Electron Paramagnetic Resonance Studies of Some Copper(II) Complexes with Organophosphorus Chelates[1]

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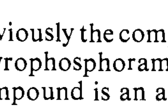
Abstract: The powder epr spectra of tris complexes of Cu(II) with octamethylpyrophosphoramide (OMPA), nonamethylimidodiphosphoramide (NIPA), octamethylmethylenediphosphonic diamide (PCP), and tetraisopropyl methylenediphosphonate (IPCP) have been obtained. At 297°K all of these tris complexes give an isotropic g value of 2.25. At 88°K all tris complexes give anisotropic g values of 2.42–2.52 for $g_{\parallel}$ and 2.08–2.13 for $g_{\perp}$. The values for $g_{\parallel}$ are among the highest known for Cu(II) complexes. The bis complexes of Cu(II) with OMPA, NIPA, and PCP give anisotropic g values at 297°K, with $g_{\parallel}$ in the range 2.41–2.50 and $g_{\perp}$ between 2.08 and 2.10.

We reported previously the complete structure of tris(octamethylpyrophosphoramide)copper(II) perchlorate.[3] This compound is an apparent exception to the Jahn–Teller theorem, since the site symmetry of Cu(II) is D_3. X-ray analysis does not eliminate the possibility of a dynamic Jahn–Teller effect. Since epr spectroscopy is more sensitive to the immediate environment of Cu(II), we have initiated an epr study of tris chelates of Cu(II) with the organophosphorus ligands illustrated below. The present paper is a report on the powder spectra.



OMPA, R = $N(CH_3)_2$; X = O
PCP, R = $N(CH_3)_2$; X = CH_2
NIPA, R = $N(CH_3)_2$; X = $N(CH_3)$
IPCP, R = $OCH(CH_3)_2$; X = O

Experimental Section

Powder spectra were obtained at 297 and 88°K with a Varian E-3 X-band epr spectrometer with 100-KHz modulation, equipped with Fieldial and an E-4551 cavity operating in the TE_{102} mode. The E-4557-9 variable-temperature accessory was used for low-temperature work. Well-resolved spectra were obtained with undoped powders. Values of g at 297°K were calculated from $g = h\nu/\beta H$, where ν = 9.53 GHz. The magnetic field was read from the chart. The scan range was ±2500 G with field centered at 3150 G. The chart was calibrated with DPPH. At 88°K the field was set at 2800 G with a scan range of ±500 G and a microwave frequency of 9.16 GHz.

The compounds studied here were prepared by procedures reported previously.[4]

The computer program used to calculate powder spectra is similar to one reported previously.[5]

Results and Discussion

The spectrum of $Cu(OMPA)_3(ClO_4)_2$ at 297°K is given in Figure 1. This is typical of the isotropic spectra obtained at 297°K for all tris chelates in this study. At 88°K the spectrum of $Cu(OMPA)_3(ClO_4)_2$ is anisotropic (solid line, Figure 2). We would like to emphasize that the well-resolved spectrum in Figure 2 is for an undoped powder. The spectrum contains a shoulder at about 3100 G which can be explained by assuming a rhombic g tensor rather than an axial one. The dotted and dashed lines in Figure 2 show the best fits obtained with computer-calculated curves. The dotted line is the best fit for a g tensor with all principal values unequal and the dashed line is the best fit for a g tensor with $g_x = g_y \neq g_z$. The three computed rhombic g values are g_x = 2.06, g_y = 2.13, and g_z = 2.52. While this calculated curve reproduces essential features of the experimental spectrum, it seems likely that improved agreement could be obtained with only slight changes in the input parameters. The computed axial tensor gives g values of 2.08 and 2.52.

The observation of an isotropic spectrum at higher temperatures and an anisotropic spectrum at lower temperatures was first reported by Bleaney and Ingram[6] for trigonal $[Cu(H_2O)_6]SiF_6$. Abragam and Pryce[7] attributed this change to a dynamic–static Jahn–Teller effect. Their theory,[8] which was later expanded by Liehr and Ballhausen,[9] assumes that three tetragonal distortions of equal energy are present. These three tetragonal distortions are mutually perpendicular and each one gives rise to an epr transition. At higher temperatures only one transition is found because the crystal field resonates among the three distortions. However, at 20°K the spectrum becomes that expected for three magnetic sites.

The similarity in our results for $Cu(OMPA)_3(ClO_4)_2$ and those of Bleaney and coworkers[6,10] for a number of trigonal Cu(II) complexes can be seen by comparing the g-tensor values in Table I. Since many consider the epr studies of Bleaney and coworkers to be the best experimental evidence for the Jahn–Teller effect, we would like to propose that our epr studies for $Cu(OMPA)_3(ClO_4)_2$ provide additional evidence in support of a dynamic–static Jahn–Teller effect.

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[1] Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

[2] (a) Department of Chemistry; (b) Department of Molecular Biology.

[3] M. D. Joesten, M. S. Hussain, and P. G. Lenhert, *Inorg. Chem.*, **9**, 151 (1970).

[4] K. P. Lannert and M. D. Joesten, *ibid.*, **8**, 1775 (1969), and references cited therein.

[5] J. H. Venable, Jr., "Magnetic Resonance in Biological Systems," Pergamon Press, Elmsford, N. Y., 1967, p 373.

[6] B. Bleaney and D. J. E. Ingram, *Proc. Phys. Soc. London, Sect. A*, **63**, 408 (1950).

[7] A. Abragam and M. H. L. Pryce, *ibid.*, *Sect. A*, **63**, 409 (1950).

[8] A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc., Ser. A*, **206**, 164 (1951).

[9] A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (*New York*), **3**, 304 (1958).

[10] B. Bleaney, K. D. Bowers, and R. S. Trenam, *Proc. Roy. Soc., Ser. A*, **228**, 147, 157 (1955).

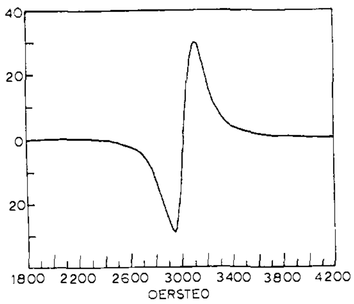

Figure 1. Epr spectrum of $Cu(OMPA)_3(ClO_4)_2$ at 297°K.

Our system also offers a number of advantages over the compounds studied by Bleaney and coworkers. First, the complete structure of $Cu(OMPA)_3(ClO_4)_2$ has been determined at room temperature. Second, the transition temperature for the change from isotropic to anisotropic g tensors is 88°K rather than the 20°K found for other compounds in Table I. For these reasons, we have initiated a low-temperature X-ray structure study of $Cu(OMPA)_3(ClO_4)_2$ to determine what changes in Cu(II) environment are indicated by X-ray diffraction techniques.

Table I. Epr Parameters for H_2O, D_2O, and OMPA

Compound	Temp, °K	g	Hfsc × 10^4
$Cu(OMPA)_3(ClO_4)_2$	88	$g_x = 2.12$	$A_x < 15$
		$g_y = 2.06$	$A_y < 15$
		$g_z = 2.52$	$A_z = 90$
$(NH_4)_2(Cu, Zn)(SO_4)_2 \cdot 6H_2O^a$	20	$g_x = 2.12$	$A_x = 25$
		$g_y = 2.05$	$A_y = 35$
		$g_z = 2.46$	$A_z = 130$
$K_2(Cu, Zn)(SO_4)_2 \cdot 6D_2O^a$	20	$g_x = 2.16$	$A_x < 17$
		$g_y = 2.04$	$A_y = 61$
		$g_z = 2.42$	$A_z = -99$
$(Cu, Mg)_3La_2(NO_3)_{12} \cdot 24D_2O^a$	20	$g_x = 2.097$	$A_x = 19.0$
		$g_y = 2.097$	$A_y = 12.3$
		$g_z = 2.470$	$A_z = -13$
$(Cu, Zn)SiF_6 \cdot 6H_2O^b$	20	$g_\perp = 2.10$	
		$g_\parallel = 2.46$	

[a] Reference 10. [b] Reference 6.

At the present time we have only preliminary results from Weissenberg photographs at 100–110°K.[11] The pattern of spots for $Cu(OMPA)_3(ClO_4)_2$ at 100°K is similar to that in Weissenberg photographs taken at 297°K. However, uneven cooling of the crystal and the capillary tube which contains the crystal has resulted in a doubling of spots in the photographs at low temperature. We hope to modify the cooling apparatus to allow even cooling of the crystal down to 88°K.

In spite of these problems, the similar patterns of spots in the Weissenberg photographs at 297 and 100–110°K are support for the presence of apparent D_3 site symmetry for Cu(II) at low temperature. Also, photographs have been taken of the same crystal cycled from room temperature to liquid nitrogen temperature several times and the results are reproducible. Since X-ray diffraction is a measure of the *average* environment, a tetragonal distortion along x, y, and z axes will give rise to three g values, but the average environment will still be D_3.[12] The distortions are probably quite small in view of the similarity in root-mean-square amplitudes for atoms in the chelate ring.[3]

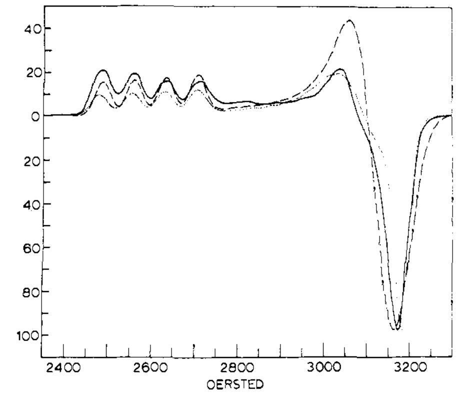

Figure 2. Epr spectrum of $Cu(OMPA)_3(ClO_4)_2$ at 88°K: —, experimental spectrum; · · ·, curve computed for a rhombic tensor model with $g_x \neq g_y \neq g_z$; - - -, curve computed for an axial tensor model with $g_x = g_y \neq g_z$.

The results described thus far provide additional experimental evidence for the Abragam–Pryce model, although it is not possible at this stage in our work to rule out the axial tensor model with two g values. Previous workers[13,14] in this area have made use of the equations

$$g_\parallel = 2 + 8|\lambda|/\Delta xy \qquad (1)$$

$$g_\perp = 2 + 2|\lambda|/\Delta xz,yz \qquad (2)$$

to calculate anisotropic g values, where λ is the spin–orbit coupling constant and Δ is the crystal-field splitting of the d orbitals of copper in an octahedral field. The equation

$$g = 2 + 4|\lambda|/\Delta \qquad (3)$$

is used to obtain the isotropic g value. Kokoszka, *et al.*,[13] have used eq 3 to calculate $|\lambda|/\Delta$ from the isotropic g value, and then eq 1 and 2 to calculate $g_\parallel$ and $g_\perp$. Good agreement is presented as support of an octahedral complex with a tetragonal Jahn–Teller distortion.

In the present study use of eq 3 gives a value of 0.0628 for $|\lambda|/\Delta$. Substitution of this value into eq 1 and 2 gives calculated values for $g_\parallel$ and $g_\perp$ of 2.50 and 2.13, respectively. The lack of good agreement between the calculated and experimental values for $g_\perp$ is an indication that an averaged crystal-field splitting is not suitable for the low-temperature g values. Polarized spectral data are needed, and Professor Palmer of Duke University has initiated such a study.[15] At the present time, only spectral data at 300°K are available. If the value of 9850 cm^{-1} is used for Δ (band maximum from unpolarized spectrum[15]), eq 3 can be used to calculate $|\lambda|$. This gives a value of 618 cm^{-1} for $|\lambda|$, compared to a free-ion value of 828 cm^{-1}, which is additional support for a negligible amount of covalent bonding in the Cu–O bond.

Since we have prepared a number of tris chelates of Cu(II) with organophosphorus ligands,[4] we were in-

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(11) M. S. Hussain and M. D. Joesten, unpublished results.

(12) Preliminary epr studies of single crystals of $Cu(OMPA)_3(ClO_4)_2$ are in support of three magnetic sites.

(13) H. C. Allen, Jr., G. F. Kokoszka, and R. G. Inskeep, *J. Amer. Chem. Soc.*, **86**, 1023 (1964).

(14) G. F. Kokoszka, C. W. Reimann, H. C. Allen, Jr., and G. Gordon, *Inorg. Chem.*, **6**, 1657 (1967).

(15) R. A. Palmer, private communication.

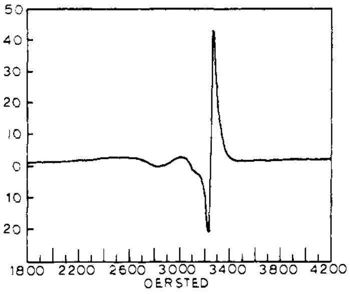

Figure 3. Epr spectrum of Cu(OMPA)$_3$(ClO$_4$)$_2$ at 297°K.

terested in whether these compounds would give epr spectra similar to those found for Cu(OMPA)$_3$(ClO$_4$)$_2$. The 88°K spectra for the other organophosphorus chelates have the appearance of intermediate spectra of the type obtained for Cu(OMPA)$_3$(ClO$_4$)$_2$ at higher temperatures (100–150°K). The spectrum of the latter compound does not become completely anisotropic until 95°K. The other organophosphorus chelates would require lowering the temperature to about 50°K to obtain completely anisotropic spectra.

Table II is a tabulation of $g_{\parallel}$ and $g_{\perp}$ for the tris chelates as determined from the experimental spectra (see the introduction section for structures of ligands and abbreviations). The g values were calculated from the experimental spectra, since all except Cu(OMPA)$_3$(ClO$_4$)$_2$ give intermediate spectra at 88°K. The values of $g_{\parallel}$ are among the highest known for Cu(II). The only other tris chelates of Cu(II) which have been investigated are dipyridyl ($g_{\perp}$ = 2.046, $g_{\parallel}$ = 2.268),[13] *o*-phenanthroline ($g_{\perp}$ = 2.064, $g_{\parallel}$ = 2.273),[14] and a mixed complex Cu(hfacac)$_2$(bipy), which has $g_{\perp}$ = 2.056 and $g_{\parallel}$ = 2.299.[16]

Table II. Epr Data for Tris Chelates

Compound	297°K	88°K	
	g	$g_{\perp}$	$g_{\parallel}$
Cu(OMPA)$_3$(ClO$_4$)$_2$	2.25	2.08	2.52
Cu(NIPA)$_3$(ClO$_4$)$_2$	2.26	2.17	2.42
Cu(PCP)$_3$(ClO$_4$)$_2$	2.24	2.12	2.44
Cu(IPCP)$_3$(ClO$_4$)$_2$	2.25	2.13	2.47

Another comparison of interest is that of epr data for bis chelates of Cu(II) with organophosphorus ligands. Table III contains g values for these systems. Figure 3 is a typical anisotropic spectrum at 297°K for the compounds listed in Table III. The X-ray structure of Cu(OMPA)$_2$(ClO$_4$)$_2$ has been reported.[17] The Cu(II) ion is in a tetragonal environment with equatorial distances of 1.94 Å and an axial distance of 2.55 Å. For a known tetragonal system of OMPA an anisotropic spectrum is observed at 297°K. However, the g values are not very different from those given in Table II for tris chelates.

Table III. Epr Data for Bis Chelates at 297°K

Compound	$g_{\parallel}$	$g_{\perp}$
Cu(OMPA)$_2$(ClO$_4$)$_2$	2.44	2.09
Cu(NIPA)$_2$(ClO$_4$)$_2$	2.45	2.10
Cu(PCP)$_2$(ClO$_4$)$_2$	2.50	2.08

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(16) M. V. Veidis, G. H. Schreiber, T. E. Gough, and G. J. Palenik, *J. Amer. Chem. Soc.*, **91**, 1859 (1969).

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A Study of Some Glycine and Leucine Peptide Complexes of Copper, Nickel, and Zinc

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Abstract: Some solid complexes of general composition M(HAA)$^+$ for copper, nickel, and zinc and M(HAA)$_2$ for nickel and zinc, with glycylglycine, glycyl-L-leucine, and L-leucylglycine, have been prepared. The magnetic susceptibilities over the temperature range 85–300°K indicate that the complexes are magnetically normal and the data are consistent with a coordination number six ligand environment. The infrared spectra of the solid-state and visible spectra of the solutions are consistent with the bonding of the peptide-amide nitrogen in the copper complexes, and the peptide-amide oxygen in the nickel (zinc) complexes.

There have been numerous reports in the literature on solution measurements of the interaction of copper(II), nickel(II), and zinc(II) ions with glycine, leucine, and their peptides; for example, see Bryce, *et al.*,[2] Martin, *et al.*,[3] Grant and Hay,[4] Nancollas, *et*

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(1) This article was based upon a dissertation submitted by M. L. Bair in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin, 1967.