resembling the ruffling of the skeleton as a mechanism for effecting inversion of five-coordinate porphyrins with sizable out-of-plane displacements, as characterized in static structures.

The rate constants in Table I and the kinetic parameters in Table II represent inversion as induced by associative halide exchange occurring exclusively via an SN2 mechanism. Any halide exchange occurring on the same side of the porphyrin goes undetected in the NMR method[15] employed here. Thus the present system represents one of the most thoroughly characterized cases of axial ligand lability in metalloporphyrins.[19]

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Solute Complexes in Aqueous Gadolinium(III) Chloride Solutions

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Abstract: The structure of the average solute species in two concentrated aqueous solutions of $GdCl_3$, with and without added hydrochloric acid, has been measured. In each solution Gd^{3+} has 8 (±0.2) nearest neighbors. The average solute species are $Gd(H_2O)_8^{3+}$ in the aqueous solution and $Cl_2Gd(H_2O)_6^+$ in the solution in which hydrochloric acid is the solvent. The average Gd-O nearest neighbor distance has been measured to be 2.37 (±0.02) Å, and the nearest neighbor Gd-Cl distance has been calculated to be ca. 2.8 Å. The ion-pair Gd···Cl distance ranges from 4.8 to 5.0 Å. On the average, dichlorohexaquogadolinium(III) appears to be pseudocubic (D_{3h}), but no satisfactory solute model of $Gd(H_2O)_8^{3+}$ has been found.

Introduction

Interest in the aqueous solution chemistry of Gd^{3+} has dramatically increased in the past few years because of its frequent use as a lanthanide shift reagent,[1] a probe in studying metal-amino acid complexes,[2,3] and because of the "gadolinium break" [4] observed in many theromodynamic measurements of solutions containing various lanthanide salts. Notwithstanding, the solution chemistry of Gd^{3+} has not been thoroughly studied and is not well understood. As noted by Mioduski and Siekierski,[5] considerable question still exists regarding the coordination number(s) of the various lan-

Table I. Solution Compositions

Soln	Molality, mol/kg	Mole fractions Gd	Cl	O	H	Density, g/ml
A[a]	2.66	0.015	0.045	0.313	0.627	1.58
B[b]	1.55	0.010	0.060	0.300	0.630	1.34

[a] The solvent is distilled deionized water. The stoichiometric ratio of chloride/gadolinium is 3:1. [b] The solvent is 10 N hydrochloric acid. The stoichiometric ratio of chloride/gadolinium is 6:1.

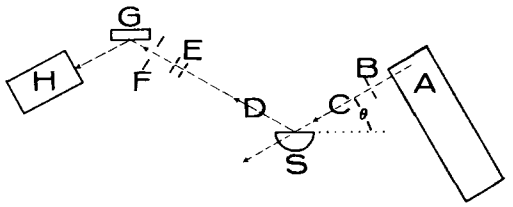

Figure 1. Schematic of the θ-θ diffractometer. The figure is not drawn to scale, and the divergence-convergence of the x-ray beam is not shown. A, X-ray tube; B, exit slit; C, incident beam; D, scattered beam; E, receiving slits; F, antiscatter slit; G, crystal monochromator; H, detector; S, sample; θ, scattering angle.

thanides in aqueous solutions[6-12] and whether the coordination number(s) change as a function of the lanthanide cation and/or other chemical parameters in such solutions.

Spedding and Mundy[13] have shown that water molecules (in a solvent of 95% water and 5% deuterium oxide) are affected differently by Gd^{3+} than by La^{3+} when the lanthanide is introduced as $LnCl_3$. These findings are consistent with the fact that La^{3+} is nine-coordinated in $LaCl_3 \cdot 7H_2O$,[14] but that Gd^{3+} is eight-coordinated in $GdCl_3 \cdot 6H_2O$.[15] However, it has recently been shown that La^{3+} is eight-coordinated in aqueous solutions of $LaCl_3$[16] and $LaBr_3$,[17] and Morgan[9] has suggested that in aqueous solutions of $Gd(ClO_4)_3$, Gd^{3+} is either eight- or nine-coordinated. The accumulation of thermodynamic,[4,5,18-25] electrochemical,[26-30] spectra,[31-36] and/or formation constant studies[37-40] have not led to definitive assignments of the coordination number(s) or to understanding of the coordination details of the various lanthanides in solutions.

In an attempt to determine the coordination details of Gd^{3+} in very concentrated aqueous solutions, we have examined two aqueous solutions of $GdCl_3$, with and without added hydrochloric acid, via x-ray diffraction methods utilizing Mo Kα x-rays.

Experimental Section

Solutions were prepared by weight from predried anhydrous $GdCl_3$. Densities were measured with a specific gravity bulb. Solution compositions are shown in Table I. Each solution was loaded into a Teflon sample holder, which had a window covered by a 1.0-mil Mylar film, and an x-ray diffraction pattern was obtained using the reflection method.[41] Scattered intensities were collected using our θ-θ diffractometer (Figure 1) as counts per preset time as a function of the scattering angle from $s = 1.23$ to 15.09 Å^{-1} ($s = 4\pi\lambda^{-1} \sin\theta$) at increments in θ of 0.25°. At least three runs over the entire angular range were made for each solution. The average intensity at each scattering point was used in subsequent calculations. For these solutions the maximum value of σ[42] < 1%, and σ is significantly lower at most of the 219 data points at which data were collected.

The scattered intensity was corrected for background (ca. 5 cpm), for polarization,[43] sample penetration,[44] multiple scattering,[45] and, after inclusion of a monochromator discrimination function, Compton scattering.[46] The corrected intensity, e.g., the coherent intensity curve $I(s)$, was then tentatively computer fitted to $\sum x_i f_i^2(s)$,[47] according to the methods of Lawrence and Kruh.[48] Final fitting of $I(s)$ to $\sum x_i f_i^2(s)$ was performed by a method similar to that used by Konnert and Karle.[49] Atomic radial distribution functions (ARDF's) were calculated at increments in Δr of 0.01 and 0.05 Å by[41]

$$D(r) = 4\pi r^2\rho_0 + (2r/\pi) \int [si(s)][M(s)][\sin sr]\, ds$$

With this method $D(r)$ provides a weighted measure of the probability of finding atom pairs in the solution separated by a distance between r and $r + dr$, ρ_0 is the bulk density of the solution, $si(s) = s[I_{coh}(s) - \sum x_i f_i^2(s)]$, and

$$M(s) = \{[\sum x_i f_i(0)/\sum x_i f_i(s)]\}^2 \{\exp(-bs^2)\}USF$$

USF is a unit step function which terminates the integral at $s_{max} = 15$ Å^{-1}.

Shown in Figure 2 are the $i(s)$ functions for the solutions, and in Figure 3 are the ARDF's obtained with $b = 0.010$. Shown in Figure 4 are the atom-pair correlation functions (APCF) (e.g., $g(r) = D(r)/4\pi r^2\rho_0$) obtained for the solutions. Summarized in Table II are the ARDF's.

The area under the first peak in each ARDF was determined via repeated graphical integration, so that deviation from the mean area of each first peak was <2% of the peak area.

For each solution the area anticipated for one Gd-Cl pair (A_{Gd-Cl}) and that for one Gd-O pair (A_{Gd-O}) were calculated by the method of Waser and Schomaker:[50] $A_{Gd-O} = 950$ and $A_{Gd-Cl} = 2400$ e^2.

Both the position of and the area under the first peak have been

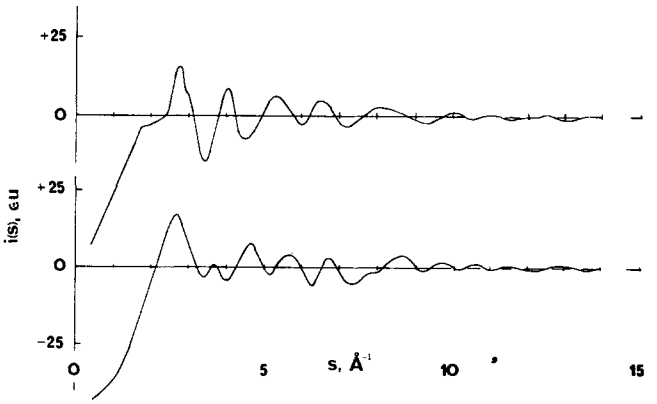

Figure 2. The $i(s)$ functions for the solutions.

Table II. Summary of the ARDF's

	Soln A	Soln B
P1, Å	2.37	2.48
P1A, e^2	114	105
Area per Gd,[a] e^2	7.6×10^3	1.05×10^4
P2, Å	3.2	3.2
P3, Å	3.9	4.0
P4, Å	4.8	5.0
P5, Å	5.9	*b*
P6, Å	6.8	6.9

[a] The area per gadolinium = P1A/mol fraction of gadolinium. [b] This peak is barely discernible in the ARDF of solution B at 5.8 Å.

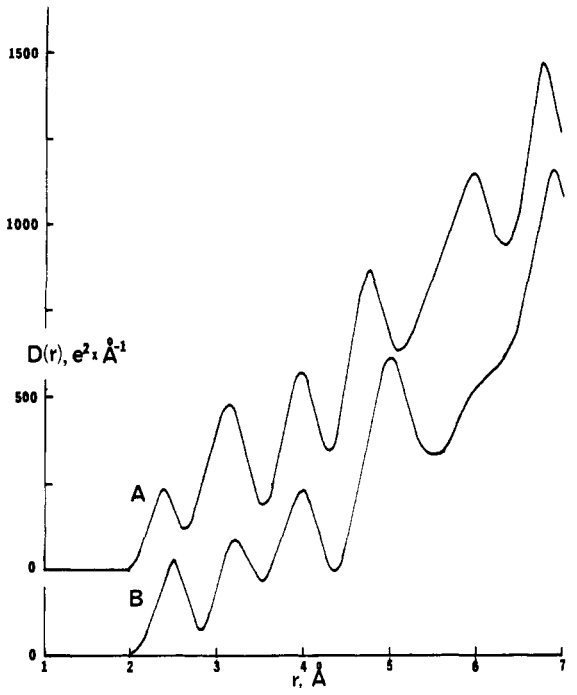

Figure 3. The ARDF's of the two solutions with $b = 0.01$.

utilized to determine the average inner-sphere coordination of Gd^{3+} in each solution by

$$P1 \simeq n_1 d_{Gd-O} + n_2 Q d_{Gd-Cl} \quad (1)$$

$$P1A = n_1 \cdot 950\ e^2 + n_2 \cdot 2400\ e^2 \quad (2)$$

In these equations, n_1 and n_2 are the average number of Gd-O and Gd-Cl contacts per Gd^{3+}, d_{Gd-X_i} are the Gd-O and Gd-Cl distances as determined in crystals, $Q \simeq A_{Gd-Cl}/A_{Gd-O}$, P1 is the location of the first peak, and P1A is the area under the peak in each ARDF.

Based upon this method of correlating the primary peak in the ARDF with the average inner-sphere coordination of a cation, the uncertainty in the determination of the coordination number of the cation is not significantly larger than the uncertainty in the area under the primary peak. In several other solutions,[51] the maximum uncertainty in the coordination number of the cation appears to be less than 0.2, and this is consistent with error estimates by Konnert and Karle.[49]

Results and Discussion

The ARDF's obtained for the two solutions are generally similar, indicating that the average coordination of Gd^{3+} in these solutions is similar. However, as the stoichometric ratio of chloride/gadolinium increases, the maximum of the first peak shifts from ca. 2.37 to ca. 2.48 Å, P4 shifts from 4.8 to 5.0 Å, and P5, a large peak in the ARDF of solution A, becomes barely discernible in the ARDF of solution B. The areas per gadolinium are $7.60 \times 10^3\ e^2$ in solution A and $1.05 \times 10^4\ e^2$ in solution B. The shift in the location of P1 and the increase in the area per gadolinium indicate that there is significantly more inner-sphere Gd-Cl bonding in solution B than in solution A.

Solution A. The location of the first peak (2.37 Å) is consistent with Gd-O inner-sphere bonding,[15,52,53] and the area per gadolinium indicates that each Gd^{3+} has, on the average, ca. eight nearest oxygen (water) neighbors.[54] An eight-coordinated species is consistent with the results obtained from a study of aqueous $LaCl_3$ solutions[16,17] and the coordination of Gd^{3+} in crystalline $GdCl_3 \cdot 6H_2O$.[15] Though P1A can be related to a six-coordinated model, this model requires extensive Gd-Cl as well as Gd-O inner-sphere bonding. The location of P1 indicates that inner-sphere Gd-Cl bonding is unimportant in this solution.

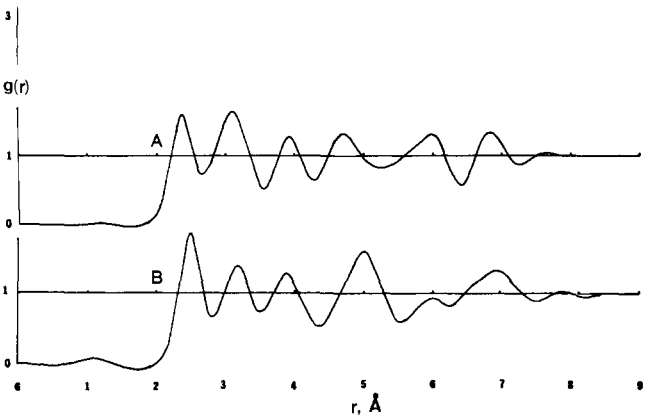

Figure 4. The APCF's of the two solutions. For each solution $g(r) = D(r)/4\pi r^2 \rho_0$.

Solution B. The similarities of the two ARDF's indicate that Gd^{3+} is, on the average, eight-coordinated in solution B as well, with P1 again describing the inner-sphere Gd-ligand interactions. From evaluation of eq 2, the area per gadolinium is consistent with $n_1 \simeq 6.0$ and $n_2 \simeq 2.0$; i.e., the average solute species in solution B is approximately $Cl_2Gd(H_2O)_6^+$.[55] From evaluation of eq 1 and assuming the Gd-O distance is 2.37 Å, the Gd-Cl (inner-sphere) bond distance is estimated to be ca. 2.8 Å. Both the average complex, $Cl_2Gd(H_2O)_6^+$, and the inner-sphere Gd-Cl distance, ca. 2.8 Å, are consistent with the complex ion found in crystalline $GdCl_3 \cdot 6H_2O$.[15]

The Second Peak. In aqueous solutions which contain chloride,[16,51,56-62] hydrogen-bonded Cl-O interactions occur at 3.15-3.30 Å. The ARDF's of both of these solutions exhibit a peak at this distance. Consequently, the existence of P2 neither supports nor eliminates any coordination models, since it is due primarily, if not totally, to hydrogen-bonded Cl-O interactions.

Speculations Concerning the Remaining Peaks. Since in aqueous $LaCl_3$[16] and $ErCl_3$ solutions,[6] ion-pair Ln···Cl interactions occur at 4.7 and 4.6 Å, respectively, P4 in each solution has been assigned to ion-pair Gd···Cl interactions. This peak occurs at 4.8 Å in solution A and 5.0 Å in solution B, where inclusion of chlorides into the inner sphere causes the average ion-pair Gd···Cl distance to be increased. Zachariasen et al. find this interaction at a distance comparable to 5.0 Å in crystalline $GdCl_3 \cdot 6H_2O$, which contains two inner-sphere chlorides.[15]

Solute Modeling. A pseudocubic model of $Cl_2Gd(H_2O)_6^+$ accounts for the ARDF obtained for solution B if it assumed that the outer-sphere chlorides occupy sites adjacent to the faces of the inner-sphere complex. The nonbonded distances consistent with this model are shown in Table III, and the model is shown in Figure 5. The peak observed at 3.2 Å may be attributed to nonbonded Cl···O interactions as well as to hydrogen-bonded Cl-O interactions. The peak at 4.0 Å may be attributed to nonbonded Cl···O interactions (at 4.0 and 4.1 Å), to nonbonded O···O interactions (at 3.9 Å) and to nonbonded Cl···Cl interactions (at 4.1 Å). The peak observed at 5.0 Å may be attributed primarily to outersphere Gd-Cl interactions and also to nonbonded O···O interactions. The peak at 6.9 Å may be attributed to nonbonded Cl···O and nonbonded Cl···Cl interactions.

We have considered several other stereochemical arrangements of this solute species, i.e., $GdCl_2(H_2O)_6^+$, but these models do not account for the ARDF obtained for solution B.

Our attempts to model the stereochemistry of the solute species in solution A, e.g., $Gd(H_2O)_8^{3+}$, have been unsuccessful. Of the several square antiprismatic models and the triangular dodecahedral models that we have considered, all

Table III. A Pseudocubic Model of $Cl_2Gd(H_2O)_6^+$

Atom pair	Distance, Å	No.	Peak in ARDF
$O_a \cdots O_b$	2.7	2 per O	*a*
$Cl_a \cdots O_a$	3.1	3 per Cl_{is}	2
$O_a \cdots O_c$	3.9	2 per O	3
$Cl_a \cdots O_d$	4.0	3 per Cl_{is}	3
$Cl_c \cdots Cl_a$	4.1	1 per Cl_{os}	3
$Cl_c \cdots O_a$	4.1	3 per Cl_{os}	3
$O_a \cdots O_d$	4.7	1 per O	4
Gd-Cl (ion pair)	5.0	1 per Cl_{os}	4
$Cl_a \cdots Cl_b$	5.6	1 per Cl_{is}	*a*
$Cl_c \cdots O_b$	6.7	3 per Cl_{os}	6
$Cl_b \cdots Cl_c$	7.0	1 per Cl_{os}	6
$Cl_c \cdots Cl_d$	7.0	*b*	6
$Cl_c \cdots Cl_e$	10.0	*b*	*a*

[a] A peak in the ARDF does not occur at this distance. [b] The number of times these interactions occur in the ARDF is dependent upon chloride simultaneously occupying these sites in the second coordination sphere.

of these models predict large peaks which do not appear in the ARDF of this solution, and none account for all of the peaks which do appear. A cubic model of $Gd(H_2O)_8^{3+}$ with the chlorides located at sites adjacent to the edges of the cube also cannot account for the ARDF. The cubic model of $Gd(H_2O)_8^{3+}$ with the outer-sphere chlorides located adjacent to faces of the inner polyhedron is consistent with the ARDF of solution A, except that it cannot account for the peak observed at ca. 6.0 Å. This model represents a possible description of the solute species in solution A only if it is assumed that P5 is not due to "rigid" solute structuring, and this assumption cannot be justified.

Consequently it may be concluded that the model described in Figure 5 is consistent with the ARDF of solution B but that no model has been found which accounts for the average solute species found in solution A.

Conclusions

In concentrated aqueous solutions, with and without added hydrochloric acid, Gd^{3+} is eight-coordinated. In the aqueous solution, $Gd(H_2O)_8^{3+}$ is the average cationic species, and the Gd-O bond distance is ca. 2.37 Å. In the presence of a large excess of hydrogen chloride, $Cl_2Gd(H_2O)_6^+$ is the average species, and the inner-sphere Gd-Cl bond distance is ca. 2.8 Å. Ion-pair Gd-Cl bond distances are ca. 4.8 Å in the aqueous solution and ca. 5.0 Å in the acidic solution. A pseudocubic model of $Cl_2Gd(H_2O)_6^+$ represents a plausible description of the stereochemistry of this species, but no model of $Gd(H_2O)_8^{3+}$ is consistent with all of the peaks observed in the ARDF of the aqueous solution.

In aqueous and acidic solutions of $LaCl_3$ and $LaBr_3$, only $La(H_2O)_8^{3+}$ is found, even when the solute is 10.0 N hydrohalic acid.[16,17] That inner-sphere Gd-Cl bonding occurs in solution B indicates that chloride ion is a far better coordinating ligand toward Gd_{aq}^{3+} than toward La_{aq}^{3+}. The different ligand affinities observed for Gd^{3+} and La^{3+} in these very concentrated solutions are consistent with the "different" Raman spectra observed for GdX_3 and LaX_3 solutions.[5] That inner-sphere Gd-Cl bonding occurs in solution B, while no La-Cl inner-sphere bonding occurs in a similar solution, may be explained in two plausible ways: (a) Gd^{3+}, with a significantly larger ionic potential than La^{3+}, is better able to polarize and subsequently to bond to chlorides; and/or (b) the 4f electrons of Gd^{3+} are involved in and necessary for the Gd-Cl inner-sphere bonding. It is, however, beyond the scope of the x-ray diffraction experiments to validate either or both of these speculations.

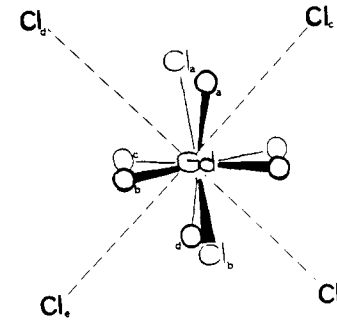

Figure 5. A pseudocubic model of $Cl_2Gd(H_2O)_6^+$. The inner-sphere Gd-O distance is 2.37 Å, and the inner-sphere Gd-Cl distance has been assumed to be ca. 2.8 Å.

The extent to which structural details obtained from these very concentrated solutions may be extrapolated to dilute solutions is unknown.

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(55) Assuming $n_1 + n_2 = 8$, then $n_1 \simeq 6.0$ and $n_2 \simeq 2.0$ to satisfy the relationship $1.05 \times 10^4\ e^2 = n_1 \times 9.5 \times 10^2\ e^2 + n_2 \times 2.4 \times 10^3\ e^2$.
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Quadrupole Coupling Constants of Square-Planar Copper(II)–Sulfur Complexes from Single-Crystal Electron Paramagnetic Resonance Spectroscopy

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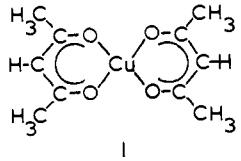
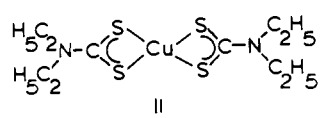
Abstract: The nuclear quadrupole coupling parameters are measured for copper in six square-planar complexes, five having sulfur donor atoms and one having both sulfur and oxygen donors. Computer simulations of the EPR spectra of the Cu-doped powders are employed to refine the principal g and A values. The secondary ($\Delta m_I = 1$) transitions of the EPR spectra of Cu-doped single crystals are analyzed for the quadrupole coupling parameters. The small quadrupole coupling constant for the $Cu-S_4$ complexes ($QD \approx 0.7 \times 10^{-4}\ cm^{-1}$) implies an effectively spherical symmetry which is attributed chiefly to the large covalent character of the Cu-S σ bond. A few anomalies are observed in the quadrupole data. A larger quadrupole coupling constant is observed for diethyl dithiophosphate, $Cu(S_2P(OC_2H_5)_2)_2$, than for other $Cu-S_4$ complexes studied, i.e., 1.8×10^{-4} cm^{-1} compared to $0.7 \times 10^{-4}\ cm^{-1}$. Also, a large asymmetry parameter (QE) is observed for the bis(maleonitriledithiolate) copperate(II), $Cu(mnt)_2^{2-}$, dianion and the mixed S-O square-planar complex copper(II) bis(*cis*-monothiodibenzoylmethanate), $Cu(SdbmO)_2$. The quadrupole coupling parameters may be sensitive to Cu-P transannular interaction in $Cu(S_2P(OC_2H_5)_2)$ and to the strong complex π bonding present in $Cu(mnt)_2^{2-}$.

I. Introduction

In the early 1950's Bleaney[1-3] suggested that quadrupole coupling data could be obtained from single-crystal EPR studies. So and Belford[4,5] examined the secondary (or forbidden $\Delta m_I = \pm 1$) transitions in the single-crystal EPR spectra of several Cu-O complexes, including four square-planar β-ketoenolates (typified by $Cu(acac)_2$, bis(2,4-pentanedionato)copper(II), I) and one square-planar copper(II)-sulfur complex ($Cu(dtc)_2$, bis(diethyldithiocarbamate)-copper(II), II). Recently we reported[6] the quadrupole coupling

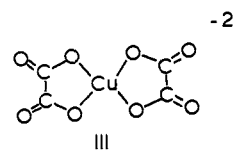


I



II

constant of another square-planar Cu-O complex ($Cu(C_2O_4)_2^{2-}$, bis(oxalato)cuprate(II) dianion, III). These studies have been continued. Here we study several copper(II)-sulfur complexes of square-planar geometry to determine the sensitivity of the quadrupole coupling parameter to more subtle aspects of the electronic structures of the molecules. The quadrupole coupling parameters are obtained from the single-crystal EPR spectra for five square-planar Cu-S complexes: $Cu(dto)_2^{2-}$, bis(dithiooxalate) cuprate(II), IV; $Cu(i\text{-}mnt)^{-2}$, bis(1,1-dicyano-2,2-dithioethylene)cuprate(II), V; $Cu(dtc)_2^{2-}$, II, EPR data repeated; $Cu(S_2P(OC_2H_5)_2)_2$, bis-(diethyl dithiophosphate)coppe!(II) (in Ni host), VI; and $Cu(mnt)_2^{2-}$, bis(1,2-dicyano-1,2-dithioethylene)cuprate(II), VII. We also report data for one mixed sulfur-oxygen donor



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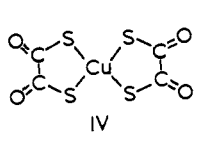

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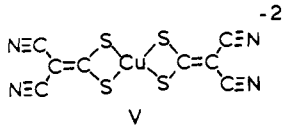

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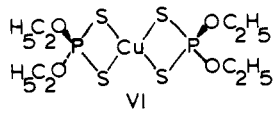

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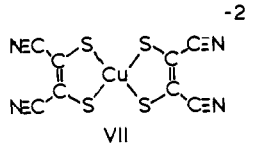
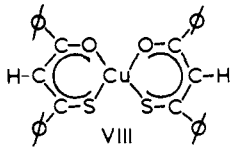


VII



VIII

complex $Cu(SdbmO)_2$, copper(II) bis(*cis*-monothiodibenzoylmethanate) (VIII).

We have employed EPR data obtained from computer simulation of powdered samples to help analyze the single-crystal EPR spectra for these nearly axial systems. The features of the EPR spectrum of a powder are extremely sensitive to the magnitude of the principal g and A values; easily obtainable precisions are ± 0.0003 for g and $\pm 0.3 \times 10^{-4}\ cm^{-1}$ for A. Since the hyperfine interaction in these compounds is much larger than either the nuclear Zeeman or nuclear quadrupole interaction, neither the line positions nor intensities of the primary ("allowed" $\Delta M_I = 0$) transitions are affected substantially by these interactions. Only the electronic Zeeman