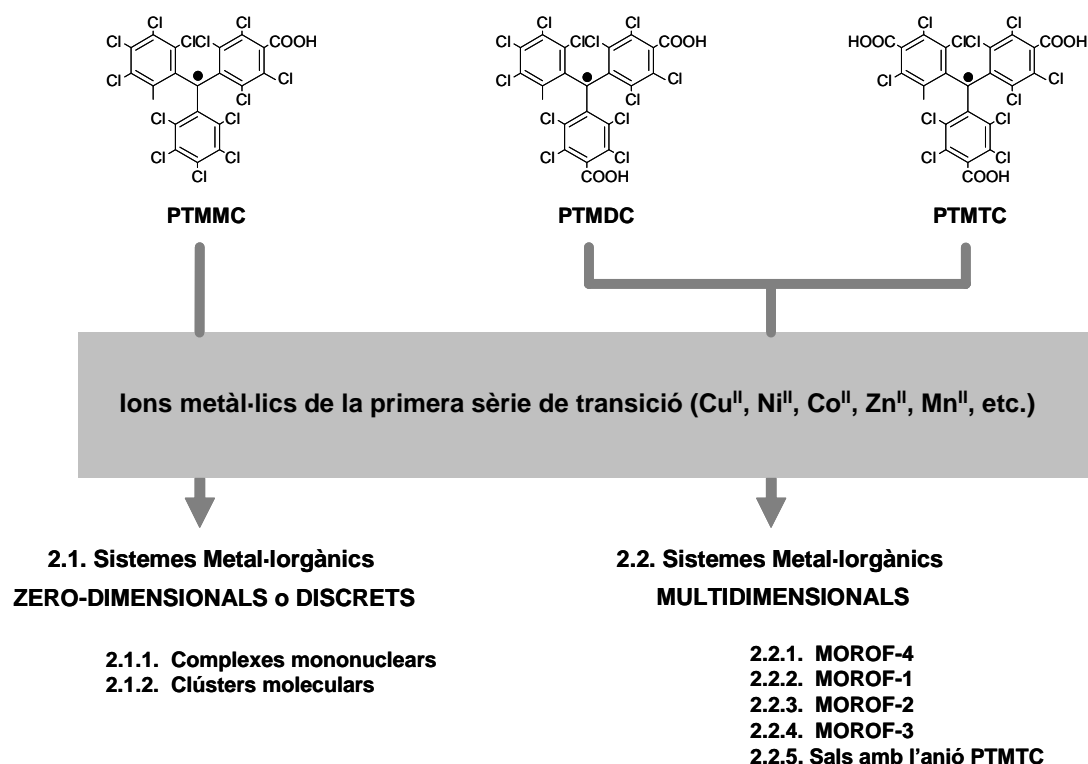


Capítol 2

Aproximació Metal·lorgànica

La funcionalització dels radicals PTM amb diversos grups carboxílics també permet l'ús d'aquests com a lligands orgànics per formar *materials moleculars metal·lorgànics nanoporosos amb propietats magnètiques*. En aquest sentit, tal i com succeïa en l'aproximació supramolecular per punts d'hidrogen, la geometria i les propietats intrínseques dels radicals PTM, combinant correctament la seva funcionalització, donen lloc a nombroses avantatges. En primer lloc, si es segueix l'aproximació metall-radical, que ja s'ha portat a terme anteriorment amb els radicals estables nitròxids,¹ nitronil o imino nitròxids,² verdazils,³ carbens⁴ i quinones,⁵ els radicals PTM amb grups carboxílics seran capaços de coordinar-se per més d'una posició, actuant com a elements paramagnètics pont entre ions metàl·lics i incrementant, així, les interaccions i la dimensionalitat magnètica del material resultant. En segon lloc, d'acord amb la seva topologia trigonal, aquests radicals, sobretot el radical PTMTC, poden actuar com a elements separadors d'ions metàl·lics a través de l'espai per formar estructures inorgàniques-orgàniques poroses. D'aquesta manera, s'espera que ambdues característiques es combinin en un mateix material, en el qual els ions metàl·lics s'allunyin en l'espai per formar estructures altament poroses sense perdre la dimensionalitat magnètica de la xarxa formada. Es pretén, doncs, dissenyar i obtenir materials porosos amb canals de dimensions grans, superiors a 1.5 nm, amb interessants propietats magnètiques. Aquests nous materials es designaran segons les sigles MOROF (Metal-Organic Radical Open-Framework).



Esq. 15. Esquematització dels diferents sistemes metal·lorgànics magnètics i porosos (MOROF) formats fent servir els radicals PTM funcionalitzats amb grups carboxílics (Capítol 1) com a lligands.

Així, amb l'objectiu de dissenyar una primera família de materials magnètics metal·lòrgànics basats en els radicals PTM, els quals puguin presentar estructures altament poroses, s'ha portat a terme un treball estructurat principalment en dos grans blocs (Esq. 15). En primer lloc, es va plantejar l'estudi de la viabilitat d'aquesta aproximació investigant la capacitat de formar complexos que té un grup carboxílic en la posició *para* dels radicals PTM. Això es va dur a terme fent servir el radical monosubstituint PTMMC per formar sistemes metal·lòrgànics magnètics discrets o zero-dimensionals. Aquests sistemes, generalment amb estructures simples, permetran, per primer cop, l'estudi de la interacció magnètica entre aquests radicals i els diferents ions metàl·lics. Seguidament, en un segon bloc, l'ús dels radicals di i trisubstituïts PTMDC i PTMTC permetrà la síntesi de sistemes multidimensionals, els quals podran presentar estructures poroses i propietats magnètiques interessants. Aquesta partició s'ha volgut definir clarament en aquesta Tesi Doctoral, dividint aquest capítol en dos subcapítols.

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Subcapítol 2.1

Sistemes Metal·lorgànics

Zero-Dimensionals

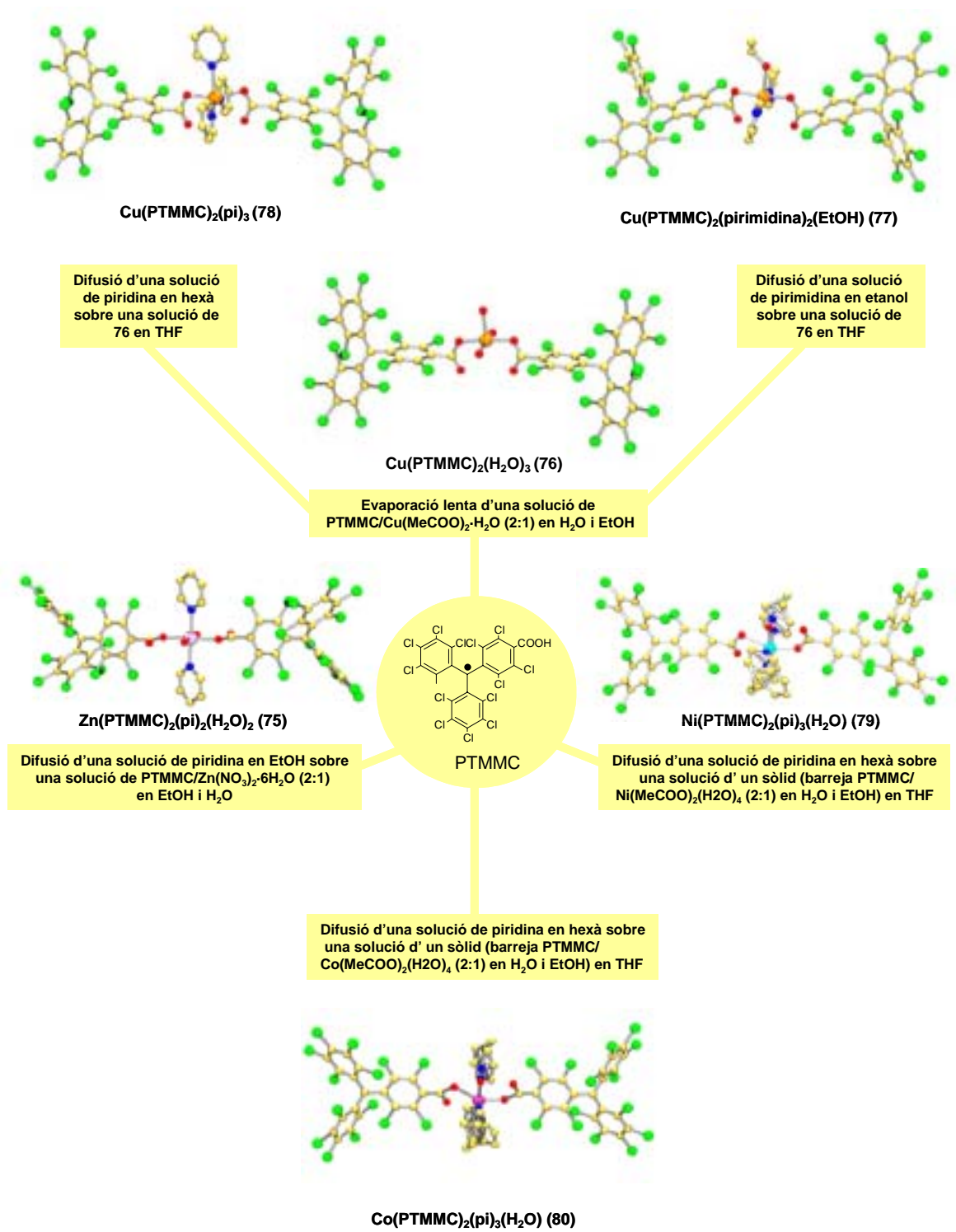
En aquest subcapítol, es presenta l'estudi estructural i magnètic de tota una família de complexos mononuclears del radical PTMMC amb diferents ions metàl·lics (Zn^{II} , Cu^{II} , Ni^{II} i Co^{II}), d'un complex rar format per la cocrystal·lització de dos complexos mononuclears de Co^{II} , i de dos clústers moleculars, que engloben un dímer de Cu^{II} i un trímer de Mn^{II} . Les estructures cristal·lines dels corresponents complexos foren resoltes pel Dr. Klaus Wurst de la Universitat d'Innsbruck. Paral·lelament, les mesures magnètiques foren realitzades utilitzant un instrument SQUID, per Neus Domingo en el grup del Prof. Javier Tejada de la Universitat de Barcelona i per José Maria Martínez en el grup del Prof. Eugenio Coronado de la Universitat de València. Qualsevol detall sobre la síntesi, aspectes cristal·logràfics o magnètics es pot consultar en els articles E, F i G del final d'aquest subcapítol.

2.1.1. Sistemes metal·lorgànics mononuclears.

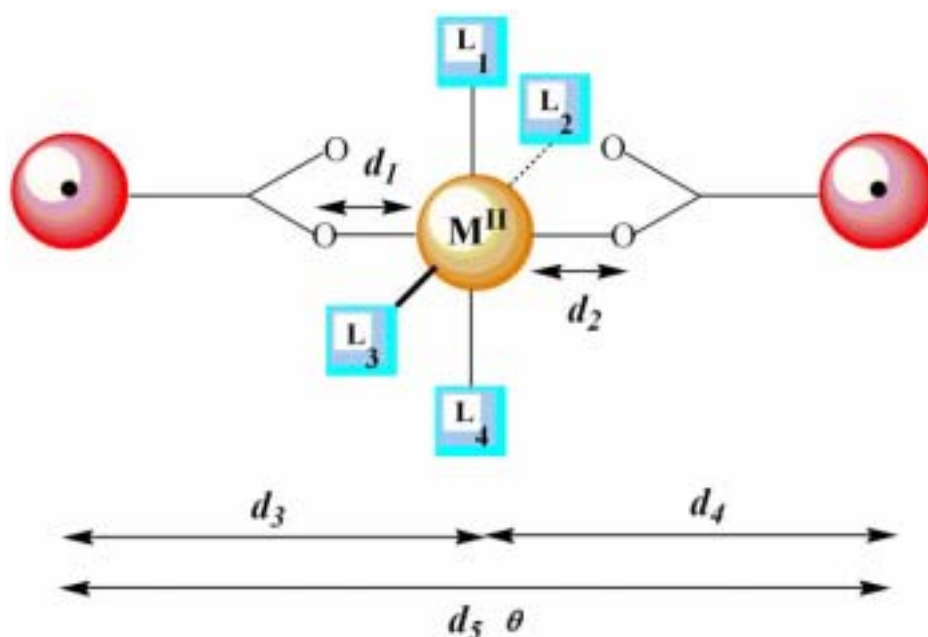
La combinació del radical PTMMC amb diversos ions metàl·lics de la primera sèrie de transició ha permès la síntesi de tota una sèrie de complexos mononuclears senzills, formats per dos radicals PTMMC coordinats a un ió metàl·lic central. Els diversos ions metàl·lics utilitzats han estat el Zn^{II} , Cu^{II} , Ni^{II} i Co^{II} , els quals presenten un nombre d'espí de $S = 0, \frac{1}{2}, 1$ i $\frac{3}{2}$, respectivament. La síntesi de tots ells es va dur a terme seguint dos mètodes sintètics diferents, utilitzant els reactius i dissolvents detallats en l'esquema 16. Un primer mètode, emprat en l'obtenció de la majoria dels complexos mononuclears, va consistir en un procés de difusió, on la reacció i el procés de cristal·lització tenen lloc al mateix temps. Alternativament, també es va utilitzar un segon mètode sintètic, on els cristalls es varen obtenir per evaporació de forma progressiva de les corresponents mesclades de reacció. D'aquesta manera, es van sintetitzar els següents complexos: $[\text{Zn}(\text{PTMMC})_2(\text{pi})_2(\text{H}_2\text{O})\cdot\text{EtOH}]$ (75), $[\text{Cu}(\text{PTMMC})_2(\text{H}_2\text{O})_3\cdot 6\text{H}_2\text{O}\cdot 2\text{EtOH}]$ (76), $[\text{Cu}(\text{PTMMC})_2(\text{pirim})_2(\text{EtOH})\cdot\text{THF}\cdot 4\text{EtOH}]$ (77), $[\text{Cu}(\text{PTMMC})_2(\text{pi})_3\cdot 2.5\text{hexà}]$ (78), $[\text{Ni}(\text{PTMMC})_2(\text{pi})_3(\text{H}_2\text{O})\cdot\text{Hexà}\cdot 2\text{THF}]$ (79) i $[\text{Co}(\text{PTMMC})_2(\text{pi})_3(\text{H}_2\text{O})\cdot\text{Hexà}\cdot 2\text{THF}]$ (80).

2.1.1.1. Geometria molecular.

Tots aquests complexos mononuclears mostren característiques estructurals molt semblants, les quals defineixen la morfologia i geometria de tots ells. Aquestes característiques són: 1) l'angle que formen els dos radicals, agafant com a referència els àtoms del carboni metílic, on la densitat d'espí és més elevada, i l'àtom metàl·lic central té un valor pròxim als 180° , dibuixant un trímer lineal format pels dos radicals PTMMC ($S = 1/2$) situats en els dos extrems i un ió metàl·lic ($S=0, \frac{1}{2}, 1, \frac{3}{2}$) central. D'aquesta manera, els dos radicals PTMMC sempre es situen en posicions coordinants oposades, degut segurament a l'impediment estèric que originen els seus múltiples àtoms de clor; 2) els radicals PTMMC es coordinen de manera monodentada, on el grup carboxílic es disposa perpendicularment a l'anell de benzè policlorat, degut, altra cop, als impediments estèrics provocats pels àtoms de clor situats a les posicions veïnes; i 3) la resta de les posicions coordinants estan ocupades en tots els casos per molècules d'aigua, piridina o etanol.

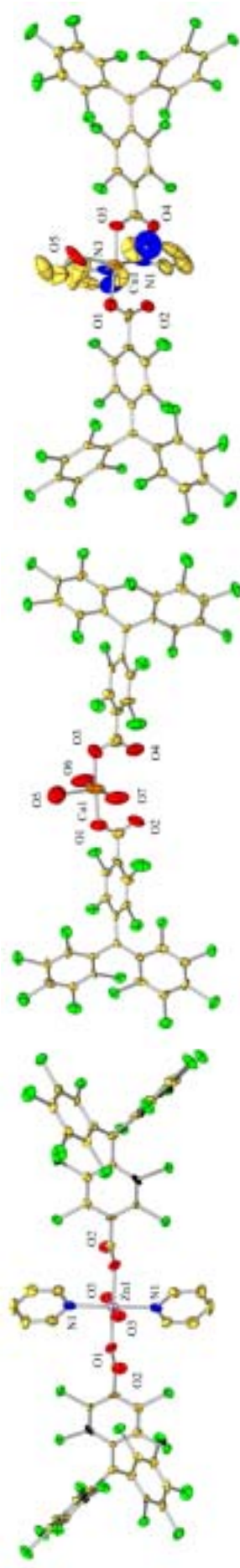


Esq. 16. Esquema indicant el mètode emprat per la síntesi dels diferents complexos mononuclears obtinguts amb el radical PTMMC i els diferents ions metàl·lics Zn^{II} (S=0), Cu^{II} (S=1/2), Ni^{II} (S=1) i Co^{II} (S=3/2).

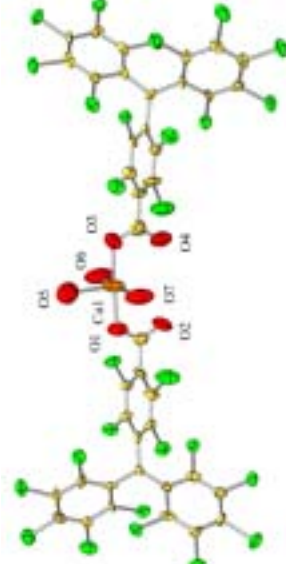


Complex	75	76	77	78	79	80
Ió Metàl·lic	Zn	Cu	Cu	Cu	Ni	Co
L₁	pi	H ₂ O	EtOH	pi	H ₂ O	H ₂ O
L₂	H ₂ O	H ₂ O	pirim	pi	pi	pi
L₃	H ₂ O	H ₂ O	pirim	pi	pi	pi
L₄	pi	-	-	-	pi	pi
d₁	2.088(16)	1.967(14)	2.068(8)	2.147(5)	2.091(19)	1.92(2)
d₂	2.088(16)	1.88(2)	1.926(6)	1.976(5)	2.091(19)	1.92(2)
d₃	8.6	8.4	8.5	8.5	8.6	8.5
d₄	8.6	8.3	8.3	8.3	8.7	8.5
d₅	17.1	16.5	16.7	16.7	17.3	17.0
χ	180	162	169	170	174	171

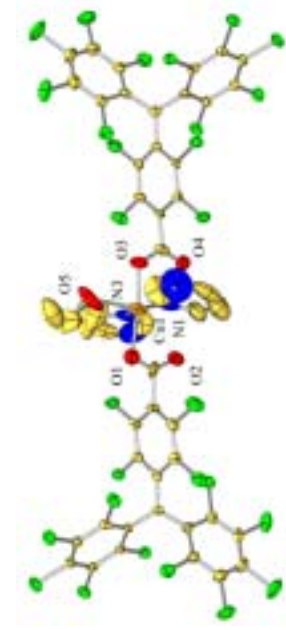
Esq. 17 i Taula 4. Representació esquemàtica d'un complex mononuclear i les corresponents dades estructurals per tots ells: [Zn(PTMMC)₂(pi)₂(H₂O)·EtOH] (**75**), [Cu(PTMMC)₂(H₂O)₃]·6H₂O·2EtOH (**76**), [Cu(PTMMC)₂(pirim)₂(EtOH)]·THF·4EtOH (**77**), [Cu(PTMMC)₂(pi)₃]·2.5hexà (**78**), [Ni(PTMMC)₂(pi)₃(H₂O)·hexà·2THF] (**79**) i Co(PTMMC)₂(pi)₃(H₂O)·hexà·2THF (**80**). Les sigles L₁₋₄ corresponen als lligands que completen l'esfera de coordinació. Els valors d₁ i d₂ corresponen a la distància entre l'oxigen coordinant del grup carboxílic del radical PTMMC i l'ió metàl·lic. Els valors d₃ i d₄ corresponen a la distància entre el carboni metílic del radical PTMMC, el qual presenta la major densitat d'espí, i l'ió metàl·lic, mentre que d₅ correspon a la distància entre aquests dos carbonis metílics. Finalment, el valor de χ correspon a l'angle entre els dos carbonis metílics i l'ió metàl·lic. A la taula 4, les distàncies es donen en Å, mentre que els angles en °. Les abreviacions pi i pirim corresponen a les molècules de piridina i pirimidina, respectivament.



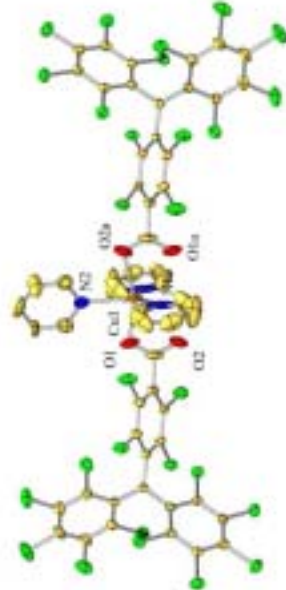
Zn(PTMMC)₂(pi)₂(H₂O)₂ (75)



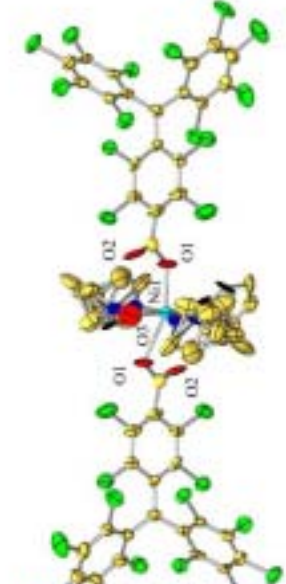
Cu(PTMMC)₂(H₂O)₃ (76)



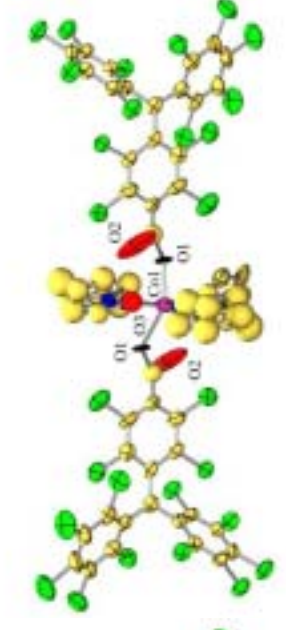
Cu(PTMMC)₂(pirimidina)₂(EtOH) (77)



Cu(PTMMC)₂(pi)₃ (78)



Ni(PTMMC)₂(pi)₃(H₂O) (79)



Co(PTMMC)₂(pi)₃(H₂O) (80)

Fig. 19. Representació ORTEP a una probabilitat del 30% de les estructures moleculars dels complexos mononuclears formats amb el radical PTMMC.

Tots els detalls estructurals d'aquests complexos s'han recopilat en l'esquema 17 i la taula 4, en les quals es pot comprovar la semblança de tots ells. En la figura 19, s'han representat les figures ORTEP de tots aquests complexos, en les quals s'observa que mentre els complexos de Cu^{II} són pentacoordinats i tenen una geometria piramidal de base quadrada lleugerament deformada, la resta presenten una coordinació octaèdrica.

2.1.1.2. Empaquetament supramolecular.

Aquests complexos s'empaqueten de tres maneres diferents, generalment dominades pels diversos contactes $\text{Cl}\cdots\text{Cl}$, que són originats perquè els radicals PTMMC queden a la part exterior dels respectius complexos degut al seu elevat volum. Així, en la part exterior d'aquests complexos predomina la presència d'àtoms de clor, que òbviament originaran aquests tipus de contactes.

A) El complex de Zn^{II} **75** s'organitza formant un entramat de contactes $\text{Cl}\cdots\text{Cl}$, en concret 28 per unitat, amb distàncies compreses entre 3.34 i 3.50 Å, entre els diferents radicals PTMMC al llarg de les tres direccions del cristall (Fig. 20). Tanmateix, aquests complexos també es troben units a través de diferents interaccions supramoleculares. Les molècules de piridina coordinades participen en interaccions tipus ϕ - ϕ febles al llarg de l'eix *a*. A més, els grups carboxilats, a través de l'àtom d'oxigen no coordinat [O(2)], formen enllaços per pont d'hidrogen amb un grup C-H d'aquestes mateixes molècules de piridina al llarg de l'eix *c*. Finalment, **75** conté una molècula d'etanol de solvatació, que també es troba formant enllaços per pont d'hidrogen amb els grups carboxilats del radical PTMMC.

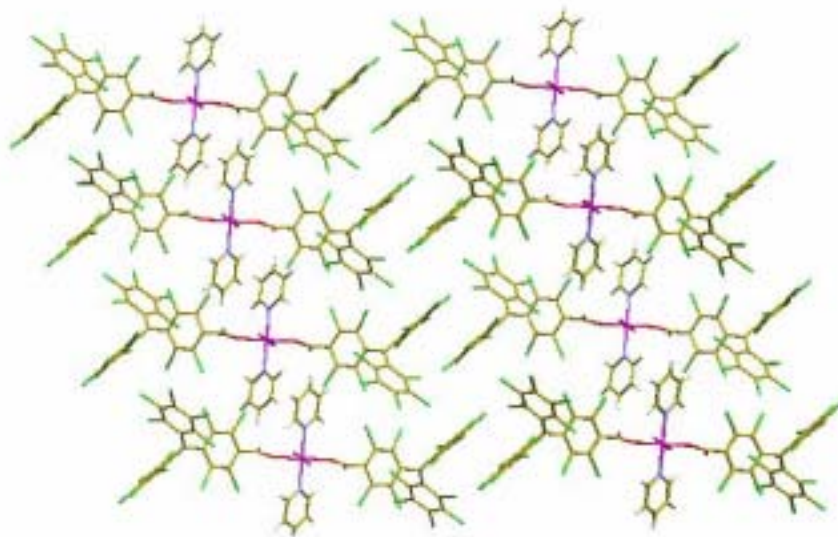


Fig. 20. Visió de l'empaquetament cristal·lí del complex $\text{Zn}(\text{PTMMC})_2(\text{pi})_2(\text{H}_2\text{O})\cdot\text{EtOH}$ (**75**) al llarg de l'eix *b*, mostrant l'estructura amb canals. Les molècules d'etanol s'han omès de l'estructura.

B) El complex de Cu^{II} **76** s'organitza formant una estructura porosa al llarg de l'eix *b*, estabilitzada principalment per diversos contactes $\text{Cl}\cdots\text{Cl}$ entre les unitats del radical PTMMC

(Fig. 21). En total, cada complex interacciona a través de 16 contactes amb distàncies compreses entre 3.25 i 3.60 Å, generant una estructura tridimensional enllaçada a través d'aquests contactes. Més específicament, la disposició confrontada de dues unitats de **76** crea un sintó supramolecular rectangular, l'empaquetament del qual genera dos canals monodimensionals quadrats separats per una hipotètica paret formada per les dues molècules d'aigua coordinada [O(5)] d'ambdós complexos. La distància dels ions Cu^{II} en aquest sintó és de 9 Å i les dimensions dels canals són d'aproximadament 5.1 x 4.6 Å, tot considerant els radis de van der Waals. Els canals de l'estructura es troben plens de molècules d'aigua i etanol, les quals es troben fortament enllaçades per ponts d'hidrogen entre elles mateixes i amb les diferents unitats metal-lorgàniques **76**.

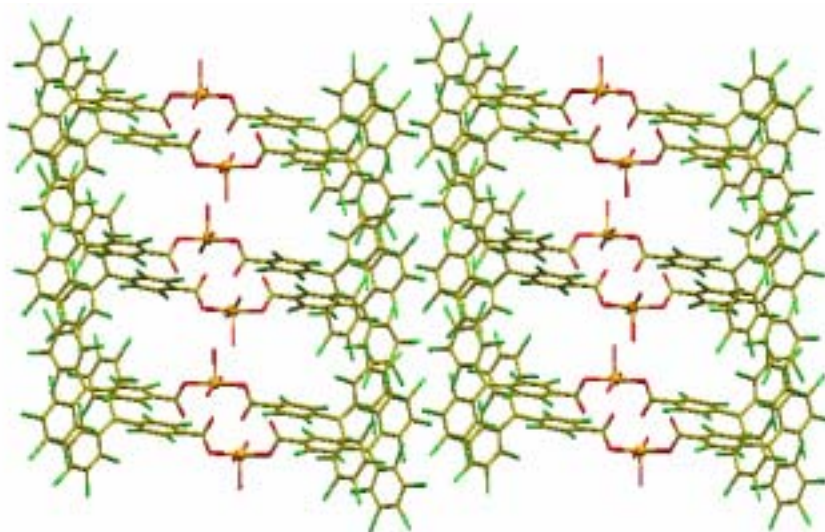


Fig. 21. Visió de l'empaquetament cristal·lí del complex $[\text{Cu}(\text{PTMMC})_2(\text{H}_2\text{O})_3] \cdot 6\text{H}_2\text{O} \cdot 2\text{EtOH}$ (**76**) al llarg de l'eix *b*, mostrant l'estructura amb canals. Les molècules de dissolvents s'han omès de l'estructura per claredat.

C) L'empaquetament dels complexos de Cu^{II} **77** i **78**, de Ni^{II} **79** i de Co^{II} **80** és el mateix, de manera que s'organitzen generant una estructura porosa, estabilitzada també per múltiples contactes Cl...Cl per unitat de PTMMC, amb distàncies compreses entre 3.33 i 3.60 Å. En concret, cadascuna de les unitats monomèriques interacciona a través de 16 (**77**), 12 (**78**), 12 (**79**) i 12 (**80**) contactes Cl...Cl amb les seves unitats anàlegs. Malgrat tot, l'estructura amb canals formada difereix de la del complex **76**, doncs en aquests casos no es forma el sintó rectangular característic de l'empaquetament d'aquest complex. El major volum de les molècules d'etanol, piridina i pirimidina en comparació amb les molècules d'aigua que conté **76**, provoca que aquests lligands no puguin estar directament enfrontats. D'aquesta manera, hi ha un lleuger desplaçament en una direcció entre ambdós complexos, generant uns canals monodimensionals rectangulars. Aquest canvi en l'empaquetament s'il·lustra pel complex **77** (Fig. 22), en el qual la separació entre els dos ions de Cu^{II} és de 15 Å, molt més gran que els 9 Å presents en el complex **76**. Les dimensions d'aquests nous canals, els quals són plens de molècules de dissolvent (hexà, THF o etanol), són d'aproximadament 7.0 x 3.0 Å en tots els casos, tot considerant els radis de van der Waals.

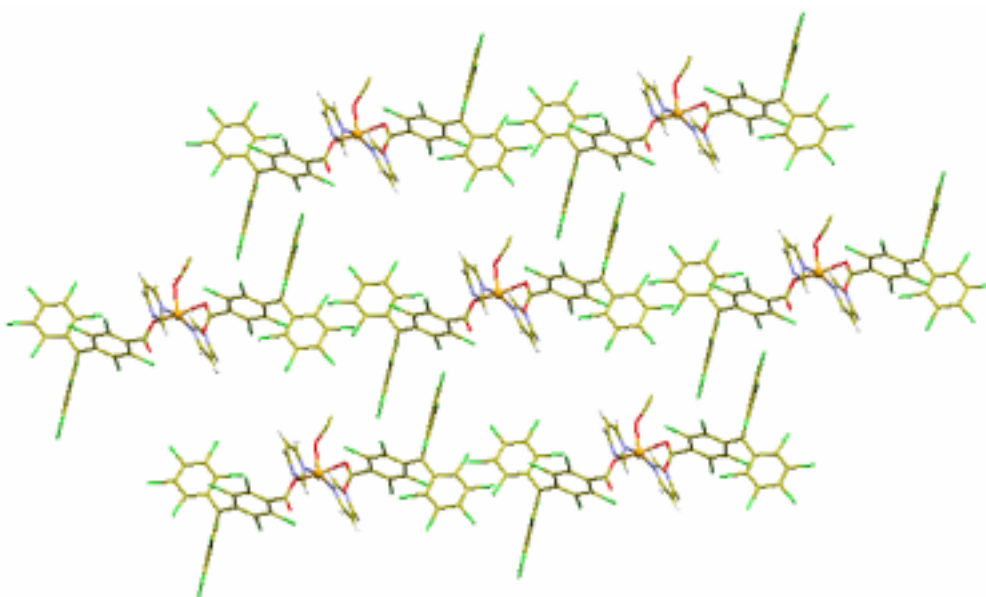


Fig. 22. Visió de l'empaquetament cristal·lí del complex $[\text{Cu}(\text{PTMMC})_2(\text{pirim})_2(\text{EtOH})]\cdot\text{THF}\cdot 4\text{EtOH}$ (**77**), mostrant l'estructura amb canals rectangulars. Les molècules de dissolvents s'han omès de l'estructura per claredat.

2.1.1.3. Propietats magnètiques.

La simplicitat i la similitud de tots aquests sistemes metal·lorgànics monomèrics ha permès conèixer, estudiar i comparar, per primer cop, la interacció d'intercanvi magnètica existent entre el radical PTMMC i un ampli ventall d'ions metàl·lics.

Les dades magnètiques del complex de Zn^{II} ($S=0$) **75** mostren un comportament paramagnètic gairebé en tot el rang de temperatures (Fig. 23). Únicament a temperatures molt baixes, a aproximadament 6 K, s'observa la presència d'interaccions antiferromagnètiques molt febles. Per conèixer la interacció intramolecular dels radicals PTMMC, aquestes dades es varen ajustar a un model dimèric d'espècies $S=1/2$ segons l'equació de Bleaney-Bowers,¹ obtenint un valor de la constant d'intercanvi magnètica intramolecular (J) de -1.0 K. No obstant, aquest valor concorda amb els valors habitualment observats per les interaccions magnètiques intermoleculars originades pels contactes $\text{Cl}\cdots\text{Cl}$ en sistemes orgànics formats únicament per radicals PTM,² per la qual cosa és difícil assignar correctament a quin dels dos tipus d'interaccions és deguda (de fet, un ajust utilitzant el mateix model, però tenint en compte la presència d'interaccions intermoleculars entre els dímers (χ), dóna uns nous valors de J de $-2\cdot 10^{-6}$ K i χ de -1.0 K). Per aquest motiu, per estudiar la resta de sistemes de Cu^{II} , Ni^{II} i Co^{II} , la interacció intramolecular entre les dues unitats de PTMMC es considerarà nul·la (o inclosa dins el valor de la constant intermolecular) i, per la qual cosa, no es tindrà en compte en el desenvolupament dels respectius Hamiltonians a l'hora d'obtenir les equacions teòriques que permetin determinar els valors de les constants d'acoblament magnètiques.

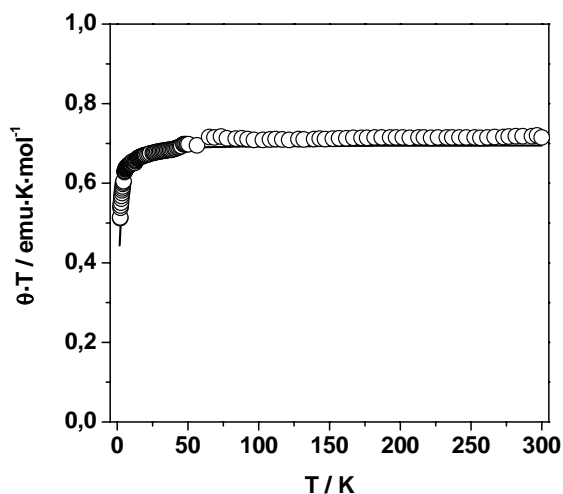
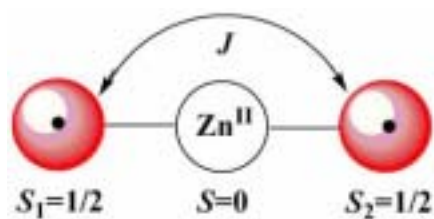


Fig. 23. Propietats magnètiques del complex **75**; producte $\theta \cdot T$ en front de T . La línia contínua indica l'ajust efectuat basant-se en l'equació de Bleaney-Bowers modificada per un camp molecular.

Tots els complexos de Cu^{II} varen presentar un comportament magnètic semblant (Fig. 24). Aquests complexos presenten un comportament paramagnètic dins un rang de temperatura d'entre 100 i 300 K, amb un valor del producte $\theta \cdot T$ de $1.125 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ a 300 K, valor que concorda amb el valor esperat per tres espècies paramagnètiques $S=1/2$ aïllades. Contràriament a l'observat en el complex de Zn, el producte $\theta \cdot T$ comença a decreixer per sota dels 100 K, el que denota la presència d'interaccions antiferromagnètiques en el sistema. A baixes temperatures, el valor de $\theta \cdot T$ s'estabilitza a un valor de $0.32 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ a 2 K, corresponent a un estat fonamental doblet $S=1/2$. Així, tenint en compte la seva estructura cristal·lina, les dades magnètiques dels successius complexos de Cu^{II} es varen ajustar a un model de tres espècies amb $S=1/2$ lineals ($S_{R1} \cdots S_{M(1/2)} \cdots S_{R2}$; $H = -2J(S_{R1}S_M + S_M S_{R2})$), modificat tenint en compte la presència d'interaccions intermoleculars (χ), d'acord amb l'aproximació del camp molecular.³ L'equació final utilitzada en aquest ajust és l'equació A.

$$\theta \left[T \right] = \frac{N \sigma_B^2 g^2 T}{3k_B(T + 4\chi)} \frac{60e^{3J/T} + 26e^{2J/T} + 26}{4(4e^{3J/T} + 22e^{2J/T} + 22)} \quad (\text{A})$$

Els millors ajustos per tots els complexos es troben tabulats en la taula 5 (pàg. 72). En ella, s'observa una constant d'intercanvi magnètica entre el radical PTMMC i l'ió Cu^{II} d'aproximadament -20K, confirmant la presència d'interaccions antiferromagnètiques moderades en aquesta classe de sistemes. Cal tenir en compte que, a l'hora d'efectuar els diferents ajustos, els corresponents valors de g s'han fixat amb els valors experimentals obtinguts utilitzant la tècnica d'EPR (veure article F).

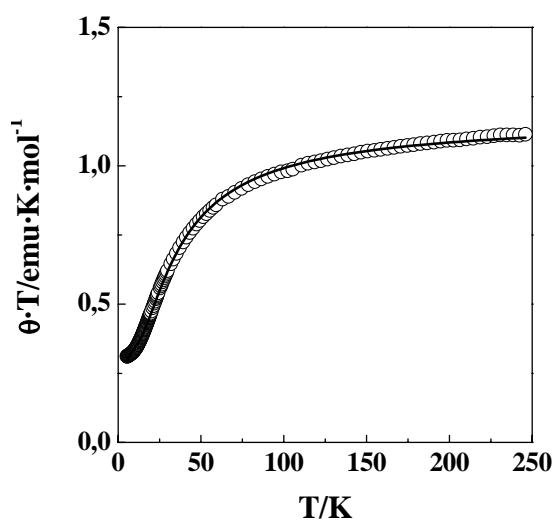
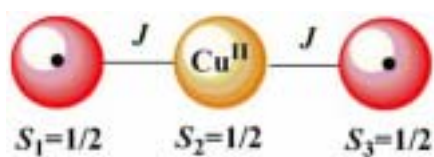
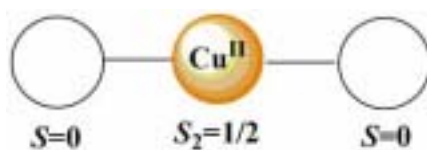


Fig. 24. Propietats magnètiques del complex **78**; producte $\theta \cdot T$ en front de T . La línia contínua indica l'ajust efectuat basant-se en l'equació teòrica per un model d'un trimer lineal de tres espècies $S = 1/2$.

Aquests resultats es varen poder comparar amb el complex $\text{Cu}(\mathbf{65})(\text{pi})_3$, similar a **78**, on les unitats radicalàries es varen substituir per unitats diamagnètiques. Aquest compost es va sintetitzar fent servir la forma hidrogenada del radical PTMMC, el compost **65** (veure capítol 1, apartat 1.1). D'aquesta manera, el complex resultant únicament presenta l'ió de Cu^{II} com a unitat paramagnètica. Les propietats magnètiques d'aquest complex van mostrar un comportament purament paramagnètic dins el rang de 2 a 300 K (Fig. 25). El valor del producte $\theta \cdot T$ a 300 K és $0.383 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$, valor que concorda amb l'esperat per una espècie Cu^{II} paramagnètica $S=1/2$ aïllada. Aquestes dades magnètiques es van ajustar seguint la llei de Curie-Weiss, obtenint un valor de la constant de Weiss de -0.3 K . Així, comparant ambdós comportaments magnètics (veure Fig. 24 i Fig. 25), es pot afirmar sense cap mena de dubte la gran influència dels radicals PTMMC en les interaccions magnètiques presents en aquesta classe de complexos.



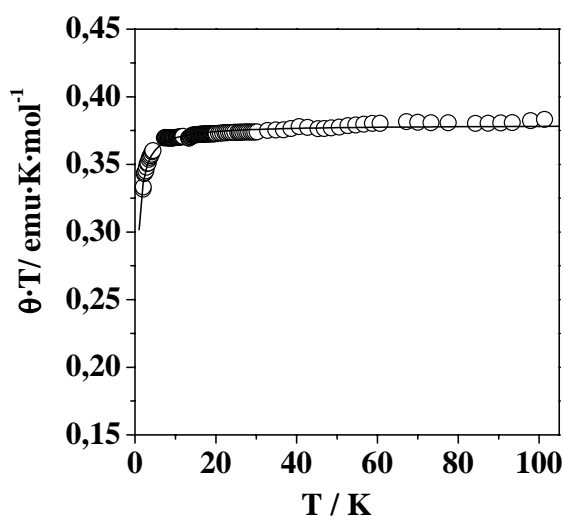
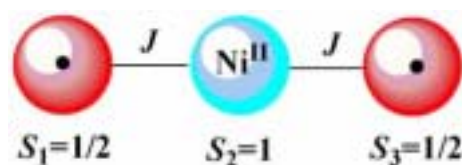


Fig. 25. Propietats magnètiques del complex Cu(65)(pi)₃, similar a 78, on els lligands PTMMC s'han substituït per les molècules hidrogenades 65; producte $\theta \cdot T$ en front de T. La línia contínua indica l'ajust efectuat seguint la llei de Curie-Weiss.

Les dades magnètiques del complex de Ni^{II} 79 mostren que el valor del producte $\theta \cdot T$ a temperatura ambient és 1.747 emu·K·mol⁻¹, que concorda amb el valor esperat per dues espècies amb un espí S=1/2 i una espècie amb espí S=1 aïllades (1.75 emu·K·mol⁻¹). A mesura que la temperatura decreix, el valor de $\theta \cdot T$ disminueix molt lentament fins a 140 K, temperatura a la qual aquest valor comença a disminuir més ràpidament, el que és característic de la presència d'interaccions antiferromagnètiques (Fig. 26). A baixes temperatures, el valor de $\theta \cdot T$ s'estabilitza a un valor lleugerament superior al zero absolut, degut a la presència d'impureses paramagnètiques (Fig. 26a). Així, les dades magnètiques d'aquest complex es varen ajustar a un model de tres espècies amb S=1/2-S=1-S=1/2 lineals ($S_{R1} \cdots S_{M(1)} \cdots S_{R2}$; $H = -2J(S_{R1}S_M + S_M S_{R2})$), modificat tenint en compte la presència d'interaccions intermoleculares (χ), d'acord amb l'aproximació del camp molecular, i tenint en compte la presència d'impureses paramagnètiques (C). Així, el millor ajust, efectuat utilitzant l'equació B, va donar uns valors de $g = 2.010$, $J/K_B = -21K$, $\chi = -3K$ i $C = 0.11$ emu·K·mol⁻¹ (Taula 5). Amb ell, s'observa que el valor de l'acoblament entre l'ió Ni^{II} i el radical PTMMC és pràcticament idèntic als observats pels complexos de Cu^{II} 76-78.

$$\theta \approx \left| \frac{N\sigma_B^2 g^2 T}{3k_B(T + \chi)} \frac{6e^{J/T} + 2e^{2J/T} + 230e^{3J/T}}{123e^{J/T} + 23e^{2J/T} + 25e^{3J/T}} \right| 2C \quad (B)$$



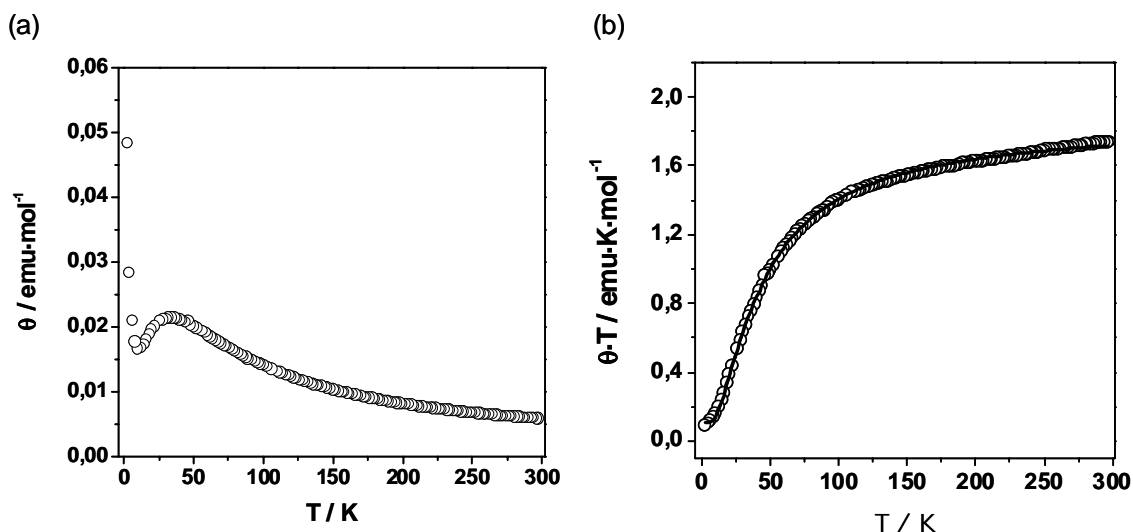
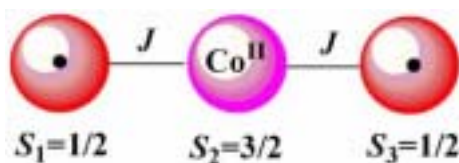


Fig. 26. Propietats magnètiques del complex de Ni^{II} **79**; (a) θ en front de T i (b) producte $\theta \cdot T$ en front de T. La línia contínua indica l'ajust efectuat seguint l'equació B.

Finalment, les dades magnètiques del complex de Co^{II} també varen constatar un comportament similar, novament amb la presència d'impureses paramagnètiques (Fig. 27). El valor del producte $\theta \cdot T$ és 3.513 emu·K·mol⁻¹, valor més elevat que l'esperat per un ió de Co^{II} ($S=3/2$) i dos radicals PTMMC ($S=1/2$) aïllats (2.63 emu·K·mol⁻¹). Aquest comportament és característic de compostos de Co^{II} i està originat per la contribució orbital. A mesura que la temperatura disminueix, el valor de $\theta \cdot T$ també decreix, símptoma de la presència d'interaccions antiferromagnètiques. A l'igual que en els darrers complexes mononuclears de Cu^{II} i Ni^{II}, les dades magnètiques també es varen ajustar a un model teòric basat en un model de tres espècies lineals amb $S=1/2$ - $S=3/2$ - $S=1/2$ ($S_{R1} \cdots S_{M(3/2)} \cdots S_{R2}$; $H = -2J(S_{R1}S_M + S_M S_{R2})$), modificat tenint en compte la presència d'interaccions intermoleculars (χ) d'acord amb l'aproximació del camp molecular. Degut a la dificultat de fer un anàlisi de la contribució orbital, les dades experimentals només es varen ajustar (Equació C) dins el rang de temperatures compreses entre 300 a 50 K, proporcionant uns valors de $g = 2.409$, $J/K_B = -11$ K i $\chi = -0.5$ K. D'aquesta manera, s'aprecia també un valor de la constant d'intercanvi magnètica entre el radical PTMMC i l'ió de Co^{II} semblant a les obtingudes pels complexes de Cu^{II} i Ni^{II} (Taula 5)

$$\theta \approx \left| \frac{N\sigma_B^2 g^2 T}{3k_B(T + \chi)} \frac{0.75215e^{2.5J/T} + 215e^{1.5J/T} + 2525e^{4J/T}}{224e^{2.5J/T} + 24e^{1.5J/T} + 26e^{4J/T}} \right| \quad (C)$$



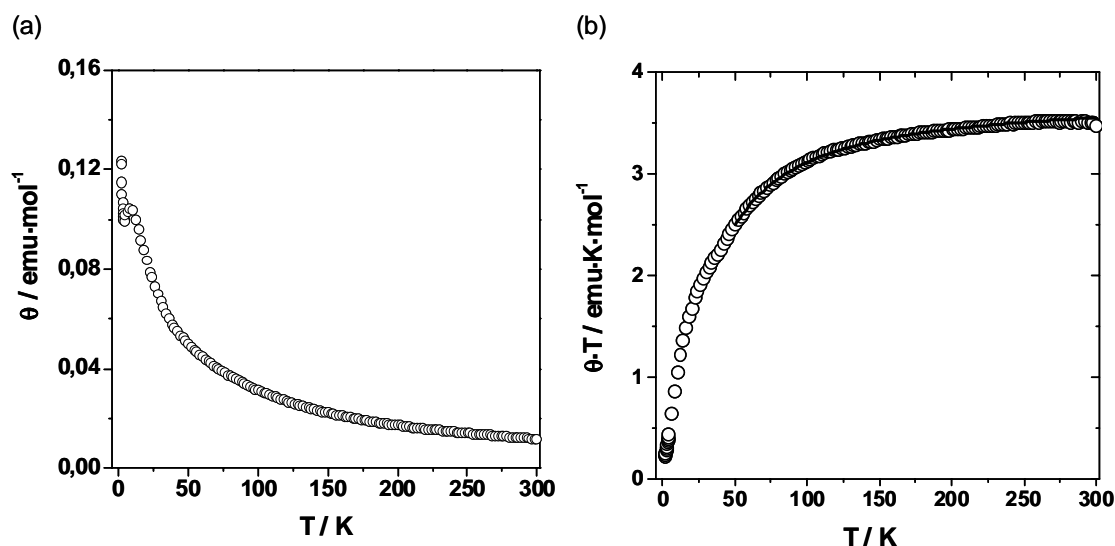


Fig. 27. Propietats magnètiques del complex de Co^{II} **80**; (a) θ en front de T i (b) producte $\theta \cdot T$ en front de T. La línia contínua indica l'ajust efectuat seguint l'equació C.

Taula 5. Dades magnètiques dels complexos mononuclears **75-80**.

Complex	75	76	77	78	79	80
J_{RR} / K	-1.0	-	-	-	-	-
J_{RM} / K	-	-25	-15	-21	-21	-11
χ / K	-	-0.7	-0.5	-1.7	-3.0	-0.5
g	-	2.063	2.046	2.045	2.010	2.409

J_{RR} , interacció entre radicals PTMMC. J_{RM} , interacció entre radical PTMMC i l'ió metàl·lic. χ és la constant d'acoblament intermolecular.

2.1.2. **[Co(PTMMC)₂(pi)₂(H₂O)₂][Co(PTMMC)(pi)₃(H₂O)(Cl)]₂·2pi·2THF (**81**): un complex rar format per la cocrystal·lització de dos complexos mononuclears.**

La mescla del carboxilat sòdic del radical PTMMC (veure article G), CoCl₂ i piridina en una solució de THF i hexà va permetre la síntesi del sistema metal·lorgànic **81**, que es pot considerar singular ja que està format per la cocrystal·lització de dos complexos mononuclears de Co^{II} diferents. Concretament, la unitat [Co(PTMMC)₂(pi)₂(H₂O)₂] és molt similar al complex **80**, doncs és un complex octaèdric de Co^{II}, on s'hi coordinen dos radicals PTMMC en posició anti, dues molècules de piridina i dues molècules d'aigua. Al contrari, la segona unitat [Co(PTMMC)(pi)₃(H₂O)(Cl)], tot i que també és un complex octaèdric de Co^{II}, únicament està coordinat per un radical PTMMC. Les posicions restants de l'esfera de coordinació les ocupen tres molècules de piridina, una molècula d'aigua i un àtom de clor. L'agrupament d'aquestes dues subunitats, en una proporció 1:2, respectivament, genera el sistema metal·lorgànic **81** (Fig. 28).

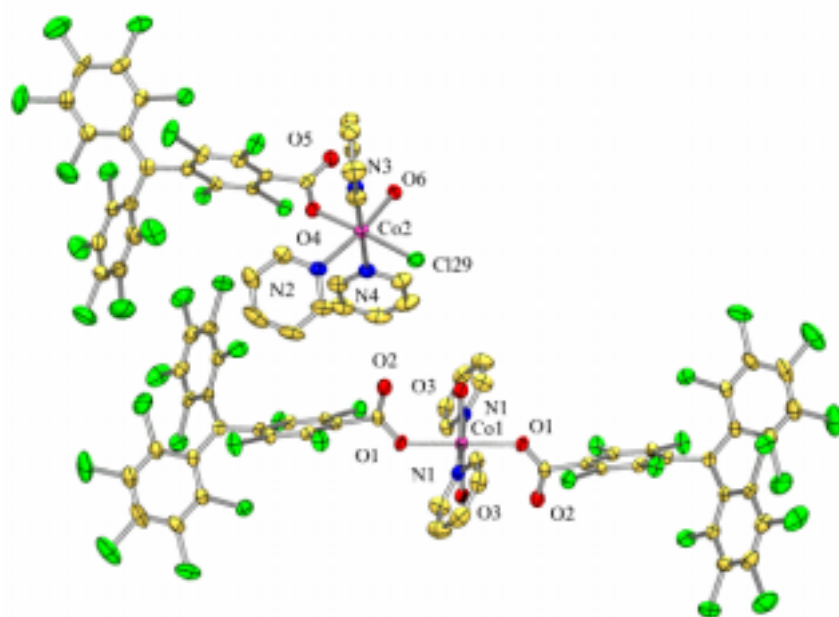


Fig. 28. Representació ORTEP al 30 % de probabilitat del complex **81**.

L'empaquetament cristal·lí mostra que aquestes subunitats s'organitzen de manera alternada al llarg de l'eix *b*. Aquest empaquetament es troba estabilitzat per diversos enllaços per pont d'hidrogen i contactes Cl...Cl intra- i intermoleculars, els quals engloben interaccions entre les diferents unitats i entre les unitats i les molècules de dissolvent. Un anàlisi detallat d'aquestes interaccions, amb les seves corresponents distàncies i angles d'enllaç, així com una representació d'aquest empaquetament, es pot consultar en l'article G del final d'aquest capítol.

Les propietats magnètiques d'aquest complex mostren que a temperatura ambient el valor del producte $\theta \cdot T$ és $8.397 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$, valor també més elevat que l'esperat per tres ions de Co^{II} ($S=3/2$) i quatre radicals PTMMC ($S=1/2$) aïllats. Tal i com s'ha comentat anteriorment, aquest comportament és característic de compostos de Co^{II} i està originat per la contribució orbital. A mesura que la temperatura disminueix, el valor de $\theta \cdot T$ també decreix, fet que es pot assignar a la presència d'interaccions antiferromagnètiques (Fig. 29). Les dades magnètiques es varen ajustar a un model teòric basat en la suma de dos models diferents; un model de tres espècies lineals similar als complexos mononuclears exposats anteriorment ($S_{R1} \cdots S_{M(3/2)} \cdots S_{R2}$; $H = -2J(S_{R1}S_M + S_M S_{R2}) - 2J'(S_{R1}S_{R2})$) i un model de dues espècies ($S_{R1} \cdots S_{M(3/2)}$; $H = -2J'(S_M S_{R3})$), modificats tenint en compte la presència d'interaccions intermoleculars (χ). Degut a la dificultat de fer un anàlisi de la contribució orbital, les dades experimentals, a l'igual que en el complex **80**, només es varen ajustar dins el rang de temperatures compreses entre 300 a 50 K, proporcionant uns valors de $J/K_B = -16.0 \text{ K}$, $J'/K_B = -2.9 \text{ K}$ i $g_{\text{Co}} = 2.437$ per la unitat trimèrica i $J''/K_B = -16.0 \text{ K}$ i $g = -2.164$ per la unitat dimèrica i $\chi = -0.7 \text{ K}$. D'aquesta manera, s'observa que els valors de l'acoblament magnètic entre el radical i l'ió metàl·lic presenten en ambdues unitats un valor de -16.0 K , el qual és semblant als obtinguts pels complexos mononuclears. En aquest cas, també s'ha tingut en compte la interacció intramolecular entre radicals dins l'espècie trimèrica (J'/K_B), el qual dona un valor de -2.9 K .

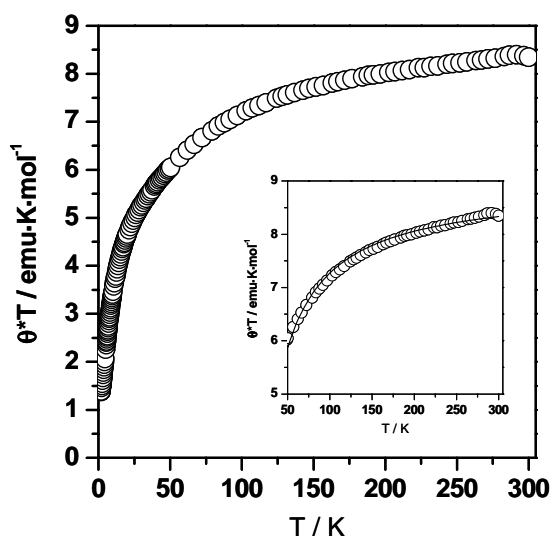


Fig. 29. Propietats magnètiques del complex **81**; producte $\theta \cdot T$ en front de T . La figura inserida mostra l'ajust efectuat seguint el model teòric corresponent.

2.1.3. Clústers moleculars.

L'ús de lligands voluminosos amb grups carboxílics s'ha convertit, en els darrers anys, en una estratègia molt bona per obtenir clústers moleculars. Amb ella, Winnpeny i col. han aconseguit la síntesi de diversos clústers amb diferent nuclearitat i interessants propietats magnètiques.⁴ En aquest sentit, la voluminositat que presenten els radicals PTM, fa que aquests també puguin ser uns bons candidats per poder formar aquesta classe de sistemes moleculars, hipòtesi que s'ha confirmat amb l'obtenció d'un dímer de Cu^{II} amb dos radicals PTMMC i, sobretot, amb la síntesi d'un trímer d'ions de Mn^{II} units per sis radicals PTMMC.

2.1.3.1. $[\text{Cu}_2(\text{PTMMC})_2(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2 \cdot 2\text{EtOH}]$ (**82**): un clúster dimèric de $\text{Cu}(\text{II})$.

Únicament variant l'estequiometria dels reactius utilitzats en la reacció realitzada per obtenir el complex mononuclear **76**, es va poder sintetitzar un dímer de Cu^{II} , on ambdós ions de Cu^{II} es troben enllaçats a través de quatre grups carboxilats pont, pertanyent a dues molècules del radical PTMMC i dues molècules d'acetat, amb distàncies d'enllaç compreses entre 1.950 i 1.971 Å (Fig. 30). Completant l'esfera de coordinació de cada ió de Cu^{II} , s'hi troba una molècula d'aigua.

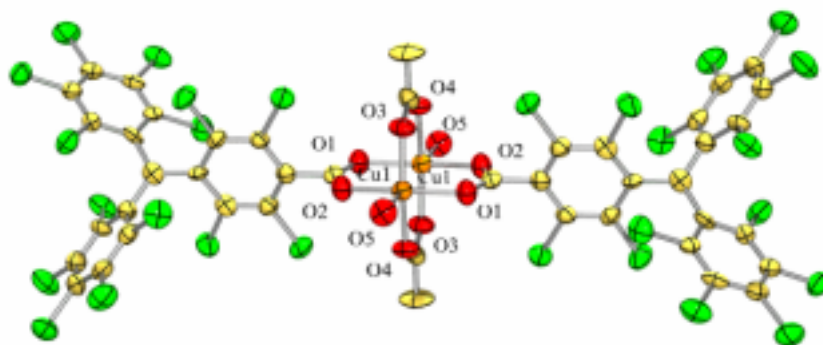


Fig. 30. Representació ORTEP al 50% de probabilitat del dímer de Cu^{II} **82**.

L'empaquetament d'aquest complex mostra la formació d'una estructura porosa estabilitzada per diversos contactes Cl...Cl, molt semblant a la del complex monomèric [Cu(PTMMC)₂(H₂O)₃]₂·6H₂O·2EtOH **76**. De fet, tal i com succeïa en el complex **76**, dues unitats de **82** s'organitzen formant un sintó supramolecular rectangular, l'empaquetament del qual forma dos canals monodimensionals quadrats de dimensions 4.2 x 4.5 Å al llarg de l'eix *c*, separats per les dues molècules d'aigua coordinades d'ambdues unitats (Fig. 31). Aquestes cavitats es troben plenes de molècules d'etanol, les quals es troben fortament enllaçades per ponts d'hidrogen als grups acetats i a les molècules d'aigua coordinades.

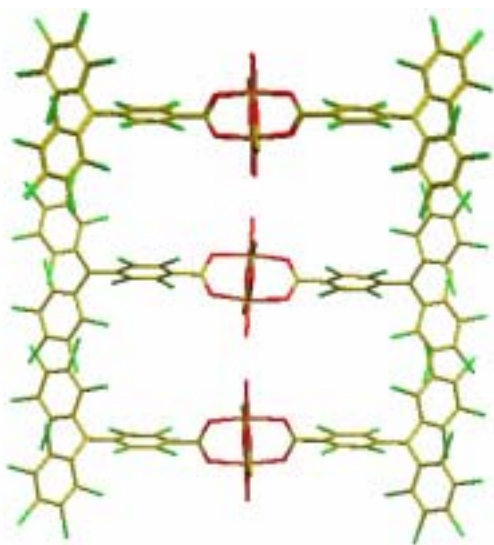


Fig. 31. Vista de l'empaquetament del clúster molecular **82** al llarg de l'eix *c*, mostrant el sintó supramolecular rectangular, el qual dibuixa dos canals monodimensionals quadrats. Les molècules de dissolvent s'han omès per claredat.

Les propietats magnètiques d'aquest complex mostren un comportament de frustració d'espí (Fig. 32). El valor del producte $\theta \cdot T$ a temperatura ambient és 0.9 emu·K·mol⁻¹, el qual és molt inferior al valor teòric esperat per quatre espècies *S*=1/2 aïllades (1.9 emu·K·mol⁻¹), fet que és consistent amb la presència d'interaccions antiferromagnètiques fortes entre els ions de Cu^{II} i entre els ions Cu^{II} i els radicals PTMMC. A mesura que la temperatura decreix, el valor del producte $\theta \cdot T$ també disminueix fins assolir un plató a aproximadament 70 K. Per sota dels 30 K, el producte $\theta \cdot T$ torna a disminuir ràpidament, arribant a un valor de 0.4 emu·K·mol⁻¹ a 2K, degut a la presència d'interaccions intermoleculars dèbils.

Aquest comportament es va ajustar a un model magnètic amb una topologia de "papallona" simètrica de dos ions metàl·lics i dos radicals PTMMC. El Hamiltonià (*H*) d'aquest sistema en forma de papallona ve donat per l'equació D,⁵ on *J* és la interacció d'intercanvi magnètica entre l'ió de Cu^{II} i el radical PTMMC i *J'* és la interacció entre els dos ions de Cu^{II}.

$$H | 42J(S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_4 + S_4 \cdot S_1) + 2J'(S_1 \cdot S_3) \quad (D)$$

Utilitzant el mètode de Kambe,⁶ els valors d'energia venen donats per l'equació E.

$$E | 4J \Psi_{S_T}(S_T 2 1) 4 S_{13}(S_{13} 2 1) 4 S_{24}(S_{24} 2 1) \beta 4 J' \Psi_{S_{13}}(S_{13} 2 1) \beta \quad (E)$$

, on els valors de S_{13} , S_{24} i S_T són respectivament: $S_{13}=S_1+S_3$, $S_{24}=S_2+S_4$ i $S_T=S_{13}+S_{24}$. Així, a partir d'aquesta equació i l'equació de Van Vleck, s'extreu una equació del producte $\theta \cdot T$ en funció de la temperatura, la qual es modifica tenint en compte les interaccions intermoleculars (χ) utilitzant l'aproximació del camp molecular. Tenint en compte el valor experimental de $g = 2.01$ obtingut per EPR (veure article F), el millor ajust per les dades magnètiques de **82** va donar uns valors de $J = -21.3$ K, $J' = -350.0$ K i $\chi = -1.7$ K. El valor de la interacció entre els dos ions de Cu^{II} , $J' = -350$ K, és similar als valors normalment observats en altres dímers de Cu^{II} amb la mateixa geometria.⁷ Per altra banda, la interacció magnètica entre els ions de Cu^{II} i les unitats de PTMMC, d'un valor de $J = -21.3$ K, és molt semblant a l'observat en la família de complexes mononuclears d'aquest ió metàl·lic **76-78**. Tal i com s'observa, els dos valors dels paràmetres d'acoblament són negatius, indicant que totes les espècies paramagnètiques veïnes tendeixen a alinear-se antiferromagnèticament. No obstant, s'observa que la topologia en forma de papallona que dibuixa aquest sistema provoca un fenomen de frustració d'espí degut a la presència d'interaccions antiferromagnètiques competitives.⁸

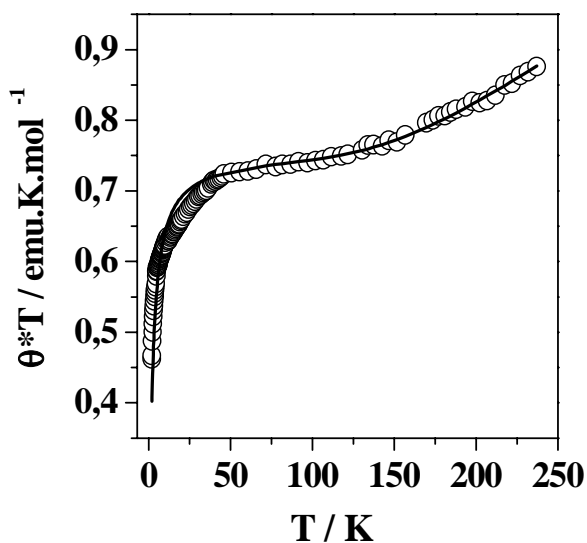
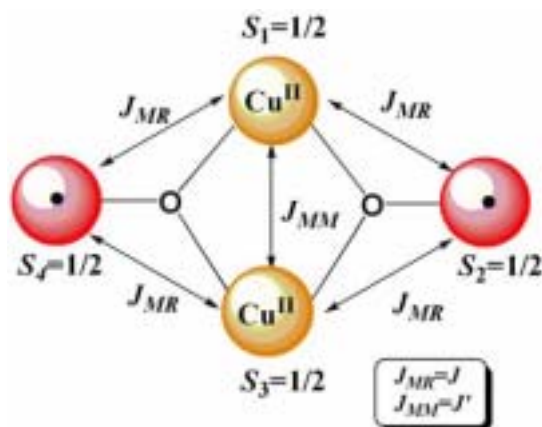


Fig. 32. Propietats magnètiques del complex **82**; producte $\theta \cdot T$ en front de T . La línia contínua indica l'ajust efectuat basant-se en l'equació teòrica per un model tipus "papallona" amb quatre espècies $S=1/2$.

2.1.2.2. $[\text{Mn}_3(\text{PTMMC})_6(\text{EtOH})_6] \cdot 6\text{EtOH}$ (**83**): un clúster trimèric de Mn^{II} ($S=5/2$).

La potencialitat del radical PTMMC per a formar clústers moleculars va quedar demostrada amb l'obtenció d'un nou clúster format per tres ions de Mn^{II} i sis radicals PTMMC. Aquest nou complex es va obtenir en mesclar a temperatura ambient acetat de Mn^{II} i PTMMC en una proporció de 1:2, respectivament. Curiosament, aquest mateix clúster es va obtenir en dues altres reaccions, efectuades de forma paral·lela. En una, es va mesclar l'acetat de Mn^{III} i el PTMMC en una proporció de 1:3 a una temperatura de 50°C. I, en l'altre, es va fer reaccionar el clúster $[\text{Mn}_{12}\text{O}_6(\text{O}_2\text{CC}_4\text{H}_9)_{16}]$ i el radical PTMMC.

Des del punt de vista estructural, aquest clúster és realment interessant, doncs està format per tres ions de Mn^{II} octaèdrics disposats en línia, els quals es troben connectats a través de grups carboxilat dels radicals PTMMC que actuen com a pont (Fig. 33). D'aquesta manera, tots els radicals PTMMC es coordinen de forma bidentada a dos ions de Mn^{II} diferents, els quals presentaran esferes de coordinació diferents segons estiguin situats al centre o als extrems del trímer lineal. Així, el ió de Mn^{II} central $[\text{Mn}(1)]$ es troba coordinat per sis grups carboxilat amb una distància $[\text{Mn}(1)\text{-O}(1)]$ de 2.154 Å, mentre que els dos ions de Mn^{II} externs $[\text{Mn}(2)]$ es troben coordinats per tres grups carboxilat amb una distància $[\text{Mn}(2)\text{-O}(2)]$ de 2.146 Å i per tres molècules d'etanol amb una distància $[\text{Mn}(2)\text{-O}(3)]$ de 2.233 Å. En aquesta disposició, els ions de Mn^{II} es troben separats amb una distància de 4.27 Å. A més, la distància entre els ions de Mn^{II} i el carboni metílic del radical PTMMC és de 8.07 Å respecte al Mn^{II} central i de 8.59 Å respecte als Mn^{II} externs.

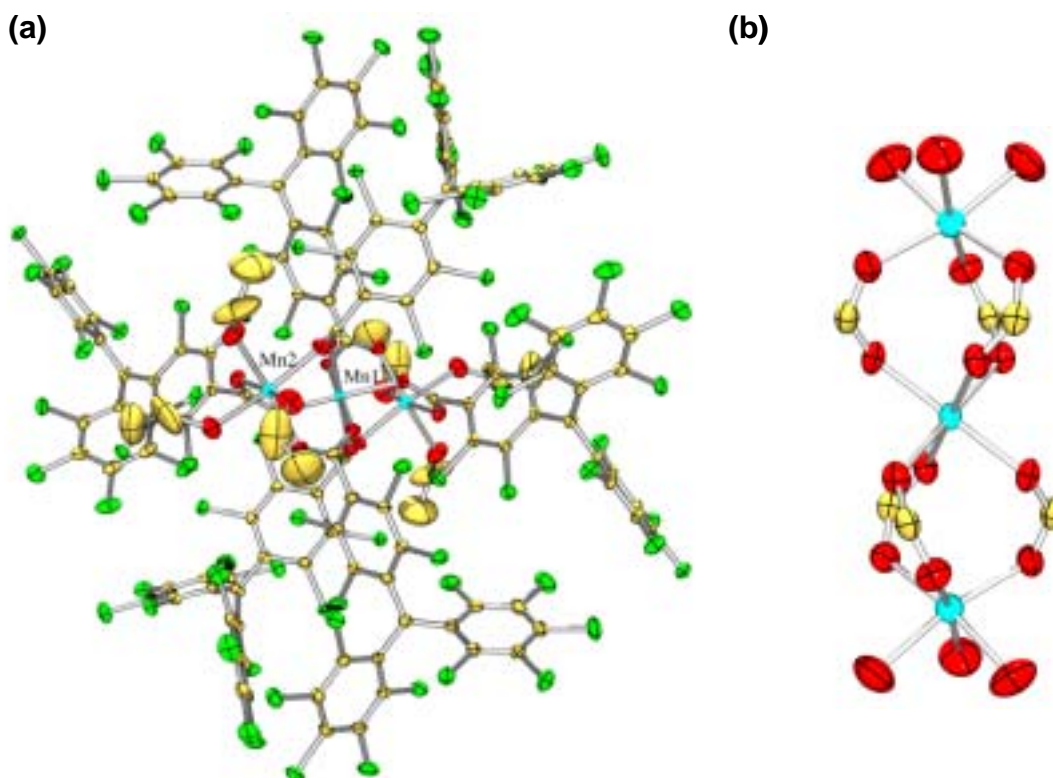


Fig. 33. Representació (a) ORTEP al 30 % de probabilitat del clúster de Mn^{II} trimèric **83**; i (b) del nucli central d'aquest clúster.

Tal i com s'ha anat succeint pels altres complexos monomèrics i el clúster dimèric, la disposició dels àtoms de clor cap a l'exterior del clúster **83** provoca un empaquetament tridimensional dominat per la presència de nombrosos contactes Cl...Cl. En concret, cada unitat de PTMMC en forma 8 (48 en el total del clúster), a través dels àtoms de clor situats als dos anells de benzè que queden exposats a l'exterior del clúster. Addicionalment, un enllaç per pont d'hidrogen C-H_(etanol)...Cl també estableix aquest empaquetament.

Les propietats magnètiques d'aquest clúster van mostrar un valor del producte $\theta \cdot T$ a 300 K de 15.713 emu·K·mol⁻¹, valor que concorda amb l'esperat per tres ions de Mn^{II} ($S=5/2$) i sis radicals PTMMC ($S=1/2$) aïllats (15.38 emu·K·mol⁻¹). A mesura que la temperatura disminueix, el valor de $\theta \cdot T$ també decreix per la presència d'interaccions antiferromagnètiques dins de cada clúster, fins arribar a un valor de 1.961 emu·K·mol⁻¹ a 1.8 K (Fig. 34). Actualment, s'estan realitzant estudis teòrics per entendre millor el comportament magnètic d'aquest sistema, per la qual cosa és aviat per extreure conclusions més detallades.

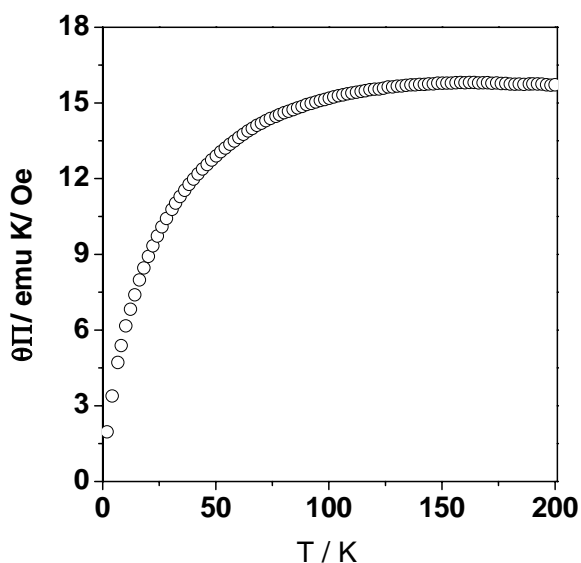
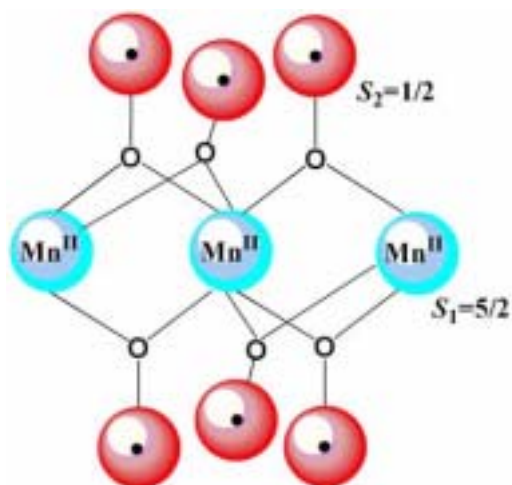


Fig. 34. Propietats magnètiques del complex **83**; producte $\theta \cdot T$ en front de T .

2.1.4. Resum i valoració dels resultats.

Els radicals PTM no s'havien utilitzat mai com a lligands orgànics en la formació de complexos de coordinació, de manera que l'obtenció d'aquesta primera família de complexos mononuclears, que constitueixen els primers exemples de sistemes metal·lorgànics basats en aquestes espècies paramagnètiques mostren que, tot i els impediments estèrics provocats pels voluminosos àtoms de clor, els radicals PTM degudament funcionalitzats són bons lligands. Aquesta circumstància origina que aquests radicals s'afegeixin a la reduïda llista de radicals orgànics emprats fins ara com a lligands, entre els quals es troben els nitròxids, els nitronil i imino nitròxids, els verdazils, els carbens i les semiquinones. A més, la simplicitat que mostren tots els complexos mononuclears obtinguts també ha permès estudiar i conèixer la interacció d'intercanvi magnètica entre aquests radicals i els diferents ions metàl·lics. S'ha determinat que aquesta interacció és de naturalesa antiferromagnètica, amb uns valors d'acoblament de l'ordre de -11 a -25 K, la qual, si bé no és tan elevada com la que presenten els nitròxids,⁹ nitronil nitròxids¹⁰ o verdazils,¹¹ sí que es pot considerar com una interacció moderadament elevada.

Paral·lelament a la síntesi d'aquests complexos, també s'ha demostrat la capacitat del radical PTMMC per formar clústers moleculars, que presentin interessants propietats magnètiques. Cal dir que, si bé en aquesta Tesi Doctoral només s'han obtingut dos exemples d'aquests sistemes, aquest és un camp molt interessant, el qual es vol explorar més intensament en un futur.

2.1.5. Referències.

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Articles relacionats amb el Subcapítol 2.1

Article E

Títol: A very bulky carboxylic perchlorotriphenylmethyl radical as a novel ligand for transition metal complexes. A new spin frustated metal system.

Autors: D. Maspoch, D. Ruiz-Molina, K. Wurst, C. Rovira, J. Veciana.

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A very bulky carboxylic perchlorotriphenylmethyl radical as a novel ligand for transition metal complexes. A new spin frustrated metal system

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Reaction of a carboxylic perchlorotriphenylmethyl radical with $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$ using different molar ratios yields two different transition metal complexes with strong intramolecular antiferromagnetic interactions, which in the case of complex **2** follows a butterfly spin frustrated model.

A great deal of work in molecular magnetism has focused on the so-called metal-radical approach that combines paramagnetic metal ions and pure organic radicals as ligating sites.¹ The electronic open-shell character of such organic ligands is particularly appealing since they are expected to interact with transition metal ions enhancing the strength of magnetic interactions. At the same time, the magnetic dimensionality of the molecular material will increase in comparison with systems made up from paramagnetic metal ions and diamagnetic coordinating ligands. However, even though a large number of metal-radical systems have been studied, the variety of radical-based ligands used up to now is fairly limited. The most extensively used family is that of nitroxide-based radicals,² although a few other examples have also been reported.^{3–5} We describe herein, for the first time, the use of perchlorotriphenylmethyl radicals to obtain complexes with paramagnetic metal ions. Among others, the main advantages of these radicals are their astonishing thermal and chemical stability and their stereochemical characteristics, with a helical (chiral) surrounding of the radical center by very bulky substituents. Here we report the first complexes of the perchlorinated monocarboxylic triphenylmethyl radical (PTMMC)⁶ with transition metals exhibiting non-conventional structural motifs and exotic magnetic behaviors. In addition, their crystal packing exhibits microporous frameworks originated by the preference to locate closely the very bulky perchlorotriphenylmethyl groups maximizing the $\text{Cl} \cdots \text{Cl}$ interactions between molecules.

Reaction of 1 eq. of $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$ with 4 eq. of PTMMC in a mixture of EtOH and H_2O at room temperature gave a high yield (89%) of a crystalline sample characterized as the complex $[\text{Cu}(\text{PTMMC})_2(\text{H}_2\text{O})_3] \cdot 6\text{H}_2\text{O} \cdot 2\text{EtOH}$ (**1**).[†] Surprisingly, complex **1** does not adopt the paddle-wheel motif with four bidentate carboxylate ligands joining two $\text{Cu}(\text{II})$ ions, characteristic of most of the copper acetate clusters. Instead, its structure consists of one $\text{Cu}(\text{II})$ ion that adopts a square pyramidal coordination polyhedron formed by two monodentate carboxylic groups and three water ligands (Fig. 1(a)). This conformation is further stabilized by strong intermolecular hydrogen bonds between non-coordinative O atoms of both carboxylate groups of PTMMC ligands and coordinated water molecules and solvent water and ethanol molecules.

The tendency to form mononuclear $\text{Cu}(\text{II})$ clusters instead of binuclear ones is attributed to the extreme steric demand of the PTMMC ligands.⁷ Indeed, due to the great steric hindrance of the chlorine atoms located at the *ortho* positions of the carboxylate group, the rotation angles (ϕ_{rot}) of the perchlorinated phenyl rings relative to the COO^- moieties are 87

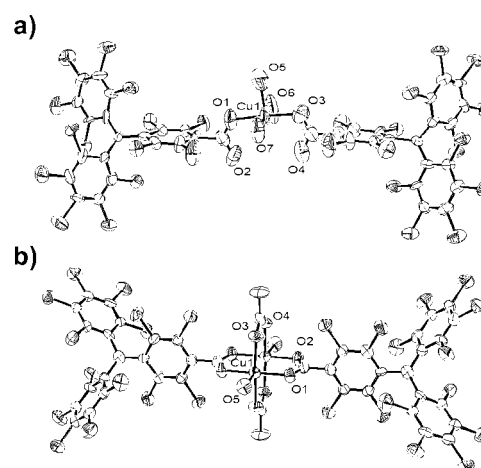


Fig. 1 ORTEP views of (a) $[\text{Cu}(\text{PTMMC})_2(\text{H}_2\text{O})_3]$ (**1**) (asymmetric unit) and (b) $[\text{Cu}_2(\text{PTMMC})_2(\text{O}_2\text{CCH}_3)_2(\text{H}_2\text{O})_2]$ (**2**).

and 89° . Such structural arrangement is expected to disrupt the formation of a binuclear complex with a paddle-wheel disposition of the four PTMMC ligands around the two $\text{Cu}(\text{II})$ units, simply due to the direct confrontation of bulky chlorine atoms of neighbouring (*syn*) PTM units. This result prompted us to control the stoichiometry of metal-radical complex by modification of the molar ratio of PTMMC in its reaction with $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$. The objective was to obtain a mixed dimeric complex with PTMMC and acetate groups. Indeed, slow addition of PTMMC over an excess of $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$ yielded (19%) a crystalline sample of complex $[\text{Cu}_2(\text{PTMMC})_2(\text{O}_2\text{CCH}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{EtOH}$ (**2**).[†] Complex **2** shows a paddle-wheel dinuclear $\text{Cu}(\text{II})$ structure, where each Cu metal ion has four O atoms of different carboxylate groups in the equatorial positions and a water molecule at the apex, completing the square pyramidal coordination geometry (Fig. 1b).

Interestingly, the crystal of complex **2** is built up by the paddle-wheel supramolecules, in such a way as to form microchannels. A view down the [001] direction reveals an

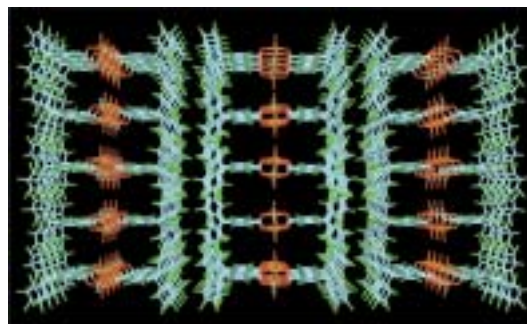


Fig. 2 View down the [001] direction of the square micropores in complex **2**.

arrangement of square microchannels stabilized by 12 chlorine–chlorine contacts ranging from 3.2 to 3.5 Å (Fig. 2). Thus, two confronted supramolecules of complex **2** along the [001] direction creates a rectangular synthon, which is partially divided in two nearly square micropores by the water ligands of both molecules. The diameter of such micropores are 7.5 and 8.0 Å, with an effective size of 4.2×4.5 Å when van der Waals radii are considered. The cavities are filled with two ethanol molecules, strongly bonded through hydrogen bonds with water and acetate ligands of molecule **2**. Similar microchannels in the [010] direction with a diameter of 8.4 and 8.1 Å (effective size 5.1×4.6 Å) are also formed in complex **1**. The channels are filled with two molecules of ethanol and six molecules of water that are disordered. The void volume of the cavities of both complexes are 2028 and 917 Å³ for **1** and **2**, respectively, which equals 28 and 24% of the unit cell volume.⁸

Variable temperature magnetic susceptibility data for a crystalline sample of complexes **1** and **2** were measured on a SQUID susceptometer (2–300 K) with an applied external field of 1 kG. The value of χT for complex **1** at 300 K (1.1 emu K mol⁻¹) (Fig. 3, left) is in excellent agreement with that expected for three non-interacting electrons (1.125 emu K mol⁻¹). Upon cooling, χT gradually decreases consistently with the presence of relatively strong antiferromagnetic interactions between the Cu(II) ion and the two coordinated PTMMC radicals. In accordance with the X-ray molecular and crystal structures, the experimental data were analyzed on the basis of a symmetrical linear three $S = 1/2$ model, modified to take into account the presence of intermolecular interactions (θ) in the molecular field approximation ($J/k_B = -23.1$ K, $\theta = -0.7$ K and $g = 2.028$).⁹

The magnetic behavior found for complex **2** differs from that reported for complex **1**. As can be seen in Fig. 3 (right), the value of χT at 300 K is 0.9 emu K mol⁻¹, which is still far from that expected for four non-interacting electrons (1.5 emu K mol⁻¹). Such a divergence is consistent with the presence of strong antiferromagnetic interactions between the Cu(II) ions and between the Cu(II) ions and the PTMMC coordinated radicals. Upon cooling, χT gradually decreases down to 70 K, where it reaches a plateau at a value of 0.7 emu K mol⁻¹. Below 30 K, the χT value abruptly decreases to 0.4 emu K mol⁻¹ at 2 K most likely due to the presence of intermolecular antiferromagnetic interactions. The data was nicely fitted to a magnetic model based on a symmetrical butterfly arrangement of the two metal ions and two organic radicals (inset of Fig. 3(b))¹⁰ modified to take into account intermolecular interactions ($\theta = -1.7$ K) in the molecular field approximation. The value of the *body/body* interaction, $J_{13} = -350$ K, is within the range of those previously reported for the same kind of interaction in other paddle-wheel Cu(II) dimers,¹¹ whereas the value of the *wing-tip/body* interaction, $J = -21.3$ K, is similar to that previously reported for the Cu(II)/PTMMC radical interaction in complex **1**. The fact that both exchange coupling parameters, J and J_{13} , are negative indicates that any two neighboring spins tend to align antiferromagnetically. However, the topological arrangement of metal ions and organic radicals in the butterfly

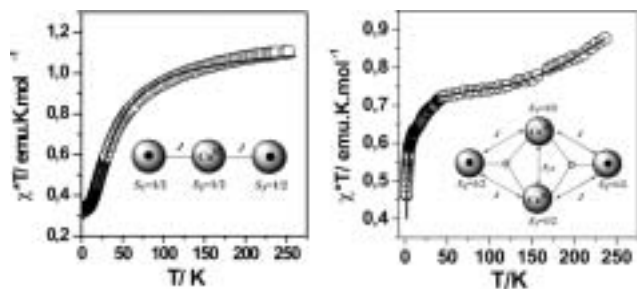


Fig. 3 Temperature dependence of the magnetic susceptibilities for complex **1** (left) and **2** (right). The solid lines were calculated as described in the text. The inset figures show the schematic arrangements of the metal ions and organic radicals.

structure results in a spin-frustration due to the presence of competing interactions. Consequently, the ground state of complex **2** is degenerated, with the following two different states, in the format (S_T, S_{13}, S_{24}), the triplet state (1,0,1) and the singlet state (0,0,0). This is one of the scarce examples of a spin-frustrated system composed of organic radicals and metal ions.¹²

In summary, we have shown that the carboxylic substituted perchlorotriphenylmethyl radical is a good coordinating ligand to obtain new complexes following the metal-radical approach. Controlling the reaction conditions, we have been able to obtain a mononuclear complex, as well as a paddle-wheel dinuclear complex exhibiting an exotic spin-frustration behaviour. Further studies to expand the range of structural motifs, structural dimensionalities and magnetic behaviours of metal-radical complexes based on polychlorinated triphenylmethyl radicals, either mono- or trifunctionalised with carboxylic groups, are currently underway.

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Notes and references

† *Crystal data for 1*: monoclinic, $P2_1/c$, $a = 25.644(4)$, $b = 15.118(3)$, $c = 18.580(3)$ Å, $\beta = 92.18(1)^\circ$, $V = 7198(2)$ Å³, $Z = 4$, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, 9744 reflections collected, 3134 independent reflections with $I > 2\sigma(I)$, $R1 = 0.071$, $wR2 = 0.168$, $\text{GOF} = 1.15$. There is a 5:1 disorder of the $\text{Cu}(\text{H}_2\text{O})_3$ unit with the coordinated Cu atom, which occurs in major part between O(1) and O(3), and in the minor part between O(2) and O(4). *Crystal data for 2*: monoclinic, $P2_1/c$, $a = 26.296(2)$, $b = 16.9040(9)$, $c = 8.5648(6)$ Å, $\beta = 93.760(3)^\circ$, $V = 3798.9(4)$ Å³, $Z = 2$, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, 12387 reflections collected, 2724 independent reflections with $I > 2\sigma(I)$, $R1 = 0.060$, $wR2 = 0.115$, and $\text{GOF} = 1.22$. Data were measured on a Nonius KappaCCD. For **1**, the structure solution was done with SHELXS86 and the refinement with SHELXL93. For **2**, SHELX97 was used. CCDC 186141 (**1**) and 186142 (**2**). See <http://www.rsc.org/suppdata/cc/b2/209884a/> for crystallographic data in CIF or other electronic format.

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Article F

Títol: Synthesis, structural and magnetic properties of a series of copper(II) complexes containing a monocarboxylated perchlorotriphenylmethyl radical as a coordinating open-shell ligand.

Autors: D. Maspoch, D. Ruiz-Molina, K. Wurst, C. Rovira, J. Veciana.

Publicació: J. Chem. Soc., Dalton Trans., en premsa.

(No presentat a la Comissió de Doctorat).

Synthesis, structural and magnetic properties of a series of copper(II) complexes containing a monocarboxylated perchlorotriphenylmethyl radical as a coordinating open-shell ligand.

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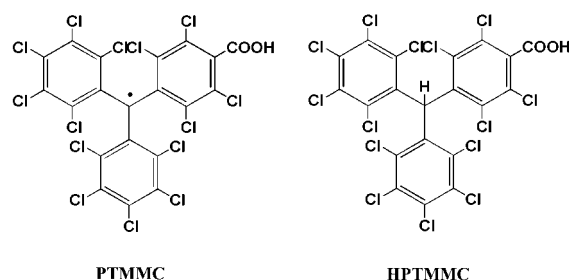
A series of complexes of copper(II)-containing a perchlorotriphenylmethyl radical properly functionalized with a carboxylic group as a new ligand is reported. The compounds [Cu(PTMMC)₂(L)₃] (PTMMC = (tetradechloro-4-carboxytriphenyl)methyl radical; L = (1) H₂O, (2) pyrimidine and ethanol or (3) pyridine), [Cu₂(PTMMC)₂(MeCOO)₂(H₂O)₂] (4) and [Cu(HPTMMC)₂(L)₃] (HPTMMC = αH-(tetradechlorotriphenyl)methane-4-carboxylic acid; L = pyridine) (5) were structurally characterized. In complexes **1**, **2**, **3** and **5**, the copper(II) ion is coordinated to two PTMMC (or HPTMMC) units in a slightly distorted square planar surrounding, while **4** shows a paddle-wheel copper(II) dimer structure, where each Cu metal ion has four O atoms of different carboxylate groups, two of them belonging to two PTMMC radicals. The copper(II)-radical exchange couplings are antiferromagnetic for complexes **1**, **2** and **3**. A linear three-spin model was applied to such complexes to give $J/k_B = -24.9$ K, $J/k_B = -15.0$ K and $J/k_B = -20.7$ K, respectively. Magnetic properties of **4** show that it is one of the scarce examples of a spin-frustrated system composed of organic radicals and metal ions. In this case, experimental data were fitted to a magnetic model based on a symmetrical butterfly arrangement to give a copper(II)-copper(II) exchange coupling of $J/k_B = -350.0$ K and a copper(II)-radical exchange coupling of $J/k_B = -21.3$ K, similar to that observed for the copper(II)-radical interactions in complexes **1**, **2** and **3**.

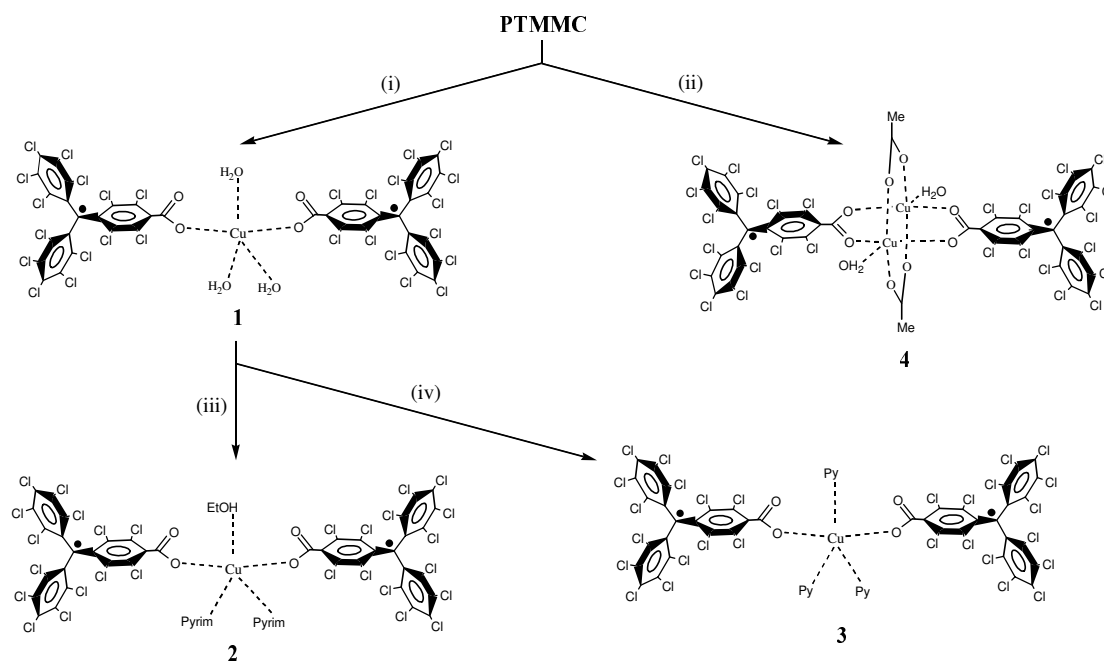
Introduction

The design and synthesis of molecular-based magnetic materials is a major focus of molecular materials research. One of the more promising strategies is the so-called metal-radical approach that combines paramagnetic metal ions and pure organic radicals as ligating sites.¹ The electronic open-shell character of such organic ligands is particularly appealing since they are expected to interact with transition metal ions enhancing the strength of magnetic interactions and increasing the magnetic dimensionality of the molecular material in comparison with systems made up from paramagnetic metal ions and diamagnetic coordinating ligands. However, even though a large number of metal-radical systems have been studied, the variety of radical-based ligands used up to now is fairly limited. Among them, one of the most extensively used families is that of nitroxide-based radicals, namely nitroxides and α-nitronyl or imino nitroxides radicals.²⁻⁵ Besides nitroxide-based radicals, other examples of open-shell ligands used up to now are: 1) derivatives of the verdazyl radical family, which turned to be very attractive because of their abundance of donor atoms and efficiency in transmitting magnetic interactions;⁶ 2) o-quinone ligands that can be found in different accessible oxidation states, including the radical semiquinones;⁷ 3) TCNE and TCNQ radical anions⁸ and 4) diphenylcarbenes substituted with chemical function able to coordinate with metal ions.⁹

Following this metal-radical approach, our group has recently initiated a scientific project focalized in the use of a perchlorinated triphenylmethyl (PTM) radicals properly functionalized with one carboxylic group, PTMMC, as new ligating sites to build magnetic molecular materials. Among others, the main advantages of these radicals are their astonishing thermal and chemical stability and their stereochemical characteristics, with a helical (chiral) surrounding of the radical center by very bulky substituents. Up to now, it has been demonstrated that the supramolecular self-assembly of PTMMC in the solid state forms hydrogen-bonded dimeric motifs that promote the presence of ferromagnetic

interactions.¹⁰ Herein, we present the controlled synthesis, crystal structures analysis, spectroscopic characterization and magnetic properties of a new family of Cu(II) complexes using the perchlorinated triphenylmethyl radical PTMMC as a new ligand.¹¹ More specifically, we report a monomeric Cu(II) complex [Cu(PTMMC)₂(H₂O)₃].6H₂O.2EtOH, **1**, in which its magnetic properties shows a relatively strong exchange coupling constant between the metal ion and the radical ligand. This result confirms that carboxylic-based PTM radicals could act as excellent ligands for the design of new magnetic complexes following the metal-radical approach. With the simple modification of the auxiliary ligands of **1**, two new monomeric complexes, [Cu(PTMMC)₂(pyrimidine)₂(EtOH)].THF.4EtOH, **2**, and [Cu(PTMMC)₂(py)₃].2.5*n*-hexane, **3**, have been synthesized. Structurally, the bulkiness of these ligands has significant implications for their microporous crystal packing. Furthermore, the simple modification of the stoichiometry of the initial reaction for obtaining **1** gives a paddle-wheel Cu(II) complex [Cu₂(PTMMC)₂(MeCOO)₂(H₂O)₂].4EtOH, **4**. Its magnetic behavior can be understood as a spin-frustrated system. Finally, the possibility to work with the non-radical analogous of PTMMC, the hydrogentaetd form HPTMMC, allow us to synthesize the non-radical Cu(II) complex [Cu(HPTMMC)₂(py)₃].4THF, **5**, for comparison purposes. Its condition of isostructurality with respect to **3** highlights the magnetic interactions between radical PTMMC and Cu(II) ions.





Scheme 1 Schematic synthesis of PTMMC-based complexes. Conditions and reagents: (i) PTMMC / $\text{Cu}_2(\text{O}_2\text{CMe})_4 \cdot 2\text{H}_2\text{O}$ (4:1) in EtOH/ H_2O ; (ii) PTMMC / $\text{Cu}_2(\text{O}_2\text{CMe})_4 \cdot 2\text{H}_2\text{O}$ (2:1) in EtOH/ H_2O ; (iii) **1** / excess of pyrimidine (pyrim) in EtOH/*n*-hexane and THF; and (iv) **1** / excess of pyridine (py) in EtOH/*n*-hexane and THF.

Results and discussion

A. Synthesis.

Complex **1** was synthesized in an initial reaction of copper acetate monohydrate and PTMMC in a solution of ethanol and water in high yields (89%). Hence, high-quality crystals of **1** suitable for single crystal X-ray diffraction analysis, were obtained by slow evaporation of the reaction liquors. Afterward, slow diffusion of an excess of pyrimidine (or pyridine) in a solution of ethanol/*n*-hexane into a solution of **2** in THF allowed to prepare complexes **2** and **3**. In both complexes the auxiliary water ligands of **1** were replaced by pyrimidine and ethanol in **2** and by pyridine in **3** (Scheme 1). Crystals suitable for single crystal X-ray diffraction were isolated directly from the diffusion method. Surprisingly, the crystal structure analysis showed that **1-3** do not adopt the paddle-wheel motif with four bidentated carboxylate ligands joining two Cu(II) ions, characteristic of most of the copper acetate clusters. The tendency to form mononuclear Cu(II) clusters instead of binuclear ones is attributed to the extreme steric demand of the molecules of PTMMC radical.¹² Indeed, due to the great steric hindrance of the chlorine atoms located at the *ortho* positions of the carboxylate group, the rotation angles of the polychlorinated phenyl rings relative to the COO^- moieties in **1-3** are in the range of 79° to 89° . Such a structural arrangement is expected to disrupt the formation of a binuclear complex with a paddle-wheel disposition of the four molecules of PTMMC around the two Cu(II) units, simply due to the direct confrontation of bulky chlorine atoms of neighboring (*syn*) radicals. This result prompted us to control the stoichiometry of metal-radical complex by the modification of the molar ratio of PTMMC in its reaction with $\text{Cu}_2(\text{O}_2\text{CMe})_4 \cdot 2\text{H}_2\text{O}$ since this may lead to the formation of a mixed dimeric complex with PTMMC and acetate groups. Indeed, slow addition of PTMMC radical over an excess of $\text{Cu}_2(\text{O}_2\text{CMe})_4 \cdot 2\text{H}_2\text{O}$ in a mixture of EtOH and H_2O at room temperature yielded a crystalline sample of complex **4**. Finally, crystals of **5** were obtained in a similar synthetic methodology as for the monomeric PTM-based complexes. Thus, an *n*-hexane solution of pyridine was diffused into a THF solution of the solid

isolated by filtration from the reaction of copper acetate monohydrate with an ethanolic solution of HPTMMC.

B. Spectroscopic properties.

The infrared spectra of **1-4** exhibit the typical vibrational modes attributed to PTM radicals. Indeed, in such PTM-based complexes, the benzenic peaks appear at 1509 and $1380\text{-}1300$ cm^{-1} , due to the highly chlorinated character of PTMMC units. Furthermore, the typical peak corresponding to the PTM moieties is found around 730 cm^{-1} .¹³ More information of these complexes can be extracted from the stretching peaks produced by the carboxylate groups. Thus, a detailed analysis of the infrared spectra of **1-3** indicates the presence of the antisymmetric COO stretching frequency around $1600\text{-}1620$ cm^{-1} , while the symmetric COO stretching frequency appears at $1410\text{-}1400$ cm^{-1} . Thus, a relatively large splitting of the COO stretching frequencies ($200\text{-}225$ cm^{-1}) is observed, being an indication a monodentate coordination.¹⁴ By contrast, the infrared spectrum of the paddle-wheel complex **4** shows a lower value of this splitting since the antisymmetric COO stretching frequency appears at 1607 cm^{-1} and the symmetric one at 1417 cm^{-1} .

The electronic absorption spectra recorded in the UV-visible region in pure THF also exhibits the absorptions corresponding to PTM radicals. Thus, the electronic absorption spectrum of **1-3** show the typical four bands, named as A, B, C and D, around 222 ($\epsilon \sim 160000$), 290 ($\epsilon \sim 17000$), 385 ($\epsilon \sim 65000$) and 500 ($\epsilon \sim 2500$) nm (Fig 1), respectively.¹⁵ Among them, C and D bands are associated with the radical character of PTMMC ligand, while the other two are the primary and secondary (1L_b) bands characteristic of substituted benzene units of such a ligand. No additional bands, that could be assigned to a radical-to-metal charge-transfer phenomenon, were observed.

As occurs in the above-described radical-based complexes, the non-radical complex **5** shows identical infrared and electronic spectrum than its precursor HPTMMC. Thus, the characteristic peak of non-radical PTM derivatives appears at 804 cm^{-1} .¹⁰ The electronic spectrum shows the presence of the primary band characteristic of substituted benzenes around 223 nm ($\epsilon \sim 265000$).

Table 1 Crystal data and structure refinement for complexes 1-5.

	1	2	3	4	5
Empirical formula	CuC ₄₄ Cl ₂₈ O ₁₅ H ₃₀	CuC ₆₂ Cl ₂₈ O ₁₀ N ₄ H ₄₆	CuC ₇₀ Cl ₂₈ O ₄ N ₃ H ₅₀	Cu ₂ C ₅₂ Cl ₂₈ O ₁₄ H ₃₄	CuC ₇₁ Cl ₂₈ O ₈ N ₃ H ₄₉
Formula weight	1854.82	2063.17	2053.27	2002.47	2128.27
T/K	223(2)	293(2)	223(2)	223(2)	293(2)
$\lambda/\text{\AA}$	0.71069 (Mo K α)	0.71069 (Mo K α)	0.71069 (Mo K α)	0.71069 (Mo K α)	0.71069 (Mo K α)
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	P2 ₁ /c	P-1	P-1	P2 ₁ /c	P-1
<i>a</i> /\AA	25.644(4)	16.2920(1)	8.774(1)	26.296(2)	8.8122(3)
<i>b</i> /\AA	15.118(3)	16.5722(8)	14.332(1)	16.9040(9)	14.3777(6)
<i>c</i> /\AA	18.580(3)	17.9520(1)	17.379(2)	8.5648(6)	17.4037(7)
α°	90	97.986(4)	84.411(6)	90.00	93.852(2)
β°	92.18(1)	102.953(4)	79.880(4)	93.760(3)	100.012(2)
γ°	90	115.831(4)	87.933(6)	90.00	90.004(2)
<i>V</i> /\AA ³	7198.(2)	4094.1(4)	2140.8(4)	3798.9(4)	2166.4(2)
Z	4	2	1	2	1
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.712	1.674	1.593	1.751	1.631
μ/mm^{-1}	1.399	1.236	1.177	1.601	1.169
F(000)	3676	2062	1028	1984	1065
Crystal size/mm	0.30 x 0.25 x 0.03	0.31 x 0.24 x 0.11	0.29 x 0.16 x 0.14	0.20 x 0.15 x 0.02	0.30 x 0.15 x 0.09
θ range/ $^\circ$	1.56-19.00	1.21-22.00	1.20-22.00	1.43-19.75	1.19-22.49
<i>hkl</i> range	-24/0, -14/13, -16/17	0/17, -17/15, -18/18	0/9, -15/15, -18/19	0/24, -16/16, -8/8	0/9, -15/15, -18/18
Reflections collected	9744	17838	8337	12387	10847
Independent reflections	4617	9965	4972	3413	5663
Parameters	754	894	503	444	506
GOF	1.049	1.049	1.044	1.218	1.104
$R^{\text{[a]}}$, $I > 2\sigma(I)$	7.07	6.68	4.84	5.95	7.72
$R_w^{\text{[b]}}$, $I > 2\sigma(I)$	16.78	18.96	11.54	11.47	21.36
Largest diff. Peak/e nm ⁻³	561, -350	921, -637	321, -452	298, -325	517, -542

^a $R = \sum |F_0 - F_c| / \sum |F_0|$, ^b $R_w = [(\sum w(|F_0 - F_c|)^2) / \sum w F_0^2]^{1/2}$

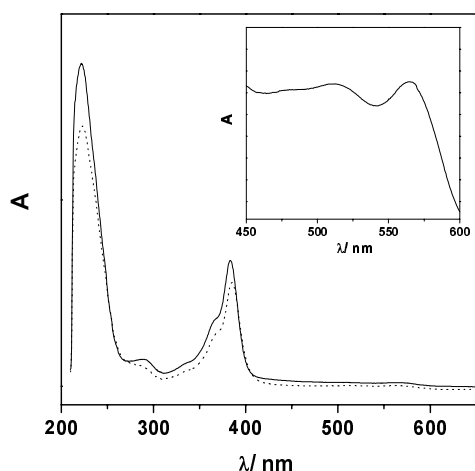


Fig. 1 Electronic absorption spectra of PTMMC radical (dash line) and complex 3 (continuous line).

C. X-Ray crystal structures.

The molecular and crystal structures of 1-5 were investigated by X-ray single crystal analysis. Crystallographic data and experimental parameters for all complexes are summarized in Table 1. Selected bond lengths and angles for metal complexes are given in Table 2. Structural disorder analysis of complexes 1-3 and 5 is described in the Experimental Section.

(i) [Cu(PTMMC)₂(H₂O)₃]·6H₂O·2EtOH, 1. Complex 1 crystallizes in the P2₁/c monoclinic space group with the cell

parameters reported in Table 1. An ORTEP drawing for the metal-radical cluster, formed by two PTMMC molecules and one Cu(II) ion, is shown in Figure 2. The Cu(II) ion displays a square pyramidal coordination geometry by binding to the two oxygen atoms of two distinct PTMMC ligands and the three oxygen atoms of water molecules acting as auxiliary ligands. The Cu-O1(carboxylate) and Cu-O3(carboxylate) distances are respectively 1.967(14) and 1.99(2) Å, so that the PTMMC anion is unidentate with the copper(II) ion. Due to the great steric hindrance of the chlorine atoms in *ortho* positions with respect to the carboxylate group in PTMMC, the latter groups are twisted by angles of 87° and 89° with respect to the phenyl plane to which they are bonded. Furthermore, the O1-Cu-O3 angle is 175.4(9)°, which draw a linear system of the three electronic open-shell units (*S*=1/2) with distances of 8.43 and 8.34 Å between the copper(II) ion and the central carbon of both PTMMC ligands, where most of the spin density is localized. The two central carbon atoms of PTMMC ligands are separated by 16.56 Å.

The self-assembly of metal-radical clusters in 1, probably steered by chlorine-chlorine contacts, generates large micropores along the [010] direction. Thus, each metal-radical cluster interacts through 16 different chlorine-chlorine contacts (3.60 and 3.25 Å) with its neighbouring clusters, building a three

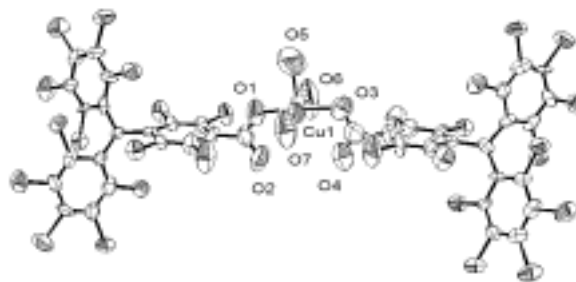
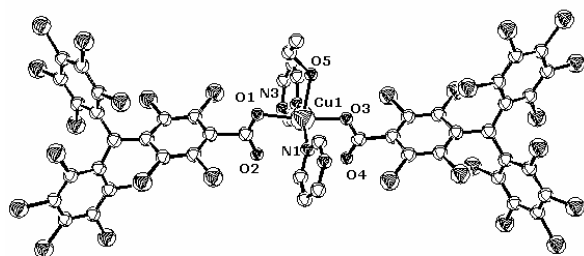


Fig. 2 ORTEP drawing of metal-radical clusters of 1 at the 50% probability level.

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1-5**.

1		2		3	
Cu(1)-O(1)	1.967(14)	Cu(1)-O(1)	2.068(8)	Cu(1)-O(1)	1.976(5)
Cu(1)-O(3)	1.99(2)	Cu(1)-O(3)	1.926(6)	Cu(1)-O(2a)	2.147(5)
Cu(1)-O(5)	2.16(12)	Cu(1)-N(1)	2.080(11)	Cu(1)-N(1)	2.184(10)
Cu(1)-O(6)	2.05(7)	Cu(1)-N(3)	1.981(8)	Cu(1)-N(2)	2.334(11)
Cu(1)-O(7)	2.27(9)	Cu(1)-O(5)	2.236(15)	Cu(1)-N(1a)	2.087(9)
O(1)-Cu(1)-O(3)	175.4(9)	O(1)-Cu(1)-O(3)	169.7(3)	O(1)-Cu(1)-O(2a)	158.2(2)
O(1)-Cu(1)-O(5)	92.3(8)	O(1)-Cu(1)-N(1)	88.8(3)	O(1)-Cu(1)-N(1)	89.1(2)
O(3)-Cu(1)-O(5)	92.2(8)	O(3)-Cu(1)-N(1)	86.7(3)	O(2a)-Cu(1)-N(1)	91.1(2)
O(1)-Cu(1)-O(6)	88.9(7)	O(1)-Cu(1)-N(3)	93.4(3)	O(1)-Cu(1)-N(2)	80.0(3)
O(3)-Cu(1)-O(6)	89.8(7)	O(3)-Cu(1)-N(3)	94.3(3)	O(2a)-Cu(1)-N(2)	79.8(3)
O(5)-Cu(1)-O(6)	95.1(12)	N(1)-Cu(1)-N(3)	157.9(5)	N(1)-Cu(1)-N(2)	112.7(5)
O(1)-Cu(1)-O(7)	89.2(6)	O(1)-Cu(1)-O(5)	87.8(5)	O(1)-Cu(1)-N(1a)	97.0(2)
O(3)-Cu(1)-O(7)	91.1(7)	O(3)-Cu(1)-O(5)	83.7(5)	O(2a)-Cu(1)-N(1a)	97.0(3)
O(5)-Cu(1)-O(7)	97.7(11)	N(1)-Cu(1)-O(5)	98.3(6)	N(1)-Cu(1)-N(1a)	139.4(2)
O(6)-Cu(1)-O(7)	167.1(11)	N(3)-Cu(1)-O(5)	103.8(6)	N(2)-Cu(1)-N(1a)	107.9(5)
4		5			
Cu(1)-O(1)	1.971(7)	Cu(1)-O(1)	2.288(11)		
Cu(1)-O(2)	1.964(7)	Cu(1)-O(2a)	1.978(7)		
Cu(1)-O(3)	1.954(7)	Cu(1)-N(1)	2.110(17)		
Cu(1)-O(4)	1.950(7)	Cu(1)-N(2)	2.340(16)		
Cu(1)-O(5)	2.102(8)	Cu(1)-N(1a)	2.070(12)		
O(1)-Cu(1)-O(2)	168.1(3)	O(1)-Cu(1)-O(2a)	152.4(4)		
O(1)-Cu(1)-O(3)	90.1(3)	O(1)-Cu(1)-N(1)	98.4(4)		
O(1)-Cu(1)-O(4)	88.2(3)	O(2a)-Cu(1)-N(1)	93.9(4)		
O(1)-Cu(1)-O(5)	97.2(4)	O(1)-Cu(1)-N(2)	69.7(5)		
O(2)-Cu(1)-O(3)	91.5(3)	O(2a)-Cu(1)-N(2)	83.1(5)		
O(2)-Cu(1)-O(4)	87.7(3)	N(1)-Cu(1)-N(2)	107.7(7)		
O(2)-Cu(1)-O(5)	94.3(4)	O(1)-Cu(1)-N(1a)	92.1(4)		
O(3)-Cu(1)-O(4)	167.6(3)	O(2a)-Cu(1)-N(1a)	90.4(2)		
O(3)-Cu(1)-O(5)	98.2(3)	N(1)-Cu(1)-N(1a)	147.9(2)		
O(4)-Cu(1)-O(5)	94.2(3)	N(2)-Cu(1)-N(1a)	104.4(8)		

dimensional network of such type of supramolecular interactions. Two confronted metal-radical clusters create a rectangular synthon, which is partially divided in two nearly square micropores, which are separated by the theoretical wall formed by the water ligands O5 of both complexes (Fig 4). The Cu-Cu distance in this configuration is 9.33 Å and the dimensions of micropores are 8.4 Å and 8.1 Å, with an effective size of 5.1 x 4.6 Å, when van der Waals radii are considered. The cavities are filled with water and ethanol molecules, which all of them are bonded through hydrogen bonds between themselves and between water ligands and the PTMMC carboxylate groups. The void volume of the cavities are 2028 Å³, which equals 28% of the unit cell volume.¹⁶


Fig. 3 ORTEP drawing of metal-radical clusters of **2** at the 50% probability level.

(ii) [Cu(PTMMC)₂(pyrimidine)₂(EtOH)]·THF·4EtOH, **2**. In complex **2**, molecules crystallize in the P-1 triclinic space group with cell parameters given in Table 1. An ORTEP drawing of **2** is shown in Figure 3. The coordination geometry of metal-radical clusters around Cu(II) ion is a distorted square pyramidal in which the Cu(II) is coordinated to the two oxygen atoms of two PTMMC, two nitrogen atoms of pyrimidine molecules and one oxygen atom of an ethanol molecule. As occurs in **1**, two molecules of PTMMC are coordinated to one Cu(II) ion through one oxygen atom of their carboxylate group, which are twisted by angles of 80° and 81° with respect to the phenyl plane to which they are bonded. The distances Cu-O1(carboxylate) and Cu-O3(carboxylate) are 2.068(8) and 1.926(6) Å and the O1-Cu-O3 angle is 169.7(3)°. Moreover, the distances between the Cu(II) ion and the central carbon of PTMMC are 8.48 and 8.33 Å and the distance between the two central carbon atoms of bonded PTMMC units are 16.72 Å.

Crystal packing of the metal-radical clusters of **2** also forms micropores stabilized through 16 chlorine-chlorine contacts in the range of 3.47 Å and 3.33 Å. In this case, four molecules of **2** form repetitive rectangular micropores, where molecules of ethanol are not confronted in comparison with water molecules of **1**. Due to the bulky nature of ethanolic and pyrimidine molecules, compared with water molecules, **2** can not adopt the same topology of **1**. Indeed, while the PTMMC moieties are confronted in **1**, these units experimented a displacement along the [0-11] direction in **2**. To illustrate this displacement, the Cu-Cu distance between to opposite walls, which forms such micropores, is 15.33 Å. The differences of the self-assembly of **1** and **2** are shown in Figure 4. This new arrangement creates rectangular micropores with dimensions of 10.7 Å and 5.9 Å,

with an effective size of $7.3 \times 3.0 \text{ \AA}$. Furthermore, such micropores are stabilized through additional π - π interactions between the chlorinated rings, which form their walls. The cavities are filled with ethanol and THF molecules. The void volume of the cavities are 1142 \AA^3 , which equals 28% of the unit cell volume.¹⁶

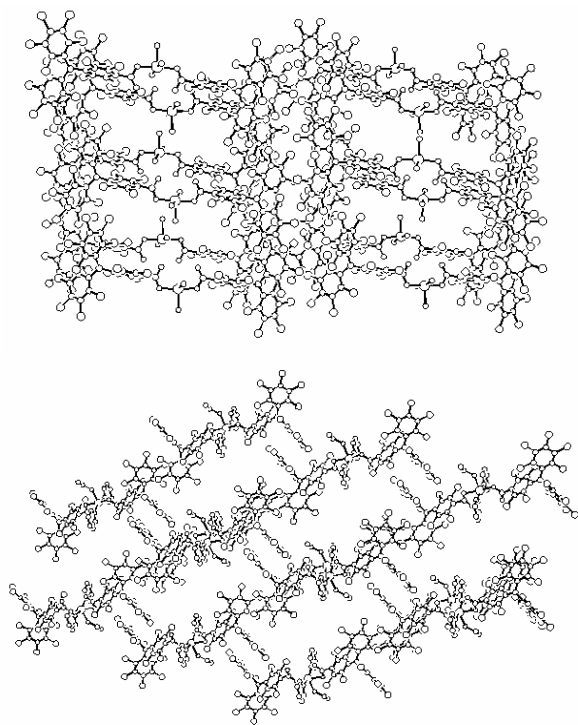


Fig 4 Crystal packing of **1** (top) and **2** (down). Water and ethanol for **1** and THF and ethanol solvent molecules for **2** have been omitted for clarity.

(iii) **[Cu(PTMMC)₂(py)₃]**·2.5hexane, **3** and **[Cu-(HPTMMC)₂(py)₃]**·4THF, **5**. The molecular structures of **3** and **5** are similar to that of **2**, but with three pyridine molecules instead of the two pyrimidine molecules and one molecule of ethanol. ORTEP drawings of metal-radical clusters present in both structures are shown in Figure 5. As for **2**, the Cu(II) ion displays a distorted square pyramidal coordination geometry by binding to the two oxygen atoms of two molecules of PTMMC (or HPTMMC) and the three nitrogen atoms of pyridine molecules. The carboxylate groups of PTMMC and HPTMMC moieties are twisted by angles of 79° in **3** and 86° in **5** with respect to the phenyl plane to which they are bonded. In complex **3** the distance between the Cu(II) ion and the central carbon atom of the PTMMC moieties are 8.47 and 8.33 \AA and the distance between the two units of PTMMC are 16.72 \AA ; values that are close to those found for complex **2**.

The self-assembly of metal-radical clusters of **3** and **5** is also similar to that of **2**, forming rectangular pores stabilized through 12 and 16 chlorine-chlorine contacts, respectively, with distances in the range of 3.46 \AA and 3.32 \AA , occurring along the three directions. Such channels are filled of *n*-hexane in **3** and THF molecules in **5**. The void volume of the cavities are 632 \AA^3 , which equals 30% of the unit cell volume.¹⁶

(iv) **[Cu₂(PTMMC)₂(MeCOO)₂(H₂O)₂]**·4EtOH, **4**. Complex **4** crystallizes in the $P2_1/c$ monoclinic space group with the cell parameters reported in Table 1. The crystal structure of **4** shows a paddle-wheel Cu(II) dimer structure, where each Cu metal ion

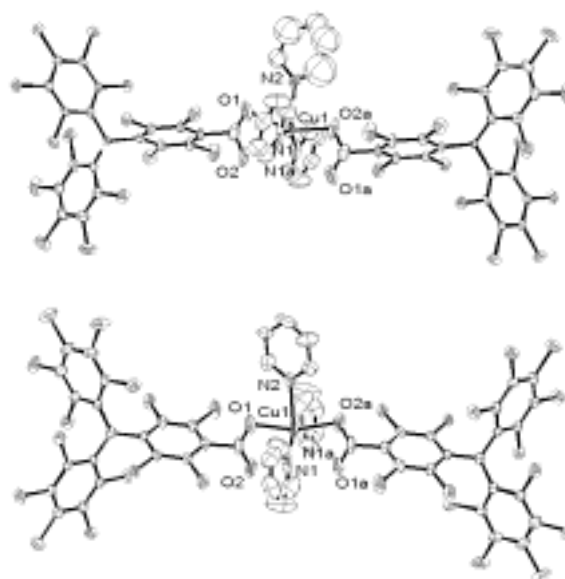


Fig. 5 ORTEP drawing of metal-radical clusters of **3** (top) and **5** (down) at the 30% probability level.

has four O atoms of different carboxylate groups in the equatorial positions, with distances in the range of 1.950-1.971 \AA , and a water molecule at 2.102 \AA at the apex, completing the square pyramidal coordination geometry (Fig 6). Two of the O atoms situated at the opposite sites in the base of the square pyramid belong to two different PTMMC ligands, while the other two belongs to two distinct acetate groups. The end-to-end distance of such metal-radical paddle-wheel supramolecules is 26 \AA .

The crystal packing is built up by the self-assembly of such supramolecules in such a way as to form microchannels. A view down in the *c* direction reveals an arrangement of square microchannels stabilized by 12 chlorine-chlorine contacts (Fig. 6). Thus, two confronted supramolecules along the *c* direction

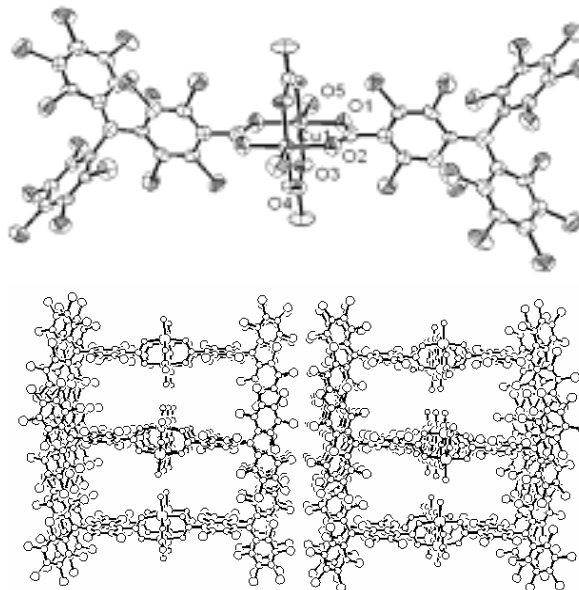


Fig 6 ORTEP plot at the 50% probability level of metal-radical supermolecule (top) and a view of the crystal packing of **4** along the *c* axes (down). Ethanol solvent molecules have been omitted for clarity.

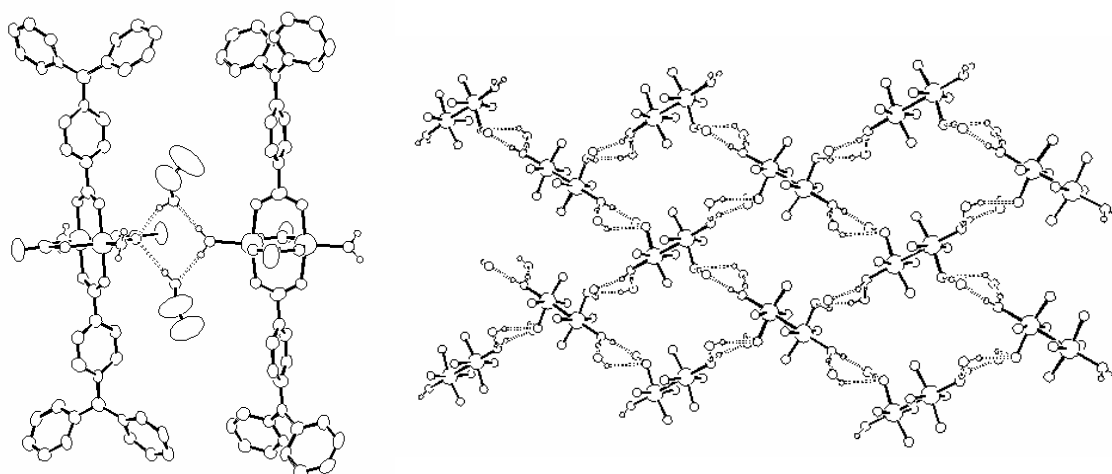


Fig 7 Hydrogen-bonded cyclic pattern formed by two molecules of **4** and two ethanol solvent molecules (left). Two-dimensional hydrogen-bonded layer along the *bc* plane (right). Chlorine atoms (left) and chlorine and carbon atoms (right) have been omitted for clarity.

creates a rectangular synthon, which is partially divided in two nearly square micropores, which are separated by a wall formed by the water ligands of both molecules. The dimensions of such a micropore are 7.5 Å and 8.0 Å, with an effective size of 4.2 x 4.5 Å when van der Waals radius are considered. The void volume are 917 Å³, which equals 24% of the unit cell volume.¹⁶ The cavities are filled with ethanol molecules, strongly bonded through hydrogen bonds with the water and acetate ligands of **4** (Table 3). More in detail, such hydrogen bonds generate a primary hydrogen-bonded cyclic motif between two molecules of ethanol and two molecules (Fig 7). In a parallel way, four of these cyclic motifs are hydrogen-bonded to create a bigger cyclic pattern composed of four ethanol solvent molecules and four molecules of **4**, which are extended along the *ab* plane generating a two-dimensional hydrogen-bonded network (Fig 7).

C. Electrochemical Properties.

Cyclic voltammograms of radical PTMMC and complexes **1-3** were done in THF at room temperature with nBu₄NPF₆ (0.1M) as supporting electrolyte (vs Ag/AgCl) and a Pt wire as a working electrode. While radical PTMMC showed only one reversible wave at +0.09 V, assigned to the one-electron

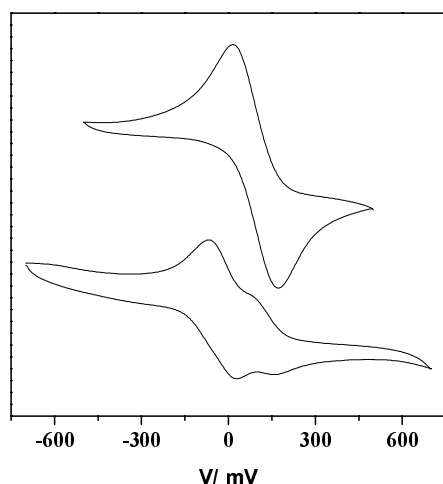


Fig 8 Cyclic voltammograms of PTMMC radical (top) and **1** (down) in THF.

reduction of the triphenylmethyl unit, all these complexes revealed two one-electron reversible waves. One of such waves corresponds to the reduction of the perchlorotriphenylmethyl radical ligands (~ 0 V) and the other to the reduction of Cu(II) ion (~ 0.1 V) (Fig. 8). The reversible waves were observed at -0.02 and 0.12 V for **1**, -0.03 and 0.13 V for **2**, and at -0.03 and 0.10 V for **3** (vs Ag/AgCl).

Table 3 Details of the hydrogen bonding distances (Å) and angles (°) of complex **4**

D-H...A	H...A ^a	D...A ^a	D-H...A ^b
O(5)-H(5A)...O(7)	1.94	2.73	154
O(5)-H(5B)...O(6)	1.89	2.74	175
O(6)-H(6)...O(4)	2.18	2.95	153
O(7)-H(7)...O(4)	2.47	3.09	132

D. Magnetic Properties.

The molar paramagnetic susceptibility data of crystalline samples of **1-5** were obtained with a SQUID magneto/susceptometer in the temperature range 2-300 K at a constant field of 0.1T using Pascal constants to calculate the diamagnetic contributions. The results are displayed in the form of the product of the molar paramagnetic susceptibility (χ_{mol}) with the temperature (T) versus the temperature. The principal components of g tensors of PTM-based complexes **1-5** (g_1 , g_2 , g_3) were determined by simulation of EPR spectra of powdered, crystalline samples (see Experimental Section), and then the averaged g values [$g_{av} = (g_1+g_2+g_3)/3$] used in the theoretical calculation, as fixed values .

(i) [Cu(PTMMC)₂(H₂O)₃]-6H₂O-2EtOH, **1**, [Cu(PTMMC)₂(pyrimidine)₂(EtOH)]·THF·4EtOH, **2** and [Cu(PTMMC)₂(py)₃]-2.5*n*-hexane, **3**. Similar magnetic behavior was observed for complexes **1-3** (Fig 9). A χT value of 1.12 emu·K·mol⁻¹ was obtained at 300 K, which is close to the theoretical one ($\chi T = 0.12505 \cdot g \cdot 2[3S(S+1)] = 0.12505 \cdot 2 \cdot 2[3/2(1/2+1)] = 1.13$ emu·K·mol⁻¹) expected for three isolated S = 1/2 spins in terms of the spin-only equation. As the temperature was decreased, the χT value also decreased until a value of 0.32 emu·K·mol⁻¹, corresponding to a S=1/2 doublet fundamental state. The resulting χT vs T curves for **1-3** were analyzed quantitatively on the basis of a linear three-spin model (Scheme 2), using the following effective Hamiltonian, $H = -2J(S_{R1}S_M+S_M S_{R2})$, modified to take into account the presence of intermolecular interactions (θ) in the molecular field

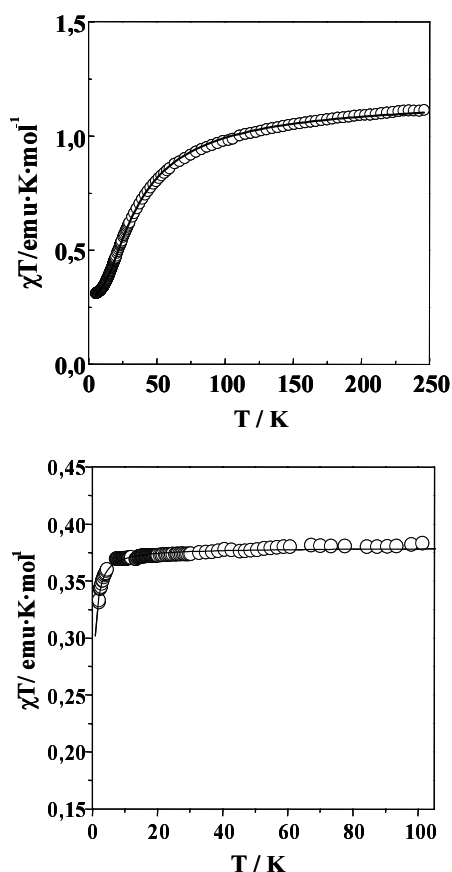


Fig. 9 Temperature dependence of the product of the magnetic susceptibilities and the temperature for complexes **3** (top) and **5** (down).

approximation.¹⁷ This model is in accordance with the X-ray molecular and crystal structure analysis previously described. Equation 1 for a system with $S_{R1}=S_{R2}=S_M=1/2$ was applied and fitted to the observed χT vs T plots by means of a least-square method.

$$\chi T = \frac{N\mu_B^2 g^2 T}{3k_B(T - \Theta)} \frac{60e^{3J/T} + 6e^{2J/T} + 6}{4(4e^{3J/T} + 2e^{2J/T} + 2)} \quad (1)$$

Fixing the evaluated g values, the resulting parameters for the best fits were $J/k_B = -24.9 \pm 0.3$ K and $\Theta = -0.68 \pm 0.05$ K for **1**, $J/k_B = -15.0 \pm 0.1$ K and $\Theta = -0.45 \pm 0.02$ K for **2**, and $J/k_B = -20.7 \pm 0.1$ K and $\Theta = -1.70 \pm 0.03$ K for **3**. Thus, the values of the copper(II)-radical exchange coupling constants for all complexes were very similar ($J/k_B \approx -20$ K) reflecting the presence of relatively strong antiferromagnetic interactions between the Cu(II) ion and the two coordinated radical PTMMC molecules.

(ii) $[\text{Cu}(\text{HPTMMC})_2(\text{py})_3] \cdot 4\text{THF}$, **5**. Magnetic measurements of a microcrystalline sample of **5** shows a quasi-ideal paramagnetic behavior (Fig 9). Thus, the χT value in the range of 300 to 10K is $0.38 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$, which is close to the theoretical one expected for one isolated $S = 1/2$ spin. Upon further cooling, χT gradually decreases to a value of $0.33 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ at 2 K. The experimental χT vs T curve for **5** was analyzed quantitatively using the Curie-Weiss equation. From these data, a molar Curie constant of $0.379 \text{ cm}^3\text{Kmol}^{-1}$ and a Weiss constant of -0.25 ± 0.01 K were obtained. The latter value is associated to the existence of very weak antiferromagnetic interactions between the supramolecules.

(iii) $[\text{Cu}_2(\text{PTMMC})_2(\text{MeCOO})_2(\text{H}_2\text{O})_2] \cdot 4\text{EtOH}$, **4**. As can be seen in Figure 10, the χT value at 300 K is $0.9 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$,

which is still far from that expected for a system with four non-interacting electrons ($1.9 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$). Such a divergence is consistent with the presence of strong antiferromagnetic interactions among the two Cu(II) ions and between the Cu(II) ions and the PTMMC coordinated radicals. Upon cooling χT gradually decreases down to 70 K, where it reaches a plateau at a value of $0.7 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$. Below 30 K, the χT value decreases abruptly to a χT value of $0.4 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ at 2 K, due to the presence of weak intermolecular interactions.

The data was nicely fitted to a magnetic model based on a symmetrical butterfly arrangement of the two metal ions and two organic radicals (Scheme 2). The spin Hamiltonian, H , for this butterfly system is given by Equation (2)¹⁸ where J is the *wing-tip/body* exchange interaction between the Cu(II) ions and the organic radicals and J_{13} is the *body/body* interaction between the two Cu(II) ions (Scheme 2).

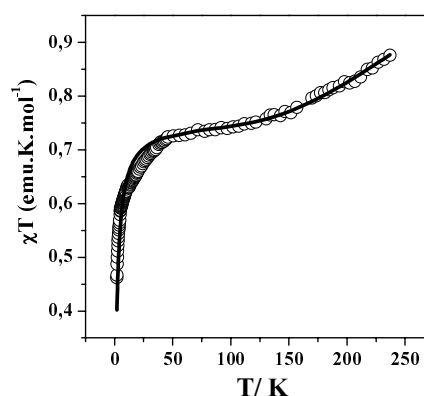


Fig. 10 Temperature dependence of the product of the magnetic susceptibility and the temperature for complex **4**.

$$\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_3 \cdot \hat{S}_4 + \hat{S}_4 \cdot \hat{S}_1) - 2J_{13} \hat{S}_1 \cdot \hat{S}_3 \quad (2)$$

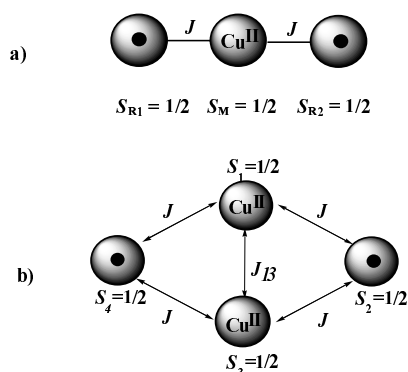
The eigenvalues E deduced from Eq. (2), using the Kambe method,¹⁹ are:

$$E = -J \cdot [S_T(S_T+1) - S_{13}(S_{13}+1) - S_{24}(S_{24}+1)] - J_{13} [S_{13}(S_{13}+1)] \quad (3)$$

where $S_{13} = S_1 + S_3$, $S_{24} = S_2 + S_4$ and $S_T = S_{13} + S_{24}$. A theoretical expression for the χT vs T behavior was derived from the use of Equation (3) and the van Vleck equation. The resulting expression, modified to take into account intermolecular interactions (θ) in the molecular field approximation, was then used to least-squares fit the experimental data of **4**. Fixing the evaluated $g = 2.01$, the best fit was obtained for $J = -21.3$ K, $J_{13} = -350.0$ K and $\theta = -1.7$ K. The value of the *body/body* [copper(II)-copper(II)] interaction, $J_{13} = -350$ K, is within the range of those previously reported for the same kind of interaction in other paddle-wheel Cu(II) dimers,²⁰ whereas the value of the *wing-tip/body* [copper(II)-radical interaction], $J_{13} = -21.3$ K, is similar to that previously reported for the Cu(II)/PTMMC radical interaction in complexes **1-3**. The fact that both exchange coupling parameters, J and J_{13} , are negative indicates that any two neighboring spins tend to align antiferromagnetically. However, the topological arrangement of metal ions and organic radicals in the butterfly structure results in a *spin-frustration* due to the presence of competing antiferromagnetic interactions. The ground state of **4** is therefore degenerated, with two different states that, in the format (S_T, S_{13}, S_{24}) , are: the triplet state (1,0,1) and the singlet state (0,0,0). This is one of the scarce examples of a spin-frustrated system composed of organic radicals and metal ions.²¹

Conclusions.

In summary, it has been demonstrated that the carboxylic substituted perchlorotriphenylmethyl radical is an excellent coordinating ligand to obtain new metal complexes with different magnetic properties following the metal-radical approach. The reaction of PTMMC radical with Cu(II) metal ion gave a series of metal-radical complexes, showing a relatively strong antiferromagnetic exchange coupling between the copper(II) ion and the PTMMC radicals of $J/k_B \approx -20$ K. Furthermore, the use of different molar ratios yield different structures for the resulting metal-radical clusters. In particular a metal-radical paddle-wheel dimer exhibiting a spin frustration phenomenon was obtained. Actually, further studies to expand the range of structural motifs, the structural dimensionality and magnetic behaviours of metal-radical complexes based on polychlorinated triphenylmethyl radicals, either mono-, bi- or trifunctionalised with carboxylic groups, are currently underway.



Scheme 2 Magnetic exchange interactions in the linear three-spin model (a) and in the symmetrical four-spin butterfly model (b).

Experimental section

Physical measurements

Microanalyses were performed at the Servei d'Anàlisi de la Universitat Autònoma de Barcelona. The FT-IR spectra were measured on a Perkin-Elmer Spectrum One spectrometer. The UV-visible spectra were obtained on a VARIAN Cary 5 instrument. Electrochemical experiments were performed with potentiostat Galvanostat 263^a de EG i PAR, using a platinum wire as working electrode and a Ag/AgCl electrode as reference electrode. Anhydrous THF was freshly distilled over sodium/benzophenone under nitrogen. Commercial tetrabutylammonium hexafluorophosphate (Fluka, electrochemical grade) was used as the supporting electrolyte. The magnetic susceptibility were measured on the bulk materials in the 2-300 K temperature range with a Quantum Design MPMS superconducting SQUID magnetometer operating at a field strength of 0.1T. The data were corrected for diamagnetism of the constituent atoms using Pascal constants. The EPR spectra have been recorded on X-band Bruker spectrometer (ESP-300E).

Materials

Solvents were distilled before use. In particular, THF was dried over sodium/benzophenone, and distilled under Argon. All the reagents were used as received and they were purchased from Aldrich and Panreac. Ligands **1** and **5** were synthesized according to the procedure previously described.^{7b} All reactions were carried out in dark.

Preparation of complexes

(i) **[Cu(PTMMC)₂(H₂O)₃]·6H₂O·2EtOH, 1.** A solution of Cu₂(O₂CMe)₄·2H₂O (0.032 g, 0.080 mmol) in 8 mL of water was dropwise added to a solution of PTMMC (0.250 g, 0.320 mmol) in 14 mL of ethanol and stirred for 15 minutes at room temperature. A red microcrystalline solid (0.246 g) was isolated through filtering. The remaining solution was allowed to stand in air for slow evaporation. After 5 days, 0.011g of red plate crystals of **1** were obtained, suitable for X-ray analysis. Total yield of the reaction was 97%. Elemental analysis (%) calcd for C₄₀H₆O₇Cl₂₈Cu: C 29.04, H 0.36; Found: C 29.41, H 0.47. FT-IR (KBr, cm⁻¹): 3393 (m), 1707 (w), 1607 (m), 1407 (m), 1335 (s), 1324 (s), 1260 (m), 1038 (w), 819 (w), 768 (w), 734 (m), 718 (m), 697 (w), 675 (w), 642 (m), 617 (w), 522 (m). UV-Vis (THF, λ in nm, ε in M⁻¹cm⁻¹): 223 (153800), 385 (62150), 508 (2412), 564 (2347). EPR (RT, powder crystalline sample): g-factors g₁ = 2.040, g₂ = 2.060, g₃ = 2.090.

(ii) **[Cu(PTMMC)₂(pyrimidine)₂(EtOH)]·THF·4EtOH, 2.** A solution containing 15.7 μL of pyrimidine in 20 mL of ethanol was layered onto a solution of **1** (0.100 g, 0.060 mmol) in 20 mL of THF. Slow diffusion over 19 days yielded 0.041 g (37%) of red prism crystals of **2**. Elemental analysis (%) calcd for C₅₀H₁₄O₅Cl₂₈N₄Cu: C 33.24, H 0.77, N 3.10; Found: C 32.87, H 0.47, N 2.73. FT-IR (KBr, cm⁻¹): 2970 (w), 1737 (w), 1611 (m), 1594 (m), 1564 (w), 1506 (w), 1470 (w), 1334 (s), 1324 (s), 1259 (m), 1226 (w), 1173 (w), 1038 (w), 819 (w), 770 (w), 734 (w), 715 (m), 674 (w), 642 (m), 616 (w), 577 (w), 540 (w), 522 (m). UV-Vis (THF, λ in nm, ε in M⁻¹cm⁻¹): 222 (176200), 385 (67340), 512 (1770), 565 (1802). EPR (RT, powder crystalline sample): g-factors g₁ = 2.018, g₂ = 2.032, g₃ = 2.090.

(iii) **[Cu(PTMMC)₂(py)₃]·2.5hexane, 3.** A solution containing 3 mL of pyridine in 15 mL of hexane was layered onto a solution of **1** (0.095 g, 0.057 mmol) in 20 mL of THF. Slow diffusion over 4 days yielded 0.040 g (39%) of red prism crystals of **3**. Elemental analysis (%) calcd for C₅₇H₂₂O₄Cl₂₈N₃Cu: C 37.03, H 1.17, N 2.23; Found: C 36.93, H 1.85, N 1.70. FT-IR (KBr, cm⁻¹): 2951 (w), 2927 (w), 2859 (w), 1617 (m), 1610 (m), 1450 (m), 1397 (m), 1334 (s), 1324 (s), 1258 (m), 1073 (m), 1048 (w), 1037 (w), 917 (w), 876 (w), 820 (w), 812 (w), 769 (m), 733 (w), 718 (w), 694 (m), 674 (w), 645 (w), 617 (w), 579 (w), 537 (w), 522 (m). UV-Vis (THF, λ in nm, ε in M⁻¹cm⁻¹): 222 (163800), 385 (67530), 512 (2615), 565 (2715). EPR (RT, powder crystalline sample): g-factors g₁ = 2.019, g₂ = 2.028, g₃ = 2.088.

(iv) **[Cu₂(PTMMC)₂(MeCOO)₂(H₂O)₂]·4EtOH, 4.** A solution of PTMMC (0.075 g, 0.098 mmol) in 40 mL of ethanol was dropwise added to a solution of Cu₂(O₂CMe)₄·2H₂O (0.051 g, 0.127 mmol) in 9 mL of water and 1 mL of ethanol during 2 hours and stirred for 5 minutes at room temperature. The reaction mixture was filtered and the remaining solution was allowed to stand in air for slow evaporation. After 15 days, 0.009 g (14%) of red prism crystals of complex **4** were obtained. Elemental analysis (%) calcd for C₄₄H₁₀O₁₀Cl₂₈Cu₂: C 31.19, H 1.70; Found: C 31.26, H 1.64. FT-IR (KBr): 1624 (m), 1607 (m), 1417 (m), 1335 (s), 1324 (s), 1259 (m), 1039 (w), 819 (w), 767 (w), 734 (m), 717 (w), 675 (w), 642 (m), 616 (w), 522 (m). EPR (110 K, powder crystalline sample): g-factors g₁ = 2.008, g₂ = 2.009, g₃ = 2.018.

(v) **[Cu(HPTMMC)₂(py)₃]·4THF, 5.** A solution of Cu₂(O₂CMe)₄·2H₂O (0.026 g, 0.130 mmol) in 7 mL of water was dropwise added to a solution of 13 mL of ethanol and 0.5 mL of ether of HPTMMC (0.200 g, 0.260 mmol) and stirred for 15 minutes at room temperature. A green solid was isolated through filtering and 100 g of it was dissolved in 20 mL of THF. A solution of 30 mL of hexane containing 3 mL of pyridine was layered onto solution of THF. Slow diffusion over 6 days yielded 0.033 g of blue prism crystals of **6**. Elemental analysis (%) calcd for C₅₅H₁₇O₄Cl₂₈N₃Cu: C 35.90, H 0.92, N 2.28; Found: C 36.46, H 1.13, N 1.82. FT-IR (KBr, cm⁻¹): 2950 (w), 2926 (w),

1742 (w), 1628 (m), 1618 (m), 1609 (m), 1556 (w), 1534 (w), 1489 (w), 1469 (w), 1450 (m), 1438 (w), 1405 (m), 1371 (m), 1334 (s), 1314 (s), 1300 (s), 1240(m), 1218 (w), 1152 (w), 1123 (w), 1048 (w), 912 (w), 872 (w), 804 (mw), 763 (m), 719 (w), 694 (m), 676 (m), 652 (w), 634 (w), 619 (w), 579 (w), 543 (w), 521 (m). UV-Vis (THF, λ in nm, ϵ in $M^{-1}cm^{-1}$): 223 (264900). EPR (RT, powder crystalline sample): g-factors $g_1 = 2.052$, $g_2 = 2.070$, $g_3 = 2.094$.

X-ray data collection and structure determination

X-ray single-crystal diffraction data were collected on a Nonius KappaCCD diffractometer with graphite-monochromized Mo-K α radiation ($\lambda=0.7106\text{\AA}$) and a nominal crystal to area detector distance of 36 mm. Intensities were integrated using DENZO and scaled with SCALEPACK. Several scans in ϕ and ω direction were made to increase the number of redundant reflections, which were averaged in the refinement cycles. This procedure replaces an empirical absorption correction. The structures were solved and refined using the SHELXTL software.²²

For **4**, the refinement runs in a normal way, all non-hydrogen atoms were refined with anisotropic displacement parameters, all hydrogen atoms were calculated or found on her positions and refined isotropically. In the refinement of the other structures the hydrogen atoms of the water, ethanol, hexane and THF molecules were omitted, because of worse crystal quality by disordering problems.

Two kinds of disorder were observed around the environment of the well ordered PTMMC radicals, one for **1** and **2**, the other for **3** and **5**. In **1**, exists a 5:1 position disorder of the Cu(H₂O)₃-unit. The Cu(1) atom of the mayor part co-ordinates to O1 and O3 (as shown in Fig.2) and in the minor part the Cu(1a) atom co-ordinates to O2 and O4 with a pretended Cu(1)-Cu(1a) distance of 2.60 Å. The oxygen atoms of the minor part and the solvent water and ethanol were refined with isotropic displacement parameters, all other non-hydrogen atoms were refined anisotropically. A similar disorder of 3:1 occurs for Cu(pyrimidine)₂(EtOH)-unit of **2** with a pretended Cu(1)-Cu(1a) distance of 1.34 Å. This short distance between the disordered Cu atoms leads to nearly overlying pyrimidine rings with high distorted anisotropic displacement parameters and separate ethanol groups in opposite direction. The ethanol molecule of the minor part and the solvent ethanol and THF were refined with isotropic displacement parameters, all other non-hydrogen atoms with refined anisotropically. In **3** and **5** is only a half molecule in the asymmetric unit and the Cu(py)₃-unit lies nearby a symmetry centre, which produces a second Cu(py)₃-unit in a 1:1 disorder with a pretended Cu(1)-Cu(1a) distance of 1.48 Å for **3** and 1.15 Å for **5**, respectively. Similar to **2**, there are two nearly overlying py-rings with also distorted displacement parameters and one separate py-ring for each Cu atom. In **3** all non-hydrogen atoms were refined with anisotropic displacement, except the solvent hexane, which were refined isotropically. In **5** exists accessorially a normal 1:1 position disorder of the methane group of the HPTMMC molecule. The solvent THF were refined isotropically and also the carbon atoms of the separate py-ring, because of a nearly overlying with an THF molecule from the disordered part, all other atoms were refined with anisotropic thermal parameters.

Interestingly, **2**, **3** and **5** have nearly the same packing motive in the crystal lattice, although the cell volume of **2** is two times greater. An examination of the intensities of **2** shows that all reflections with $h+k = 2n+1$ are systematically weak in direction to a C-centred unit cell, which is not defined in a triclinic system. The relationship to **3** and **5** is, that the 1:1 disorder of the Cu-units leads to a complete extinction of these weak reflections and formally to a C-centered unit cell. The transformation matrix from the C-centered to the correct primitive P cell is 0.5 0.5 0; -0.5 0.5 0; 0.5 0.5 1 (row by row). If the unit cell of **2** would be transformed in this manner, the cell

constants are comparable to **3** and **5** with 8.729, 13.923, 17.076 Å and 86.52, 81.22, 88.91°. This shows in an imposing way that a simply 1:1 disorder from a small part of the molecule can generate a new unit cell.

Further crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication n°. CCDC-186141 (**1**), CCDC-226899 (**2**), CCDC-226900 (**3**), CCDC-186142 (**4**) and CCDC-226898 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk].

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