Electron Paramagnetic Resonance Studies of Low-Spin d^5 Complexes. Tris-Bidentate Complexes of Iron(III), Ruthenium(III), and Osmium(III) with Sulfur-Donor Ligands[1]

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Abstract: Results of a detailed magnetic resonance investigation of iron group complexes of the form $M^{III}(S\text{-}S)_3{}^{n-}$ (M = Fe, Ru, Os; S-S = bidentate sulfur donor ligand) are reported. The apparently near-isotropic *g* values of these complexes, in contrast to those of most other $t_{2g}{}^5$ complexes, are explained in terms of a consistent model of the bonding which requires a *large* low symmetry distortion both geometric and electronic in origin. This conclusion, contrary to that reached in previous epr studies, is supported by analysis of the hyperfine coupling arising from ^{101}Ru. It is found that the extensive metal–ligand covalent interaction reduces the spin–orbit coupling constant of Ru(III) to about 40% of its free-ion value and that the hyperfine coupling originates from both the usual indirect or polarization mechanism as well as a direct mechanism. Difficulties which arise from a purely $^2T_2$ model are considered, and their effect on interpretation of the data is discussed. It is concluded that, when properly applied, the simple crystal field model will qualitatively yield the correct results, but, in the limit of large distortion from octahedral symmetry, the quantitative results of this treatment are of dubious value.

Since the original paramagnetic resonance work on $Fe^{III}(CN)_6{}^{3-}$,[2] a large number of $d^5(t_{2g}{}^5)$ complexes has been studied by electron spin resonance; this has been especially true during the last few years.[3–11] One finds in general that the low-spin d^5 configuration is a good probe of molecular structure and bonding since the observed *g* values vary widely and are sensitive to small changes in structure and to the covalent interaction with the ligands of the complex.

In contrast to this "normal" behavior, one comes across an apparent anomaly when considering the tris-bidentate chelate complexes with sulfur donor ligands, $Fe(S\text{-}S)_3{}^{n-}$ (n = 0 or 3); here one finds the *g* values are markedly closer to $|g| = 2.0$ and apparently insensitive to the differences among the various ligands. These results have in general been interpreted as arising from very small low-symmetry distortions,[6,9] a conclusion which is surprising, since the results of Mössbauer[8,9,12,13] and magnetic susceptibility[8,14] experiments as well as structural investigations[8] often do not support this conclusion. Since the model invoked in all of these experiments is essentially the same, it is not clear how such drastically different results are obtained. In view of the ambiguities which exist in this area and in view of the continuing interest in sulfur coordination in a number of metalloenzyme systems[15–20] as well as in the numerous models proposed for these biological systems, it was felt that a detailed epr study of these complexes was warranted. It is hoped that the conclusions reached herein will shed some light on the nature and origins of the electronic distortions induced in metal complexes of sulfur bonded ligands.

The approach taken involves the study of the entire iron group, Fe(III), Ru(III), and Os(III), all of which form similar low-spin complexes with the ligands of interest. There are a number of advantages in studying the complexes of the heavier members of the series. First, for comparative purposes, there are many more low-spin complexes to be found here; a comparatively small number of Fe(III) complexes are low spin while this behavior is universal for Ru(III) and Os(III). Second, the approximations inherent in the model[6,21] by which the epr results are interpreted are much less important where free-ion term and primary crystal field splittings are large as in the second- and third-row elements. Third, the possibility of observing electronic splittings within the $^2T_{2g}$ ground level is a good possibility for Os(III) and perhaps even for Ru(III). This allows a check on the resonance results.

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Experimental Section

Reagents. "$RuCl_3 \cdot nH_2O$," $OsCl_3$, and Ph_4PBr were obtained from Alfa Inorganics; $(NH_4)_2OsBr_6$ was synthesized from OsO_4 (Fisher Scientific) by the method of Dwyer and Hogarth.[22] $Ph_4AsCl \cdot H_2O$ was obtained from Aldrich Chemical Co. All ligands were commercially available except for sacsac⁻ which was synthesized *in situ* as described in the literature.[14] Potassium dithiooxalate (K_2dto), sodium dimethyl- and diethyldithiocarbamates (Nadtc and Nadetc, respectively) were obtained from Eastman Organic Chemicals. Sodium *cis*-1,2-dicyanoethylene-1,2-dithiolate (Na_2mnt) was purchased from Strem Chemicals, and diphenyldithiophosphinic acid (Hdtp) was obtained from Alfred Bader Chemicals. Where dry solvents were found necessary, drying was accomplished with Linde 4A molecular sieves. All other chemicals were reagent grade.

Preparation of Complexes. Previously reported compounds were prepared by standard methods. Where possible, spectral and physical data were compared if such data were available. Microanalyses were satisfactory. Details of new complexes are reported here.

Ru(sacsac)₃. The method of Heath and Martin[14] did not produce the desired product after three attempts. A modification of their method for Os(sacsac)₃[14] was used. $RuCl_3 \cdot nH_2O$ (0.5 g) was dissolved in approximately 20 ml of absolute ethanol containing 1.0 ml of acetylacetone and cooled in a CH_2Cl_2 slush bath. H_2S (5–10 ml) was condensed into the cold solution which was then saturated with HCl and allowed to warm overnight to room temperature. The dark brown solid was washed thoroughly with ethanol and then dissolved in warm benzene. The remaining residue was discarded and the solution was evaporated to dryness. The solid from evaporation was boiled in diethyl ether until the small amount of soluble material had dissolved. The remaining solid Ru(sacsac)₃ was recrystallized from benzene–hexane (2:1 v/v) yielding dark brown crystals which appeared identical with those reported by Martin and Heath.

Ru(dtp)₃. $RuCl_3 \cdot nH_2O$ (0.21 g) was dissolved in 50 ml of methanol and added slowly to 0.75 g of Ph_2PS_2H in 100 ml of acetone. A purple solution formed immediately and turned green upon gentle warming, depositing a lump of dark solid which was separated and washed with 2–3 ml of cold acetone. The solid was then dissolved in dry CH_2Cl_2 and filtered, yielding a deep purple solution from which purple crystals were obtained on addition of hexane followed by evaporation to approximately 25% of the original volume. This compound is slightly unstable in solvents such as $CHCl_3$, CH_3CN, and acetone. Decomposition is readily detected by epr. CH_2Cl_2 seems to be the best solvent in which to work with this compound.

Anal. Calcd for $C_{36}H_{30}P_3S_6Ru$: C, 50.93; H, 3.56. Found: C, 50.03; H, 3.55.

(Ph₄P)₃[Ru(mnt)₃]. The entire preparation of this compound was carried out under nitrogen. All solvents were degassed with N_2. $RuCl_3 \cdot nH_2O$ (0.25 g) was dissolved in 30 ml of $EtOH–H_2O$ (50:50 by vol) and added to 1.4 g of Na_2mnt in 10 ml of H_2O. After mixing and stirring gently for 0.5 hr, the solution had turned from green to a deep golden brown color. Ph_4PBr (1.8 g) in 10 ml of EtOH was added all at once, whereupon a dark brown precipitate immediately formed. This solid was washed well with a small volume of H_2O followed by a large quantity of absolute ethanol and dried under vacuum. The brown solid appears stable, but microanalyses from two independent laboratories did not produce consistent results. Three of the five elements analyzed gave acceptable results and two were unstatisfactory in both cases, indicating perhaps a difficulty in analysis of this compound. It is felt that the epr spectra reported for this compound are correct and not due to a sulfur radical or to the dimeric purple compound which results from the above preparation with less ligand than used here. Further attempts to obtain better analytical results are underway.

(Ph₄P)₃[Os(mnt)₃]. $(NH_4)_2OsBr_6$ (0.7 g) in H_2O was reduced with sodium dithionite to give a pale yellow-gray solution. Na_2mnt (0.56 g) in $EtOH–H_2O$ and a few milligrams more of dithionite were added to the osmium solution which immediately darkened. Ph_4PBr in $EtOH–H_2O$ was added to precipitate the deep brown desired complex. The crystals were thoroughly washed with absolute ethanol and dried.

Anal. Calcd for $C_{84}H_{60}P_3OsS_6N_6$: P, 5.71; S, 11.81; N, 5.16. Found: P, 5.15; S, 11.71; N, 5.36. Carbon and hydrogen are not determined due to interference of volatile OsO_4.

(Ph₄As)₃[Ru(dto)₃]. $RuCl_3 \cdot nH_2O$ (0.42 g) was dissolved in 60 ml of H_2O and 0.6 g of K_2dto was added directly as the solid. This mixture was stirred for a few minutes, then filtered, and the filtrate was added to aqueous Ph_4AsCl to give a dark precipitate. This was filtered and dissolved in $CHCl_3$. Some residue remains and the chloroform solution was again filtered; the desired compound is precipitated with diethyl ether.

Anal. Calcd for $C_{78}H_{60}As_3RuS_6O_6$: C, 58.13; H, 3.75; S, 11.94. Found: C, 57.10; H, 4.07; S, 11.67.

Spectra. Spectra were recorded on either a Varian E-4 or V-4500 spectrometer system at X-band frequencies at 77°K. Calibration was within 1%, and spectra were referenced relative to a sample of DPPH, with a g value of 2.0036, which was taped to the wall of the quartz dewar as close to the sample as possible. Both solid-state and frozen solution (acetone or $CHCl_3$–toluene glass) spectra were obtained and in all cases indicated the same species in solution as in the solid state. Solutions of the dithiolates and dithiooxalates were frozen rapidly to prevent decomposition; all other complexes were stable for at least several hours in solution.

Results

Since much of the work to follow will involve Ru and Os, it should first be established that these metals indeed do behave in the same way as Fe. In Table I are presented results from spectra of Fe(III) low-spin complexes. These are divided into two groups: (a) the tris-bidentate sulfur chelates and (b) other representative types. The difference in these two groups is immediately apparent. The sulfur-donor chelates are all very similar; g values, especially g_3, are quite close to 2.0 and all appear rhombic. The remaining types all show marked g-tensor anisotropy consistent with varying degrees of distortion of either sign. In Table II now, are presented similar data for Ru(III) and Os(III) complexes, where it is readily seen that this pattern still prevails.

Table I. Typical g Values Found in Low-Spin Fe(III) Complexes[a]

	g_1	g_2	g_3	Ref
$Fe(CN)_6^{3-}$	2.35	2.10	0.91	2
$Fe(bipy)_3^{3+}$	2.61	2.61	1.61	3a
$Fe(bipy)_2(CN)_2^+$	2.74	2.47	1.54	11
$Fe(en)_3^{3+}$	2.68	2.68	<0.6	*b*
$Fe(diars)_2Cl_2^+$	3.05	1.86	1.64	*c*
Fe(sacac)₃	2.341	2.182	1.930	6
Fe(sacsac)₃	2.161	2.090	2.004	6, 7, 8
Fe(exan)₃	2.210	2.143	1.985	6,*b*
Fe(dtc)₃	2.111	2.076	2.015	9
$Fe(mnt)_3^{3-}$	2.225	2.114	1.986	6
Fe(dtb)₃	2.155	2.094	2.008	6
Fe(ttd)(dtt)₂	2.156	2.097	2.018	12

[a] Absolute values. Signs undetermined from experiment. [b] R. DeSimone, unpublished data. [c] R. DeSimone, Ph,D. Thesis, University of Illinois, 1970.

Theory

The theory of electron resonance in the $d^5(t_{2g}{}^5)$ configuration was first put forward by Stevens[23] and then in more complete form by Bleaney and O'Brien.[2b] The d^5 system is treated as a d^1 system *via* the hole formalism. For d^5 one is pretty much forced to use this approach or a minor modification thereof,[10] although for d^1 a more complete treatment[24] is feasible.

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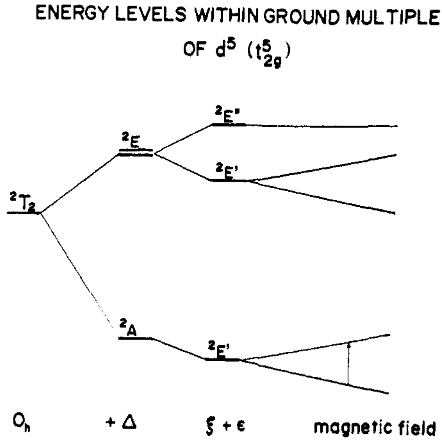

Figure 1. Energy level diagram for the $^2T_2$ term of $d^5(t_{2g}^5)$ under the combined influence of low-symmetry field, spin–orbit, and magnetic field perturbation. Diagram is constructed for a positive trigonal field. Primed *term* symbols are of the D_3 double group.

Table II. Typical g Values Found in Ru(III) and Os(III) Complexes[a]

	g_1	g_2	g_3	Ref
$Ru(bipy)_3^{3+}$	2.64	2.64	(~1.1)	3a
$Os(bipy)_3^{3+}$	2.49	2.49	<0.6	3a
$Ru(en)_3^{3+}$	2.64	2.64	0.33	*c*
$Os(en)_3^{3+}$	(~2.5)			*d*
$Ru(diars)_2Cl_2^{+}$	3.22	1.72	1.41	*b*
$Os(diars)_2Cl_2^{+}$	3.46	1.29	<0.6	*b*
$Ru(ox)_3^{3-}$	2.30	2.02	1.76	*d*
$Ru(acac)_3$	2.45	2.16	1.45	*d, e*
$Ru(sacsac)_3$	2.109	2.031	1.992	This work
$Os(sacsac)_3$	2.138	1.89	1.76	
$Ru(mnt)_3^{3-}$	2.120	2.026	1.968	
$Os(mnt)_3^{3-}$	2.19	2.01	1.82	
$Ru(dtc)_3$	2.156	2.109	1.979	
$Ru(dtp)_3$	2.085	2.055	1.982	
$Ru(dto)_3^{3-}$	2.04	2.04	1.98	

[a] Absolute values. Signs undetermined from experiment. [b] R. DeSimone, Ph.D. Thesis, University of Illinois, 1970. [c] J. A. Stanko, H. J. Peresie, R. A. Bernheim, R. Wang, and P. S. Wang, *Inorg. Chem.*, **12**, 634 (1973). [d] R. DeSimone, unpublished data. [e] The results for $Ru(acac)_3$ in $Al(acac)_3$, quoted in ref 5, do not reflect accurately the properties of the $Ru(acac)_3$ molecule. See B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc. A*, 422 (1966). Values quoted in Table II reflect those of pure $Ru(acac)_3$ and $Ru(acac)_3$ in various glasses and are felt to be more indicative of the true molecular distortion.

The major assumption made is that only the $^2T_2$ ground term need be considered; *i.e.*, only the octahedral t_{2g} orbitals need be included in the basis set. As long as the crystal field or the spin–orbit interaction causes only a small amount of mixing with the lower lying excited states, the error introduced by this approximation is not expected to be serious. In the case of the iron complexes a substantial reduction in interelectronic repulsion parameters usually associated with sulfur ligands may be a source of error. In the case of the osmium complexes, the large magnitude of the spin–orbit coupling probably necessitates the use of modified equations, such as given by Hill[10] to take into account the mixing of excited states into the ground state *via* the spin–orbit coupling. Since the present purposes do not require precise data for the osmium complexes, this has not been done.

A brief summary of the necessary equations will be given here since considerable variation and some error exists in the literature on this point. We assume the following form for our basis orbitals so that we may adopt the hole formalism.[21a,b]

$$-|1\rangle = 1/\sqrt{2}(d_{xz} + id_{yz}) \qquad (1a)$$

$$|-1\rangle = 1/\sqrt{2}(d_{xz} - id_{yz}) \qquad (1b)$$

$$\xi_1 = id_{xy} = 1/\sqrt{2}(|2\rangle - |-2\rangle) \qquad (1c)$$

In trigonal quantization, $d_{z^2} = t_0 = |0\rangle$ is associated with d_{xy} in tetragonal quantization, while $t_\pm = \sqrt{2/3}|\mp 2\rangle \pm \sqrt{1/3}|\pm 1\rangle$ are associated with the d_{xz} and d_{yz} set of tetragonal orbitals. As indicated in Figure 1, the combined action of low symmetry field and spin–orbit interaction resolves the sixfold degeneracy of the $^2T_2$ term producing three well-separated Kramers' doublets. In these calculations and in the equations which follow, ξ is the one-electron spin–orbit coupling constant defined as positive, Δ is the splitting of the t_{2g} orbitals by the axial component of the crystal field and is defined as positive if the orbital singlet, (*i.e.*, t_0 or d_{xy}) lies lowest. For d^1 this corresponds to a ^2A *term* as ground state and for d^5 to a ^2E *term*. The rhombic splitting of d_{xz} and d_{yz} in the absence of spin–orbit interactions is defined as 6ϵ. Of course the actual separations of the three Kramers' doublets are functions of all three of these parameters.

In the most general case, the ground doublet in which resonance is observed may be written as

$$\psi = A|1^+\rangle + B|\xi_1^-\rangle + C|-1^+\rangle \qquad (2a)$$

$$\psi' = A|-1^-\rangle - B|\xi_1^+\rangle + C|^-\rangle \qquad (2b)$$

where $\psi' = i\psi^*$ and $A^2 + B^2 + C^2 = 1$. In the case of axial symmetry $C = 0$. Operating on these functions with the magnetic moment operator ($k\mathrm{L} + g_e\mathrm{S}$) yields equations for the g-tensor components in terms of the coefficients A, B, C, and the orbital reduction factor k.[25] k is expected to be ≤ 1.0 but is not necessarily so, as many factors enter into its value. As has been pointed out,[2,25] it is quite risky to equate k with delocalization or covalency. The equations for g_i are

$$g_x = 2[2AC - B^2 + k\sqrt{2}B(C - A)] \qquad (3a)$$

$$g_y = -2[2AC + B^2 + k\sqrt{2}B(C + A)] \qquad (3b)$$

$$g_z = -2[k(A^2 - C^2) + A^2 - B^2 + C^2] \qquad (3c)$$

Change of sign of any pair of these equations produces the same physical result.[26] The present signs are favored since they yield the value of $g_i = -2.0$ when the octahedral values of A, B, and C are plugged in with $k = 1.0$, and they give $g_x = g_y$ if $C = 0$. A normal resonance experiment of course does not determine the signs of the g_i[27,28] and this is the source of the ambiguity associated with the data at all times. One must consider all sign combinations which yield consistent and acceptable solutions. The values of A, B, and C may be used to calculate the orbital energies

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and the crystal field parameters as functions of ξ. We get

$$\epsilon/\xi = -\left(\frac{A\sqrt{2} + B}{3\sqrt{2}}\right)\left(\frac{C}{C^2 - A^2}\right) \tag{4}$$

$$\Delta/\xi = -A/B\sqrt{2} - 1/2 + (3A/C)(\epsilon/\xi) \tag{5}$$

$$E_1/\xi = -A/B\sqrt{2} - (2/3)(\Delta/\xi) \tag{6}$$

ξ must be determined independently from temperature-dependent susceptibility or Mössbauer measurements or may be estimated from the value of $\langle r^{-3}\rangle$ derived from the hyperfine interaction.

Within the same $^2T_2$ model, expressions for the hyperfine coupling constants A_x, A_y, and A_z may be obtained from consideration of the $A\mathbf{I}\cdot\mathbf{S}$ operator. This has been done,[2b,4] but only the results for axial symmetry, $A_x = A_y$, are presented here since the data do not justify the use of the general equations.

$$A_{\parallel} = P[4/7 - (16/7)A^2 - (2\sqrt{2}/7)AB + \kappa(A^2 - B^2)] \tag{7a}$$

$$A_{\perp} = P[2/7 - (15\sqrt{2}/7)AB + \kappa B^2] \tag{7b}$$

where the constant P is

$$P = 2\gamma\beta_e\beta_n\langle r^{-3}\rangle \tag{8}$$

κ is the so-called core-polarization constant,[29,30] $\gamma = \mu_n/I$ and other terms have their usual meanings. A useful derived parameter by which to measure the contact interaction is defined as

$$\chi = -(3/2)\kappa\langle r^{-3}\rangle \tag{9}$$

the core polarization hyperfine field per unit spin.[30]

For the sulfur chelates under consideration here, one finds that the experimental data, combined with the above equations, can be made to yield at most two acceptable solutions: (1) hole in d_{xy} or t_0, large Δ/ξ corresponding to a large distortion and (2) hole in $(d_{xz} \pm d_{yz})$ or $t_{\pm}$, small Δ/ξ corresponding to a very small distortion. Solution 1 requires $g_z < g_x$, g_y and g_z positive, g_x, g_y negative. Solution 2 requires $g_z > g_x$, g_y and g_z, g_x, g_y all negative. Throughout the remainder of this paper, solutions 1 and 2 will refer to these two sets of solutions as defined here.

Discussion

Application of the preceding theory to the iron(III) dithio chelates previously studied by epr has led to the conclusion that the ground-state Kramers' doublet wave functions ψ and ψ' are basically composed of the $(d_{xz} \pm d_{yz})$ or $t_{\pm}$ hole,[6-9] implying a very small distortion of only a few inverse centimeters from octahedral symmetry. Only in the case of the $Fe(ttd)(dtt)_2$ and $Fe(dtt)(ttd)_2$ complexes (dtt = dithio-*p*-toluate; ttd = trithioperoxy-*p*-toluate), did Rickards, Johnson, and Hill[12] propose a ground state consisting of a d_{xy} hole and here more in order to obtain agreement with their Mössbauer results than to fit the epr data. They were not able to reproduce g_z well (this turns out to be the key to the whole problem as we shall see) and in fact a much better fit is obtained with solution 2. The Mössbauer study of $Fe(sacsac)_3$ by Reiff and Szymanski[13] indicated a d_{xy} hole, but their calculation based on reported[7,8] epr g values indicated an acceptable fit could only be achieved with a $(d_{xz} \pm d_{yz})$ hole and small distortion. This is clearly inconsistent with not only the sign of the distortion but also with the large magnitude of ΔE_Q, ≈ 1.9 mm/sec at 300°K.[8,13] They rejected this interpretation in favor of that indicated by their Mössbauer results.

The previous epr studies then, indicate for all of these Fe–sulfur chelates a *small* distortion from octahedral symmetry. Many of these same complexes show large quadrupole splittings,[8,9,12] X-ray structures of $Fe(exan)_3$[31] $Fe(dtt)_3\cdot CHCl_3$,[32] and $Fe(sacsac)_3$[8] show considerable distortion from idealized geometry, and magnetic moments are generally low and rather temperature independent. This is not the kind of behavior which one would expect from slightly distorted molecules with T ground states. These should show little asymmetry in the electric field gradient at the Fe nucleus and should have large temperature-dependent second-order Zeeman contributions to the magnetic moments, which should thus be higher than are observed.[33]

The values of the orbital reduction factor for these complexes as determined from solution 2 are very similar, as in fact are all of the parameters, and range from 1.03–1.08.[6] There has recently been considerable discussion of the orbital reduction factor, its expected magnitude, its interpretation as a covalency parameter, and, in this context, as a "sink" into which all other unaccounted for effects are drawn.[2,25] Griffith,[28] Thornley,[34] and more recently Cotton[35] have considered modification of these high values of k, and Cotton has shown that for $Fe(dtc)_3$ and $Fe(exan)_3$ k can be reduced from approximately 1.07–1.08 to 0.83–0.87 by considering $t_2^4(^3T_1)e$ and $t_2^4(^1T_2)e$ configurations mixed into $t_{2g}^5(^2T_2)$ by electrostatic interactions. Spin–orbit and charge transfer mixing have been assumed relatively unimportant. Steps of this sort are undoubtedly in the right direction, but cannot really be expected to attach any more significance to the value of k. The reasonableness of k must clearly *not* be taken as the sole criterion of acceptability for a solution, even though this is quite tempting. In view of the factors delineated above, a reinterpretation of the epr results seems warranted.

The data in Tables I and II establish the essential similarity of Ru(III) and Os(III) complexes to their Fe(III) counterparts. Fitting the results for Ru(III) to the theoretical equations is a bit more illuminating, however. Table III presents the two acceptable fits for several Ru(III) complexes, and Table IV compares the results for Fe(III), Ru(III), and Os(III) with the same ligands, namely $sacsac^-$ and mnt^{2-}. Examination of these tables shows that in fact for Ru(III) and Os(III) there are two solutions which cannot be rejected out of hand. (As the results for $Fe(sacsac)_3$ and $Fe(mnt)_3^{3-}$

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Table III. Comparison of the Results of the Two Possible "Fits" to the Epr Data Obtained for Ru(III) Sulfur Chelates[a,b]

	No.	k	Δ/ξ[c]	ϵ/ξ[c]	A	B	C
Ru(sacsac)$_3$	1	0.96	32.72	−5.36	0.029	0.999	−0.013
	2	1.03	−0.03	+0.003	0.823	0.568	0.004
Ru(dtc)$_3$	1	0.70	10.20	−0.53	0.074	0.997	−0.010
	2	1.06	−0.05	+0.003	0.805	0.593	0.005
Ru(dto)$_3$$^{3-}$	1	0.26	11.05	0.0	0.066	0.998	0.0
	2	1.01	−0.02	0.0	0.812	0.583	0.0
Ru(dtp)$_3$	1	0.46	12.56	−0.71	0.060	0.998	−0.009
	2	1.03	−0.03	+0.001	0.810	0.586	0.003
Ru(mnt)$_3$$^{3-}$	1	0.41	11.94	−1.69	0.075	0.997	−0.030
	2	1.03	−0.04	+0.003	0.825	0.566	0.006
Ru(ox)$_3$$^{3-}$	1	0.44	4.0	−0.48	0.215	0.974	−0.067
	2	1.02	−0.146	+0.01	0.788	0.615	0.028
Ru(acac)$_3$	1	0.60	2.4	−0.16	0.323	0.945	−0.050
	2	1.03	−0.30	+0.02	0.754	0.656	0.029

[a] Rows labeled 1 and 2 refer to solutions 1 and 2 as defined in the text. [b] Ru(ox)$_3$$^{3-}$ and Ru(acac)$_3$ have been included for comparison. [c] In units of ξ.

Table IV. Comparison of Acceptable "Fits" for Complexes of Fe(III), Ru(III), and Os(III) with the Same Ligands[a]

	No.	k	Δ/ξ[b]	ϵ/ξ[b]	ΔE_1[b]	ΔE_2[b]	A	B	C
Fe(sacsac)$_3$	1	1.98	35.93	−3.47	25.54	46.37	0.022	0.999	−0.006
	2	1.06	−0.042	0.005	1.48	1.52	0.824	0.566	0.009
Ru(sacsac)$_3$	1	0.96	32.72	−5.36	15.68	48.82	0.029	0.999	−0.013
	2	1.03	−0.037	0.002	1.48	1.52	0.823	0.568	0.004
Os(sacsac)$_3$	1	0.20	4.21	−0.634	2.33	6.36	0.219	0.971	−0.085
	2	0.94	−0.123	0.008	1.46	1.55	0.838	0.546	0.014
Fe(mnt)$_3$$^{3-}$	1	1.35	17.75	−1.85	12.22	23.39	0.045	0.999	−0.014
	2	1.08	−0.064	0.007	1.48	1.52	0.827	0.560	0.012
Ru(mnt)$_3$$^{3-}$	1	0.41	11.94	−1.69	6.92	17.12	0.075	0.997	−0.030
	2	1.03	−0.044	0.003	1.48	1.52	0.825	0.566	0.006
Os(mnt)$_3$$^{3-}$	1	0.33	4.37	−0.463	2.96	6.01	0.191	0.980	−0.053
	2	1.01	−0.100	0.011	1.46	1.54	0.834	0.550	0.019

[a] Rows labeled 1 and 2 refer to solutions 1 and 2 as defined in the text. [b] In units of ξ.

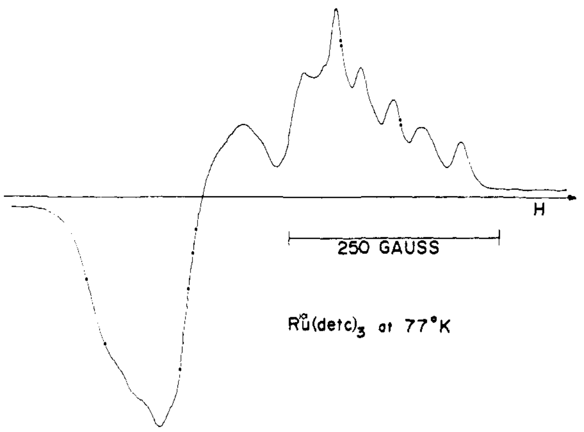

Figure 2. Epr spectrum of ^{101}Ru(detc)$_3$ at 77°K, showing hyperfine splitting due to ^{101}Ru.

in Table IV indicate, solution 1 is likely to be considered unreasonable for Fe(III) on the basis of k = 1.98 and 1.35, respectively, leaving only one apparently acceptable fit.) Confining our attention to the Ru(III) complexes, we see that fit 2 is virtually identical with that assumed valid for the Fe(III) complexes; *i.e.*, very small Δ/ξ, ϵ/ξ, k slightly greater than 1.0, and $\Delta E_1 \approx \Delta E_2 \approx 1.5\xi$. Fit 1 produces large distortions relatively consistent in magnitude, with the exception of Ru(sacsac)$_3$ for which Δ/ξ and ϵ/ξ are much larger, and k values ranging from 0.26 to 0.96.

These Ru(III) complexes, like their Fe(III) counterparts show low, relatively temperature-independent magnetic moments;[14] Ru(dtc)$_3$ for example is structurally quite distorted,[36] and one is led to believe that their magnetic properties are essentially those of their Fe(III) counterparts. The data in Table IV for the Os(III) complexes likewise appear quite reasonable for solution 1, which seems unacceptable for the Fe(III) complexes. In view of this continuing ambiguity, more data are needed to resolve the problem. It seems reasonable to expect that perhaps the parameters of solution 1 for the iron (III) complexes are not reliable enough to allow their use in predicting other properties such as ΔE_q or hyperfine splittings. For Ru(III), however, one has no good reason for assuming this, and one might hope to obtain the desired information by further investigation of these Ru(III) complexes.

Obtaining Mössbauer data for Ru complexes is quite difficult and nobody has yet determined the sign of V_{zz} for a Ru(III) complex, although this would be most welcome. Furthermore, the sign of V_{zz} and its correlation with either a ^2A or ^2E ground term depends on whether one considers the molecule as trigonal or tetragonal. Since all of these systems possess symmetry lower than axial, interpretation of V_{zz} is not clear. In view of these considerations, it was decided to pursue the hyperfine interaction in the hope of resolving the ambiguity in the epr results derived from g values alone.

A small quantity of ^{101}Ru(detc)$_3$ was prepared from 97% enriched RuCl$_3$·nH$_2$O; the spectrum at 77°K of this complex is shown in Figure 2. For ^{101}Ru I =

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Table V. Hyperfine Interaction for ^{101}Ru(detc)$_3$

$A_{\parallel} = 38 \pm 1$ G $= 35 \pm 1 \times 10^{-4}$ cm^{-1}			
$A_{\perp} = 21 \pm 3$ G $= 21 \pm 3 \times 10^{-4}$ cm^{-1}			
Solution 1	$A_{\perp} = 0.0741$, $B = 0.9972$	Solution 2	$A = 0.8053$, $B = 0.5928$
$A_{\parallel}/A_{\perp} > 0$	$P = -94 \times 10^{-4}$ cm^{-1} $\kappa = 0.161$ $\langle r^{-3}\rangle = 10.75$ au	$A_{\parallel}/A_{\perp} > 0$	$P = -141 \times 10^{-4}$ cm^{-1} $\kappa = 2.88$ $\langle r^{-3}\rangle = 16.04$ au
$A_{\parallel}/A_{\perp} < 0$	$P = -24 \times 10^{-4}$ cm^{-1} $\kappa = 0.945$ $\langle r^{-3}\rangle = 2.71$ au $\chi = +3.84$ au	$A_{\parallel}/A_{\perp} < 0$	$P = -431 \times 10^{-4}$ cm^{-1} $\kappa = 3.44$ $\langle r^{-3}\rangle = 49.10$ au
Calculated free ion value of $\langle r^{-3}\rangle = 6.5$ au[38]			
Calculated free ion value of $\chi = -8.5$ au[38]			

5/2, and the six $A_{\parallel}$ hyperfine components of the $g_{\parallel}$ resonance are nicely resolved. The six $A_{\perp}$ components of the $g_{\perp}$ resonance (the spectrum of this compound appears nearly axial so we use the designation of $\parallel$ and $\perp$ rather than x, y, z) are not all resolved; however, we can readily see the uniform spacing of four of the six lines. This spectrum will be further investigated to 4.2° to obtain more accurate results. Our hyperfine calculations will thus not be as precise as they could be, but simply knowing that $A_{\parallel}$ is nearly twice $A_{\perp}$ is sufficient to provide all the information we need. With reasonable estimates of error, $A_{\parallel} = 38 \pm 1$ G, $A_{\perp} = 21 \pm 3$ G.

As with the g values, we do not know the signs of $A_{\parallel}$ and $A_{\perp}$. We do know, however, that the sign of P must be negative since for ^{101}Ru $\mu_n = -0.69$, and this is reflected in the sign of γ. This simplifies things a bit since solutions to equations (7) which yield positive values of P may be rejected. We are left with four solutions, two each for the two fits to the g values. These are given in Table V, along with the calculated parameters P, κ, $\langle r^{-3}\rangle$, and χ.

Little is known of the nature of the hyperfine interaction in second-row transition metals, in large part because of the paucity of experimental data.[4,37] Freeman and Watson[30,38] using unrestricted Hartree–Fock methods have calculated, for a great many ions, values of χ and $\langle r^{-3}\rangle$. For first-row transition ions, $\chi = -3$ au, increasing only slightly as one moves across the series. This was first noted by Abragam and Pryce and has since been demonstrated[39] for a large number of complexes. Among the second-row elements χ and $\langle r^{-3}\rangle$ are expected to be larger, but any such constancy in χ has not been noted. The values calculated for Ru^{3+} by Freemen and Watson are $\langle r^{-3}\rangle_{4d} = 6.5$ au and $\chi = -8.5$ au.[38] Covalent interactions are expected to decrease both of these quantities; χ is less predictably affected than $\langle r^{3-}\rangle$ due to the dependence on κ. From the data in Table V, it is seen that three of the four possible solutions yield $\langle r^{-3}\rangle$ much greater than the free ion value and may be discarded. One might be induced to allow a value close to or slightly greater than the free ion value if it appeared that weaknesses in the theory might be responsible. However, as we have seen, this is not the case for Ru(III) and these values are clearly unreasonable, even in view of error associated with the Hartree–Fock calculation. The only acceptable solution then, is one corresponding to $B \gg A$, $A_{\parallel}/A_{\perp} < 0$ of the configuration in which the hole resides in the d$_{xy}$ (or t_0) orbital. This conclusion is consistent with the large low-symmetry distortion expected on other grounds. The value of $\langle r^{-3}\rangle = 2.7$ au represents a reduction to 40% of the free-ion value, indicating considerable metal ligand interaction. Since the spin–orbit coupling constant depends directly on $\langle r^{-3}\rangle$,[40] we may infer a similar reduction in ξ upon complex formation giving a value of $\xi_{\text{eff}} \approx 480$ cm^{-1} based on $\xi \approx 1200$ cm^{-1}. This of course depends upon the correctness of the calculated value of $\langle r^{-3}\rangle_{4d}$ for Ru^{3+}, but the results seem reasonable.

Perhaps most interesting is the negative value of κ which in turn produces a positive value of $\chi = +3.84$ au. A few comments are in order concerning the origin of χ. For most transition metals in high symmetry environments, χ is presumed to arise from polarization of filled inner s-orbital electrons by exchange interaction with unpaired electrons residing in the d orbitals,[39] thus the term core polarization and the negative sign associated with χ. It is possible, however, in certain instances, to have a direct interaction between s and d orbitals containing the unpaired spin. In this case the contribution to χ would be positive and of course only a very small amount of direct admixture of s and d orbitals would be required to offset the relatively small effects of polarization. This situation is allowed in complexes of D_3 symmetry (and in most, but not all lower symmetries) and has been found to exist in complexes of vanadium, chromium, and molybdenum with dithio chelates. A discussion has been given by McGarvey.[39] The results which we have found here are thus not unacceptable in any way, and it is felt that the problem is adequately resolved.

Conclusions

Having established conclusively the situation which exists in Ru(detc)$_3$, the remaining task is to extend this to the other Ru(III) and of course to the Fe(III) complexes. The essential question is this: is it reasonable to assume that all of these complexes share the feature of a large low-symmetry distortion and a ^{2}A ground term? As was discussed previously, there is independent evidence for large distortions in many of these complexes. Complexes with four-membered chelate rings obviously are subject to considerable strain due to the small S–M–S angle, often as small as 73°.[32,36] Complexes with larger chelate rings would

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(39) B. R. McGarvey, *J. Phys. Chem.*, 71, 51 (1967).

(40) M. Blume, A. J. Freeman, and R. E. Watson, *Phys. Rev.*, **134**, A320 (1964).

not be expected to show such pronounced distortion, but available structural evidence indicates that these too are not as close to octahedral as one might expect; Rh(sacsac)$_3$[41] and Fe(sacsac)$_3$[8] both show considerable distortion. It therefore does not seem reasonable to assume that any of these complexes have only slightly distorted structures, and it seems that only one alternative is open, that found in this work.

The question of *why* this situation exists is more complicated but not surprising when one considers all of the facts. From a purely geometric standpoint, many complexes coordinated *via* oxygen and nitrogen are equally distorted but do not manifest this large distortion in the epr. If one partially substitutes oxygen for sulfur in the sacsac$^-$ complexes, producing monothio–acac complexes, this difference is noticeably reflected in the epr spectra; the g values begin deviating considerably from 2.0. (See Table I for Fe(sacac)$_3$.) One cannot rule out the possibility that much of the distortion in these complexes is electronic in nature. If the reduction in $\langle r^{-3} \rangle$ and by implication the reduction in ξ, is as large as indicated by the hyperfine couplings in Ru(detc)$_3$, then these are very covalent complexes indeed, and anisotropy in the covalent interaction—due to the electronic configuration rather than the structure—would contribute significantly to large electronic distortions. The fact that the ground state is as pure a $t_0(d_{xy})$ hole as it appears to be, would indicate considerable anisotropy in the covalent bonding, at least more than would be the case if all of the t_{2g} orbitals participated more or less equally in the ground state. Thus we have a situation where in these compounds a moderate geometric distortion coupled with a high degree of covalency produces a large anisotropy, characterized by spectra differing markedly from the less covalent complexes of oxygen and nitrogen donors of comparable structural features.

Finally we must evaluate the Bleaney–Stevens theory in regard to these complexes. Looking at the raw data, in the form of the g values, one sees that the greatest difficulty arises when the lowest g value, g_z, is closest to $+2.0$. The problem is most serious when the value of $g_z > 2.0$ as in Fe(dtc)$_3$ and Fe(sacsac)$_3$, a situation which is strictly not allowed within the framework of the $^2T_2$ model. This points out two important considerations. The existence of complexes in which all three g values are $> |2.0|$ clearly indicates that the model is in some way incomplete, either by virtue of neglect of configuration interaction and/or anisotropic covalent interaction with the ligand. Fe(sacac)$_3$, as noted, appears quite normal, much more like the Ru(III) complexes than the Fe(III) complexes, (with $k = 0.94$, $A = 0.108$, $B = 0.993$, $C = 0.026$, and $\Delta/\xi = 7.38$) so that perhaps less importance should be attached to the configuration interaction than has been so far assumed. Strong covalent bonding may be much more important in limiting the applicability of the theory. The other important point bears on the uncertainty in the derived parameters. Parameters like Δ/ξ and k "blow up" rapidly as g_z approaches $+2.0$ from the low side. For an increment Δg between 1.99 and 2.00, for example, there is a tremendous change in the derived parameters, quite independent of reality, it seems. This is purely the fault of the mathematics; in the limit of large distortion (g_x, $g_y = -2.0$, $g_z = +2.0$), any derived parameters can be quite meaningless. In the limit of large distortion, the g values are in fact virtually independent of k. The lower values of k in Table III ($k \approx 0.4$) are most likely to be as good as this ligand field approach is capable of providing. It seems that the source of the incorrect assignments previously made for many of the Fe(III) complexes lies with the nature of the fitting process and the criteria used for an acceptable fit. Within limitations of both the model and experimental data, these tris-bidentate dithiochelates of Fe(III), Ru(III), and Os(III) can be fitted to a consistent electronic model, and use of the information contained in the hyperfine coupling provides an effective means of resolving the ambiguities arising from less complete data.

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