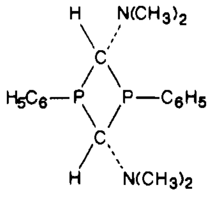
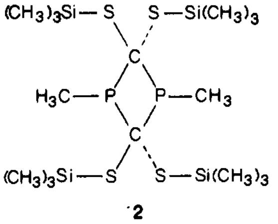
The C—P=C angle (108.8 (8)°) is considerably larger than these phosphorus valence angles in $HP{=}CH_2$ (97.4 (4)° [25]) or $ClP{=}CH_2$ (103.0 (7)° [29]) and may be interpreted as a consequence of steric interactions. A similar CPC angle of 106.7 (1)° has been reported for bis((trimethylsilyl)sulfano)methylenephenylphosphine.[27]

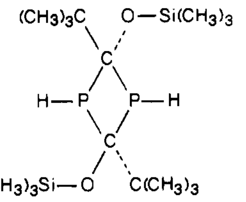
In the dimeric species, $(CF_3PCF_2)_2$, the strong puckering of the four-membered CPCP ring (θ = 35.4 (12)°) and the very small CPC ring angle of 77.6 (8)° are striking. Similar rings containing large substituents, such as **1**,[30] **2**,[31] and **3**,[32] have smaller puckering angles in the crystal or are planar as in the case of **3**. The reported CPC angles in these compounds range from 83–87°. The exo P–C bonds in $(CF_3PCF_2)_2$ are again typical for P–CF_3 bonds (see above) and are considerably longer than these P–C bonds in **1** and **2** (1.83–1.84 Å). The endo P–C bond lengths in $(CF_3PCF_2)_2$ are very similar to these bonds in **1**–**3** (1.87–1.91 Å).



1



2



3

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Registry No. $CF_3P{=}CF_2$, 72344-34-4; *trans*-$(CF_3PCF_2)_2$, 37896-36-9; $(CH_3)_3SnP(CF_3)_2$, 39185-13-2.

---

[28] Bartell, L. S.; Brockway, L. O. *J. Chem. Phys.* **1960**, *32*, 512.

[29] Kroto, H. W.; Nixon, J. F.; Ohashi, O.; Ohno, K.; Simmons, N. P. C. *J. Mol. Spectrosc.* **1984**, *103*, 113.

[30] Becker, G.; Massa, W.; Mundt, O.; Schmidt, R. *Z. Anorg. Allg. Chem.* **1982**, *485*, 23.

[31] Becker, G.; Massa, W.; Schmidt, R. E.; Uhl, G. *Z. Anorg. Allg. Chem.* **1984**, *517*, 75.

[32] Becker, G.; Uhl, W. *Z. Anorg. Allg. Chem.* **1981**, *475*, 35.

Contribution from the Department of Chemistry, University of Florence, and ISSECC, CNR, Florence, Italy,
Laboratoire de Spectrochimie des Elements de Transition, University of Paris Sud, Orsay, France,
and Department of Inorganic Chemistry, University of València, València, Spain

EPR Evidence for an Unexpected Symmetric Dinuclear Species Present in the Lattice of an Asymmetric Dinuclear Copper Complex

Alessandro Bencini,[1a] Dante Gatteschi,*[1b] Claudia Zanchini,[1b] Olivier Kahn,*[1c] Michel Verdaguer,[1c] and Miguel Julve[1d]

Received February 24, 1986

The low-temperature single-crystal EPR spectra of $[(dien)Cu(ox)Cu(tmen)(H_2O)_2](ClO_4)_2$ (I: dien = diethylenetriamine; ox = oxalato; tmen = *N,N,N′,N′*-tetramethylethylenediamine) revealed that the paramagnetic species that caused the deviation of the magnetic susceptibility from the Bleaney–Bowers equation is a spin triplet containing two equivalent copper ions. The comparison of the magnetic properties of the impurity with those reported in the literature for similar compounds leads us to suggest that $[(dien)Cu(ox)Cu(dien)]^{2+}$ species are present in the lattice.

Introduction

The presence of paramagnetic species, often called impurities, in the lattice of dinuclear copper(II) complexes is well-established, evidence arising from both EPR and magnetic susceptibility measurements.[2–6] In fact, in the EPR spectra beyond the signals attributable to the $S = 1$ coupled state, quite often signals of $S = {}^1/_2$ species are observed. Generally the **g** tensors of the $S = {}^1/_2$ species are practically identical with those of the triplet.

In the temperature dependence of the magnetic susceptibility of antiferromagnetically coupled pairs both a maximum and a minimum are observed: the former is due to the coupling between the ions; the latter is attributed to the presence of the paramagnetic impurity, which is generally associated with defective dinuclear units in which one of the two copper ions is missing, but, to our knowledge, no attempt has ever been made to proceed to a detailed characterization of the nature of the impurity.

Recently three of us reported[7] the synthesis of an asymmetric dinuclear copper(II) complex of formula $[(dien)Cu(ox)Cu(tmen)(H_2O)_2](ClO_4)_2$ (I: dien = diethylenetriamine; ox = oxalato; tmen = *N,N,N′,N′*-tetramethylethylenediamine), in which the two inequivalent copper ions are antiferromagnetically coupled, with a singlet–triplet separation of 75.5 cm^{-1}. The magnetic data revealed the presence of a paramagnetic species, which determined the value of the magnetic susceptibility below 25 K. The asymmetric nature of the complex in this case poses some problems about the possible nature of the impurity, since, with the above explanation, two different defective complexes might be formed. By recording the low-temperature EPR spectra of I, we found that the paramagnetic species corresponds to a spin triplet. We characterized this impurity by single-crystal EPR spectroscopy, and we report here the results of such analysis in order to show how this species is symmetric and presumably rather different from the parent compound.

Experimental Section

A blue-violet precipitate of I was formed immediately when equimolar methanolic solutions of $[Cu(dien)](ClO_4)_2$ and $Cu(tmen)(ox)\cdot 4H_2O$ were mixed.[7,8] The solid was dissolved in warm water, and EPR-suitable

---

[1] (a) ISSECC, CNR. (b) University of Florence. (c) University of Paris Sud. (d) University of València.

[2] Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, A* **1952**, *214*, 451.

[3] O'Young, C. L.; Dewan, J. C.; Lilienthal, H. R.; Lippard, S. J. *J. Am. Chem. Soc.* **1978**, *100*, 7291.

[4] O'Connor, C. J.; Romananch, R. J.; Robertson, D. M.; Eduok, E. E.; Fronczek, F. R. *Inorg. Chem.* **1983**, *22*, 449.

[5] Ginsberg, A. P. *Inorg. Chim. Acta, Rev.* **1971**, *5*, 45.

[6] Sikorav, S.; Bkouche-Waksman, I.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 490.

[7] Julve, M.; Verdaguer, M.; Gleizes, A.; Philoche-Levisalles, M.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 3808.

[8] Julve, M.; Verdaguer, M.; Gleizes, A.; Philoche-Levisalles, M.; Kahn, O. *Inorg. Chem.* **1983**, *22*, 368.

0020-1669/86/1325-3181$01.50/0

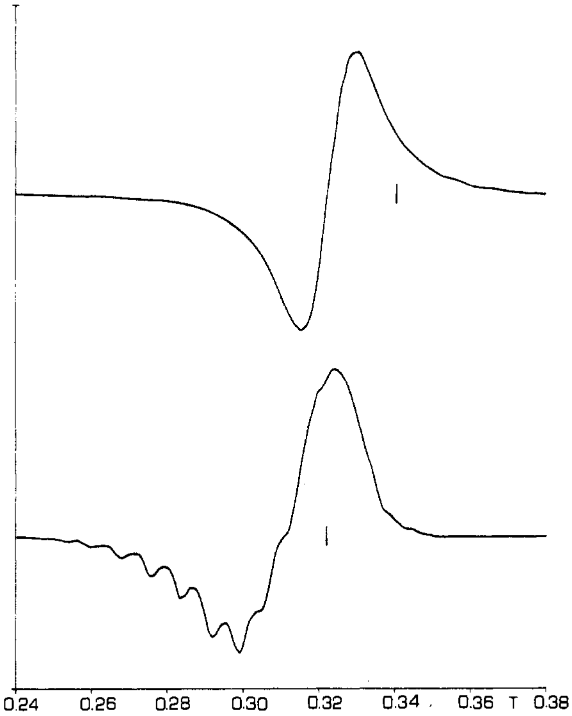


Figure 1. Polycrystalline powder EPR spectra of $[(dien)Cu(ox)Cu(tmen)(H_2O)_2](ClO_4)_2$ at X-band frequency at room temperature (upper line) and at 4.2 K (lower line). The vertical lines indicate the DPPH resonating field.

single crystals of the compound were obtained by slow evaporation at room temperature. Attempts to isolate $[(dien)Cu(ox)Cu(tmen)(H_2O)_2](ClO_4)_2$ from aqueous solutions of $[Cu(tmen)](ClO_4)_2$ and $Cu(dien)(ox)\cdot 4H_2O$ were unsuccessful, yielding mainly the corresponding symmetric complexes. In this case the synthesis in methyl alcohol can not be carried out due to the insolubility of the mononuclear species $Cu(dien)(ox)\cdot 4H_2O$ in this solvent. The crystals were oriented with a Philips PW1100 diffractometer and were found to correspond to the reported structure[7] with prominent ($\bar{1}02$) and ($10\bar{2}$) faces. EPR spectra in the temperature range 4.2–300 K were recorded at X-band frequency with a Bruker ER-200 spectrometer equipped with an Oxford Instruments ESR9 cryostat.

Results

The polycrystalline powder EPR spectra of I at room temperature and X-band frequency are quasi-isotropic, with a signal at $g = 2.11$ (Figure 1). Q-band spectra reveal an axial structure with $g_{\parallel} = 2.06$ and $g_{\perp} = 2.12$. The single-crystal spectra show only one signal for each orientation in the static magnetic field. Since the unit cell is monoclinic, this is an evidence of intermolecular exchange, averaging the signals of the two expected magnetically nonequivalent sites[9] and washing out also the fine and hyperfine splittings. The principal g values are $g_X = 2.12$, $g_Y = 2.14$, and $g_Z = 2.06$, where Y is parallel to b and Z is orthogonal to the $10\bar{2}$ face. The line widths in the XY plane, where the **g** tensor is quasi-isotropic, have a $1 + \cos^2 2\vartheta$ angular dependence at X-band frequency (where ϑ is the angle with the Y axis) and a more complicated pattern at Q-band frequency, with maxima at $\vartheta = 0°$ and $\vartheta = 90°$ and minimum at $\vartheta \simeq 55°$. In the other two rotations a pattern with maxima and minima separated by 90° are observed. The line widths tend to be slightly larger at X-band frequency.

The polycrystalline powder spectra of I at 4.2 K are typical of a triplet, with a hyperfine splitting into seven components neatly resolved on the low-field edge of the $\Delta M = 1$ transition (Figure 1). Single-crystal spectra showed at most two fine-structure components, with neat hyperfine splitting into seven lines resolved in most crystal orientations. A typical spectrum is shown in Figure 2. There is no evidence of the presence of another magnetic site.

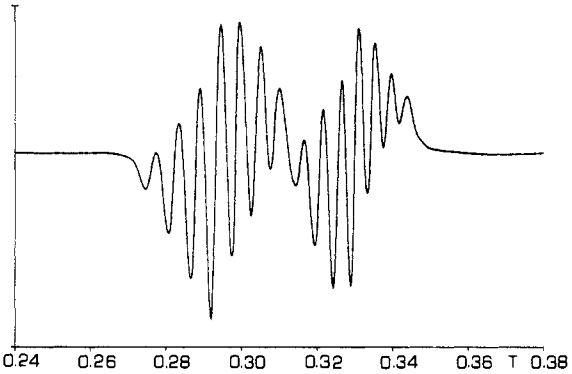


Figure 2. Single-crystal EPR spectrum of $[(dien)Cu(ox)Cu(tmen)(H_2O)_2](ClO_4)_2$ at X-band frequency and 4.2 K recorded with the static magnetic field parallel to the Z axis.

Table I. Principal **g** and **D** Values and Directions for the Symmetric Dinuclear Species Present in the Lattice of $[(dien)Cu(ox)Cu(tmen)(H_2O)_2](ClO_4)_2$[a]

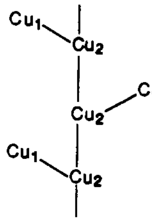
$g_{xx} = 2.063$ (2)	$g_{yy} = 2.185$ (4)	$g_{zz} = 2.087$ (2)
−0.89 (3)	0.0000	−0.45 (6)
0.0000	1.0000	0.0000
0.45 (6)	0.0000	−0.89 (3)
$D_{x'x'}$[b] = 0.0081 (3)	$D_{y'y'}$[b] = 0.0031 (2)	$D_{z'z'}$[b] = −0.0112 (2)
−0.9997 (3)	0.0000	0.02 (1)
0.0000	1.0000	0.0000
−0.02 (1)	0.0000	−0.9997 (3)

[a] The principal directions are given by their direction cosines referred to the orthogonal crystal axes X, Y, and Z, with Y parallel to b and Z orthogonal to the $10\bar{2}$ face. [b] In cm^{-1}.

The spectra were satisfactorily analyzed by a previously described technique[10] including only one magnetic site per unit cell. The principal **g** and **D** values and directions are given in Table I. The g_{yy} and D_{yy} directions are parallel to the b crystal axis, while the two tensors are slightly rotated in the ac plane, g_{xx} and $D_{x'x'}$ making an angle of about 28°. The hyperfine splitting was complicated by large second-order effects[11] and it was not further analyzed.

Discussion

The room-temperature single-crystal EPR spectra of I show only one signal for every orientation in the static magnetic field: apparently intermolecular exchange is large enough to yield exchange narrowing. In the present case several factors may determine broadening effects, namely (i) **g** anisotropy, (ii) **A** anisotropy, and (iii) zero-field splitting. The first contribution is of the order of 200 G, the second slightly smaller, and the third is perhaps half as large. In order to justify the observed line width, the modulating exchange frequency[12,13] must be larger than 700 G. The origin of this exchange can be attributed to the interaction between the pairs: indeed, the crystal structure determination[7] showed that the copper ions in the dien environment have additional bonds to the oxygen atom of the oxalato ion of another dinuclear species, so that a chain along the b axis is formed. For the magnetic interactions, therefore, the compound can be schematized as



---

(9) Bencini, A.; Gatteschi, D. *Transition Met. Chem. (N.Y.)* **1982**, *8*, 1.

(10) Banci, L.; Bencini, A.; Gatteschi, D.; Zanchini, C. *J. Magn. Reson.* **1982**, *48*, 9.

(11) Banci, L.; Bencini, A.; Gatteschi, D. *Inorg. Chem.* **1984**, *23*, 2138.

(12) Kubo, R.; Tomita, K. *J. Phys. Soc. Jpn.* **1954**, *9*, 888.

(13) Anderson, P. V.; Weiss, P. R. *Rev. Mod. Phys.* **1953**, *25*, 269.

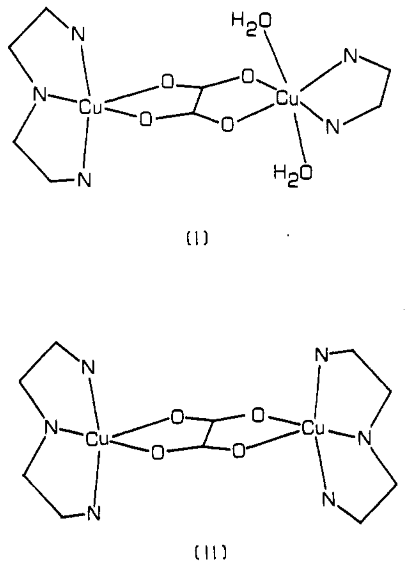


Figure 3. Schematic representations of the [(dien)Cu(ox)Cu(tmen)$(H_2O)_2$] (I) and [(dien)Cu(ox)Cu(dien)] (II) moieties.

Since the Cu_2 ions are bridged by one oxygen atom with a long (2.461 (5) Å) and a short (1.969 (5) Å) bond, it is conceivable that the exchange interaction between the dinuclear units can be strong enough to give exchange-narrowed spectra.

The *g* values have a reversed pattern, $g_{\parallel} < g_{\perp}$, as compared to the usual behavior for tetragonal complexes.[14] An approximate analysis of these values can be performed by looking at the structure of I. Recalling that the *z* molecular axis in copper(II) complexes is determined by the direction of the long metal–ligand bonds, we see that the pseudooctahedral Cu(tmen) moiety has the *z* molecular axis orthogonal to the oxalato plane, while the five-coordinate Cu(dien) moiety has the molecular *z* axis roughly in the oxalato plane. Therefore, the *z* axis of one moiety is parallel to an axis in the equatorial plane of the other. According to this, the **g** tensor of the pair is expected to have two *g* values that are intermediate between the $g_{\parallel}$ and $g_{\perp}$ values of the two individual copper ions and a third that is given by the average of two $g_{\perp}$ values. The observed pattern conforms to this. It is not possible for us to evaluate the individual **g** tensors of the two copper ions, due to the low symmetry of the pair and to the fact that exchange narrowing averages further the **g** tensors of the pairs.

The low-temperature spectrum indicates the presence of a triplet spin species containing two equivalent copper atoms. In fact, the hyperfine splitting into seven lines can be explained only by the interaction with two equivalent copper atoms. Since this species remains paramagnetic down to 4.2 K, the two copper ions are only weakly coupled ($J < 4$ K). A possible candidate for this is a noncentrosymmetric dimer of formula $[(dien)Cu(ox)Cu(dien)]^{2+}$.[15] Indeed, it has been reported[16] that only a weak coupling between copper ions is operative in $[(dien)Cu(ox)Cu(dien)](ClO_4)_2 \cdot H_2O$ and $[(dien)Cu(ox)Cu(dien)](ClO_4)_2$. In these complexes the two copper ions are not rigorously equivalent; the crystal structure shows a noncentrosymmetric dication, but with N-substituted tetramethyl and tetraethyl dien derivatives, the dimeric units are centrosymmetric.[15-18] The structure of $[(dien)Cu(ox)Cu(dien)]^{2+}$ is as shown schematically in Figure 3, with an oxygen atom of the bridge occupying an equatorial position and another oxygen atom occupying an axial position of the copper coordination environment.

The fact that one site is observed in the low-temperature spectra implies that the resonating species has either C_s or C_2 symmetry and one principal direction of the **g** and **D** tensors must be parallel to *b*. The *g* value observed parallel to *b*, g_{yy}, is 2.185 (4), i.e. the largest, suggesting that *b* is closely parallel to the *z* molecular axis of the symmetric pair. Looking at the structural data of $[(dien)Cu(ox)Cu(tmen)(H_2O)_2](ClO_4)_2$, we see that the directions of the long copper–oxygen bonds, which define the molecular *z* axes, are fairly close to the *b* axis, so that it is reasonable to assume that the symmetric species is similarly oriented in the lattice.

The zero-field splitting tensor has its largest value orthogonal to g_{yy}, suggesting that exchange contributions are not dominant.[17] It seems reasonable to assume then that the $D_{z'z'}$ direction is close to the copper–copper direction, as is to be expected for a dipolar-determined zero-field splitting tensor. The actual value of $D_{z'z'}$ is in fairly good agreement with the expected value for two copper ions[18] separated by more than 5 Å. For this hypothesis it is useful to compare the z' direction with the copper–copper direction seen in the structure[7] of I at room temperature. Indeed, the latter makes an angle of 36° with the *c* axis, which corresponds to the z' axis of the **D** tensor. If our structural hypothesis on the nature of the paramagnetic impurity is correct, some nonsymmetric dinuclear units in the lattice are replaced by [(dien)Cu(ox)Cu(dien)] symmetric units. This replacement is accompanied by distortions in the coordination environment such that a difference of 30–40° in the copper–copper directions between the symmetric and asymmetric species might be reasonable.

Conclusions

The analysis of the EPR spectra of I at low temperature revealed that in the lattice of the asymmetric dinuclear species a symmetric dinuclear complex can be accommodated. This is evidence of how flexible the lattice of a coordination compound can be and how its properties can be modulated by a doping procedure, analogous to that well-known for ionic lattices.

Registry No. $[(dien)Cu(ox)Cu(tmen)(H_2O)_2](ClO_4)_2$, 83928-11-4; $[(dien)Cu(ox)Cu(dien)]^{2+}$, 48190-95-0.

---

(14) Bertini, I.; Gatteschi, D.; Scozzafava, A. *Coord. Chem. Rev.* **1979**, *29*, 67.

(15) Curtis, N. F.; McCormik, I. R. N.; Waters, T. N. *J. Chem. Soc., Dalton Trans.* **1973**, 1537.

(16) Felthouse, T. R.; Laskowski, E. J.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 1077.

(17) Gatteschi, D.; Bencini, A. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Dordrecht, Holland, 1985; pp 241–268.

(18) Bencini, A.; Di Vaira, M.; Fabretti, A. C.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1984**, *23*, 1620.