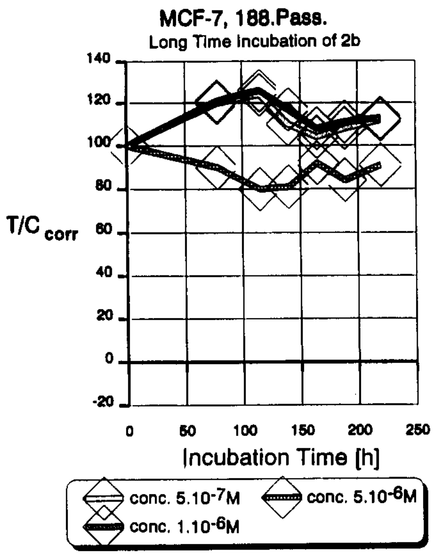

**Figure 4.** Effect of **2b** on the hormone-sensitive human breast cancer cell line MCF-7 plotted as in Figure 2.

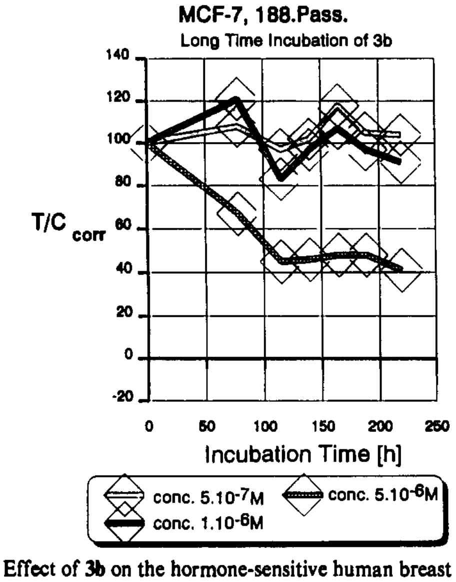

**Figure 5.** Effect of **3b** on the hormone-sensitive human breast cancer cell line MCF-7 plotted as in Figure 2.

liferation kinetics of MCF-7. Cell proliferation is not significantly affected by the nature of the organic solvent. The results of the in vitro chemosensitivity tests against MCF-7 are summarized in Figures 2–5. Figure 2 demonstrates that cell proliferation is inhibited by $10^{-5}$ M Tamoxifen, a clinically established drug in the hormonal treatment of breast cancer. The hormone-sensitive cell line was also inhibited by Cisplatinum (Figure 3). Within the selected concentration range ($5 \times 10^{-7}$, $1 \times 10^{-6}$, and $5 \times 10^{-6}$ M) inhibition was clearly dose-related. No effect was observed for the neutral Pt complex $[\mathrm{PtCl_2(NH_3)(am)}]$ (**2b**) (Figure 4), whereas the cationic compound *cis*-$[\mathrm{PtCl(NH_3)_2(am)}]\mathrm{Cl}$ (**3b**) was cytostatic in a concentration of $5 \times 10^{-6}$ M with a final $T/C_{\mathrm{cor}}$ value of around 40% (Figure 5). The extent of inhibition is comparable with the effect of Tamoxifen. Although we observed a marked antiproliferative effect on the estrogen receptor positive cell line MCF-7, a direct hormonal action seems unlikely because of the cytotoxic potential of **3b** against the L 1210 leukemia of the mouse. According to the generally accepted mechanism of action for platinum anticancer drugs, the positively charged complex must have crossed the cell membrane prior to cross-link formation with the bases of the DNA. Both compounds **2b** and **3b** showed activity against the L 1210 cell line of the mouse (EC 90 = 0.3 μg/mL, 6 days exposure). Complex **3b** was also active in vivo (P388; 46.4 mg/kg: $T/C$ = 150%; $\mathrm{LD}_{50}$ = 158 mg/kg). Compound **3a** showed ED 90 > 1 μg/mL (L 1210).

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# EPR Spectrum and Metal–Ligand Bonding Parameters of a Low-Spin (Hexaamine)iron(III) Complex

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## Introduction

Comparatively few detailed investigations of the EPR spectra of low-spin iron(III) complexes have been undertaken,[1,2] and for those compounds which have been studied, the interpretation of their spectra has been complicated by the fact that the *g* values are very sensitive to the splitting of the $^2T_{2g}$ ground state. This may be difficult to estimate, as the $^2T_{2g}$ state is both Jahn–Teller unstable and strongly influenced by the $\pi$-bonding properties of the ligands. Past studies have sometimes required orbital reduction factors greater than unity, which is chemically unreasonable unless the parameters are modified to include the effects of configuration interaction.[3]

Recently, the preparation of a novel complex of iron(III) with the sexidentate ligand 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (diammac), was reported.[4] The geometry of the cation $[\mathrm{Fe(diammac)}](\mathrm{ClO_4})_3$ is shown in Figure 1. This provides an ideal system to investigate the relationship between the **g** tensor and the metal–ligand bonding parameters of a low-spin iron(III) complex, since simple bonding considerations suggest that $\pi$-bonding interactions with a saturated amine of this kind should be negligible. Moreover, the unit cell of $[\mathrm{Fe(diammac)}](\mathrm{ClO_4})_3$ contains two complex cations in the asymmetric unit, possessing slightly different geometries,[4] which allows the influence of changes in the stereochemistry upon the EPR spectrum to be probed. In contrast to previous studies in which perturbation formulas have been used to relate the *g* values to the energies of higher states,[1] in the current work the **g** tensors are interpreted by carrying out calculations using the computer program CAMMAG, extended to treat the complete $d^5$ basis set. This program, developed in its original version by Gerloch and co-workers,[5] has recently been used to successfully interpret the energy levels and *g* values of a wide range of transition-metal complexes within the framework of the angular overlap model (AOM).[6] The present paper reports the single-crystal EPR spectrum of $[\mathrm{Fe(diammac)}](\mathrm{ClO_4})_3$. The **g** tensors of the two $[\mathrm{Fe(diammac)}]^{3+}$ units present in the complex are interpreted and compared with those reported for other polyamine complexes of Fe(III).

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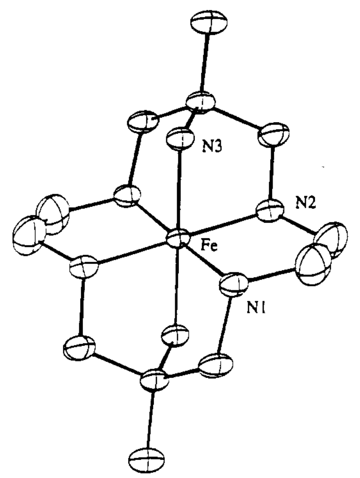

**Figure 1.** Geometry of the [Fe(diammac)]$^{3+}$ complex.

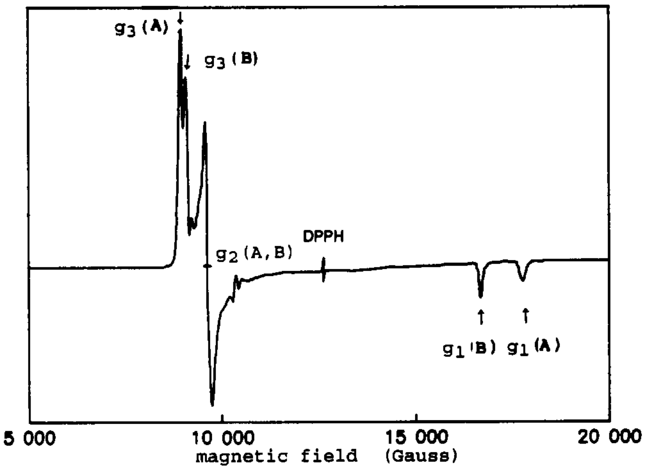

**Figure 2.** EPR Q-band powder spectrum of [Fe(diammac)](ClO$_4$)$_3$ at 4.2 K.

## Experimental Section

The preparation and characterization of [Fe(diammac)](ClO$_4$)$_3$ have been described previously.[4] EPR spectra were recorded by using JEOL JES-FE X-band (single crystals) and Varian E15 Q-band (powder) spectrometers. Crystals were mounted on a quartz rod, cooled, and rotated with respect to the applied magnetic field by using the standard JEOL accessories. The *g* values were measured with reference to the signal of a speck of powdered DPPH (diphenylpicrylhydrazyl, *g* value 2.0037).

The signals observed at room temperature were very broad, but they sharpened considerably on cooling with only minor shifts in the position of the peaks. The spectrum of powdered [Fe(diammac)](ClO$_4$)$_3$ at 4.2 K, recorded at Q-band frequency, is shown in Figure 2. The spectra of several crystals were recorded at ~130 K at X-band frequency for rotations in three orthogonal planes. In general, four signals were observed, due to the four Fe(diammac)$^{3+}$ polyhedra in the unit cell of the compound. Because of the symmetry requirements of the monoclinic space group ($P2_1/c$), these coalesced to two signals, associated with the two magnetically inequivalent FeN$_6$ molecules in the asymmetric unit, when the magnetic field was parallel or normal to the [010] crystal axis. Sets of *g* values for the different polyhedra for three typical rotations are shown in Figure 3. Misalignments of the crystal are responsible for the slight deviations of the angular dependence of the *g* values from the ideal behavior predicted by the crystal symmetry.

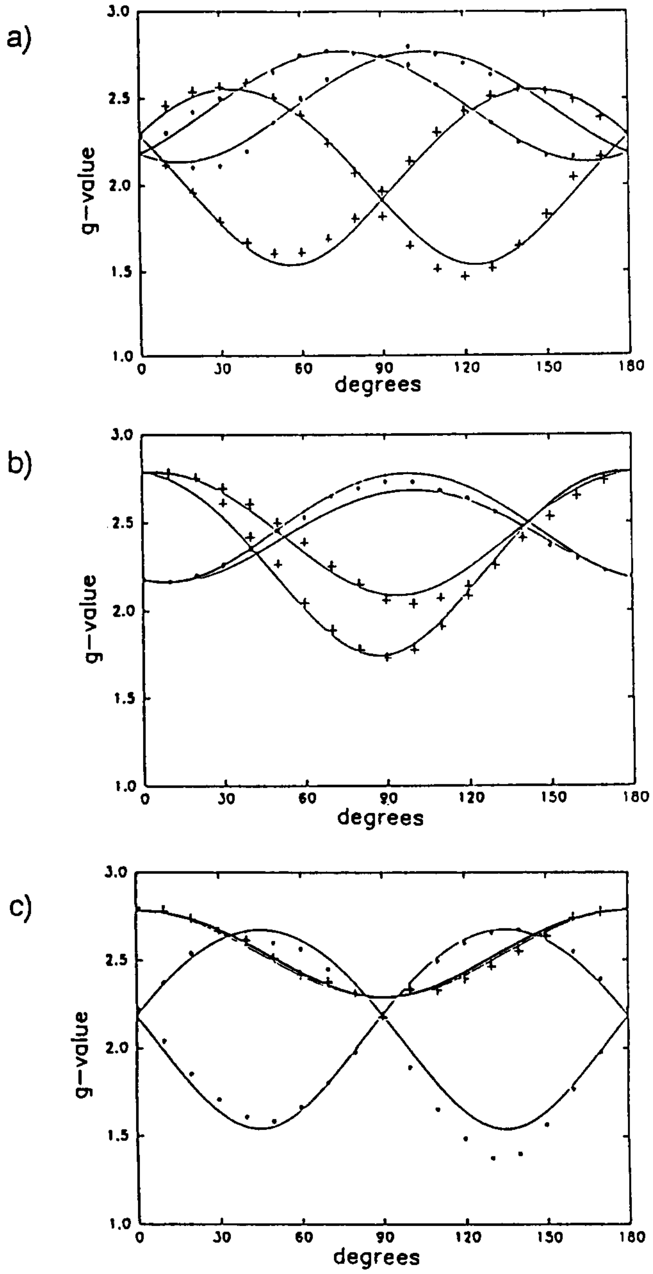

**Figure 3.** Experimental and calculated *g* values of [Fe(diammac)](ClO$_4$)$_3$ for rotations of the magnetic field in (a) the *bc** plane ($\Phi = 90°$, $\theta = 90°$), (b) a plane inclined at 10° to the *ac* plane ($\Phi = 0°$, $\theta = 10°$), and (c) the *ab* plane ($\Phi = 0°$, $\theta = 90°$). See ref 7 for a precise definition of $\Phi$ and $\theta$. Signals assigned to molecule A are shown as dots, and those assigned to molecule B, as crosses.

## Results and Discussion

**Symmetry of the Fe(diammac)$^{3+}$ Complex.** The two complexes in the asymmetric unit of [Fe(diammac)](ClO$_4$)$_3$ have very similar geometries, this being indicated schematically in Figure 1. Both complexes lie on an inversion center and are therefore rigorously centrosymmetric. The equatorial bond lengths to the secondary amines of the macrocyclic ring are nearly equal (1.965 (3) and 1.965 (5) Å for molecule B and 1.951 (4) and 1.961 (4) Å for molecule A) and somewhat shorter than those to the primary amines of the terminal groups (1.982 (4) Å for molecule B and

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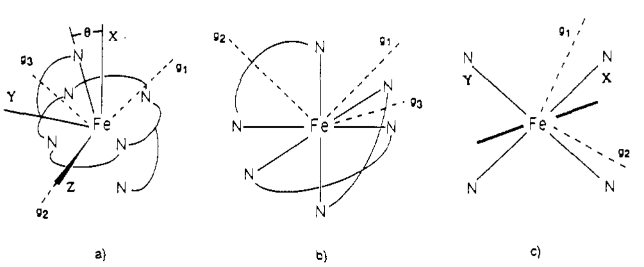

**Figure 4**. Schematic diagram illustrating the orientation of the principal *g* axes of the low-spin Fe(III) complexes: (a) $[Fe(diammac)]^{3+}$; (b) $[Fe(o\text{-}phenan)_3]^{3+}$; (c) $[Fe(TPP)L_2]^+$. See text for the meaning of the ligand abbreviations.

1.985 (4) Å for molecule A). The bonds to the in-plane nitrogen atoms are almost exactly at right angles (at 91.9 and 92.3° for molecules B and A, respectively). However, those to the terminal nitrogen ligands deviate somewhat from the normal to the plane formed by the metal and the four macrocyclic nitrogen atoms (angles of 82.3 and 82.5° are made with the bonds to nitrogen atoms 1 and 2 of molecule B; 83.3 and 83.5° are found for molecule A). The main distortion from a regular octahedral coordination geometry thus involves a rotation of the terminal Fe–N bonds by ~10° in the plane which contains these bonds and bisects the angle between the Fe–N bonds to the secondary N1 and N1′ nitrogen atoms (shown by the angle $\theta$ in Figure 4a). Here, the primes indicate atoms related to their unprimed counterpart by the inversion center (Figure 1). The complex cations thus conform closely to the $C_{2h}$ point group with the 2-fold symmetry axis (**z**) bisecting the angle between the metal–ligand bonds to the secondary amines N1 and N2, as indicated schematically in Figure 4a.

***g* Values of the Complexes.** The principal *g* values and orientations of the **g** tensors with respect to the bond directions of the complexes were deduced by using a computer program and a method described in detail elsewhere.[7] Here, the **g** tensor is calculated by a least-squares fitting procedure in a chosen molecular coordinate system **x**, **y**, **z**. Diagonalization of this tensor yields the principal *g* values and the orientation of the *g* axes with respect to this coordinate system. In the present case, **z** was defined as the vector from the metal to the midpoint of N1 and N2, **x** as the cross product of **z** and the vector from the metal to the midpoint of N1 and N2′, and **y** as the cross product of **z** and **x**.

The *g* value data occur in two sets of symmetry-related signals, and to define the **g** tensors of the two molecules, it is necessary to know which set of resonances is associated with each molecule in the unit cell. Several possibilities were investigated, but only one combination was found to yield **g** tensors which conform to the point group of the complexes by having one principal axis approximately parallel to the molecular symmetry axis **z**. The principal values and the angles made with the molecular axis **x** or **z** axis are shown for the two molecules in Table I. The *g* values associated with these are shown in Figure 3. The values deduced from the powder spectrum are also shown in Table I, with the assignment to the different molecules being that suggested by the calculations (see following section). The powder and crystal values correspond reasonably well; it is likely that the powder values are more accurate, both because better resolution is obtained at Q-band frequency and because the results are not influenced by crystal misalignments. The latter effects are expected to be relatively large because the crystals of the complex invariably formed with poorly defined faces. Moreover, overlapping of the signals often made it hard to resolve the resonances accurately in the single-crystal spectra. However, it is only from the single-crystal spectra that the orientation of the **g** tensors may be established.

**Table I.** Observed and Calculated **g** Tensors of $[Fe(diamac)](ClO_4)_3$

| | obsd | | | calcd | |
|---|---|---|---|---|---|
| | single-crystal | | | | |
| | values | orientation,[a] deg | powder values | values | orientation,[a] deg |
| | | | Molecule A | | |
| $g_1$ | 1.53 | 49/**x** | 1.417 | 1.520 | 51/**x** |
| $g_2$ | 2.55 | 9/**z** | 2.609 | 2.541 | 1/**z** |
| $g_3$ | 2.80 | 48/**x** | 2.812 | 2.882 | 39/**x** |
| | | | Molecule B | | |
| $g_1$ | 1.52 | 44/**x** | 1.514 | 1.665 | 50/**x** |
| $g_2$ | 2.60 | 3/**z** | 2.609 | 2.480 | 2/**z** |
| $g_3$ | 2.81 | 46/**x** | 2.783 | 2.767 | 40/**x** |

[a] Angles are with respect to the molecular axis indicated (see text and Figure 4a).

The **g** tensors of the two independent molecules in the asymmetric unit are quite similar, as is to be expected, given the structural similarity of the complexes. The *g* values have approximate tetragonal symmetry, with $g_1$ considerably lower and $g_2$ and $g_3$ significantly higher than the free-electron value. However, the higher *g* values are split by a significant rhombic contribution, and it is interesting that it is the axis of the middle *g* value which is approximately parallel to the $C_2$ symmetry axis of the complexes. The principal axes of the smallest and largest *g* values lie approximately midway between the molecular **x** and **y** axes, with the axes of the largest *g* values lying in the quadrants containing the terminal Fe–N bonds. The **g** tensor orientation is shown in Figure 4a.

**Metal–Ligand Bonding in the Complexes.** Although the $[Fe(diammac)]^{3+}$ complex cations deviate only slightly from a regular octahedral geometry, it is this lowering in symmetry which must be responsible for the highly anisotropic nature of the **g** tensors. The effects of the angular distortions and differences in the metal–ligand bonding parameters upon the electronic structure of the complexes were investigated with use of the computer program CAMMAG developed by Gerloch and co-workers.[5] This program calculates the **g** tensor and electronic transitions of a complex within the framework of the angular overlap model (AOM), using as input the crystal structure data and a set of metal–ligand bonding parameters. In the original version, only a limited basis set was used for the $d^5$ electron configuration, but for the present problem CAMMAG was extended to include all the terms of all multiplicities as basis functions for the calculations. To check the modification of the program, the energies from a full $d^5$ calculation, including interelectron repulsion and spin–orbit coupling, were compared with results given in the literature for complexes involving cubic[8] and trigonal[9] ligand fields. As the calculation requires the diagonalization of a 252 × 252 matrix, several strategies have been used to minimize the computing time.

For a complex of $C_{2h}$ symmetry, the matrix can be halved so that only one member of the Kramers doublet needs to be calculated.[10] In contrast to symmetry blocking, where a number of smaller matrices need to be diagonalized, in this case only a single matrix of half the size needs diagonalization. Although a calculation with a complete basis set is necessary to obtain accurate ground-state wave functions, only this ground state wave function is required to calculate the *g* values. The problem is then ideally suited for diagonalization using the Lanczos algorithm,[11] which finds extreme eigenvalues and eigenvectors very efficiently. Typical CPU times on a VAX 6410 computer for a full basis $d^5$ calculation of the ground-state *g* values were 520 s for the full diagonalization of the 252 × 252 matrix, 200 s for the full diagonalization of the "halved" matrix, and 10 s for a Lanczos

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diagonalization of the "halved" matrix.

An approximate estimate of the metal–ligand bonding parameters in $[Fe(diammac)]^{3+}$ may be obtained from the electronic spectrum of the analogous chromium(III) complex (the transition energies observed for the Fe(III) complex cannot easily be used directly for this purpose, as they depend upon interelectron repulsion as well as the metal–ligand interaction). The structures[12] of the $[Cr(diammac)]^{3+}$ units in $[Cr(diammac)](ClO_4)_3$ are very similar to those in the analogous Fe(III) compound, suggesting that the two complexes should have similar bonding parameters. The lowest energy spin-allowed band in the electronic spectrum of an aqueous solution of $[Cr(diammac)](ClO_4)_3$ occurs at 23 420 $cm^{-1}$, and the spectrum of a single crystal also consist of a single, essentially unpolarized peak at this energy. Simple bonding theory suggests that the $\pi$-bonding parameters of the saturated amines should be negligible, and the energy of the first spin-allowed transition then occurs at $3e_\sigma$, where $e_\sigma \cong 7800$ $cm^{-1}$ is the average $\sigma$-antibonding parameter of the amine ligands. The fact that the bonds to the terminal nitrogen atoms are slightly longer than those involving the macrocyclic ring nitrogen atoms suggests that the terminal ligands form slightly weaker $\sigma$-bonds than the in-plane ligands. However, the fact that no splitting of the bands is resolved in the electronic spectrum indicates that the difference between the bonding parameters of the in-plane and terminal amines is small.

The parameters

$$e_\sigma(\text{terminal}) = 7500\ cm^{-1} \qquad e_\sigma(\text{in-plane}) = 8000\ cm^{-1}$$

are consistent with the optical spectrum of $[Cr(diammac)](ClO_4)_3$, and these were used to calculate the energy levels and **g** tensors of the complexes in $[Fe(diammac)](ClO_4)_3$ by using the computer program CAMMAG. The Condon–Shortly parameters $F_2 = 786$ $cm^{-1}$ and $F_4 = 57$ $cm^{-1}$ reported previously for the complex $[Fe(ethane\text{-}1,2\text{-}diamine)_3]Cl_3$ were used in these calculations.[13]

As expected from their similar geometries, molecules A and B were calculated to have very similar energy levels, with spin-doublet ground states lying some 13 000 $cm^{-1}$ below the nearest spin-quartet states. The $^2T_{2g}$ ground state of a regular octahedral low-spin Fe(III) complex is expected to split into a lower level of $^2A_g$ symmetry and two higher levels of $^2B_g$ and $^2A_g$ symmetries in a complex having the idealized $C_{2h}$ symmetry illustrated in Figure 4a. In the absence of spin–orbit coupling, the two upper levels were calculated to lie at ~1330 and ~1675 $cm^{-1}$ for $[Fe(diammac)]^{3+}$, with the assignment being unknown. The next nearest spin-doublet levels were calculated to occur in two groups of closely spaced levels lying between 20 500 and 24 600 $cm^{-1}$ and between 27 000 and 35 000 $cm^{-1}$, respectively. This agrees with the electronic spectrum reported[4] for an aqueous solution of $[Fe(diammac)](ClO_4)_3$, which shows bands centered at ~21 000, 24 000, 30 000, and 34 000 $cm^{-1}$.

**Calculated g Tensors of the $Fe(diammac)^{3+}$ Complexes.** The molecular *g* values calculated for the two $[Fe(diammac)]^{3+}$ complexes by using CAMMAG are also in reasonable agreement with the observed values (Table I), assuming a value of the spin–orbit coupling constant of 375 $cm^{-1}$ and an orbital reduction parameter $k = 0.95$. The spin–orbit coupling constant is reduced somewhat from the value[14] of 460 $cm^{-1}$ for a free $Fe^{3+}$ ion. This is to be expected, first because the effective charge on the metal will be reduced from the free-ion value (a reduction to an effective charge of 2+ would produce a value of 400 $cm^{-1}$)[14] and second because the unpaired spin density is delocalized onto the ligands. In the present case, the latter effect is expected to be relatively small. This is because spin–orbit coupling influences the *g* values by mixing excited states into the ground state, and both the low-lying $^2B_g$ and $^2A_g$ states and the ground state itself are composed of d orbitals which only interact weakly with the $\sigma$-bonding amine ligands. The parameter *k* describes the reduction of orbital angular momentum within the ground state, so that for the same reason a value marginally less than unity seems reasonable for the present complexes. Previous interpretations[3] of the *g* values of low-spin Fe(III) complexes which have used perturbation methods have sometimes required the use of *k* values greater than unity, which seems chemically unreasonable unless the interpretation of this parameter is extended to include the effects of configuration interaction.

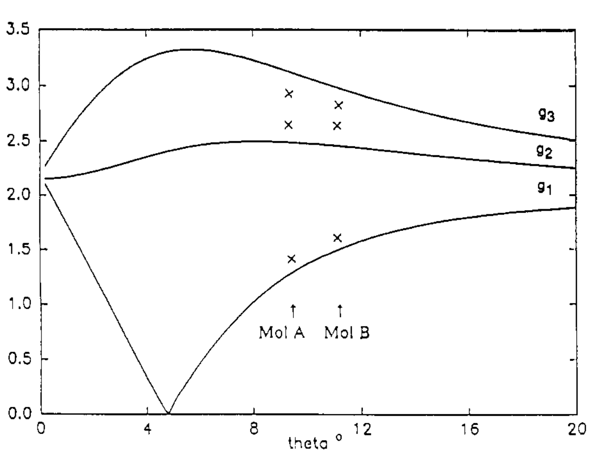

**Figure 5.** Dependence of the *g* values of a model octahedral Fe(III) complex $ML_6$ upon the angular distortion ($\theta$) of a pair of trans M–L bonds in the plane bisecting opposite angles LML formed by the remaining M–L bonds. Such a distortion is shown schematically in Figure 4a; an angle $\theta = 0°$ corresponds to a regular octahedral geometry.

**Influence of the Ligand Field Symmetry on the g Tensor.** In agreement with experiment, the middle *g* value is calculated to lie close to the symmetry axis of each complex, with the lowest *g* value rotated ~50° away from the normal to the macrocycle ring in an opposite sense to the rotation of the bonds to the terminal amine groups (Figure 4a). Also in agreement with experiment, the two higher *g* values of molecule A are quite similar to those of molecule B, but the smallest *g* value of the second molecule is slightly larger than that of the first molecule.

In order to investigate the effects of the different low-symmetry components of the ligand field, CAMMAG was used to model the influence upon the **g** tensor of the angular distortion of the bonds and the difference in $\sigma$-bond strength of the amines. Varying the difference between the $\sigma$-bonding parameters of the terminal and in-plane amines was found to have little effect upon the **g** tensor. This is not surprising, as such a $\sigma$-anisotropy affects the splitting of the $e_g$ orbitals of the parent octahedral complex, and these contribute little to the ground-state wave function of a low-spin $d^5$ complex. However, the distortion of two bonds away from the normal to the other four toward the bisector of the in-plane bond angles (to mimic the geometry shown in Figure 4a) has a pronounced effect upon the *g* values, as indicated in Figure 5. Here, identical values were assumed for the amine bonding parameters ($e_\sigma = 7500$ $cm^{-1}$). It may be seen that the **g** tensor very rapidly diverges from cubic symmetry, with one value falling steeply toward zero and the other two rising to maxima at a distortion angle of ~5°. A rapid rise of the lowest *g* value is then accompanied by a slow fall of the two higher *g* values. The direction of the mid *g* value lies exactly along the molecular **z** axis (the symmetry axis of the model complex). The effects of the distortion upon the principal directions of the highest and lowest *g* values were also investigated. It was found that essentially as soon as $\theta$ becomes nonzero (>0.2°), these *g* axes orientate to lie close to the bisectors of the molecular **x** and **y** axes (defined as in Figure 4a) and remain in this position over the whole range of $\theta$ values investigated. It should be noted that the choice of the directions of **x** and **y** is quite arbitrary in a complex of $C_{2h}$ symmetry, since these axes do not conform to a symmetry element of the point group. The present definition was chosen so that **x** and **y** coincide with the axes of the regular octahedral which occurs when the angular distortion reduces to zero.

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Despite the fact that the model complex deviates from a regular octahedral only as a result of a single angular distortion, the **g** tensor is always highly rhombic. This is consistent with the low symmetry of the point group produced by the distortion ($C_{2h}$). With the coordinate system defined as in Figure 4a, the unpaired electron is expected to be in an orbital of $A_g$ symmetry, largely $d_{xy}$ in character. The experimental *g* values observed for the two $[Fe(diammac)]^{3+}$ complexes are also shown in Figure 5, and it may be seen that the lowest *g* values of the two molecules are readily resolved in the Q-band EPR spectrum, despite the similarity of their geometries, because of the extreme sensitivity of this parameter to the angular distortion. Although this is only marginally greater for molecule B than for molecule A (11.0° compared with 9.5°), it produces a readily detectable difference in the value of $g_1$ (Figure 2 and Table I). It is noteworthy that the effect is expected to be even more pronounced for a similar complex with a smaller distortion, and "strain broadening" might make this component of the **g** tensor difficult to detect in a powder or solution EPR spectrum of such a molecule.

**Comparison with Other Low-Spin Fe(III) Complexes.** It is of interest to compare the **g** tensor of $[Fe(diammac)]^{3+}$ with those reported for iron(III) complexes involving other amines. The *g* values reported[15] for the complex $[Fe(o\text{-phen})_3]^{3+}$ ($g_1 = 1.459$, $g_2 = 2.615$, $g_3 = 2.727$; *o*-phen = 1,10-phenanthroline) are rather similar to those of the present complex, except that they approach axial symmetry more closely. However, the symmetry of the 1,10-phenanthroline complex is quite different from that formed by the hexadentate diammac ligand. All six Fe–N bond lengths in $[Fe(o\text{-phen})_3]^{3+}$ are equal within experimental error, and the dominant distortion from octahedral symmetry is caused by the small "bite" of the three chelate rings (83.0°). This lowers the point group to $D_3$, and it was found that the smallest *g* value lies very close to the $C_3$ symmetry axis of the complex, as illustrated schematically in Figure 4b. It was proposed[15] that the slight inequivalence of the two higher *g* values is caused by minor distortions away from exact $D_3$ symmetry.

The magnetic properties of $[Fe(o\text{-phen})_3]^{3+}$ are not readily explicable on the basis of crystal field theory,[16] and it is of interest to see whether *g* values in reasonable agreement with experiment may be reproduced by using the angular overlap model. The sensitivity of the **g** tensor of $[Fe(o\text{-phen})_3]^{3+}$ to the $\sigma$- and $\pi$-bonding parameters of the amine was therefore investigated by using the computer program CAMMAG and the reported crystal structure[15] of the perchlorate salt. Taking the values of the interelectron repulsion and spin–orbit coupling parameters to be identical with those used for $[Fe(diammac)]^{3+}$ yielded *g* values for $[Fe(o\text{-phen})_3]^{3+}$ in excellent agreement with experiment ($g_1 = 1.463$, $g_2 = 2.615$, $g_3 = 2.758$ compared with the experimental values $g_1 = 1.459$, $g_2 = 2.615$, $g_3 = 2.727$) assuming an orbital reduction parameter of $k = 0.9$, and bonding parameters $e_\sigma = 8000$ cm$^{-1}$ and $e_{\pi y} = -500$ cm$^{-1}$ for the *o*-phenanthroline ligand. Here, $e_{\pi y}$ refers to the out-of-plane $\pi$-bonding parameter, with the in-plane parameter being set to zero, as has generally been assumed for aromatic amines. Not only do the magnitudes of the *g* values agree well, but $g_1$ was calculated to lie parallel to the $C_3$ symmetry axis of the complex, as observed experimentally (the calculated and observed directions of $g_2$ and $g_3$ do not agree well, but as already noted, the orientation of these *g* axes is poorly defined, since their slight anisotropy is caused by minor deviations from $D_3$ symmetry).

The negative sign of $e_{\pi y}$ implies that *o*-phenanthroline is functioning as a weak $\pi$-acceptor. Similar $\pi$-acceptor character has been inferred for other aromatic amines.[17] A range of possible bonding parameters were explored in the calculations, and agreement with experiment was always poorer when positive values of $e_{\pi y}$ were used. For instance, values of $g_1 = 1.281$, $g_2 = 2.732$, $g_3 = 2.783$ were obtained, leaving all other parameters unaltered but setting $e_\sigma = 9000$ cm$^{-1}$ and $e_{\pi y} = 500$ cm$^{-1}$ (note that a higher value of $e_\sigma$ is required to maintain a similar splitting of the $\sigma$- and $\pi$-bonding orbitals when a positive value is taken for $e_{\pi y}$). The above bonding parameters imply that for $Fe(o\text{-phen})_3{}^{3+}$, in the absence of spin–orbit coupling, the $^2T_{2g}$ ground state of the parent octahedral complex is split to give an orbital singlet ground state and slightly split components of an upper $^2E$ state at 1055 and 1210 cm$^{-1}$. The average splitting is fairly similar to the estimate of ~800 cm$^{-1}$ inferred[16] from the magnetic susceptibility of this complex by assuming a somewhat lower orbital reduction parameter for the complex.

The *g* values of the $[Fe(diammac)]^{3+}$ ions are also rather similar to those observed[2] for a range of Fe(III) porphyrin complexes in which the axial coordination sites are occupied by amines such as substituted imidazoles. Although the ligands involved in these latter complexes are quite different from that in $[Fe(diammac)]^{3+}$, their general symmetry also conforms closely to the $C_{2h}$ point group. This may be seen from the schematic diagram in Figure 4c, which pictures a typical complex viewed down the normal to the porphyrin ring. The imidazole rings are coplanar, this plane making an angle which ranges from 6 to 41° to the closest in-plane Fe–N bonds. For these complexes, the **z** axis of the $C_{2h}$ point group lies along the Fe–N(imidazole) bonds.

Calculations using CAMMAG were carried out for the complexes $[FeTPP(tMU)_2]SbF_6$ and $[FeTPP(cMU)_2]SbF_6$ (TPP = tetraphenylporphyrinato; tMU/cMU = *trans-cis*-methylurocanate) for a range of possible metal–ligand bonding parameters. The latter complex contains two magnetically different polyhedra in the asymmetric unit.[2] Reasonable agreement of the *g* values with those observed experimentally ($g_1 = 1.47$, $g_2 = 2.27$, $g_3 = 2.96$ for $[FeTPP(tMU)_2]SbF_6$ compared with calculated values of $g_1 = 1.39$, $g_2 = 2.27$, $g_3 = 2.87$; $g_1 = 1.48$ (A), 1.49 (B), $g_2 = 2.26$ (A), 2.30 (B), $g_3 = 3.00$ (A), 2.96 (B) for $[FeTPP(cMU)_2]SbF_6$ compared with calculated values of $g_1 = 1.41$ (A), 1.38 (B), $g_2 = 2.26$ (A), 2.30 (B), $g_3 = 2.85$ (A), 2.86 (B)) was obtained by using interelectron repulsion and spin–orbit coupling parameters identical with those of $[Fe(diammac)]^{3+}$, with an orbital reduction parameter of $k = 0.9$ and bonding parameters of $e_\sigma = 8000$ cm$^{-1}$ and $e_{\pi y} = 400$ cm$^{-1}$ for the porphyrin nitrogen atoms and $e_\sigma = 8500$ cm$^{-1}$ and $e_{\pi y} = 400$ cm$^{-1}$ for the imidazole ligands. The in-plane $\pi$-bonding of the amines was again assumed to be negligible. These parameters imply that both the porphyrin and the imidazole ligands function as weak $\pi$-donors, and the use of negative values of $e_{\pi y}$ in calculations, corresponding to $\pi$-acceptor character for the amines, was found to produce an orientation of the **g** tensors in disagreement with experiment. The $\pi$-donor character of these ligands is in agreement with previous interpretations of the EPR parameters.[2] Moreover, substituted imidazole ligands have also been found to act as $\pi$-donors in several complexes of Ni(II).[18,19]

It is interesting to compare the splitting of the $^2T_{2g}$ ground state implied by the present calculations with those obtained by Strouse et al.[2] using the formulas of Taylor,[20] which were derived by assuming that the *g* shifts are dominated by the distribution of the unpaired spin density within the $(t_{2g})^5$ configuration of the parent octahedral complex. In the latter calculations,[2] the energy levels were estimated as multiples of the spin–orbit coupling constant, and assuming this to have a value of 375 cm$^{-1}$, the energy of the baricenter of the upper $^2E_g$ state, $\Delta$, was estimated as 1155 cm$^{-1}$ for $[FeTPP(tMU)_2]SbF_6$ and 1208 cm$^{-1}$ (A), 1133 cm$^{-1}$ (B) for $[FeTPP(cMU)_2]SbF_6$, while the splitting of the $^2E_g$ state, *V*, was estimated as 675 cm$^{-1}$ and as 664 cm$^{-1}$ (A), 690 cm$^{-1}$ (B), respectively. The present calculations imply values of $\Delta = 1538$ cm$^{-1}$ and $\Delta = 1547$ cm$^{-1}$ (A), 1533 cm$^{-1}$ (B) and of $V = 797$ cm$^{-1}$ and $V = 816$ cm$^{-1}$ (A), 813 cm$^{-1}$ (B), for the two complexes, respectively. The overall pattern implied by the two calculations

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is very similar, though the present approach involving diagonalization of the $d^5$ ligand field matrix yields estimates of the splitting of the $^2T_{2g}$ ground state which are ~15–25% larger than those derived by using the formulas of Taylor.

The orientations of the **g** tensors calculated for the porphyrin complexes are in excellent agreement with those observed experimentally. The largest *g* value was found to be parallel to the $C_2$ axis of each complex (the Fe–N(imidazole) bond directions). The other principal *g* axes are rotated away from the Fe–N(porphyrin) bond vectors, and the calculated rotation angles (23° for $[FeTPP(tMU)_2]SbF_6$ and 26° (A), 11° (B) for $[FeTPP(cMU)_2]SbF_6$) agree well with those observed experimentally (22° and 29° (A), 15° (B), respectively). Here, the rotation angle refers to the smallest *g* value, and rotation occurs in the direction opposite to that of the plane of the imidazole ligand (Figure 4c). It has been pointed out[2,21] that, in complexes such as these, the orientation of the **g** tensor will be dominated by the $\pi$-interactions with the amine ligands. The unpaired electron density is likely to be concentrated in the orbital of $\pi$-symmetry normal to the plane of the axial ligands. For the coordinate system shown in Figure 4c, the ground state will be of $^2B_g$ symmetry and will consist largely of a linear combination of the $d_{xz}$ and $d_{yz}$ orbitals. The rotation of the principal *g* axes away from the Fe–N bond directions is caused largely by coupling with the low-lying $^2A_g$ state, in which the unpaired electron occupies the $d_{xy}$ orbital.[2,21]

For $[Fe(diammac)]^{3+}$, the dominant distortion from octahedral symmetry is due to the angular distortion of the terminal amine groups, and a simplistic interpretation might infer that, for the coordinate system shown in Figure 4a, the unpaired density should occupy the $d_{xy}$ orbital. This would imply that the principle axis of the approximately axially symmetric **g** tensor, $g_1$, should lie along the **z** axis of the complex. Instead, $g_1$ approximately bisects the molecular **x** and **y** axes. In the $C_{2h}$ point group of the complex, $d_{xy}$, $d_{x^2-y^2}$, and $d_{z^2}$ all belong to the $A_g$ representation, and it seems likely that the unpaired electron occupies an orbital composed of a mixture of these d functions, having lobes approximately normal to the $g_1$ principal axis. In both $[Fe(diammac)]^{3+}$ and $[Fe(o\text{-}phen)_3]^{3+}$, the deviation of the ligand field from octahedral symmetry is largely caused by angular distortions, and the orientation of the **g** tensors of the two complexes is remarkably similar when considered in this light. In $[Fe(o\text{-}phen)_3]^{3+}$, the deviation is due to the "bite" of each chelate ring being less than 90°, and the lowest *g* value is directed away from the three acute NFeN angles (Figure 4b). In just the same way, the lowest *g* value of $[Fe(diammac)]^{3+}$ is directed away from the two acute NFeN angles in this complex (Figure 4a).

## Conclusions

It has been found that the rhombic **g** tensors measured for the two $[Fe(diammac)]^{3+}$ complexes present in $[Fe(diammac)](ClO_4)_3$ may be interpreted satisfactorily by using the angular overlap model. This model has also been applied successfully to the interpretation of the **g** tensors reported for iron(III) *o*-phenanthroline and porphyrin complexes. The orientation of the **g** tensor has been related to the way in which the ligand field deviates from octahedral symmetry in each complex. As expected, the **g** tensor in each case conforms to the point group symmetry of the complex. However, the relationship of the electronic structure to the molecular geometry of $[Fe(diammac)]^{3+}$, of $C_{2h}$ symmetry, seems more closely analogous to that of $[Fe(o\text{-}phen)_3]^{3+}$, of $D_3$ symmetry, than to the porphyrin complexes which also belong to the $C_{2h}$ point group.

Because the angular overlap model relates the **g** tensor directly to the molecular geometry and metal–ligand bonding parameters, both features of interest to nontheoretical chemists, it should provide a particularly useful method of interpreting the **g** tensors of biologically important molecules. Low-spin iron(III) complexes of biological significance have been the subject of numerous EPR investigations, and we are currently applying the model to the interpretation of the **g** tensors reported for a range of molecules of this kind.

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# Cysteine Complexes of Oxoruthenium(VI): Synthesis and Characterization of $Ru(O)_2L_2\{SCH_2CHRC(O)O\}$ (L = py, $^1/_2$ bpy; R = H, NHCHO, NHCOMe)

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## Introduction

In the biosynthesis of isopenicillin N, it has been proposed that coordination of $\alpha$-aminoadipoyl-L-cysteinyl-D-valine to an oxidized (ferryl) iron center occurs through the cysteinyl sulfur and the valine nitrogen.[1] The active site of this metalloenzyme, isopenicillin N synthetase (IPNS), has been studied spectroscopically by several groups who found that the iron center in the reduced enzyme is non-heme and is coordinated to histidine, water, and a cysteine residue.[2]

Transition-metal complexes of cysteine(2−) derivatives possessing monodentate coordination of the ligand through sulfur,[3] bidentate coordination through sulfur and nitrogen,[4] or tridentate coordination with sulfur, nitrogen, and oxygen atoms[5] have been previously prepared. Other species are insoluble polymers, presumably with bridging cysteine ligands.[6]

As a part of our efforts to model the active site of isopenicillin N synthetase, we have prepared high-oxidation-state complexes

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