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Spectroscopic and Magnetic Properties of Cu_2(terpy)Cl_4 (terpy = 2,2′:6′,2″-Terpyridine). A Magnetic System constructed of Two Exchange-coupled Dimers†

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The complex Cu_2(terpy)Cl_4 (terpy = 2,2′:6′,2″-terpyridine) has been prepared and characterized through spectroscopic and magnetic properties. The results emphasize the presence of two dimeric moieties, identified as $[\{Cu(terpy)Cl\}_2]^{2+}$ and $[Cu_2Cl_6]^{2-}$. Magnetic susceptibility data show that both dimers are antiferromagnetically coupled, with $J_1 = -1.2$ and $J_2 = -54.3$ cm^{-1}, giving a satisfactory explanation for the thermal evolution of the e.s.r. spectra. These results are compared with those for similar entities and structural predictions are discussed.

In recent years there has been significant interest by inorganic chemists in magneto and spectral correlations with the structure of transition metal complexes. In particular for polymetallic magnetic systems, significant progress has been made in the understanding of the chemical and structural effects that govern exchange coupling interactions.[1–6]

Magnetic correlations are especially worthwhile in these compounds because it is often difficult to obtain single crystals for structural studies.[7] Thus, the arrangement of the metal ions in the solid (as dimers, chains, *etc.*) may eventually be determined from magnetic experiments alone. On the other hand, complementary information, concerning the local environment of the metal ion can be deduced from spectroscopic measurements.

In this work we show the usefulness of these measurements for the elucidation of structural characteristics of the complex Cu_2(terpy)Cl_4.

2,2′:6′,2″-Terpyridine (terpy) is a tridentate rigid 'quasi-planar' ligand that forms complexes with all divalent 3*d* transition ions. The co-ordination chemistry of terpy includes two kinds of complexes: firstly, monomers of formulation $M(terpy)_nX_2$ (n = 1 or 2; X = halogen or pseudohalogen);[8,9] second, dimers and polymers which contain the entity $[\{M(terpy)X\}_n]^{n+}$ (where n = 2 or ∞). Our interest is focussed in the study of magnetic interactions of these polymetallic systems particularly for M = Cu^{II}.

We have recently synthesized and characterized the chain complexes $[Cu(terpy)(pyz)][ClO_4]_2$[10] (pyz = pyrazine), or dimers $[\{Cu(terpy)X\}_2]A_2$[11–13] (X = Cl, Br, SCN, or CNO; A = PF_6, ClO_4, or BF_4). The geometry of the dimers consists of two square-parallel $[Cu(terpy)X]^+$ entities bridged by the X^- anions, showing a weak antiferromagnetic coupling between the Cu^{II} ions.[11]

It is of particular interest to design new complexes containing the $[\{Cu(terpy)X\}_2]^{2+}$ dimer and a magnetic anion, since in this case new magnetic situations will be produced. We envisage a wide range of possibilities varying from isolated magnetic moieties to extended magnetic systems.

Experimental

Synthesis of Cu_2(terpy)Cl_4.—$CuCl_2\cdot 2H_2O$ (0.853 g, 5 mmol) was dissolved in boiling ethanol (20 cm^3). Then terpy (0.233 g, 1 mmol) dissolved in warm ethanol (10 cm^3) was added to the above solution with heating and stirring, and a dark green solid appeared. The mixture was carried to reflux during 35 or 40 min After filtration of the warm suspension, the crystalline solid wa washed with warm ethanol, dried with cold diethyl ether and stored in a desiccator over silica gel. Yield 85—90% (Found: C, 36.0; Cu, 25.1; N, 8.3. $C_{15}H_{11}Cl_8Cu_4N_3$ requires C, 35.9; Cu, 25.3; N, 8.4%).

The dark green solid is decomposed in contact with water and other solvents having good donor properties, and is very poorly soluble in common organic solvents. Up to now, attempts to grow suitable single crystals for *X*-ray structure determination have failed.

Physical Measurements.—Infrared spectra were obtained with KBr pellets in the 4 000—250 cm^{-1} region, using a Pye-Unicam SP 2000 spectrophotometer. Electronic spectra were recorded on a Pye-Unicam SP 180 spectrophotometer using the filter paper/Nujol mull technique. E.s.r. spectra were recorded on a Bruker E.R. 200 D *X*-band spectrometer. Magnetic measurements were performed in the temperature range 4—200 K using a pendulum-type apparatus. The susceptibilities were corrected for the diamagnetism of the constituent atoms and for the temperature-independent paramagnetism (estimated to be -137×10^{-6} and 60×10^{-6} cm^3 mol^{-1} per Cu^{II} ion, respectively).

Results and Discussion

Vibrational Spectrum.—In the 4 000—400 cm^{-1} region, the i.r. spectrum is basically identical to the observed one for $[\{Cu(terpy)Cl\}_2]A_2$ dimeric complexes.[13] This fact indicates that the existence of the $[\{Cu(terpy)Cl\}_2]^{2+}$ entity is very plausible.

On the other hand, two new bands are observed in the low-energy region (located at 310 and 295 cm^{-1}). These may be associated with Cu–Cl vibrations. As will be confirmed later on, this result agrees with the presence of the dimeric $[Cu_2Cl_6]^{2-}$ anion. In this assumption, we may assign these bands to Cu–Cl(terminal) and Cu–Cl(bridging) stretching vibrations, respectively.[14]

Electronic Spectrum.—The electronic spectrum exhibits two well defined bands centred at 22 900 and 18 400 cm^{-1}, and a broad complex one located between 11 500 and 17 000 cm^{-1}, with a maximum around 14 000 cm^{-1}. The presence of the $[Cu_2Cl_6]^{2-}$ dimeric anion is confirmed by the former two bands, corresponding to charge-transfer transitions, especially by the band at 18 400 cm^{-1} associated with the characteristic π-dimer transition.[15] Furthermore, this value may be indicative, as suggested previously,[14] of a quasiplanar dimeric chloro-

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† *Non-S.I. unit employed:* G = 10^{-4} T.

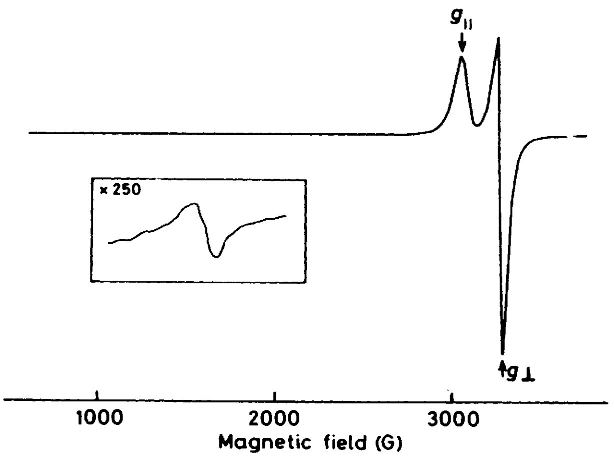

Figure 1. Polycrystalline powder e.s.r. spectrum (*X*-band) of $Cu_2(terpy)Cl_4$ at 4.2 K

cuprate (values around 19 000 cm^{-1} agree with a planar geometry, whereas an increase of the energy up to 21 000 cm^{-1} may result from a large departure from planarity). Nevertheless, some exceptions to this rule are known, and further experimental data, such as the energies of the *d–d* transitions, may improve our understanding. Unfortunately, the presence of two different Cu^{II} chromophores in our complex prevents an accurate determination of them. Thus, other physical properties, such as magnetic measurements, may be helpful in such a case.

Electron Spin Resonance.—Polycrystalline powder e.s.r. spectra were recorded in the temperature range 4.2—300 K. At 4.2 K an axial spectrum with $g_{\parallel} > g_{\perp}$ is obtained (Figure 1). The most relevant feature is the observation at half field (*ca.* 1 600 G) of a very weak signal that clearly indicates the presence of a dimeric magnetically coupled Cu^{II} moiety. Further, it can be emphasized that the spectrum is identical to that reported for $[\{Cu(terpy)Cl\}_2][PF_6]_2$ ($g_{\parallel} = 2.22$, $g_{\perp} = 2.06$),[13] confirming unambiguously the presence in the complex under consideration of the dimeric $[\{Cu(terpy)Cl\}_2]^{2+}$ cation.

The e.s.r. spectra are shown to be greatly temperature dependent. This results from the appearance of a broad isotropic signal, superimposed onto the initial one, which becomes significant above 30 K (Figure 2). The former signal increases with temperature to mask nearly completely the lower intensity original narrow line (150 G) at room temperature. Then, this broad signal (500 G) envelopes the initial one, and only two shoulders centred around an estimated mean *g* value ($\bar{g} = 2.12$) may be detected at room temperature (Figure 2).

Finally, as might be implied from the chemical composition, thermal evolution of e.s.r. spectra can be interpreted in terms of $[Cu_2Cl_6]^{2-}$ units. The known complexes containing this anionic group have shown either a singlet or triplet ground state due to the magnetic coupling within the dimer.[14] The variation of e.s.r. intensity data with temperature agrees with a single ground state and thus indicates an antiferromagnetic coupling for this entity. This result is confirmed below.

Magnetic Measurements.—The magnetic behaviour of the title compound is reported in the range 4—200 K. Curie-Weiss behaviour is observed above $T \simeq 40$ K corresponding to $C = 0.36$ and $\theta = -60$ K. Below 40 K, a change of slope arises ($C = 0.18$ and $\theta = -3$ K). This result indicates that one half of the Cu^{II} ions are strongly antiferromagnetically coupled, so that at low temperature only the other half contributes to the magnetic moment. Further, the small θ value in this temperature range suggests a weak antiferromagnetic coupling between these Cu^{II} ions. Such an assumption is confirmed from the plot of $\chi_A \cdot T$ (Figure 3) which shows a constant value ($C = 0.18$) in the range 20—30 K, then decreasing and tending to zero on cooling.

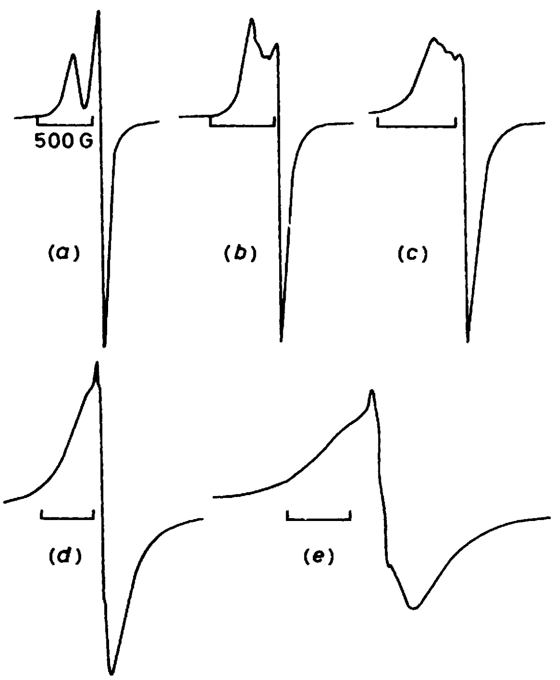

Figure 2. Temperature dependence of the e.s.r. spectrum (*X*-band) of $Cu_2(terpy)Cl_4$: (*a*) 4 K, (*b*) 40 K, (*c*) 50 K, (*d*) 110 K, (*e*) room temperature

The observed behaviour can be understood from a set of two $S = \frac{1}{2}$ independent dimers with different exchange constants and Landé factors (namely J_1, J_2 and g_1, g_2, respectively). The best fit was obtained from the set of parameters given below, $2J_i$ ($i = 1$ or 2) being the singlet–triplet splitting.

$$\text{Dimer 1: } J_1 = -1.2\ cm^{-1},\ g_1 = 2.09$$
$$\text{Dimer 2: } J_2 = -54.3\ cm^{-1},\ g_2 = 2.26$$

The theoretical curve (full line in Figure 3) describes very satisfactorily the experimental data (the agreement criterion, previously defined,[10] is $R = 1.5 \times 10^{-4}$). The dashed lines in Figure 3 are the curves for each sub-unit; the g_2 value from this fitting is undoubtedly too large. It could arise from the uncertainties of the experimental data and from the fitting procedure. Note that the only significant contribution to the magnetic moment arises below $T = 30$ K from dimer 1 whereas at higher temperatures it is due to both dimers. This fact could explain the larger discrepancy of the g_2 parameter with the e.s.r. results. On the other hand, the *J* values remain practically unaffected by small changes (± 0.1) in the *g* values. Further, the large difference between the exchange parameters J_1 and J_2 warrants the good accuracy of the resulting values (better than 3—5%).

Let us now relate this result to the thermal variation of e.s.r. spectra. It is clear that low-temperature spectra reflect the behaviour of the dimer 1, identified previously as $[\{Cu(terpy)Cl\}_2]^{2+}$. The significant variation above 30 K arises from the thermal population of the triplet state lying 108.6 cm^{-1} above the ground state in the dimer 2. Thus, J_2 can be only associated with the $[Cu_2Cl_6]^{2-}$ entity, in agreement with e.s.r. conclusions.

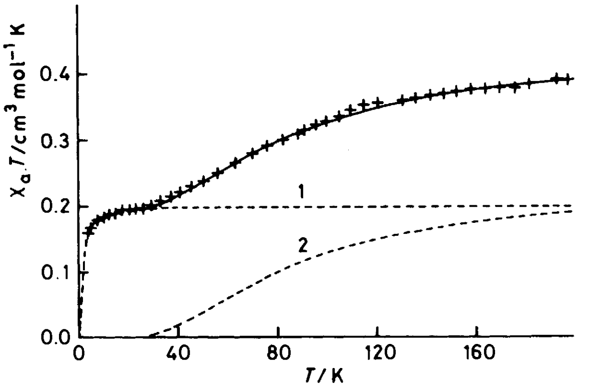

Figure 3. Plot of $\chi_a{\cdot}T$ *versus* *T*: (——) best fit obtained considering two $S = \frac{1}{2}$ exchange coupled dimers; (— — —) contribution of each dimer (1 and 2) to the susceptibility; χ_a is the corrected magnetic susceptibility per Cu^{II} ion

The magnetic and structural features of known Cu^{II} complexes containing $[\{Cu(terpy)Cl\}_2]^{2+}$ or $[Cu_2Cl_6]^{2-}$ entities are listed in the Table. We first note that the weak antiferromagnetic exchange constant obtained for the cationic moiety agrees fairly well with the other known values. This behaviour results from the poor effective overlap between the magnetic orbitals involved in the unit. Then, the weak variation of the *J* value with the structural parameters prevents a valuable magneto-structural correlation.[16,17] Owing to the rigidity of the entity imposed by the terpy ligand we can expect a very poor influence of the counter ion on the geometry of $[\{Cu(terpy)Cl\}_2]^{2+}$, according to observed *J* values. Thus, it is reasonable to expect a negligible variation in the molecular parameters.

On the contrary, the geometry of the anion is strongly influenced by the nature of counter ion which, in the solid state, is a decisive factor determining the co-ordination of copper(II), as well as the planarity and stacking of the dimers.[14]

From a magnetic point of view, such systems have been well studied in order to establish the structural factors which control the exchange mechanisms. In this way, it has been emphasized that the strength (and sign) of the *J* parameter is mainly determined by the angle θ (defined by the two Cu^{II} ions and the bridging chlorines, Cl$_b$) and by the twist angle φ [the angle between the planes defined by the $\mathrm{Cu}{<}^{\mathrm{Cl_b}}_{\mathrm{Cl_b}}{>}\mathrm{Cu}$ skeleton and the $\mathrm{Cu}{<}^{\mathrm{Cl_t}}_{\mathrm{Cl_t}}$ end (t = terminal)]. This last parameter gives the planarity of the dimer.

From extended Hückel calculations, Hay *et al.*[18] showed that in a planar $[Cu_2Cl_6]^{2-}$ moiety, the orthogonality between magnetic orbitals occurs for θ = 90°, whereas the singlet–triplet splitting becomes significant when this angle increases. Therefore, a very sensitive *J* value variation with this angle is expected. Obviously, the result will depend on the planarity of the unit. The effect of the angle φ is to reduce the splitting between magnetic orbitals, thus shifting the crossover toward θ values larger than 90°. This analysis provides a very simple description of the influence of the structural parameters on the *J* value, allowing approximate explanation of the magnetic results of known complexes having the $[Cu_2Cl_6]^{2-}$ entity (Table). A simple magneto-structural correlation, as shown for OH-bridged Cu^{II} dimers[19] seems unrealistic here, due to the very wide variety of geometries encountered in this anion. However, from the Table, some experimental trends can be indicated. (*i*) Only a large departure from planarity may be associated with ferromagnetic dimers. (*ii*) For the known complexes, it seems that both θ and ψ parameters are not fully independent. All ferromagnetic dimers show both an angle θ ≃ 93° and a large angle φ, while in antiferromagnetic ones θ is somewhat larger (θ ≃ 95—96°) and a small departure from the planarity is observed.

Table. Magnetic properties and geometric parameters of known complexes containing the $[\{Cu(terpy)Cl\}_2]^{2+}$ and $[Cu_2Cl_6]^{2-}$ moieties

Compound	$\bar{g}$	*J*/cm^{-1}	θ[a]/°	φ[a]/°	Ref.
$[\{Cu(terpy)Cl\}_2][PF_6]_2$	2.11	−2.5			11
$[\{Cu(terpy)Cl\}_2][ClO_4]_2$	2.11	−1.9			13
$[\{Cu(terpy)Cl\}_2][Cu_2Cl_6]$[b]	2.11	−1.2			*c*
K[CuCl$_3$]	2.12	−20.0	95.9	0	*d*
$[NH_2Me_2][CuCl_3]$	2.11	−1.5	95.6	≃0	*d*
$[NH_3Pr^i][CuCl_3]$		−16.0	95.5	19.5	*e*
$[AsPh_4][CuCl_3]$	2.17	+23.0	93.6	48	*f*
$[PPh_4][CuCl_3]$	2.12	+43.0	93.3	50	*g*, *h*
$[SbPh_4][CuCl_3]$	2.09	+52.0			*h*
$[PPh_3Pr][CuCl_3]$	2.09	+45.0			*h*
$[Cu(terpy)Cl][CuCl_3]$[i]	≃2.12	−54.3	>96	Small	*c*

[a] These angles are defined in the text. [b] Values correspond to the $[\{Cu(terpy)Cl\}_2]^{2+}$ moiety. [c] This work. [d] R. D. Willett, C. D. Dwiggins, R. F. Kruh, and R. E. Rundle, *J. Chem. Phys.*, 1963, **38**, 2429. [e] S. A. Roberts, D. R. Bloomquist, R. D. Willett, and H. W. Dodgen, *J. Am. Chem. Soc.*, 1981, **103**, 2603. [f] R. D. Willett and C. Chow, *Acta Crystallogr.*, 1974, **30**, 207. [g] M. Textor, E. Dubler, and H. R. Oswald, *Inorg. Chem.*, 1974, **13**, 2860. [h] W. Estes, J. R. Wasson, J. W. Hall, and W. E. Hatfield, *Inorg. Chem.*, 1978, **17**, 3657. [i] Values correspond to $[Cu_2Cl_6]^{2-}$ moiety.

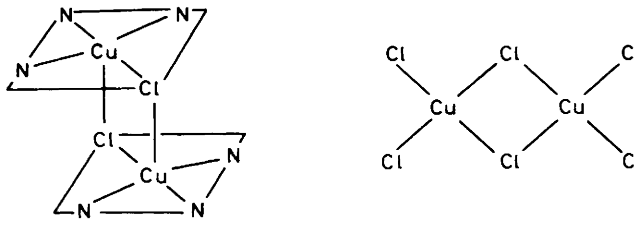

Figure 4. Proposed constitution of Cu$_2$(terpy)Cl$_4$: the $[\{Cu(terpy)Cl\}_2]^{2+}$ cation and $[Cu_2Cl_6]^{2-}$ anion

In the title compound, the calculated *J* parameter is the largest reported so far to our knowledge. Then, allowing for the above remarks, this very large antiferromagnetic interaction agrees with a planar dimer, as suggested above from the electronic spectra, and indicates a θ angle larger than 96°. This results seems somewhat surprising: until now, a planar geometry was associated with chlorocuprates having small counter ions (*e.g.* Li$^+$, K$^+$, or NH$_4$$^+$) whereas bulkier cations led to isolated dimers with a pronounced tetrahedral distortion[19] (see Table). The reasons for this unexpected geometry can surely be related to the 'non-innocent' nature of the $[\{Cu(terpy)Cl\}_2]^{2+}$ cation, which differs significantly from the other bulk cations, in both geometry (planar instead of spherical) and reactivity.

Finally, a question not yet discussed is the presence of interdimer magnetic interactions that may be significant due to the magnetic nature of the two ions. We can envisage interactions of the type anion–anion, cation–cation, and anion–cation. The first are present in many chlorocuprates, being related to the polymeric arrangements exhibited by these entities. However, with bulk cations, the dimers are well isolated. In the present case, allowing for the very large volume of the cation, we can expect this situation and thus, the anion–

anion interactions must be negligible. The interdimer interaction between cationic moieties is unexpected and will be too weak to affect the magnetic behaviour in the temperature range studied.

A similar situation arises with the anion–cation interactions since, although possible (assuming a Cl_t weakly semi-co-ordinated to Cu^{II} of the cation) this is expected to be very weak because of the orientation of the magnetic orbitals (approximate $d_{x^2-y^2}$) of Cu^{II} in the cation (placed in the terpy plane).

From the above remarks, we can consider the complex $Cu_2(terpy)Cl_4$ as a magnetic system constructed of two 'independent' magnetic coupled dimers: the $[\{Cu(terpy)Cl\}_2]^{2+}$ cation and the $[Cu_2Cl_6]^{2-}$ anion (Figure 4). Then the correct formulation for the solid must be $[\{Cu(terpy)Cl\}_2][Cu_2Cl_6]$.

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