

Supplementary Material Available. Tables I, II, and IV–IX, showing analytical data, relevant ir bands, and magnetic susceptibility data, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number AIC40741N.

References and Notes

- (1) Esso Fellow, 1971–1972; Mobil Fellow, 1972–1973; University of Illinois Fellow, 1973–1974.
- (2) Camille and Henry Dreyfus Fellow, 1972–1977.
- (3) G. A. Rodley and W. T. Robinson, *Nature (London)*, **235**, 438 (1972), and references therein.
- (4) C. Busetto, F. Cariate, A. Fusi, M. Gullotti, F. Morazzoni, A. Pasini, R. Ugo, and V. Valenti, *J. Chem. Soc., Dalton Trans.*, 754 (1973).
- (5) R. Morassi, I. Bertini, and L. Sacconi, *Coord. Chem. Rev.*, **11**, 343 (1973), and references therein.
- (6) P. W. Ball and A. B. Blake, *J. Chem. Soc., Dalton Trans.*, 852 (1974).
- (7) P. W. Ball and A. B. Blake, *J. Chem. Soc. A*, 1415 (1969).
- (8) M. E. Lines, *J. Chem. Phys.*, **55**, 2977 (1971).
- (9) D. M. Duggan, R. G. Jungst, K. R. Mann, G. D. Stucky, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **96**, 3443 (1974); D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, **13**, 1911 (1974).
- (10) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, **13**, 2929 (1974).
- (11) E. J. Laskowski, D. M. Duggan, and D. N. Hendrickson, unpublished results.
- (12) D. M. Duggan and D. N. Hendrickson, "Extended Interactions between Transition Metal Ions", L. Interranti, Ed., American Chemical Society Symposium Series, No. 5, Washington, D.C., 1974.
- (13) G. A. Barclay and A. K. Barnard, *J. Chem. Soc.*, 2540 (1958).
- (14) P. Paoletti, M. Ciampolini, and L. Sacconi, *J. Chem. Soc.*, 3589 (1963).
- (15) I. Bertini, M. Ciampolini, and D. Gatteschi, *Inorg. Chem.*, **12**, 693 (1973).
- (16) M. Di Vaira and P. L. Orioli, *Inorg. Chem.*, **6**, 955 (1967).
- (17) Supplementary material.
- (18) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966).
- (19) J. S. Wood, *Inorg. Chem.*, **7**, 852 (1968); J. S. Wood, *J. Chem. Soc. A*, 1582 (1969).
- (20) J. S. Wood, *Prog. Inorg. Chem.*, **16**, 227 (1972).
- (21) D. Gatteschi and I. Bertini, Abstracts, Third National Meeting of the Italian Association of Inorganic Chemists, 1970, No. C34, and unpublished results.
- (22) E. J. Laskowski and D. N. Hendrickson, unpublished results.
- (23) D. M. Duggan and D. N. Hendrickson, *J. Chem. Soc., Chem. Commun.*, 411 (1973).
- (24) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, **13**, 2056 (1974).
- (25) C. G. Pierpont, D. N. Hendrickson, D. M. Duggan, F. Wagner, and E. K. Barefield, *Inorg. Chem.*, **14**, 604 (1975).
- (26) C. Postmus, J. R. Ferraro, A. Quattrochi, K. Shobatake, and K. Nakamoto, *Inorg. Chem.*, **8**, 1851 (1969).
- (27) M. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, *J. Chem. Soc. A*, 540 (1967).
- (28) M. Ciampolini and I. Bertini, *J. Chem. Soc. A*, 2241 (1968).
- (29) A. D. Liehr, *J. Phys. Chem.*, **67**, 1314 (1963).
- (30) F. S. Kennedy, H. A. O. Hill, T. A. Kaden, and B. L. Vallee, *Biochem. Biophys. Res. Commun.*, **48**, 1533 (1972).
- (31) D. M. Duggan, E. K. Barefield, and D. N. Hendrickson, *Inorg. Chem.*, **12**, 985 (1973).
- (32) R. L. Belford, P. H. Davis, and G. G. Belford, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., 1974, No. INOR 108.
- (33) G. R. Hall, D. M. Duggan, and D. N. Hendrickson, *Inorg. Chem.*, in press.
- (34) E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra", Cambridge University Press, London, 1959.

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Magnetic Exchange Interactions in Transition Metal Dimers. V. Copper(II)–Diethylenetriamine Complexes with Oxalate, Cyanate, Thiocyanate, and Azide Inner- and Outer-Sphere Bridging Units. Electron Paramagnetic Resonance of Alkali Halide Pelleted Copper Complexes

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Variable-temperature magnetic susceptibility and EPR are used to investigate compounds of the composition $[\text{Cu}_2(\text{dien})_2\text{X}_2](\text{BPh}_4)_2$ where $\text{X} = \text{Ox}^{2-}/2$, N_3^- , NCO^- , and NCS^- and dien is diethylenetriamine. The oxalate (Ox) compound is inner-sphere bridged wherein the oxalate is bis-bidentate. In contrast to $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2$ (X-ray structure is available) where no signs of an exchange interaction are seen in either the susceptibility to 4.2°K or the EPR spectrum, the susceptibility of $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$ shows an antiferromagnetic interaction characterized by $J = -7.4 \text{ cm}^{-1}$, $g = 2.16$, and $\Theta = 1.3^\circ$ via least-squares fitting to the copper dimer equation. The structural changes of the dimeric cation required to account for this anion dependence are discussed. The weak ($|J| < \sim 0.5 \text{ cm}^{-1}$) exchange interaction and relatively large zero-field splitting seen in the EPR of $[\text{Cu}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$ are shown to be explicable in terms of a structure where two square-planar copper complexes are outer-sphere associated (hydrogen bonding) such that the Cu–Cu vector is normal to the copper coordination planes. Powdered-sample Q-band EPR spectra are computer simulated partially to substantiate this and the effects of Cu–Cu distance and g tensor– D tensor (i.e., Cu–Cu vector) orientation are illustrated for this azide as well as for $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$. No exchange interactions are seen to 4.2°K in the susceptibility of $[\text{Cu}_2(\text{dien})_2(\text{NCO})_2](\text{BPh}_4)_2 \cdot 2\text{H}_2\text{O}$; however, the Q-band spectra of this compound and the analogous anhydrous thiocyanate compound give evidence of electron exchange; probable structures are proposed for the dimeric cations in these two compounds. EPR is used to study the effects on $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2$, which potentially has open copper coordination sites, of pelleting in KBr, KCl, KI, NaBr, and NaCl.

Introduction

We have investigated^{4–9} exchange interactions in the series $[\text{Ni}_2(\text{tren})_2\text{X}_2](\text{BPh}_4)_2$, where tren is the tetraamine 2,2',-2''-triiminotriethylamine and $\text{X} = \text{Ox}^{2-}/2$ (Ox = oxalate), $\text{Sq}^{2-}/2$ (Sq = squarate), N_3^- , NCO^- , NCS^- , and NCS^- . These nickel(II) compounds have been shown^{8–10} with X-ray crystallography to be dimeric with two X anions end-to-end bridging such that the nickel centers are octahedrally coordinated. It was found that it is the precise geometry of the bridging system in these nickel inner-sphere dimers that determines the sign (i.e., antiferromagnetic vs. ferromagnetic)

and magnitude of the exchange interaction. Attempts to replace the nickel(II) atoms with copper(II) atoms in these tren compounds gave outer-sphere $[\text{Cu}_2(\text{tren})_2\text{X}_2](\text{BPh}_4)_2$ ($\text{X}^- = \text{NCO}^-$, NCS^- , CN^- , Cl^- , and Br^-) dimers where each copper center is trigonal bipyramidal and one end of the X group is hydrogen bonding to a tren nitrogen on the second copper center. The structural details of most of these interesting outer-sphere copper dimers^{11–13} and two related outer-sphere manganese dimers,¹⁴ $\text{X}^- = \text{NCS}^-$ and NCO^- , have been determined by X-ray techniques.

In the present paper results are reported for a study of the

electronic and magnetic properties of complexes analogous to the above tren-Cu complexes where the ligand tren is now replaced by the triamine dien (diethylenetriamine) to give the complexes $[\text{Cu}_2(\text{dien})_2\text{X}_2](\text{BPh}_4)_2$ ($\text{X}^- = \text{NCO}^-$, NCS^- , N_3^- , and $\text{Ox}^{2-}/2$). An interesting effect of anion (i.e., ClO_4^- vs. BPh_4^-) on the magnetism of $[\text{Cu}_2(\text{dien})_2(\text{Ox})]^{2+}$ will be presented.

In our earlier work⁶ the magnetic susceptibility curves of $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2$ and $[\text{Cu}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$ were found to exhibit *no* signs of interactions down to 4.2°K. The complicated EPR of the latter compound is analyzed in this paper to suggest a structure for the *green* form of this compound; *blue* solvated forms of $[\text{Cu}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$ have also been identified in this work. At least three dimeric metal-diethylenetriamine complexes have been reported in the literature. As expected, $[\text{Ni}_2(\text{dien})_2(\text{H}_2\text{O})_2(\text{Ox})](\text{ClO}_4)_2$ has (distorted) octahedrally coordinated nickel ions with the oxalate as a bis-bidentate inner-sphere bridging ligand and nickel-coordinated water.¹⁵ More relevant to this paper is the X-ray single-crystal structural work¹⁶ for $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2$, where again the oxalate is acting as a bis-bidentate inner-sphere bridge and an oxygen of the perchlorate is semicoordinated (average Cu-O = 2.9 Å) to the copper atom. Semicoordination of perchlorate is also found¹⁷ in $[\text{Cu}_2(\text{dien})_2(\text{NCS})_2](\text{ClO}_4)_2$ where the two thiocyanate groups are end-to-end inner-sphere bridging the copper centers. An observation of differences in our ir spectra for Nujol mulls vs. KBr pellets of these semicoordinated copper systems prompted an EPR study of the effects of alkali halide pelleting of various copper complexes; the initial results of this study are presented in this paper.

Experimental Section

Compound Preparation. All chemicals were reagent grade. Diethylenetriamine was generally used as purchased (light yellow coloration); for a few compound preparations it was vacuum distilled (colorless); however, the final copper compounds were found to be essentially identical. Microanalytical analyses were carried out in the University of Illinois microanalytical laboratory and the results are given in Table I.¹⁸

Samples of $[\text{Cu}_2(\text{dien})_2(\text{NCS})_2](\text{ClO}_4)_2$ were prepared as reported and this also gave a sample of $\text{Cu}(\text{dien})(\text{NCS})_2$.¹⁷

A sample of $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2$ was prepared as reported.¹⁹ The BPh_4^- salt is prepared by dissolving the perchlorate in H_2O and adding an aqueous solution of NaBPh_4 ; attempts at a direct preparation of the BPh_4^- salt were unsuccessful. As per the reported recipe it was also possible to prepare a hydrate which, as Table I¹⁸ shows, analyzed as $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$. Blue crystals of the monomer analog $\text{Cu}(\text{dien})(\text{Ox}) \cdot 4\text{H}_2\text{O}$ were prepared as recently reported.²⁰

Samples of $[\text{Cu}_2(\text{dien})_2\text{X}_2](\text{BPh}_4)_2 \cdot n\text{H}_2\text{O}$, where $\text{X} = \text{NCO}^-$ ($n = 2$), $\text{X} = \text{N}_3^-$ and NCS^- ($n = 0$), were prepared by dissolving ~3.7 g of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and ~1.0 g of dien in ~150 ml of H_2O and adding ~100 ml of aqueous solution of ~3.2 g of NaX . A blue solid forms immediately upon addition of an aqueous solution of NaBPh_4 in the NCO^- and NCS^- cases; these blue solids are washed several times with H_2O and then with several ~30-ml portions of absolute Et_2O and finally dried in vacuo over P_2O_5 to give analytically pure samples (see Table I¹⁸). In the case of the azide compound the initial compound upon addition of aqueous BPh_4^- is colored bluish steel gray and on several occasions had a lustrous microcrystalline appearance. If this compound is washed only with H_2O , it retains its blue color only changing to a green color after considerable (more than 1 day) air and/or in vacuo P_2O_5 drying. If the compound is washed with H_2O followed by a few 30-ml portions of absolute Et_2O , it immediately turns green.

Dissolution of $[\text{Cu}_2(\text{dien})_2\text{X}_2](\text{BPh}_4)_2 \cdot n\text{H}_2\text{O}$ ($\text{X}^- = \text{NCO}^-$, NCS^- , and N_3^-) in CH_3CN followed by evaporation yields crystalline $[\text{Cu}_2(\text{dien})_2\text{X}_2](\text{BPh}_4)_2 \cdot 2\text{CH}_3\text{CN}$. It is interesting to note that the azide-acetonitrile compound is dark blue. Other solvates (e.g., acetone) can be prepared and the analytical data for some of these are given in Table I.¹⁸ EPR and ir (CH_3CN bands) data point to similar structures for the solvated and nonsolvated compounds.

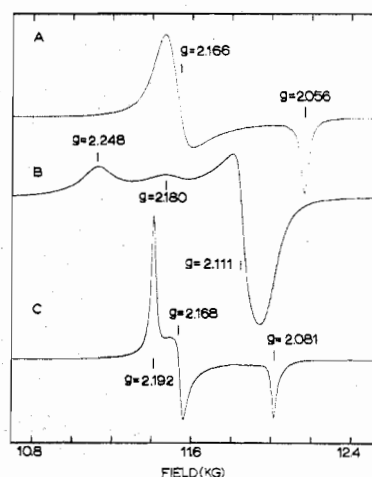


Figure 1. Room-temperature Q-band EPR spectra of three powdered copper diethylenetriamine oxalates: $\text{Cu}(\text{dien})(\text{Ox}) \cdot 4\text{H}_2\text{O}$ (A); $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2$ (B); $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (C).

The zinc analogs of many of the above Cu-dien complexes were prepared with the same procedures. These samples were generally prepared for EPR doping and ir experiments and analytical data are given in Table I.¹⁸

A sample of $[\text{Ni}_2(\text{dien})_2(\text{H}_2\text{O})_2(\text{Ox})](\text{BPh}_4)_2$ was prepared as per the above copper procedure.

It should be noted that if $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is used in place of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, the copper preparations frequently give either impure products or none of the desired product.

Physical Measurements. Molecular weight measurements were performed with a Mechrolab Model 301A vapor pressure osmometer. Infrared, electronic absorption, X-ray powder pattern, X- and Q-band EPR, and variable-temperature magnetic susceptibility measurements were carried out as mentioned in our recent paper.⁷ Alkali halide pelleting of the various copper complexes was done with a hydraulic press (typically, 20,000 lbs on a 13-mm pellet) in conjunction with a standard 13-mm pellet die and press. The alkali halides were quite frequently of spectroscopic quality and were extensively dried in an oven at $\geq 120^\circ$. Descriptions of quantities of alkali halide and compound used are given in the following sections.

Results and Discussion

Because it is felt that the structural characteristics are somewhat different for the different Cu-dien complexes, they will be discussed separately. The oxalates are probably the best structurally characterized of the systems under discussion and as such we will turn to them first.

Oxalate Bridging. The magnetic properties of $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2$ and $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$ will be compared in this section. The X-ray structure¹⁶ of the former compound shows that the oxalate group is bis-bidentate and bound in such a way as to complete a five- rather than a four-membered ring with each metal. The bridging is essentially planar and the stereochemistry about the copper ions is square pyramidal with the oxalate oxygen atoms occupying one basal and one apical site. There is a slight tetrahedral distortion and the metal ions are displaced toward the apical atom by 0.15 Å. Each copper atom completes a very distorted octahedron by semicoordinating in the remaining apical position with an oxygen of the perchlorate (for the two copper atoms in a dimer the Cu-O distances are 2.96 and 2.78 Å). We have reported⁶ the variable-temperature (4.2–283°K) magnetic susceptibility of this perchlorate compound and, as indicated in the Introduction, no exchange interaction was detected. The room-temperature Q-band EPR spectrum of $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2$ was run and a reproduction is shown in Figure 1 (tracing B). Three signals are seen at $g_1 = 2.248$, $g_2 = 2.180$, and $g_3 = 2.111$. This type of three-g-value signal is reasonable for the elongated rhombic symmetry that is found

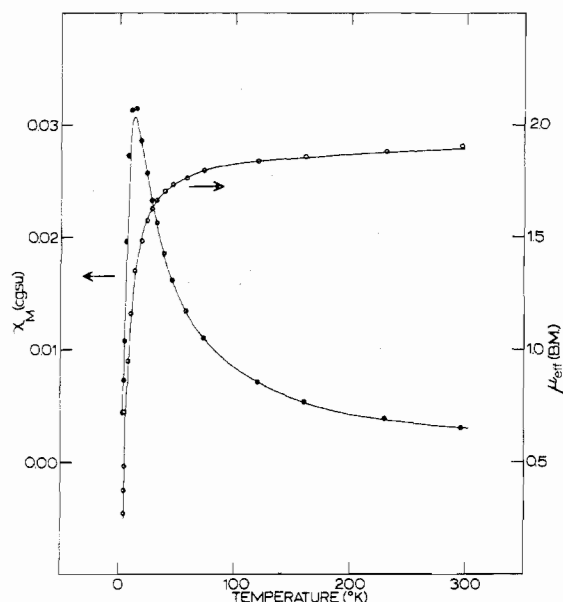


Figure 2. Corrected molar paramagnetic susceptibility, χ_M (cgsu/mol of dimer) and μ_{eff} (BM/Cu ion) vs. temperature for $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$. The solid lines are least-squares theoretical lines fit to the Bleaney-Bowers equation with $J = -7.4 \text{ cm}^{-1}$, $g = 2.16$, and a Curie-Weiss constant of $\Theta = -1.3^\circ$.

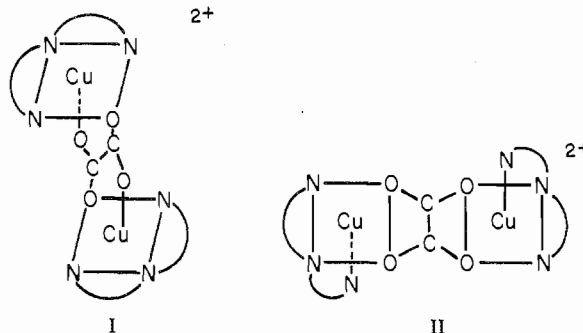
for the copper sites in this oxalate-bridged compound and can be taken to indicate that the ground state is $d^1_{x^2-y^2}$ where the square-pyramidal plane is the xy plane. The hydrate compound, $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, has been found to have properties different from those of the above anhydrous salt. For example, Figure 1 shows that the room-temperature Q-band spectra are different with the hydrate having three signals at $g_1 = 2.192$, $g_2 = 2.168$, and $g_3 = 2.081$.

An X-ray structure²¹ has also been reported for monomeric $\text{Cu}(\text{dien})(\text{Ox}) \cdot 4\text{H}_2\text{O}$ and the local copper geometry is found to be very similar to that in the oxalate-bridged dimer. In this case the oxalate is only coordinated to one copper atom. A characteristic of these five-coordinate Cu-dien complexes is that the sixth apical site is taken by some semicoordinated ligand. For $\text{Cu}(\text{dien})(\text{Ox}) \cdot 4\text{H}_2\text{O}$, the sixth (apical) site is taken by an oxygen atom of the oxalate ion of another molecule at a distance of 2.994 Å from the copper atom. The similarity of local copper sites in $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{dien})(\text{Ox}) \cdot 4\text{H}_2\text{O}$ is reflected in the similarity (see Figure 1) of their EPR; the latter compound has a two- g -value Q-band spectrum with $g_{\perp} = 2.166$ and $g_{\parallel} = 2.056$. There is nothing in the EPR spectra of these three diethylenetriamine oxalates that would indicate appreciable exchange interaction where the exchange interaction parameter J is greater than the copper hyperfine interaction parameter. Unsuccessful attempts were made to detect singlet-to-triplet EPR transitions that would allow of a direct determination of small J values.⁷

In contrast, variable-temperature magnetic susceptibility data for $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$ (Figure 2 and Table II¹⁸) show that there is an antiferromagnetic exchange present such that a maximum in the susceptibility is seen at a temperature of 13°K. Least-squares fitting of the data to the Bleaney-Bowers equation²² for a copper dimer (solid lines in Figure 2) with a TIP of 120×10^{-6} cgsu/mol of dimer gives $J = -7.4 \text{ cm}^{-1}$, $g = 2.16$, and a Curie-Weiss constant Θ of -1.3° . Thus, the energy separation between the singlet and triplet states of this copper dimer is 14.8 cm^{-1} . The good fit illustrated in Figure 2 is testimony to the fact that there is a dimeric $[\text{Cu}_2(\text{dien})_2(\text{Ox})]^{2+}$ in this salt.

The change in counterion from ClO_4^- to BPh_4^- probably appreciably changed the lattice forces and also left the

oxalate-bridged dimer with no ligands to semicoordinate to the copper in the second apical site. Infrared spectra (Nujol mull and KBr pellet) of the BPh_4^- salt show that there is not any water present (also in agreement with analysis; see Table I¹⁸) and that the oxalate is still bis-bidentate. It is more than likely that the structure of the dimer changed. The known structure of the dimer in the perchlorate salt is sketched as I, and one possible structure for the dimeric cation in $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$ is given as II. It should be noted



that the cis (i.e., facial) configuration of the dien ligand in II has not been seen in the X-ray structural work^{16,17} on Cu-dien systems, but it has been seen for $\text{Mo}(\text{dien})(\text{CO})_3$ ²³ and $[\text{Co}(\text{en})(\text{dien})\text{Cl}]\text{Cl}$.²⁴ The zero or negligible exchange interaction in I is the result of the fact that the unpaired electron associated with each copper center is in a $d_{x^2-y^2}$ orbital which is in the plane of the square pyramid. For the two unpaired electrons of I, exchange via a σ density pathway of the oxalate bridge would have to be effected through a



moiety and this would be minimal. If the oxalate dimer in the BPh_4^- compound has structure II, the increased exchange interaction is explicable in that now the unpaired electrons are in $d_{x^2-y^2}$ orbitals that are coplanar with the oxalate bridge and an interaction can be propagated through the two



moieties. A study⁵ of exchange interactions between octahedral Ni(II) centers bridged by either oxalate ($\text{C}_2\text{O}_4^{2-}$) or squarate ($\text{C}_4\text{O}_4^{2-}$) found exchange parameters of $J \approx -17$ and -0.4 cm^{-1} , respectively. In this case the



pathway is some 40 times more viable for interaction than the



pathway. We do *not* contend that the structure of the dimeric cation in $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$ necessarily approximates that of cation II but only that the distortion from structure I by removal of the semicoordinated perchlorate is such that the $d_{x^2-y^2}$ orbital with the unpaired electron bonds to a certain degree into both arms of the oxalate and thus a partial Cu-O-C-O-Cu pathway is effective. It would be very interesting to know the structure of the BPh_4^- salt. Blue crystals of the compound can be obtained by slow evaporation of an acetonitrile solution; however, the few times that we tried the crystals were not totally suitable for X-ray structural work.

The liquid nitrogen temperature Q-band spectrum, depicted as tracing A in Figure 3, also shows the effects of electron

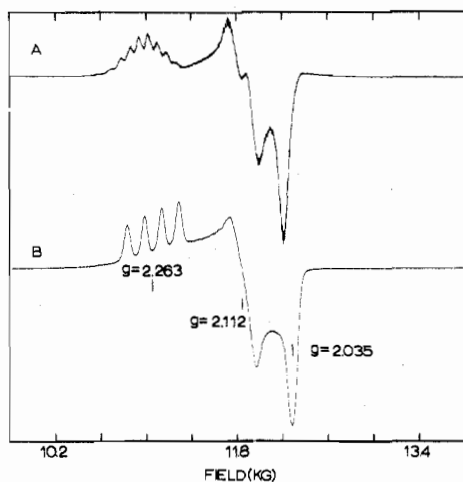


Figure 3. Liquid nitrogen temperature Q-band spectrum of a powdered sample of $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$ (A) and room-temperature Q-band spectrum of a powdered sample of Cu-doped $[\text{Zn}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$ (B).

exchange in $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$. It should be noted that the room-temperature Q-band spectrum is of appreciably lower resolution and the $\Delta M_s = 1$ region in the X-band spectrum shows closely spaced (e.g., ~ 90 G) parallel copper hyperfine lines; however, the parallel signal is extensively overlapping with the perpendicular signal. On the other hand, in the Q-band spectrum in Figure 3 there appear to be two signals in the "perpendicular" region and each is zero-field split. Eight copper hyperfine lines are seen in the "parallel" region with spacings between 75 and 90 G with an average of 83 G. In an effort to understand the appearance of this spectrum a sample of $[\text{Zn}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$ was prepared with considerable Cu^{2+} doped into the compound. The sample was prepared by dissolving equal amounts of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in H_2O and adding dien and then an aqueous solution of $\text{Na}_2\text{C}_2\text{O}_4$, followed by an aqueous solution of NaBPh_4 . The Q-band spectrum of $[\text{Cu}/\text{Zn}(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$ is shown in Figure 3(B) and it can be seen that a three-g-value spectrum is obtained with the "parallel" signal at $g_1 = 2.263$ (four Cu hyperfine lines with an average spacing of $A = 149$ G) and the "perpendicular" split into two signals at $g_2 = 2.112$ and $g_3 = 2.035$. Inspection of Figure 3 shows that the three g values of the doped compound are aligned reasonably well with features in the more complicated undoped sample spectrum. Incorporation of zero-field splittings and exchange interactions could change the "doped" sample spectrum to resemble that obtained for the dimer. This can be partially substantiated as we turn to simulations.

We have carried out some simulations of powdered copper dimer EPR spectra using a computer program written by Dr. D. Gibbons following the mathematical development of Professors R. L. Belford and G. G. Belford.²⁵ For each magnetic field orientation (relative, of course, to the magnetic axes of the copper centers) the matrices including zero-field and Zeeman interactions are diagonalized, and because of prohibitive costs, copper hyperfine was *not* treated. In passing it should be noted that the present simulation analysis is not based on a perturbation treatment as has been set out in recent papers.^{26,27}

Interion-dipolar zero-field splitting (D_{dd}) in a copper dimer can be gauged as

$$D_{dd} = (3/4)g^2\beta^2 \left\langle \frac{1 - 3 \cos^2 \theta}{r^3} \right\rangle$$

where θ is the angle between the Cu-Cu vector and the magnetic field and r is the Cu-Cu interion distance. In short, the relative orientation of the g and D tensors (principal axis

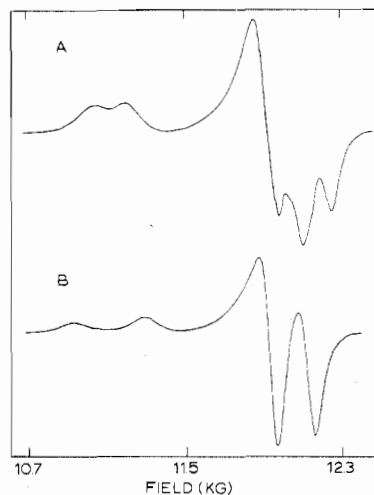


Figure 4. Computer-simulated powdered-sample Q-band spectra for two different orientations of the interion D tensor. In each case the Cu-Cu distance was taken as 5.5 Å, $g_x = 2.060$, $g_y = 2.068$, $g_z = 2.237$, and the isotropic exchange parameter J was taken as zero; the copper dimer is assumed to have a center of inversion. In case A the D tensor (i.e., Cu-Cu vector) is taken to lie along the x axis of the g tensor, whereas, in case B it is taken to lie along the z axis of the g tensor. All copper dimer spectral simulations were carried out assuming the two copper ions are related by a center of inversion and by summing over 900 field orientations and assuming lorentzian line shapes.

of the D tensor is assumed to be along the Cu-Cu vector) will determine the magnitude of zero-field splitting that is seen on a particular g-value signal. With g_z directed along the Cu-Cu vector the zero-field splitting of the g_z signal will be twice the zero-field splittings of the g_x and g_y signals, because $\theta = 0^\circ$ for the g_z orientation and $\theta = 90^\circ$ for the g_x and g_y orientations. Figure 4 illustrates the effects of g-D tensor orientation with $r = 5.5$ Å, $g_x = 2.060$, $g_y = 2.068$, and $g_z = 2.237$; two g-D tensor alignments were selected for illustration.

If the cation in $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$ has a structure approximating structure II, the Cu-Cu vector (i.e., the z axis of D) would be in the square-pyramidal plane (xy plane) and this would lead to a situation where the zero-field splitting on the g_z (i.e., the "parallel") signal would be small, as is seen in the experimental spectrum (see Figure 3). The many parameters were varied to simulate the oxalate spectrum; two important simulations are presented in Figure 5. In tracing A the r vector is taken to be along the x axis of the g tensor and it is seen that in this case the appearance of the g_z "parallel" signal is not unlike that of the experimental spectrum; the "perpendicular" signals, however, are not similar. In tracing B the r vector is in the xy plane and bisects the angle between the x and y axes of the g tensor. In this case the overall appearance of the simulated spectrum is not unlike that of the experimental spectrum. It is probably possible to increase the anisotropy in the "perpendicular" signal and sharpen the features to simulate more closely the experimental spectrum.

Eight hyperfine lines are seen on the g_z signal for $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$. With $r = 5.5$ Å and $g_z = 2.26$, the component of the dipolar zero-field splitting along the z axis is calculated to be ~ 90 G. If it is assumed that the pseudodipolar contribution to the zero-field splitting is negligible in comparison to the dipolar term,²² then a nine-line g_z hyperfine pattern arising from the superposition of two seven-line hyperfine patterns separated by $2D_{||}$ could result. This is because in this case $D_{||} \approx A_{||}(\text{Cu})$ (recall that the copper hyperfine parameter for a dimer is expected to be half that of the monomer as seen, for example, in the doped sample) and the spectrum appears quite simple and relatively evenly spaced due to the coincidence of hyperfine lines from two

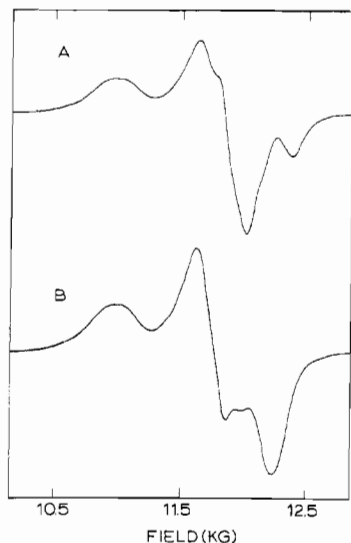


Figure 5. Two computer-simulated powdered-sample Q-band spectra for $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$ where in both cases $J = -7.4 \text{ cm}^{-1}$ and the Cu-Cu distance was taken as 5.5 Å. In A the Cu-Cu vector is taken along x axis of the g tensor, $g_x = 2.035$, $g_y = 2.112$, and $g_z = 2.263$, while in B the Cu-Cu vector is in the xy plane and bisects the angle between the x and y axes of the g tensor, $g_x = 2.035$, $g_y = 2.112$, and $g_z = 2.263$.

different components of the zero-field split g_z signal. Perhaps the ninth line is masked by the tail of the "perpendicular" signal. An alternate explanation of this eight-line hyperfine pattern in terms of two overlapping four-line patterns with $A_{\parallel}(\text{Cu}) = 180 \text{ G}$ is precluded because of the magnitude of the exchange in this compound and the observed intensity pattern.

The absence of any zero-field splitting in the EPR spectra of $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2$ and $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (see Figure 1) could indicate that the orientation of the Cu-Cu vector with respect to the g tensors on the two copper centers is such that the appropriate components of the zero-field tensor are very small and this seems reasonable in terms of the structure of the former compound.

Azide Bridging. In light of the above results for the copper-diethylenetriamine-oxalate compounds, the report⁶ of an unusual X-band EPR spectrum of $[\text{Cu}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$, combined with the observation of no exchange interactions to 4.2°K in the magnetic susceptibility, prompted a more detailed study of this copper-diethylenetriamine-azide compound. First, it was found that the preparation scheme we reported⁶ would only yield a good compound occasionally. However, by merely changing from the $\text{Cu}(\text{SO}_4) \cdot 5\text{H}_2\text{O}$ to a $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ reactant, as indicated in the Experimental Section, analytically pure samples can be prepared consistently.

The ir spectrum of green $[\text{Cu}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$ shows (either KBr or Nujol mull) a strong $\nu_{\text{as}}(\text{N}_3^-)$ band at 2070 cm^{-1} and a medium-intensity $\nu_s(\text{N}_3^-)$ band at 1345 cm^{-1} . The ir data exclude the possibility of end-to-end di- μ -azide bridging and two reasonable structures for the cation in green $[\text{Cu}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$ can be represented as structures III and IV. In structure III the cation is dimeric by virtue of an outer-sphere association established by hydrogen-bonding contacts between the azide group bonded to one copper atom and one primary nitrogen atom of the dien bonded to the other copper atom. In addition, structure III is drawn such that the Cu-Cu vector would be expected to be coincidental with the z axis of the g tensor at each copper center, and because there are four nitrogen atoms in a square plane about each copper atom, the copper centers are magnetically axial. Structure III is suggested, in part, by the very recent X-ray structure of $\text{Cu}(\text{dien})(\text{NCS})_2$.²⁸ The copper environment is five-coordinate square-pyramidal with one NCS^- group bonded

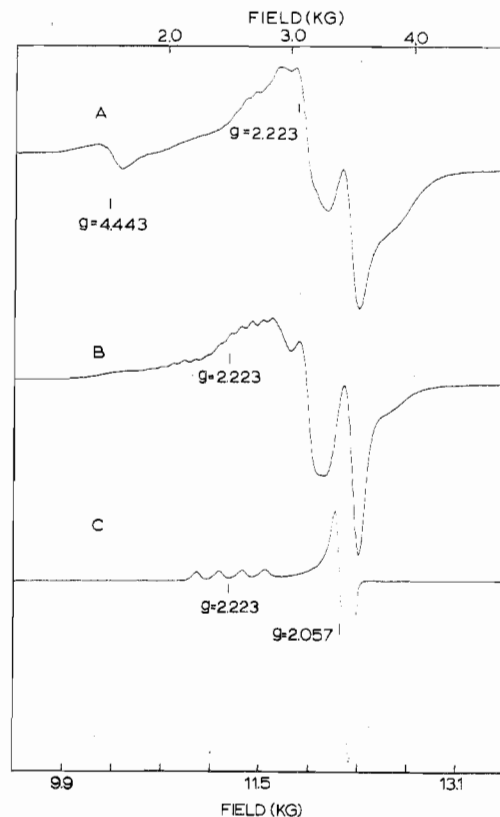
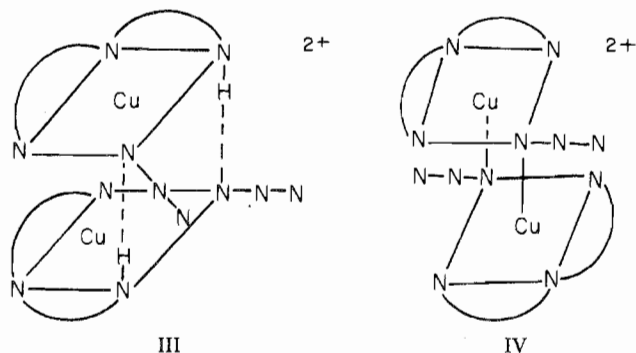


Figure 6. Room-temperature powdered-sample EPR spectra: A and B, X- and Q-band spectra, respectively, of a sample of green $[\text{Cu}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$; C, Q-band spectrum of a Cu-doped sample of $[\text{Zn}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$. The top scale is for the X-band spectrum and the lower for the two Q-band spectra.



in the plane and the other as the only axial ligand. Two of these "monomer" units are outer-sphere associated with two hydrogen bonds, a structure that is very analogous to structure III. Thiocyanate bonds to a copper in a less angular fashion than azide and in the $\text{Cu}(\text{dien})(\text{NCS})_2$ solid the square bases of the two outer-sphere associated pyramids have slipped by each other to some degree. The results of a detailed EPR study, summarized below, clearly point to structure III for the cation of $[\text{Cu}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$.

An improved X-band EPR spectrum has been obtained for green $[\text{Cu}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$ and this and the newly obtained Q-band spectrum are illustrated in Figure 6. In contrast to our previously reported⁶ X-band spectrum, copper hyperfine signals can be seen in the "parallel" region with spacings between successive peaks of $\sim 90 \text{ G}$, which is suggestive of an exchange-interacting dimer. Furthermore, the intense half-field $\Delta M_s = 2$ transition at $\sim 1500 \text{ G}$ in the X-band tracing (A) is indicative of a short (i.e., in range of 3–5 Å) Cu-Cu distance, because the intensity of such formally forbidden transitions reflects the magnitude of the interion-

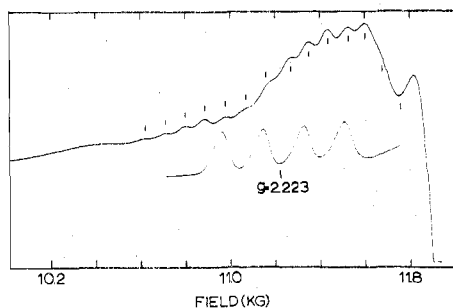


Figure 7. The "parallel" signal in the Q-band spectrum of powdered green $[\text{Cu}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$. Two zero-field split seven-line copper hyperfine lines are indicated by dashes. The parallel signal for the doped sample is indicated in the insert.

dipolar interaction. Strong support for structure III is found in the zero-field splittings seen in both the parallel and perpendicular signals. For comparison, trace C illustrates the axial Q-band spectrum for Cu-doped ($\sim 1\%$) $[\text{Zn}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$ where $g_{\parallel} = 2.223$ and $g_{\perp} = 2.057$ (copper hyperfine structure on the parallel signal of 182 G).

A $\sim 320\text{-G}$ ($=2D_{\perp}$) zero-field splitting in the perpendicular signal for $[\text{Cu}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$ is evident by comparing X- and Q-band spectra (note that the doped sample g_{\perp} signal falls in the center of the zero-field split g_{\perp} signal of the pure compound). The parallel region of the Q-band spectrum of the pure copper complex is presented in Figure 7 and by assigning, as indicated, the two expected seven-line copper hyperfine patterns one obtains $2D_{\parallel} = 640\text{ G}$. These relative values of D_{\parallel} and D_{\perp} for $[\text{Cu}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$ indicate that the Cu-Cu vector for the dimeric cation in this salt is aligned fairly closely to the z axis of the g tensor.

Computer simulations of copper dimer Q-band spectra were generated with ranges of g values and structural parameters (for Cu-Cu distance and g -D tensor orientation used see figure caption) for structures III and IV and typical simulations are given in Figure 8. Tracing B simulated for the Q-band spectrum structure III on the whole looks remarkably like the experimental spectrum (the reader, of course, has to imagine the seven-line hyperfine patterns on each of the low-intensity broad parallel signals). The same cannot be said for tracing A (Figure 8) for structure IV. Structure III for the cation in green $[\text{Cu}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$ is also reasonable in light of the variable-temperature magnetic susceptibility of this compound which shows no signs of exchange interactions to 4.2°K . The two unpaired electrons would be located, one to each copper center, in $d_{x^2-y^2}$ orbitals in the basal planes of the copper complexes. The exchange interaction needs to be propagated in the z direction through the two hydrogen bonds. It is recalled that in the structurally characterized $[\text{Cu}_2(\text{tren})_2\text{X}_2](\text{BPh}_4)_2$ series, where outer-sphere associated dimers are found, the greatest exchange interaction occurs with $\text{X}^- = \text{Br}^-$ where $J = -3.8\text{ cm}^{-1}$ ($H = -2JS_1 \cdot S_2$).⁴ In the tren outer-sphere dimer where $\text{X}^- = \text{SCN}^-$ it was only possible to gauge the exchange parameter J ($= -0.05\text{ cm}^{-1}$ at room temperature) by the position of weak singlet-to-triplet EPR transitions. With green $[\text{Cu}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$ it has not been possible with the wide range of spectral features to locate definitively singlet-to-triplet transitions; however, there are two broad unassigned low-intensity features (one at the lowest and the other at the highest field) in the $\Delta M_s = 1$ region. These are reproducible with different compound preparations. At present it is only possible to conclude that for $[\text{Cu}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$ $|J| < \sim 0.5\text{ cm}^{-1}$ from the magnetism and $|J| > \sim 0.02\text{ cm}^{-1}$ from the seven-line EPR hyperfine patterns (i.e., in the latter case $J > A_{\parallel}(\text{Cu})$).

Cyanate and Thiocyanate Bridging. The $[\text{Cu}_2(\text{dien})_2\text{X}_2](\text{BPh}_4)_2 \cdot n\text{H}_2\text{O}$ systems where $\text{X}^- = \text{OCN}^-$ ($n = 2$)

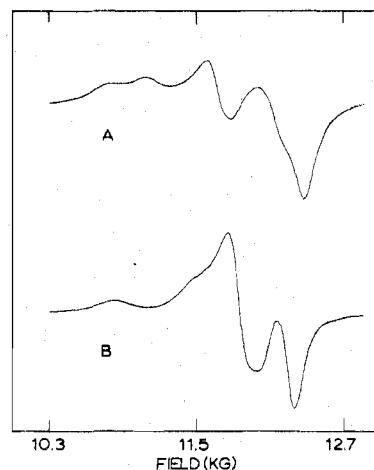


Figure 8. Typical computer-simulated powdered-sample Q-band spectra for the two possible structures of the dimeric cation in $[\text{Cu}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$. Tracing B is for III and A for IV. In the case of tracing B, Cu-Cu = 4.2 Å, $g_x = 2.055$, $g_y = 2.065$, $g_z = 2.220$, the angle between the Cu-Cu vector and the z axis of the g tensor was taken as 20° , and the angle between the projection of the Cu-Cu vector on the xy plane (i.e., basal plane) of one copper complex and the x axis of the g tensor was taken as equal to 20° . In the case of tracing A, the corresponding numbers are 3.5 Å, 2.068, 2.068, 2.220, 45° , and 0° , respectively.

and SCN^- ($n = 0$) are probably outer-sphere dimer systems as proposed for the azide analog. The ir spectra of the azide, cyanate, and thiocyanate compounds are the same except for bands due to the different bridging groups [$\nu_{\text{as}}(\text{NCO}^-)$ 2225 cm^{-1} , $\nu_{\text{s}}(\text{NCO}^-)$ 1330 cm^{-1} , $\nu_{\text{CN}}(\text{SCN}^-)$ 2100 cm^{-1}]. In addition, the cyanate compound has water bands consisting of a sharp doublet for ν_{OH} at 3525, 3585 cm^{-1} and a bending mode at 1613 cm^{-1} . We have found that the compound $[\text{Ni}_2(\text{dien})_2(\text{Ox})(\text{H}_2\text{O})_2](\text{BPh}_4)_2$, which is expected to have coordinated water,¹⁵ also has a doublet at 3515, 3565 cm^{-1} (the lower energy band is obscured by an intense oxalate band).

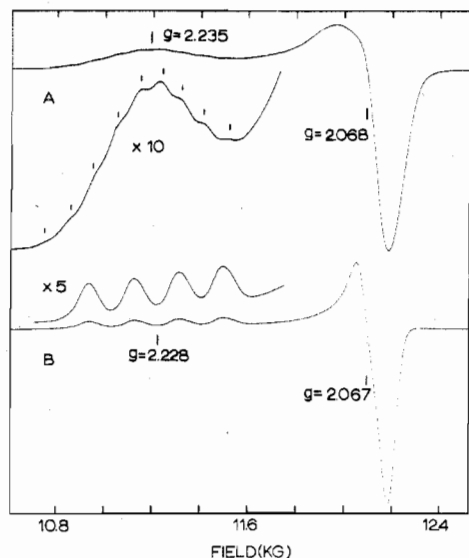
Analogous to the azide compound, the cyanate and thiocyanate compounds can be prepared as CH_3CN adducts. As with azide, the CH_3CN molecules are probably semicoordinated since the $\nu(\text{CN})$ bands are only shifted 5–20 cm^{-1} to higher energy than for free CH_3CN . In fact, the ir spectra of all three CH_3CN adducts are all identical (except for bridging group bands) and they each differ from the spectrum of the nonadduct compound in the absence of a $\sim 3220\text{-cm}^{-1}$ band and the addition of a $\sim 1365\text{-cm}^{-1}$ band. We have also prepared $[\text{Cu}_2(\text{dien})_2(\text{NCO})_2](\text{BPh}_4)_2 \cdot 2(\text{CH}_3)_2\text{CO}$ and this acetone adduct has a $\nu(\text{CO})$ band that is only shifted by $\sim 15\text{ cm}^{-1}$ to lower frequency than that for free acetone.

The ir spectrum of $\text{Cu}(\text{dien})(\text{NCS})_2$, which has both an apical and a basal NCS^- group, has two $\nu(\text{CN})$ bands at 2070 and 2098 cm^{-1} . Since the apical NCS^- is more weakly bonded to the copper (i.e., the apical Cu-N bond is 0.29 Å longer than the basal one), the 2098- cm^{-1} band can be assigned to the apical NCS^- . The compound $[\text{Cu}_2(\text{dien})_2(\text{NCS})_2](\text{BPh}_4)_2$ has a $\nu(\text{CN})$ band at 2094 cm^{-1} and the above analysis would tend to say that this is characteristic of an apical NCS^- ; however, in our opinion, caution has to be exercised in view of the difference in charge.

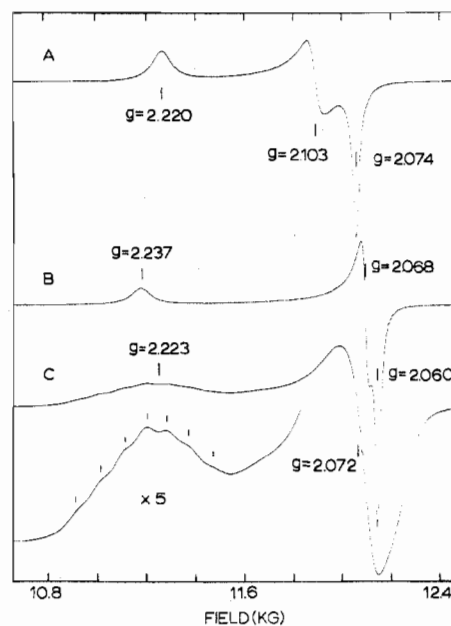
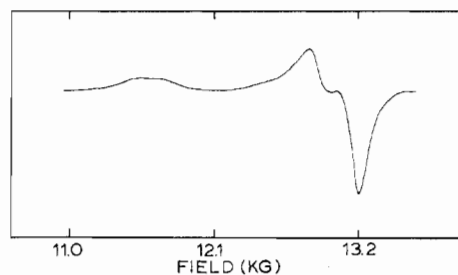
The electronic absorption spectra of these three compounds, $[\text{Cu}_2(\text{dien})_2\text{X}_2](\text{BPh}_4)_2$, where $\text{X}^- = \text{N}_3^-$, OCN^- , and SCN^- , are also very similar in that they each have one broad band in the visible region with no evidence at room temperature of any shoulders. The band positions are as follows: N_3^- , 16.3 kK (KBr), 16.6 kK (CH_3CN); OCN^- , 15.6 kK (KBr), 15.7 kK (CH_3CN); SCN^- , 16.3 kK (KBr), 16.3 kK (CH_3CN), with the extinction coefficients per metal for the solution spectra

Table III. Magnetic Susceptibility Data for $[\text{Cu}_2(\text{dien})_2(\text{NCO})_2](\text{BPh}_4)_2 \cdot 2\text{H}_2\text{O}^a$

$T, ^\circ\text{K}$	$10^3 \chi_M,$ cgsu/mol	$\mu_{\text{eff}}/\text{Cu},$ BM	$T, ^\circ\text{K}$	$10^3 \chi_M,$ cgsu/mol	$\mu_{\text{eff}}/\text{Cu},$ BM
296.1	3.01	1.888	28.4	28.60	1.802
230.3	3.71	1.850	24.1	33.37	1.794
196.5	4.34	1.849	19.2	41.35	1.782
161.0	5.35	1.857	14.4	52.92	1.746
120.0	7.13	1.851	10.7	74.15	1.781
73.1	11.67	1.847	8.2	96.18	1.776
58.0	14.48	1.833	6.6	120.31	1.782
46.5	17.80	1.820	5.4	145.86	1.775
39.1	21.01	1.813	4.8	164.86	1.779
32.6	25.08	1.808	4.2	192.65	1.799

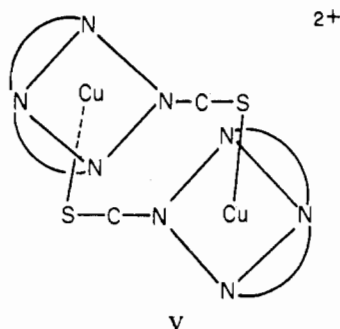
^a Diamagnetic correction from tables ($= -5.99.2 \times 10^{-6}$).**Figure 9.** Room-temperature powdered-sample Q-band spectra for $[\text{Cu}_2(\text{dien})_2(\text{NCO})_2](\text{BPh}_4)_2 \cdot 2\text{H}_2\text{O}$ (A) and Cu-doped $[\text{Zn}_2(\text{dien})_2(\text{NCO})_2](\text{BPh}_4)_2$ (B). The inserts are increased gain tracings of the parallel regions.in the range of $100\text{--}300 \text{ M}^{-1} \text{ cm}^{-1}$.

Variable-temperature ($4.2\text{--}296^\circ\text{K}$) magnetic susceptibility data were obtained for $[\text{Cu}_2(\text{dien})_2(\text{NCO})_2](\text{BPh}_4)_2 \cdot 2\text{H}_2\text{O}$ and they are summarized in Table III. As can be seen there is no indication of an exchange interaction, with μ_{eff} at 4.2°K set at 1.80 BM per copper ion. The presence of an exchange interaction is seen, however, in the room-temperature Q-band spectrum of this compound as reproduced in Figure 9 (no improvement in resolution is obtainable at lower temperatures). A somewhat broadened perpendicular signal is seen at $g = 2.068$ and nine copper hyperfine lines, spaced at 80–95 G, are seen on the parallel signal centered at $g = 2.235$. A doped sample was prepared containing $\sim 1\%$ Cu in $[\text{Zn}_2(\text{dien})_2(\text{NCO})_2](\text{BPh}_4)_2$ and the Q-band spectrum in Figure 9 shows signals at $g_{\parallel} = 2.228$ and $g_{\perp} = 2.067$. Thus, there is electron exchange present in $[\text{Cu}_2(\text{dien})_2(\text{NCO})_2](\text{BPh}_4)_2 \cdot 2\text{H}_2\text{O}$, for with nine parallel hyperfine lines it is not possible to account for the pattern with a superposition of two four-line monomer signals; the intensity pattern is also to be noted. Comparison of the cyanate spectrum with that for the azide shows that the former has appreciably less zero-field splitting in either the parallel or the perpendicular signals. This, taken with the fact that there is appreciable intensity in the $\nu_8(\text{OCN}^-)$ ir band (eliminating the possibility of an end-to-end dicyanate-bridged dimer), can tentatively be explained by a dimeric cation structure similar to III only with appreciable slipping of the basal planes to pick up a different hydrogen-bonding configuration. The resulting larger Cu–Cu distance and D–g tensor orientation would lead to smaller zero-field splittings.

**Figure 10.** Room-temperature powdered-sample Q-band spectra for $\text{Cu}(\text{dien})(\text{NCS})_2$ (A), $[\text{Cu}_2(\text{dien})_2(\text{NCS})_2](\text{ClO}_4)_2$ (B), and $[\text{Cu}_2(\text{dien})_2(\text{NCS})_2](\text{BPh}_4)_2$ (C). In the last case an increased gain version of the parallel signal is inserted.**Figure 11.** Computer-simulated powdered-sample Q-band spectrum of $[\text{Cu}_2(\text{dien})_2(\text{NCS})_2](\text{ClO}_4)_2$; for the parameters used see text.

The decreased zero-field interaction is also manifested in a weak half-field $\Delta M_s = 2$ transition for the cyanate, approximately $1/1000$ the intensity of the $\Delta M_s = 1$ transition as compared to the $\sim 1/10$ intensity ratio for the azide compound.

Decreased zero-field splittings resulting from basal slipping of structure III can be demonstrated with computer simulations, but perhaps the best documentation is found in the Q-band spectrum of the structurally characterized $\text{Cu}(\text{dien})(\text{NCS})_2$ as reproduced in Figure 10. Three signals are seen at g values of 2.220, 2.103, and 2.074. There is no zero-field splitting on the parallel signal at $g = 2.220$ and the X-band spectrum of this same compound shows that the two features in the perpendicular signal are the g_x and g_y transitions and are not due to zero-field splitting in spite of a Cu–Cu distance of 4.30 \AA . A similarly appearing rhombic Q-band spectrum is found (see Figure 10) for $[\text{Cu}_2(\text{dien})_2(\text{NCS})_2](\text{ClO}_4)_2$, which has been shown to have a dimeric cation V. The perchlorate anions are semicoordinated in the open apical positions. Neither of these crystallographically characterized compounds show any indications of exchange interactions in their EPR spectra. The Cu–Cu distance in this inner-sphere bridged dimer is 5.51 \AA and the crystal structure shows an angle of 42.5° between the Cu–Cu vector and the Cu–NCS vector (assumed to be collinear with g_z). These two values in combination with $g_x = 2.05$, $g_y = 2.06$, and $g_z = 2.21$ result in the simulated spectrum in Figure 11 which shows little in the way of zero-field splitting.



The Q-band spectrum of $[\text{Cu}_2(\text{dien})_2(\text{NCS})_2](\text{BPh}_4)_2$ in Figure 10 is very similar in appearance to that for the cyanate only now there are only seven hyperfine lines (see insert) discernible on the parallel signal and as such one could conclude that as in the cyanate there is a weak exchange interaction with a structure where the zero-field splitting is even smaller.

Alkali Halide Pelleting. Previous workers have pointed out the dangers of alkali halide pelleting in that anion exchange can and does occur. For example, anion exchange has been reported for polynuclear cyanides²⁹ and organic hydrohalides.³⁰ The extent of anion exchange appears to depend on the moisture content and the physical properties (e.g., lattice energies and relative ionic dimensions) of the host and guest compounds. In the initial stages of this work we observed differences between the ir spectra of samples of $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2$ either pelleted in KBr or prepared as a Nujol mull. Because many of these Cu-dien complexes have open or semicoordinated sites and because little or nothing has been reported on alkali pelleting of copper complexes using the EPR technique, we initiated such a study using some of the above complexes, particularly the structurally characterized $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2$.

The compound $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2$ occurs either as an anhydrous or as a monohydrated salt. As we pointed out earlier, the perchlorate anions are semicoordinated to the copper ions in the anhydrous form and it is possible that in the hydrated form the H_2O molecule is in some way interacting with one or more copper ions since the EPR and ir properties for the two forms are quite different. The anhydrous and hydrated compounds were each pelleted in an 100:1 excess of either well-dried (>1 week at temperatures greater than 120°) KI, KBr, KCl, NaBr, or NaCl. The resultant 13-mm pellets were studied by ir and then were ground and studied by Q-band EPR spectroscopy.

At the outset it seemed that there were basically three possibilities for the interaction of $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2$ with the various pelleting agents. There could simply be a hydration of the compound, or the halide ion could become (semi)coordinated to the copper ion, or there could be a major change in ligandcy as for instance by having the halide ion(s) (partially) replacing the oxalate ligand. It is clear that if the halide ion is involved in any interconversion, then the final products should reflect the halide ions and the sensitivity of the EPR technique should be very beneficial in such determinations. It is not to be expected, however, that any alkali salt of the same halide ion would give the same results; that is, lattice energy effects could be important.

Figure 12 and Table IV summarize the EPR signals seen for either $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2$ or $[\text{Cu}(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ pressed into various alkali halide hosts. Essentially the same Q-band spectrum results from pelleting either the anhydrous or hydrated compound in either KI or KBr. As can be seen in Figure 12 (tracing A) the spectrum is very similar in appearance to that in Figure 1 (tracing C) for the hydrated compound (the anhydrous compound pelleted in KBr did show extra weak features at $g = 2.243$ and $g =$

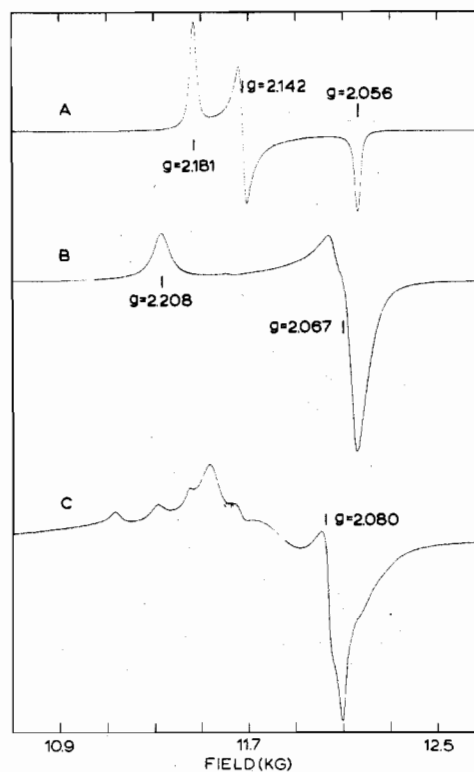


Figure 12. Room-temperature Q-band spectra for 1% by weight samples of three compounds pelleted in an alkali halide host: $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ in KI (A); $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ in NaBr (B); $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$ in KBr (C).

Table IV. Room-Temperature Q-Band Features Seen for $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ Pelleted in Various Alkali Halide Hosts^a

Host	$n = 0$	$n = 1$	Host	$n = 0$	$n = 1$
Pure solid	2.248	2.191	NaCl	2.228	2.209
	2.180	2.168		2.173	2.175
	2.111	2.081		2.162	2.149
KI	2.182	2.181		2.094	2.077-2.057 ^b
	2.144	2.142	NaBr	2.307	
	2.058	2.056		2.207	2.206
KBr	2.243 w			2.074	2.067
	2.180	2.180	KCl	2.178	2.176
	2.141	2.142		2.155	2.154
	2.072 w ^b			2.084	
	2.056	2.056		2.063	2.063

^a Unless indicated otherwise, each g value is ± 0.002 . ^b Clear indications of more than one feature.

2.072). The g values (~ 2.180 , ~ 2.142 , and ~ 2.056) obtained for these four pelleted samples are, however, appreciably different from those (2.192, 2.168, and 2.081) recorded for $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2$. Apparently, the dried samples of KI and KBr had sufficient water content to hydrate the anhydrous compound in the pelleting process.

An axial spectrum results (see Figure 12, tracing B) from pelleting a sample of $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ in NaBr. The anhydrous compound gives an extra weak feature at low field with $g = 2.307$. In the former case the appearance of the spectrum is reminiscent of that for $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2$ (see Figure 1) except that there is no signal at $g = 2.180$. It is tempting to say that the copper environment of the pelleted species in NaBr resembles the copper site of the anhydrous copper compound for which there is a structure. It appears, however, that the degree of distortion in the basal plane is different. Pelleting in NaCl is similar in that an apparently axial spectrum is obtained, but in the case of either the anhydrous or hydrated compound there is indication of the presence of a certain amount of hydrated species.

The hydrated compound pelleted in KCl gives a spectrum like that obtained for the KI pelleting; however, the anhydrous compound in KCl yields a spectrum where the low-field signal at 2.178 is quite weak and the high-field feature at 2.063 is shouldered with a signal at ~ 2.084 .

All in all, it looks like hydration and dehydration are the major occurrences with pelleting of these two oxalatocopper perchlorates. The pelleted species, however, do not seem to have exactly the same copper environments as are found in the hydrated or anhydrous material and as such additional work is needed to eliminate the possibility of anation, partial dissociation of oxalate, etc. This becomes more than amply clear when one views the Q-band spectrum (see Figure 12, tracing C) of a sample of $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$ pelleted in KBr. This spectrum seems to be a superposition of spectral features from at least two different copper species.

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Registry No. $\text{Cu}(\text{dien})(\text{Ox})\cdot 4\text{H}_2\text{O}$, 37072-95-0; $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2$, 50797-94-9; $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{ClO}_4)_2\cdot\text{H}_2\text{O}$, 55401-14-4; $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$, 40961-76-0; $[\text{Zn}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$, 55520-75-7; $[\text{Cu}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$, 55401-16-6; $[\text{Zn}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$, 55520-76-8; $[\text{Cu}_2(\text{dien})_2(\text{NCO})_2](\text{BPh}_4)_2\cdot 2\text{H}_2\text{O}$, 55401-19-9; $[\text{Zn}_2(\text{dien})_2(\text{NCO})_2](\text{BPh}_4)_2$, 55520-74-6; $\text{Cu}(\text{dien})(\text{NCS})_2$, 52690-20-7; $[\text{Cu}_2(\text{dien})_2(\text{NCS})_2](\text{ClO}_4)_2$, 52588-10-0; $[\text{Cu}_2(\text{dien})_2(\text{NCS})_2](\text{BPh}_4)_2$, 55401-20-2.

Supplementary Material Available. Tables I and II, showing analytical results and $[\text{Cu}_2(\text{dien})_2(\text{C}_2\text{O}_4)](\text{BPh}_4)_2$ magnetic susceptibility data, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105×148 mm, $24\times$ reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number AIC40832K.

References and Notes

- (1) NSF traineeship, 1970-1974.
- (2) Mobil Fellow, 1972-1973; University of Illinois Fellow, 1973-1974.
- (3) Camille and Henry Dreyfus Fellow, 1972-1977.
- (4) D. N. Hendrickson and D. M. Duggan, "Extended Interactions between Transition Metal Ions", L. Interranti, Ed., American Chemical Society Symposium Series, No. 5, 1974.
- (5) D. M. Duggan, E. K. Barefield, and D. N. Hendrickson, *Inorg. Chem.*, **12**, 985, (1973).
- (6) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, **12**, 2422 (1973).
- (7) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, **13**, 2929 (1974).
- (8) C. G. Pierpont, D. N. Hendrickson, D. M. Duggan, F. Wagner, and E. K. Barefield, *Inorg. Chem.*, **14**, 604 (1975).
- (9) D. M. Duggan and D. N. Hendrickson, *J. Chem. Soc., Chem. Commun.*, 411 (1973).
- (10) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, **13**, 2056 (1974).
- (11) D. M. Duggan, R. G. Jungst, K. R. Mann, G. D. Stucky, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **96**, 3443 (1974).
- (12) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, **13**, 1911 (1974).
- (13) E. J. Laskowski, D. M. Duggan, and D. N. Hendrickson, submitted for publication.
- (14) E. J. Laskowski and D. N. Hendrickson, unpublished results.
- (15) N. F. Curtis, *J. Chem. Soc.*, 4109 (1963).
- (16) N. F. Curtis, I. R. N. McCormick, and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1537 (1973).
- (17) M. Cannas, G. Carta, and G. Marongiu, *J. Chem. Soc., Dalton Trans.*, 556 (1974).
- (18) Supplementary material.
- (19) N. F. Curtis, *J. Chem. Soc. A*, 1584 (1968).
- (20) M. J. Bew, B. J. Hathaway, and R. J. Fereday, *J. Chem. Soc., Dalton Trans.*, 1229 (1972).
- (21) F. S. Stephens, *J. Chem. Soc. A*, 2493 (1969).
- (22) B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, **214**, 451 (1952).
- (23) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 314 (1965).
- (24) A. V. Ablov, M. D. Mazus, E. V. Popa, T. I. Malnowskii, and V. N. Biyushkin, *Dokl. Akad. Nauk SSSR*, **194**, 821 (1970).
- (25) G. G. Belford, R. L. Belford, and J. F. Burkhalter, *J. Magn. Reson.*, **11**, 251 (1973).
- (26) P. D. W. Boyd, A. D. Toy, T. D. Smith, and J. R. Pilbrow, *J. Chem. Soc., Dalton Trans.*, 1549 (1973).
- (27) T. Lund and W. E. Hatfield, *J. Chem. Phys.*, **59**, 885 (1973).
- (28) M. Cannas, G. Carta, and G. Marongiu, *J. Chem. Soc., Dalton Trans.*, 553 (1974).
- (29) D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nucl. Chem.*, **21**, 33 (1961).
- (30) D. M. Drew and J. T. van Gemert, *Appl. Spectrosc.*, **25**, 465 (1971).

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Complexes with Sulfur and Selenium Donors. XI. Metal 2-Amino-1-cyclopentene-1-dithiocarboxylates^{1,2}

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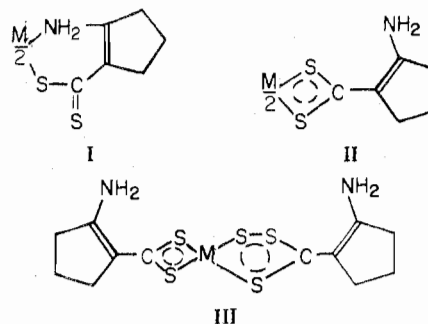
AIC40601D

A variety of complexes of the 2-amino-1-cyclopentene-1-dithiocarboxylate (acdc) anion have been investigated with a view to elucidation of the bonding sites employed by the acdc ligand. Electron spin resonance spectra of $\text{VO}(\text{acdc})_2$ and $\text{Cu}(\text{acdc})_2$ and proton NMR spectra of $\text{Zn}(\text{acdc})_2$, $\text{Cd}(\text{acdc})_2$, $\text{Hg}(\text{acdc})_2$, $\text{Ni}(\text{acdc})_2$, and $\text{In}(\text{acdc})_3$ as well as the electronic spectra of the complexes support the exclusive use of sulfur atoms by the ligand in metal bonding.

Introduction

Metal complexes with sulfur donor ligands exhibit a wide variety of chemical behavior. The physical and chemical properties of these compounds have been extensively reviewed.³⁻⁶ A series of complexes of the type ML_2 (M = divalent Ni, Co, Pt, Zn, and Cd; L = the 2-amino-1-cyclopentene-1-dithiocarboxylate (acdc) anion) were investigated by Pattnaik and Sen.⁷ They suggested that these complexes contained MS_2N_2 chromophores (I). In view of previous work with sulfur donor ligands we considered the formation of quadratic MS_4 chromophores (II) a more likely possibility and, thus, undertook the present study. A referee kindly pointed out the work of Thomas and Poveda,⁸ who investigated acdc complexes with divalent Co, Ni, Cu, Zn, and Cd ions. They proposed⁸ on the basis of rather limited measurements of

physical properties that MS_4 chromophores were obtained and that Co(II) and Ni(II) formed complexes of type III. Pattnaik



and Sen's suggestion⁷ of involvement of the amino group in