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Synthesis, crystal structure and magnetic properties of $[Cu_2(bpym)(N_3)_4]$ (bpym = 2,2′-bipyrimidine)

Giovanni De Munno

Dipartimento di Chimica, Università della Calabria, 87030 Arcavacata di Rende (Cosenza) (Italy)

J. Antonio Real and Miguel Julve*

Departament de Química Inorgànica, Facultat de Química, Universitat de València, Dr. Moliner 50, 46100 Burjassot (València) (Spain)

M. Carmen Muñoz

Departamento de Física Aplicada, Universidad Politécnica de València, Camino de Vera s/n, 46071 València (Spain)

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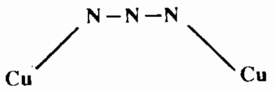
Abstract

The compound of formula $[Cu_2(bpym)(N_3)_4]$ (bpym = 2,2′-bipyrimidine) has been synthesized and its crystal structure determined by X-ray diffraction methods. It crystallizes in the monoclinic space group $P2_1/n$ with cell constants: $a = 10.071(2)$, $b = 6.376(1)$, $c = 11.617(2)$ Å and $\beta = 95.93(1)°$; $V = 742.0(2)$ Å^3, D (calc., $Z = 2$) = 2.029 g cm^{-3}, $M_r = 453.4$, $F(000) = 448$, λ (Mo Kα) = 0.71073 Å, μ (Mo Kα) = 29.1 cm^{-1} and $T = 298$ K. A total of 2027 reflections was collected over the range $3 \leq 2\theta \leq 55°$; of these, 1723 were unique and 1427 were considered as observed ($I > 3\sigma(I)$) and used in the structural analysis. The final R and R_w residuals were 0.0275 and 0.0328, respectively. The structure consists of dinuclear Cu^{II}_2(bpym) units held together by azido groups in such a way to form a 2D polymer. Each copper atom is in a distorted octahedral environment with two nitrogen atoms of bpym and two nitrogen atoms of azide in the equatorial plane and two other nitrogen atoms of azide groups from neighbouring units occupying the axial position. Magnetic susceptibility data as a function of the temperature exhibit a rounded maximum at 160 K evidencing a large antiferromagnetic interaction. The relevant parameters are $g = 2.17$ and $J = -178$ cm^{-1} with the interaction Hamiltonian defined as $\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2$. The singlet–triplet energy gap is compared to that reported for the related cyanato and thiocyanato copper(II) complexes and the influence of the nature of the pseudohalide ligand on the resulting structure is analyzed.

Introduction

Azide-containing copper(II) complexes have been a subject of great interest from both structural and magnetic viewpoints in the last decade [1]. In fact, the azide group is a very versatile ligand and it can coordinate to copper(II) either in a monodentate or bridging fashion to yield mono or polynuclear species, respectively [2, 3]. Two bridging modes of N_3^- are known, the end-to-end (μ-1,3) fashion as in **1** and the end-on (μ-1,1) fashion as in **2**, the magnetic interaction being antiferromagnetic in the former situation [4–10] and ferromagnetic in the latter one [5b, 11, 12]. A simple orbital model [13] and the concept of spin polarization [14] were used to understand this specific ability of the azido ligand to stabilize either the singlet or the triplet ground state in azido-bridged copper(II) dinuclear complexes.



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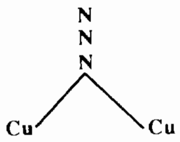

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On the other hand, some of us have shown that 2,2′-bipyrimidine (bpym) can mediate a strong antiferromagnetic coupling between bpym-bridged copper(II) ions (J (singlet–triplet energy gap) from -236 to -191 cm^{-1}) [15] which can be tuned by using both the Cu(II): bpym stoichiometry and the nature of the counterion [16, 17]. In particular, nD arrays ($n = 1$–3) of copper(II) ions have been achieved in the compounds of formula $[Cu(bpym)(NCS)_2]$ ($n = 1$), $[Cu_2(bpym)(NCO)_4]$ ($n = 2$) and $[Cu_2(bpym)(NCS)_4]$ ($n = 3$) [17].

In this paper we report the synthesis, structural characterization and magnetic properties of a new

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*Author to whom correspondence should be addressed.

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polynuclear copper(II) complex of formula [Cu_2(bpym)$(N_3)_4$] in which both bpym and azido ligands are involved. The magneto-structural role of the pseudohalide ligand (X = NCS, NCO, N_3) in the ternary complexes Cu(II)–bpym–X is analyzed and discussed.

Experimental

Reagents

Copper(II) nitrate trihydrate and sodium azide were Merck analytical grade reagents and they were used as received. 2,2′-Bipyrimidine was purchased from Lancaster Synthesis and used without further purification. Elemental analyses (C, H, N) were conducted by the Microanalytical Service of the Universidad Autónoma de Madrid (Spain). The copper content was determined by atomic absorption spectrometry.

Preparation of single crystals of [Cu_2(bpym)$(N_3)_4$]

Single crystals of the title compound were grown in aqueous solution by a slow-diffusion method using an H-double-tube glass vessel. The starting solutions were aqueous solutions of [Cu_2(bpym)$(NO_3)_4$] [15b] (0.1 mmol) in one arm and NaN_3 (0.5 mmol) in the other one. After a few weeks, brown needles were formed and they were collected, washed with water and dried over calcium chloride. *Anal.* Calc. for $C_8H_6N_{16}Cu_2$: C, 21.20; H, 1.32; N, 49.43; Cu, 28.04. Found: C, 21.14; H, 1.40; N, 49.20; Cu, 27.70%.

Physical measurements

IR spectra were taken on a Perkin-Elmer 1750 FTIR spectrophotometer as KBr pellets in the 4000–250 cm^{-1} region and X-band EPR spectra were recorded using a Brüker ER-200D spectrometer equipped with a helium continuous-flow cryostat. Magnetic susceptibility measurements were carried out at 300–30 K with a fully automatized AZTEC DSM5 pendulum-type susceptometer equipped with a TBT continuous-flow cryostat and a Brüker BE15 electromagnet, operating at 1.8 T. The apparatus was calibrated with mercury tetrakis(thiocyanato)cobaltate(II). The correction for the diamagnetism of [Cu_2(bpym)$(N_3)_4$] was estimated from Pascal's constants as -280×10^{-6} cm^3 mol^{-1}. Experimental susceptibility was also corrected for the temperature-independent paramagnetism (60×10^{-6} cm^3 mol^{-1} per Cu(II)).

X-ray structure determination

A suitable single crystal of [Cu_2(bpym)$(N_3)_4$] of approximate dimensions $0.12 \times 0.28 \times 0.14$ mm was put in a Siemens R3m/V automatic four-circle diffractometer to collect reflection data. Lattice parameters were determined and refined from least-squares fitting of the setting angles of 25 well centered reflections in the range $15 \leqslant 2\theta \leqslant 30°$. A summary of crystal data and refinement conditions is given in Table 1. The intensities were measured at 298 K using the ω–2θ scan technique. Examination of two standard reflections, monitored after every 150, showed no sign of crystal deterioration. The index ranges of data collection were $0 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 8$ and $-15 \leqslant l \leqslant 14$. Corrections were applied for Lorentz and polarization factors. ψ-Scan absorption correction [18] was also applied to the intensity data. The maximum and minimum transmission factors were 0.546 and 0.456, respectively.

TABLE 1. Crystallographic data for [Cu_2(bpym)$(N_3)_4$]

Chemical formula	$C_8H_6N_{16}Cu_2$
Formula weight	453.4
Crystal system	monoclinic
a (Å)	10.071(2)
b (Å)	6.376(1)
c (Å)	11.617(2)
β (°)	95.93(1)
V (Å^3)	742.0(2)
Z	2
Space group	$P2_1/n$
T (°C)	25
D_{calc} (g cm^{-3})	2.029
Radiation	graphite monochromated Mo Kα ($\lambda = 0.71073$ Å)
$F(000)$	448
μ (cm^{-1})	29.1
Scan method	ω–2θ
Scan speed (°/min)	2.00
Scan range (°)	$3 \leqslant 2\theta \leqslant 55$
No. collected reflections	2027
No. unique data	1723
Cutoff observed data	$3\sigma(I)$
No. observed reflections	1427
No. refined parameters	118
R_{int}	0.007
R^a	0.0275
$R_w{}^b$	0.0328
s^c	1.10

$^aR = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. ^{c}Goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

The structure was solved by standard Patterson methods and subsequently completed by Fourier recycling. The full-matrix least-squares refinement was based on $|F_o|$. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of bpym were set in calculated positions and refined as riding atoms. A common thermal parameter (50×10^{-3} Å^2) was assigned to them. The full-matrix least-squares refinement was carried out by minimizing the function $\Sigma w(\|F_o| - |F_c\|)^2$, the weighting scheme used in the last refinement cycles being $w = 1.0000/[\sigma^2(F_o) + 0.0011(F_o)^2]$. The final discrepancy indices R and R_w were 0.0275 and 0.0328, respectively. The number of reflections/number of variable parameters was 12.1. The maximum and minimum peaks in the final difference synthesis were 0.65 and -0.41 e Å^{-3}, respectively. The largest and mean Δ/σ are 0.029 and 0.009. Atomic scatterings factors and corrections for anomalous dispersion for Cu were taken from ref. 19. Solution and refinement were performed with the SHELXTL-PLUS system [20] on a MICRO-VAX II computer. The geometrical calculations were carried out with the PARST program [21] and the graphical manipulations were performed using the XP utility of the SHELXTL-PLUS system. The final atomic coordinates for non-hydrogen atoms and interatomic bond distances and angles are listed in Tables 2 and 3, respectively.

Results and discussion

Description of the structure

The structure of the title compound consists of neutral dinuclear [Cu_2(bpym)$(N_3)_4$] units (Fig. 1) which are linked by azide groups acting simultaneously in asymmetrical end-on and end-to-end bridging fashions to yield a 2D-arrangement (Fig. 2). The resulting layers are interconnected only by weak van der Waals forces.

The copper atom is in a distorted octahedral surrounding: the basal plane is formed by four nitrogen atoms, two from azide groups and the other two from bpym, whereas the axial positions are filled by azide-nitrogen atoms from neighbouring units. In fact, two kinds of azide groups are present, the N(6)N(7)N(8) one which is coordinated to copper only though N(6) as a monodentate ligand (1.949(3) Å for Cu(1)–N(6)) and the N(3)N(4)N(5) one which is bound to the metal atom through N(3) and N(5) in asymmetrical end-on and end-to-end bridging fashions (1.978(2), 2.480(2) and 2.743(3) Å for Cu(1)–N(3), Cu(1b)–N(3) and Cu(1c)–N(5), respectively). The Cu–N(bpym) bond distances (2.065(2) and 2.056(2) Å for Cu(1)–N(1) and Cu(1)–N(2a), respectively) are close to that reported for related bpym-bridged copper(II) complexes. The equatorial Cu–N(azide) bond lengths (av. value 1.97 Å) are shorter than the axial ones (mean value 2.61

TABLE 2. Final atomic coordinates for non-hydrogen atoms[a] and equivalent isotropic displacement parameters[b] for [Cu_2(bpym)$(N_3)_4$]

Atom	*x/a*	*y/b*	*z/c*	$U_{eq} \times 10^3$ (Å^2)
Cu(1)	0.1279(1)	0.0825(1)	0.2169(1)	23(1)
N(1)	0.1633(2)	0.0977(3)	0.0452(2)	22(1)
C(1)	0.2721(3)	0.1570(5)	−0.0038(2)	27(1)
C(2)	0.2748(3)	0.1507(5)	−0.1222(2)	30(1)
C(3)	0.1625(3)	0.0837(4)	−0.1897(2)	26(1)
N(2)	0.0539(2)	0.0207(3)	−0.1412(2)	21(1)
C(4)	0.0596(2)	0.0322(3)	−0.0264(2)	18(1)
N(3)	0.3034(2)	0.2091(4)	0.2684(2)	28(1)
N(4)	0.3905(3)	0.0884(4)	0.2986(3)	36(1)
N(5)	0.4756(3)	−0.0242(5)	0.3271(4)	79(2)
N(6)	0.0613(3)	0.0860(4)	0.3686(2)	38(1)
N(7)	0.1341(3)	0.1326(4)	0.4524(2)	34(1)
N(8)	0.2043(4)	0.1703(6)	0.5344(2)	63(1)

[a] e.s.d.s are given in parentheses. [b] *U* values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$.

TABLE 3. Bond distances (Å) and bond angles (°) for [Cu_2(bpym)$(N_3)_4$][a, b]

Copper environment			
Cu(1)–N(1)	2.065(2)	Cu(1)–N(6)	1.949(3)
Cu(1)–N(2a)	2.056(2)	Cu(1)–N(3b)	2.480(2)
Cu(1)–N(3)	1.978(2)	Cu(1)–N(5c)	2.743(3)
N(1)–Cu(1)–N(2a)	80.6(1)	N(2a)–Cu(1)–N(3)	171.2(1)
N(1)–Cu(1)–N(3)	92.0(1)	N(6)–Cu(1)–N(3)	95.9(1)
N(1)–Cu(1)–N(3b)	92.1(1)	N(6)–Cu(1)–N(3b)	93.9(1)
N(1)–Cu(1)–N(5c)	82.9(1)	N(6)–Cu(1)–N(5c)	89.9(1)
N(1)–Cu(1)–N(6)	169.3(1)	N(3)–Cu(1)–N(3b)	97.9(1)
N(2a)–Cu(1)–N(6)	90.9(1)	N(3)–Cu(1)–N(5c)	89.7(1)
N(2a)–Cu(1)–N(3b)	87.2(1)	N(3b)–Cu(1)–N(5c)	171.2(1)
N(2a)–Cu(1)–N(5c)	84.7(1)		
2,2′-Bipyrimidine ligand			
N(1)–C(1)	1.340(4)	C(3)–N(2)	1.343(4)
N(1)–C(4)	1.334(3)	N(2)–C(4)	1.331(3)
C(1)–C(2)	1.380(4)	C(4)–C(4a)	1.462(5)
C(2)–C(3)	1.376(4)		
Cu(1)–N(1)–C(1)	130.8(2)	C(2)–C(3)–N(2)	120.7(2)
Cu(1)–N(1)–C(4)	112.7(2)	C(3)–N(2)–C(4)	116.9(2)
N(1)–C(4)–C(4a)	116.7(3)	C(3)–N(2)–Cu(1a)	130.1(2)
C(4)–N(1)–C(1)	116.5(2)	N(2)–C(4)–N(1)	126.3(2)
N(1)–C(1)–C(2)	121.1(2)	N(2)–C(4)–C(4a)	117.0(3)
C(1)–C(2)–C(3)	118.5(3)	Cu(1a)–N(2)–C(4)	113.0(2)
Azide ligand			
N(3)–N(4)	1.192(3)	N(6)–N(7)	1.195(3)
N(4)–N(5)	1.141(4)	N(7)–N(8)	1.152(4)
Cu(1)–N(3)–N(4)	115.7(2)	Cu(1)–N(6)–N(7)	120.0(2)
N(3)–N(4)–N(5)	178.7(3)	N(6)–N(7)–N(8)	177.6(3)
Cu(1)–N(3)–Cu(1b)	130.3(1)		

[a] e.s.d.s are given in parentheses. [b] Symmetry code: (a) $-x, -y, -z$; (b) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (c) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

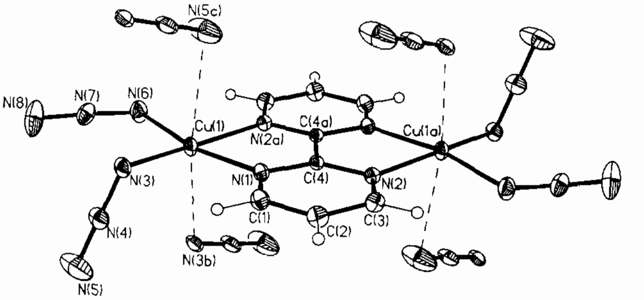

Fig. 1. Perspective drawing of [Cu_2(bpym)$(N_3)_4$] showing the atom numbering. Thermal ellipsoids are drawn at the 30% probability level.

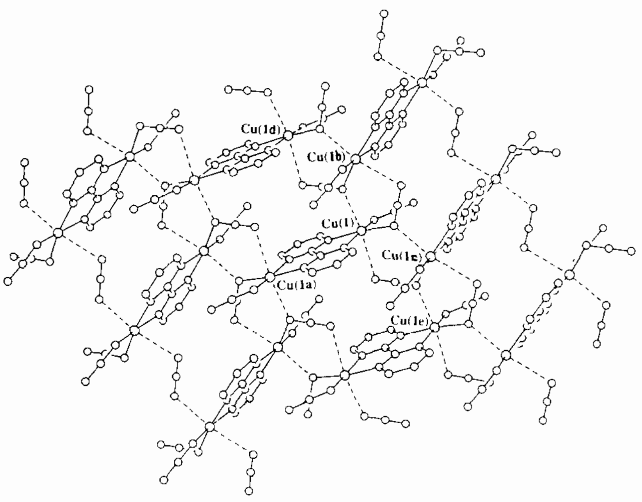

Fig. 2. A view showing the packing of [$Cu_2(bpym)(N_3)_4$] in the crystal. Symmetry code: (a) $-x$, $-y$, $-z$; (b) $\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$; (c) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; (d) x, $y-1$, z; (e) x, $1+y$, z.

Å) and the values of the former compare well with those found in related systems in which the azide occupies equatorial positions acting either as terminal or bridging ligand. The four equatorial atoms are nearly coplanar with deviations from the least-squares plane lower than 0.018(3) Å, the copper atom being displaced 0.104(1) Å towards the axial N(3b) nitrogen atom. The value of the angle subtended at the metal atom by the chelating bpym (80.6(1)° for N(1)–Cu(1)–N(2a)) is significantly reduced with respect to the ideal value of 90° in agreement with the small bite parameter of free bpym [22].

The pyrimidyl rings of the bpym ligands are planar as expected, the maximum deviation from the mean planes being 0.010(2) Å at C(3). The ligand as a whole is also planar and the dihedral angle between this plane and the equatorial one is only 2.4(1)°. The intra-ring carbon–carbon bond length (mean value 1.38 Å) is shorter than the inter-ring carbon–carbon distance (1.462(5) Å for C(4)–C(4a)) in agreement with the greater double bond character of the former.

The azido groups are quasi-linear (178.7(3) and 177.6(3)° for N(3)–N(4)–N(5) and N(6)–N(7)–N(8), respectively) and the values of the angles Cu(1)–N(3)–N(4) (115.7(2)°) and Cu(1)–N(6)–N(7) (120.0(2)°) are consistent with a sp^2-hybridization of N(3) and N(6) atoms. Two different nitrogen–nitrogen bond distances occur around the central nitrogen atom in both azido groups (1.192(3) and 1.141(4) Å for N(3)–N(4) and N(4)–N(5), 1.195(3) and 1.152(4) Å for N(6)–N(7) and N(7)–N(8)), the shorter bond involving the end which is strongly bound to the metal ion as observed in other copper(II) complexes containing terminal [1b, 5, 7, 8, 23], end-on [3, 5b, 11ab, 23c, 24–26] or asymmetrical end-to-end [4, 10, 11a, 25, 27] azido ligands.

The intramolecular Cu(1)···Cu(1a) separation is 5.520(1) Å, whereas the shortest intermolecular metal–metal distance is significantly shorter (4.051(1) for Cu(1)···Cu(1b) or Cu(1)···Cu(1c)).

IR and EPR spectra

Examination of IR data is useful to infer the coordination modes of azido and bpym ligands. As far as the azido group is concerned, the relevant features on the IR spectrum of the title complex are two stretching frequencies: a split sharp and strong peak at 2060 and 2030 cm^{-1} ($\nu_{as}(N_3)$) and two medium peaks at 1335 and 1280 cm^{-1} ($\nu_s(N_3)$) [28]. The strong feature is at its usual position [29] independently of the coordination mode of the azide. However, the occurrence of medium intensity bands near 1300 cm^{-1} supports the presence of end-on and/or terminally bound azide [29a, 30]. In [$Cu_2(bpym)(N_3)_4$] both coordination modes are present. In the far-IR region (*c.* 400 cm^{-1}) bands due to Cu–N stretching vibrations are clearly detectable. Dealing with bpym, the occurrence of a very asymmetric doublet at 1585(vs) and 1560(vw) supports the presence of bis-chelating bpym [17a] in full agreement with the structural data.

The powder X-band EPR spectrum of the compound at room temperature exhibits a quasi-symmetric feature at 3160 G ($g = 2.12$) whose intensity quickly vanishes when cooling down, thus supporting its triplet nature. No half-field forbidden transition was detected either at room or low temperatures.

Magnetic properties

The magnetic properties of [$Cu_2(bpym)(N_3)_4$] are shown in Fig. 3 in the form of the molar magnetic susceptibility (χ_M) versus *T*. The curve exhibits a behaviour characteristic of antiferromagnetically coupled copper(II) ions with a smooth maximum in the susceptibility occurring at about 160 K. The experimental

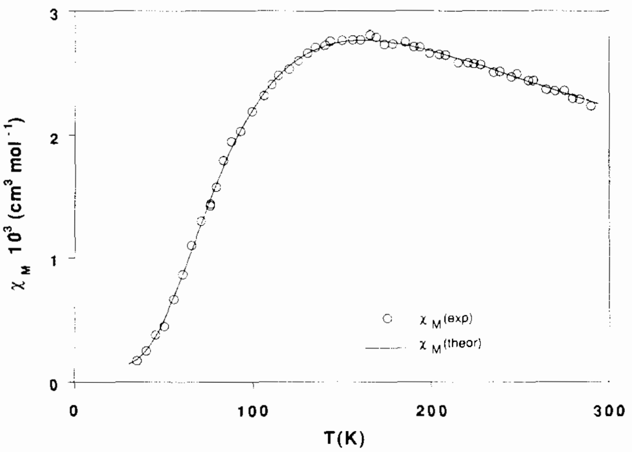

Fig. 3. Thermal dependence of χ_M for **1**.

data were fitted to a simple Bleaney-Bowers expression (eqn. (1))

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

for a dinuclear copper(II) complex, where J is the singlet–triplet energy gap defined by the Hamiltonian (eqn. (2))

$$\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2 \tag{2}$$

J accounts for the intramolecular exchange interaction, S_1 and S_2 are quantum spin operators, and N, g, β and T have their usual meaning. J and g were determined by minimizing $R = \Sigma[\chi_M^{obs} - \chi_M^{calc}]^2/\Sigma[\chi_M^{obs}]^2$ and found as $J = -178$ cm^{-1} and $g = 2.17$ with $R = 8.0 \times 10^{-5}$, a value which actually corresponds to a good experiment–theory agreement.

A strong antiferromagnetic coupling between copper(II) ions is thus achieved in the present compound. As shown in previous works [15a, 17a], $-J$ values of *c.* 200 cm^{-1} were found for bpym-bridged copper(II) complexes (see Table 4). This large singlet–triplet energy gap for copper(II) ions separated by more than 5.3 Å is due to the overlap between the $d_{x^2-y^2}$ magnetic orbitals centred on each metal ion (the x and y axes are roughly defined by the Cu(1)–N(1) and Cu(1)–N(2a) bonds, respectively) through the bpym bridge, where they are partially delocalized. Due to the fact that the axial distances around the copper are long (2.480(2) and 2.743(3) Å for Cu(1)–N(3b) and Cu(1)–N(5c), respectively) the admixture of d_{z^2} orbital in the ground state is weak and consequently, the overlap between the $d_{x^2-y^2}$ orbitals through N(3b) or N(5c) is expected to be very small. Furthermore, there is no overlap between the bpym units both within the layer (see Fig. 2) and between the layers. We recall that in the context of the model of interaction of localized non-orthogonal magnetic orbitals [31] and for extended bridges such as bpym, the value of the exchange coupling for the dinuclear Cu(bpym)Cu unit is proportional to S^2 [32, 13c], S being the overlap integral between the two magnetic orbitals centred on the two copper(II) ions. Keeping in mind these considerations, is not surprising that the magnetic behaviour of the present sheet-like polymer can be matched by a theoretical expression for the dinuclear bpym-bridged copper(II) unit. The copper–copper separation through bpym in the azido complex (5.520(1) Å) lies within the range observed for related species (5.371(1)–5.545(1) Å from Table 4). An inspection of the values of the inter-ring carbon–carbon distances in bridging bpym reveals that they are all shorter than those found in the free ligand in both gaseous and solid states (1.511(2) and 1.497(1) Å, respectively) [22]. As shown in Table 4, the somewhat reduced $-J$ value obtained for the azido complex is mainly due to the larger displacement of the metal atom from the equatorial plane which is found in it. The influence of this and other structural factors on the magnitude of the exchange interaction in the parent oxalato-bridged dinuclear copper(II) complexes was reported by some of us in a previous work [33].

We would like to finish the present contribution with a brief comment on the magneto-structural role of the counterion X in the complexes of formula $[Cu_2(bpym)X_4]$ (X = Cl, Br, NO_3, NCS, NCO and N_3). This family of complexes has in common the occurrence of dinuclear Cu(bpym)Cu units which are interconnected through the counterion X to yield 1D (X = NO_3), 2D (X = Cl, Br, NCO and N_3) and 3D (X = NCS) assemblies. In the nitrato compound, two kinds of nitrate ligands are present: one acts in a chelating fashion whereas the other one acts as a bis-monodentate bridge linking the dinuclear Cu(bpym)Cu entities to build a zigzag chain. In the isostructural chloro and bromo compounds, the halogen atoms act as bridging groups between copper atoms occupying simultaneously basal and axial positions around copper building 1D CuX_2 chains which are linked by bpym groups. Concerning the cyanato compound, the dinuclear Cu(bpym)Cu entities grow in one direction through cyanate groups acting in an asymmetrical end-on bridging fashion, the

TABLE 4. Relevant structural and magnetic data for the complexes $[Cu_2(bpym)X_4]$

X	Network	Donor set[a]	γ[b] (°)	h_M[c] (Å)	d(C–C)[d] (Å)	d(Cu–Cu)[e] (Å)	J[f] (cm^{-1})	Ref.
NO_3	1D	N_2O_4	3.5	0.000	1.432(8)	5.371(1)	−191	15
Cl	2D	$N_2Cl_2Cl_2$	2.7	0.000	1.472(3)	5.528(2)	−225	15a
Br	2D	$N_2Br_2Br_2$	2.0	0.000	1.470(7)	5.545(1)	−236	15a
N_3	2D	N_2N_4	2.6	0.104	1.462(5)	5.520(1)	−178	this work
NCO	2D	N_2N_3O	5.8	0.007	1.450(9)	5.520(1)	−199	7a
NCS	3D	$N_2N_2S_2$	0.8	0.000	1.461(10)	5.492(2)	−230	7a
			0.6	0.000	1.475(10)	5.506(3)		

[a] The two first atoms are those of bpym and the four first ones build the equatorial plane. [b] Dihedral angle between the mean equatorial plane around copper(II) and the bpym plane. [c] The height of the metal atom above the basal plane. [d] The inter-ring carbon–carbon distance. [e] Metal–metal separation through bridging bpym. [f] Singlet–triplet energy gap.

polymerization in the second direction being achieved via end-to-end cyanato bridges between chains. Two kinds of azido groups are present in the title compound, one which acts as a terminal ligand whereas the other one exhibits both end-on and end-to-end coordination modes leading to a 2D arrangement of copper(II) ions. Finally, the dinuclear Cu(bpym)Cu units in the thiocyanate derivative are linked by thiocyanate groups acting in an asymmetrical end-to-end bridging fashion to yield a polymeric 3D arrangement. Summarizing, the choice of the counterion X allows not only the growing of single crystals but can be crucial in the determination of the type of network of the resulting compound. Unfortunately, this relevant structural role of X in the present family of complexes exerts only a minor influence on their magnetic behaviour which can be explained on the basis of simple dinuclear Cu(bpym)Cu units.

Supplementary material

Tables of thermal parameters, hydrogen coordinates, mean planes (4 pages) as well as a listing of observed and calculated structure factors (7 pages) are available from the authors on request.

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