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Spectroscopic and Magnetic Properties of a Novel Pyrazine-Bridged Copper(II) Chain: $[Cu(Terpy)(pyz.)](ClO_4)_2$

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The $[Cu(Terpy)(pyz.)](ClO_4)_2$ *complex (were Terpy = 2,2′:6′,2″-terpyridine and pyz. = pyrazine) was synthesized and characterized by means of spectral and magnetic properties. UV–visible and EPR spectra indicate a square pyramidal coordination for the copper(II) ion. Magnetic susceptibility measurements, reported in the temperature range 2–125 K, are analyzed in terms of regular and alternating Heisenberg-chain models giving* $2J = -4.4$ *K,* $g = 2.19$ *(regular chain) and* $2J = -5.6$ *K,* $2J' = -1.7$ *K,* $g = 2.15$ *(alternating chain). The better agreement obtained with the alternating-chain model allows us to propose a dimerized zig–zag chain structure with the pyz. ligand bridging the copper(II) ions.*

Introduction

Recent studies on the structure–magnetic property correlations in polynuclear transition metal complexes have alowed significant progress to be made in the understanding of exchange mechanisms [1–9]. Thus, the relevant factors which control the magnitude, sign and dimensionality of the magnetic interaction are better defined. In particular, the role of the orbital symmetry of both interacting paramagnetic centres and bridging ligands has been emphasized.

Non-bridging ligands can also have an influence on the magnetic behaviour by determining the geometry around the metallic ions and, thus, the relative orientation of d-orbitals.

2,2′:6′,2″-terpyridine (hereafter abbreviated as Terpy) is a tridentate rigid quasi-planar ligand that forms complexes with all divalent 3d transition ions. Coordination numbers are shown to be six for $M(Terpy)_2^{2+}$ complex ions and four or five for monoterpyridine mixed ligand complexes as $M(Terpy)Cl_2$. In the presence of coordinating counterions (as halide or pseudohalide), the formation of pentacoordinated complexes $M(Terpy)X_2$ is highly favoured [10–13].

Rossi and Hoffmann [14] have shown that for the pentacoordinated complexes all conformations between the trigonal-bipyramidal (TBP) and the square-pyramidal ones (SP) are close in energy. Consequently, the conformation adopted by these complexes in the solid state is often governed by packing forces. This phenomenon is enhanced for Cu(II) complexes owing to the 'plasticity effect' [15]. Furthermore, this ion has a well-established tendency to be engaged in a 4 + 1 coordination mode adopting a 'normal' deformed square-pyramidal (DSP) conformation characterized by a long axial bond and a mean trans-basal ligand angle of 165 ± 2° [16].

In the present paper, we describe a new synthesis procedure leading to polymeric structures of exchange coupled copper(II) ions. So far, only two families of Cu(II)–Terpy complexes showing such a behaviour are known. The first, reported by Anderson *et al.* [17], consists of one-dimensional polymeric chains containing cyanide bridged copper(II) (Fig. 1-a), while the second is made of dimeric entitites Cu(II)–Terpy bridged by two halogen (Cl, Br) [12] or pseudohalogen (SCN, CNO) [18] ions (Fig. 1-b). The 'normal' DSP conformation adopted by isolating monomeric complexes is conserved for the first family; on the other hand, the conformation of the second corresponds better to an ideal square planar pyramid, probably resulting from a repulsion between $[Cu\ Terpy\ X]^+$ entities [13].

Furthermore, pyrazine (pyz.) and derivatives have shown to bridge copper(II) ions forming low-dimensional systems [19]. Hatfield, Hendrikson *et al.* [7–9] have proposed a mechanism for describing the exchange interaction in such systems. Using this ligand, we have synthesized the mixed complex $[Cu(Terpy)(Pyz)](ClO_4)_2$ which exhibits a one-dimensional behaviour described by the Heisenberg chain model.

Experimental

Preparation of the Complexes

The synthesis scheme comprises the isolation of the $[Cu(Terpy)H_2O](ClO_4)_2$ complex, and the

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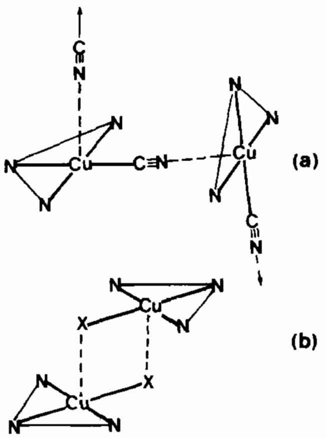

Fig. 1. Known magnetically coupled copper(II) complexes with the Terpy ligand. (a) Chain of $[Cu(Terpy)CN]NO_3 \cdot H_2O$. (b) Dimers of $[Cu(Terpy)X]^+$ (X = Cl, Br, SCN, CNO).

subsequent substitution reaction of the water molecule by a stronger nucleophilic ligand. These reactions are achieved in a non-aqueous solvent which avoids the formation of the bis-Terpy complex.

Synthesis of [Cu(Terpy)H₂O](ClO₄)₂ (I)

A 0.25 g (1.07 mmol) portion of Terpy was dissolved in a 15 ml chloroform solution. An ethyl acetate solution of $Cu(ClO_4)_2 \cdot 3H_2O$ (0.35 g, 1.13 mmol) was added with stirring to the above solution. A copious blue precipitate was obtained. This solid complex was then separated by filtration, washed with hexane and dried in air. *Anal.* Calcd. for $[Cu(C_{15}H_{11}N_3)H_2O](ClO_4)_2$: C, 35.05; H, 2.55; N, 8.18. Found C, 34.88; H, 2.50; N, 7.94.

Synthesis of [Cu(Terpy)(pyz.)]ClO₄)₂ (II)

0.20 g (0.40 mmol) of I was dissolved with heating and stirring in the minimal quantity of a methanol–acetal 99:1 (v:v) solution. 0.30 g (4 mmol) of pyz., dissolved in 5 ml of the methanol solution, was added to the warm solution of I. After filtration of the warm mixture, the greenish-blue filtrate was cooled down slowly to room temperature. The resulting blue crystals were filtered, washed with cold methanol and ether, and stored in a desiccator over silica gel. *Anal.* Calcd. for $[Cu(C_{15}H_{11}N_3)(C_4H_4N_2)](ClO_4)_2$: C, 39.60; H, 2.62; N, 12.16; Cu, 11.04. Found: C, 38.58; H, 2.46; N, 11.76; Cu, 11.30. This compound is very poorly soluble in all common organic solvents.

Physical Measurements

Electronic spectra were recorded on a PYE-UNICAM SP8-100 spectrophotometer using the filter paper/mull technique.

Infrared spectra were obtained with Nujol mulls between CsI plates in the 4000–300 cm^{-1} region using a PERKIN-ELMER 597 I.R. spectrophotometer.

E.P.R. spectra were recorded on a BRUKER E.R. 200 D X-Band spectrometer.

Magnetic measurements were performed in the temperature range 2–150 K using a pendulum-type apparatus. The susceptibilities were corrected for the diamagnetism of the constituent atoms (estimated to be -268×10^{-6} e.m.u./mol) and from the T.I.P. (taken to be 60×10^{-6} e.m.u. per Cu(II) ion).

Results and Discussion

Infrared Spectrum

Complex II shows a strong band at 488 cm^{-1}, which may be identified as a vibrational mode of the coordinated pyz. (for the free ligand the value is 420 cm^{-1}). The simplicity of this band suggests that pyz. is bidentate (D_{2h} symmetry as in the free ligand). A greater complexity of the ligand modes could indicate the presence of unidentate pyz. [20] (then, the symmetry is lowered to C_{2v}). This situation, observed for pelleted samples in KBr, suggests that the pyz. bridge is surely broken under high pressure to give a terminal pyz. linkage. Similar phenomena were described for the cyanide bridge in the $[Cu(Terpy)CN] \cdot NO_3 \cdot H_2O$ [17].

Electronic and EPR Spectra

The complex exhibits in the UV–visible region an asymmetric band which may be deconvoluted into two gaussians; one centered at 17.8 kK (strong) and the other at 15.6 kK (weak). Band assignments of the lower energy d–d transitions are as follows:

$$^2B_1(d_{x^2-y^2}) \longrightarrow {}^2A_1(d_{z^2}), \quad 15.6\ kK;$$

$$^2B_1(d_{x^2-y^2}) \longrightarrow {}^2E(d_{xz,yz}), \quad 17.8\ kK.$$

These results are consistent with a SP stereochemistry for the chromophore $\{CuN_5\}$ [21].

EPR spectra of the powdered complex were recorded at room temperature and at 4.2 K. No appreciable variation with temperature was observed. An axial spectrum was obtained with $g_{\parallel} = 2.12$ and $g_{\perp} = 2.054$ ($\bar{g} = 2.08$). These values are indicative of a $d_{x^2-y^2}$ ground state for the Cu(II) ion in agreement with stereochemistry predicted through electronic spectra. It should be noted that the nature of Terpy ligand provokes a distortion of the coordination polyhedron and a displacement of the Cu(II) ion over the basal plane giving rise to a DSP conformation [22].

A far too low $g_{\parallel}$ value is observed and so, a G value (defined as $\dfrac{2 - g_{\parallel}}{2 - g_{\perp}}$ [21]) smaller than 4 results (G = 2.2). This value may result from the presence of significant magnetic exchange between the copper(II) ions. The existence of an axial Cu(II)–pyz. π-bonding could also contribute to this G value diminution.

Magnetic Properties

The corrected magnetic susceptibility which shows a rounded maximum at about 3 K agrees with an antiferromagnetic interaction between Cu(II) ions. The plot of the $\chi_m T$ product, preferable to χ_m for interacting systems, confirms the presence of such interactions through the low temperature behaviour (Fig. 2).

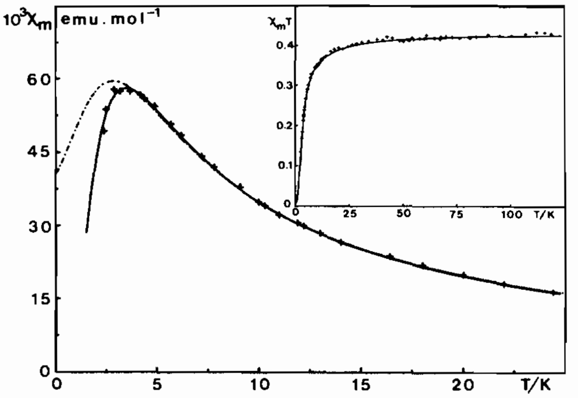

Fig. 2. Magnetic behaviour of the [Cu(Terpy)(pyz.)]$(ClO_4)_2$ complex. Theoretical curves correspond to the best fits obtained by the Heisenberg-regular chain model (dashed line) and Heisenberg-alternating one (solid line). The values of the parameters are given in Table I.

The ability of pyz. to act as a bidentate ligand, thus forming polymeric structures, and the obtained IR data suggest that the magnetic behaviour may be analyzed in terms of one-dimensional exchange-coupled system.

Up to now, attempts to grow suitable single crystals of [Cu(Terpy)(pyz.)]$(ClO_4)_2$ for X-ray structure determinations have failed. However, from the previous stereochemistry remarks, two extreme molecular schemes, depending on the bond sequences between copper(II) ions and pyz. nitrogens, may be investigated: the one corresponding to the sequence ...(ee)–(aa)–(ee)... (Fig. 3a), and the other to the sequence ...(ea)–(ea)–(ea)... (Fig. 3b) where *a* and *e* refer to axial and equatorial positions respectively. The magnetic properties will then be described either by the J-alternating chain model (conformation *a*) or by the J-regular chain model (conformation *b*). The problem of J-alternating chain was first resolved by Duffy and Barr [23] through a numerical treatment of S = 1/2 finite closed chains of increasing length. The exchange Hamiltonian is then expressed as:

$$\mathcal{H} = -2J \sum_{i=1}^{N/2} (S_{2i}S_{2i-1} + \alpha S_{2i}S_{2i+1})$$

where J and Jα = J$'$ are the alternating exchange parameters with α ranging from 0 to 1.

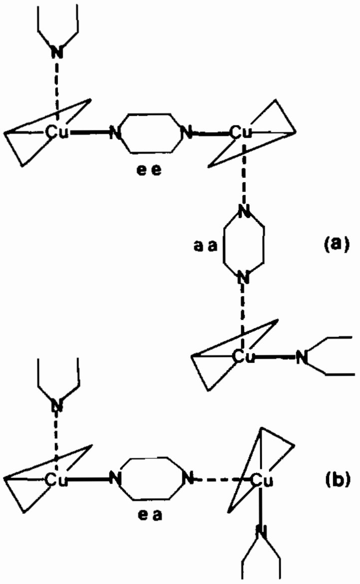

Fig. 3. Chain configurations with pyz. bridging [Cu(Terpy)]$^{2+}$ entitites. (a) Pyz. bridge alternatively in (ee) and (aa) position. (b) Pyz. bridge in (ea) position. *e* and *a* refer, respectively to the equatorial and axial bondings of the square pyramid.

The limit $\alpha = 1$ corresponds to the regular chain solved equally by Bonner and Fischer [24]. From these results, Hall *et al.* [25] have recently proposed rational expressions making the comparisons with experiment an easy task. Using these expressions we have determined from a least squares refinement of the experimental data the best Lande and exchange parameters in the two molecular configurations. The results are reported in Table I with the corresponding agreement criteria (R) defined as the sum of the squares of the relative deviations. As can be seen from Fig. 2, the two approaches, which are in excellent agreement with experiment up to about 4 K, differ drastically at lower temperatures. Then, the regular chain model ($\alpha = 1$) leads to a finite susceptibility as the temperature approaches zero Kelvin while the experimental data decrease quickly when cooling down. These results, together with the obtained g value which is in fairly good agreement with the one estimated by EPR measurement ($\bar{g} = 2.08$), suggest that conformation *a* is the more probable of the two.

TABLE I. Magnetic Parameters of the Cu(Terpy)(Pyz.)$(ClO_4)_2$ Complex.

Model	2J (K)	2J$'$ (K)	$\bar{g}$	R
Alternating chain	–5.6	–1.7	2.15	0.4×10^{-4}
Regular chain	–4.4	–	2.19	0.8×10^{-4}

TABLE II. Exchange Coupling and Geometric Parameters of Pyrazine-bridged Copper(II) Complexes with SP Coordination.

Compound[a]	pyz.[b] bridging	β[c]	2J (K)	Ref.
$Cu(pyz.\ A)_2(ClO_4)_2$	(ee)	0	0	26
$Cu(pyz.)_4(ClO_4)_2$	(ee)	66	−10.6	27
$Cu(pyz.)(NO_3)_2$	(ee)	48	−10.7	7, 28
$Cu(hfac)_2(pyz.)$	(aa)	0	0	8
$Cu(Terpy)(pyz.)(ClO_4)_2$	(ee); (aa)	—	−5.6; −1.7	Present work

[a] pyz. A = pyrazine-2-carboxamide; hfac = hexafluoroacethylacetonate. [b] a = axial; b = equatorial. [c] β is the canting angle between the pyz. ring and the copper(II) coordination plane (*XY* for (ee) and *XZ* for (aa) systems).

An anisotropic exchange interaction could equally be invoked in order to explain the low temperature behaviour. In fact, the isotropic model is generally thought to be more satisfying for copper(II) in such an environment. Furthermore, agreement with experiment is not as good around the susceptibility maximum.

Finally, the results are reported in Table II with those relative to known pyz.-bridged copper(II), allowing a correlation between structure and magnetic properties.

Hatfield *et al.* [7–9] have proposed an exchange mechanism in the pyz.-bridged copper(II) complexes which involves the b_{1g} and a_u pyrazine orbitals. Clearly, the exchange coupling only occurs if the heterocyclic ring is slightly tilted with respect to the copper(II) coordination plane, thus leading to a significant overlap between the $d_{x^2-y^2}$ and $\pi(b_{1g})$ orbitals.

According to this exchange process, the following remarks can be made:

(i) Assuming the same Cu–N bond length as in the other pyrazine complexes, the angle of canting of the heterocyclic ring is expected to be smaller than 48° if we refer to the obtained J value.

(ii) The $[Cu(Terpy)(pyz.)](ClO_4)_2$ complex is the first example to our knowledge showing, for an axial pyz. conformation, a non-zero exchange coupling between copper(II) ions. The exchange mechanisms proposed for this complex are displayed in Fig. 4.

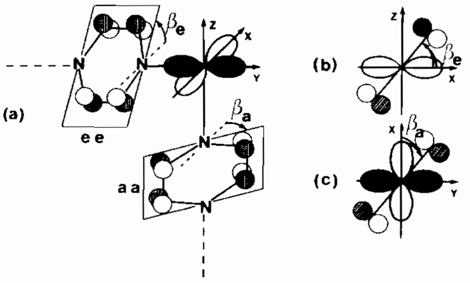

Fig. 4. Superexchange mechanism showing the tilt of the pyz. ring and the $d_{x^2-y^2} - \pi(b_{1g})$ overlap (a). The projection of the involved orbitals is given in the xz (b) and xy (c) planes.

Finally, the alternation between axial and equatorial pyz. conformation along the chain allows an explanation of the low temperature behaviour. Such a study clearly shows how correlation studies between structure and magnetic properties are essential in modern inorganic chemistry.

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