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Contribution from the Department of Inorganic
Chemistry, University of Melbourne, Parkville,
Victoria, Australia 3052

Paramagnetic Anisotropy and Electronic Structure of β-Copper(II) Phthalocyanine

By R. L. Martin and S. Mitra

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The electronic structures of square-planar paramagnetic transition metal compounds have been the subject of extensive studies.[1-4] Optical absorption and electron spin resonance spectroscopy are the only methods which have been widely used for this purpose. While absorption spectroscopy in the visible and ultraviolet regions is quite versatile in its applications, the occurrence of intense charge-transfer bands often obscures the much weaker d–d transitions and so makes the identification and assignment of ground and excited electronic states rather difficult. Electron paramagnetic resonance has been successfully applied to several square-planar systems, but its application is sometimes limited by relaxation and other phenomena.

We have been interested recently in using the method of paramagnetic anisotropy to deduce the electronic structure of square-planar transition metal compounds and have applied it successfully to square-planar cobalt(II) and manganese(II) compounds.[5,6] In the present communication, we apply this method to deduce the electronic structure of β-copper(II) phthalocyanine, where the copper ion almost achieves a perfect square-planar stereochemistry.[7,8] Because of the extensive charge-transfer bands, no information about the d–d transitions has been obtained from optical absorption spectra. Although the electron spin resonance spectrum for this compound has been determined by several groups of workers,[9-12] there is still considerable controversy over the electronic structure, particularly concerning the excited states. Accordingly, copper(II) phthalocyanine provides a very good example to illustrate the usefulness of magnetic anisotropy in deducing the electronic structure of square-planar compounds.

The single crystals used in the present measurements belong to the monoclinic system with two inequivalent molecules in the unit cell.[7,8] The magnetic anisotropy was measured in the liquid nitrogen temperature range by the apparatus described earlier.[13] The correction for diamagnetic anisotropy was found to be very important in this case, and the observed anisotropies were corrected for diamagnetism using the data from our recent measurements on the isomorphous diamagnetic zinc(II) phthalocyanine.[14] The molecular anisotropy was calculated assuming a uniaxial symmetry for the molecule, which is in conformity with the available electron spin resonance and structural data. The experimental data are shown graphically (circles) in Figure 1.

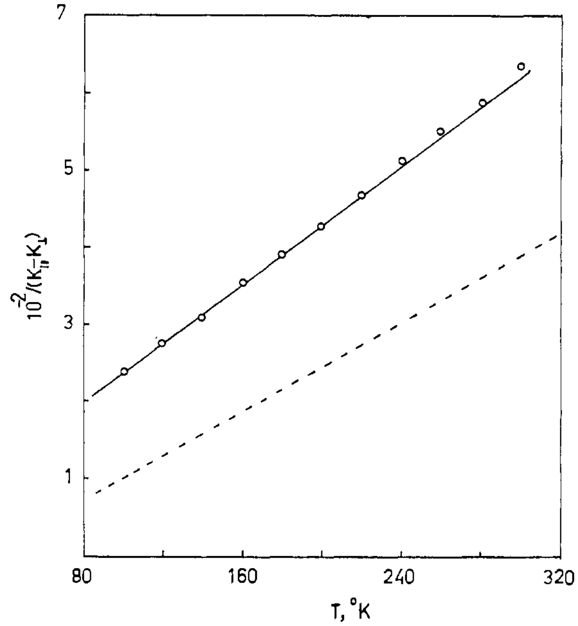

Figure 1.—Variation of molecular magnetic anisotropy with temperature for β-copper phthalocyanine. The open circles are the experimental data. The solid and dashed lines are the theoretically calculated ones, using the energy separations as suggested by Harrison and Assour[12] and Kivelson and Nieman,[10] respectively (see the text).

The copper ion in copper phthalocyanine has the $3d^9$ configuration, and the nine d electrons can be arranged[4,9] as in Figure 2. The ground state is, therefore, deduced to be $^2B_1$ (hole in $d_{x^2-y^2}$). The sign of magnetic anisotropy ($K_{\|} > K_{\perp}$) is inconsistent with $^2A_1$ (hole in d_{z^2}) being the ground state. For a $^2B_1$ ground state the expressions for the principal molecular susceptibilities are

$$K_{\|} = \frac{N\beta^2}{4kT}\left[2 + \frac{8\zeta}{\Delta E_{\|}}\right]^2 + \frac{8N\beta^2\kappa^2}{\Delta E_{\|}}$$

$$K_{\perp} = \frac{N\beta^2}{4kT}\left[2 + \frac{2\zeta}{\Delta E_{\perp}}\right]^2 + \frac{2N\beta^2\kappa^2}{\Delta E_{\perp}} \qquad (1)$$

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where $E_{||}$ and $E_{\perp}$ are the ${}^2B_1 \rightarrow {}^2B_2$ and ${}^2B_1 \rightarrow {}^2E$ positive hole transitions, respectively; ζ is the one-electron spin–orbit coupling parameter and κ is the orbital reduction factor. $K_{||}$ and $K_{\perp}$ are the principal molecular susceptibilities parallel and perpendicular to the symmetry axis of the molecule.

As indicated above, there have been conflicting interpretations of the ordering and separation of the ${}^2B_2$ (hole in d_{xy}) and ${}^2E$ (hole in d_{xz}, d_{yz}) states, as inferred from the electron spin resonance studies. For instance, the relative ordering of these two states as deduced recently by Harrison and Assour[12] (${}^2B_2$ being above the ${}^2E$) is at variance with the earlier calculation of Kivelson and Nieman[10] and also, to some extent, with that deduced by Gibson, *et al.*[9] However, Gibson, *et al.*, placed these two states very close together, and their calculation was somewhat uncertain because of their failure to observe the ${}^{14}N$ superhyperfine structure which was observed by all later workers. Further, the magnitudes of $E_{||}$ and $E_{\perp}$ deduced by various workers differ very widely among themselves. Roberts and Koski[11] have even taken the π–π optical transitions of the organic ring as being the d–d transitions.

In Figure 1, we have plotted two theoretical curves with different $E_{||}$ and $E_{\perp}$, taking $\zeta = 500$ cm^{-1} and $\kappa^2 = 0.7$. The solid curve has been drawn assuming $E_{||} = 27{,}000$ cm^{-1} and $E_{\perp} = 17{,}000$ cm^{-1} which are very close to the values deduced by Harrison and Assour. The dashed curve has been drawn taking the values of $E_{||}$ and $E_{\perp}$ deduced by Kivelson and Nieman (17,000 and 25,000 cm^{-1}, respectively). The close agreement of our experimental results with the solid curve confirms the ordering of ${}^2B_2$ and ${}^2E$ states as deduced by Harrison and Assour (*i.e.*, as shown in Figure 2). The values of ζ and κ assumed in the present calculation are in good agreement with the degree of covalency deduced from the observed ${}^{14}N$ superhyperfine structure in this compound. For no reasonable values of ζ and κ can our experimental data be fitted to the energy separations used by Kivelson and Nieman.

This result illustrates the usefulness of the paramagnetic anisotropy in deducing the electronic structure of square-planar copper compounds. Unfortunately, neither magnetic anisotropy nor electron spin resonance can be used to locate the relative position of the ${}^2A_1$ state beyond confirming that it lies higher in energy than ${}^2B_1$.

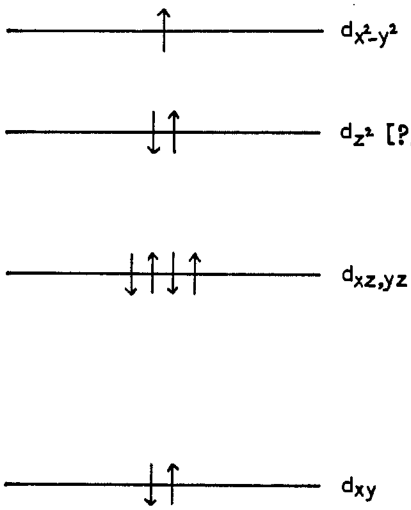

Figure 2.—A schematic representation of the electronic structure of β-copper(II) phthalocyanine.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
POLYTECHNIC INSTITUTE OF BROOKLYN,
BROOKLYN, NEW YORK 11201

Electronic Structure of CrO_4^{3-} in $Ca_2(CrO_4,PO_4)Cl$

BY C. SIMO,[1] E. BANKS, AND S. L. HOLT[2]

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In the past 10 years there has been a rapidly increasing application of Wolfsberg–Helmholz type of molecular orbital calculations to the problem of electronic structure of transition metal ions.[3-5] It is interesting to note, however, that while this method is widely used, the original system to which this method was applied, namely, MnO_4^-, has yet to have its electronic structure satisfactorily described.[6-10] Indeed no small part of this problem has been the fact that until recently[11] all calculations pertaining to the MnO_4^- ion were based on inadequate data.

The study of CrO_4^{3-} was undertaken as part of a program to provide a sound experimental basis for calculations pertaining to the electronic structure of higher oxidation states.

Banks, Greenblatt, and McGarvey[12] reported the esr spectra of CrO_4^{3-}-doped single crystals of Ca_2PO_4Cl and showed that the unpaired electron is in an orbital having largely d_{z^2} character. They also reported some unpolarized absorption spectra at liquid nitrogen temperature showing bands at 37,250, 27,940, 24,500, and 17,400 cm^{-1}. These were compared to the results of Carrington, *et al.*,[13] on MnO_4^{2-} and CrO_4^{3-} and were shown to be similar. Extended optical measurement, however, produced important new features[14] which

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(1) NSF–SDP postdoctoral fellow.

(2) Author to whom correspondence should be addressed at the Chemistry Department, University of Wyoming, Laramie, Wyo. 82070.

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