Crystal Structures and Magnetic Properties of the Mono-μ-halogeno-bridged Copper(II) Chains Cu(pcpci)X [pcpci = *N*-(2′-pyridylcarbonyl)pyridine-2-carboximidate, X = Cl or Br]†

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Compounds Cu(pcpci)Cl (**1**) and Cu(pcpci)Br (**2**) [pcpci = *N*-(2′-pyridylcarbonyl)pyridine-2-carboximidate] are isostructural and crystallize in the monoclinic space group *Pc* with two formula units in cells of dimensions [(**1**)/(**2**)]: a = 3.963(2)/3.888(3), b = 8.48(3)/8.641(3), c = 18.21(12)/17.944(11) Å, and β = 94.9(2)/92.63(6)°. The crystal and molecular structure of (**2**) has been determined by *X*-ray diffraction methods. Least-squares refinement of 1 351 reflections with $I > 2.5\sigma(I)$ and 189 parameters gave a final R' = 0.065. The complex exhibits a chain arrangement built up of Cu(pcpci)Br units linked through the bromine atoms. The copper(II) ions are five-co-ordinate and the co-ordination geometry is near square pyramidal. Magnetic susceptibility measurements were analyzed in terms of the Heisenberg model yielding antiferromagnetic exchange interactions of $J(\mathbf{1}) = -0.4$ and $J(\mathbf{2}) = -0.8$ cm^{-1}. These values are discussed on the basis of the structural features and correlated with published magnetostructural data.

Magnetostructural correlations in exchange-coupled systems are becoming increasingly well established.[1] Since the earlier study of Crawford *et al.*[2] on the dimeric planar di-μ-hydroxo complexes [{Cu(L)(OH)}$_2$] (L = bidentate ligand), other correlations have been developed in similar planar chloride-bridged dimers[3] and dibridged linear chains.[4] However, the experimental magnetic data accumulated for other simple systems such as parallel square-planar halogeno-bridged copper(II) dimers have been shown to have only approximate dependences on topological features.[5–7] On the other hand, results on mono-μ-halogeno-bridged copper(II) chains are scarce.[8,9]

Our current interest in this area is focused on the design of new polymetallic complexes of copper(II). In this context, we have reported recently the synthesis and magnetic characterization of a wide range of five-co-ordinated copper(II) compounds containing the entity [Cu(L–L–L)X]$^{n+}$, where L–L–L is a tridentate rigid quasi-planar ligand such as terpy (2,2′:6′,2″-terpyridine) (n = 1), paphy (pyridine-2-carbaldehyde 2′-pyridylhydrazone) (n = 1), tpt [2,4,6-tris(2′-pyridyl)-1,3,5-triazine] (n = 1), or pcpci [*N*-(2′-pyridylcarbonyl)pyridine-2-carboximidate] (n = 0), and X a halide, pseudohalide, or one half of bidentate bridging anions such as oxalate or chloranilate [2,5-dichloro-3,6-dihydroxycyclohexa-2,5-diene-1,4-dionate].[5,6,10–16] Planarity of these ligands favours the stacking of square-parallel [Cu(L–L–L)X]$^{n+}$ moieties bridged by the X groups to give dimers[5,6,11–15] or more extended magnetic systems (linear or ladder-like chains).[16]

In this work we report the crystal structures and magnetic properties of two new mono-μ-halogeno-bridged copper(II) chains. These results are compared with those reported previously for analogous systems and some magnetostructural trends are discussed.

Experimental

Preparation of the Complexes.—The synthesis of Cu(pcpci)Cl (**1**) and Cu(pcpci)Br (**2**) as microcrystalline solids has been previously described.[14] Single crystals of these isostructural compounds were obtained by slow evaporation, at room temperature, of aqueous solutions of the precursor species [Cu(tpt)X$_2$]·nH$_2$O (X = Cl or Br) which were prepared as described.[12] The green solutions became blue after several hours, indicating hydrolysis of the tpt ligand,[14] and yielded, by slow evaporation, blue crystals after several days. The crystals were separated by filtration, washed with cold water, and ethanol, and stored in a desiccator over silica gel [Found for (**1**): C, 44.5; H, 2.6; Cu, 19.7; N, 12.9. $C_{12}H_8ClCuN_3O_2$ requires C, 44.3; H, 2.5; Cu, 19.6; N, 12.9%. Found for (**2**): C, 39.1; H, 2.3; Cu, 17.2; N, 11.5. $C_{12}H_8BrCuN_3O_2$ requires C, 39.0; H, 2.2; Cu, 17.2; N, 11.6%].

Crystallographic Study.—*Crystal data.* The crystal data for (**1**) and (**2**) are summarized in Table 1. Since both compounds were isostructural, the structure determination of (**2**) was carried out due to the superior quality of the crystals. Data for (**2**) were derived as indicated below while those for (**1**) were obtained through indexation of *X*-ray powder diffraction patterns performed on a Kristalloflex 810 Siemens diffractometer (Cu-K_α radiation, $5 \leqslant 2\theta \leqslant 50°$), using silicon powder as an internal reference.

Data collection for Cu(pcpci)Br (**2**). A well formed blue prismatic crystal with dimensions 0.18 × 0.12 × 0.08 mm was selected and mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator. The cell dimensions were obtained by least-squares refinement of 24 well centred reflections ($8 < 2\theta < 30°$) using Mo-K_α radiation (λ =

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: Oe = 1 000/4π A m^{-1}.

Table 1. Crystallographic data for Cu(pcpci)Cl (**1**) and Cu(pcpci)Br (**2**)

Complex	(**1**)	(**2**)
Formula	$C_{12}H_8ClCuN_3O_2$	$C_{12}H_8BrCuN_3O_2$
M	325.0	369.5
System	Monoclinic	Monoclinic
Space group	*Pc*	*Pc*
a/Å	3.963(2)	3.888(3)
b/Å	8.48(3)	8.641(3)
c/Å	18.21(12)	17.944(11)
β/°	94.9(2)	92.63(6)
U/Å^3	610(6)	602(2)
Z	2	2
D_c/g cm^{-3}	1.77	2.04
F(000)		362
μ(Mo-K_α)/cm^{-1}		51.0

0.709 26 Å). From systematic absences (00*l*, *l* odd; *h*0*l*, *l* odd) the space group *Pc* was assumed. Examination of four standard reflections [(0 2 6), (0 3 4), (1 1 10), (0 1 4)] monitored after each 50 reflections showed no substantial intensity decay. A total of 1 912 reflections were measured ($2 < 2\theta < 60°$; $-5 < h < 5$, $0 < k < 12$, $0 < l < 25$) with the variable-speed ω–2θ technique, of which 1 351 were unique with $I > 2.5\sigma(I)$ and used in the determination of the structure. Lorentz and polarization corrections were applied, but not absorption.

Structure solution and refinement. The positions of copper, bromine, two oxygen, and two nitrogen atoms were obtained by direct methods (MULTAN 11/84).[17] The remaining non-hydrogen atoms were located from subsequent Fourier syntheses. The model obtained was refined with the SHELX 76 system[18] by weighted anisotropic full-matrix least squares. After refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms, difference maps indicated the positions of four H atoms. The co-ordinates of the four remaining H atoms [H(1), H(4), H(11), and H(12)] were calculated. All the hydrogen atoms were included in the final refinement with common fixed isotropic thermal parameters (U = 0.02 Å^2). The final *R* values were *R* = 0.066 and *R'* = 0.065 (189 parameters refined); $\Sigma w(|F_o| - |F_c|)^2$ was minimized, where $w = 2.8226/[\sigma^2(F_o) + 0.0025F_o^2]$ with $\sigma^2(F_o)$ from counting statistics. In the final difference map the residual maximum was a peak of 1.9 e Å^{-3} near the copper atom. Atomic scattering factors and corrections for anomalous dispersion for Cu and Br atoms were taken from ref. 19. The geometrical calculations were performed with XANADU[20] and DISTAN[21] and molecular illustrations drawn with PLUTO 78.[22]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Magnetic Measurements.—Differential magnetic susceptibility measurements were performed in the temperature range 4.2—0.05 K for compound (**2**). An a.c. method based on SQUID detection with an excitation frequency of 16 Hz and an oscillating field of 10 mOe was used on a polycrystalline sample. Measurements from 4.2 to 1 K were made in a glass cryostat with pumped liquid helium for both compounds (**1**) and (**2**). An a.c. method with a small oscillating field was also used and each data point was calibrated against cerium magnesium nitrate, $Ce_2Mg_3(NO_3)_{12}\cdot24H_2O$. Measurements from 298 to 4.2 K were performed, for (**1**) and (**2**), as described in a recent paper.[15]

Table 2. Fractional atomic co-ordinates ($\times 10^4$) for Cu(pcpci)Br (**2**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	−2 988(5)	1 722(1)	7 609(1)
Br	1 326	273(1)	8 318
N(1)	−2 909(32)	3 600(13)	8 286(7)
N(2)	−5 396(36)	3 109(12)	6 944(7)
N(3)	−3 453(29)	282(13)	6 723(6)
O(1)	−7 880(46)	5 595(15)	6 865(10)
O(2)	−7 939(51)	3 313(18)	5 737(8)
C(1)	−1 518(41)	3 760(19)	8 971(9)
C(2)	−1 647(54)	5 086(21)	9 379(12)
C(3)	−3 222(60)	6 388(30)	9 031(17)
C(4)	−4 748(51)	6 261(21)	8 336(14)
C(5)	−4 488(42)	4 844(17)	7 965(11)
C(6)	−6 172(46)	4 563(19)	7 189(11)
C(7)	−6 446(43)	2 598(19)	6 232(8)
C(8)	−5 185(39)	964(17)	6 126(7)
C(9)	−5 914(46)	157(23)	5 467(9)
C(10)	−4 778(52)	−1 350(28)	5 405(11)
C(11)	−3 071(47)	−2 006(19)	6 021(11)
C(12)	−2 432(43)	−1 164(19)	6 655(8)

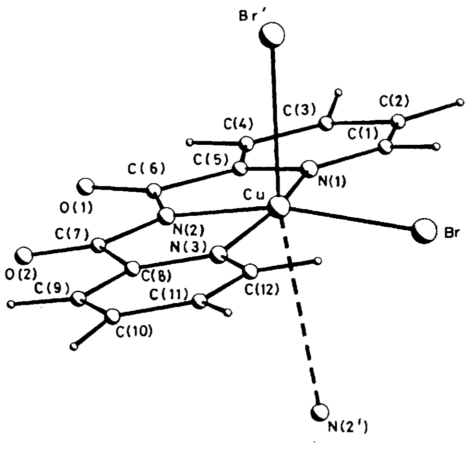


Figure 1. Perspective view and atomic numbering of Cu(pcpci)Br

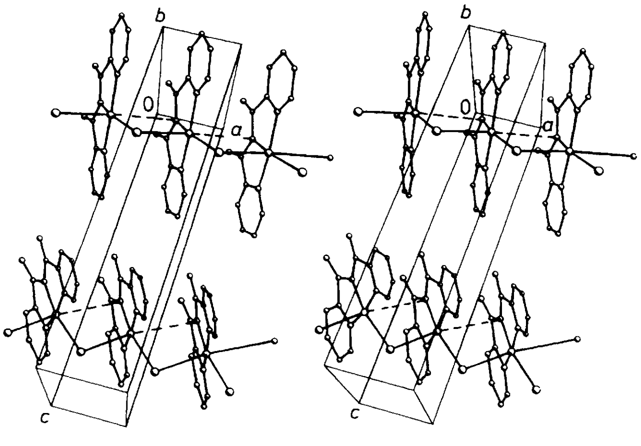


Figure 2. Stereoscopic view of the unit cell of Cu(pcpci)Br

Results and Discussion

Crystal Structure of Cu(pcpci)Br (**2**).—The atomic parameters are given in Table 2. Figure 1 shows a perspective view of the molecule with the atomic numbering scheme and Figure 2 shows a stereoscopic view of the unit cell. Selected bond distances and angles are listed in Table 3. The structure consists of infinite chains along (1 0 0) built up of parallel Cu(pcpci)Br units, related by the symmetry operation $x + 1, y, z$. These units are linked through the bromine atoms which bridge two copper(II) ions. Adjacent chains interact only through van der Waals contacts.

The co-ordination polyhedron around copper(II) is best described as a distorted square pyramid. The basal positions are occupied by the three nitrogen atoms from pcpci$^-$ and the bromine atom while the apical site is occupied by another bromine atom (Br′) belonging to a neighbouring molecule. The Cu–N distances [1.906(11)—2.027(12) Å] are similar to those found in related N-heterocyclic copper(II) complexes,[13,15] whereas the Cu–Br distances are 2.409(2) (basal) and 2.887(2) Å (apical). The basal atoms are practically coplanar within ±0.10 Å and the copper atom lies 0.19 Å above the least-squares plane. The plane defined by Cu, Br, and Br′ makes an angle of 91.1(9)° with the basal plane; the bridging angle Cu–Br–Cu′ (as well as Br–Cu–Br′) is 94.0(2)° and the Cu–Cu′ distance 3.888(3) Å.

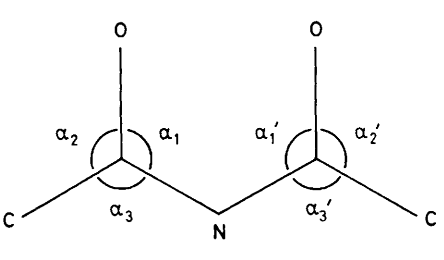
It is interesting to compare the stacking adopted by the Cu(pcpci)X entities with that observed in the [{Cu(L–L–L)X}$_m$]$^{m+}$ cations (L–L–L = terpy, m = 2; L–L–L = paphy, $m = \infty$).[5,6,16] Thus, while in the former compound two adjacent planar units are related by a translation along the Cu–Cu axis, in the latter these are related by the translation followed by a rotation of 180°. The origin of this difference may lie in the stronger basicity of the central nitrogen atom of pcpci$^-$ (when compared to the neutral ligands) since it originates from a deprotonated imide group. In such an arrangement (see Figures 1 and 2) each N(2) atom could be considered as semi-co-ordinated to a second copper atom belonging to an adjacent molecule [Cu–N(2′) 3.449(12) Å] giving rise to strongly elongated octahedral metallic sites [*i.e.*, a copper(II) '4 + 1 + 1' co-ordination mode]. Similar Cu–N(bridging) situations have been previously found in the chain compound *catena*-dichloro(oxamide oxime)copper(II),[23] and in the [bis(8-quinolinyl)amido-*N*,*N*′,*N*″]chlorocopper(II) dimeric complex.[24] In such cases the Cu–N distances are 3.223(20) and 3.093(2) Å, respectively. The larger Cu–N distance observed in compound (**2**) may arise from repulsion of the π clouds from pcpci$^-$ entities. In view of this distance compound (**2**) is considered as a mono-μ-bromo-bridged copper(II) chain.

Table 3. Selected bond distances (Å) and angles (°) for Cu(pcpci)Br (**2**) with e.s.d.s in parentheses*

Cu–Br	2.409(2)	Cu–N(2)	1.906(11)
Cu–Br′	2.887(2)	Cu · · · N(2′)	3.449(12)
Cu–N(1)	2.027(12)	Cu–N(3)	2.019(12)
Br′–Cu–Br	94.0(2)	N(2′)–Cu–N(1)	86.5(5)
N(1)–Cu–Br	96.2(4)	N(2)–Cu–N(2′)	88.2(5)
N(1)–Cu–Br′	94.2(4)	N(3)–Cu–Br	97.5(3)
N(2)–Cu–Br	165.3(4)	N(3)–Cu–Br′	92.1(3)
N(2′)–Cu–Br	77.1(4)	N(3)–Cu–N(1)	164.4(5)
N(2)–Cu–Br′	100.6(4)	N(3)–Cu–N(2)	82.6(5)
N(2′)–Cu–Br′	171.2(4)	N(3)–Cu–N(2′)	89.4(5)
N(2)–Cu–N(1)	82.3(5)		

* The atoms Br′ and N(2′) are related to the atoms listed in Table 1 by the symmetry operations $x - 1, y, z$ and $x + 1, y, z$ respectively.

The pcpci$^-$ ligand can be considered as practically planar within ±0.11 Å (non-hydrogen atoms). Notwithstanding, the ligand is better described by two pyridylcarbonyl halves that show no deviations from planarity greater than ±0.02 and ±0.07 Å, respectively. The dihedral angle between the least-squares planes defined by these two halves is 3.1°, which is very close to that found by Lerner and Lippard[25] in triaqua[*N*-(2′-pyrimidinylcarbonyl)pyrimidine-2-carboximidato]copper(II) nitrate dihydrate (2.9°). With regard to the ligand geometry, another point to note is the value of the angles around the carbon atoms [C(6) and C(7)] of the carbonyl groups. These angles show significant deviations from the expected value of 120° for sp^2 hybridation. Table 4 shows these angles for Cu(pcpci)Br and for other terpy and tpt related complexes, using the notation given in the Scheme. Deviations are larger in Cu^{II} than in Co^{II} and Ni^{II} complexes; the largest deviations correspond to the Cu^{II}–pcpci complexes. Clearly, the need for short metal–nitrogen bonds lies at the origin of the angular strain, which is more pronounced in the case of copper complexes due to the smaller ionic radii of this cation (usual Cu–N distances are 2.0 Å, while Ni–N or Co–N are 2.10—2.12 Å). It has been suggested previously by Lerner and Lippard that angular strain is the principal reason for the copper(II)-promoted hydrolysis of tpt,[25] which is not observed when tpt is co-ordinated to Ni^{II} or Co^{II}, or to another bulkier cation such as Pb^{II}.[26] On the other hand, although angular strain is also present in terpy complexes, the stability of the pyridine ring when compared to the *s*-triazine ring ensures that hydrolysis does not take place.



Scheme.

Magnetic Properties.—Variable-temperature magnetic measurements have been performed down to 1.0 K for

Table 4. Values of the α_i(°) angles in some complexes of pcpci, terpy, and tpt

Compound	α_1 (α_1')	α_2 (α_2')	α_3 (α_3')	σ^a	Ref.
Cu(pcpci)Br	129 (129)	121 (122)	110 (109)	7.0	This work
[Cu(pcpci)(O$_2$CMe)(OH$_2$)]·H$_2$O	128.4 (128.3)	121.1 (121.2)	110.4 (110.6)	6.3	*b*
[Cu(terpy)(O$_2$CH)(OH$_2$)]ClO$_4$	119.0 (119.0)	127.5 (127.5)	113.5 (113.5)	5.0	13
[Ni(terpy)$_2$][PF$_6$]$_2$	118.8 (117.0)	127.0 (126.6)	113.1 (116.2)	4.8	*c*
[Co(terpy)(NCO)$_2$]	117.3 (117.3)	126.1 (126.1)	116.6 (116.6)	4.1	*d*
[Ni(Htpt)(OH$_2$)$_3$]Br$_3$·H$_2$O	124 (120)	121 (124)	115 (116)	3.0	*e*
[Co$_2$(tpt)Cl$_4$(OH$_2$)]·H$_2$O	118 (118)	119 (125)	122 (117)	2.5	*f*

[a] $\sigma = \Sigma|\alpha_i - 120|/6$. [b] J. V. Folgado, Ph.D. Thesis, University of Valencia, 1987. [c] M. I. Arriortua, T. Rojo, J. M. Amigo, G. Germain, and J. P. Declercq, *Bull. Soc. Chim. Belg.*, 1982, **91**, 337. [d] D. L. Kepert, E. S. Kucharski, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1980, 1932. [e] G. A. Barclay, R. S. Vagg, and E. C. Walton, *Acta Crystallogr., Sect. B*, 1977, **33**, 3487. [f] G. A. Barclay, R. S. Vagg, and E. C. Walton, *Acta Crystallogr., Sect. B*, 1978, **34**, 1833.

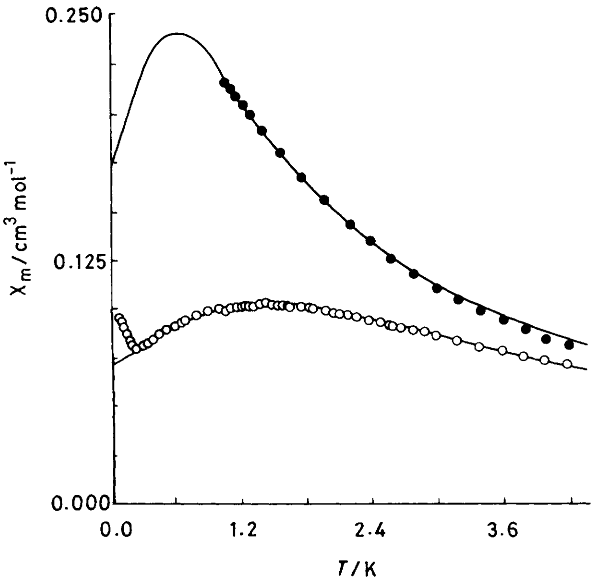


Figure 3. Low-temperature magnetic susceptibility data for Cu(pcpci)-Cl (●) and Cu(pcpci)Br (○). The solid lines correspond to the best fits of the Heisenberg chain model to the experimental data (see text)

Table 5. Magnetic and structural parameters[a] for mono-μ-halogeno-copper(II) chains

Compound[b]	J/cm^{-1}	R/Å	θ/°	φ/°	Ref.
$[Cu(dmso)_2Br_2]$	−7.9	2.777	146.1	144.6	9,30
$[Cu(dmso)_2Cl_2]$	−6.1	2.702	146.1	144.6	8
$[Cu(Him)_2Cl_2]$	−2.1	2.751	166.9	117	8
$[Cu(H_2oao)Cl_2]$	−1.0	2.776	165.6	95.6	23
Cu(pcpci)Br	−0.8	2.887	165.3	94.0	This work
Cu(pcpci)Cl	−0.4				This work
$[Cu(paphy)Cl]PF_6\cdot H_2O$	+0.5	2.805	167.6	102.3	16
$[Cu(caf)(OH_2)Cl_2]$	+0.5	2.788	178.8	128.1	8
$[Cu(maep)Cl_2]$	+1.6	2.785	176.0	113.6	7

[a] R, θ, and φ are defined in the text. [b] Abbreviations: dmso = dimethyl sulphoxide, Him = imidazole, H_2oao = oxamideoxime, pcpci = *N*-(2′-pyridylcarbonyl)pyridine-2-carboximidate, paphy = pyridine-2-carbaldehyde 2′-pyridylhydrazone, caf = 1,3,7-trimethylpurine-2,6-dione (caffeine), maep = 2-(2′-methylaminoethyl)pyridine.

compound (**1**) and 0.05 K for (**2**). Figure 3 illustrates the low-temperature susceptibility data of both compounds. The observation of a very broad maximum in the case of (**2**) is indicative of weak antiferromagnetically coupled copper(II) ions. Although such a maximum is not observed for (**1**), the effective magnetic moment per copper(II) ion goes from 1.9 μ_B at room temperature to 1.4 μ_B at 1.01 K. The variation of the magnetic susceptibility with temperature for both compounds can be satisfactorily fitted to the $S = \frac{1}{2}$ Heisenberg regular chain model.[27,28] The resulting exchange parameters are J(**1**) = −0.4 and J(**2**) = −0.8 cm^{-1}. In the fits, the g parameters were kept constant and equal to the values (g = 2.10) calculated from e.s.r. powder spectra.[14] The susceptibility increase below 0.25 K observed in compound (**2**) may be due to the presence of a small amount of paramagnetic impurity in the sample which can be estimated to be less than 0.5%, or to residual errors in the background correction since the measured signal is very small.

Hatfield and co-workers[29] have pointed out that a smooth correlation exists, in di-μ-halogeno-bridged copper(II) dimers, between the exchange parameter J and the ratio φ/R (φ is the Cu–X–Cu bridging angle and R the longest Cu–X distance) which reflects the significance of the geometrical aspects of the bridge plane in the magnetic behaviour. More recently, Beltrán-Porter and co-workers[5,6] and Landee and Greeney[7] have suggested that the X–Cu–L_t angle, θ, is a better parameter for the correlation (L_t = ligand *trans* to X). This angle gives an indication of the distortion of the co-ordination polyhedron of copper(II) with respect to the square-pyramidal geometry. On the contrary, there are only a few examples of structural and magnetically characterized copper(II) complexes containing mono-μ-halogeno-bridges,[8,9,23,30] and up to now only a mono-μ-bromide chain has been reported.[30] Structural and magnetic properties of these compounds are summarized in Table 5.

From an inspection of Table 5 it is evident that a simple magnetostructural correlation does not exist in the reported chains. However, some experimental trends can be indicated. Thus, it is significant that the largest exchange parameters are for the dmso derivatives, which exhibit the largest deviations away from the ideal square-pyramidal geometry. These deviations are reflected in the θ angle which is 180° in the ideal square-pyramidal geometry and decreases as the distortion toward the trigonal-byramidal geometry increases. For the reported compounds the bridging halide atom occupies a basal position in the distorted square-pyramidal copper(II) and an axial position in the adjacent copper(II) environment. This geometry determines a weak superexchange interaction since it allows a poor effective overlapping between the magnetic orbitals, essentially of $x^2 - y^2$ type, which are localized on the basal planes. However, when the copper(II) environment becomes more distorted, that is when the co-ordination polyhedron acquires greater trigonal-bipyramidal character, the magnetic orbital becomes more strongly mixed with the d_{z^2} orbital and, consequently, the magnetic interaction becomes stronger. An additional factor that favours the exchange strength in the dmso derivatives is that the values of φ are the largest (and significantly larger than 90°).

The other complexes listed in Table 5 exhibit interactions weaker than for the dmso derivatives. All these compounds are characterized by θ angles close to 180° and φ angles near to 90°. Although the complexes which exhibit a greater distortion from the square-pyramidal geometry are those which possess, at the same time, greater φ bridging angles, the trend that we can extract is that the smaller the θ angle from 180° as well as the larger the φ angle from 90° the greater the antiferromagnetic coupling is favoured.

Acknowledgements

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