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Magnetic Coupling and EPR Spectra of *catena*-Bis(μ-perchlorato)-[bis(μ-imidazolato)bis(perchlorato)octakis(imidazole)tricopper(II)]

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The temperature dependence of the magnetic susceptibility and the EPR spectra of *catena*-bis(μ-perchlorato)[bis(μ-imidazolato)bis(perchlorato)octakis(imidazole)tricopper(II)] showed that the compound behaves like a chain of weakly coupled trinuclear species; the best fit of the experimental points showed that the magnetic coupling between the internal and the external copper(II) atoms in the trinuclear unit is given by $J = 116.9$ (9) cm^{-1} (J is defined through the Hamiltonian $H = JS_1 \cdot S_2$). This value is compared to those previously reported for other imidazolato-bridged copper(II) complexes.

Introduction

Imidazolate-bridged copper(II) complexes have been actively studied,[2-7] mainly to understand the factors determining the extent of coupling between the two metal ions and to use these simple compounds as models for metalloenzymes that contain the same structural units.[8,9]

Several studies have already been reported in which structural data have been used to find useful correlations between structure and magnetic coupling[2,10-12] as has been done for other series of copper(II) complexes.[13-16] Unfortunately until now not much success has been achieved, and more experiments appear to be required.

Some years ago some Swedish authors reported[17] the crystal structure of *catena*-bis(μ-perchlorato)[bis(μ-imidazolato)bis(perchlorato)octakis(imidazole)tricopper(II)], $Cu_3(iz^-)_2(iz)_8(ClO_4)_4$, which is built up of trinuclear units consisting of three distorted octahedrally coordinated copper atoms connected to each other through two imidazolato bridges, as shown in Figure 1. The trinuclear units are linked together by two perchlorate groups forming a chain along the c direction of the monoclinic unit cell. For this compound no magnetic data were reported, and we decided to collect them, together with EPR spectra, in order to characterize the magnetic coupling and hopefully add a new brick to the construction of the correlation between structure and exchange coupling in imidazolate-bridged copper(II) complexes.

Experimental Section

Single crystals of the title compound were grown from aqueous solutions according to the reported procedure.[17] The crystal was oriented with a Philips PW 1000 diffractometer. The unit cell corresponds to that previously reported: $P2_1/a$, $a = 16.644$ Å, $b = 15.524$ Å, $c = 9.226$ Å, and $\beta = 94.68°$ with two formula units.

Magnetic susceptibility measurements in the range 4.2–300 K were performed with a homemade Faraday balance equipped with a Bruker electromagnetic balance and a R-100 Cahn microbalance. The cooling apparatus was a CF200 flow cryostat from Oxford Instruments Co. The uncertainty in the temperature is about 0.1 K and in the susceptibility about 50×10^{-6} cm^3 mol^{-1}. $Ni(en)_3S_2O_3$ (en = 1,2-diaminoethane) was used as the susceptibility standard over the entire temperature range. The Pascal contribution was calculated to be -440×10^{-6} cm^3 mol^{-1}.[18]

EPR spectra were recorded with a Varian E9 spectrometer equipped with standard X-band (9 GHz) and Q-band (35 GHz) frequencies. Variable-temperature spectra in the range 4.2–300 K were recorded with Oxford Instruments ESR 9 and ESR 35 cryostats.

Results

Magnetic Susceptibility. The temperature dependence of χ and the effective magnetic moment μ vs. T of $Cu_3(iz^-)_2(iz)_8(ClO_4)_4$ are shown in Figure 2. The experimental points were fit by using the spin Hamiltonian[19]

$$\hat{H} = J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3) + J'\hat{S}_1 \cdot \hat{S}_3 \qquad (1)$$

where 1 and 3 refer to the external copper atoms and 2 to the internal one, as shown in Figure 1. By coupling S_1 and S_3 to give an intermediate spin state S^* and then coupling S^* to S_2 to give a total spin state S, we can label the spin states of the triple as $^3/_2(1)$, $^1/_2(1)$, and $^1/_2(0)$ using the notation $S(S^*)$. Different g values correspond to the different $S(S^*)$ states, according to the relations previously reported.[20] Therefore, the most general expression for the magnetic susceptibility of a symmetric triple is

$$\chi = (N\beta^2/4kT)\{10(2g_e/3 + g_i/3)^2 e^{-J/2kT} + (4g_e/3 - g_i/3)^2 e^{J/kT} + g_i^{\,2} e^{J'/kT}\}/\{2e^{-J/2kT} + e^{J/kT} + e^{J'/kT}\}$$

where g_e and g_i refer to the external and to the internal copper ions in the triple, respectively.

This equation demands at least four parameters. In order to reduce their number, we started by setting $J' = 0$ and $g_e = g_i = g$. The two-parameter least-squares fit yielded the calculated curves shown in Figure 2 with $g = 2.243$ (7), $J = 117.8$ (4) cm^{-1}, and an agreement factor[21] $R = 1.65 \times 10^{-2}$. When all four independent parameters were allowed to vary, i.e. g_i, g_e, J, and J', the fit was not substantially improved, R being 1.62×10^{-2} with the parameter values $g_e = 2.20$ (2), $g_i = 2.08$ (9), $J = 116.9$ (9) cm^{-1}, and $J' = -77$ (54) cm^{-1}. The very large inaccuracy in J' reflects the inaccuracy of the

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(21) $R = [\sum_i(\chi^i_{obsd} - \chi^i_{calcd})^2/\sum_i(\chi^i_{obsd})^2]^{1/2}$.

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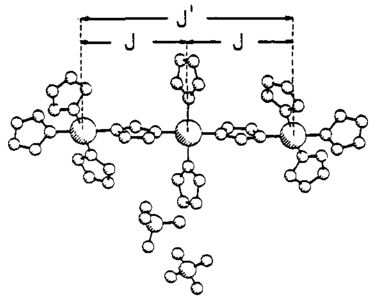

Figure 1. A sketch of the trinuclear units of $Cu_3(iz^-)_2(iz)_8(ClO_4)_4$.

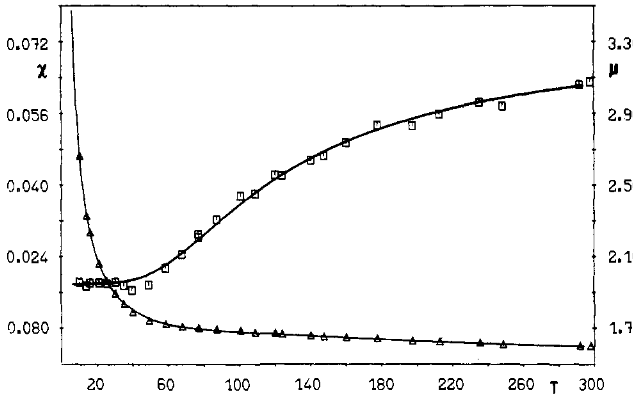

Figure 2. Temperature dependence of the magnetic susceptibility (△) and the effective magnetic moment (□) of $Cu_3(iz^-)_2(iz)_8(ClO_4)_4$.

fit. Also, it is extremely instructive to look at the correlation matrix

	g_e	g_i	J	J'
g_e	1	0.9997	−0.7249	−0.9874
g_i		1	−0.7213	−0.9880
J			1	0.6274
J'				1

which shows an almost complete correlation among g_e, g_i, and J'.

Therefore, we feel that the only parameter that is determined with a reasonable accuracy is J, and we will not further discuss the J' value but will assume it to be zero.

EPR Spectra. Polycrystalline powder EPR spectra of $Cu_3(iz^-)_2(iz)_8(ClO_4)_4$ show only one feature in the range 4.2–300 K, centered at $g = 2.08$ (Figure 3). At room temperature a weak feature at ~0.15 T is also observed, which decreases in relative intensity as the temperature is decreased, and it is practically absent at 4.2 K. Single-crystal spectra were recorded at room and liquid-helium temperatures by rotating around a, b, $c^* = a \times b$ directions. The spectra at room temperature are so broad that no useful information can be obtained from them. Even at liquid-helium temperature the lines are so broad that the angular dependence of the transitions can hardly be followed. However, there is evidence of two transitions in a general setting of the crystal in the static magnetic field corresponding to the two magnetically nonequivalent sites. In some orientations of the crystal a hyperfine splitting into seven lines, with an intensity ratio 1:2:3:4:3:2:1, is also resolved. The largest splitting of ~14 mT, for a g value of 2.21 (see Figure 4), was recorded in the rotation around a with the static magnetic field making an angle of 10° with c^*. A more detailed analysis of the spectra was impossible due to the broadness of the signals.

Discussion

The X-ray crystal structure determination showed that $Cu_3(iz^-)_2(iz)_8(ClO_4)_4$ has a chain structure,[17] but the EPR spectra clearly indicate that the trinuclear units are only weakly coupled through the perchlorato bridges, so that magnetically the compound is better described as a trimer than as a polymer. In fact the single-crystal EPR spectra show one signal for either magnetically nonequivalent site present in the monoclinic cell, thus showing that intermolecular coupling is weak.[22] Since in some orientations a hyperfine splitting of 14 mT is observed, the upper limit to intermolecular exchange is 0.013 cm^{-1}.

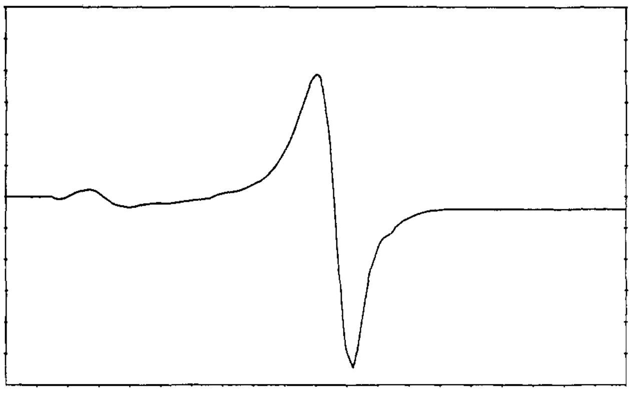

Figure 3. Polycrystalline powder spectra of $Cu_3(iz^-)_2(iz)_8(ClO_4)_4$.

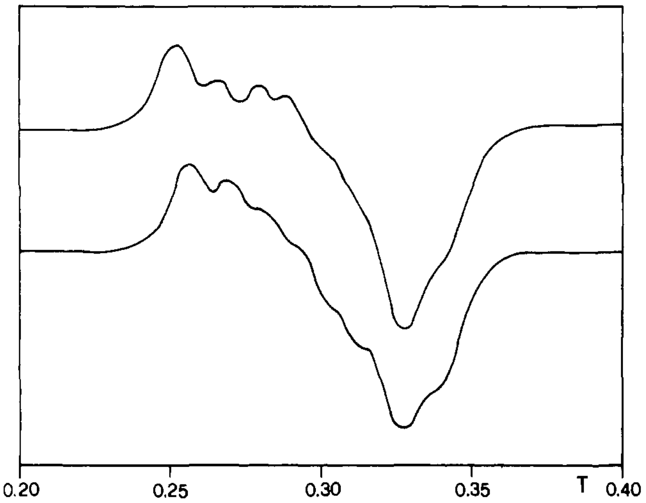

Figure 4. Single-crystal EPR spectra of $Cu_3(iz^-)_2(iz)_8(ClO_4)_4$ at 4.2 K with the static magnetic field in the bc^* plane. Upper trace: the field makes an angle of 20° with c^*. Lower trace: the field makes an angle of 10° with c^*.

The magnetic susceptibility data show that the coupling between the internal and the two external copper ions of the trimer is antiferromagnetic; therefore, the **g** tensor of the ground spin doublet is given by[20]

$$\mathbf{g} = \tfrac{4}{3}\mathbf{g}_e - \tfrac{1}{3}\mathbf{g}_i \qquad (2)$$

For the copper hyperfine interaction

$$\mathbf{A}_{e,t} = \tfrac{2}{3}\mathbf{A}_e \qquad \mathbf{A}_{i,t} = -\tfrac{1}{3}\mathbf{A}_i \qquad (3)$$

where $\mathbf{A}_{e,t}$ and $\mathbf{A}_{i,t}$ are the hyperfine splitting tensors in the trinuclear unit for external and internal copper nuclei, respectively. The coordination environment of the three copper atoms is essentially square planar, with weak axial interaction with perchlorate groups. The trinuclear units are centrosymmetric so that the coordination planes of the two external copper atoms are parallel to each other, but they make an angle of 57.5° with the coordinate plane of the central copper atom. Therefore $\mathbf{g}_e$ ($\mathbf{A}_e$) and $\mathbf{g}_i$ ($\mathbf{A}_i$) must be not parallel to each other. At the crystal settings in the static magnetic field

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Table I. Magnetic and Structural Parameters for Some Imidazolate-Bridged Copper(II) Complexes

compd	J, cm^{-1}	r_1, pm	α_1, deg	θ_1, deg	r_2, pm	α_2, deg	θ_2, deg	r, pm	η	ref
$Cu_3(iz^-)_2(iz)_8(ClO_4)_4$	117	197.4	162.9	70.0	197.7	160.9	60.0	197.6	0.9032	17, *a*
$Cu_2(TMDT)_2(iz)(ClO_4)_2{}^{+}$ [b]	52	194.4	161.9	91.8	196.6	160.2	90.0	195.5	0.8943	3
$Cu(macro)^{2+}$ [c]	42	191.9	158.9	68.8	198.4	166.3	79.1	195.1	0.9064	28
$Cu_2(Gly\text{-}GlyO)_2(iz)^-$ [d]	38	192.8	157.5	5.8	194.0	157.2	10.4	193.4	0.8517	25
Cu_2bpim^{3+} [e]	163	194.6	176.2	4.7	194.6	171.1	13.4	194.6	0.9858	24

[a] This work. [b] TMDT = 1,1,7,7-tetramethyldiethylenetriamine. [c] macro = 30-membered "N_6O_4" macrocyclic Schiff base prepared from 2,6-diacetylpyridine and 3,6-dioxaoctane-1,8-diamine. [d] Gly-GlyO = glycylglycinate.[2] [e] bpim = 4,5-bis[((2-(2-pyridyl)ethyl)imino)methyl]-imidazolate.

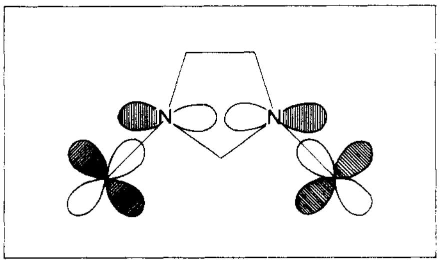

Figure 5. Schematic representation of the magnetic orbitals for a Cu–iz$^-$–Cu moiety.

where we observed a well-resolved hyperfine splitting into seven lines, one of the trinuclear units in the cell is oriented in such a way to have its coordination plane orthogonal to the static magnetic field. It seems therefore reasonable to assume that $\mathbf{g}_e$ and $\mathbf{A}_e$ reach their maxima[22,23] while $\mathbf{g}_i$ and $\mathbf{A}_i$ are in some intermediate positions between maxima and minima. Not knowing g_i, it is impossible to calculate g_e, or vice versa. As regards the hyperfine splitting, the two equivalent external copper ions are expected to give a seven-line pattern with intensity ratios 1:2:3:4:3:2:1, each line being further split into a quartet by the interaction with the internal copper ion. The observed seven-line pattern can tentatively be attributed to $\mathbf{A}_{e,t}$, the four-line pattern due to $\mathbf{A}_{i,t}$ being too broad to be detected (in fact, A_i is not at its maximum but is intermediate between maximum and minimum, and further, according to (3), its splitting is weighted by a coefficient $-{}^1/_3$). Using (3) and the observed splitting of 14 mT, we may calculate that A_e = 21 mT, which is close to the value expected for a square-planar CuN_4 unit.[22,23]

The value of J is the highest reported for imidazolate-bridged copper(II) complexes,[2] as shown in Table I. Higher J values were reported for chelating imidazolate.[2] The first observation to be made is that the present data are in conflict with the claim of a correlation of J and pK_a of the ligand.[2] In fact, while the three previously fully characterized imidazolate-bridged complexes showed[2,24,25] relatively small variation in J (varying from 38 to 52 cm^{-1}), in the present compound with the same ligand J is more than twice as large as the highest value previously reported. It has been stated that since the magnetic orbitals on copper are essentially $x^2 - y^2$, which are σ antibonding for square-planar complexes, the relevant exchange pathway through the imidazolate bridge is of the σ type.[2] The imidazolate orbitals that are responsible for this sort of interaction are of the type sketched in Figure 5, and they are essentially parallel to the N–N′ direction.[5] The extent of the coupling between the two copper ions depends on the overlap of the magnetic orbitals.[26,27] This, in turn, can be expected to depend on three factors: the metal–nitrogen distance, the angle Cu–N–N′ (α), and the dihedral angle θ between the copper coordination plane and the imidazolate plane. The last parameter might become relevant only in the hypothesis of π Cu–imidazolate interactions. All these parameters are shown in Table I for the complexes for which structural and magnetic data are available. From Table I it is apparent that some complexes have symmetric and some nonsymmetric bridges. Also, the Cu–N distances show a fairly consistent variability, ranging from 191.9 to 198.4 pm. In this respect these complexes show a much more consistent variability than observed in bis(μ-hydroxo)-bridged complexes.[13,14] An increase in the Cu–N distance is expected to decrease the antiferromagnetic contribution, J_{AF}, to J and also the ferromagnetic one, J_F.[27] The exact dependence of S, the overlap between the metal and the ligand orbitals, on the distance is not known, but it seems to be a reasonable approximation to assume that it depends on r^{-2}. If all the bridges were symmetric, it would be easy to scale them according to the Cu–N distance. Unfortunately they are not; therefore, a possible way of putting all of them to scale might be to use the geometric average of the Cu–N distances. From the data of Table I we see that the order of r is the same as the order of J, which means that the complexes with the largest antiferromagnetic coupling have the largest Cu–N distances! Perhaps this absurd result only means that J is not much affected by r.

The second parameter, α, also shows some variability, ranging from 157.2 to 166.3° for the imidazolate bridges.[3,17,25,28] In the chelating imidazolate bridge species, Cu_2bpim^{3+}, it is even larger,[24] 171.1 and 176.2°. α is expected to affect the magnetic coupling between the two metal ions, giving rise to larger J_{AF} the closer it is to 180°. As a matter of fact the high J value observed for Cu_2bpim^{3+} was attributed[24] also to the fact that α is very close to 180°. The overlap between the $x^2 - y^2$ orbital and the ligand orbital is expected to vary as cos α; therefore, in order to put all the complexes to scale, it seems reasonable to use $[(\cos \alpha_1)(\cos \alpha_2)]^{1/2} = \eta$. η has its maximum corresponding to Cu_2bpim^{3+}, but the second highest value is achieved for $Cu(macro)^{2+}$, which has one of the smallest J values.

The third parameter, θ, varies from 5.8 to 91.8° throughout the series, but also in this case no relationship is apparent.

It is rather disappointing that no obvious trend emerges as yet, but it must be recalled that also for other series of dinuclear complexes, such as chloride-bridged copper(II)[29] and hydroxo-bridged chromium(III) complexes,[30] the structural magnetic correlation, which has many more experimental points available, is not yet fully satisfactory. More data therefore appear to be required from both the experimental and the theoretical points of view.

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Registry No. $Cu_3(iz^-)_2(iz)_8(ClO_4)_4$, 11127-74-5.

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