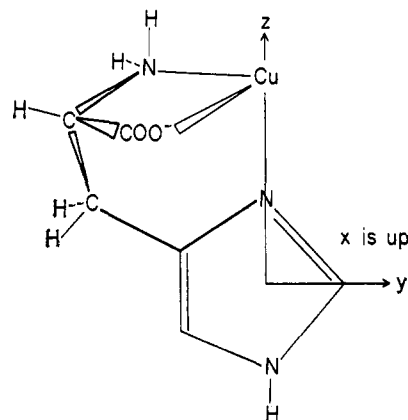


Fig. 10.—Rotatory dispersion curve of the L-histidine-copper complex resolved into a simple Cotton effect and a Cotton effect similar to those of the cobalt, nickel, and zinc complexes.

the many-electron model to this chromophoric electron. Looking at complex I (imidazole plane), it would be reasonable to take the most polarizable  $z$ -direction in the direction of charge transfer. The  $y$ -direction would be in the imidazole plane and the  $x$ -direction would be perpendicular to that plane. All of the groups lie in



Complex I (imidazole plane)

or very near a plane except the carboxylate anion which is clearly the principal perturbation of the "chromophoric ellipsoid." As it is a negative group, the product  $Axyz$  would be positive in this direction, that is, the static charge effect is assumed to be dominant, and as  $xyz$  is negative,  $A$  must be negative, *i.e.*, a negative Cotton effect might be expected. Figure 10 shows that the curve for the L-histidinocopper(II) can be resolved into a curve similar to those of the other transition metals and a negative Cotton effect curve.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

## Electron Paramagnetic Resonance Studies of the Electronic Structures of Bis(maleonitriledithiolato)copper(II), -nickel(III), -cobalt(II), and -rhodium(II) Complexes

BY A. H. MAKI, N. EDELSTEIN, A. DAVISON, AND R. H. HOLM<sup>1</sup>

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The electron paramagnetic resonance spectra of the low spin ( $S = 1/2$ ) planar complexes  $[\text{CuS}_4\text{C}_4(\text{CN})_4]^{-2}$ ,  $[\text{CoS}_4\text{C}_4(\text{CN})_4]^{-2}$ ,  $[\text{RhS}_4\text{C}_4(\text{CN})_4]^{-2}$ , and  $[\text{NiS}_4\text{C}_4(\text{CN})_4]^{-}$  have been obtained at room temperature in magnetically dilute single crystals of diamagnetic  $(n\text{-Bu}_4\text{N})_2[\text{NiS}_4\text{C}_4(\text{CN})_4]$  and  $(n\text{-Bu}_4\text{N})[\text{CuS}_4\text{C}_4(\text{CN})_4]$ , respectively, whose crystal structures are known. It was found that the principal axes of the tensors  $\mathbf{g}$  and  $\mathbf{A}$  lie along the symmetry axes of the complex in the crystal, within experimental error. Calculations of  $\mathbf{g}$  and  $\mathbf{A}$  are made for several possible ground-state configurations of the metal ion in the complex and are compared with the experimental spin-Hamiltonian. The following probable ground-state hole configurations are deduced:  $[\text{CuS}_4\text{C}_4(\text{CN})_4]^{-2}$ ,  $|\epsilon\rangle$ ;  $[\text{CoS}_4\text{C}_4(\text{CN})_4]^{-2}$ ,  $[\text{NiS}_4\text{C}_4(\text{CN})_4]^{-}$ ,  $|\epsilon^2y\rangle$ ;  $[\text{RhS}_4\text{C}_4(\text{CN})_4]$ ,  $|\epsilon^20\rangle$  ( $\epsilon \equiv d_{xy}$ ,  $y \equiv d_{yz}$ ,  $0 \equiv d_{z^2-x^2}$ , where the  $z$ -axis is perpendicular to the molecular plane and the  $y$ -axis bisects each ligand). Configurational excitation energies estimated from the spin-Hamiltonians are compared with the optical spectra, and assignments of certain observed electronic transitions are made.

### Introduction

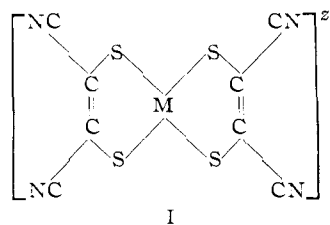
Paramagnetic resonance spectroscopy has been extensively utilized in the study of planar chelates of Cu(II), which have a  $d^9$ -electron configuration.<sup>2-9</sup>

- (1) Alfred P. Sloan Foundation Fellow.
- (2) B. R. McGarvey, *J. Phys. Chem.*, **60**, 71 (1956).
- (3) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 31, 35 (1958).
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- (6) D. Kivelson and R. Neiman, *ibid.*, **35**, 149 (1961).
- (7) R. Petterson and T. Vännngård, *Arkiv Kemi*, **17**, 249 (1961).
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- (9) H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962).

We have recently reported on the synthesis and characterization of a series of planar four-coordinate complexes of transition metal ions of the 3d, 4d, and 5d groups which readily undergo oxidation-reduction reactions.<sup>10</sup> These complexes are remarkable in that the geometry of the complex is unaffected by oxidation-reduction reactions, and one can obtain planar complexes containing the transition metal ions in a series of formal oxidation states. The object of this paper is to report on the results of paramagnetic resonance

- (10) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964), and papers referred to therein.

measurements of magnetically dilute single crystals containing certain of the paramagnetic complexes described earlier<sup>10,11</sup> as solutes. The compounds in-



vestigated here are the paramagnetic tetra-*n*-butylammonium salts of the planar complexes I in which  $M = \text{Cu}$ ,  $\text{Co}$ ,  $\text{Rh}$ ,  $z = -2$ , and  $M = \text{Ni}$ ,  $z = -1$ . The diamagnetic host crystals employed in this investigation were  $M = \text{Ni}$ ,  $z = -2$ , for the paramagnetic  $z = -2$  complexes, and  $M = \text{Cu}$ ,  $z = -1$  for the paramagnetic  $z = -1$  complex.

Preliminary paramagnetic resonance data have been reported for several complexes<sup>10,11</sup> but up to now these data have been obtained either in liquid solutions, frozen glasses, polycrystalline solids, or magnetically dilute single crystals without the benefit of a crystal structure. Although data obtained from disoriented samples may be used to obtain the spin-Hamiltonian<sup>12</sup> parameters of the complex, they suffer from the very important defect that the magnetic principal axis system cannot be related to a molecule-fixed coordinate system by purely experimental means. The usefulness of the spin-Hamiltonian for the assignment of the electronic configurations of complexes is largely lost without this information.

Complete structure determinations of  $(n\text{-Bu}_4\text{N})\text{[CuS}_4\text{C}_4(\text{CN})_4]$  and  $(n\text{-Bu}_4\text{N})_2\text{[CoS}_4\text{C}_4(\text{CN})_4]$  (isomorphous with the corresponding nickel complex<sup>13</sup>) have recently been completed by Forrester, *et al.*,<sup>14</sup> and reveal that the ligands form a planar array about the central metal atom.

From the crystallographic structures of the  $z = -2$  and  $z = -1$  host complexes, we obtain the orientation of the principal axis systems of  $\mathbf{A}$ , the hyperfine tensor, and  $\mathbf{g}$ , the  $g$ -value tensor in a molecule-fixed coordinate system. Conclusions are then drawn about the probable  $d$ -electron ground-state configurations of the central metal ions by comparison of the observed  $\mathbf{A}$  and  $\mathbf{g}$  with those calculated from various configurations. Estimates of configurational excitation energies are obtained and discussed.

### Experimental

Single crystals containing 1 to 5 mole % of the paramagnetic complex were grown by solvent evaporation from solutions of the  $z = -1$  crystals in dichloromethane-chloroform, and from solutions of the  $z = -2$  crystals in acetone-2-butanol. Faces of the doped  $(\text{Bu}_4\text{N})_2\text{[NiS}_4\text{C}_4(\text{CN})_4]$  and  $(\text{Bu}_4\text{N})\text{[CuS}_4\text{C}_4(\text{CN})_4]$  crystals were identified by optical goniometry.

Crystals were mounted on a polystyrene wedge with an identified face attached with Apiezon N to one of the surfaces. The wedge was attached to a polystyrene post with an indicator which could be rotated against a fixed angular scale. By means of this arrangement, the crystals were each rotated inside the microwave cavity of the paramagnetic resonance spectrometer through  $180^\circ$ ,

(11) E. Billig, S. I. Shupack, J. H. Waters, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 926 (1964).

(12) M. H. L. Pryce, *Proc. Phys. Soc. (London)*, **A63**, 25 (1950).

(13) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963).

(14) J. D. Forrester, A. Zalkin, and D. H. Templeton, *ibid.*, **3**, 1500, 1507 (1964).

measurements being made either at  $20$  or  $15^\circ$  intervals. Crystals were remounted, and rotations made about two axes orthogonal to the first. The rotation axis was perpendicular to the magnetic field.

The paramagnetic resonance measurements were made on a conventional spectrometer operating at about  $9.8$  Gc./sec. employing  $30$  kc./sec. magnetic field modulation. The klystron frequency was measured with a transfer oscillator and frequency counter for each crystal orientation. The magnetic field was measured by means of a proton gaussmeter monitored by the same frequency counter.

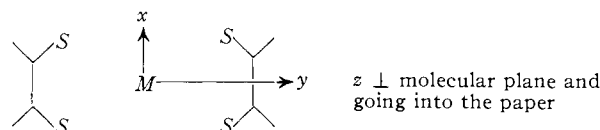
### Analysis of Data and Experimental Results

The observed  $g$ -values and hyperfine splittings for each rotation were averaged by a least-squares analysis and the resulting parameters were treated according to the procedure of Schonland.<sup>15</sup> We have assumed that  $\mathbf{g}$  and  $\mathbf{A}$  have the same principal axis system (discussed below) and write the spin-Hamiltonian<sup>12</sup> as

$$\begin{aligned} \mathcal{H} &= \beta_0 \vec{S} \vec{H} + \vec{I} \vec{A} \vec{S} \\ &= \beta_0 (g_{xx} S_x H_x + g_{yy} S_y H_y + g_{zz} S_z H_z) + A_{xx} I_x S_x + \\ &\quad A_{yy} I_y S_y + A_{zz} I_z S_z \end{aligned}$$

where  $\beta_0$  is the Bohr magneton,  $\vec{H}$  is the magnetic field, and  $\vec{S}$  and  $\vec{I}$  are the electron and nuclear spin operators, respectively. We obtain the principal values of  $\mathbf{g}$  ( $g_{xx}$ ,  $g_{yy}$ ,  $g_{zz}$ ) and  $\mathbf{A}$  ( $A_{xx}$ ,  $A_{yy}$ ,  $A_{zz}$ ) from the analysis of the data. The analysis also gives the direction angles of the magnetic principal axis system in relation to the coordinate system defined by the three orthogonal crystal rotation axes.

We now define a right-handed molecule-fixed axis system as



The direction angles of  $x$ ,  $y$ , and  $z$  were calculated from the crystallographic data in the crystal rotation axis system and compared with the direction angles of the principal axes of  $\mathbf{g}$  and  $\mathbf{A}$ . For each crystal analyzed, agreement was found to be, on the average, within  $2$ - $3^\circ$ , which indicates that the magnetic axis systems in the crystal are coincident with the symmetry axes of the complex ion, within experimental error. This agreement also shows the assumption that  $\mathbf{g}$  and  $\mathbf{A}$  have the same principal axis system is correct, within experimental error.

Table I lists the crystals measured, the principal  $\mathbf{g}$  and  $\mathbf{A}$  values, and the calculated and experimental direction angles.  $(\text{Bu}_4\text{N})_2\text{[NiS}_4\text{C}_4(\text{CN})_4]$  has one molecule per unit cell, while  $(\text{Bu}_4\text{N})\text{[CuS}_4\text{C}_4(\text{CN})_4]$  has eight molecules per unit cell, but only two magnetically inequivalent sites.<sup>14</sup> In the case of  $[\text{NiS}_4\text{C}_4(\text{CN})_4]^-$ ,  $\mathbf{A}$  for  $^{61}\text{Ni}$  was obtained from the glass spectrum of an isotopically enriched sample. The most significant differences between the principal values of  $\mathbf{g}$  reported here and previously reported values from glass spectra occur in the case of the  $g_{zz}$  for  $[\text{NiS}_4\text{C}_4(\text{CN})_4]^-$  (found to be  $2.140$  in a  $\text{CHCl}_3$ -dimethylformamide glass<sup>10</sup>). There is also a significant difference in the maximum principal  $g$ -value reported by Billig, *et al.*,<sup>11</sup> for polycrystalline  $(n\text{-Bu}_4\text{N})_2\text{[RhS}_4\text{C}_4(\text{CN})_4]$  ( $2.35$ ) and our

(15) D. S. Schonland, *Proc. Phys. Soc. (London)*, **73**, 788 (1959).

TABLE I

Crystal	Molecular axis	Calculated direction angles, deg.				$g^a$	Experimental							
		Direction angles, deg.		$A, \text{cm.}^{-1} \times 10^3$			Direction angles, deg.		$A, \text{cm.}^{-1} \times 10^3$		Direction angles, deg.			
(Bu <sub>4</sub> N)NiS <sub>4</sub> C <sub>4</sub> (CN) <sub>4</sub> <sup>b</sup>	x	78.2	34.3	58.2	2.160	74.1	34.7	60.0	1.5 ± 0.2 <sup>c</sup>					
diluted in (Bu <sub>4</sub> N)CuS <sub>4</sub> C <sub>4</sub> (CN) <sub>4</sub>	y	76.2	55.2	38.1	2.042	76.9	55.9	37.2	0.29 ± 0.1 <sup>c</sup>					
	z	18.2	88.0	71.8	1.998	20.8	83.9	70.2	<0.2 <sup>c,d</sup>					
(Bu <sub>4</sub> N) <sub>2</sub> CoS <sub>4</sub> C <sub>4</sub> (CN) <sub>4</sub>	x	22.9	-67.2	-89.1	2.798 ± 0.003	23.5	-66.5	-88.5	5.0 ± 0.1	23.7	-66.3	89.5		
diluted in (Bu <sub>4</sub> N) <sub>2</sub> NiS <sub>4</sub> C <sub>4</sub> (CN) <sub>4</sub>	y	71.5	43.1	-52.8	2.025 ± 0.003	73.6	46.2	-48.4	2.8 ± 0.1	70.2	40.6	-56.2		
	z	77.0	55.7	37.3	1.977 ± 0.003	73.6	53.0	41.6	2.3 ± 0.1	77.5	59.2	33.8		
(Bu <sub>4</sub> N) <sub>2</sub> CuS <sub>4</sub> C <sub>4</sub> (CN) <sub>4</sub>	x	22.9	-67.2	-89.1	2.026	24.8	-65.3	89.3	3.9 ± 0.1 <sup>e</sup>		f			
diluted in (Bu <sub>4</sub> N) <sub>2</sub> NiS <sub>4</sub> C <sub>4</sub> (CN) <sub>4</sub>	y	71.5	43.1	-52.8	2.023	70.2	44.2	-52.5	3.9 ± 0.1 <sup>e</sup>		f			
	z	77.0	55.7	37.3	2.086	75.8	56.1	37.5	16.2 ± 0.2 <sup>e</sup>	75.1	55.6	38.3		
(Bu <sub>4</sub> N) <sub>2</sub> RhS <sub>4</sub> C <sub>4</sub> (CN) <sub>4</sub> <sup>g</sup>	x	37.2	64.8	64.5	2.447	36.8	66.7	63.2	<0.4 <sup>d</sup>					
diluted in (Bu <sub>4</sub> N) <sub>2</sub> NiS <sub>4</sub> C <sub>4</sub> (CN) <sub>4</sub>	y	-54.2	44.9	66.8	2.019	-54.7	44.9	66.1	0.75 ± 0.1	-55.6	43.6	66.7		
	z	-82.1	-55.5	35.6	1.936	-80.9	-54.2	37.3	<0.4 <sup>d</sup>					

<sup>a</sup> Estimated accuracy in  $g$ -value measurements  $\pm 0.001$  except where noted. <sup>b</sup> In this crystal there are two magnetically inequivalent molecules per unit cell; the  $g$ -values are the same within experimental error; we list the direction angles for only one of the molecules. <sup>c</sup> Values obtained from an enriched Ni<sup>91</sup> sample in a CHCl<sub>3</sub>-DMF glass at 100°K. <sup>d</sup> Hyperfine splitting too small to be measured. <sup>e</sup> Refers to <sup>63</sup>Cu. <sup>f</sup> Because of the near axial symmetry, meaningful direction angles could not be obtained. <sup>g</sup> A different crystal rotation axis system was used than in the Co- or Cu-doped crystals.

value of  $g_{zz}$  for the magnetically dilute single crystal. The effect on  $g_{zz}$  of the nickel complex may be due to a solvent effect to be discussed more fully below, but there is no ready explanation for the large discrepancy in the case of the rhodium complex. Normally, paramagnetic resonance data of magnetically concentrated crystals may be suspect because of the possible averaging of  $g$ -values of magnetically nonequivalent sites by electron spin exchange. Such averaging occurs in crystals of Cu(NH<sub>3</sub>)<sub>4</sub>SO<sub>4</sub>·H<sub>2</sub>O, for instance,<sup>16</sup> containing two magnetically nonequivalent sites in a unit cell. The crystal structure of the isomorphous (*n*-Bu<sub>4</sub>N)<sub>2</sub>[CoS<sub>4</sub>C<sub>4</sub>(CN)<sub>4</sub>]<sup>14</sup> reveals only one molecule per unit cell, so averaging of principal  $g$ -values by spin exchange is not expected to occur, even with a considerable spin-exchange rate.

### Preliminary Discussion

Previous magnetic susceptibility work<sup>10,11,13</sup> has shown that the complexes investigated here have a low spin ( $S = 1/2$ ) ground state. This is particularly true of the complex [CoS<sub>4</sub>C<sub>4</sub>(CN)<sub>4</sub>]<sup>-2</sup> which has been shown<sup>10</sup> to have a susceptibility consistent with  $S = 1/2$  in several solid crystalline salts, in magnetically diluted salts, as well as in solutions of acetone, DMSO, and DMF. Our previous findings are thus inconsistent with the earlier claim<sup>17</sup> that [CoS<sub>4</sub>C<sub>4</sub>(CN)<sub>4</sub>]<sup>-2</sup> is a high-spin ( $S = 3/2$ ) square-planar cobaltous complex. In the next section we will present evidence for the correct ground-state configuration of this cobalt complex derived from the paramagnetic resonance results.

Beginning with the complex [CuS<sub>4</sub>C<sub>4</sub>(CN)<sub>4</sub>]<sup>-2</sup>, we find that  $|g_{zz}| > |g_{xx}|, |g_{yy}|$ , and  $g_{zz} \sim |g_{xx}| \sim |g_{yy}|$ . We also find  $|A_{zz}| \gg |A_{xx}|, |A_{yy}|$ . These results are typical of square-planar Cu(II) complexes with the electronic configuration  $d^9$ , or a vacancy configuration  $d^7$ . Previous paramagnetic resonance studies<sup>2-4</sup> on single crystals of square-planar Cu(II) complexes makes it highly likely that the vacancy is in a  $d_{xy}$  orbital in  $D_{2h}$  symmetry. The polarized optical absorption spectra of bis(acetylacetonato)copper(II) were interpreted by Ferguson,<sup>18</sup> who concluded that the vacancy occupies a  $d_{yz}$  orbital in  $D_{2h}$  symmetry. Ferguson's analysis has,

however, been disputed by Piper and Belford,<sup>19a</sup> who point out that the analysis was based upon an inaccurate crystallographic structure. This reinterpretation has been accepted by Ferguson, *et al.*<sup>19b</sup> It should be pointed out that the spin-Hamiltonian of bis(acetylacetonato)copper(II) is completely inconsistent with a  $d_{yz}^1$  vacancy configuration.<sup>3</sup> Turning to the other complexes investigated here, we find that they contain two less valence electrons than does [CuS<sub>4</sub>C<sub>4</sub>(CN)<sub>4</sub>]<sup>-2</sup> and are thus presumably  $d^7$  complexes. It has been suggested<sup>20</sup> that [NiS<sub>4</sub>C<sub>4</sub>(CN)<sub>4</sub>]<sup>-</sup> is, in fact,  $d^9$  with spin-paired monoanion radical ligands. It should be noted, however, from Table I that the largest  $g$ -value is  $g_{xx}$ , not  $g_{zz}$ , and that  $g_{xx}$  and  $g_{yy}$  are significantly different. In fact,  $g_{zz}$  is the smallest  $g$ -value, which is difficult to reconcile with a  $d^9$  metal ion configuration in which the vacancy occupies a  $d_{xy}$  orbital. We will thus begin by assuming that the metal ion in the nickel, cobalt, and rhodium complexes can be treated as a  $d^7$  electronic configuration with  $S = 1/2$  and attempt in the next sections to reconcile this assumption with the observed spin-Hamiltonians and, to some extent, with the optical spectra.

### Theoretical Results

It would be preferable to develop spin-Hamiltonians for the complexes under discussion through the use of a basis set of molecular orbitals consisting of linear combinations of metal and ligand orbitals.<sup>21,22</sup> Although this has been done for square-planar Cu(II),<sup>3,5,8</sup> an analogous theory would be exceedingly cumbersome for a  $d^7$  configuration. We will, therefore, not attempt to use molecular orbitals, but rather approach the problem with a basis set of the  $d$  atomic orbitals. We will later attempt to account for delocalization of the wave functions by reducing the spin-orbit coupling parameter,  $\zeta$ , and  $r^{-3}$ , the mean inverse cube electron-nuclear distance, which are deduced from the electronic spectra of the free ions. Our development will be similar to that of Griffith<sup>23</sup> for the  $d^n$  strong field complexes, except that we use a basis set of real  $d$ -orbitals.

- (19) (a) T. S. Piper and R. L. Belford, *Mol. Phys.*, **5**, 169 (1962); (b) J. Ferguson, R. L. Belford, and T. S. Piper, *J. Chem. Phys.*, **37**, 1569 (1962).  
 (20) H. B. Gray and E. Billig, *J. Am. Chem. Soc.*, **85**, 2019 (1963).  
 (21) J. H. Van Vleck, *Phys. Rev.*, **41**, 203 (1932).  
 (22) M. Tinkham, *Proc. Roy. Soc. (London)*, **A236**, 535, 549 (1956).  
 (23) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, London, 1961.

(16) E. H. Carlson and R. D. Spence, *J. Chem. Phys.*, **24**, 471 (1956).

(17) H. B. Gray, R. Williams, I. Bernal, and E. Billig, *J. Am. Chem. Soc.*, **84**, 3596 (1962).

(18) J. Ferguson, *J. Chem. Phys.*, **34**, 1609 (1961).

We will abbreviate the orbital basis set as  $\epsilon$ ,  $\mu$ ,  $y$ ,  $x$ , and  $0$ , which stand for the real d-orbitals  $d_{xy}$ ,  $d_{x^2-y^2}$ ,  $d_{yz}$ ,  $d_{zx}$ , and  $d_{3z^2-r^2}$ , respectively. The d-orbital phases are chosen to be those prescribed by Condon and Shortley.<sup>24</sup> We will be discussing vacancy (*i.e.*, hole), rather than electron configurations, throughout;  $\zeta$  is thus negative.<sup>25</sup> We begin with Cu(II),  $\epsilon^1$ , and proceed to the various likely  $d^3$  configurations.

**1. Zero-Order Kramers' Doublet**  $|\bar{\epsilon}\rangle$ ,  $|\bar{\mu}\rangle$ .<sup>25</sup>—The first-order improved configurational wave functions are obtained by applying the spin-orbit interaction Hamiltonian,  $\sum_k \zeta \vec{l}_k \cdot \vec{s}_k$ , as a perturbation, using standard first-order perturbation theory. We find

$$\psi_{\alpha}^{+} = N_{\alpha} |\bar{\epsilon}\rangle + i\alpha_1 |\bar{\mu}\rangle - 1/2\alpha_2 |\bar{y}\rangle - \frac{i}{2}\alpha_3 |\bar{x}\rangle \quad (1)$$

$$\psi_{\alpha}^{-} = N_{\alpha} |\bar{\epsilon}\rangle - i\alpha_1 |\bar{\mu}\rangle + 1/2\alpha_2 |\bar{y}\rangle - \frac{i}{2}\alpha_3 |\bar{x}\rangle \quad (2)$$

for the first-order ground-state Kramers' doublet.  $N_{\alpha}$  is a normalization constant which is close to one if the mixing parameters,  $\alpha_i$ , are small.  $\alpha_i = \zeta/E_{i\alpha}$ , where  $E_{i\alpha}$  is a configurational excitation energy.  $E_{1\alpha} = E(|\mu\rangle) - E(|\epsilon\rangle)$ ,  $E_{2\alpha} = E(|y\rangle) - E(|\epsilon\rangle)$ , etc. With  $N_{\alpha} = 1$ , the following expressions are found for the spin-Hamiltonian parameters

$$g_{xx} = 2\langle\psi_{\alpha}^{+}|\sum_k(l_{zk} + 2s_{zk})|\psi_{\alpha}^{-}\rangle = 2 - 2\alpha_3 \quad (3a)$$

$$g_{yy} = 2i\langle\psi_{\alpha}^{+}|\sum_k(l_{yk} + 2s_{yk})|\psi_{\alpha}^{-}\rangle = 2 - 2\alpha_2 \quad (3b)$$

$$g_{zz} = 2\langle\psi_{\alpha}^{+}|\sum_k(l_{zk} + 2s_{zk})|\psi_{\alpha}^{+}\rangle = 2 - 8\alpha_1 \quad (3c)$$

and

$$A_{xx} = 2P\langle\psi_{\alpha}^{+}|\sum_k(l_{zk} - \kappa s_{zk} + 1/7a_{zk})|\psi_{\alpha}^{-}\rangle = P[-2\alpha_3 - \kappa + 2/7 + 3/7\alpha_2] \quad (4a)$$

$$A_{yy} = 2iP\langle\psi_{\alpha}^{+}|\sum_k(l_{yk} - \kappa s_{yk} + 1/7a_{yk})|\psi_{\alpha}^{-}\rangle = P[-2\alpha_2 - \kappa + 2/7 + 3/7\alpha_3] \quad (4b)$$

$$A_{zz} = 2P\langle\psi_{\alpha}^{+}|\sum_k(l_{zk} - \kappa s_{zk} + 1/7a_{zk})|\psi_{\alpha}^{+}\rangle = P[-8\alpha_1 - \kappa - 4/7 - 3/7(\alpha_2 + \alpha_3)] \quad (4c)$$

In these expressions, the summation is over the electron vacancies (one in this case), and  $P = 2g_N \beta_0 \beta_N r^{-3}$ , where  $g_N$  and  $\beta_N$  are the nuclear  $g$  value, and nuclear magneton, respectively,  $\beta_0$  is the Bohr magneton, and  $r^{-3}$  is the mean inverse cube vacancy-metal nucleus distance.  $\vec{a}_k = 4\vec{s}_k - (\vec{l}_k \cdot \vec{s}_k)\vec{l}_k - \vec{l}_k(\vec{l}_k \cdot \vec{s}_k)$ , and  $\kappa$  is a parameter referring to the Fermi hyperfine coupling energy in units of  $P$ .

**2. Zero-Order Kramers' Doublet**  $|\epsilon^2\mu^+\rangle$ ,  $|\epsilon^2\mu^-\rangle$ .—We will assume that in the  $d^3$  configurations  $\epsilon$  remains the lowest energy orbital for the vacancies, and consequently in an  $S = 1/2$  configuration is doubly occupied. We will consider the four possibilities for the ground-state configuration based upon  $|\epsilon^2\rangle$ .

(24) E. U. Condon and G. H. Shortley, "Theory of Atomic Spectra," Cambridge University Press, Cambridge and New York, 1935.

(25) The + and - symbols above the orbital wave functions refer to the eigenvalues of  $h^{-1}S_z$ ,  $+1/2$ , and  $-1/2$ , respectively, according to standard usage.

Applying the spin-orbit coupling Hamiltonian to  $|\epsilon^2\mu^+\rangle$ ,  $|\epsilon^2\mu^-\rangle$  we obtain, in first order

$$\psi_a^{+} = N_a |\epsilon^2\mu^+\rangle + \frac{i}{2}a_1 |\epsilon^2y^-\rangle - 1/2a_2 |\epsilon^2x^-\rangle - ia_3 |\epsilon^+\mu^2\rangle \quad (5)$$

$$\psi_a^{-} = N_a |\epsilon^2\mu^-\rangle + \frac{i}{2}a_1 |\epsilon^2y^+\rangle + 1/2a_2 |\epsilon^2x^+\rangle + ia_3 |\epsilon^-\mu^2\rangle \quad (6)$$

We have truncated the complete first-order wave functions to exclude configurations which do not contribute to the spin-Hamiltonian.

With  $N_a = 1$ , we find

$$g_{xx} = 2 - 2a_1 \quad (7a)$$

$$g_{yy} = 2 - 2a_2 \quad (7b)$$

$$g_{zz} = 2 + 8a_3 \quad (7c)$$

and

$$A_{xx} = P[-2a_1 - \kappa + 2/7 + 3/7a_2] \quad (8a)$$

$$A_{yy} = P[-2a_2 - \kappa + 2/7 + 3/7a_1] \quad (8b)$$

$$A_{zz} = P[8a_3 - \kappa - 4/7 - 3/7(a_1 + a_2)] \quad (8c)$$

**3. Zero-Order Kramers' Doublet**  $|\epsilon^2 0^+\rangle$ ,  $|\epsilon^2 0^-\rangle$ .—The spin-orbit interaction mixes in many excited configurations in first order. Of these, we include only those which contribute to  $\mathbf{g}$  and  $\mathbf{A}$  in the following truncated first-order ground-state doublet.

$$\psi_b^{+} = N_b |\epsilon^2 0^+\rangle + \frac{i\sqrt{3}}{2} b_1 |\epsilon^2 y^-\rangle + \frac{\sqrt{3}}{2} b_2 |\epsilon^2 x^-\rangle \quad (9)$$

$$\psi_b^{-} = N_b |\epsilon^2 0^-\rangle + \frac{i\sqrt{3}}{2} b_1 |\epsilon^2 y^+\rangle - \frac{\sqrt{3}}{2} b_2 |\epsilon^2 x^+\rangle \quad (10)$$

Using this ground state, we find the spin-Hamiltonian parameters

$$g_{xx} = 2 - 6b_1 \quad (11a)$$

$$g_{yy} = 2 - 6b_2 \quad (11b)$$

$$g_{zz} = 2 \quad (11c)$$

and

$$A_{xx} = P[-6b_1 - \kappa - 2/7 - 3/7b_2] \quad (12a)$$

$$A_{yy} = P[-6b_2 - \kappa - 2/7 - 3/7b_1] \quad (12b)$$

$$A_{zz} = P[-\kappa + 4/7 + 3/7(b_1 + b_2)] \quad (12c)$$

where we have made the approximation that  $N_b = 1$ .

**4. Zero-Order Kramers' Doublet**  $|\epsilon^2 y^+\rangle$ ,  $|\epsilon^2 y^-\rangle$ .—We obtain the perturbed ground-state doublet wave functions

$$\psi_c^{+} = N_c |\epsilon^2 y^+\rangle - \frac{i\sqrt{3}}{2} c_1 |\epsilon^2 0^-\rangle + \frac{i}{2} c_2 |\epsilon^2 x^+\rangle - \frac{i}{2} c_3 |\epsilon^2 \mu^-\rangle - 1/2c_4 |\epsilon^2 y^2\rangle \quad (13)$$

$$\psi_c^- = N_c |\epsilon^2 y^- \rangle - \frac{i\sqrt{3}}{2} c_1 |\epsilon^2 0^+ \rangle - \frac{i}{2} c_2 |\epsilon^2 x^- \rangle - \frac{i}{2} c_3 |\epsilon^2 \mu^+ \rangle + \frac{1}{2} c_4 |\epsilon^+ y^2 \rangle \quad (14)$$

which again include only those admixed configurations which contribute to **g** and **A**. With  $N_c = 1$ , the spin-Hamiltonian parameters obtained from eq. 13 and 14 are

$$g_{xx} = 2 - 6c_1 - 2c_3 \quad (15a)$$

$$g_{yy} = 2 - 2c_4 \quad (15b)$$

$$g_{zz} = 2 - 2c_2 \quad (15c)$$

and

$$A_{xx} = P[-6c_1 - 2c_3 - \kappa - \frac{4}{7} - \frac{3}{7}(c_2 + c_4)] \quad (16a)$$

$$A_{yy} = P[-2c_4 - \kappa + \frac{2}{7} + \frac{3}{7}(c_1 + c_2 - c_3)] \quad (16b)$$

$$A_{zz} = P[-2c_2 - \kappa + \frac{2}{7} + \frac{3}{7}(c_3 - c_1 - c_4)] \quad (16c)$$

**5. Zero-Order Kramers' Doublet**  $|\epsilon^2 x^+ \rangle, |\epsilon^2 x^- \rangle$ .—We will not develop this case separately, since it can be shown readily that the spin-Hamiltonian obtained is of the same form as that obtained from the doublet  $|\epsilon^2 y^+ \rangle, |\epsilon^2 y^- \rangle$ , but with interchanged magnetic  $x$ - and  $y$ -axes. The coefficients,  $c_i$ , must be changed to refer to different excitation energies, however.

#### Comparison with Observed Spin-Hamiltonians

The observed **g**, Table I, will be compared with each of the theoretical expressions developed in the previous sections. The resulting parameters,  $\alpha_i, a_i, b_i, c_i$ , will then be introduced into the expressions for **A**. The best over-all agreement of the calculated **A** with experiment will be taken to indicate the probable ground-state configuration.

**1. [CuS<sub>4</sub>C<sub>4</sub>(CN)<sub>4</sub>]<sup>-2</sup>.**—In this case we assume that the configuration is  $|\epsilon \rangle$ . We will also assume, for simplicity, that  $g_{xx} = g_{yy}$ , neglecting the small rhombic distortion and taking their average value as  $g_{\perp}$ . Substitution of  $g_{zz}$  and  $g_{\perp}$  into eq. 3a, 3b, and 3c gives  $\alpha_1 = -0.0105, \alpha_2 \sim \alpha_3 = -0.0105$ . Substituting these parameters into eq. 4a-c, we obtain  $A_{xx} \sim A_{yy} = P[0.30 - \kappa], A_{zz} = P[-0.48 - \kappa]$ . The observed hyperfine coupling constant in solution,  $\langle a \rangle = \frac{1}{3}(A_{xx} + A_{yy} + A_{zz}) \sim 76$  gauss, is consistent only with  $A_{xx}, A_{yy}$ , and  $A_{zz}$  of the same sign, and since  $|A_{zz}| \gg |A_{xx}|, |A_{yy}|$ , the sign of each must be negative ( $P$  is positive for <sup>63,65</sup>Cu). The observed hyperfine parameters of Table I give  $P = 1.6 \times 10^{-2}$  cm.<sup>-1</sup>, and  $\kappa = 0.55$ . For the free ion,  $P_0 \sim 3.5 \times 10^{-2}$  cm.<sup>-1</sup>,<sup>26</sup> so in this complex  $r^{-3}$  has roughly one-half the free ion value, indicating strongly covalent  $\sigma$ -bonding.

The more accurate molecular orbital theory for planar Cu(II) complexes<sup>3</sup> has been applied by Pettersson and Vänngård<sup>7</sup> to bis(N,N-disubstituted dithiocarbamate)Cu(II) complexes, which have spin-Hamiltonians similar to [CuS<sub>4</sub>C<sub>4</sub>(CN)<sub>4</sub>]<sup>-2</sup> and in which the metal is coordinated only by sulfur. Similar conclusions have been drawn regarding the high degree of covalency of the Cu-S bonds.

**2. [NiS<sub>4</sub>C<sub>4</sub>(CN)<sub>4</sub>]<sup>-</sup>.**—The configuration  $|\epsilon^2 \mu \rangle$  leads to  $a_1 = -0.079, a_2 = -0.020$ , and  $a_3 \sim -0.001$ , by solving eq. 7a-c with the observed  $g$  values. The hyperfine interaction is then given from eq. 8a-c by  $A_{xx} = P[0.43 - \kappa], A_{yy} = P[0.29 - \kappa]$ , and  $A_{zz} = P[-0.53 - \kappa]$ . The observed  $|A_{zz}| \ll |A_{xx}|$  would require a negative value for  $\kappa$  which is not unreasonable in this configuration due to the possibility of mixing  $|4s \rangle$  with  $|3d \rangle$  in D<sub>2h</sub> symmetry. However, if  $\kappa$  is negative, it is not possible to obtain  $|A_{xx}| \gg |A_{yy}|$  which is observed experimentally. We thus consider the  $|\epsilon^2 \mu \rangle$  ground-state configuration unlikely.

The configuration  $|\epsilon^2 0 \rangle$  leads to  $b_1 = -0.027, b_2 = -0.007$  by substitution of the experimental **g** into eq. 11a-c. We then find from eq. 12 a-c that  $A_{xx} = P[-0.13 - \kappa], A_{yy} = P[-0.23 - \kappa]$ , and  $A_{zz} = P[0.56 - \kappa]$ . A positive  $\kappa$  which is required to reduce  $|A_{zz}|$  to a value less than  $|A_{xx}|$  simultaneously yields  $|A_{yy}| > |A_{xx}|$ , contrary to observation. The configuration  $|\epsilon^2 0 \rangle$  is thus also unlikely.

We next examine the configuration  $|\epsilon^2 y \rangle$ . We find  $3c_1 + c_3 = -0.079$ , and  $c_4 = -0.020$  by solution of eq. 15a and b. The theory is not sufficiently accurate to enable the determination of  $c_2$  from eq. 15c, but it is probably small, and we shall ignore it in eq. 16. It will be shown below that with  $N_c < 1$ , as is required for normalization,  $g_{zz}$  can be reduced below 2.0023. By substitution of the  $c_i$  into eq. 16a-c, we find  $A_{xx} = P[-0.41 - \kappa], A_{yy} = P[0.33 - \kappa]$ , and  $A_{zz} = P[0.29 - \kappa]$ , where we have made the approximation  $c_1 = c_3 = -0.02$  when these coefficients appear in the smaller terms. If it is assumed that  $A_{xx}$  and  $A_{yy}$  are of the same sign, the experimental values may be fit with  $\kappa = 0.51$ , and  $P = 1.6 \times 10^{-3}$  cm.<sup>-1</sup>; whereas, a fit is obtained with  $\kappa = 0.21$ , and  $P = 2.5 \times 10^{-3}$  cm.<sup>-1</sup> if they are of opposite signs. The predicted values of  $A_{zz}$  are  $-0.35 \times 10^{-3}$  cm.<sup>-1</sup>, and  $0.20 \times 10^{-3}$  cm.<sup>-1</sup>, respectively. The <sup>61</sup>Ni hyperfine interaction in solution,  $\langle a \rangle = 4.5 \pm 1$  gauss, favors the assignment of  $A_{xx}$  and  $A_{yy}$  with opposite signs. The sign of  $A_{xx}$  is predicted to be negative. If we use the most recent value of the nuclear moment of <sup>61</sup>Ni,  $\mu = 0.70 \pm 0.04\beta_N$ ,<sup>27</sup> we can estimate  $P_0$  for the free ion. We use an equation given by Trees,<sup>28</sup> derived from formulas of Goudsmit,<sup>29</sup> which relates  $\zeta$  to  $r^{-3}$  for the free ion. We take  $\zeta = 715$  cm.<sup>-1</sup> for Ni(III),<sup>30</sup> and find  $P_0 = 0.010$  cm.<sup>-1</sup>. Reduction of  $r^{-3}$  for the ion in the complex might be expected to reduce  $P$  to about  $6 \times 10^{-3}$  cm.<sup>-1</sup>, but not much lower. However, the order of magnitude is correct, and we accept the  $|\epsilon^2 y \rangle$  configuration as consistent with the observed spin-Hamiltonian. Inspection quickly shows that the configuration  $|\epsilon^2 x \rangle$  is inconsistent with the spin-Hamiltonian, so  $|\epsilon^2 y \rangle$  is the probable ground-state configuration of [NiS<sub>4</sub>C<sub>4</sub>(CN)<sub>4</sub>]<sup>-</sup>.

**3. [CoS<sub>4</sub>C<sub>4</sub>(CN)<sub>4</sub>]<sup>-2</sup>.**—Beginning with the assumed ground-state configuration  $|\epsilon^2 \mu \rangle$ , we find  $a_1 = -0.400, a_2 = -0.011, a_3 = -0.003$ . These parameters yield the principal hyperfine couplings  $A_{xx} = P[1.08 - \kappa], A_{yy} = P[0.14 - \kappa]$ , and  $A_{zz} = P[-0.42 - \kappa]$ . The observed values of  $A_{xx}, A_{yy}$ , and  $A_{zz}$

(27) R. L. Streever, *Phys. Rev. Letters*, **10**, 232 (1963).

(28) R. E. Trees, *Phys. Rev.*, **92**, 308 (1953).

(29) S. Goudsmit, *ibid.*, **43**, 636 (1933).

(30) T. M. Dunn, *Trans. Faraday Soc.*, **57**, 1441 (1961).

(26) A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc. (London)*, **A206**, 164 (1951).

can be fit approximately with  $\kappa = -1.4$ ,  $P = 2 \times 10^{-3} \text{ cm.}^{-1}$ , provided these parameters are all positive.  $P_0$  for the Co(II) free ion has been deduced to be  $0.022 \text{ cm.}^{-1}$  by Abragam and Pryce.<sup>31</sup> It seems unlikely that  $P$  could be reduced by an order of magnitude in this complex, so we conclude that  $|\epsilon^2\mu\rangle$  is an unlikely ground-state configuration.

We next assume that the ground-state configuration is  $|\epsilon^20\rangle$ , and obtain  $b_1 = -0.133$ ,  $b_2 = -0.004$ . We will not be concerned at this point that  $g_{zz}$  is less than 2. It will be shown below that if terms in  $b_1^2$  are retained in the development of the spin-Hamiltonian,  $g_{zz} = 2 - 3b_1^2$  is obtained which yields  $g_{zz} \sim 1.95$ , a value in tolerable agreement with the experimental one. Substitution of  $b_1$  and  $b_2$  into eq. 12a-c gives  $A_{xx} = P[0.51 - \kappa]$ ,  $A_{yy} = P[-0.21 - \kappa]$ , and  $A_{zz} = P[0.51 - \kappa]$ . These values predict that  $A_{xx} \sim A_{zz}$  for any value of  $\kappa$  and  $P$  and thus cannot be reconciled with the observed hyperfine tensor. These expressions are not changed significantly by retaining terms of order  $b_1^2$ . The ground-state configuration  $|\epsilon^20\rangle$  is thus considered an unlikely one.

If the ground-state configuration is  $|\epsilon^2y\rangle$ , we find  $c_1 = -0.13$  and  $c_4 = -0.011$ , where we have assumed  $|c_3| < |c_1|$ . We shall examine this configuration using a more accurate theory below. For now, we will assume that  $c_2$  and  $c_3$  are small and can be ignored. From eq. 16a-c, we find  $A_{xx} = P[0.23 - \kappa]$ ,  $A_{yy} = P[0.25 - \kappa]$ ,  $A_{zz} = P[0.35 - \kappa]$ . Taking  $P = 0.018 \text{ cm.}^{-1}$ ,  $\kappa = 0.48$ , we find  $A_{xx} = -4.5 \times 10^{-3}$ ,  $A_{yy} = -4.1 \times 10^{-3}$ , and  $A_{zz} = -2.3 \times 10^{-3} \text{ cm.}^{-1}$ , values which are in tolerable agreement with experiment, considering the crudeness of the theory at this stage. The value of  $P$  required for this fit is reasonable in comparison with the free ion value.<sup>31</sup>

The agreement can be improved considerably by retaining terms in  $c_1^2$  in the development of the spin-Hamiltonian. We will justify the assumption that  $c_3$  is small in comparison with  $c_1$ , below. The equivalents of eq. 11a-c and 12a-c are found to be

$$g_{zz} = 2 - 6c_1 - 2c_3 \quad (17a)$$

$$g_{yy} = 2 - 2c_4 - 3c_1^2 \quad (17b)$$

$$g_{xx} = 2 - 2c_2 - 3c_1^2 \quad (17c)$$

and

$$A_{xx} = P[-6c_1 - 2c_3 - \kappa + 1/7\{-4 + 3/2c_1^2 - 3(c_2 + c_4)\}] \quad (18a)$$

$$A_{yy} = P[-2c_4 - \kappa + 1/7\{2 + 3(c_1 + c_2 - c_3)\}] \quad (18b)$$

$$A_{zz} = P[-2c_2 - \kappa + 1/7\{2 - 3/2c_1^2 - 3c_1 + 3(c_3 - c_4)\}] \quad (18c)$$

We may now obtain a crude estimate of  $c_3$ , and verify that it is smaller than  $c_1$ . Neglecting interelectronic repulsion terms,  $c_3$  refers to the excitation  $|y\rangle \rightarrow |\mu\rangle$  for a vacancy; whereas,  $c_4$  refers to the excitation  $|\epsilon\rangle \rightarrow |y\rangle$ . In the Cu(II) complex,  $\alpha_1$  refers to the vacancy excitation  $|\epsilon\rangle \rightarrow |\mu\rangle$  directly. Assuming little change in the quantity  $(|\epsilon\rangle - |\mu\rangle)$  the one electron energy level difference between Cu(II) and Co(II),

(31) A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc. (London)*, **A206**, 173 (1951).

we obtain the equation

$$c_3 \sim c_4 \left[ \frac{c_4 \zeta_{\text{Cu}}}{\alpha_1 \zeta_{\text{Co}}} - 1 \right]^{-1} \quad (19)$$

A value of  $c_4$  is obtained from eq. 17b and the experimental  $g_{yy}$ , assuming  $c_1 \sim -0.13$ . The ratio  $\zeta_{\text{Cu}}/\zeta_{\text{Co}}$  is taken from the free ion values.<sup>30</sup> We find  $c_3 = -0.01$  from eq. 19, and from eq. 17a-c we obtain  $c_1 = -0.13$ ,  $c_2 = -0.013$ , and  $c_4 = -0.037$ . Substitution of these values into eq. 18a-c gives  $A_{xx} = P[0.25 - \kappa]$ ,  $A_{yy} = P[0.30 - \kappa]$ , and  $A_{zz} = P[0.37 - \kappa]$ . With  $P = 0.020 \text{ cm.}^{-1}$  and  $\kappa = 0.47$ , we obtain  $A_{xx} = -4.4 \times 10^{-3}$ ,  $A_{yy} = -3.4 \times 10^{-3}$ , and  $A_{zz} = -2.0 \times 10^{-3} \text{ cm.}^{-1}$ . It is noteworthy that reasonable quantitative agreement is obtained with  $P$  near the free ion value.

By similar arguments it is found that no reasonable agreement with experiment is obtained with the ground-state configuration  $|\epsilon^2x\rangle$ . We conclude that the probable ground-state configuration of  $[\text{CoS}_4\text{C}_4(\text{CN})_4]^{-2}$  is  $|\epsilon^2y\rangle$ .

**4.  $[\text{RhS}_4\text{C}_4(\text{CN})_4]^{-2}$ .**—Assuming the configuration  $|\epsilon^2\mu\rangle$ , we find  $a_1 = -0.223$ ,  $a_2 = -0.009$ ,  $a_3 = -0.008$ , from which are obtained  $A_{xx} = P[0.73 - \kappa]$ ,  $A_{yy} = P[0.21 - \kappa]$ , and  $A_{zz} = P[-0.54 - \kappa]$ . For any value of  $\kappa$ , either positive or negative,  $|A_{xx}|$  or  $|A_{zz}|$  is larger than  $|A_{yy}|$ . Since these possibilities are in qualitative disagreement with the experimental observation  $|A_{yy}| > |A_{xx}|$ ,  $|A_{zz}|$ , we discard  $|\epsilon^2\mu\rangle$  as unlikely.

If we next assume that the configuration is  $|\epsilon^20\rangle$ , we find, using eq. 11a-c,  $b_1 = -0.074$ ,  $b_2 = -0.003$ , whereupon, from eq. 12a-c, we find  $A_{xx} = P[0.16 - \kappa]$ ,  $A_{yy} = P[-0.24 - \kappa]$ , and  $A_{zz} = P[0.54 - \kappa]$ . It is consistent with these expressions that  $|A_{yy}| > |A_{xx}|$ ,  $|A_{zz}|$ . We may estimate  $P_0$  for the free ion Rh(II), as outlined previously, and we find  $P_0 \sim -3.2 \times 10^{-3} \text{ cm.}^{-1}$ . If we assume that  $r^{-3}$  is reduced to about one-half the free ion value in this complex, and use the experimentally determined  $|A_{yy}| = 0.74 \pm 0.1 \times 10^{-3} \text{ cm.}^{-1}$ , we find  $\kappa = 0.22 \pm 0.06$ ,  $A_{xx} = +0.1 \pm 0.1 \times 10^{-3}$ , and  $A_{zz} = -0.51 \pm 0.1 \times 10^{-3} \text{ cm.}^{-1}$ .  $A_{yy}$  is predicted to be positive. A more accurate set of equations can be developed for this configuration which retain terms of order  $b_1^2$ . These are

$$g_{zz} = 2 - 6b_1 \quad (20a)$$

$$g_{yy} = 2 - 6b_2 - 3b_1^2 \quad (20b)$$

$$g_{xx} = 2 - 3b_1^2 \quad (20c)$$

and

$$A_{xx} = P[-6b_1 - \kappa - 1/7(2 + 3b_2 + 3/2b_1^2)] \quad (21a)$$

$$A_{yy} = P[-6b_2 - \kappa - 1/7(2 + 3b_1)] \quad (21b)$$

$$A_{zz} = P[-\kappa + 1/7(4 + 3b_1 + 3b_2 - 3/2b_1^2)] \quad (21c)$$

From eq. 20a-c, we obtain  $b_1 = -0.074$  and  $b_2 = -0.0056$ . Substitution into eq. 21a-c gives  $A_{xx} = P[0.16 - \kappa]$ ,  $A_{yy} = P[-0.22 - \kappa]$ , and  $A_{zz} = P[0.53 - \kappa]$ . If we again estimate  $P = -1.6 \times 10^{-3} \text{ cm.}^{-1}$ , we obtain  $\kappa = 0.24 \pm 0.06$ ,  $A_{xx} = +0.13 \pm 0.1 \times 10^{-3}$ , and  $A_{zz} = -0.46 \pm 0.1 \times 10^{-3} \text{ cm.}^{-1}$ . The agreement with the experimental data is only fair,  $A_{zz}$  being calculated to be somewhat too large. These values are very sensitive to the magnitude of  $P$ , however. A 10% reduction gives extremely good agree-

ment. There is a discrepancy in the observed and calculated values of  $g_{zz}$  which is probably the result of a general inadequacy of our theory in dealing quantitatively with the heavier 4d and 5d transition series.

For the configuration  $|\epsilon^2y\rangle$ , we obtain  $c_1 = -0.071$ ,  $c_2 \sim 0$ ,  $c_4 \sim -0.016$ , and have estimated  $c_3 \sim -0.01$ . Substitution into eq. 18a-c gives  $A_{xx} = P[-0.12 - \kappa]$ ,  $A_{yy} = P[0.29 - \kappa]$ , and  $A_{zz} = P[0.31 - \kappa]$ . These expressions are incompatible with the observed  $|A_{yy}| > |A_{xx}|$ ,  $|A_{zz}|$ , and we think that the configuration  $|\epsilon^2y\rangle$  is unlikely for the rhodium complex.

It is found that the configuration  $|\epsilon^2x\rangle$  leads to  $A_{xx} = P[0.73 - \kappa]$ ,  $A_{yy} = P[-0.45 - \kappa]$ , and  $A_{zz} = P[0.38 - \kappa]$ . A value of  $\kappa$  may be found such that  $|A_{yy}| > |A_{xx}|$ ,  $|A_{zz}|$  by a factor of roughly two which is the experimental criterion, but this requires  $\kappa \gtrsim 0.33$ . In order to fit the experimental value of  $A_{yy}$ ,  $P = -1.0 \times 10^{-3} \text{ cm.}^{-1}$  would be required. Although a value of  $P$  this small can not be ruled out, it seems less likely than the larger value discussed in connection with the  $|\epsilon^20\rangle$  configuration above. We conclude that the probable ground-state configuration of  $[\text{RhS}_4\text{C}_4(\text{CN})_4]^{-2}$  is  $|\epsilon^20\rangle$ .

### Comparison with Optical Spectra

Evaluation of the parameters  $\alpha_i$ ,  $a_i$ , etc., from the expressions for  $\mathbf{g}$  in the previous section allows an estimate of configurational excitation energies to be made. No great accuracy can be expected, since the one-electron parameter,  $\zeta$ , is reduced from the free ion value because of the covalency of the orbitals in the complex, by an undetermined factor. For these complexes, it is probably reasonable in general to take  $\zeta$  to be about 0.5 to 0.7 of the free ion value,  $\zeta_0$ .

$[\text{CuS}_4\text{C}_4(\text{CN})_4]^{-2}$ .—For Cu(II), the free ion value of the spin-orbit coupling parameter is  $\zeta_0 = 828 \text{ cm.}^{-1}$ . Since it was found that  $\alpha_1 \sim \alpha_2 \sim \alpha_3 \sim -0.010$  in order to fit the paramagnetic resonance data, we conclude that the states  $|\mu\rangle$ ,  $|x\rangle$ , and  $|y\rangle$  lie between 40,000 and 60,000  $\text{cm.}^{-1}$  above the configuration  $|\epsilon\rangle$ . These excitation energies arise from assuming  $\zeta = 0.5\zeta_0$  and  $\zeta = 0.7\zeta_0$ , respectively. The energy of  $|0\rangle$  cannot be obtained from the paramagnetic resonance data, since  $|0\rangle$  is not mixed with the ground state,  $|\epsilon\rangle$ , by spin-orbit coupling.

We find one optical transition in  $[\text{CuS}_4\text{C}_4(\text{CN})_4]^{-2}$  at 8330  $\text{cm.}^{-1}$ ,  $\epsilon = 94$ , which could possibly be assigned to a d-d transition—most likely  $|\epsilon\rangle \rightarrow |0\rangle$ . Some doubt is cast upon the interpretation of this transition as  $|\epsilon\rangle \rightarrow |0\rangle$  by our failure to observe any transition of  $\epsilon \gtrsim 10$  in the range 5000–12,000  $\text{cm.}^{-1}$  in bis(N,N-diethyldithiocarbamate)copper(II). This complex has  $g_x$  and  $g_z$  essentially the same as those of  $[\text{CuS}_4\text{C}_4(\text{CN})_4]^{-2,7}$  and consequently the d-electron excitation energies would be expected to be similar.

$[\text{NiS}_4\text{C}_4(\text{CN})_4]^{-}$ .—In Ni(III),  $\zeta_0 = 715 \text{ cm.}^{-1}$ , and we will assume that  $\zeta$  is reduced to  $430 \pm 70 \text{ cm.}^{-1}$  in the complex. If  $c_1 \sim c_3$ , we find  $c_1 \sim c_3 \sim c_4 \sim -0.02$ . From the paramagnetic resonance data, we predict that the excited configurations  $|\epsilon^20\rangle$ ,  $|\epsilon^2\mu\rangle$ , and  $|\epsilon^2y\rangle$  lie between 18,000 and 25,000  $\text{cm.}^{-1}$  above the ground-state configuration  $|\epsilon^2y\rangle$ . In terms of one-electron energies, we have consistency with the results for  $[\text{CuS}_4\text{C}_4(\text{CN})_4]^{-2}$  for which the excitation  $|\epsilon\rangle \rightarrow |\mu\rangle$  was predicted to occur in the vicinity of

50,000  $\text{cm.}^{-1}$ . The paramagnetic resonance data are again consistent with a strong tetragonal field.

The optical spectrum of the ion in acetone reveals at least one band with  $\epsilon \lesssim 100$  near 19,000  $\text{cm.}^{-1}$  appearing as a shoulder to a more intense band ( $\epsilon \sim 2500$ ) peaking at 21,000  $\text{cm.}^{-1}$ . The weak shoulders are reasonably assigned to any of the d-d transitions  $|\epsilon^2y\rangle \rightarrow |\epsilon^20\rangle$ ,  $|\epsilon^2\mu\rangle$ ,  $|\epsilon^2y\rangle$ , since they are of reasonable intensity and occur in the frequency region predicted by the paramagnetic resonance data. A band with  $\epsilon \sim 300$  occurring as a shoulder at  $\sim 8850 \text{ cm.}^{-1}$  on an extremely intense band at 11,590  $\text{cm.}^{-1}$  ( $\epsilon \sim 8000$ ) can not be assigned as a d-d transition.

$[\text{CoS}_4\text{C}_4(\text{CN})_4]^{-2}$ .—The Co(II) free ion has  $\zeta_0 = 515 \text{ cm.}^{-1}$ . Using  $\zeta = 310 \pm 50 \text{ cm.}^{-1}$  for the complex, and the values  $c_1 = -0.13$ ,  $c_2 = -0.013$ ,  $c_3 = -0.01$ , and  $c_4 = -0.037$ , we find that the energies of the configurations  $|\epsilon^20\rangle$ ,  $|\epsilon^2x\rangle$ ,  $|\epsilon^2\mu\rangle$ , and  $|\epsilon^2y\rangle$  are  $2400 \pm 400$ ,  $24,000 \pm 4000$ ,  $31,000 \pm 5000$ , and  $8400 \pm 1400 \text{ cm.}^{-1}$  above the ground-state configuration  $|\epsilon^2y\rangle$ . In the visible region, transitions  $|\epsilon^2y\rangle \rightarrow |\epsilon^2y\rangle$ ,  $|\epsilon^2y\rangle \rightarrow |\epsilon^20\rangle$  would be predicted to occur at approximately  $8400 \pm 1400 \text{ cm.}^{-1}$  and  $10,800 \pm 1800 \text{ cm.}^{-1}$ , whereas all other d-d transitions would be expected either in the ultraviolet or in the far-infrared range.

Two weak bands are, in fact, observed in the visible spectrum in dimethylformamide solution and occur as shoulders on a strong band peaking at 18,000  $\text{cm.}^{-1}$  ( $\epsilon \sim 3500$ ). The weak bands have maxima at  $\sim 12,500 \text{ cm.}^{-1}$  ( $\epsilon \sim 70$ ) and  $\sim 15,000 \text{ cm.}^{-1}$  ( $\epsilon \lesssim 100$ ). The agreement with the observed positions of the bands may be improved considerably by using a larger value of  $\zeta$  for the complex. The paramagnetic resonance hyperfine structure of the cobalt complex was fit with a value of  $P$  approximately 90% of the free ion value, and since  $P$  has the same dependence on  $r^{-3}$  as does  $\zeta$ , a value of  $\zeta$  about 90% of the free ion value would seem more reasonable in this case. With  $\zeta \sim 0.9\zeta_0 \sim 460 \text{ cm.}^{-1}$ , the visible transitions are predicted to occur at approximately 12,400 and 15,900  $\text{cm.}^{-1}$ . The approximate energies of the excited configurations  $|\epsilon^20\rangle$ ,  $|\epsilon^2x\rangle$ , and  $|\epsilon^2\mu\rangle$  based upon the larger value of  $\zeta$  are then 3500, 35,000, and 46,000  $\text{cm.}^{-1}$ , respectively.

$[\text{RhS}_4\text{C}_4(\text{CN})_4]^{-2}$ .—In Rh(II),  $\zeta_0 = 1220 \text{ cm.}^{-1}$ . Assuming  $\zeta \sim (0.6 \pm 0.1)\zeta_0$ , and using  $b_1 = -0.074$  and  $b_2 = -0.0056$ , we find that the energies of the configurations  $|\epsilon^2y\rangle$  and  $|\epsilon^2x\rangle$  are  $9900 \pm 1600$  and  $130,000 \pm 22,000 \text{ cm.}^{-1}$ , respectively, above the ground-state configuration  $|\epsilon^20\rangle$ . The latter excitation energy is probably not reliable, since it is obtained from the rather small  $\Delta g_{yy}$ , and inadequacies in the theory for 4d complexes would be expected to affect conclusions drawn from the smaller  $\Delta g$  values to the greatest extent. The energy of  $|\epsilon^2y\rangle$  is probably a better estimate since it is obtained from the relatively large  $\Delta g_{zz}$ .

The optical spectrum of  $[\text{RhS}_4\text{C}_4(\text{CN})_4]^{-2}$  contains one weak band which could be assigned to a d-d transition. The band has  $\epsilon \sim 30$ , and a maximum at 7810  $\text{cm.}^{-1}$ . It is reasonable to assign this transition to  $|\epsilon^20\rangle \rightarrow |\epsilon^2y\rangle$ .

### Summary

From measurements of the paramagnetic resonance spectra of the complexes  $[\text{CuS}_4\text{C}_4(\text{CN})_4]^{-2}$ ,  $[\text{NiS}_4\text{C}_4(\text{CN})_4]^{-}$ ,  $[\text{CoS}_4\text{C}_4(\text{CN})_4]^{-2}$ , and  $[\text{RhS}_4\text{C}_4(\text{CN})_4]^{-2}$  in

magnetically dilute single crystals of known structure, we have concluded that the probable ground-state vacancy configurations are  $|\epsilon\rangle$ ,  $|\epsilon^2y\rangle$ ,  $|\epsilon^2y\rangle$ , and  $|\epsilon^2()\rangle$ , respectively. In  $D_{2h}$  symmetry,  $\epsilon \equiv d_{xy}$ ,  $y \equiv d_{yz}$ , and  $() \equiv d_{3z^2 - r^2}$ . The  $z$ -axis is perpendicular to the molecular plane, and the  $y$ -axis bisects each ligand. The configurational excitation energies predicted from spin-Hamiltonians have been compared with the optical spectra of solutions of the complexes, and observed weak transitions were assigned. The agreement between predicted and observed optical transition energies is satisfactory considering the uncertainty in the spin-orbit coupling parameter,  $\zeta$ , for the complex. From the value of  $r^{-3}$  and  $\zeta$  required to fit the hyperfine structure, and the optical transition energies of the cobalt complex, the d-orbitals are considerably less covalent in this complex than in the other three. In the other complexes, the hyperfine structure of the paramagnetic resonance and the optical spectra are best fit with  $r^{-3}$  and  $\zeta$  about 0.5–0.6 of the calculated free ion values.

We find that the strength of the tetragonal field of maleonitriledithiolate dianion as measured by the one-electron energy  $\epsilon \rightarrow \mu$  (where  $\mu \equiv d_{x^2 - y^2}$ ) is large, this energy difference being estimated in the region of 40,000  $\text{cm}^{-1}$  for the copper, nickel, and cobalt complexes.

The parameter  $g_{xx}$  is reduced in  $\text{CHCl}_3$ -DMF glass of  $[\text{NiS}_4\text{C}_4(\text{CN})_4]^-$  below its value in the single crystal. According to the theory this implies a reduction in the parameter  $c_1$ , or in  $c_3$ . Since  $c_1$  refers to the excitation  $|\epsilon^2y\rangle \rightarrow |\epsilon^2()\rangle$ , whereas  $c_3$  refers to  $|\epsilon^2y\rangle \rightarrow |\epsilon^2\mu\rangle$ , it is more reasonable that the solvent would affect the energy of the former excitation, which ap-

pears to be increased by the order of 10% in the glass over its value in the single crystal.

The common feature of our interpretation of the electronic configurations of the  $d^3$ -hole complexes is the proximity of the energies of the configurations  $|\epsilon^2y\rangle$  and  $|\epsilon^2()\rangle$ . The splitting is largest in the nickel(III) complex, with  $|\epsilon^2y\rangle$  lower (by about 20,000  $\text{cm}^{-1}$ ), smaller in the cobalt(II) complex ( $\sim 3500 \text{ cm}^{-1}$ ), and the  $|\epsilon^2()\rangle$  has become the ground-state configuration in the rhodium(II) complex (with  $|\epsilon^2y\rangle$  at about 8000  $\text{cm}^{-1}$ ). No reliable estimate can be obtained of the energy of the  $|\epsilon^2x\rangle$  configuration from the theory, but it may be stated that the energy of this configuration is well above that of  $|\epsilon^2y\rangle$ , probably by  $> 15,000 \text{ cm}^{-1}$ . The large splitting of  $|\epsilon^2y\rangle$  and  $|\epsilon^2x\rangle$  implies an extensive interaction of the metal  $|y\rangle$  and  $|x\rangle$  orbitals with  $\pi$ -orbitals of the ligands.

Finally, molecular orbital calculations of the ground-state configurations of  $[\text{NiS}_4\text{C}_4(\text{CN})_4]^-$  and  $[\text{CoS}_4\text{C}_4(\text{CN})_4]^{2-}$  using the extended Hückel theory correctly predict the  $|\epsilon^2y\rangle$  configuration.<sup>32</sup>

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(32) R. Hoffmann and R. H. Holm, unpublished work.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY, BALTIMORE, MARYLAND 21218]

## Piperidinate Complexes of Nickel and Copper Mesoporphyrin IX<sup>1</sup>

By EARL W. BAKER, MAURICE S. BROOKHART, AND ALSOPH H. CORWIN

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By spectrophotometric techniques, it is shown that copper and nickel mesoporphyrin IX form, respectively, a mono- and a dicomplex with piperidine. The thermodynamic constants for these reactions are reported. The crystal field stabilization energy of the structure of the transition metal ion is correlated with the structure of metalloporphyrin ligand complexes and a relationship of spectral shifts to ligand number is shown.

The formation of complexes of copper and nickel mesoporphyrin with a variety of ligands was reported by Corwin, Whitten, Baker, and Kleinspehn.<sup>2</sup> Previously, Caughey, Deal, McLees, and Alben<sup>3</sup> had shown that nickel porphyrins form complexes with pyridine. Miller and Dorough studied the formation of pyridine complexes of several metallo derivatives of tetraphenylporphine and reported equilibrium constants of their formation.<sup>4</sup>

This article reports a spectrophotometric study of the reaction of piperidine with copper and nickel meso-

(1) Porphyrin Studies. XXXII. Paper XXXI: E. W. Baker, M. Ruccia, and A. H. Corwin, *Anal. Biochem.*, **8**, 512 (1964). This work was supported in part by Research Grant A-2877 from the National Institutes of Health and in part by the Petroleum Research Fund administered by the American Chemical Society. Presented in part at the 146th National Meeting of the American Chemical Society, Denver, Colo., 1964.

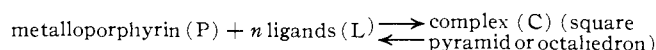
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(4) J. R. Miller and G. D. Dorough, *ibid.*, **74**, 3977 (1952).

porphyrin IX dimethyl ester. The changes in absorption spectra accompanying complex formation may be used to study the reaction quantitatively. Two distinct electronic transitions in the region of 25,000  $\text{cm}^{-1}$  are observed. The shorter wave length transition is associated with the uncomplexed metalloporphyrin and the longer wave length transition with a state of higher ligancy.

The equilibrium under consideration is



for which the equilibrium constant,  $K$ , is given by

$$K = \frac{[\text{C}]}{[\text{P}] [\text{L}]^n} \quad (1)$$

where the quantities in brackets are expressed in units of moles/l. Equation 1 may be rewritten as