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# The Electron Paramagnetic Resonance Spectrum of Some Tris-Complexes of Copper(II)[1a]

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The e.p.r. spectrum of the tris-coordination compound of $Cu^{+2}$ with 1,10-phenanthroline and 2,2′-dipyridine has been examined as a function of temperature. At high temperatures a single absorption is observed in each compound indicating an isotropic $g$-value. At liquid nitrogen temperature, each compound exhibits an absorption pattern corresponding to an anisotropic $g$-tensor with two unique principal values. The measured $g$-values are: phenanthroline complex, $g = 2.134$ at high temperature, $g_{\|} = 2.273$, $g_{\perp} = 2.062$ at liquid nitrogen temperature; dipyridine complex, $g = 2.114$ at high temperature, $g_{\|} = 2.268$, $g_{\perp} = 2.046$ at liquid nitrogen temperature. These spectra have been interpreted as arising from a Jahn–Teller tetragonal distortion, frozen in at the lower temperatures as described in the theoretical treatment of Liehr and Ballhausen.

## Introduction

There has been considerable recent interest in the e.p.r. spectra of bis-$Cu^{+2}$ chelates[2]; however, up to the present, no work has been reported on tris-$Cu^{+2}$ chelates. These complexes should be of considerable interest since they are expected to be octahedrally coordinated and exhibit a Jahn–Teller distortion. The theory of the Jahn–Teller effect, recently worked out by Liehr and Ballhausen[3] for octahedral coordination, seems to account for the e.p.r. spectrum of copper fluorosilicate hexahydrate and $Cu^{+2}$ in some inorganic salts,[4] but as yet no example has been found in a chelate.

Recent work on the infrared spectra of the tris-$Cu^{+2}$ complex with 2,2′-dipyridine gives some reason to believe that there is a Jahn–Teller distortion in this complex.[5]

This evidence is lacking in the infrared spectrum of the tris-1,10-phananthroline complex.

We have investigated the e.p.r. spectra of the tris-complexes of $Cu^{+2}$ with these ligands as a function of temperature in the range from liquid helium temperature to 130°. The result seems to be accounted for by the Liehr–Ballhausen theory.

## Experimental

The tris-2,2′-dipyridine and 1,10-phenanthroline complexes were prepared as nitrate salts by the method described by Inskeep.[5] In order to obtain magnetically dilute samples, the diamagnetic tris-$Zn^{+2}$ complexes were prepared containing small amounts of $Cu^{+2}$. Percentages of $Cu^{+2}$ ranged from 0.1 to 3. Compositions of the complexes were checked for C, H, N, and metal by chemical analysis. All samples corresponded to the tris-complex. Owing to difficulties encountered in the interpretation of the complexes containing naturally occurring copper with its two isotopes 63 and 75, samples were also prepared by the same procedure containing only the $^{63}Cu$ isotope.

The e.p.r. spectra were recorded on a Varian Model 4500 e.p.r. spectrometer using 100 kc. modulation except at liquid He temperature. At the latter temperature a modulation of 400 c.p.s. was used. The spectra were recorded on polycrystalline samples and the $g$-values determined by the method of Sands[6a] and Kneubuhl.[6b]

TABLE I

MAGNETIC PARAMETERS OF $Cu(phen)_3{}^{+2}$ AND $Cu(dipy)_3{}^{+2}$

| | $Cu(phen)_3(NO_3)_2$ | $Cu(dipy)_3(NO_3)_2$ |
|---|---|---|
| | High temperature | |
| $g$ | $2.134 \pm 0.002$ | $2.114 \pm 0.002$ |
| | Liquid $N_2$ | |
| $g_{\|}$ | $2.273 \pm 0.003$ | $2.268 \pm 0.003$ |
| $g_{\perp}$ | $2.062 \pm 0.003$ | $2.046 \pm 0.003$ |
| $A_{\|}$, cm.$^{-1}$ | $161 \pm 2 \times 10^{-4}$ | $164 \pm 2 \times 10^{-4}$ |
| $A_{\perp}$, cm.$^{-1}$ | $36 \pm 4 \times 10^{-4}$ | [a] |
| | Obsd. spacing of nitrogen hyperfine splitting, cm.$^{-1}$ | |
| Parallel | $10 \pm 1 \times 10^{-4}$ | $9 \pm 1 \times 10^{-4}$ |
| Perpendicular | $12 \pm 1 \times 10^{-4}$ | $12 \pm 1 \times 10^{-4}$ |

[a] Too small to be observed at available resolution. Values of constants were taken from J. A. Bearden and J. S. Thomsen, "A Survey of Atomic Constants," The Johns Hopkins University, Baltimore, Md., 1955.

A typical spectrum of these two complexes containing naturally occurring copper at 130° is shown in Fig. 1. Although this is for the phenanthroline complex, the spectrum of the bipyridine complex is quite similar. There is a single absorption indicative of an isotropic $g = 2.134$. Figure 2 shows a typical spectrum at liquid nitrogen temperature. The high-field strong absorption at $g = 2.062$ shows no measurable indication of a coupling of the unpaired electron to the copper nucleus. The structure appearing on this absorption arises from a coupling with the nitrogen nuclei in the ligand molecules. The three smaller absorptions at lower field with $g_{\|} = 2.273$ are three of the four components resulting from the coupling of the unpaired electron with the copper nucleus. Evidence for the fourth component is discernible on traces run at high amplification as a perturbation on the large absorption pattern. The signal shape at low temperatures is quite characteristic of those generally obtained from powders and glasses.[6a,b]

Examination of these spectra under higher amplification at liquid nitrogen temperature clearly revealed the hyperfine structure due to the coupling of the unpaired electron with the nitrogen nuclei of the ligands. For samples containing naturally occurring copper, 13 such components were observed indicating a coupling with six equivalent nitrogen nuclei. Six equivalent nitrogen nuclei are not compatible with any distortion of an octahedron except along one of the threefold axes. Such a distortion is not compatible with the $g$-values observed.

Because of this anomaly, samples containing only $^{63}Cu$ were prepared and examined with the result that in the spectrum of both compounds only 9 components were found. One of the parallel components is shown in Fig. 3. This observation indicates that there are four equivalent nitrogen nuclei interacting with the unpaired electron. Four equivalent nuclei are compatible with a tetragonal distortion, as are the observed $g$-values. There is no change in the spectrum below liquid nitrogen temperature as far down as liquid helium temperature. This experiment with a single isotope points out the very real danger of depending on ligand hyperfine structure to determine the number of nitrogen atoms coordinated equivalently to the central copper ion.

The general aspects of the $^{63}Cu^{+2}$ spectra are similar to those in Fig. 1 and 2, except that for the phenanthroline complex a small coupling of the unpaired electron to the copper nucleus is observed in the perpendicular direction.

## Interpretation

The low temperature spectra could be fitted to the usual spin Hamiltonian

$$H = \beta_0[g_{\|} H_z S_z + g_{\perp}(H_x S_x + H_y S_y)] + A_{\|} I_z S_z + A_{\perp}(I_x S_x + I_y S_y) \quad (1)$$

The high temperature spectra required only an isotropic $g$-value which is denoted by $g$ in Table I. The

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(1) (a) Presented at the 114th National Meeting of American Chemical Society, March 31–April 6, 1963, Los Angeles, Calif.; (b) National Bureau of Standards; (c) University of Hawaii.

(2) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 31, 35 (1958); D. Kivelson and R. Nieman, *ibid.*, **35**, 149, 156, 162 (1961); H. R. Gersmann and J. D. Swalen, *ibid.*, **36**, 3221 (1962).

(3) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, **3**, 304 (1958).

(4) B. Bleaney, K. D. Bowers, and R. S. Trenham, *Proc. Roy. Soc.* (London), **A228**, 157 (1955); J. H. M. Thornley, B. W. Mangum, J. H. E. Griffiths, and J. Owen, *Proc. Phys. Soc.* (London), **78**, 1263 (1961).

(5) R. G. Inskeep, *J. Inorg. Nucl. Chem.*, **24**, 763 (1962).

(6) (a) R. H. Sands, *Phys. Rev.*, **99**, 1222 (1955); (b) F. K. Kneubuhl, *J. Chem. Phys.*, **33**, 1074 (1960).

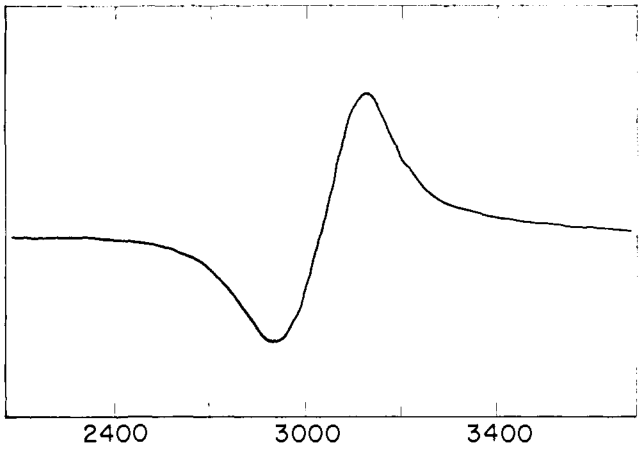

Fig. 1.—The e.p.r. spectrum of tris-1,10-phenanthrolinecopper nitrate at 130°

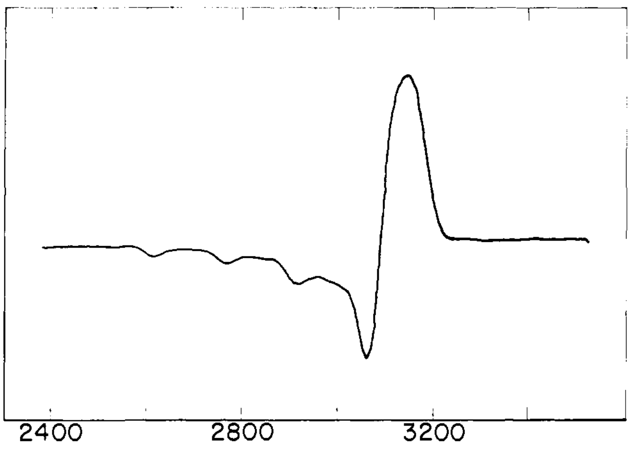

Fig. 2.—The e.p.r. spectrum of the Cu$^{+2}$ tris-1,10-phenanthroline complex at liquid nitrogen temperature.

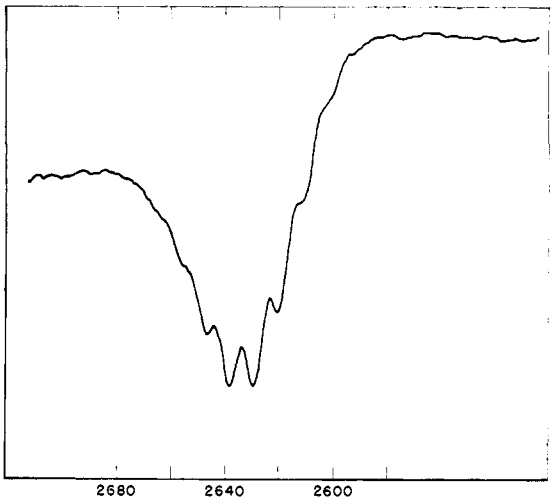

Fig. 3.—The hyperfine structure due to the coupling of the unpaired electron to the nitrogen nuclei of the ligands. This example is the dipyridine complex at liquid nitrogen temperature.

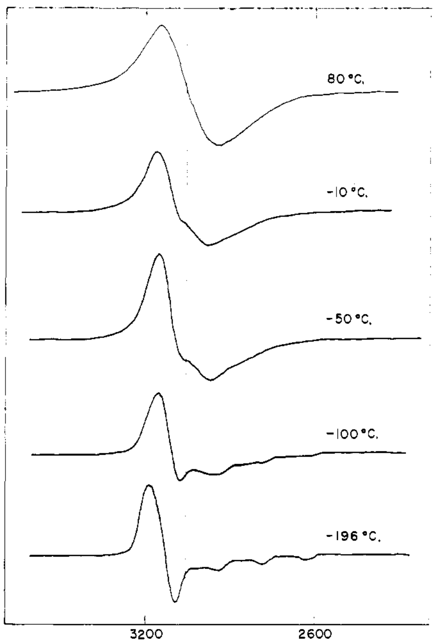

Fig. 4.—The variation of the e.p.r. spectrum of the Cu$^{+2}$ tris-1,10-phenanthroline complex with temperature.

magnetic parameters deduced for the $^{63}$Cu compounds are given in Table I. The uncertainties given in the table are merely indications of the reproducibility of the measurements.

The temperature dependence of these spectra is reminiscent of the behavior predicted by Liehr and Ballhausen[3] for an octahedral complex with a tetragonal Jahn–Teller distortion.

In their picture, at a sufficiently high temperature, the system resonates among the three equivalent tetragonal distortions along the three fourfold axes of the octahedron. The result of this resonance is an effective octahedron which will give rise to an isotropic $g$-value. If the temperature is lowered sufficiently, the complexes are frozen into one of the distortions and an anisotropic $g$-value is expected. If their phenomenological parameter $\beta > 0$, the crystal-field approximation expressions for the $g$-values are, when the distortion is frozen in

$$g_{\parallel} = 2 + \frac{8|\lambda|}{\Delta}$$
$$g_{\perp} = 2 + \frac{2|\lambda|}{\Delta} \qquad (2)$$

in which $\lambda$ is the spin-orbit coupling constant and $\Delta$ is the crystal-field splitting of the d-orbitals of the copper in an octahedral field. For the high temperature case

$$g = 2 + \frac{4|\lambda|}{\Delta} \qquad (3)$$

For the phenanthroline spectrum, one can evaluate $|\lambda/\Delta|$ from the high temperature $g$-value and, using this value, calculate the expected $g$-value for the low-temperature spectrum. The results are summarized in Table II. The agreement between the observed and calculated values is about 2 parts in 1000, which is remarkable agreement for this crude approximation.

TABLE II

COMPARISON OF OBSERVED AND CALCULATED $g$-VALUES

| Complex | | Obsd. | Calcd. |
|---|---|---|---|
| Phenanthroline | $g_{\parallel}$ | 2.273 | 2.268 |
| | $g_{\perp}$ | 2.062 | 2.067 |
| Dipyridine | $g_{\parallel}$ | 2.268 | 2.228 |
| | $g_{\perp}$ | 2.046 | 2.057 |

In the dipyridine complex, the agreement is not nearly as good as in the phenanthroline complex, although the results still agree to about 2%. This is the complex for which the infrared evidence suggests a Jahn–Teller distortion. For the effect to be apparent in the infrared it must be quite large. This is reasonable because the dipyridine ligand is much less rigid than the phenanthroline ligand and so is more easily distorted. If the distortion is large enough, it is no longer sufficient to use an averaged crystal field splitting in the formulas for the low temperature *g*-values. Assuming that $\lambda$ remains constant, this reasoning leads to a splitting of about 2000 cm.$^{-1}$ of the degenerate electronic state in the distorted configuration. This figure is reasonable when compared to other studies in which the ligands around the Cu$^{+2}$ are tetragonally distorted.

The spectrum does not show a sharp transition point with temperature but rather goes over slowly from one limiting spectrum to the other. Figure 4 shows a series of spectra run at various temperatures. It is not possible to account for these spectra quantitatively at the intermediate temperatures, but they seem to be superpositions of the two limiting spectra.

## Conclusion

The line width of the high temperature spectrum is equal to the line width of the two components observed at low temperature. This observation would seem to lend weight to the interpretation given here. One would expect that the hyperfine structure would be washed out at the high temperature owing to the breadth of the energy levels involved in the transitions.

This work on polycrystalline samples poses some questions to be answered. Single crystals of the diluted compounds are being grown to help answer these questions. The optical spectrum will be investigated at low temperature to see if the Jahn–Teller splitting of the electronic state can be observed. Similarly, since the Liehr–Ballhausen treatment assumes that the distortion arises from a vibronic coupling to the E-modes of vibration, the infrared spectrum should be investigated as the vibrational states should also be perturbed. Observation of these effects would eliminate any doubts that may exist concerning the origin of the observed effects. X-Ray diffraction investigations should be done on the crystals at various temperatures to see if any information can be deduced as to the extent of the distortion.

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# Machine Computation of Association Constants from Spectrophotometric Data: An Analysis of Errors

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Fortran language programs have been written which successfully calculate equilibrium constants, *K*, and molar absorptivities, $\epsilon$, from experimental data for self-association and heteroassociation. The calculated parameters are, however, inordinately sensitive to variations in the input data. Experiments using the programs with synthetic data reveal the results to be most sensitive to concentration errors. The errors are discussed in terms of the Rose–Drago treatment of this kind of data. Suggested approaches for the improvement of this situation are given.

The simplicity and accuracy of spectrophotometric measurements have led to their use in the determination of a great variety of association constants, especially where the association occurs between two different species. A wide variety of methods has been devised for the treatment of the experimental data, but owing to the complexity of the problem it has usually been necessary to limit the approach to special cases (such as special concentration relationships) or to make simplifying approximations.[2] The best known methods are graphical and are comparatively tedious and often imprecise. One digital method has been proposed for the determination of self-association constants[3] but it has been shown to fail.[4] A digital method has been presented by Liptay for the calculation of association constants of electron donor–acceptor complexes which avoids many of the restrictions implicit in the earlier methods but which, too, necessarily makes simplifying assumptions in order to keep the labor of the calculation within bounds.[5]

In the current work we sought to write a program for a digital computer which would accept spectrophotometric data and fit to it, without simplifying approximations, equilibrium constants and molar absorptivities according to the least-squares criterion. Activity coefficient effects were assumed to be negligible; Beer's law was assumed to hold for every species involved. The kind of approach used in developing the computer program is akin to that used by Coburn and Grunwald[6] and more recently by Sillén.[7]

The problem may be stated as follows: The three independent variables which have an effect on the value of the optical density (at a given temperature in a given solvent) are the initial concentration of substrate(s), the values of the equilibrium constants for the equilibria involved, and the values of the molar absorptivities for the species involved. Of these three independent variables, only the concentration is experimentally controlled.

The task which confronts one is to deduce values of the equilibrium constants and molar absorptivities which predict the experimentally determined values of the optical density ($D_m$) at various wave lengths and experimental values of the concentration of substrate(s). The variety of possible ways this might be done is summarized with the following diagram. To illustrate the interpretation of this diagram consider the upper left leg. If one knows the values of $K$ and the initial concentrations ($C_0$) one can calculate the equilibrium concentrations ($C_e$) of the species. Conversely, if one knows the equilibrium concentrations and the initial concentrations one can derive the equilibrium constant.

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(1) National Science Foundation Research Participation for College Teachers Fellow.

(2) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961.

(3) P. A. D. de Maine and A. G. Goble, *Trans. Faraday Soc.*, **53**, 427 (1957); P. A. D. de Maine, M. M. de Maine, A. A. Briggs, and G. E. McAlonie, *J. Mol. Spectry.*, **4**, 398 (1960).

(4) B. Musulin, W. Lee, and R. L. Foley, *ibid.*, **9**, 254 (1962).

(5) W. Liptay, *Z. Elektrochem.*, **65**, 375 (1961).

(6) W. C. Coburn and E. Grunwald, *J. Am. Chem. Soc.*, **80**, 1318, 1322 (1958).

(7) D. Dyrssen, N. Ingre, and L. G. Sillén, *Acta Chem. Scand.*, **15**, 694 (1961); L. G. Sillen, *ibid.*, **16**, 159, 191 (1962).