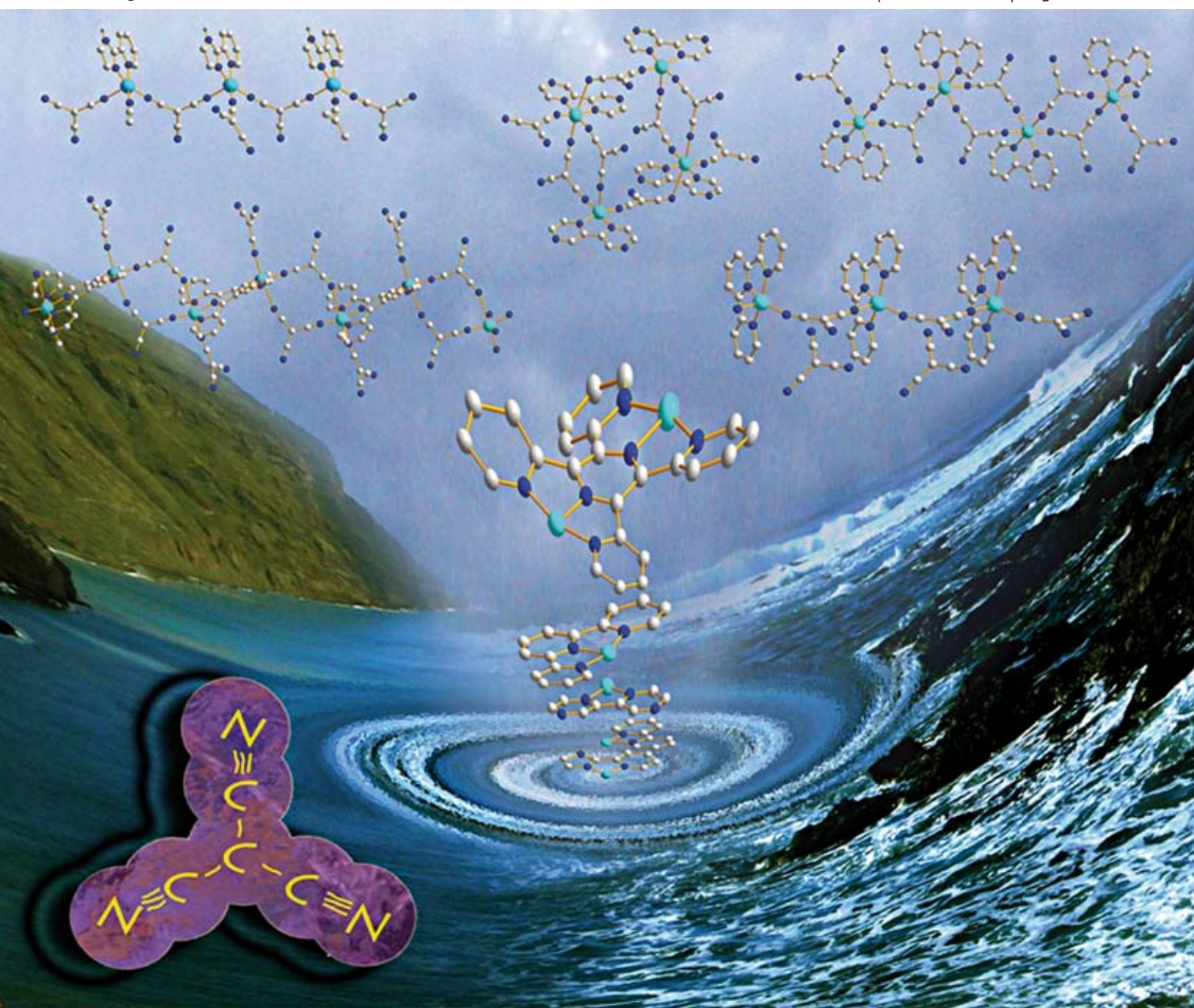


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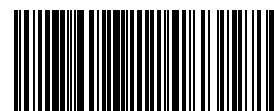
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Synthesis, crystal structures and magnetic properties of tricyanomethanide-containing copper(II) complexes†

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The preparation, crystal structures and magnetic properties of the copper(II) complexes of formula [Cu(pyim)(tcm)₂]_n (**1**), [Cu(bpy)(tcm)₂]_n (**2**), [Cu₄(bpz)₄(tcm)₈] (**3**), {[Cu(terpy)(tcm)]·tcm}_n (**4**) and {[Cu₂(tppz)(tcm)₄]·3/2H₂O}_n (**5**) [pyim = 2-(2-pyridyl)imidazole, tcm = tricyanomethanide, bpy = 2,2'-bipyridine, bpz = 2,2'-bipyrazine, terpy = 2,2':6',2''-terpyridine and tppz = 2,3,5,6-tetrakis-(2-pyridyl)pyrazine] are reported. Complexes **1**, **2** and **4** are uniform copper(II) chains with single- (**1** and **4**) and double-(**2**) μ-1,5-tcm bridges with values of the intrachain copper–copper separation of 7.489(1) (**1**), 7.520(1) and 7.758(1) (**2**) and 7.469(1) Å (**4**). Each copper atom in **1**, **2** and **4** is five-coordinate with bidentate pyim (**1**)/bpy (**2**) and tridentate terpy (**4**) ligands and nitrile-nitrogen atoms from bridging (**1**, **2** and **4**) and terminal (**1**) tcm groups building a distorted square pyramidal surrounding. The structure of **3** is made up of neutral centrosymmetric rectangles of (2,2'-bipyrazine)copper(II) units at the corners, the edges being built by single- and double-μ-1,5-tcm bridges with copper–copper separations of 7.969(1) and 7.270(1) Å, respectively. Five- and six-coordinated copper atoms with distorted square pyramidal and elongated octahedral environments occur in **3**. Compound **5** is a neutral copper(II) chain with regular alternating bis-tridentate tppz and double μ-1,5-tcm bridges, the intrachain copper–copper distances being 6.549(7) and 7.668(1) Å, respectively. The two crystallographically independent copper atoms in **5** have an elongated octahedral geometry with three tppz nitrogen atoms and a nitrile-nitrogen atom from a bridging tcm group in the equatorial positions, and two nitrile nitrogen atoms from a terminal and a bridging tcm ligand occupying the axial sites. The investigation of the magnetic properties of **1–5** in the temperature range 1.9–295 K has shown the occurrence of weak ferro- [$J = +0.11(1) \text{ cm}^{-1}$ (**2**)] and antiferromagnetic interactions [$J = -0.093(1)$ (**1**), $-0.083(1)$ (**4**), $-0.04(1)$ and $1.21(1) \text{ cm}^{-1}$ (**3**)] across the μ-1,5-tcm bridges and intermediate antiferromagnetic coupling [$-J = 37.4(1) \text{ cm}^{-1}$ (**5**)] through bis-tridentate tppz. The values of the magnetic interactions are analyzed through simple orbital symmetry considerations and compared with those previously reported for related systems.

Introduction

The structures and magnetic properties of the extended magnetic systems with paramagnetic metal ions and the pseudohalide ligands dicyanamide [dca, C(CN)₂⁻] and tricyanomethanide [tcm, C(CN)₃⁻] have attracted a lot of attention since the discovery of long range magnetic ordering in the binary d-block series of complexes α-M(dca)₂.^{1–4}

They are three-dimensional (3D) compounds with the same topology as that of rutile. In the case of tcm, the larger void space provided by the additional nitrile group leads to two fold interpenetrating lattices and reduced magnetic ordering.^{5–15} Dca and tcm have in common Lewis base character, negative charge and planar geometry with nominal C_{2v} (dca) and D_{3h} (tcm) symmetries, two (dca) and three (tcm) potentially coordinating nitrile-nitrogens and a five-atom super-exchange pathway, the former also has a three-atom pathway which is accessible. In the presence of a coligand (L), ternary species of formula M(dca)₂(L)_x or M(tcm)₂(L)_x are obtained, which display a diverse range of nD (n = 0–3) structural types.^{16–18} A survey of the literature shows that there are a very great number of structures of metal complexes which combine dca and L whereas in the case of tcm, the number of reports is comparatively much smaller.

Focusing on the use of tcm as a ligand, its triangular topology with three nitrile-nitrogen atoms as donors makes this unit very suitable to design triangular, magnetically frustrated lattices, as shown in a recent report.¹⁵ The versatility of tcm in its metal complexes is illustrated by the variety of its structurally characterized coordination modes: terminal monodentate, and

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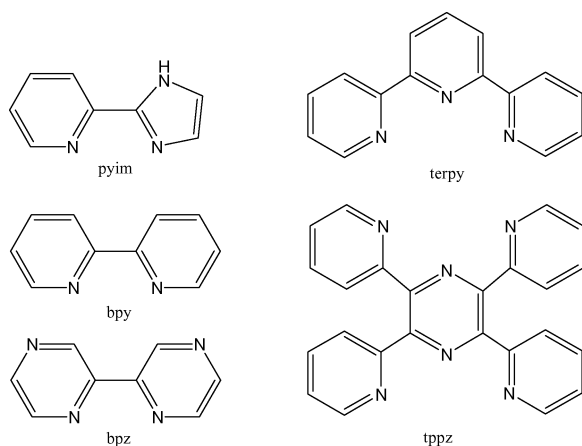
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bridging $\mu_{1,5}$, $\mu_{1,5,7}$ and $\mu_{1,1,5,7}$. Herein we report the synthesis, structural characterization and magnetic investigation of five novel tcm-containing copper(II) chains of formula $[\text{Cu}(\text{pyim})(\text{tcm})_2]_n$ (**1**), $[\text{Cu}(\text{bpy})(\text{tcm})_2]_n$ (**2**), $[\text{Cu}_4(\text{bpz})_4(\text{tcm})_8]$ (**3**), $\{[\text{Cu}(\text{terpy})(\text{tcm})] \cdot \text{tcm}\}_n$ (**4**) and $\{[\text{Cu}_2(\text{tppz})(\text{tcm})_4] \cdot 3/2\text{H}_2\text{O}\}_n$ (**5**) where pyim [2-(2-pyridyl)imidazole], bpy (2,2'-bipyridine), bpz (2,2'-bipyrazine), terpy (2,2':6',2''-terpyridine) and tppz [2,3,5,6-tetrakis(2-pyridyl)pyrazine] are the coligands (see Scheme 1). These coligands were chosen to prepare low dimensional tcm-containing magnetic compounds and also to compare their structural role *versus* the binary Cu(II)–tcm system as a function of their denticity and chelating or bis-chelating ability.



Scheme 1

Experimental

Materials

Copper(II) nitrate trihydrate, potassium tricyanomethanide, 2,2'-bipyridine and 2,2':6',2''-terpyridine were purchased from commercial sources and used as received. The nitrogen heterocycles pyim, bpz and tppz were prepared by following previously reported methods.^{19–21} Elemental analyses (C, H, N) were carried out by the Microanalytical Service of the University of València.

Preparations

[Cu(pyim)(tcm)₂]_n (1). This compound separates as a brown crystalline solid by adding an aqueous solution of Ktcm (1/2 mmol) to an aqueous mixture of Cu(NO₃)₂·3H₂O (1/4 mmol) and pyim (1/4 mmol). The yield is practically quantitative. Single crystals of **1** as brown needles were grown by slow diffusion in an H-shaped tube of aqueous solutions containing Ktcm (0.5 mmol) in one arm and [Cu(pyim)](NO₃)₂ (1/4 mmol) [mixture of Cu(NO₃)₂·3H₂O and pyim in stoichiometric amounts] in the other. The diffusion was complete at room temperature after three weeks. Anal. Found: C, 49.31; H, 1.70; N, 32.29. Calc. for C₁₆H₇CuN₉: C, 49.44; H, 1.80; N, 32.42%.

[Cu(bpy)(tcm)₂]_n (2). This compound is obtained as a green crystalline solid by reaction of concentrated aqueous solutions of Ktcm (1/2 mmol) and 2,2'-bipyridylcopper(II) nitrate (1/4 mmol) [generated *in situ* by mixing stoichiometric amounts of Cu(NO₃)₂·3H₂O and bpy]. X-Ray quality crystals of **2** as green cubes were grown by slow diffusion in an H-shaped tube

of aqueous solutions of Ktcm (0.5 mmol) and [Cu(bpy)](NO₃)₂ (1/4 mmol). The diffusion was complete at room temperature after one month. Anal. Found: C, 53.94; H, 1.92; N, 27.91. Calc. for C₁₈H₈CuN₈: C, 54.08; H, 2.00; N, 28.02%.

[Cu₄(bpz)₄(tcm)₈] (3). Single crystals of **3** as dark green parallelepipeds were grown by slow diffusion in water using an H-shaped tube as for **1** and **2**, the source of the copper(II) ion being [Cu(bpz)](NO₃)₂ [mixture of Cu(NO₃)₂·3H₂O and bpz in stoichiometric amounts (1/4 mmol each)]. The diffusion is complete after one month and the yield is *ca.* 90%. Anal. Found: C, 47.69; H, 1.42; N, 34.72. Calc. for C₃₂H₁₂Cu₂N₂₀: C, 47.84; H, 1.49; N, 34.85%.

{[Cu(terpy)(tcm)]·tcm}_n (4). X-Ray quality crystals of **4** as dark green prisms were grown by slow diffusion in an H-shaped tube of aqueous solutions of Ktcm (0.5 mmol) and (2,2':6',2''-terpyridyl)copper(II) nitrate (1/4 mmol) [mixture of Cu(NO₃)₂·3H₂O and terpy in stoichiometric amounts]. The diffusion is finished after one month and the yield is practically quantitative. Anal. Found: C, 57.83; H, 2.25; N, 26.31. Calc. for C₂₃H₁₁CuN₉: C, 57.94; H, 2.31; N, 26.43%.

{[Cu₂(tppz)(tcm)₄]·3/2H₂O}_n (5). Single crystals of **5** in the form of brown parallelepipeds were obtained by the same technique used in the preceding compounds. In a typical experiment, aqueous solutions of Cu(NO₃)₂·3H₂O (0.625 mmol) and tppz (0.25 mmol) at one hand and of Ktcm (1 mmol) at the other were placed on each arm of the H-tube. The diffusion is practically complete after five weeks and the yield is *ca.* 85% based on tppz. Anal. Found: C, 53.05; H, 2.04; N, 27.80. Calc. for C₄₀H₁₉CuN₁₈O_{1.5}: C, 53.23; H, 2.11; N, 27.92%.

Physical techniques

IR spectra of **1–5** (4000–400 cm⁻¹) were performed with a Bruker IF S55 spectrophotometer on samples prepared as KBr pellets. Variable temperature (1.9–295 K) magnetic susceptibility measurements were carried out with a SQUID susceptometer using applied magnetic fields of 1000 G for **1–5** (over the whole temperature range) and of 250 G for **2** ($T < 50$ K). The complex (NH₄)₂Mn(SO₄)₂·6H₂O was used as a susceptibility standard. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants²² and found to be -176×10^{-6} (**1**), -193×10^{-6} (**2**), -752×10^{-6} (**3**), -222×10^{-6} (**4**) and -413×10^{-6} cm³ mol⁻¹ (**5**) [per one (**1**, **2** and **4**), two (**5**) and four copper atoms (**3**)]. A value of 60×10^{-6} cm³ mol⁻¹ was used for the temperature-independent paramagnetism of the copper(II) ion.

Crystallography

X-Ray diffraction data on single crystals of **1–5** were collected on Nonius KappaCCD (**1** and **5**), Bruker-Nonius X8APEXII CCD area detector (**2** and **4**) and Bruker R3m/V four-circle (**3**) diffractometers with graphite-monochromated Mo–K α radiation ($\lambda = 0.71073$ Å). Crystal parameters and refinement results for **1–5** are summarized in Table 1.† Orientation matrix and lattice parameters for **1** and **5** were determined by least-squares refinement of the reflections obtained by a θ - χ scan (Dirac/lsq method). Data collection, data reduction and empirical absorption corrections were done for **1** and **5** through the

Table 1 Summary of the crystal data for [Cu(pyim)(tcm)₂]_n (**1**), [Cu(bpy)(tcm)₂]_n (**2**), [Cu₄(bpz)₄(tcm)₈] (**3**), {[Cu(terpy)(tcm)]·tcm}_n (**4**) and {[Cu₂(tppz)(tcm)₄]·3/2H₂O}_n (**5**)

Compound	1	2	3	4	5
Formula	C ₁₆ H ₇ CuN ₉	C ₁₈ H ₈ CuN ₈	C ₃₂ H ₁₂ Cu ₂ N ₂₀	C ₂₃ H ₁₁ CuN ₉	C ₄₀ H ₁₉ Cu ₂ N ₁₈ O _{1.5}
<i>M_r</i>	388.84	399.86	803.70	476.95	902.81
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	7.4889(4)	7.7136(8)	9.998(3)	7.4688(4)	9.8741(6)
<i>b</i> /Å	11.0496(5)	10.061(1)	12.583(2)	13.225(1)	12.8989(7)
<i>c</i> /Å	11.5924(5)	12.637(2)	14.391(3)	21.046(2)	16.0258(8)
<i>a</i> /°	116.319(4)	107.932(6)	97.370(10)	90	80.965(6)
<i>β</i> /°	90.635(4)	104.904(6)	106.10(2)	93.657(2)	88.684(6)
<i>γ</i> /°	108.260(4)	101.699(4)	93.20(2)	90	89.289(4)
<i>U</i> /Å ³	803.75(7)	858.3(2)	1717.1(7)	2074.5(2)	2015.2(2)
<i>Z</i>	2	2	2	4	2
<i>T</i> /K	293(2)	293(2)	293(2)	293(2)	293(2)
<i>D_c</i> /g cm ⁻³	1.607	1.555	1.554	1.527	1.488
<i>F</i> (000)	390	406	804	964	910
μ(Mo-Kα)/mm ⁻¹	1.380	1.293	1.296	1.085	1.115
Reflect. collod (indep.)	7681 (3599)	12798 (5940)	6447 (6067)	44419 (4601)	18852 (8862)
Reflect. obs. [<i>I</i> > 2σ(<i>I</i>)]	3324	5256	4866	3916	5267
No. param.	263	244	487	298	559
<i>R</i> ₁ ^a [<i>I</i> > 2σ(<i>I</i>)] (all)	0.0268 (0.0308)	0.0268 (0.0314)	0.052 (0.065)	0.0278 (0.0353)	0.057 (0.125)
<i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)] (all)	0.0675 (0.0697)	0.0771 (0.0796)	0.136 (0.146)	0.0743 (0.0787)	0.091 (0.109)
Goodness-of-fit on <i>F</i> ²	1.070	1.066	1.081	1.066	1.027
Largest diff. in peak and hole/e Å ⁻³	0.44 and -0.43	0.36 and -0.27	0.94 and -1.21	0.26 and -0.33	0.33 and -0.37

^a $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^b $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ and $w = 1/[\sigma^2(F_o^2) + (mP)^2 + nP]$ with $P = (F_o^2 + 2F_c^2)/3$, $m = 0.031$ (**1**), 0.0393 (**2**), 0.1000 (**3**), 0.0392 (**4**) and 0.0280 (**5**) and $n = 0.4532$ (**1**), 0.1696 (**2**), 0.0000 (**3**), 0.6505 (**4**) and 1.9272 (**5**).

COLLECT,^{23a} EVALCCD^{23b} and SADABS^{23c} programs, respectively. The data reduction, structure solution and refinement of **1** and **5** were performed through standard procedures using the WINGX²⁴ program. The data of **2–4** were processed through the SAINT²⁵ reduction and SADABS^{23c} absorption software. Lorentz-polarization and empirical absorption corrections through the ψ-scan program^{23d} were applied for compound **3**. The structures of **1–5** were solved by direct methods and subsequently completed by Fourier recycling using the SHELXS-97 and SHELXL-97²⁶ (**1** and **5**) and SHELXTL²⁷ (**2–4**) software packages. All non-hydrogen atoms of **1–5** were refined anisotropically. The hydrogen atoms of pyim (**1**), bpy (**2**), bpz (**3**), terpy (**4**) and tppz (**5**) and those of the uncoordinated water molecules (**5**) were placed in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. The final full-matrix least-squares refinements on *F*², minimising the function $\sum w(|F_o| - |F_c|)^2$, reached convergence with the values of the discrepancy indices given in Table 1. The final geometrical calculations were carried out with the PARST97²⁸ program whereas the graphical manipulations were performed with the DIAMOND²⁹ program and the XP utility of the SHELXTL system. Main interatomic bond lengths and angles are listed in Tables 2 (**1**), 3 (**2**), 4 (**3**), 5 (**4**) and 6 (**5**).

Results and discussion

Synthesis and infrared spectra

The reaction of aqueous solutions of [Cu_xL]^{2x+} and tcm⁻ [L = pyim, bpy, bpz and terpy (*x* = 1) and tppz (*x* = 2)] yielded highly insoluble compounds as polycrystalline powders. Aiming at obtaining suitable X-ray diffraction crystals, we tried the

Table 2 Selected interatomic distances (Å) and angles (°) for compound **1** with esds in parentheses^a

<i>Copper environment</i>			
Cu(1)–N(1)	2.036(2)	Cu(1)–N(14)	1.962(2)
Cu(1)–N(2)	1.981(2)	Cu(1)–N(12a)	2.193(2)
Cu(1)–N(11)	1.992(2)		
N(1)–Cu(1)–N(2)	80.67(6)	N(2)–Cu(1)–N(11)	157.68(7)
N(1)–Cu(1)–N(14)	166.88(7)	N(2)–Cu(1)–N(12a)	102.40(7)
N(1)–Cu(1)–N(11)	91.21(6)	N(14)–Cu(1)–N(11)	91.95(7)
N(1)–Cu(1)–N(12a)	95.11(6)	N(14)–Cu(1)–N(12a)	96.97(8)
N(2)–Cu(1)–N(14)	91.73(7)	N(11)–Cu(1)–N(12a)	99.00(6)
<i>Bridging tcm</i>			
N(11)–C(12)	1.141(2)	C(11)–C(12)	1.392(2)
N(13)–C(14)	1.137(3)	C(11)–C(13)	1.400(3)
N(12)–C(13)	1.146(2)	C(11)–C(14)	1.398(3)
C(12)–C(11)–C(13)	118.05(11)	C(11)–C(13)–N(12)	178.17(19)
C(12)–C(11)–C(14)	120.71(18)	C(11)–C(14)–N(13)	178.8(4)
C(13)–C(11)–C(14)	120.93(17)	C(12)–N(11)–Cu(1)	170.56(16)
C(11)–C(12)–N(11)	177.1(2)	C(13)–N(12)–Cu(1b)	173.92(15)
<i>Terminal tcm</i>			
N(14)–C(16)	1.146(2)	C(15)–C(16)	1.386(3)
N(15)–C(17)	1.144(3)	C(15)–C(17)	1.403(3)
N(16)–C(18)	1.138(3)	C(15)–C(18)	1.413(3)
C(16)–C(15)–C(17)	121.10(17)	C(15)–C(17)–N(15)	179.5(2)
C(16)–C(15)–C(18)	118.28(17)	C(15)–C(18)–N(16)	178.1(3)
C(17)–C(15)–C(18)	120.54(17)	C(16)–N(14)–Cu(1)	174.79(16)
C(15)–C(16)–N(14)	177.9(2)		

^a Symmetry transformations used to generate equivalent atoms: (a) = *x*–1, *y*, *z*; (b) = *x*+1, *y*, *z*.

slow diffusion technique of the corresponding chemicals in an H-shaped tube. This simple technique provided us with single crystals of the copper(II) complexes of formula [Cu(pyim)(tcm)₂]_n (**1**), [Cu(bpy)(tcm)₂]_n (**2**), [Cu₄(bpz)₄(tcm)₈] (**3**), {[Cu(terpy)(tcm)]·tcm}_n (**4**) and {[Cu₂(tppz)(tcm)₄]·3/2H₂O}_n (**5**). They are all neutral species with L adopting bi- (**1–3**), tri- (**4**) and bis-tridentate

Table 3 Selected interatomic distances (Å) and angles (°) for compound **2** with esds in parentheses^a

Cu(1)–N(1)	1.992(1)	Cu(1)–N(4a)	1.982(1)
Cu(1)–N(2)	1.989(1)	Cu(1)–N(6)	1.981(1)
Cu(1)–N(3)	2.466(1)	Cu(1)–N(8b)	2.663(2)
N(1)–Cu(1)–N(2)	81.35(4)	N(2)–Cu(1)–N(8b)	87.60(5)
N(1)–Cu(1)–N(4a)	176.76(5)	N(4a)–Cu(1)–N(6)	88.13(5)
N(1)–Cu(1)–N(6)	94.51(5)	N(4a)–Cu(1)–N(3)	86.64(5)
N(1)–Cu(1)–N(3)	94.75(4)	N(4a)–Cu(1)–N(8b)	92.90(5)
N(1)–Cu(1)–N(8b)	85.47(4)	N(6)–Cu(1)–N(3)	99.71(5)
N(2)–Cu(1)–N(4a)	95.79(5)	N(6)–Cu(1)–N(8b)	85.15(5)
N(2)–Cu(1)–N(6)	171.94(5)	N(3)–Cu(1)–N(8b)	175.05(4)
N(2)–Cu(1)–N(3)	87.58(4)		
<i>Bridging tcm</i>			
N(3)–C(12)	1.146(2)	C(11)–C(12)	1.401(2)
N(4)–C(13)	1.148(2)	C(11)–C(13)	1.392(2)
N(5)–C(14)	1.141(2)	C(11)–C(14)	1.409(2)
N(6)–C(15)	1.1532(16)	C(15)–C(16)	1.386(2)
N(7)–C(17)	1.1433(19)	C(15)–C(17)	1.411(2)
N(8)–C(18)	1.1472(18)	C(15)–C(18)	1.408(2)
C(12)–C(11)–C(13)	121.5(1)	C(11)–C(14)–N(5)	177.7(2)
C(12)–C(11)–C(14)	118.0(1)	C(15)–C(16)–N(6)	179.4(2)
C(13)–C(11)–C(14)	120.4(1)	C(12)–N(3)–Cu(1)	120.8(1)
C(11)–C(12)–N(3)	175.7(1)	C(13)–N(4a)–Cu(1)	160.1(1)
C(16)–C(15)–C(17)	119.8(1)	C(15)–C(17)–N(7)	178.0(2)
C(16)–C(15)–C(18)	119.8(1)	C(15)–C(18)–N(8)	178.6(2)
C(17)–C(15)–C(18)	120.3(1)	C(16)–N(6)–Cu(1)	144.7(1)
C(11)–C(13)–N(4)	178.3(1)	C(18b)–N(8b)–Cu(1)	124.5(1)

^a Symmetry transformation used to generate equivalent atoms: (a) = $x-1, y, z$; (b) = $-x, -y+2, -z$.

(5) coordination modes. **1**, **2**, **4** and **5** are one-dimensional compounds whereas **3** is a cyclic tetranuclear species. Their neutral nature and polynuclear character account for their insolubility in water. The structural knowledge of **1**, **2** and **5** and that of the related compounds $[\text{Cu}(\text{pyim})(\text{H}_2\text{O})(\text{dca})]_n(\text{NO}_3)_n$,³⁰ $[\text{Cu}(\text{bpy})(\text{dca})_2]_n$ ³¹ and $[\text{Cu}_2(\text{tpz})(\text{dca})_3(\text{H}_2\text{O})]_n \cdot \text{dca} \cdot 3/2\text{H}_2\text{O}$ ³² which contain dca instead of tcm seems appropriate in order to show the differences between the two polynitrile ligands. These last three compounds were also prepared in aqueous solution by using the above mentioned slow diffusion technique. The coordination modes of L in both families are the same and the dca compounds with pyim and bpy are also chains. However, important structural differences occur which are associated with the coordination of the solvent in the dca compounds with pyim and tppz. A cationic chain (pyim) and a cationic dinuclear species (tppz) with uncoordinated nitrate and dca as counterions, result in these two last compounds. Finally, the bpy/dca compound is a neutral chain like **2** but with only one μ -1,5-dca bridge, the electroneutrality being achieved by a terminally bound dca group.

As far as the infrared spectra of **1–5** are concerned, apart from the peaks due to the coligands L and to the crystallization water molecules (strong and broad peak centered at 3435 cm^{-1} in the ir spectrum of **5**), the most important absorptions occur in the region $2250\text{--}2150\text{ cm}^{-1}$ [2245 m , 2190 sh and 2185 vs cm^{-1} (**1**), 2235 m , 2190 s , 2175 sh and 2160 vs cm^{-1} (**2**), 2250 w , 2240 m , 2205 sh and $2174\text{ br,vs cm}^{-1}$ (**3**), 2250 w , 2190 s and 2155 vs cm^{-1} (**4**) and 2245 w and 2170 vs cm^{-1} (**5**)] which correspond to the $\nu(\text{C}\equiv\text{N})$ stretching of the tcm group. In this respect, it deserves to be noted that a single and very strong intensity peak occurs in this region at *ca.* 2178 cm^{-1} for the free tcm as the potassium salt. The shift toward higher wavenumbers and the splitting of the $\nu(\text{C}\equiv\text{N})$ stretching of the tcm group in **1–5** are consistent with the

Table 4 Selected interatomic distances (Å) and angles (°) for compound **3** with esds in parentheses^a

<i>Copper environment</i>			
Cu(1)–N(1)	2.036(3)	Cu(2)–N(5)	2.006(3)
Cu(1)–N(3)	1.992(3)	Cu(2)–N(7)	2.016(3)
Cu(1)–N(9)	1.992(3)	Cu(2)–N(17)	1.984(3)
Cu(1)–N(12)	1.972(3)	Cu(2)–N(18)	1.948(3)
Cu(1)–N(15)	2.174(3)	Cu(2)–N(14)	2.246(3)
		Cu(2)–N(10a)	2.882(3)
N(1)–Cu(1)–N(3)	80.4(1)	N(5)–Cu(2)–N(7)	80.6(1)
N(1)–Cu(1)–N(9)	161.2(1)	N(5)–Cu(2)–N(18)	168.5(1)
N(1)–Cu(1)–N(12)	92.7(1)	N(5)–Cu(2)–N(17)	94.1(1)
N(1)–Cu(1)–N(15)	96.9(1)	N(5)–Cu(2)–N(14)	92.0(1)
N(3)–Cu(1)–N(9)	94.3(1)	N(5)–Cu(2)–N(10a)	73.5(1)
N(3)–Cu(1)–N(12)	171.3(1)	N(7)–Cu(2)–N(18)	95.0(1)
N(3)–Cu(1)–N(15)	94.6(1)	N(7)–Cu(2)–N(17)	174.7(1)
N(9)–Cu(1)–N(12)	90.6(1)	N(7)–Cu(2)–N(14)	92.0(1)
N(9)–Cu(1)–N(15)	101.6(1)	N(7)–Cu(2)–N(10a)	86.3(1)
N(12)–Cu(1)–N(15)	91.4(1)	N(17)–Cu(2)–N(18)	90.1(3)
		N(17)–Cu(2)–N(14)	88.9(1)
		N(17)–Cu(2)–N(10a)	91.6(1)
		N(18)–Cu(2)–N(14)	98.9(1)
		N(18)–Cu(2)–N(10a)	95.6(1)
		N(14)–Cu(2)–N(10a)	165.5(1)
<i>Bridging tcm</i>			
N(9)–C(18)	1.151(5)	C(17)–C(18)	1.385(5)
N(10)–C(19)	1.154(5)	C(17)–C(19)	1.405(6)
N(11)–C(20)	1.148(6)	C(17)–C(20)	1.411(5)
N(12)–C(22)	1.158(5)	C(21)–C(22)	1.386(5)
N(13)–C(23)	1.143(6)	C(21)–C(23)	1.391(6)
N(14)–C(24)	1.138(5)	C(21)–C(24)	1.398(5)
N(15)–C(26)	1.144(5)	C(25)–C(26)	1.406(5)
N(16)–C(27)	1.139(6)	C(25)–C(27)	1.409(6)
N(17)–C(28)	1.151(5)	C(25)–C(28)	1.395(5)
C(22)–C(21)–C(23)	121.9(4)	C(26)–C(25)–C(27)	120.3(3)
C(22)–C(21)–C(24)	117.9(3)	C(26)–C(25)–C(28)	118.1(3)
C(23)–C(21)–C(24)	120.1(3)	C(27)–C(25)–C(28)	121.3(4)
C(21)–C(22)–N(12)	177.4(4)	C(25)–C(26)–N(15)	178.7(4)
C(21)–C(23)–N(13)	179.4(6)	C(25)–C(27)–N(16)	178.0(7)
C(21)–C(24)–N(14)	178.8(4)	C(25)–C(28)–N(17)	177.4(4)
C(22)–N(12)–Cu(1)	155.1(3)	C(26)–N(15)–Cu(1)	168.0(3)
C(24)–N(14)–Cu(2)	168.5(3)	C(28)–N(17)–Cu(2)	162.6(3)
C(18)–C(17)–C(19)	123.7(3)	C(18)–C(17)–C(20)	118.5(3)
C(19)–C(17)–C(20)	117.7(3)	C(17)–C(18)–N(9)	176.7(4)
C(17)–C(19)–N(10)	176.0(5)	C(17)–C(20)–N(11)	178.4(5)
C(18)–N(9)–Cu(1)	172.4(3)	C(19)–N(10)–Cu(2a)	120.0(3)
<i>Terminal tcm</i>			
N(18)–C(30)	1.150(5)	C(29)–C(30)	1.390(5)
N(19)–C(31)	1.117(7)	C(29)–C(31)	1.400(7)
N(20)–C(32)	1.143(6)	C(29)–C(32)	1.406(6)
C(30)–C(29)–C(31)	121.9(4)	C(29)–C(31)–N(19)	177.4(6)
C(30)–C(29)–C(32)	118.0(4)	C(29)–C(32)–N(20)	177.9(6)
C(31)–C(29)–C(32)	120.1(4)	C(30)–N(18)–Cu(2)	161.2(3)
C(29)–C(30)–N(18)	175.6(4)		

^a Symmetry transformation used to generate equivalent atoms: (a) = $1-x, 1-y, 1-z$.

occurrence of terminally bound (**1**, **3** and **4**) and bridging μ -1,5-tcm (**1–5**) ligands.^{18a,33} The lower wavenumber peak at 2155 cm^{-1} in the IR spectrum of **4** suggests the occurrence of uncoordinated tcm. These spectral suggestions concerning the presence of coordinated and uncoordinated tcm groups are confirmed by the respective crystal structures (see below).

Description of the structures

[Cu(pyim)(tcm)]_n (1). The structure of **1** consists of linear chains of copper(II) ions of formula $[\text{Cu}(\text{pyim})(\text{tcm})_2]_n$ (Fig. 1) growing parallel to the crystallographic *a* axis and which are

Table 5 Selected interatomic distances (Å) and angles (°) for compound **4** with esds in parentheses^a

Copper environment			
Cu(1)–N(1)	2.026(2)	Cu(1)–N(4)	1.966(1)
Cu(1)–N(2)	1.942(1)	Cu(1)–N(5a)	2.124(2)
Cu(1)–N(3)	2.034(2)		
N(1)–Cu(1)–N(2)	79.92(6)	N(2)–Cu(1)–N(4)	151.30(6)
N(1)–Cu(1)–N(3)	158.84(6)	N(2)–Cu(1)–N(5a)	107.25(6)
N(1)–Cu(1)–N(4)	98.20(6)	N(3)–Cu(1)–N(4)	96.72(6)
N(1)–Cu(1)–N(5a)	93.71(6)	N(3)–Cu(1)–N(5a)	97.94(6)
N(2)–Cu(1)–N(3)	79.78(6)	N(4)–Cu(1)–N(5a)	101.45(6)
Bridging tcm			
N(4)–C(17)	1.144(2)	C(16)–C(17)	1.394(2)
N(5)–C(18)	1.142(2)	C(16)–C(18)	1.397(2)
N(6)–C(19)	1.141(2)	C(16)–C(19)	1.407(4)
C(17)–C(16)–C(18)	118.4(2)	C(16)–C(18)–N(5)	178.54(2)
C(17)–C(16)–C(19)	121.6(1)	C(16)–C(19)–N(6)	178.9(2)
C(18)–C(16)–C(19)	119.9(1)	C(17)–N(4)–Cu(1)	161.5(2)
C(16)–C(17)–N(4)	177.8(2)	C(18)–N(5)–Cu(1b)	175.3(2)
Free tcm			
N(7)–C(21)	1.159(3)	C(20)–C(21)	1.391(3)
N(8)–C(22)	1.147(3)	C(20)–C(22)	1.407(3)
N(9)–C(23)	1.140(3)	C(20)–C(23)	1.408(3)
C(21)–C(20)–C(22)	120.10(18)	C(20)–C(21)–N(7)	179.2(2)
C(21)–C(20)–C(23)	120.26(19)	C(20)–C(22)–N(8)	179.4(3)
C(22)–C(20)–C(23)	119.62(19)	C(20)–C(23)–N(9)	179.5(3)

^a Symmetry transformations used to generate equivalent atoms: (a) = $x-1, y, z$; (b) = $x+1, y, z$.

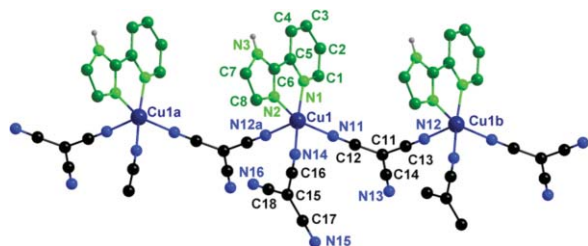


Fig. 1 Perspective view of a fragment of the neutral $[\text{Cu}(\text{pyim})(\text{tcm})_2]_n$ chain (**1**) showing the atom numbering. Symmetry codes: (a) = $x-1, y, z$; (b) = $x+1, y, z$.

grouped by pairs through very weak π – π type interactions involving the pyridyl rings of the pym ligands [3.5986(2) and 3.9414(2) Å for Py1...Py1c and Py1...Py1d centroids, respectively; symmetry code: (c) = $-x, -y, -z+1$ and (d) = $-x+1, -y, -z+1$] (Fig. 2). Further interchain interactions through

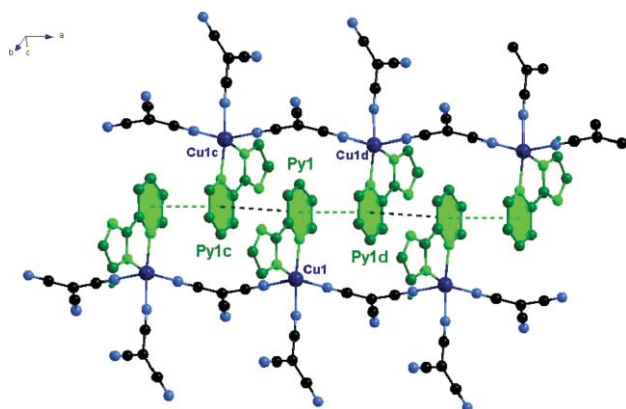


Fig. 2 A view of the pairing of the chains in **1** showing the π – π stacking (dashed lines) between the pyridyl rings of neighbouring pyim ligands.

Table 6 Selected interatomic distances (Å) and angles (°) for compound **5** with esds in parentheses^a

Copper environment			
Cu(1)–N(1)	2.000(3)	Cu(2)–N(3)	1.994(3)
Cu(1)–N(2)	2.006(3)	Cu(2)–N(4)	2.004(3)
Cu(1)–N(5)	1.962(3)	Cu(2)–N(6)	1.961(3)
Cu(1)–N(32)	1.944(4)	Cu(2)–N(40)	1.949(3)
Cu(1)–N(36)	2.038(4)	Cu(2)–N(44)	2.174(4)
Cu(1)–N(42a)	2.685(4)	Cu(2)–N(34b)	2.897(6)
N(1)–Cu(1)–N(2)	159.99(12)	N(3)–Cu(2)–N(4)	160.31(13)
N(1)–Cu(1)–N(5)	80.32(11)	N(3)–Cu(2)–N(6)	80.57(12)
N(1)–Cu(1)–N(32)	99.54(13)	N(3)–Cu(2)–N(40)	98.99(13)
N(1)–Cu(1)–N(36)	96.37(11)	N(3)–Cu(2)–N(44)	96.19(14)
N(1)–Cu(1)–N(42a)	81.63(12)	N(3)–Cu(2)–N(34b)	75.1(2)
N(2)–Cu(1)–N(5)	80.02(11)	N(4)–Cu(2)–N(6)	80.07(12)
N(2)–Cu(1)–N(32)	99.30(13)	N(4)–Cu(2)–N(40)	98.31(13)
N(2)–Cu(1)–N(36)	89.42(11)	N(4)–Cu(2)–N(4)	90.57(13)
N(2)–Cu(1)–N(42a)	94.37(12)	N(4)–Cu(2)–N(34b)	98.5(2)
N(5)–Cu(1)–N(32)	171.17(13)	N(6)–Cu(2)–N(40)	162.12(13)
N(5)–Cu(1)–N(36)	96.10(11)	N(6)–Cu(2)–N(44)	99.68(13)
N(5)–Cu(1)–N(42a)	89.22(11)	N(6)–Cu(2)–N(34b)	81.61(14)
N(36)–Cu(1)–N(32)	92.69(14)	N(40)–Cu(2)–N(44)	98.15(14)
N(36)–Cu(1)–N(42a)	173.92(13)	N(40)–Cu(2)–N(34b)	81.03(15)
N(42a)–Cu(1)–N(32)	82.04(13)	N(34b)–Cu(2)–N(44)	170.9(2)
Bridging tcm			
N(32)–C(32)	1.136(5)	N(40)–C(40)	1.145(4)
N(33)–C(33)	1.143(7)	N(41)–C(41)	1.141(5)
N(34)–C(34)	1.139(7)	N(42)–C(42)	1.139(5)
C(31)–C(32)	1.394(5)	C(39)–C(40)	1.382(5)
C(31)–C(33)	1.411(8)	C(39)–C(41)	1.408(6)
C(31)–C(34)	1.406(8)	C(39)–C(42)	1.405(5)
C(32)–C(31)–C(33)	117.9(4)	C(40)–C(39)–C(41)	118.9(3)
C(32)–C(31)–C(34)	118.3(5)	C(40)–C(39)–C(42)	118.3(4)
C(33)–C(31)–C(34)	123.8(4)	C(41)–C(39)–C(42)	122.8(3)
C(31)–C(32)–N(32)	179.8(6)	C(39)–C(40)–N(40)	177.9(4)
C(31)–C(33)–N(33)	177.2(6)	C(39)–C(41)–N(41)	177.4(5)
C(31)–C(34)–N(34)	177.9(7)	C(39)–C(42)–N(42)	179.1(4)
C(32)–N(32)–Cu(1)	176.8(4)	C(40)–N(40)–Cu(2)	168.5(3)
C(42a)–N(42a)–Cu(1)	141.5(4)	C(34b)–N(34b)–Cu(2)	145.1(5)
Terminal tcm			
N(36)–C(36)	1.144(4)	N(44)–C(44)	1.142(5)
N(37)–C(37)	1.142(4)	N(45)–C(45)	1.157(6)
N(38)–C(38)	1.148(4)	N(46)–C(46)	1.131(6)
C(35)–C(36)	1.400(5)	C(43)–C(44)	1.395(6)
C(35)–C(37)	1.409(5)	C(43)–C(45)	1.401(8)
C(35)–C(38)	1.410(5)	C(43)–C(46)	1.412(8)
C(36)–C(35)–C(37)	120.1(3)	C(44)–C(43)–C(45)	117.6(4)
C(36)–C(35)–C(38)	120.3(3)	C(44)–C(43)–C(46)	120.7(4)
C(37)–C(35)–C(38)	119.6(3)	C(45)–C(43)–C(46)	121.2(4)
C(35)–C(36)–N(36)	179.0(4)	C(43)–C(44)–N(44)	179.0(5)
C(35)–C(37)–N(37)	178.9(5)	C(43)–C(45)–N(45)	178.6(5)
C(35)–C(38)–N(38)	178.4(4)	C(43)–C(46)–N(46)	179.4(5)
C(36)–N(36)–Cu(1)	172.2(3)	C(44)–N(44)–Cu(2)	173.4(3)
Intermolecular contacts ^b			
D	A	D...A/Å	
O(1w)	O(2wc)	3.26(2)	
O(2w)	O(1we)	2.71(2)	
O(1w)	N(41d)	3.23(1)	
O(2w)	N(34c)	3.25(2)	

^a Symmetry transformations used to generate equivalent atoms: (a) = $x, y-1, z$; (b) = $x, y+1, z$; (c) = $-x+1, -y+1, -z+2$; (d) = $x+1, y-1, z$; (e) = $x-1, y+1, z$. ^b A = acceptor and D = donor.

hydrogen bonds between the N(3)–H(5) imidazole fragment and one of the free nitrile-nitrogen atoms of the terminally bound tcm group [2.9003(2) Å for N(3)...N(15e); (e) = $x-1, y-1, z-1$] leads to a layered structure in the bc plane (Fig. 3).

Each copper atom is distorted square pyramidal (trigonality parameter $\tau = 0.15$),³⁴ the equatorial positions being occupied by four nitrogen atoms, two from pyim [N(1) and N(2)] and the

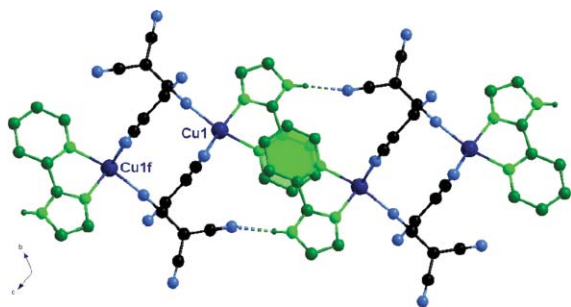


Fig. 3 A view along the *a* axis showing the hydrogen bonds (dashed lines) connecting adjacent chains in **1**. Symmetry code: (f) = $-x + 1, -y + 1, -z + 2$.

other two from monodentate [N(14)] and bridging [N(11)] tcm groups, whereas the apical position is filled by other nitrile nitrogen [N(12a)] of the symmetry related tcm bridge. The equatorial Cu–N bond distances vary in the range 1.962(2)–2.036(2) Å, values somewhat shorter than the axial bond [2.193(2) for Cu(1)–N(12a)]. The atoms defining the equatorial plane of the copper atom are approximately coplanar [maximum atomic deviation is 0.099(2) Å at N(14)] and the metal is shifted by 0.292(1) Å from this mean plane toward the apical nitrogen. The reduced value of the angle subtended at the copper atom by the chelating pyim ligand [80.67(6)° for N(1)–Cu(1)–N(2)] is the main source of distortion of the metal environment. The bidentate coordination mode of the pyim molecule in **1** was previously observed in a few structural reports with other pyim-containing copper(II) complexes of formula [Cu(pyim)(H₂O)(dca)]_n(NO₃)_n,³⁰ [Cu(pyim)(C₂O₄)(H₂O)]·2H₂O³⁵ (C₂O₄²⁻ = oxalate) and [Cu(pyim)(C₄O₄)(H₂O)₂]·2H₂O³⁵ (C₄O₄²⁻ = dianion of the squaric acid).

The pyim ligand in **1** is not far from being planar [the dihedral angle between the imidazole and pyridyl rings of pyim is *ca.* 5.8(1)°]. This quasi planarity is derived from the significant percentage of double bond character of the inter-ring carbon-carbon bond [1.450(3) Å for C(5)–C(6)]. The bond distances and angles of the pyim ligand are in agreement with those observed for this molecule in other metal complexes.^{30,35,36}

Two types of coordinated tcm groups are present in **1**, one is terminal monodentate [C(15)] and the other act as a μ -1,5 bridge [C(11)] linking an equatorial position of one copper atom with the apical position of the adjacent metal atom. Both tcm groups are practically planar [largest deviations are 0.095(5) and 0.023(3) Å at N(13) and N(16), respectively] and their mean planes form a dihedral angle of 86.34(6)°. Their coordination to the copper atom do not affect significantly their geometry and the N–C and C–C bond lengths and CCC bond angles vary in very narrow ranges, 1.138(3)–1.146(2) Å, 1.386(3)–1.413(3) Å and 118.28(17)–121.10(17)° (terminal), 1.137(3)–1.146(2) Å, 1.392(2)–1.400(3) Å and 118.05(16)–120.93(17)° (bridging), respectively. These features are in agreement with almost ideal sp² hybridization of the central carbon atoms. The intrachain copper–copper separation is 7.4889(4) Å [Cu(1)···Cu(1a); (a) = $x - 1, y, z$], a value which is very close to that observed [7.446(1) Å] in the related linear chain of formula [Cu(2,3-dpq)(tcm)₂]_n [2,3-dpq = 2,3-bis(2-pyridyl)quinoxaline] which exhibits the same bridging pathway.³³ The shortest interchain metal–metal distance in **1** is somewhat

shorter than the intrachain one [5.2743(3) Å for Cu(1)···Cu(1f); (f) = $-x + 1, -y + 1, -z + 2$].

[Cu(bpy)(tcm)₂]_n (2). A zigzag chain structure is present in this compound, two tcm groups serving as bridges in μ -1,5 coordination modes (Fig. 4). Each chain extends along the direction of the diagonal line between *a* and *b* axes and it interacts with the two adjacent ones through weak off-set π – π type interactions between the bpy ligands [the interplanar distance is *ca.* 3.44 Å] leading to a layered structure (Fig. 5).

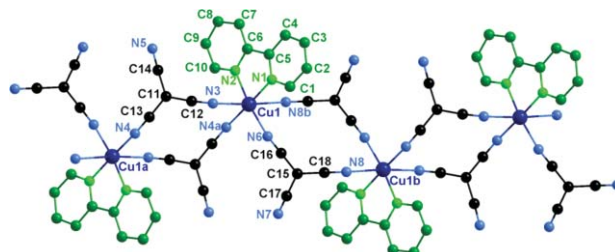


Fig. 4 Section of the neutral [Cu(bpy)(tcm)₂]_n chain (**2**) showing the atom numbering. Thermal ellipsoids are drawn at the 30% probability level. Symmetry code: (a) = $-x + 1, -y, -z$; (b) = $-x, -y + 1, -z$.

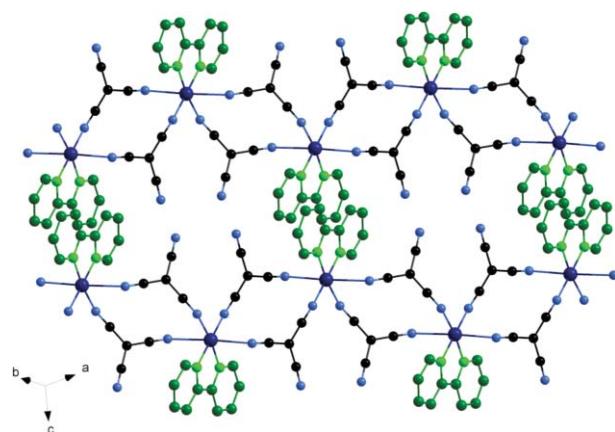


Fig. 5 A view of the bpy stacking of neighbouring chains in **2**.

Tcm anions are also involved in π – π type interactions. In particular, one of the two bridging tcm [N(6)/N(8)] (A) and its symmetrically equivalent [N(6a)/N(8a)] (B) interact with the corresponding ones of the nearest chains, following an ABAB sequence [interplanar distances of 3.18 Å] (Fig. 6).

The copper atom is in an elongated octahedral environment, the equatorial plane being defined by four nitrogen atoms, two from the chelating bpy ligand [N(1) and N(2)] and the other two from two crystallographically independent tcm groups [N(4a) and N(6)] and the axial positions being filled by two nitrogen atoms [N(3) and N(8b)] from the two independent tcm ligands. The most important distortions of this polyhedron deal with the lengths of the axial Cu–N bonds which are significantly longer [2.466(1) and 2.663(2) Å] than the equatorial ones [1.982(2)–1.992(1) Å] and the reduced bite of the bidentate bpy ligand [81.35(4)° for N(1)–Cu(1)–N(2)]. The four nitrogen atoms in the equatorial positions are quasi coplanar [the largest deviation is 0.047(1) Å at N(1)]. The copper atom is displaced only by 0.075(1) Å from the mean basal plane toward the axial N(3) atom. Each pyridyl ring of the bpy ligand is essentially planar, the dihedral angle between the

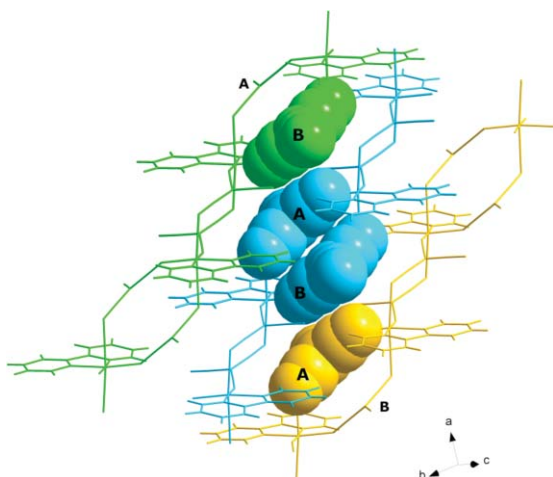


Fig. 6 A view of the tcm interactions within the nearest chains in **2**.

two rings being $7.3(1)^\circ$. Average C–C and C–N bond lengths are in agreement with those reported previously for the free bpy and other bpy-containing copper(II) complexes.^{37,38} The dihedral angle between the equatorial plane and the bpy mean plane is $6.5(1)^\circ$. Bond lengths and angles within the two bridging tcm groups are very close and they agree with those observed in the previous structure. The values of the intrachain copper–copper separation are $7.520(1)$ [Cu(1)···Cu(1a)] and $7.758(1)$ Å [Cu(1)···Cu(1b)] whereas the shortest interchain metal–metal distance is $5.852(1)$ Å [Cu(1)···Cu(1d); (d) = $-x, -y, -z$].

[Cu₄(bpy)₄(tcm)₈] (3). The structure of compound **3** is made up of discrete cyclic tetracopper(II) units of formula [Cu₄(bpy)₄(tcm)₈] which exhibit a rectangular shape with single- and double- μ -1,5-tcm bridges alternating at the edges (Fig. 7). These neutral and centrosymmetric units are stacked along the crystallographic *b* axis in an eclipsed conformation (Fig. 8). Bpy rings are involved in both π – π overlap between them [with an interplanar distance of *ca.* 3.50 Å] and in CN··· π interactions with the terminal tcm, following an ABCCBA sequence [interplanar distances of 3.30 and 3.37 Å for AB and BC, respectively] (Fig. 9).

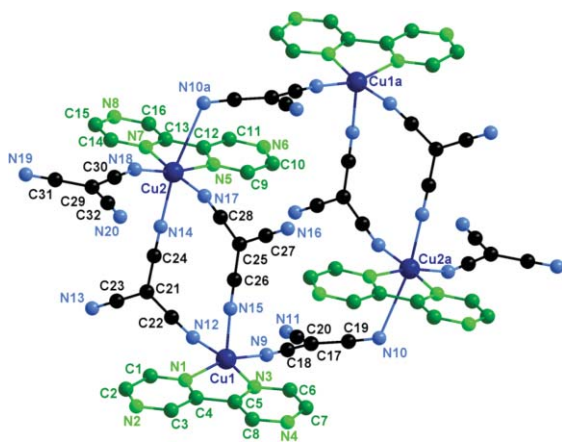


Fig. 7 Perspective view of the tetranuclear [Cu₄(bpy)₄(tcm)₈] complex (**3**) showing the atom numbering. Thermal ellipsoids are drawn at the 30% probability level. Symmetry code: (a) = $1 - x, 1 - y, 1 - z$.

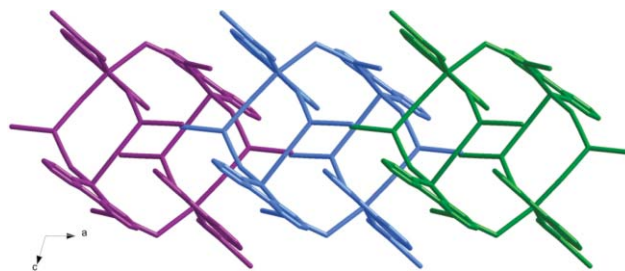


Fig. 8 A view of the packing of **3** along the *b* axis.

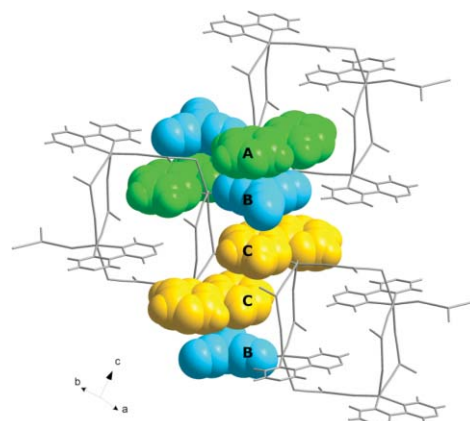


Fig. 9 Side view of a summary of π -type interactions in **3**.

Two crystallographically independent copper atoms noted Cu(1) and Cu(2) occur in **3**. Cu(1) has a distorted square pyramidal coordination geometry ($\tau = 0.17$) with two nitrogen atoms from a bidentate bpy ligand [N(1) and N(3)] and two nitrile-nitrogen atoms from two independent and bridging tcm groups [N(9) and N(12)] in the equatorial positions and other nitrile-nitrogen atom from another independent and bridging tcm ligand [N(15)] in the apical position. The Cu–N bond lengths in the basal plane vary in the range $1.973(3)$ – $2.036(3)$ Å, values which are somewhat shorter than the axial one [$2.174(4)$ Å for Cu(1)–N(15)].

The value of the angle subtended at Cu(1) by the chelating bpy is $80.4(1)^\circ$. The nitrogen atoms in equatorial positions are quite coplanar [maximum atomic deviation is $0.110(2)$ Å for N(1)] and the copper atom is shifted by $0.214(2)$ Å from this mean plane toward the apical position. The coordination of Cu(2) may be described as elongated octahedral of the $4 + 1 + 1'$ type: two nitrogen atoms from a bidentate bpy ligand [N(5) and N(7)] and two nitrile-nitrogen atoms from two tcm groups, one being terminal [N(18)] and the other bridging [N(17)], occupy the equatorial positions whereas two other nitrile-nitrogen atoms from two bridging tcm groups [N(14) and N(10a)] complete the coordination sphere. As for Cu(1), the short bite of the chelating bpy [$80.6(1)^\circ$ for N(5)–Cu(2)–N(7)] is one of the most important sources of the distortion of the coordination polyhedron around Cu(2), together with the lengths of the axial Cu–N bonds which are significantly longer [$2.246(4)$ Å for Cu(2)–N(14) and $2.882(3)$ Å for Cu(2)–N(10a)] than the equatorial ones. The equatorial set of atoms around Cu(2) are practically coplanar [maximum deviation is *ca.* $0.084(2)$ Å for N(5)] and the copper atom is shifted by $0.103(2)$ Å from this mean plane toward the N(14) atom.

The two bpz ligands in **3** are quasi planar, the values of the dihedral angle between their mean pyrazine planes being 1.1(2) and 5.0(2)°. The bond lengths and angles of the two bpz groups in **3** compare well with those reported for the free molecule³⁹ and other bpz-containing copper(II),⁴⁰ iron(II)⁴¹ and cobalt(II)⁴² complexes.

Four crystallographically independent tcm groups occur in **3**, one acting as a terminally bound ligand and the other three adopting the μ -1,5-bridging mode and linking an equatorial position of one copper atom with an axial position at the adjacent metal atom. They are all planar in agreement with the sp^2 hybridization of the central carbon atoms [C(17), C(21), C(25) and C(29)] and their bond lengths and angles are not unexceptional. The values of the dihedral angle between the equatorial planes of the two copper atoms is 11.5(2)°. The metal–metal separations along the edges of the rectangle are 7.969(2) [Cu(1) \cdots Cu(2a)] and 7.270(2) Å [Cu(1) \cdots Cu(2)] whereas those through the diagonals are 11.818(2) [Cu(1) \cdots Cu(1a)] and 9.646(3) Å [Cu(2) \cdots Cu(2a)]. These values are longer than the shortest intermolecular copper–copper distance [5.828(2) Å for Cu(2) \cdots Cu(2h); (h) = $-x, 1 - y, -z$].

{[Cu(terpy)(tcm)]-tcm}_n (**4**). The structure of compound **4** contains cationic linear chains of formula [Cu(terpy)(tcm)]_n⁺ with single μ -1,5-tcm ligands connecting the adjacent copper atoms (Fig. 10), the electroneutrality being achieved through uncoordinated tcm⁻ anions. The chains extend along the crystallographic *a* axis and they are grouped by pairs with a partial π - π overlap between pyridyl rings [interplanar distance of *ca.* 3.43 Å] of neighbouring terpy ligands in the *ac* plane (Fig. 11) The resulting structure could be viewed as pairs of chains intercalating free tcm

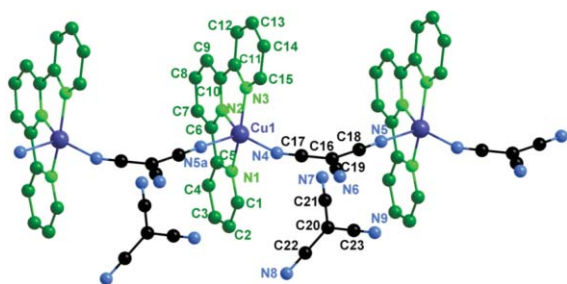


Fig. 10 Section of a fragment of the neutral {[Cu(terpy)(tcm)]-tcm}_n chain (**4**) showing the atom numbering. Thermal ellipsoids are drawn at the 30% probability level. Symmetry code: (a) = $x - 1, y, z$.

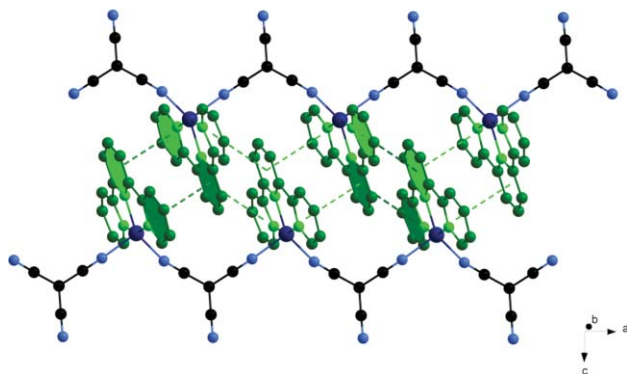


Fig. 11 A view along the *b* axis of the stacking of two adjacent chains in **4**.

groups that weakly interact with the coordinated ones. In fact, the chains and free tcm groups are arranged in layers developing in the *xy* plane, wherein the tcm planes are sandwiched between planes defined by terpy ligand.

Each copper atom is five-coordinated in a distorted square pyramidal surrounding, the trigonality parameter being $\tau = 0.13$. The equatorial positions are defined by the three terpy-nitrogen atoms [N(1), N(2) and N(3)] and a nitrile-nitrogen from a tcm group [N(4)] whereas the apical position is occupied by another nitrile-nitrogen of a symmetry-related tcm ligand [N(5a)]. The equatorial Cu–N bond lengths vary in the range 1.942(1)–2.026(2) Å, values which are somewhat shorter than the axial Cu–N bond [2.124(2) Å for Cu(1)–N(5a)]. The Cu(1)–N bond of the central pyridyl ring of the terpy ligand is significantly shorter than those of the outer pyridyl rings, as previously observed in other terpyridyl-containing copper(II) complexes.⁴³ The constrained terpyridyl geometry when acting as a tridentate ligand accounts for this pattern. The small bite of this type of chelating ligand is reflected by the reduced values of the angles it subtends at the copper atom [79.92(6) and 79.78(6)° for N(1)–Cu(1)–N(2) and N(2)–Cu(1)–N(3), respectively]. The equatorial plane of the copper atom has a significant tetrahedral distortion [maximum and minimum atomic deviations from the mean plane of 0.171(1) and 0.119(1) Å at N(2) and N(4), respectively] and the metal atom is displaced by 0.339(1) Å from this mean plane toward the axial nitrogen atom. The individual pyridine rings of the terpy ligand are planar and the ligand as a whole is not far from planarity [dihedral angles between the inner and outer pyridyl rings are 1.25(8) and 3.57(7)°]. Average C–C bond lengths within the rings (1.379 Å), C–N bonds (1.345 Å) and C–C inter-ring bonds (1.479 Å) compare well with those reported in the literature.⁴³ Two independent tcm groups occur in **4**, one adopting the μ -1,5-bridging mode [C(16)] and the other acting as a counterion [C(20)]. Both are planar in agreement with the sp^2 hybridization of their central carbon atoms.

A comparison between the values of the C–C–C bond angles of the free and bridging tcm shows that the former has a closer symmetry to D_{3h} , as expected because of its noncoordination. Anyway, their bond distances and angles are in agreement with the observed ones for the terminal and bridging tcm ligands in the previous structures. The intrachain copper–copper separation is 7.469(1) Å [Cu(1) \cdots Cu(1a); (a) = $x - 1, y, z$], a value which is somewhat greater than the shortest interchain metal–metal distance 6.394(1) [Cu(1) \cdots Cu(1c); (c) = $1 - x, 1 - y, -z$]. Finally, it is worthy of note that **4** is the second structurally characterized example of uniform copper(II) chain with a single μ -1,5-tcm bridge, the first one being the compound of formula [Cu(bpca)(tcm)]_n where bpca is the tridentate ligand bis(2-pyridylcarbonyl)amidate.⁴⁴ The copper–copper separation through the μ -1,5-tcm bridge in this neutral chain is 7.688(3) Å, a value which compares well with that observed in **4**.

{[Cu₂(tppz)(tcm)₄]-3/2H₂O}_n (**5**). The structure of compound **5** consists of neutral zigzag chains of copper(II) ions of formula [Cu₂(tppz)(tcm)₄]_n running parallel to the *b* axis (Figs. 12 and 13) and crystallization water molecules. Regular alternating bis-tridentate tppz and double μ -1,5-tcm bridges occurs in them, the electroneutrality being achieved by terminally bound tcm groups. The crystallization water molecules are interlinked by hydrogen bonds resulting in tetrameric cyclic units of the R₄⁴ (**8**) type⁴⁵

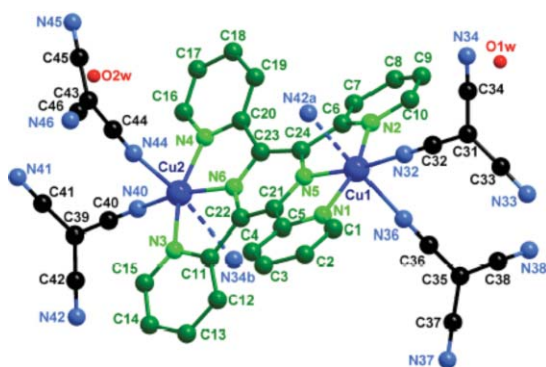


Fig. 12 Perspective view of a dicopper(II) fragment of the chain $\{[\text{Cu}_2(\text{tppz})(\text{tcm})_2]_n\}$ (**5**) showing the atom numbering. Symmetry code: (a) = $x, y - 1, z$; (b) = $x, y + 1, z$.

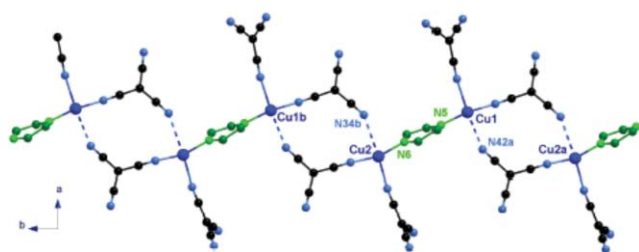


Fig. 13 A view of a section of **5** showing the alternating tppz (only its pyrazine ring is drawn for the sake of clarity) and double μ -1,5-tcm bridges.

which are further attached to four neutral chains through hydrogen bonds with some of the free nitrile-nitrogen atoms of the tcm groups [see end of Table 6 and Fig. 14(top)] leading to a layered structure in the yz plane. Off-set π - π type interactions between the pyridyl rings of tppz ligands of adjacent chains along the x axis contribute to the stabilization of the resulting three-dimensional structure [Fig. 14(bottom)].

Two crystallographically independent copper atoms [Cu(1) and Cu(2)] are present in **5**. Both have elongated octahedral surroundings with three tppz-nitrogen atoms [N(1), N(2) and N(5) at Cu(1) and N(3), N(4) and N(6) at Cu(2)] and a nitrile-nitrogen atom from a bridging tcm group [N(32) and N(40) at Cu(1) and Cu(2), respectively] in the equatorial positions and two nitrile-nitrogen atoms from two tcm groups, one being terminal [N(36) at Cu(1) and N(44) at Cu(2)] and the other bridging [N(42a) at Cu(1) and N(34b) at Cu(2)] in the axial positions. The equatorial Cu–N bond distances vary in the range 1.944(3)–2.006(3) [Cu(1)] and 1.949(3)–2.004(3) Å [Cu(2)], values which are shorter than the axial interactions [2.308(4) and 2.685(4) Å at Cu(1) and 2.174(4) and 2.897(6) Å at Cu(2)]. The nitrogen atoms in the equatorial positions are practically coplanar in the case of Cu(1) [maximum deviation is 0.035(4) Å at N(32)] whereas they exhibit a small tetrahedral distortion in the case of Cu(2) [maximum atomic deviation is 0.104(3) Å at N(3)]. The dihedral angle between the mean equatorial planes is 13.73(9)°. The copper atoms are displaced by 0.1189(5) [Cu(1)] and 0.2130(5) Å [Cu(2)] from these mean planes toward the axial N(36) and N(44) atoms, respectively.

The tppz ligand is appreciably twisted, the dihedral angles between the pyrazine ring and each of the pyridyl rings being 20.15(13)°, 20.04(11)°, 23.03(12)° and 17.90(10)° [arranged in order of rings containing N(1), N(2), N(3) and N(4)]. The pyrazine

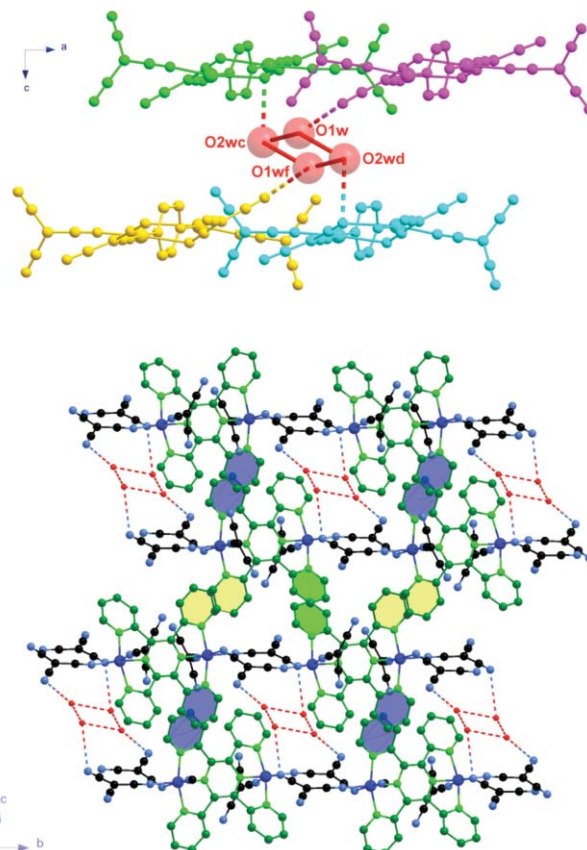


Fig. 14 (top) Perspective view along the b -axis of **5** showing the cyclic tetrameric water unit which is connected to four chains through hydrogen bonds (broken lines). (bottom) A projection of the packing in **5** down the x axis showing the hydrogen bonds (dashed lines) and the off-set π - π type interactions. The hydrogen atoms have been omitted for clarity.

ring itself is puckered with a maximum atomic deviation from the best plane being 0.100(3) Å at C(22). The dihedral angle between the two C–N–C planes of the pyrazine ring is 9.0(2)°. The values of the dihedral angle between the mean plane of the pyrazine ring and those of the equatorial planes at the copper atoms are practically identical [8.43(9) and 8.28(9)° for Cu(1) and Cu(2), respectively]. The copper–copper separation through the bridging tppz ligand in **5** is 6.5446(7) Å, a value which remains within the range of those observed in other structurally characterized tppz-bridged copper(II) complexes [6.497(2)–6.6198(14) Å].^{46–50}

The tcm groups present in **5** adopt two different coordination modes, monodentate and double μ -1,5-bismonodentate. Each of the bridging tcm ligands links one equatorial position at one copper atom with an axial position at the neighbouring copper atom. The two types of tcm groups are all planar and their C–C and C–N bond distances and C–C–C bond angles are as expected in agreement with the sp^2 hybridization of the respective central carbon atoms [C(35) and C(43) for the terminal and C(31) and C(39) for the bridging tcm ligands]. No significant differences are observed between these values when comparing the two types of tcm ligands in spite of their different coordination modes, as previously observed in **1**, **3** and **4**. The copper–copper separation through the double μ -1,5-tcm bridges is 7.6680(7) Å [Cu(1)⋯Cu(2a)], a value which compares well with those observed through the same bridging pathway in **2** and **4**. The

shortest interchain metal–metal distance in **5** is 9.1580(8) Å [Cu(1)⋯Cu(2f); (f) = x + 1, y, z], a value which is much greater than the intrachain ones.

Magnetic properties

The magnetic properties of compounds **1**, **2** and **4** under the form of $\chi_M T$ against T [χ_M is the magnetic susceptibility per copper(II) ion] are shown in Fig. 15.

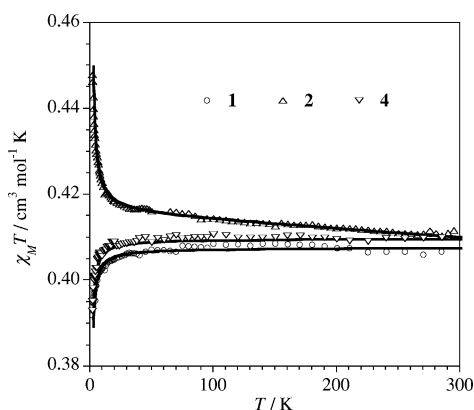


Fig. 15 $\chi_M T$ versus T plot for compounds **1**, **2** and **4**: (○, △, ▽) experimental data; (—) best-fit curves through eqn (1) (**1** and **4**) and (2) (**2**).

At room temperature the values of $\chi_M T$ are 0.396 (**1**), 0.406 (**2**) and 0.414 $\text{cm}^3 \text{mol}^{-1} \text{K}$ (**3**). They are as expected for a magnetically isolated spin doublet. Upon cooling, those of **1** and **4** follow a Curie law until 40 K and further decrease smoothly to 0.381 (**1**) and 0.397 (**4**) at 1.9 K whereas in the case of **2**, $\chi_M T$ continuously increases to attain a value of 0.448 $\text{cm}^3 \text{mol}^{-1} \text{K}$ at 1.9 K. These features are characteristic of very weak antiferro- (**1** and **4**) and ferromagnetic (**2**) interactions between the copper(II) ions in these compounds.

Given that **1** and **4** are one-dimensional compounds where the copper(II) ions are bridged by single μ -1,5-tcm bridges linking one equatorial position of one copper atom with the apical one at the neighbouring copper atom, their magnetic data were analysed through the theoretical expression (the Hamiltonian being $\hat{H} = -J \sum_i \hat{S}_i \hat{S}_{i+1}$) proposed by Hall^{51a} for a uniform chain of interacting spins $S = 1/2$, eqn (1)

$$\chi_M = (N\beta^2 g^2 / kT) [0.25 + 0.14995x + 0.30094x^2] / (1 + 1.9862x + 0.68854x^2 + 6.0626x^3) \quad (1)$$

where N , β and g have their usual meanings, $x = |J|/kT$ and J is the exchange coupling constant describing the magnetic interaction between the two nearest-neighbour spin doublets. This expression which derives from the numerical results from Bonner and Fisher,^{51b} has been widely used to treat the magnetic data of uniform copper(II) chains. Least-squares fit of the magnetic data of **1** and **4** through eqn (1) leads to the following set of parameters: $J = -0.093(1) \text{ cm}^{-1}$, $g = 2.09(1)$ and $R = 1.5 \times 10^{-4}$ for **1** and $J = -0.086(1) \text{ cm}^{-1}$, $g = 2.10$ and $R = 1.2 \times 10^{-4}$ for **4** (R is the agreement factor defined as $\sum_i [(\chi_M T)_{\text{obs}(i)} - (\chi_M T)_{\text{calc}(i)}]^2 / \sum_i [(\chi_M T)_{\text{obs}(i)}]^2$).

The magnetic data of the chain compound **2** has been analysed through the numerical expression proposed by Baker and

Rushbrooke⁵² for a ferromagnetically coupled uniform chain of spin doublets [eqn (2)]

$$\chi_M = (N\beta^2 g^2 / 4kT) [(1 + Ax + Bx^2 + Cx^3 + Dx^4 + Ex^5) / (1 + A'x + B'x^2 + C'x^3 + D'x^4)]^{2/3} \quad (2)$$

where $x = |J|/kT$, $A = 5.7979916$, $B = 16.902653$, $C = 29.376885$, $D = 29.832959$, $E = 14.036918$, $A' = 2.7979916$, $B' = 7.0086780$, $C' = 8.6538644$ and $D' = 4.5743114$. The best-fit parameters obtained through this procedure are: $J = +0.11(1) \text{ cm}^{-1}$, $g = 2.11$ and $R = 1.1 \times 10^{-5}$.

The magnetic properties of a polycrystalline sample of the cyclic tetracopper(II) complex **3** under the form of $\chi_M T$ versus T plot [χ_M is the magnetic susceptibility per four copper(II) ions] are shown in Fig. 16. $\chi_M T$ at room temperature is 1.69 $\text{cm}^3 \text{mol}^{-1} \text{K}$, a value which is as expected for four magnetically non-interacting copper(II) ions [1.65 $\text{cm}^3 \text{mol}^{-1} \text{K}$ with $g = 2.10$]. A Curie law behaviour is observed for **3** until ca. 100 K and then, $\chi_M T$ slightly decreases to 1.26 $\text{cm}^3 \text{mol}^{-1} \text{K}$ at 1.9 K. No maximum is observed in the magnetic susceptibility in the temperature range explored. The smooth decrease of $\chi_M T$ in the low temperature range is indicative of weak but significant antiferromagnetic interactions between the copper(II) ions.

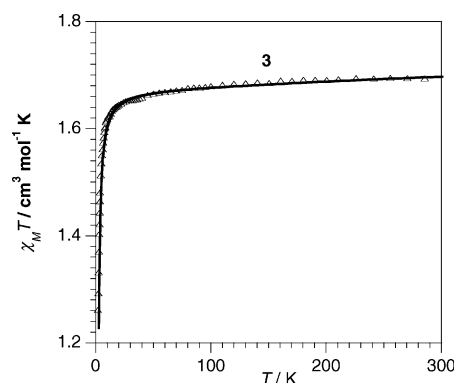
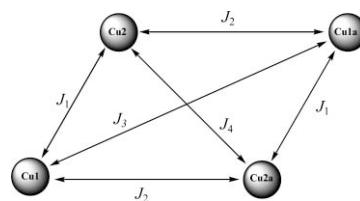


Fig. 16 $\chi_M T$ versus T plot for compound **3**: (△) experimental data; (—) best-fit curve.

For a cyclic tetranuclear compound such as **3**, the exchange coupling topology is that depicted in Scheme 2 where J_i ($i = 1-4$) are the magnetic coupling parameters through the edges (J_1 and J_2) and diagonals of the rectangle, the corresponding isotropic spin Hamiltonian being $\hat{H} = -J_1(\hat{S}_{\text{Cu1}}\hat{S}_{\text{Cu2}} + \hat{S}_{\text{Cu1A}}\hat{S}_{\text{Cu2A}}) - J_2(\hat{S}_{\text{Cu1}}\hat{S}_{\text{Cu2A}} + \hat{S}_{\text{Cu2}}\hat{S}_{\text{Cu1A}}) - J_3(\hat{S}_{\text{Cu1}}\hat{S}_{\text{Cu1A}}) - J_4(\hat{S}_{\text{Cu2}}\hat{S}_{\text{Cu2A}})$.



Scheme 2

The analysis of the magnetic data of **3** through the expression of the magnetic susceptibility derived from this Hamiltonian⁵³ leads to the following best-fit parameters: $J_1 = -1.21(2) \text{ cm}^{-1}$,

$J_2 = -0.04(1) \text{ cm}^{-1}$, $J_3 = J_4 = 0$, $g = 2.12(1)$ and $R = 1.7 \times 10^{-5}$. In order to avoid overparametrisation, a common g value was assumed for the two crystallographically independent copper(II) ions. It deserves to be noted that practically the same quality fit is obtained when analysing the magnetic data of **3** as two magnetically non-interacting copper(II) dimers (that is $J_2 = J_3 = J_4 = 0$), with $J_1 = 1.23(1)$ and $g = 2.12$. Anyway, it seems reasonable to assign the stronger magnetic coupling to the Cu(1)⋯Cu(2) fragment given the presence of two tcm bridges *versus* only one for Cu(1)⋯Cu(2a), the exchange pathway being of the out-of-plane type in both cases. The fact that length of the axial Cu(2a)–N(10) bond [2.883(4) Å] is greater than those in the Cu(1)⋯Cu(2) fragment [2.174(3) and 2.247(3) Å] reinforces this assignment.

The temperature dependence of χ_M and $\chi_M T$ product [χ_M is the magnetic susceptibility per two copper(II) ions] for compound **5** is shown in Fig. 17. At room temperature, $\chi_M T$ is ca. $0.78 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, a value which is as expected for two magnetically isolated spin doublets. Upon cooling, this value continuously decreases and it vanishes at very low temperatures. The susceptibility curve exhibits a maximum at 29 K. These features are indicative of the occurrence of an intermediate antiferromagnetic coupling. Although alternating bis-tridentate tppz and double μ -1,5-tcm bridges occur in the chain compound **5**, the weak magnetic coupling through the tcm bridge in **1–4** and the known ability of the tppz to mediate relatively large antiferromagnetic interactions between the copper(II) ions when acting as a bis-tridentate bridging ligand,^{46–50} allowed us to analyse the magnetic data of **5** by a simple Bleaney-Bowers expression for two magnetically interacting spin doublets [eqn (3)]⁵⁴

$$\chi_M = (2N\beta^2 g^2 / kT) [3 + \exp(-J/kT)]^{-1} \quad (3)$$

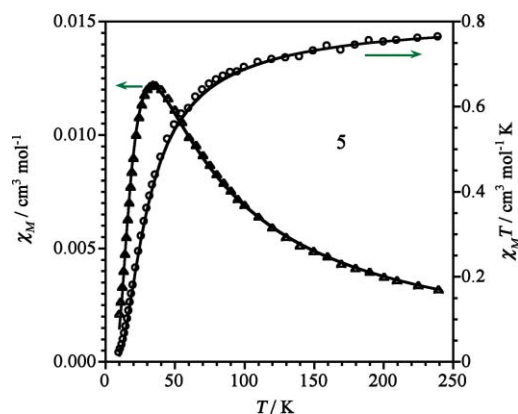


Fig. 17 χ_M and $\chi_M T$ versus T plots for compound **5**: (o,Δ) experimental data; (—) best-fit curves through eqn (3).

where J is the magnetic coupling parameter and g is the average Landé factor. Least-squares fit of the experimental magnetic data of **5** with eqn (3) leads to the following set of parameters: $J = -37.4(1) \text{ cm}^{-1}$, $g = 2.08$ and $R = 9.1 \times 10^{-6}$ (R is the agreement factor defined as $\sum_i [(\chi_M)_{\text{obs}(i)} - (\chi_M)_{\text{calc}(i)}]^2 / \sum_i [(\chi_M)_{\text{obs}(i)}]^2$). As seen on Fig. 14, the calculated curve matches very well the magnetic data in the whole temperature range investigated.

The magneto-structural study of **1–5** together with those of previous reports show that the ability of the tcm and tppz as

bridges to mediate magnetic interactions between the copper(II) ions linked by them is very different (see Tables 7 and 8). Let us to focus first on the tcm case. As illustrated by the data listed in Table 7, the magnetic coupling between copper(II) ions through either single or double μ -1,5-tcm bridges is very weak and of antiferromagnetic nature in most of the cases. The magnetic interaction is found to be ferromagnetic only for **2** and for the dinuclear species $[\text{Cu}_2(\text{Hpz})_6(\text{tcm})_4]$ (hpsz = pyrazole),⁵⁵ At this respect, a weak intramolecular ferromagnetic coupling was recently reported through a double μ -1,5-tcm bridge for the dinuclear nickel(II) complex $[\text{Ni}_2(\text{teten})(\text{tcm})_2](\text{ClO}_4)_2$ (teten = triethylenetetramine) ($J = +0.15 \text{ cm}^{-1}$).^{18c} The out-of-plane exchange pathway which exhibits the tcm bridge in the copper(II) complexes of Table 7 (the tcm bridge links one equatorial position at one copper atom with an axial one of the adjacent copper atom) together with the large copper-copper separation (values greater than 7 Å) account for the weak magnetic couplings observed. The unpaired electron of each copper(II) ion (the magnetic orbital) in the series of compounds listed in Table 7 is of the $d_{x^2-y^2}$ type [the x and y axes being roughly defined by the equatorial copper to nitrogen bonds]. In such a case, the spin density in the axial position is predicted to be weak and thus, the overlap between the two parallel magnetic orbitals through the one or two N–C–C–N five-atoms out-of-plane exchange pathway would be very weak or zero. Consequently, a weak antiferromagnetic coupling is expected for the cases with a net overlap (the first six compounds in Table 7). Also a weak ferromagnetic coupling could be observed in the case of accidental orthogonality (two last compounds in Table 7), as previously observed in other families where the out-of-plane exchange pathway is operative either through monoatomic (μ -chloro and di- μ -chloro)⁵⁶ or polyatomic (μ -oxalato and μ -oximato) bridges.^{57,58} Anyway, in the light of the data listed in Table 7, it is clear that the the magnetic coupling for the equatorial-axial exchange pathway through the μ -1,5-tcm bridge will be very weak and as far as its sign is concerned, it will be strongly dependent on fine structural details such as Cu–N bond distances and degree of structural distortions. The small number of magneto-structural studies of tcm-bridged copper(II) complexes contrasts with the great number of this type of study with the related dca group as bridge, but both ligands have in common the poor ability to mediate magnetic interactions between the paramagnetic centers that they link.

Dealing with the antiferromagnetic coupling through tppz in **5**, one can see in Table 8 that its magnitude lies within the range of those previously reported for other magneto-structurally characterized tppz-bridged copper(II) complexes. The good overlap between the two $d_{x^2-y^2}$ type magnetic orbitals of the copper(II) atoms [the x and y axes being roughly defined by the copper to pyrazine and copper to pyridyl bonds, respectively] through the bis-tridentate tppz accounts for the relatively large antiferromagnetic coupling observed in this family. Parameters such as the planarity of the pyrazine ring, the deviation from the mean pyrazine plane (h) and the intramolecular copper–copper separation are very important and indeed, the largest antiferromagnetic interaction is observed for the first compound of Table 8 where the pyrazine is planar, h is practically zero and the copper–copper separation is the shortest one. The efficiency of tppz to mediate antiferromagnetic interactions between the copper(II) ions when acting as a bridge contrasts with that of the

Table 7 Selected magneto-structural data for single- and double- μ -1,5-tcm bridged copper(II) complexes

Compound ^a	Nuclearity	No. of tcm bridges	Exchange pathway ^b	Cu–N _{ax} ^c	d _{Cu...Cu} ^d	J ^e	Ref
[Cu(2,3-dpq)(tcm) ₂] _n	chain	1	eq-ax	2.158(1)	7.446(1)	–0.18	33
[Cu(bpca)(tcm) _n] _n	chain	1	eq-ax	2.210(2)	7.688(3)	–0.64	44
[Cu(tn)(tcm) ₂] _n	chain	1	eq-ax	2.341(2)	7.5157(4)	–0.70	18
[Cu(pyim)(tcm) ₂] _n	chain	1	eq-ax	2.729(3)	7.7455(4)		
(1)				2.193(2)	7.4889(4)	–0.09	This work
{[Cu(terpy)(tcm)]·tcm} _n (4)	chain	1	eq-ax	2.124(2)	7.469(1)	–0.086	This work
[Cu ₄ (bpz) ₄ (tcm) ₈] (3)	tetranuclear	1	eq-ax	2.883(4)	7.969(2)	–0.04	This work
		2	eq-ax	2.174(3) 2.247(3)	7.469(1)	–1.21	
[Cu(bpy)(tcm) ₂] _n (2)	chain	2	eq-ax	2.467(2) 2.659(2)	7.520(1) 7.758(1)	+0.11	This work
[Cu ₂ (Hpz) ₆ (tcm) ₄]	dinuclear	2	eq-ax	2.472(4)	*	+3.2 ^f	55

^a Abbreviations used: 2,3-dpq = 2,3-bis(2-pyridyl)quinoxaline; bpca = bis(2-pyridylcarbonyl)amidate; tn = 1,3-diaminopropane; Hpz = pyrazole. ^b Eq and ax refer to equatorial and axial positions, respectively, in square pyramidal or elongated octahedral copper surroundings. ^c Value of the axial copper to tcm-nitrogen bond (in Å). ^d Copper–copper separation across bridging tcm (in Å). ^e Value of the magnetic coupling (in cm^{–1}). ^f This value is the Curie–Weiss term θ . *Value not given by the authors.

Table 8 Selected magneto-structural data for tppz-bridged copper(II) complexes

Compound	d.s. ^a	geom. ^b	Cu–N _{pyz} ^c	pyz twist. ^d	h ^e	g ^f	d _{Cu...Cu} ^g	J ^h	Ref
[Cu ₂ (tppz)(H ₂ O) ₄](ClO ₄) ₄ ·2H ₂ O	N ₃ O ₂	dsp	1.962(3)	0	0.012	13.7	6.497(2)	–61.1	46
[Cu ₂ (tppz)(dca) ₃ (H ₂ O)]·dca·3H ₂ O	N ₅	dsp	1.962(4) 1.977(4)	11.5	0.121	14.0/15.1	6.562(1)	–43.7	48a
[Cu ₂ (tppz)Br ₄]	N ₃ Br ₂	dsp	2.005(6) 2.001(6)	10.7	0.117	14.5/21.6	6.620(1)	–40.9	46b
[Cu ₂ (tppz)(N ₃) ₁₀] _n	N ₆	eo	1.976(2)	10.2	0.107	17.5/11.6	6.561(1)	–37.5	48a
{[Cu ₂ (tppz)(tcm) ₄]·1.5H ₂ O} _n (5)	N ₆	eo	1.962(3) 1.961(3)	9.0(2)	0.100	8.3/8.4	6.545(1)	–37.4	This work
[Cu ₂ (tppz)Cl ₄]·5H ₂ O	N ₃ Cl ₂	dsp	1.975(4)	9.9(9)	0.106	10.7/8.5	6.565(1)	–34.1	46b
[Cu ₂ (tppz)(dca)Cl ₂]·dca·H ₂ O	N ₃ Cl ₂	dsp	1.980(2)	10.7	*	*	6.560	–20.5	50
[Cu ₃ (tppz)(C ₅ O ₅) ₃ (H ₂ O) ₃]·7H ₂ O	N ₃ O ₃	eo	1.953(4) 1.966(4)	10.1	0.107	7.7/9.3	6.542(1)	–19.9	48b

^a Donor set. ^b dsp = distorted square pyramidal, eo = elongated octahedral. ^c Copper to pyrazine-nitrogen bond length (in Å). ^d Dihedral angle (in °) between the two C–N–C planes of the pyrazine ring. ^e Maximum deviation from the mean pyrazine plane (in Å). ^f Dihedral angle (in °) between the mean pyrazine plane and the copper mean equatorial plane. ^g Metal-metal separation across bridging tppz (in Å). ^h Value of the magnetic coupling (in cm^{–1}). *Values not given by the authors.

pyrazine (pyz) molecule for which the largest antiferromagnetic interaction reported in its copper(II) complexes is $J = -12.37 \text{ cm}^{-1}$ for [Cu(pyz)₂(ClO₄)₂]_n.⁵⁹ It is clear that the presence of four pyridyl substituents in tppz plays a significant role not only to make possible the bis-chelation of tppz in its metal complexes but also on enhancing the transmission of electronic effects. A comparative theoretical study on magneto-structurally characterized pyrazine- and tppz-bridged copper(II) complexes would provide deeper insights on the structural/electronic factors accounting for such a different efficiency.

Conclusions

The combined action of tcm and bidentate [pyim (**1**), bpy (**2**) and bpz (**3**), tridentate [terpy (**4**)] and bis-tridentate [tppz (**5**)] nitrogen donors on copper(II) ions in aqueous solution afforded a new family of low-dimensional compounds [tetranuclear (**3**) and chain (**1**, **2**, **4** and **5**) species]. The ligand tcm adopts the μ -1,5 bridging mode in this series and it connects equatorial and axial positions of adjacent copper atoms. These structures are very different from those previously reported for the three-dimensional [M(tcm)₂]_n compounds where the polynitrile tcm group acts as a $\mu_{1,5,7}$ -bridging ligand. The presence of the coligand in **1–5** partially blocks the coordination sphere of the copper atom and

decreases the dimensionality of the resulting metal assembling. Weak ferro- (**2**) and antiferromagnetic (**1**, **3** and **4**) interactions between the copper(II) ions separated by more than 7.4 Å across this type of bridge are observed whereas a relatively important antiferromagnetic coupling occurs through the extended tppz bridge (**5**) with a copper–copper separation of ca. 6.5 Å.

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