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Structure and Magnetic Properties of Two New Polynuclear Copper(II) Complexes: $[Cu(terpy)(NCO)(H_2O)](Y)$ ($Y = NO_3, PF_6$)

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Abstract

Compounds $[Cu(terpy)(NCO)(H_2O)](NO_3)$ (**I**) and $[Cu(terpy)(NCO)(H_2O)](PF_6)$ (**II**) (terpy = 2,2′:6′,2″-terpyridine) have been synthesized and the crystal structures have been determined. Complex **I** is monoclinic with space group $P2_1/n$ and lattice parameters $a = 9.698(2)$, $b = 10.391(2)$, $c = 16.681(2)$ Å, $\beta = 95.54(4)°$, $U = 1673(1)$ Å^3 and $Z = 4$. Complex **II** is triclinic, with space group $P\bar{1}$ and lattice parameters $a = 9.129(1)$, $b = 10.489(2)$, $c = 11.106(3)$ Å, $\alpha = 104.90(2)°$, $\beta = 86.61(1)°$, $\gamma = 113.93(1)°$, $U = 938.1(5)$ Å^3 and $Z = 2$. The complexes consist of $[Cu(terpy)(NCO)(H_2O)]^+$ and NO_3^- or PF_6^- ions. The $[Cu(terpy)(NCO)(H_2O)]^+$ cationic units are stacked to make a chain or dimeric arrangements for the nitrate and hexafluorophosphate compounds, respectively. Magnetic susceptibility measurements (2–100 K) and EPR spectra provide evidence of the existence of very weak antiferromagnetic exchange coupling for both complexes. The magnetic behaviour is discussed on the basis of the structural findings.

Introduction

The study of exchange-coupled polynuclear complexes is an active area of coordination chemistry. In particular, significant progress has been made in the understanding of the exchange interactions phenomenon [1]. In general, a close dependence of the isotropic exchange parameter J on some structural factors has been demonstrated and understood on the basis of the orbital mechanism of the exchange interaction [2].

Exchange interactions that are propagated by discrete polyatomic bridging moieties (OCN^-, SCN^-, N_3^-, CN^- etc.) between the paramagnetic centers have been the subject of several papers [3–6]. Interesting relationships between rather subtle changes in molecular structure (inter and outer-sphere dimers, linear chains) and the net electron-exchange interactions have been detected [7, 8].

A part of the activity of our laboratory has been devoted to the study of the interaction between paramagnetic metal ions in coupled systems. In this way, we have established a synthetic strategy of new one-dimensional systems of copper(II) with tridentate ligands of general formula $[CuL_{III}XY]$ (L_{III} = tridentate ligand, X = coordinating anion, Y = coordinating or non-coordinating anion), which include bi- and polynuclear species [9–11].

In this work, we have determined the crystal structures and the sign of the exchange-interactions in two new polynuclear copper(II) complexes, with general formula $[Cu(terpy)(NCO)(H_2O)](Y)$ ($Y = NO_3, PF_6$), which differ only by the nature of their counterions.

Experimental

Synthesis

$[Cu(terpy)(NCO)(H_2O)](NO_3)$ (I)

A 0.200 g (0.86 mmol) portion of 2,2′:6′,2″-terpyridine (terpy) was dissolved in a 20 ml aqueous solution containing 0.207 g (0.86 mmol) of $Cu(NO_3)_2 \cdot 3H_2O$. Heating and stirring dissolved the terpy, with subsequent formation of a Cu(II)–terpy complex. The resulting solution was treated with 0.070 g (0.86 mmol) of KNCO, added dropwise (with stirring) to the warm solution of the Cu(II)–terpy complex. Slow evaporation at room temperature yield green prismatic crystals after several hours, which were separated by filtration, washed with diethyl ether, and stored in a desiccator over P_2O_5 for 48 h. *Anal.* Calc. for $C_{16}H_{13}O_5CuN_5$: C, 45.8; H, 3.1; N, 16.7. Found: C, 45.3; H, 2.9; N, 16.3%.

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[Cu(terpy)(NCO)(H$_2$O)](PF$_6$) (II)

Samples of this compound were prepared by addition of an excess of a KPF$_6$ saturated aqueous solution to a warm aqueous solution containing 0.200 (0.48 mmol) of complex **I**. A green precipitate was separated by vacuum filtration and readily recrystallized from a saturated aqueous solution. The crystals were isolated after filtration, washed with diethyl ether, and stored in a desiccator over P$_2$O$_5$ for 48 h. *Anal.* Calc. for C$_{16}$H$_{13}$O$_2$PF$_6$CuN$_4$: C, 39.7; H, 2.7; N, 11.6. Found: C, 39.5; H, 2.6; N, 11.4%.

X-ray and Structure Determination

Crystals of [Cu(terpy)(NCO)(H$_2$O)](NO$_3$) (**I**) and [Cu(terpy)(NCO)(H$_2$O)](PF$_6$) (**II**) as green needles were mounted in an Enraf-Nonius CAD4 automatic diffractometer with their long dimensions roughly parallel to the phi axis of the goniometer. The cell dimensions and orientation matrix were determined from the setting angles of 25 reflections with a Mo Kα monochromated radiation. A fast data collection of reflections in the θ range 3–12° allowed us to choose the space group on looking at the systematic extinctions. Details of the data collection together with structure refinement are summarized in Table 1. Orientation (every 50 reflections) and intensity control (every 3600 s) by means of two standard reflections showed no significant changes during data collection. The intensity data were corrected for Lorentz polarization factors. Absorption effects were neglected. The structures were solved using the direct methods, MULTAN84 [12] and successive Fourier syntheses (SHELX76) [13]. Anisotropic thermal parameters were introduced for all atoms except hydrogen atoms whose thermal parameters were isotropic. The hydrogen positions could be derived from a difference Fourier map. Final difference maps revealed no significant regions of electron density with max. 0.58 and min. −0.28 e Å^{-3} for compound **I** and max. 0.71 and min. −0.45 e Å^{-3} for compound **II**. Final values of the discrepancy indices are R = 0.041 (R_w = 0.049) for com-

TABLE 1. Physical properties and parameters of data collection and refinement of the [Cu(terpy)(NCO)(H$_2$O)](Y) (Y = NO$_3$, PF$_6$) complexes

Compound	I	II
Formula	[C$_{16}$H$_{13}$O$_5$CuN$_5$]	[C$_{16}$H$_{13}$O$_2$PF$_6$CuN$_4$]
Dimensions (mm)	0.27 × 0.15 × 0.12	0.45 × 0.12 × 0.07
Molecular weight (g)	398.5	501.5
System	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	9.698(2)	9.129(1)
b (Å)	10.391(2)	10.489(2)
c (Å)	16.681(2)	11.106(3)
α (°)	90	104.90(2)
β (°)	95.54(4)	86.61(1)
γ (°)	90	113.93(1)
U (Å^3)	1673(1)	938.1(5)
Z	4	2
ρ_{obs} (g cm^{-3})	1.66(4)	1.70(2)
ρ_{calc} (g cm^{-3})	1.66	1.78
μ(Mo Kα) cm^{-1}	13.5	13.3
F(000)	852	498
Measurements		
Radiation Mo Kα, λ (Å)	0.7107	0.7107
Scan type	$\omega/2\theta$	$\omega/2\theta$
θ range (°)	1–25	1.5–25
Check reflections int.	−1 1 −4, −2 −1 −6	2 1 0, 0 1 2
Check reflections orient.	−2 −1 −6, −2 1 −6, −2 5 1	2 −3 1, 2 1 2, 1 −2 2
No. measured reflections	8934	6842
No. of averaged reflections	2935	3291
Refinements		
No. variables NV =	296	323
No. unique reflections with	$I \geqslant 2.5\sigma(I)$	$I \geqslant 2.5\sigma(I)$
NO	1924	2191
Weighting scheme		
$w = 1/[\sigma^2\lvert F_o\rvert + (p\lvert F_o\rvert)^2]$ p =	0.057	0.028
$R = (\Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/(\Sigma\lvert F_o\rvert)$	4.12	4.46
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	4.90	5.42

TABLE 2. Final atomic coordinates ($\times 10^4$) and equivalent thermal parameters (Å^2) with e.s.d.s. in parentheses of the [Cu(terpy)(NCO)(H_2O)](Y) (Y = NO_3, PF_6) complexes

Atom	*x/a*	*y/b*	*z/c*	B_{eq}[a]	Atom	*x/a*	*y/b*	*z/c*	B_{eq}[a]
Compound I					Compound II				
Cu	8662(1)	885(1)	631(0)	4.168(2)	Cu	6720(1)	811(1)	9090(1)	3.71(1)
N(1)	7323(4)	1562(4)	−297(2)	4.324(6)	N(1)	7933(6)	2690(5)	10392(4)	3.84(1)
N(2)	7802(4)	−713(3)	241(2)	4.214(3)	N(2)	6063(5)	2099(5)	8516(4)	3.520(4)
N(3)	9813(4)	−429(4)	1317(2)	4.745(8)	N(3)	5184(6)	−601(5)	7638(5)	4.00(1)
C(1)	7137(6)	2787(5)	−527(3)	5.266(5)	P	8510(2)	−2564(2)	5525(2)	4.392(3)
C(2)	6109(7)	3133(6)	−1121(3)	5.572(1)	F(1)	9204(5)	−3783(5)	5265(4)	6.77(1)
C(3)	5287(6)	2224(6)	−1486(3)	5.753(1)	F(2)	9712(9)	−1824(7)	4604(6)	10.48(4)
C(4)	5445(6)	962(5)	−1263(3)	5.066(9)	F(3)	7797(5)	−1358(4)	5765(4)	5.86(1)
C(5)	6483(5)	657(5)	−654(2)	4.403(7)	F(4)	9809(7)	−1614(7)	6623(5)	8.97(1)
C(6)	6752(5)	−659(5)	−352(3)	4.18(2)	F(5)	7395(9)	−3275(8)	6491(8)	14.24(2)
C(7)	6058(6)	−1775(6)	−606(3)	4.98(1)	F(6)	7231(9)	−3534(6)	4446(8)	12.09(7)
C(8)	6483(7)	−2916(5)	−238(3)	5.790(9)	C(1)	8907(8)	2905(7)	11348(5)	4.67(1)
C(9)	7563(6)	−2958(5)	363(3)	5.14(1)	C(2)	9658(9)	4236(7)	12171(6)	4.90(1)
C(10)	8214(5)	−1824(5)	592(3)	4.545(3)	C(3)	9415(8)	5386(7)	12012(5)	4.43(2)
C(11)	9374(5)	−1649(5)	1218(3)	4.798(5)	C(4)	8418(8)	5200(6)	11035(5)	4.113(8)
C(12)	9991(7)	−2635(6)	1667(4)	6.132(7)	C(5)	7705(6)	3834(5)	10234(5)	3.534(9)
C(13)	11060(8)	−2364(8)	2244(4)	6.89(2)	C(6)	6648(7)	3512(6)	9141(5)	3.769(7)
C(14)	11487(7)	−1113(8)	2364(4)	6.90(4)	C(7)	6222(8)	4455(7)	8724(6)	4.72(2)
C(15)	10847(7)	−162(7)	1877(3)	5.598(2)	C(8)	5190(9)	3907(8)	7669(7)	6.014(6)
N(4)	9810(5)	2344(4)	839(3)	5.948(8)	C(9)	4553(8)	2459(8)	7077(6)	5.219(5)
C(16)	10215(6)	3341(6)	1034(4)	5.88(2)	C(10)	5041(7)	1568(6)	7521(5)	4.074(5)
O(1)	10696(7)	4355(4)	1232(4)	10.13(5)	C(11)	4525(7)	−15(7)	7006(6)	4.248(9)
Ow(1)	7154(4)	1222(3)	1521(2)	4.898(9)	C(12)	3482(7)	−827(9)	5986(7)	5.19(2)
N(5)	6926(5)	4419(4)	1800(3)	5.011(7)	C(13)	3100(8)	−2288(9)	5589(8)	5.49(2)
O(2)	6449(6)	3995(5)	1144(3)	8.68(2)	C(14)	3774(8)	−2882(8)	6214(9)	5.43(3)
O(3)	7478(6)	3715(4)	2321(3)	7.55(2)	C(15)	4805(8)	−2029(7)	7240(7)	4.86(2)
O(4)	6834(6)	5567(4)	1940(3)	8.19(5)	N(4)	6925(8)	−514(6)	9894(5)	5.72(2)
					C(16)	7583(9)	−1155(6)	10142(6)	4.60(2)
					O(1)	8219(8)	−1842(6)	10440(6)	8.08(2)
					Ow(1)	8981(6)	1139(5)	7964(4)	4.464(5)

[a] $B_{eq} = 8\pi^2[(U_{11} + U_{22} + U_{33})/3]$.

pound I and $R = 0.045$ ($R_w = 0.054$) for compound II.

Final positional and equivalent thermal parameters of [Cu(terpy)(NCO)(H_2O)](NO_3) (I) and [Cu(terpy)(NCO)(H_2O)](PF_6) (II) complexes are given in Table 2.

Scattering factors were taken from the International Tables for X-ray Crystallography [14]. All calculations were carried out on a MicroVAX VT220 computer at the computer centre of the Basque University. The geometric calculations were performed with XANADU [15] and molecular illustrations were drawn with PLUTO [16]. See also 'Supplementary Material'.

Physical Measurements

Infrared spectra were obtained with KBr pellets in the 4000–250 cm^{-1} region, using a Perkin-Elmer spectrophotometer. A Bruker ER 200 tt spectrometer equipped with a standard low-temperature device, operating at X-band calibrated by NMR probe for the magnetic field and a HP 5342 A frequency counter for the microwave frequency, was used to record the EPR powder spectra of the complexes at different temperatures. Magnetic susceptibility measurements were performed on powdered samples in the temperature range 2–100 K using a SQUID SHE magnetometer. Experimental susceptibilities were corrected for the diamagnetic contributions and for the temperature independent paramagnetism estimated to be 60×10^{-6} cm^3 mol^{-1} per copper(II) ion.

Results and Discussion

Description of the Structures

The main interatomic distances and angles of compounds I and II are listed all together in Table 3 in order to facilitate their comparison. The X-ray crystal structures of both the title compounds consist of [Cu(terpy)(NCO)(H_2O)]$^+$ and NO_3^- or PF_6^- ions. The copper complex, presented with labeling in Fig. 1, is stacked to make a chain or dimeric ar-

TABLE 3. Selected bond distances (Å) and angles (°) in the [Cu(terpy)(NCO)(H_2O)](Y) (Y = NO_3, PF_3) complexes

Distance/angle	I	II	Distance/angle	I	II
Copper coordination sphere					
Cu–N(1)	2.047(4)	2.038(4)	Cu–N(2)	1.942(3)	1.933(6)
Cu–N(3)	2.043(4)	2.028(5)	Cu–N(4)	1.893(4)	1.906(8)
Cu–Ow(1)	2.210(4)	2.298(5)	O(w)–O(3)	2.917(5)	
O(4)–O(w)^{i}	2.744(6)		Cu–Cu^{i}	8.583(2)	
Cu–Cu^{ii}	3.950(2)		Cu–Cu^{iii}	7.442(1)	
Cu–Cu^{iv}		7.369(2)	Cu–Cu^{v}		3.678(1)
Cu–N(4)^{v}		3.368(7)			
O(w)–Cu–N(1)	92.3(1)	90.6(2)	O(w)–Cu–N(2)	94.0(1)	97.3(2)
O(w)–Cu–N(3)	95.2(1)	94.6(2)	O(w)–Cu–N(4)	99.5(2)	96.6(3)
N(1)–Cu–N(2)	79.6(2)	80.1(2)	N(2)–Cu–N(3)	79.0(2)	79.7(2)
N(3)–Cu–N(4)	98.8(2)	99.7(2)	N(1)–Cu–N(4)	100.5(2)	99.3(2)
N(1)–Cu–N(3)	157.8(2)	159.6(3)	N(2)–Cu–N(4)	166.4(2)	166.1(2)
N(4)^{v}–Cu–N(1)		94.5(2)	N(4)^{v}–Cu–N(2)		69.8(2)
N(4)^{v}–Cu–N(3)		75.9(2)	N(4)^{v}–Cu–N(4)		96.5(2)
O(w)–Cu–N(4)^{v}		165.1(2)	Cu–N(4)–Cu^{v}		83.5(3)
Average values in the terpyridine					
C–N	1.341(9)	1.34(2)	C–C(intracycle)	1.376(15)	1.382(19)
C–C(intercycle)	1.471(8)	1.48(1)	C–H	0.92(10)	0.93(12)
C–C–C(intracycle)	119(1)	119(1)	C–C–C(intercycle)	123.8(6)	124(1)
C–C–N(intracycle)	121.0(9)	121(1)	C–C–N(intercycle)	112.5(5)	112.6(8)
C–N–C	120(1)	119(2)			
Cyanate					
N(4)–C(16)	1.144(8)	1.154(12)	C(16)–O(1)	1.186(8)	1.204(12)
Cu–N(4)–C(16)	163.1(5)	153.6(6)	N(4)–C(16)–O(1)	176.9(7)	177.0(8)
Counterions					
N(5)–O(2)	1.228(7)		N(5)–O(3)	1.219(6)	
N(5)–O(4)	1.220(6)		O(2)–N(5)–O(3)	121.4(5)	
O(3)–N(5)–O(4)	119.0(5)		O(4)–N(5)–O(2)	119.5(5)	
P–F(1)		1.602(6)	P–F(2)		1.561(7)
P–F(3)		1.603(5)	P–F(4)		1.573(5)
P–F(5)		1.552(9)	P–F(6)		1.552(8)
F(3)...Ow(1)		2.953(5)			

i = $\frac{3}{4} - x, \frac{1}{4} + y, \frac{1}{4} - z$; ii = $1 - x, -y, -z$; iii = $\frac{1}{2} - x, -y, -z$; iv = $1 - x, -y, 1 - z$; v = $\frac{1}{2} - x, -y, 1 - z$.

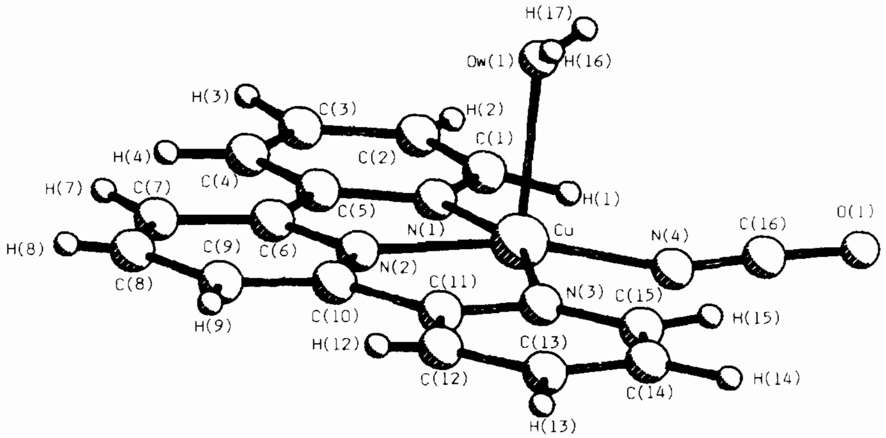

Fig. 1. Perspective view of the [Cu(terpy)(NCO)(H_2O)]$^+$ unit showing the atom numbering.

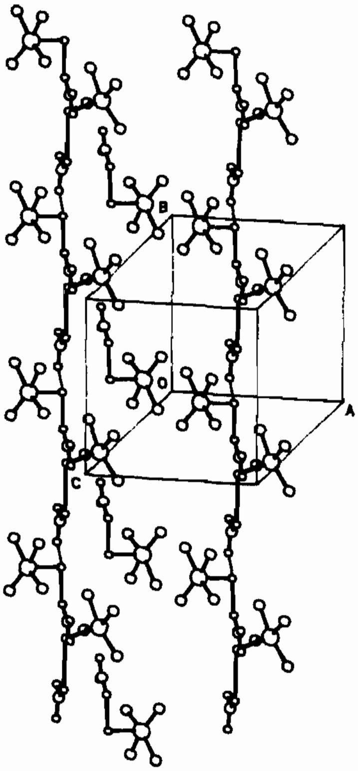

Fig. 2. Perspective view of the chaining up of the [Cu(terpy)-(NCO)(H_2O)](NO_3) complex in the |010| direction.

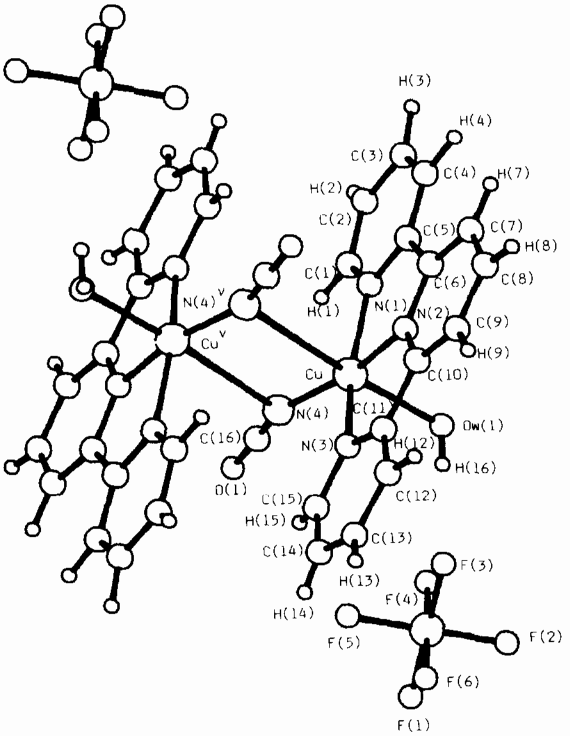

Fig. 3. Perspective view of the [Cu(terpy)(NCO)(H_2O)]-(PF_6) dimeric complex.

rangement for the nitrate and hexafluorophosphate compounds, respectively.

The structure of compound I consists of [Cu-(terpy)(NCO)(H_2O)]$^+$ units linked by hydrogen bonds between the water molecules and the nitrate anions (Fig. 2). The Ow(1)...O(3) and O(4)...Ow(1)^i [i = $\frac{3}{4} - x$, $\frac{1}{4} + y$, $\frac{1}{4} - z$] distances are 2.917(5) and 2.744(6) Å, respectively. An helicoidal binary axis serves to propagate the chain along the |010| direction. The copper(II) ions of the [Cu(terpy)-(NCO)H_2O)]$^+$ units belonging to two different chains are alternately separated by 3.950(2) [ii = $1 - x$, $-y$, $-z$] and 7.442(1) Å [iii = $\frac{1}{2} - x$, $-y$, $-z$].

The coordination sphere of the copper(II) ion is better described as a distorted square pyramid. The basal positions are occupied by the three nitrogen atoms of the terpyridine ligand [Cu–N(1), N(2), N(3); 2.047(4), 1.942(3), 2.043(4) Å, respectively] and the N-cyanate group [Cu–N(4), 1.893(4) Å]. The apical site is occupied by the water molecule [Cu–Ow(1), 2.210(4) Å]. The average value of the angles Ow(1)–Cu–N(basal) is 95(3)°, while the *trans*-basal angles, N(1)–Cu–N(3) and N(2)–Cu–N(4) are 157.8(2) and 166.4(2)°, respectively. The basal atoms are coplanar within ±0.04 Å and the copper(II) ion is displaced 0.19 Å from the mean plane.

The structure of compound II consists of cationic [Cu(terpy)(NCO)(H_2O)]$_2^{2+}$ units and hexafluorophosphate anions (Fig. 3). The dimeric complex cation is built by two [Cu(terpy)(NCO)(H_2O)]$^+$ units linked through two N-cyanate bridge groups and related by a molecular inversion center. The water molecule makes a hydrogen bond with the fluorine atom F(3) of the PF_6 group [Ow(1)...F(3) = 2.953(5) Å]. The [Cu(terpy)(NCO)(H_2O)]$_2$(PF_6)$_2$ dimeric molecules are isolated, with the shorter interdimeric distance Cu–Cu^{iv} being 7.369(2) Å, iv = $1 - x, -y, 1 - z$.

The coordination around the copper(II) ion can be described as distorted elongated tetragonal octahedral. The equatorial positions are occupied by the three nitrogen atoms from the terpy ligand [Cu–N(1), N(2), N(3); 2.038(4), 1.933(6), 2.028(5) Å] and the nitrogen atom from the N-cyanate group [Cu–N(4), 1.906(8) Å]. The water molecule occupies an axial site, with a Cu–Ow(1) distance of 2.298(5) Å. The coordination sphere is completed by the nitrogen atom of the other μ-N-cyanate group, belonging to the other half of the dimer, in which the Cu–N(4)^v distance is 3.368(7) Å (v = $\frac{1}{2} - x$, $-y$, $1 - z$). The four equatorial atoms are coplanar in the range 0.06 for N(3) to −0.07 for N(2) Å. The copper(II) ion is displaced 0.16 Å from the equatorial least-squares plane. The average values of the angles Ow(1)–Cu–N(equatorial) and N(4)^{v}–Cu–N(equatorial) [v = $\frac{1}{2} - x, -y, 1 - z$] are 95(3) and 84(12)°, respectively. The '*trans*' angles Ow(1)–Cu–N(4)^{v} and N(2)–Cu–N(4) are 165.1(2) and 166.1(2)°, respectively, while the other N(1)–Cu–N(3) is 159.6(3)°. In the bridging unit, the intradimeric Cu–Cu^{v} distance is 3.678(1) Å and the bridging angle Cu–N(4)–Cu^{v} is 83.5(3)°.

For both complexes the interatomic bond distances and angles of the ligand terpyridine are similar to those found in other related compounds [9, 10, 17, 18]. The planarity of the terpy ligand, as well as its rigidity, is once again confirmed. The terpy ligand is planar within ±0.02 Å for the nitrate compound and exhibits deviations from 0.03 for N(2) to –0.05 Å for C(4) in the hexafluorophosphate compound. In both compounds, because of the rigidity of the terpyridine rings the angles N(2)–Cu–N(1) and N(2)–Cu–N(3) deviate from 90° by about 10° and the Cu–N(2) bond length is smaller than Cu–N(1), N(3) by ≈0.1 Å.

The angles formed by the copper(II) ions with the NCO groups [Cu–N(4)–C(16)] are 163.1(5) and 153.6(6)° for compounds **I** and **II**, respectively. The values of the Cu–N(4)–C(16)–O(1) torsion angles [12.5(1)° and 10.9(8)°] show that the copper(II) ion is more separated from the plane defined by N(4),C(16),O(1) in compound **I** than in compound **II**. However, these values do not show significantly different distances Cu–N(4) [1.893(5) and 1.906(8) Å]. It suggests that there is a similar π-donor character in the Cu–N(4) bond, for both complexes.

The nitrate ion is found to be highly planar. The largest deviation from the N(5),O(2),O(3),O(4) mean plane is 0.004 Å for the N(5) atom. The values obtained for N–O bond distances [1.222(8) Å] and O–N–O bond angles [120(1)°] are in good agreement with those found in other studies [8, 19]. In the hexafluorophosphate group, the values of the P–F bond distances and the high isotropic thermal parameters for the fluorine atoms are similar to those found in other terpy coordination compounds containing the PF_6 anions [6, 9, 10]. The mobility for the F(3) is smaller than for the other fluorine atoms due, probably, to hydrogen bonding with the water molecule.

Infrared Spectroscopy

The interest of the IR spectra of the title compounds lies mainly in the bands due to the water, cyanate and counterion groups.

In compound **I** the stretching and bending vibrations of the water molecule appear at 3500, 3280 and 1640 cm^{-1}, respectively. The band of the cyanate ligand corresponding to the antisymmetric stretching vibration, ν_{as}(NCO), appears at 2225 cm^{-1}. The symmetric stretching vibration, ν_{s}(NCO), is obscured by the nitrate group. The characteristic band of the bending mode δ(NCO) is observed at 615 cm^{-1}. The $\nu_s(NO_3)$ vibration of the nitrate group appears as a broad and splitted band centered at 1370 cm^{-1}, due to the hydrogen bonds between the water molecule [Ow(1)] and the nitrate anion [O(3), O(4) atoms].

For compound **II**, the stretching and bending vibrations of the water molecule are observed at 3500, 3430 and 1645 cm^{-1}, respectively. As for compound **I**, the two values observed for the stretching vibration are consistent with the existence of two different O–H distances in the water molecules. The ν_s(NCO) vibration of the cyanate ligand appears like a weak band at 1390 cm^{-1}, in the range found for N-bonded cyanates [6, 20–22]. The ν_{as}(NCO) vibration is observed at 2230 cm^{-1}. The δ(NCO) vibration is splitted (640–615 cm^{-1}) in good agreement with the existence in this compound of a NCO bridged group [6, 20–22]. The F_{1u} active modes of the PF_6 group are at 850 and 570 cm^{-1}. The band at 850 cm^{-1} is splitted, due to hydrogen bonding between the F(3) and Ow(1) atoms. This splitting has been observed in other hexafluorophosphate compounds [6].

Magnetic Behaviour and Electron Paramagnetic Resonance

The study of magnetic susceptibility data for the title compounds has been performed within the temperature range 2.0–100 K. Compound I follows a Curie–Weiss behaviour for $T > 5$ K with a negative temperature intercept of about –0.5 K. The slope corresponds to a Curie constant of 0.42 emu K mol^{-1}. The product χT lies practically constant (0.42 emu K mol^{-1}) when cooling down from 100 to about 5 K. However, this product decreases from 0.42 to 0.29 emu K mol^{-1} when cooling from 5 to 2 K. This variation indicates a weak antiferromagnetic coupling ($|J| < 0.5$ cm^{-1}). The magnetic susceptibility data for compound **II** are well described by a Curie–Weiss law above 6 K with $\theta \approx -1$ K and $C =$ 0.44 emu K mol^{-1}. The negative θ value and the overall appearance of the χT *versus* T curve (χT decreases from 0.44 emu K mol^{-1} at 100 K to 0.29 emu K mol^{-1} at 2 K) are indicative of a weak antiferromagnetic interaction between the Cu(II) centers. In both cases, the J parameters could not be accurately determined using an isotropic Heisenberg Hamiltonian due to the weakness of the magnetic couplings. Measurements at lower temperatures ($T < 1$ K) would be desirable.

The X-band EPR spectra of polycrystalline powdered samples of the title compounds are shown in Fig. 4. The spectra remain unchanged over the range 4.2–300 K. The spectrum of the nitrate complex shows a large linewidth, which does not allow a good resolution of the g tensor. For the hexafluoro-

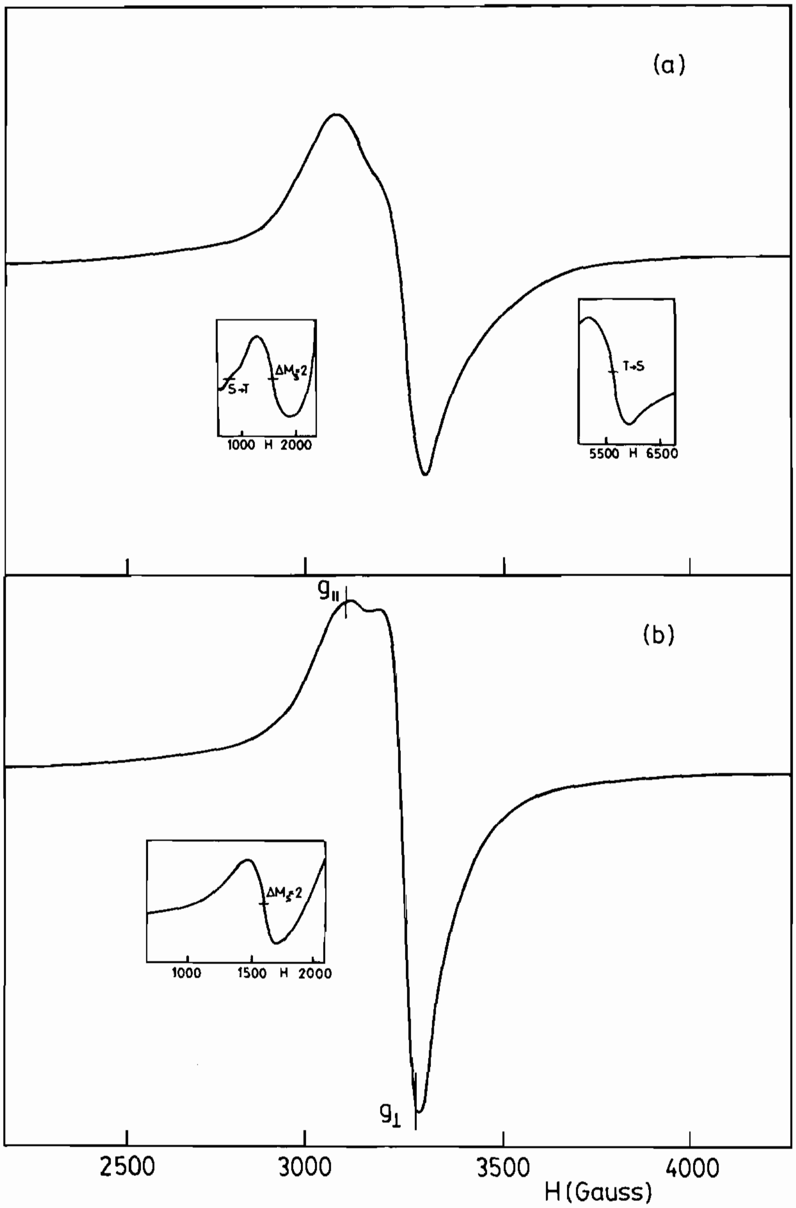

Fig. 4. X-band EPR spectra of powdered samples of [Cu(terpy)(NCO)(H_2O)](Y) complexes: (a) Y = NO_3; (b) Y = PF_6.

phosphate complex the EPR spectrum is characteristic of an axial g tensor and by comparison with the simulated spectra we can determine the components of g, $g_\parallel = 2.205$ and $g_\perp = 2.075$, and the linewidths, $\Gamma_\parallel = 260$ and $\Gamma_\perp = 175$ Gauss. Besides these large signals, which correspond to the triplet $\Delta Ms = \pm 1$ allowed transitions (3200 G), both complexes show a feature at $\approx$1650 G corresponding to the $\Delta Ms = \pm 2$ forbidden transition, which indicates a magnetic coupling between two Cu(II) ions. Furthermore, two very weak signals, symmetrically located at lower (720 G) and higher (5600 G) field values of the normal $\Delta Ms = \pm 1$ transitions, are seen for compound I. These can be assigned as forbidden transitions between the singlet electronic state of a weakly exchange-coupled copper(II) dimer and the $Ms = \pm 1$ components of the triplet state [23]. When it is taken into account that each of these transitions are separated from the allowed transitions by a field value of $2\ |J|\ (g\beta)^{-1}$, $|J| = 0.12\ \text{cm}^{-1}$ can be calculated assuming a mean g value equal to 2.12, obtained from the Curie constant. This $|J|$ value is in good agreement with the magnetic susceptibility measurements.

In the hexafluorophosphate compound, the exchange between copper(II) pairs is clearly propagated through N-cyanate groups. In contrast, the structural arrangement found in the nitrate compound could involve several potential interaction pathways.

(i) A direct dipolar interaction due to the relatively short interchain Cu–Cu^{ii} distance: 3.950(2) Å. The corresponding calculated dipolar parameter is $D_d = 0.05$ cm^{-1}, which *a priori* cannot be neglected versus the J value obtained from the EPR spectra (0.12 cm^{-1}).

(ii) A superexchange path through an extended bridging network formed by two water molecules and one nitrate anion connected by hydrogen bonds (see Fig. 2). The Cu–Cu^{i} intrachain distance (through the extended bridging network) is 12.5 Å, and for such distance the expected $|J|$ value must be less than 10^{-2}–10^{-3} cm^{-1} according to the experimentally determined function for long-range antiferromagnetic superexchange proposed by Coffman and Buettner [24]. The $|J| = 0.12$ cm^{-1} observed is significantly higher than that expected, nevertheless this is not conclusive since several exceptions to the Coffman rules have been found.

(iii) An alternative superexchange path involves a 'quasi-directed' interaction between two copper(II) ions through the cyanate groups and a portion of the terpyridine ligands belonging to two chains related by an inversion center (see Fig. 2), which are separated by ≈3.3 Å. This exchange mechanism seems to be the most reasonable according to the results obtained from EPR and magnetic data.

Supplementary Material

Thermal parameters, bond lengths and angles, mean average planes and structure factors are available from the authors on request.

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