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Prediction and Interpretation of EPR Spectra of Low-Spin Iron(III) Complexes with the MM–AOM Method

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The *g*-values of low-spin iron(III) complexes of *trans*-diammac (*trans*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine), tris-en (ethane-1,2-diamine), tris-phen (1,10-phenanthroline), tris-bipy (2,2′-bipyridine), and bis-terpy (2,2′:6′,2″-terpyridine) have been determined with angular overlap model (AOM) calculations based on structural parameters calculated with molecular mechanics (MM) calculations (MM–AOM approach). A constant set of e_σ and e_π parameters, corrected for bond length differences, was employed. There is good agreement between calculated and experimental EPR data. Regions of possible inaccuracies due to very strong dependency of the *g*-values from certain normal modes were identified by model AOM calculations as a function of the corresponding geometric parameter. In the case of [Fe(*trans*-diammac)]$^{3+}$ the conformations of the five-membered chelate rings (disordered in the published crystal structures) are discussed in some detail. The calculated *g*-values of [Fe(en)$_3$]$^{3+}$ are discussed on the basis of a previously reported spectrum, and some inconsistencies with the calculations are discussed on the basis of a remeasured spectrum. The calculated spectra of [Fe(bpy)$_3$]$^{3+}$ and [Fe(phen)$_3$]$^{3+}$ are in good agreement with the reported experimental data. With [Fe(terpy)$_2$]$^{3+}$ it is demonstrated that the published EPR spectrum is, in contrast to earlier analyses, due to a highly distorted species (C_1), and this is also in agreement with other published observations.

Introduction

Iron is an important metal in a number of biological systems. Of special interest are iron–sulfur cluster compounds and low-spin iron(III) porphyrins. Therefore, the electronic properties of low-spin iron(III) complexes have attracted considerable attention.[1,2] EPR spectra are of special interest because of the generally large variation of *g*-values. Earlier interpretations have involved ligand field models.[3] Major problems with these included chemically unreasonable values for the orbital reduction factor *k* of larger than unity and the fact that the structures of the chromophores could not be related to the experimental spectra on more than a qualitative basis.[4–10] In a recent publication it was demonstrated that the electronic properties of low-spin iron(III) complexes may be interpreted with angular overlap model (AOM) calculations.[11] With this approach the *g*-values and the orientation of the **g**-tensors are calculated accurately with a chemically reasonble parameter set.

One of my aims is to design transition metal chromophores with given properties, a scheme which might be particularly important in the synthesis of (spectroscopic) model compounds for biological systems. The general approach involves the prediction of structures and their influence on spectroscopic properties. It was shown previously that the molecular mechanics (MM) technique is a powerful tool for accurate predictions of geometries of transition metal complexes.[12,13] The *interpretation* of electronic properties of transition metal complexes with the AOM formalism, based on experimental structural data, has been applied successfully in many cases.[11,14,15] *Prediction* of spectroscopic properties requires a prior knowledge of the structure of the chromophore and some electronic parameters. Of particular importance are two questions: (i) Are the calculated structures (MM) accurate enough such that at meaningful prediction of the energy levels is possible and (ii) are the AOM e_σ and e_π parameters predictable, viz. transferable within transition metal complexes of a given metal ion and donor set? The transferability of ligand field parameters is questionable, and this has been discussed in some detail in the literature.[16–18] The fact that in studies involving the MM–AOM approach I use a constant set of ligand field parameters for a given chromophore, adjusted only for structural changes based on the structures that have been optimized via force field calculations, does not imply that I understand full transferability as a fact. However, the results presented here and in similar studies[19,20] indicate that the errors due to this approximation are acceptable, especially in view of the appealing approach to

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predict and interpret spectroscopic properties of structurally unknown transition metal compounds with a rather simple and general method and with acceptable accuracy.

The MM–AOM approach has already been used successfully for hexaamines of chromium(III), cobalt(III), and nickel(II),[19] and it is presently tested with other chromophores. Two rather demanding systems are copper(II) and low-spin iron(III) systems: (i) Copper(II) complexes are known to exhibit a number of different geometries involving four-, five-, and six-coordination. Also, the usually Jahn–Teller labile ground states lead to coordination geometries which are not easy to predict accurately within the strain energy minimization formalism. Jahn–Teller-distorted structures with distortion modes predetermined by the ligand system as in the N_4O_2 chromophores of tetraazamacrocycles have already been calculated with high accuracy,[12,13] and a general algorithm for the optimization of Jahn–Teller-distorted systems is presently being developed.[21] The major inconsistencies in terms of the computed spectroscopic properties have been traced back to misdirected valences (bent bonds), and once this problem has been addressed there is acceptable agreement between calculated and experimental data.[20] (ii) The high sensitivity of low-spin iron(III) *g*-values to structural variations and their large anisotropy imply that a meaningful prediction must be based on rather accurate structural parameters. On the basis of a number of examples presented herein, the MM–AOM method will be shown to be a powerful tool for the prediction and interpretation of EPR spectra of low-spin iron(III) complexes.

Experimental Section

$[Fe(en)_3]Cl_3$ and [Fe(*trans*-diammac)]Cl_2·ClO_4 were prepared as described in the literature.[22,23] X-band EPR spectra (undiluted powders) were recorded at 4 K (tris-en complex) and 77 K (diammac complex). The spectra were analyzed by simulations using EPR50F.[24] The *g*-values of the final simulations are given in Tables 2, 4, and 8, and the line widths (half-width at half-height of absorption for Lorentzian and half-peak to peak width of the first derivative for Gaussian lines; line widths determined by the *g*- and *A*-strain formalism[24]) were varied between ca. 100 and 500 G to obtain optimal fit of the spectral profiles.

Molecular Mechanics Calculations were performed with MOMECPC.[25] The functional forms and force field used have been described previously.[12] ORTEP[26] files were produced with the program CONVERSION.[25]

AOM Calculations were performed with a modified version[11] of the FORTRAN program CAMMAG.[27] In this approach the *g*-values are assumed to be those due to isolated Kramers doublets. The Zeeman operator is applied to the wave functions after ligand field diagonalization.[14,28] The methods used for matrix diagonalization involving the full d^5 basis with chromophores of various point groups have been described in the literature.[11,29] The e_σ and e_π parameters were similar to those used in previous work.[11] They were adjusted for metal–ligand bond length differences (X-ray or MM structural parameters) with $1/r^6$[19,20,30] from $e_\sigma = 7500\ cm^{-1}$ and $e_\pi = 0\ cm^{-1}$ for Fe–N = 1.985 Å (aliphatic amines; π-bonding of saturated amines is negligible) and $e_\sigma = 7900\ cm^{-1}$ and $e_{\pi y} = -500\ cm^{-1}$ for Fe–N = 1.968 Å (aromatic amines; $e_{\pi y}$ refers to the out-of-plane π-bonding parameter with the in-plane π-bonding parameter, as is generally assumed, being set to zero). In contrast to similar studies involving Cu(II) complexes no corrections for misdirected valences were required.[20] This might be due to the fact that the dependence of relevant energy levels on the bond lengths is rather small (see ahead). All the other electronic parameters are as given in a previous publication.[11] For model calculations, where the *g*-values were calculated for geometries based on a distortion from octahedral symmetry along a relevant normal mode (Figures 1, 2, and 4), all Fe–N bond lengths were assumed to be identical. While these diagrams reflect the influence of some of the major modes of distortion on the values of the *g*-factors of low-spin iron(III) complexes, the experimentally observed and calculated (MM–AOM) *g*-values (see Tables) are not *directly* related to these curves.

Results and Discussion

[Fe(*trans*-diammac)]$^{3+}$. Few low-spin iron(III) complexes with saturated amine ligands are extant, and most of them have not been suitable for detailed spectroscopic analysis.[11,22,23,31–36] The tris-en[22] and hexaamine cage[34,35] complexes are relatively unstable in solution, and for the former no single crystal data are available. Fast spin–lattice relaxation caused by doublet states being close in energy to the ground state results in line broadening which can make recording of EPR spectra impossible. No EPR spectra of the relatively stable $[Fe(tacn)_2]^{3+}$ ion (tacn = 1,4,7-triazacyclononane) have been reported.[33] [Fe(*trans*-diammac)]$^{3+}$ (*trans*-diammac = *trans*-6,13-dimethyl-1,4,8,11-tetraazatetradecane-6,13-diamine) is stable in solution and in the solid state, presumably due to the ligand geometry preventing efficiently the formation of coordinated imines and because of a relatively high Fe^{2+}/Fe^{3+} couple caused by a relatively large ligand field due to the small cavity size. Moreover, the complex yields an EPR spectrum at 77 K.[11,23]

Three molecular structures of [Fe(*trans*-diammac)]$^{3+}$ have been reported, that of the mixed chloride/perchlorate salt[23] and that of the perchlorate salt which yielded two crystallographically distinct molecules in the unit cell.[36] Both X-ray structures exhibit conformational disorder in the macrocyclic five-membered chelate rings.[23,36] The three nondegenerate conformations of [Fe(*trans*-diammac)]$^{3+}$ are shown in Figure 1. Strain energy minimization has indicated that the observed structures might be mixtures of the $\delta\delta,\lambda\lambda$ and $\lambda\delta$ conformations ($U_{total}{}^{\delta\delta(\lambda\lambda)} = 90.7$ kJ/mol; $U_{total}{}^{\lambda\delta} = 91.5$ kJ/mol; $U_{total}{}^{\delta\lambda} = 112.2$ kJ/mol).[37]

The analysis of the electronic properties of [Fe(*trans*-diammac)]$^{3+}$ with AOM calculations based on a chemically reasonable set of electronic parameters and crystal structure data leads to excellent agreement between calculated and observed *g*-values, orientations of the **g**-tensors, and electronic transitions.[11] The doublet ground state (^2A_g in C_{2h} symmetry, largely d_{xy} in character) is well separated from the ^2B_g and ^2A_g levels by ca. 1300 and ca. 1700 cm^{-1}, respectively. It therefore was

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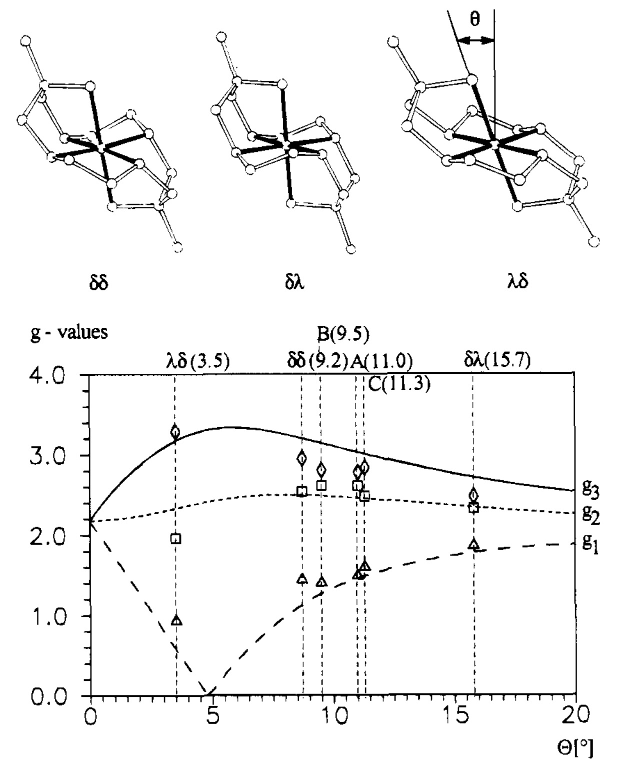

Figure 1. ORTEP plots of the calculated structures of the three nondegenerate conformations of $[Fe(\textit{trans}\text{-diammac})]^{3+}$ and dependence of the *g*-values on the angle θ (calculated curves from AOM model calculations; see text), including experimental (*A*, *B*, *C*) and calculated ($\lambda\delta$, $\delta\delta$, $\delta\lambda$) values.

not surprising that well-resolved EPR signals were observed even at 77 K, and no Jahn–Teller lability was expected to occur. There is a large anisotropy of the *g*-values of $[Fe(\textit{trans}\text{-diammac})]^{3+}$, and the rhombic nature of the **g**-tensor was shown by model calculations to be a result of a strong dependence of the *g*-values on the angle θ (see Figure 1).[11]

Generally, in molecular mechanics of this type of compound metal–ligand bond lengths may be reproduced to ca. 0.01 Å.[12,13] On the basis of averaged Fe–N distances, there is good agreement between the three sets of experimental data and the corresponding calculated parameters for the $\delta\delta$ and $\lambda\delta$ conformations (see Table 1). The $\delta\lambda$ species can be excluded on the basis of the calculated Fe–N bond lengths in comparison with the three sets of X-ray data and also on the strain energy being some 20 kJ/mol higher than for the other two conformers.

The difference between axial and in-plane Fe–N distances is a little underestimated in the molecular mechanics calculations. This may be due to small inaccuracies in the force field parametrization. It should be kept in mind that the force field parameters are based on X-ray structures of a range of low-spin iron(III) complexes including $[Fe(\textit{trans}\text{-diammac})]^{3+}$ as just one example.[12,13] Also, the experimental structures are affected by crystal packing effects while the calculated geometries rather represent "naked" molecules; i.e., environmental effects (crystal lattice and solvation) are usually excluded in molecular mechanics calculations.[13] The presence of effects of crystal packing are exemplified with the identification of two distinct molecular cations (A and B) which crystallize in the unit cell of the perchlorate salt and a third one (C) identified in the mixed chloride/perchlorate salt. Not only are the bond lengths and the distortion angles θ of the two molecules A and B of the perchlorate salt different but also the geometry of the five-membered macrocyclic chelates: In molecule B these rings are more puckered by ca. 10°. AOM model calculations indicate that there is only a rather small dependence of *g*-values on the Fe–N distance. However, the calculated structural data indicate that the distortion angle θ is critically dependent on the Fe–N distances (see Table 1), and this might lead to some error in the calculated *g*-values.

Table 1. Experimental and Calculated Structural Parameters of $[Fe(\textit{trans}\text{-diammac})]^{3+}$

	X-ray			MM		
structural param	A[a]	B[b]	C[c]	$\delta\delta$	$\lambda\delta$	$\delta\lambda$
$Fe{-}N_1{}^d$ (Å)	1.965	1.951	1.969	1.982	1.966	2.006
$Fe{-}N_2{}^d$ (Å)	1.965	1.961	1.974	1.982	1.966	2.006
$Fe{-}N_3{}^d$ (Å)	1.965	1.951	1.969	1.982	1.966	2.006
$Fe{-}N_4{}^d$ (Å)	1.965	1.961	1.974	1.982	1.966	2.006
$Fe{-}N_5{}^e$ (Å)	1.982	1.985	1.984	1.984	1.979	1.992
$Fe{-}N_6{}^e$ (Å)	1.982	1.985	1.984	1.984	1.979	1.992
θ^f (deg)	11.0	9.5	11.3	9.2	3.5	15.7
U_{total} (kJ/mol)				90.7	91.5	112.2

[a] Perchlorate, molecule A.[36] [b] Perchlorate, molecule B.[36] [c] Chloride/perchlorate.[23] [d] In-plane. [e] Axial. [f] Defined in Figure 1.

Table 2. Observed and calculated *g*-Values (AOM and MM–AOM) of $[Fe(\textit{trans}\text{-diammac})]^{3+}$

experiment	g_1	g_2	g_3
A[a]	1.42	2.61	2.81
B[b]	1.51	2.61	2.78
C[c]	1.62	2.48	2.84
solution[d]	1.63	2.46	2.84
A (AOM)[e]	1.52	2.54	2.88
B (AOM)[f]	1.66	2.48	2.77
C (AOM)[g]	1.61	2.50	2.83
$\delta\delta$ (MM–AOM)	1.45	2.54	2.95
$\lambda\delta$ (MM–AOM)	0.95	1.96	3.29
$\delta\lambda$ (MM–AOM)	1.89	2.05	2.46

[a] Perchlorate, molecule A; powder, Q-band.[11] [b] Perchlorate, molecule B; powder, Q-band.[11] [c] Chloride/perchlorate; powder, X-band. [d] DMF/H_2O (1:2); 77 K. [e] Perchlorate, molecule A.[11] [f] Perchlorate, molecule B.[11] [g] Chloride/perchlorate.

The **g**-tensors calculated with the MM–AOM method (see Figure 1 and Table 2) indicate that the disorder observed in the crystal structures[23,36] is a result of mixing $\delta\delta$ and $\lambda\lambda$ conformers. The frozen solution spectrum is similar to the crystal spectra and again in good agreement with the MM–AOM parameters of the $\delta\delta$ conformers. In the $\lambda\delta$ conformer the AOM calculations produce doublets rather close to the ground state (separated by ca. 600 and 800 cm^{-1}), a configuration that would lead to fast spin–lattice relaxation preventing observation of EPR spectra at 77 K. For the $\delta\delta$ conformer the separation between the nearest doublet levels are 1100 and 1500 cm^{-1}, for the $\delta\lambda$ conformation it is over 3000 cm^{-1}. The calculated doublet excited states for the $\delta\delta$ conformer are similar to the ones reported for an AOM analysis based on crystal coordinates,[11] viz. compatible with the experimental UV–vis–near-IR data;[23,36] those for the $\lambda\delta$ and $\delta\lambda$ conformers are not. On the basis of the calculated strain energies, the $\delta\lambda$ conformer may be excluded whereas the $\lambda\delta$ geometry might contribute up to ca. 25% to an equilibrated solution. Also, some participation of the $\lambda\delta$ conformer was proposed to contribute to the disordered crystal structures.[37] With the appreciable error limits inherent to the MM–AOM method, an estimation of a mixed $\delta\delta{-}\lambda\delta{-}\lambda\lambda$ structure, based on the relative strain energies, and of the corresponding electronic parameters is not warranted.

$[Fe(en)_3]^{3+}$. The synthesis of $[Fe(en)_3]Cl_3$ (en = ethane-1,2-diamine) was reported 25 years ago.[22] The fact that, apart from unpublished EPR data,[39] no further spectroscopic studies have been reported is probably related to the instability of solutions

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Table 3. Details of the Calculated Structures of the Four Conformations of $[Fe(en)_3]^{3+}$

param	lel_3	lel_2ob	$lelob_2$	ob_3
Fe—N (Å)	1.992	1.993 1.993 1.992	1.993 1.993 1.993	1.993
ϕ^a (deg)	51.7	~52.6	~53.6	54.9
h^b (Å)	2.321	~2.291	~2.268	2.246
U_{total} (kJ/mol)	31.7	32.7	33.5	33.7

[a] Twist angle (octahedron, $\phi = 60°$; trigonal prism, $\phi = 0°$). [b] Distance between the two trigonal planes; for a regular octahedron $h = 2r/\sqrt{3}$.[38]

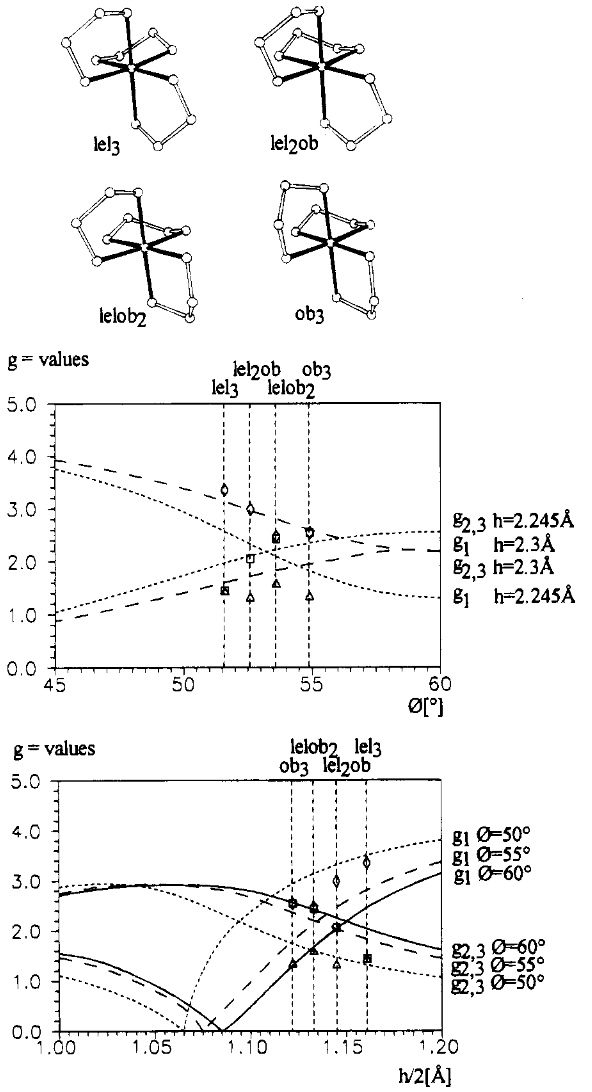

Figure 2. ORTEP plots of the calculated structures of the four nondegenerate conformations of $[Fe(en)_3]^{3+}$ and dependence of the g-values upon the twist angle ϕ and the trigonal compression parameter h (calculated curves from AOM model calculations; see text), including the calculated (MM−AOM) g-values. In the two sets of curves one structural parameter (h, top, or ϕ, bottom) was fixed at various positions, while the other was varied continuously.

of this compound. The excellent agreement between calculated and observed structural and electronic parameters found for [Fe(*trans*-diammac)]$^{3+}$, $[Fe(phen)_3]^{3+}$, and $[Fe(bpy)_3]^{3+}$ (see ahead) have encouraged me to compare the experimental EPR spectrum with calculated parameters based on combined MM−AOM calculations.

Table 4. Observed and Calculated (MM−AOM) g-Values of $[Fe(en)_3]^{3+}$

conformer	g_1	g_2	g_3
exptl[39]	≤0.6	2.68	2.68
exptl[a]	b	2.69	2.69
lel_3	1.45	1.45	3.34
lel_2ob	1.35	2.05	2.97
$lelob_2$	1.60	2.42	2.48
ob_3	1.35	2.55	2.55

[a] Powder, 4 K X-band. [b] Not observed; see text.

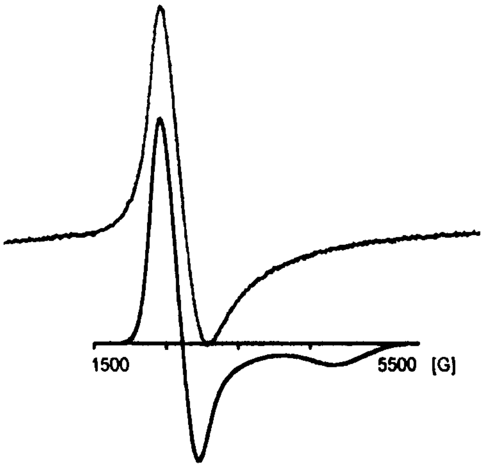

Figure 3. Observed (top; undiluted powder of the chloride salt, 4 K) and simulated (bottom; ob_3 conformer, for parameters see Table 4 and Experimental Section) EPR spectra of $[Fe(en)_3]^{3+}$.

Details of the calculated structures of the four possible conformers of $[Fe(en)_3]^{3+}$ are summarized in Table 3. As for $[Co(en)_3]^{3+}$, the four conformers have similar strain energies with the lel_3 ($\Delta\lambda\lambda\lambda$ or $\Lambda\delta\delta\delta$) complex being the most stable structure (for $[Co(en)_3]^{3+}$ the relative strain energies using the same force field[12] are 0.0, 1.2, 2.3, and 2.7 kJ/mol for the lel_3, lel_2ob, ob_2lel, and ob_3 conformers). In an equilibrated solution the four conformers of $[Fe(en)_3]^{3+}$ are calculated to be of similar abundence (no entropy terms included: 39, 25.5, 18.5, and 17%) and the conformer that precipitates might simply do so because of environmental effects. That one pure conformer, not necessarily the most stable one, precipitates is therefore not unexpected. In terms of the geometry of the chromophore the main differences of the four structures are related to a change from D_3 (lel_3 and ob_3) to C_2 (lel_2ob and ob_2lel) site symmetry and to an increasing twist and a compression along the (pseudo) C_3 axis (parameters ϕ, h) with an increasing number of ob conformations.

The model calculations presented in Figure 2 are based on geometries with D_3 symmetry, and they illustrate the behavior of the g-values in the function of distortions along the trigonal axis. The calculated g-values (MM−AOM) for the four conformers together with the experimental data are presented in Table 4 and also included in Figure 2, to illustrate that these distortions are the major factors for the **g**-tensor anisotropy. However, it is obvious that additional perturbations due to rhombic distortions and bond length differences might also be of importance. A factor that so far has not been addressed is the magnitude of effects due to the Jahn−Teller lability of the ground state.

The lowest g-value was reported to be outside the field range studied ($g_1 \leq 0.6$).[39] This does not agree with our calculations, and we therefore decided to remeasure the spectrum which is presented in Figure 3. No additional signal was observed up to 11 000 G. Two possible explanations for the observed spectrum may be offered: (i) The third line expected to occur around 4000−5000 G, which is already rather broad and ill-defined (see Figure 3, where the simulated spectrum of the calculated transition for the ob_3 conformer is shown), is further

Table 5. Details of the Experimental and Calculated Structures of $[Fe(phen)_3]^{3+}$ and $[Fe(bpy)_3]^{3+}$

	$[Fe(phen)_3]^{3+}$		$[Fe(bpy)_3]^{3+}$	
param	X-ray[9]	MM	X-ray[10]	MM
Fe—py (Å)	1.976, 1.980, 1.974, 1.968, 1.972, 1.967	1.969	1.967, 1.964, 1.958, 1.960, 1.960, 1.959	1.967
ϕ^a (deg)	~55.7	57.7	~55.1	58.3
h^b (Å)	2.097	2.074	2.068	2.023

[a] Twist angle (octahedron, $\phi = 60°$; trigonal prism, $\phi = 0°$). [b] Distance between the two trigonal planes; for a regular octahedron $h = 2r/\sqrt{3}$.[38]

broadened by g-strain broadening and therefore not observable. (ii) The three g-values are all similar, viz. close to one of the crossing points shown in Figure 2. However, this should lead to $g \sim 2.1$, which disagrees with the observed spectrum. Simulations indicate that already moderate anisotropies would lead to observable shoulders. For the same reason, a mixture of conformers may be excluded, and it is assumed that the pure ob_3 conformer is precipitated.

From Figure 2 it emerges that the lowest g-value of the ob_3 and ob_2lel conformations is strongly dependent on the elongation h of the polyhedron, and the calculated g_1 values might therefore be less accurate than the other parameters. For this reason it cannot be excluded that the observed spectrum is due to the ob_2lel conformer. Therefore, the presented data are in agreement with an attribution of the spectrum to a single conformer (ob_3 or ob_2lel) and an unresolved g_1 value caused by line broadening.

The predicted eletronic absorptions are similar for all four conformers, and therefore, they do not allow support of the assignment of the conformation of $[Fe(en)_3]^{3+}$ as ob_3. However, the calculated absorptions (doublet levels clustered around 19 500, 21 500, 27 500, and 32 000 cm^{-1}) are in good agreement with the observed spectrum[22] (an additional transition observed at 16 250 cm^{-1} and assigned as $^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$ [22] has to be attributed to a transition to a quartet level). The closest spin doublets are calculated to be displaced by ca. 600 and 700 cm^{-1} from the ground state. These doublets must lead to rather fast spin—lattice relaxation, and they are therefore consistent with the observed large line widths, even at 4 K.

$[Fe(phen)_3]^{3+}$. The calculated structure of $[Fe(phen)_3]^{3+}$ (phen = 1,10-phenanthroline) is in good agreement with the published X-ray data[9] (see Table 5). Apart from a small distortion in the crystal from D_3 point symmetry, probably due to crystal lattice effects, the major discrepancy is found in an exaggerated compression (h) and a larger twist angle (ϕ) in the optimized structure. However, these errors are in the expected range of accuracy for molecular mechanics calculations (see also Conclusions).

It was demonstrated that AOM calculations based on the experimental structural parameters of $[Fe(phen)_3]^{3+}$ and a chemically reasonable set of electronic parameters lead to calculated **g**-tensor properties that are in excellent agreement with the observed values.[11] The series of reported experimental spectral parameters of $[Fe(phen)_3]^{3+}$ in various lattices (see Table 6) indicates that environmental effects might be of some importance, and these clearly cannot be modeled with molecular mechanics calculations. However, apart from the very low value of g_1 for $[Fe(phen)_3]^{3+}$ in a Co(III) hexafluorophosphate lattice, the entire set of calculated parameters is rather constant. The model calculations presented in Figure 4 indicate that the inaccuracies of the calculated trigonal twist ($\phi \sim 55°$) do not lead to large errors in the predicted g-values. However, in the range of $h \sim 2-2.2$ Å, the lowest g-values are strongly dependent on the elongation of the C_3 polyhedron, and a discrepancy of up to 0.2 in g_1 is therefore not unexpected. An elongation due to crystal lattice effects might therefore be the origin of the unexpectedly low value for g_1 of $[Fe(phen)_3]^{3+}$ in the Co(III) hexafluorophosphate lattice—if this effect is reproducible. In general, the agreement between experimental data and MM—AOM calculations is satisfactory.

Table 6. Observed and Calculated (AOM and MM—AOM) g-Values of $[Fe(phen)_3]^{3+}$ and $[Fe(bpy)_3]^{3+}$

experiment	g_1	g_2	g_3
	$[Fe(phen)_3]^{3+}$		
perchlorate[a,9]	1.46	2.62	2.73
perchlorate[7]	1.49	2.65	2.65
hexafluorophosphate[b,5]	1.19	2.69	2.69
hexafluorophosphate[c,7]	1.51	2.69	2.69
AOM	1.45	2.61	2.78
MM—AOM	1.61	2.62	2.62
	$[Fe(bpy)_3]^{3+}$		
perchlorate[a,10]	1.47	2.60	2.77
perchlorate[7]	1.46	2.57	2.72
hexafluorophosphate[b,5]	1.61	2.61	2.61
hexafluorophosphate[c,7]	1.63	2.64	2.64
AOM	1.54	2.59	2.72
MM—AOM	1.74	2.53	2.53

[a] Single crystal study. [b] In a Co(III) lattice. [c] Undiluted.

The lowest dd-absorptions are predicted to occur above ca. 22 000 cm^{-1}, in an area where they would be obscured by charge transfer transitions.[40] The closest spin doublets are calculated to be displaced by ca. 1200 and 1600 cm^{-1} from the ground state. Therefore, it is not unexpected that well-resolved EPR spectra are observed at liquid nitrogen temperature.

$[Fe(bpy)_3]^{3+}$. The calculated structure of $[Fe(bpy)_3]^{3+}$ (bpy = 2,2′-bipyridine) is compared to experimental data in Table 5. It refined as expected to a D_3 symmetrical molecule, and the calculated bond lengths are in good agreement with the average of the experimental Fe—N distances. The largest difference between experimental and calculated structure again is found in the compression h and the trigonal twist ϕ.

The parameters obtained by the MM—AOM calculations are in good agreement with the experimental parameters of the single crystal and a number of powder studies (see Table 6). The first doublet transitions are expected around 24 000 cm^{-1}, and also the displacement of doublet levels close to the ground state is a little larger than for $[Fe(phen)_3]^{3+}$. From the structural parameters (see Table 5) and the model calculations (see Figure 4) it emerges that the electronic properties of $[Fe(phen)_3]^{3+}$ and $[Fe(bpy)_3]^{3+}$ should be very similar, and this is evidently so (see Table 6).

$[Fe(terpy)_2]^{3+}$. The EPR spectrum of $[Fe(terpy)_2]^{3+}$ (terpy = 2,2′:6′,2″-terpyridine) was assigned as being consistent with axial symmetry and due to a distorted octahedral complex.[8] No crystallographic data for this compound have been reported. This is not astonishing in view of the instability of the complex.[8,40,41] The structure was therefore optimized with molecular mechanics calculations (see Table 7). From the calculated structure the electronic properties were estimated with AOM calculations. The resulting **g**-tensor is not in agreement with the experimental

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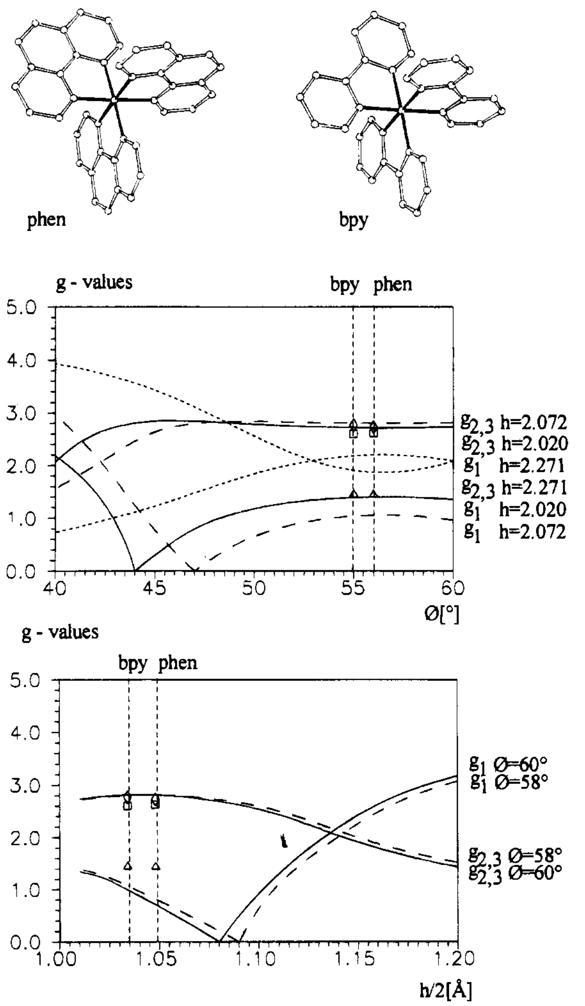

Figure 4. ORTEP plots of the calculated structures of $[Fe(phen)_3]^{3+}$ and $[Fe(bpy)_3]^{3+}$ and dependence of the g-values on the twist angle ϕ and the trigonal compression parameter h (calculated curves from AOM model calculations; see text), including the calculated (MM−AOM) g-values. In the two sets of curves one structural parameter (h, top, or ϕ, bottom) was fixed at various positions, while the other was varied continuously.

Table 7. Details of the Calculated Structures of $[Fe(terpy)_2]^{3+}$

	molecular mechanics		
param	octahedral[a]	five coordinate	octahedral[b]
Fe—$py_{terminal}$ (Å)	1.976	1.964, 1.965, 1.937	1.979, 1.984, 1.988[c]
Fe—py_{middle} (Å)	1.949	1.948, 1.949	1.960
τ^d (deg)	8.9	9.8	10.2
U_{total} (kJ/mol)	86.5	68.8	93.9

[a] Two tridentate terpy ligands. [b] One tridentate, one bidentate terpy, ammonia. [c] $Fe-NH_3$. [d] $\tau = (180° - 2\alpha)/2$; α = bite angle.

Table 8. Observed and Calculated (MM−AOM) g-Values of $[Fe(terpy)_2]^{3+}$

experiment	g_1	g_2	g_3
perchlorate[6]	1.76	2.54	2.54
MM−AOM oct[a]	0.38	0.45	4.05
MM−AOM pent[b]	1.54	2.42	2.69
MM−AOM oct[c]	1.73	2.27	2.73
AOM oct[d]	1.72	2.18	2.64

[a] Two tridentate terpy ligands. [b] One tridentate, one bidentate terpy, pentacoordinate. [c] One tridentate, one bidentate terpy, ammonia. [d] Unsymmetrically distorted (see text).

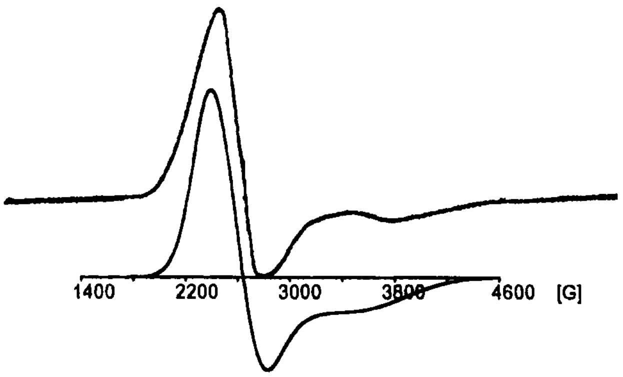

Figure 5. Observed (top; redrawn from ref 38) and simulated (bottom; experimental data; for parameters see Table 8 and Experimental Section) EPR spectra of $[Fe(terpy)_2]^{3+}$.

data (see Table 8). Also, a calculated energy difference of only ca. 500 cm^{-1} between the ground state and the closest doublet levels is not compatible with an observed EPR spectrum at liquid nitrogen temperature.

Mössbauer and magnetic data indicated that $[Fe(terpy)_2]^{3+}$ has a large axial distortion.[8,41] The origin of this was assumed to be the inflexibility of the three fused pyridyl rings enforcing relatively small bite angles (~80−83° in the case of the rather small iron(III) cation; for larger metal ions values down to ~75° have been reported[42]) and a short central Fe—N bond length. Such axial symmetry is well-known for a number of transition metal complexes of terpy.[42] However, the earlier analyses of the electronic properties did not make it possible to quantify the structural parameters in relation to the electronic properties, and the exact nature of the structure could not be ascertained.[8,41] Therefore, the **g**-tensor properties were analyzed with model AOM calculations in dependence of three symmetrical distortion modes, including the angular distortion angle τ ($2\tau = 180° - 2\alpha$, where α is the bite angle of a terpy ligand; $\tau = 0-20°$), the axial compression c (c = Fe—N distance of the central pyridyl unit; $c = 1.97-1.89$ Å), and the torsion angle ω (torsion along to pyridyl−pyridyl bond; $\omega = 0-8°$). Interestingly, the g-values and the energy levels were not greatly dependent on these three distortion modes and axial spectra with two very low g-values and one large g-value were obtained over the whole ranges of τ, c, and ω.

With further model calculations I have found two possible nonsymmetrical modes of distortion leading to electronic ground states compatible with the published experimental data: (i) Distortion of the bite angles (τ) of only one coordinated terpy ligand or (ii) coordination of a tridentate and a bidentate terpy ligand. Both chromophores lead to similar sets of g-values (see Figure 5 and Table 8), to an energy gap between the ground state and the first doublet states of over ca. 1200 cm^{-1} (expected well-resolved EPR spectra at 77 K), and to magnetic moments compatible with the experimental data.[8]

An asymmetrical distortion in the solid might be induced by the crystal lattice and account for the solid state spectrum. The anisotropy of $g_{2,3}$ emerging from the model AOM calculations might be obscured by rather large line widths in the not well resolved experimental spectrum.[8] However, in solution asymmetrical distortion is not expected to occur. Pentacoordinate complexes of iron(III) are well-known,[41,43] but with few exceptions they all are high spin.[44] Bidentate coordination of terpy was suggested in a number of cases,[45−49] and chelate ring

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opening was proposed or detected with similar ligand systems.[50–52] Conclusive evidence for bidentate coordination of terpy was presented with crystal structures[53,54] and a recently reported NMR study.[55] Most importantly, a structure involving one bidentate terpy ligand is not in disagreement with any of the reported properties of this compound.[6,8,40,41,43]

The MM–AOM studies do not give conclusive information on the type of structure resulting from a chelate ring opening since six-coordinate species (capture of a monodentate ligand), distorted square pyramidal, and distorted trigonal bipyramidal coordination polyhedra all have the required symmetry and lead to similar calculated electronic properties. However, we assume that an extra ligand is coordinated leading to a distorted octahedral chromophore. Note that in our model calculations we have used NH_3 as model for an additional ligand since so far we only have parametrized Fe—N bonds. The fact that the calculated EPR spectra were not strongly dependent on the $Fe—NH_3$ bond distance, which was varied over a larg range, indicates that coordination of other, chemically more reasonable, ligands will lead to similar EPR spectra. The release of strain (ca. 30 kJ/mol) upon dissociation of one pyridyl ring might be an important reason for the suggested coordination mode, and the strongly acidic environment used for recording the frozen solution spectrum[8] clearly assists dissociation of a pyridyl moiety. Note, however, that our molecular mechanics model does not include electronic factors which possibly oppose the proposed mechanisms, and the use of harmonic potentials to model the bonding function does not allow the estimate of any bond dissociation.

The force constant for the torsion around two connected pyridyl rings has not previously been determined with any measure of accuracy.[12] Ligands such as bpy and terpy tended to be refined to nearly planar geometries, even with a rather small force constant. With one dissociated pyridyl group this obviously is a different matter. The force constant used is in agreement with a conformational analysis based on ab initio calculations of various bipyridinium dications,[56] and the strain energy minimized structures are in agreement with X-ray data of similar compounds.[52–54]

The structure of $[Fe(terpy)_2]^{3+}$ discussed here is in agreement with all of the reported experimental data, and it is chemically reasonable. However, the calculations reported do not prove it. Two aspects which so far have not been addressed quantitatively are distortions resulting from the Jahn–Teller labile ground state and the effect of misdirected valences on the d_π-orbitals (the reduction of σ-bonding has been modeled and not found to be of any importance). Therefore, an iron(III) species with one tri- and one bidentate terpy ligand is just one reasonable explanation of the experimental facts, and future work has to be awaited to solve this structural and spectroscopic problem unambiguously.

Conclusions

There is generally excellent agreement between EPR spectra of low-spin iron(III) complexes and calculated properties of the **g**-tensors based on AOM calculations with a constant set of electronic parameters and experimentally determined structures of the chromophores.[11] The structures of these compounds may be calculated accurately with MM calculations (Fe—N = ca. $\pm$ 0.01 Å, N—Fe—N = ca $\pm 3°$).[12] We have shown in the present paper that a prediction of EPR spectra of low-spin iron(III) compounds with the MM–AOM method is possible with an error limit of ca. ± 0.2 in g-values, and this is satisfactory in view of the generally very large anisotropy and dependence of the g-values on small structural deviations.

The problem of cancellation (or possible propagation) of errors due to the combination of slightly inconsistent parametrization schemes (MM and AOM) has been discussed in a previous publication.[19] While this cannot be excluded, the entire set of satisfactory data from various systems, including Cr(III),[19] Co(III),[19] Ni(II),[19] Cu(II),[20] and Fe(III) complexes, implies that the MM–AOM approach is generally rather consistent. However, the simplicity of the MM–AOM approach clearly has to be paid with a limited accuracy (g ca. ± 0.2). AOM calculations for g-values as a function of a particular distortion mode have been rather useful for the determination of "problem areas" where errors on calculated g-values are most important. Two possible improvements, relating to inaccuracies of the calculated structures due to neglecting electronic effects (Jahn–Teller distortion of the ground state and computation of the ligand–metal–ligand valence angles), indicate the direction of future studies. The latter problem has already been observed in an earlier MM–AOM study,[19] and both effects are presently addressed with the development of new algorithms and parameter sets.[21,57]

The approach described here is useful for detailed analyses of spectroscopic properties of compounds where structural data are not available. Also, as shown in the cases of $[Fe(en)_3]^{3+}$ and $[Fe(terpy)_2]^{3+}$, the MM–AOM method allows one to determine structural properties of low-spin iron(III) complexes. Moreover, the predictive power of the MM–AOM approach is important in view of a rather quick and accurate design of low-spin iron(III) compounds, and of transition metal compounds in general, with given electronic properties.

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