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EPR Spectra of Trinuclear Complexes. Octachlorodiadeniniumtricopper(II) Tetrahydrate

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The single-crystal and polycrystalline powder EPR spectra of the trinuclear complex octachlorodiadeniniumtricopper(II) tetrahydrate have been recorded in the range 4.2–298 K. The temperature dependence of the spectra has been justified by considering that they are a thermal average of the multiplet spin states expected for a system of three coupled $S = \frac{1}{2}$ spins. The nature of the magnetic orbitals involved supports a mechanism of superexchange through the bridging adeninium ligands.

Introduction

Among metal complexes containing interacting metal ions the oligonuclear metal complexes are perhaps the least characterized. As a matter of fact, the studies of the spectral and magnetic properties of dinuclear metal complexes have allowed us to go a long way to understand the mechanism of exchange interactions and of their relation to the electronic structure of the metal ions.[2-5] Also for polymeric materials numerous studies are available and the structural implications leading to one-, two-, and three-dimensional magnetic behaviors are reasonably well understood.[7] Much fewer studies are available for trinuclear complexes involving paramagnetic ions.[8-10] Copper(II) complexes are extremely indicative in this respect: there are hundreds of reports on the crystal structures, magnetic properties, and EPR spectra of dinuclear and polynuclear complexes, but to our knowledge only a few structure reports are available for trinuclear copper(II) complexes, and only for some of them are magnetic data available. In no case have detailed EPR studies been reported.

It is apparent that a deeper insight into the magnetic properties of trinuclear, and in general oligonuclear, complexes cannot be any longer delayed, especially having in mind the efforts that are being made for characterizing iron ferrodoxins containing three and four metal ions.[11]

We wish to report here the single-crystal EPR spectra of octachlorodiadeniniumtricopper(II) tetrahydrate, Cu$_3$-(ade)$_2$Cl$_8$, whose crystal structure[12] and magnetic susceptibility[13] have been previously reported, together with room-temperature polycrystalline powder EPR spectra.

Experimental Section

Octachlorodiadeniniumtricopper(II) tetrahydrate was prepared according to the procedure previously reported,[13] with mixing of 10 mmol of copper(II) chloride dihydrate and 5 mmol of adenine in about 30 mL of 2 M hydrochloric acid. The solution was reduced to a small volume and then cooled, yielding the complex as bright green crystals. Single crystals were grown by slow evaporation of a 4 M hydrochloric acid solution of the trinuclear complex.

The unit cell was determined with a Philips PW1100 diffractometer using Mo Kα radiation. All the crystals used were twinned, with

(1) (a) Università di Firenze. (b) ISSECC, CNR.
(2) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.
(3) Kahn, O.; Briat, B. *J. Chem. Soc., Faraday, Trans. 2* **1976**, *72*, 268.
(4) Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173.
(5) Hatfield, W. E. *ACS Symp. Ser.* **1974**, *No. 5*, 108.
(6) Bencini, A.; Gatteschi, D. *Inorg. Chim. Acta* **1978**, *31*, 11.
(7) Willett, R. D. *Ann. N.Y. Acad. Sci.* **1978**, *313*, 113.
(8) Rakitin, Yu. V.; Yablokov, Yu. V.; Zelentsov, V. V. *J. Magn. Reson.* **1981**, *43*, 288.
(9) Dziobkowski, C. T.; Wrobleski, J. T.; Brown, D. B. *Inorg. Chem.* **1981**, *20*, 671.
(10) Gruber, S. J.; Harris, C. M.; Sinn, E. *J. Chem. Phys.* **1968**, *49*, 2183.
(11) Kent, T. A.; Huynh, B. H.; Münck, E. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6574.
(12) De Meester, P.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* **1972**, 2400.
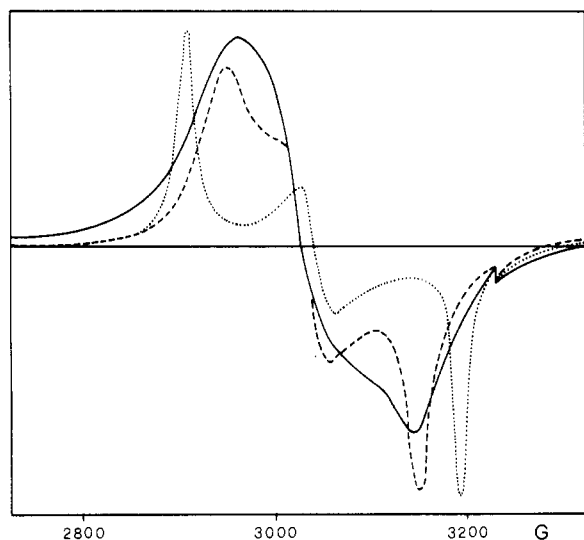(13) Brown, D. B.; Wasson, J. R.; Hall, J. W.; Hatfield, W. E. *Inorg. Chem.* **1977**, *16*, 2526.

Table I. Principal *g* Values and Directions for Cu$_3$(ade)$_2$Cl$_8$ at Room and Liquid-Helium Temperature

	room temp	liquid-He temp
$g_1{}^a$	2.049 (∓0.3090, 0, 0.9511)	2.027 (∓0.4695, 0, 0.8829)
$g_2{}^a$	2.144 (0, 1, 0)	2.127 (0, 1, 0)
$g_3{}^a$	2.190 (0.9511, 0, ∓0.3090)	2.230 (0.8829, 0, ∓0.4695)

a The values in parentheses are the direction cosines of the indicated g_i values relative to the *a*, *b*, *c** crystal axes.

individuals of different dimensions, as confirmed by Weissenberg diffraction patterns. The unit cell was determined for the larger individuals and found to correspond to the reported one, space group $P2_1/c$, $a = 11.134$ Å, $b = 12.726$ Å, $c = 10.404$ Å, $\beta = 119°30'$, and two molecules in the unit cell.[12]

Results

The temperature dependence of the polycrystalline powder EPR spectra of Cu$_3$(ade)$_2$Cl$_8$, recorded at X-band frequency, is shown in Figure 1. The room-temperature spectra correspond well to those previously reported.[13] They were interpreted as axial with $g_\parallel = 2.060$ and $g_\perp = 2.136$. However, Q-band spectra do show three *g* values, $g_1 = 2.057$, $g_2 = 2.140$, and $g_3 = 2.200$, and the X-band spectra appear to be better interpreted with similar values: $g_1 = 2.059$, $g_2 = 2.140$, and $g_3 = 2.189$. On lowering of the temperature the spectra sharpen up and also the *g* values vary: at 44 K $g_1 = 2.049$, g_2 2.133, and $g_3 = 2.194$, and at 4.2 K $g_1 = 2.028$, $g_2 = 2.127$, and $g_3 = 2.226$.

The single-crystal spectra were recorded by rotating around the *a* crystal axis. In all the orientations of the crystal in the static magnetic field one signal was observed. The minimum *g* value in this rotation was observed parallel to *b*, the maximum parallel to *c**. The spectra were found to be temperature dependent: the *g* value parallel to *b* is 2.144 at room temperature and 2.127 at 4.2 K. The variation was found to be steady, becoming steeper in the range 30–20 K. The angular dependence of g^2 at liquid-helium temperature is given in Figure 2. The crystal spectra were recorded also at Q-band frequency, from room to liquid-nitrogen temperature, yielding results identical within error with those of X-band frequency. In particular also in this case only one signal was detected in all the orientations of the crystal in the static magnetic field.

Since the minimum *g* value in this rotation corresponds nicely to the g_2 value of the powder spectra, a second rotation was performed around *b*, by using a Perspex wedge. In this rotation two signals of different intensities were in general recorded. The intensity ratios apparently varied with use of different crystals. The resonance fields of the two signals are symmetrical around *a*, as shown in Figure 2, so that they correspond to sites that have identical *g* values within error. Also in this case the spectra are temperature dependent. The minimum *g* value, g_1, is 2.027 ± 0.003 at liquid-helium temperature and 2.049 ± 0.005 at room temperature; the maximum *g* value, g_3, is 2.230 ± 0.002 at liquid-helium temperature and 2.190 ± 0.004 at room temperature. The directions of

Figure 1. Polycrystalline powder EPR spectra of $Cu_3(ade)_2Cl_8$: (—) 298 K; (---) 44 K; (⋯) 4.2 K.

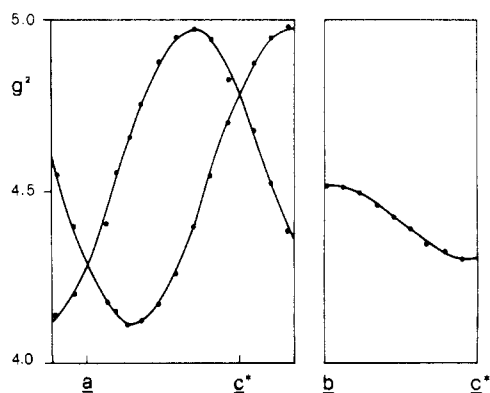**Figure 2.** Angular dependence of g^2 values of $Cu_3(ade)_2Cl_8$ at liquid-helium temperature in the (010) and (100) planes.

Figure 3. Sketch of one $Cu_3(ade)_2Cl_8$ molecules projected on the (010) plane.

Figure 4. Energies of the three spin states for linear symmetric three ($S = {}^1/_2$) spin-coupled systems (see also Table II).

Table II. g Tensors of Trinuclear Complexes Containing Two Equivalent Metal Ions as a Function of the g Tensors of the Individual Ions[a]

spin multiplet[b]	g tensor	spin multiplet[b]	g tensor
$\|{}^3/_2\rangle$	${}^1/_3 g_1 + {}^1/_3 g_2 + {}^1/_3 g_3$	$\|{}^1/_2,0\rangle$	g_2
$\|{}^1/_2,1\rangle$	${}^2/_3 g_1 - {}^1/_3 g_2 + {}^2/_3 g_3$		

[a] The subscripts refer to the metal ions as indicated in Figure 3. [b] The two spin doublets are labeled as $\|S,S^*\rangle$. S^* is defined as $S^* = S_1 + S_3$.

maximum and minimum g values in this rotation are also temperature dependent: g_3 makes an angle of 28 ± 1° with a at liquid-helium temperature and 18 ± 2° at room temperature. The principal g values and directions at the two temperatures are shown in Table I.

Discussion

The Spin Hamiltonian and the Energy Levels of a Linear Symmetric Three ($S = {}^1/_2$) Spin System. The X-ray crystal structure[12] of $Cu_3(ade)_2Cl_8$ has shown that the three copper(II) ions lie on the same straight line in the arrangement shown in Figure 3. The spin Hamiltonian appropriate to describe the exchange interaction in a linear symmetric trimer has the form[14]

$$H = J(S_1 \cdot S_2 + S_2 \cdot S_3) + J'S_1 \cdot S_3$$

where J describes the interaction between adjacent nuclei and J' describes the interaction between nonadjacent nuclei. The spin states can be labeled according to the eigenvalues of the square of the total spin operator $S = S_1 + S_2 + S_3$. The resulting spin multiplets are two doublets and one quartet, $S = {}^1/_2$ and $S = {}^3/_2$, respectively. The two doublets can be identified by an intermediate coupling quantum number, S^*, defined through the relation $S^* = S_1 + S_3$. The energies of the three spin states are as shown in Figure 4. As long as the trinuclear complex has two equivalent ions, as in the present case, the two spin doublets are not mixed and the g values for the various multiplets can be easily expressed as a
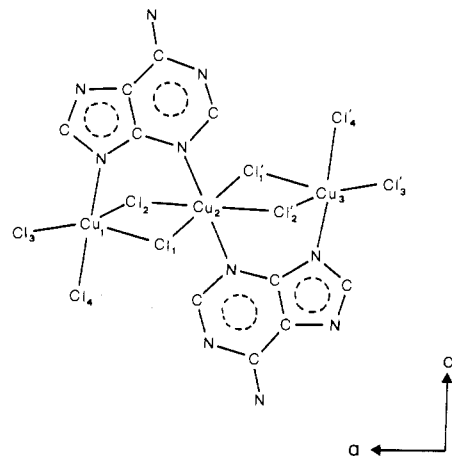
linear combination of the g values of the individual ions, through an extention of methods reported for pairs of metal ions.[15,16] If the two equivalent ions, Cu_1 and Cu_3, are coupled first, a singlet and a triplet are obtained and the g values of the triplet can be easily calculated. If these states are coupled then with the doublet of Cu_2, the formulas shown in Table II are obtained.

Analysis of the EPR Spectra. The polycrystalline powder and the single-crystal spectra are typical of a spin doublet. No evidence of signals attributable to spin quartets was found.

The single-crystal EPR spectra recorded at both X- and Q-band frequencies in the plane (100) show that intermolecular exchange interactions are operative, since only one signal is observed and no copper hyperfine is resolved. The fact that two signals differing in intensity but corresponding to sites with identical g values are observed in the (010) plane, where symmetry requires only one signal from the two magnetic sites of the monoclinic cell[17] even if intermolecular exchange is not operative, can be explained on the basis of twinning of the

(14) Griffith, J. S. *Struct. Bonding (Berlin)* **1972,** *10,* 87.

(15) Scaringe, J.; Hodgson, D. J.; Hatfield, W. E. *Mol. Phys.* **1978,** *35,* 701.
(16) Gatteschi, D. In "The Coordination Chemistry of Metalloenzymes;" Bertini, I.; Drago, R. S.; Luchinat, C., Eds.; D. Reidel Publishing Co.: Dordrecht, 1983; p 215.
(17) Bencini, A.; Gatteschi, D. *Transition Met. Chem. (N.Y.)* **1982,** *8,* 1.

crystal. This hypothesis is confirmed by the X-ray data and by the fact that the ratio of the intensity of the two signals varies from crystal to crystal. It may be recalled here that in the original structural report the twinning of the crystals was noticed and that the structure was made on a fragment of a twinned crystal.[12] The two individual crystals forming the twinned unit must have the (001) face in common. In fact, according to this view, when the crystal is rotated around the *a* axis, the two individuals give coincident EPR spectra for every orientation in the static magnetic field because both of them have principal directions along the *b* axis. When the crystal is rotated around *b*, two signals are detected because a principal direction of *g* is not parallel to *a*.

An alternative assignment that attributes the two signals to the two different doublet states is ruled out by the above considerations and by the fact that the relative intensities of the two signals do not depend on temperature.

The temperature dependence of the *g* values might in principle be due to structural variations. However, no abrupt change of the ESR spectra is observed, suggesting that no phase transition occurs. Since in a nondilute material sizable structural variations are expected to induce a phase transition[18-20] due to cooperative effects, we prefer an alternative explanation of the experimental data.[21]

The expressions of Table II show that the *g* values of the two spin doublets and of the spin quartet are different provided that the individual g_i values are different.[23] If we assume that the rate of transition from the lowest to the excited multiplets is fast on the EPR time scale, the observed spectrum at a given temperature would be a thermal average of the spectra of the three different multiplets. If this interpretation is correct, therefore, the liquid-helium spectra should be those of the lowest doublet, while those at higher temperatures should bear also the contribution of the excited multiplets.

The magnetic susceptibility data[13] were fit with the assumption that the separation between the two doublets is in the range 32–49 cm^{-1}, the quartet being 48–50 cm^{-1} higher than the lowest doublet. Using these values, it is possible to predict semiquantitatively the temperature dependence of the *g* values: the excited multiplets are depopulated at relatively high temperatures, so that in the range 4.2–25 K the values should remain constant.

Although our data are not accurate enough to give a detailed temperature dependence of the *g* values, they do show a small variation of *g* between room temperature and liquid-nitrogen temperature and a much steeper variation in the range 40–10

K becoming then almost constant only below 10 K, thus suggesting a smaller separation between the two doublets. It is worth recalling here, as previously reported, that the *J* and *J'* parameters are strongly correlated in determining the temperature dependence of the magnetic susceptibility.[13,24,25] Brown et al.[13] is reported similar "good fits" for both *J* = −32.2 cm^{-1}, *J'* = 0, *g* = 2.14 and *J* = +33.2 cm^{-1}, *J'* = −16.1 cm^{-1}, *g* = 2.14. However, also with *J* = +28 cm^{-1}, *J'* = −18 cm^{-1}, *g* = 2.15 a curve almost superimposable on the other two can be obtained. In this case the energy separation of the two doublets is only 10 cm^{-1}. These considerations show how difficult it can be to obtain meaningful values of the spin Hamiltonian parameters for trinuclear complexes. As a matter of fact, *J* can be obtained with a reasonable accuracy but *J'* is much less well determined.

The analysis of the *g* values is complicated by the fact that those observed are not "molecular" *g* values but are crystal average of them.

The highest *g* values are observed in the (010) plane close to the *a* axis. The molecular structure data show that both the internal and the external copper ions are in an elongated-octahedral geometry. In the (010) plane the long Cu_1–Cl_1 bond, which should define the *z* axes for the external copper atoms, makes an angle of ∼18° with the *a* axis, while the Cu_2–Cl_2 bond, which should define the *z* axis of the internal copper atom, is practically parallel to the *a* axis. The **g** tensor of the excited doublet is expected to be identical with the **g** tensor of the central metal ion, while the **g** tensor of the lowest doublet is given by a linear combination in which the external copper(II) ions have a heavier weight (Table II). Therefore, it is expected that the highest *g* value is closer to the *a* axis at room than at liquid-helium temperature, as observed.

Further, the fact that the highest *g* value is indeed found close to the *z* axes shows that the unpaired electrons are located in orbitals that can be mainly described as $x^2 - y^2$ on each copper center.[26] Since these orbitals are pointing toward the nitrogen atoms of the bridging adenine groups, it seems that the exchange is mainly occurring through this group. For the exchange through the chlorine atoms the geometry of the magnetic orbitals is ineffective to yield a substantial coupling.[27] Similar conclusions were reached previously, although the interpretation of the EPR data was not correct.

For a concluding remark we would like to state that EPR spectroscopy can be of help in the interpretation of exchange interaction of trinuclear copper(II) complexes when magnetic susceptibility alone cannot be enough to determine all the required spin Hamiltonian parameters. However, also the interpretation of EPR spectra can be difficult if, as in the present case, it is not possible to have independent information on the **g** tensor of each individual copper ion. We are at present looking for some system that can give all the required information.

(18) Bertini, I.; Gatteschi, D.; Scozzafava, A. *Coord. Chem. Rev.* **1979**, *29*, 67.
(19) Bencini, A.; Benelli, C.; Gatteschi, D. *Inorg. Chem.* **1980**, *19*, 1632.
(20) Bari, R. A.; Sivardiere, J. *Phys. Rev. C* **1972**, *5*, 4466.
(21) A reviewer points out that a *g*-value shift such as the one here reported is not uncommon in normal copper(II) monomers, and it might be due to second-order effects. To our knowledge second-order effects have been claimed to be operative in a trigonal-bipyramidal copper(II) complex,[22] but in that case the larger *g* shift was 0.008, which is less than half the smallest *g* shift observed in the present case (0.017). Jahn–Teller distortions also can in principle yield temperature-dependent *g* values, but the low symmetry of the copper(II) centers in the present case makes such a mechanism rather improbable.
(22) Barbucci, R.; Bencini, A.; Gatteschi, D. *Inorg. Chem.* **1977**, *16*, 2117.
(23) In the case of the quartet the spectra might bear also zero-field splitting effects, determined by both exchange and magnetic dipolar effects. Using the same formalism used for the **g** tensors, we find that the zero-field splitting tensor should be given by **D** = $^1/_9 D_{12}$ + $^1/_9 D_{13}$ + $^1/_9 D_{23}$, where D_{ij} is the zero-field splitting tensor originating from the interaction between the *i* and *j* metal ions.

(24) Banci, L.; Bencini, A.; Benelli, C.; Di Vaira, M.; Gatteschi, D. *Inorg. Chem.* **1982**, *21*, 3801.
(25) Long, G. J.; Lindner, D.; Lintvedt, R. L.; Guthrie, J. W. *Inorg. Chem.* **1982**, *21*, 1431.
(26) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 147.
(27) Watkins, N. T.; Dixon, E. E.; Crawford, V. H.; McGregor, K. T.; Hatfield, W. E. *J. Chem. Soc., Chem. Commun.* **1973**, 133.