Magnetic Resonance Studies of Some Low-Spin d^5 Tris Diimine Complexes

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Abstract: A detailed magnetic resonance investigation of the Fe(III), Ru(III), and Os(III) complexes with 2,2′-bipyridyl and 1,10-phenanthroline has been carried out with the purpose of obtaining an accurate estimate of the dipolar contribution to the observed shifts, to establish, if possible, trends in σ and π delocalization in this series of metal ion complexes and to compare our results for these t_{2g}^5 systems with the previously reported nickel(II) complexes with the same ligand. We find a large dipolar contribution to the shift which cannot be neglected and, as a result, show that the conclusions of a previous study of the Fe(III) complex are basically incorrect. Significantly, too, we find that the mechanisms of spin delocalization are radically different in the iron(III) and nickel(II) complexes and a model to account for this is proposed. Finally, we are able to say that Ru(III) exhibits a significantly greater degree of π delocalization than either Fe(III) or Os(III) and that σ delocalization appears most important in the Fe(III) complexes.

We have been interested in the application of nmr contact shift studies to problems concerning bonding in transition metal complexes. Numerous studies have appeared which attempt to relate electron nuclear hyperfine coupling constants and calculated unpaired spin densities to the mode of metal–ligand bonding or the type of delocalization of unpaired spin onto the ligand.[1] Very little good quantitative work has been done,[2] however, and virtually all work of any sort has been on first-row transition metal complexes. Previous work in our laboratory[3] using 2,2′-bipyridyl as a ligand has encouraged us to continue its use as a probe of the metal–ligand interaction and to extend our studies to several of the heavier metals.

For this study, we have chosen the series of metals, iron(III), ruthenium(III), and osmium(III), all of which form tris chelates with 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen). We have here an unusual series of complexes in that iron(III), as well as ruthenium(III) and osmium(III), forms *low-spin* species providing us the opportunity to study trends in delocalization in a series of completely analogous compounds.

Previous quantitative work on complexes of metals other than octahedral nickel(II) or tetrahedral cobalt(II) has been hampered considerably by the pseudo-contact shift problem which has only rarely been treated properly.[2] As a result, any speculation as to spin delocalization mechanisms is likely to be in error by enough to make any analysis meaningless. Fortunately, in these complexes, study of both nmr and esr is possible and g-tensor anisotropy can be determined, enabling us to carry out a thorough treatment of the pseudo-contact interaction and to show that in these and other complexes, where appreciable magnetic anisotropy exists, it is of sufficient importance that it cannot be neglected if any truly meaningful interpretation of spin delocalization and bonding is to be made. Indeed, we shall show that a previously reported delocalization mechanism[4] for the iron(III) complex is incorrect because of elimination of pseudo-contact contributions. This[4] is an excellent example of how one can go wrong by ignoring this effect even in a qualitative interpretation of mechanism.

Experimental Section

Reagents. 2,2′-Bipyridyl and 1,10-phenanthroline were used as purchased from Aldrich Chemical Company and J. T. Baker Chemical Company, respectively. Methyl-substituted phenanthrolines and bipyridines were purchased from G. F. Smith Company, except for 5,5′-dimethyl-2,2′-bipyridine, which was synthesized by the procedure of Sasse.[5] Ruthenium trichloride, rhodium trichloride, and potassium hexachloroosmate(IV) were obtained from Research Inorganics, Inc. Deuterated solvents were obtained from either Merck or Diaprep. Potassium hexafluorophosphate was obtained from Ozark Mahoning Corp. and was recrystallized from hot water before use. All other chemicals were reagent grade.

Preparation of Complexes. All of the compounds reported have been prepared previously except that the ruthenium(III) complexes have never been isolated in stable form. The quality of the preparations varies considerably, and with several complexes, considerable difficulty in obtaining reproducibility was encountered. The preparative procedures given below are those which we have found to be on the whole most satisfactory.

$Fe(bipy)_3(PF_6)_3$. 2,2′-Bipyridyl (1.56 g, 0.01 mol) and 0.92 g (0.0033 mol) of $FeSO_4 \cdot 7H_2O$ were added to 25 ml of H_2O and warmed gently until all solid had dissolved. The solution was then filtered into a flask immersed in an ice bath and 2–3 ml of 1 M H_2SO_4 added. After further cooling, an excess of PbO_2 was added and the solution was mixed thoroughly until all traces of red color had disappeared leaving a blue solution. This solution was filtered into a cold aqueous solution of KPF_6 whereupon blue crystals of the desired complex precipitated immediately. The product was filtered, washed first with a small amount of cold water, then with ethanol and ether, and dried over P_2O_5 under vacuum. As with all compounds reported here, this complex is unstable toward reduction and should be stored in a cool dark place.

Anal. Calcd for $C_{30}H_{24}N_6P_3F_{18}Fe$: C, 37.56; H, 2.25; N, 8.76; Fe, 5.56. Found: C, 37.10; H, 2.88; N, 8.57; Fe, 5.58.

$Fe(phen)_3(PF_6)_3$. Exactly the same procedure was used as for the bipyridine complex, beginning with 2.0 g (0.01 mol) of 1,10-phenanthroline and 0.92 g of $FeSO_4 \cdot 7H_2O$.

Anal. Calcd for $C_{36}H_{24}N_6P_3F_{18}Fe$: C, 41.92; H, 2.35; N, 8.15. Found: C, 42.02; H, 2.37; N, 7.70.

All methyl-substituted complexes were prepared in an exactly analogous manner. Microanalyses were satisfactory.

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[1] (a) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, 37, 347 (1962); (b) G. N. LaMar, W. D. Horrocks, Jr., and L. C. Allen, *ibid.*, 41, 2126 (1964); (c) J. A. Happe and R. L. Ward, *ibid.*, 39, 1211 (1963); (d) R. J. Fitzgerald and R. S. Drago, *J. Amer. Chem. Soc.*, 89, 2879 (1967); (e) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, 1, 103 (1965).

[2] J. P. Jesson, *J. Chem. Phys.*, 47, 582 (1967).

[3] (a) M. Wicholas and R. S. Drago, *J. Amer. Chem. Soc.*, 90, 2196 (1968); (b) *ibid.*, 90, 6946 (1968).

[4] G. N. LaMar and G. R. Van Hecke, *ibid.*, 91, 3442 (1969).

[5] W. H. F. Sasse, *Org. Syn.*, 46, 5 (1966).

$Co(bipy)_3(PF_6)_3$. Preparation was analogous to that of the iron(III) complex, except that only mild oxidizing conditions are necessary. More dilute acid solutions were used and there is no need to keep the solutions cold. The bright yellow powder may be recrystallized from 50:50 acetone–water to give well-formed crystals of what appears to be the monohydrate.

Anal. Calcd for $C_{30}H_{24}N_6P_3F_{18}Co \cdot H_2O$: C, 36.75; H, 2.67; N, 8.57. Found: C, 36.53; H, 2.69; N, 8.08.

All other cobalt complexes were prepared in a similar manner and recrystallized from acetone–water mixtures.

$Ru(bipy)_3(PF_6)_3$.[6] $RuCl_3$ and an excess of bipyridyl were fused in a test tube and kept at 260–270° for 1 hr. After cooling, the residue was extracted with hot benzene to remove excess bipyridyl. This was followed by boiling with hot water and filtering, after which bright orange crystals of $Ru(bipy)_3Cl_2 \cdot nH_2O$ were collected upon evaporation of the aqueous solution. The above product was dissolved in $\sim$6 *M* H_2SO_4 and cooled in an ice bath at 0°. (Throughout, the remainder of the preparation solutions should be kept as cold as possible.) Addition of PbO_2, with mixing, results in an emerald green solution of $Ru(bipy)_3{}^{3+}$. Filtering into KPF_6 results in formation of bright green hydrated $Ru(bipy)_3(PF_6)_3 \cdot nH_2O$, which is very unstable toward reduction if filtered immediately. If the precipitate is left in the acid solution for a few hours, it converts to a more stable crystalline form which can be filtered and washed with cold water without decomposition. Rapid drying over P_2O_5 *in vacuo* produces a di- or trihydrate, which is stable for several days *if kept cold.* Under favorable but somewhat unreproducible circumstances, we have been able to produce a stable anhydrous product as follows. If, after precipitation with PF_6, more H_2SO_4 is added until the precipitate begins to dissolve slightly, we have found that the light green crystals dehydrate with formation of deep green anhydrous microcrystals. This usually requires several hours, but once the process begins, it seems to proceed rather quickly. These crystals may be filtered, washed with water, and dried over P_2O_5 to give an anhydrous product which is stable for several weeks. All spectral properties of the hydrated and anhydrous complexes were identical. The stability of the anhydrous crystals leads one to suspect that reduction of Ru^{3+} in the hydrates takes place *via* the water of hydration. The high potential (+1.26 V) of the $Ru(bipy)_3{}^{2+}$/$Ru(bipy)_3{}^{3+}$ couple appears to be enough to accomplish such a reaction.

Anal. Calcd for $C_{30}H_{24}N_6P_3F_{18}Ru$: C, 35.87; H, 2.41; N, 8.37. Found: C, 35.71; H, 2.36; N, 8.43.

$Ru(phen)_3(PF_6)_3$. This compound was prepared in the same way as the bipyridyl complex. However, it is even more unstable and difficult to isolate in a pure form. Sulfuric acid solutions are a deep blue-green.

Anal. Calcd for $C_{36}H_{24}N_6P_3F_{18}Ru$: C, 40.05; H, 2.24; N, 7.79. Found: C, 39.95; H, 2.33; N, 8.28.

Methyl-substituted complexes were prepared in the same manner, but were found to be considerably more stable and easier to isolate.

$Rh(bipy)_3(PF_6)_3$.[7] $RhCl_3 \cdot H_2O$ (1.1 g) and 2.7 g of bipyridyl were fused in a test tube and heated to 270° for 10–15 min. The mixture was cooled and taken up in 40 ml of 50:50 ethanol–water. This solution was refluxed for 4 hr. Upon cooling and addition of a large volume of acetone, $Rh(bipy)_3Cl_3$ is precipitated. This product is usually tinted pink with a small amount of intensely colored impurity which may be removed as follows. The pink powder is dissolved in a minimum amount of water (2–3 ml) to give a very concentrated and fairly viscous solution. A few drops of acetone at a time are added with gentle swirling so as not to mix the nearly immiscible layers. Removal of the upper acetone layer removes some of the pink contaminant. This is repeated several times until all traces of pink color are gone. Dilution with H_2O and addition of $PF_6{}^-$ precipitates the pure white $Rh(bipy)_3(PF_6)_3$ complex which is recrystallized from acetone–water as for the cobalt complexes.

Anal. Calcd for $C_{30}H_{24}N_6P_3F_{18}Rh$: C, 35.80; H, 2.40; N, 8.35. Found: C, 35.68; H, 2.53; N, 8.59.

Anal. Calcd for $C_{30}H_{24}N_6F_{18}Rh$: C, 35.80; H, 2.40; N, 8.35. Found: C, 35.68; H, 2.53; N, 8.59.

$Rh(phen)_3(PF_6)_3$. Exactly the same procedure was followed as for the bipyridyl complex.

Anal. Calcd for $C_{36}H_{24}N_6P_3F_{18}Rh$: C, 40.02; H, 2.42; N, 7.77. Found: C, 40.11; H, 2.42; N, 8.09.

$Os(bipy)_3(PF_6)_3$.[8] K_2OsCl_6 and excess bipyridyl were fused in a test tube for 1 hr at 260°. The residue was extracted with benzene to remove excess bipyridine. The remaining solid was extracted with hot water and filtered. The light brown residue was discarded and the filtrate evaporated until all $[Os(bipy)_2Cl_2]Cl$ in the form of red plates had precipitated from the olive green solution. A small amount of 2 *M* NaOH was added and the solution boiled for a few minutes. Upon cooling, the solution was filtered and neutralized with HCl. Evaporation to dryness was followed by extraction with absolute ethanol, and the solution again was evaporated. The almost black crystals of $Os(bipy)_3Cl_2$ were dissolved in an acetonitrile–H_2O mixture and Cl_2 was bubbled through the solution until it had turned bright red. Addition of $PF_6{}^-$ and more H_2O resulted in precipitation of the complex $Os(bipy)_3(PF_6)_3$ which was washed with ethanol and ether and air-dried.

Anal. Calcd for $C_{30}H_{24}N_6P_3F_{18}Os$: C, 32.95; N, 7.80; Os, 17.4. Found: C, 32.31; N, 7.80; Os, 20.2.

$Os(phen)_3(PF_6)_3$.[9] K_2OsCl_6 and a twofold excess of phenanthroline were heated to 120° in 40 ml of glycerol until all water had been driven off. The temperature was raised and kept at 265° for 20 min. The solution was cooled and poured into 150 ml of warm water. Aqueous KPF_6 was added and the precipitate was filtered. The solid was extracted thoroughly with benzene to remove excess phenanthroline and taken up in CH_2Cl_2. The insoluble residue was discarded. After evaporation to dryness, the remaining solid was extracted with $CHCl_3$ to remove a large quantity of red compound, possibly $[Os(phen)_2Cl_2]PF_6$, leaving black crystals of $Os(bipy)_3(PF_6)_2$. This was dissolved in CH_3CN and treated with Cl_2, and upon addition of aqueous KPF_6, the desired complex precipitated. It was washed with ethanol and ether and air-dried.

Anal. Calcd for $C_{36}H_{24}N_6P_3F_{18}Os$: C, 37.06, N, 7.20; Os, 16.30. Found: C, 36.79; N, 7.22; Os, 17.5.

Microanalyses were performed at the University of Illinois microanalytical laboratory.

Physical Measurements. The 60-MHz nmr spectra were recorded on a Jeolco C60-H spectrometer and 100-MHz spectra were recorded on a Varian HA-100 spectrometer. Sideband calibration was employed in all cases. Shifts in D_2SO_4 were measured relative to $N(CH_3)_4Cl$ whose resonance was taken to be -3.1 ppm from TMS. Spectra in CD_3CN were referred directly to TMS.

Visible spectra to confirm the identity of species in solution were run as solutions and mulls on a Cary Model 14RI spectrophotometer equipped with a high-intensity source.

Epr spectra were measured at 77°K on a Varian V-4502 spectrometer system at X-band frequencies with 100-kHz modulation. The magnetic field was precalibrated with a gaussmeter and individual spectra were measured relative to a standard DPPH sample taped to the liquid nitrogen dewar.

Results

Nmr. Spectra of all iron and ruthenium complexes have been obtained in D_2SO_4 solutions, the only solvent in which these compounds are stable for any length of time. Previously reported spectra[10] of the iron(III) phenanthroline complexes recorded in D_2O containing Cl_2 do not agree with ours in all aspects. Another spectral report of iron(III) bipyridines in D_2O agrees somewhat better, but reference was made to the free ligand rather than a diamagnetic complex.[4] For this reason and in view of the acknowledged instability and decomposition noted by the above workers, we prefer to use our own data for interpretation. Stability studies[11a] in concentrated H_2SO_4 have shown the tris complexes of iron(III) to be stable for several days at temperatures well above room temperature. The same is apparently true for the even more unstable ruthenium(III) species, as we have not been able to detect any

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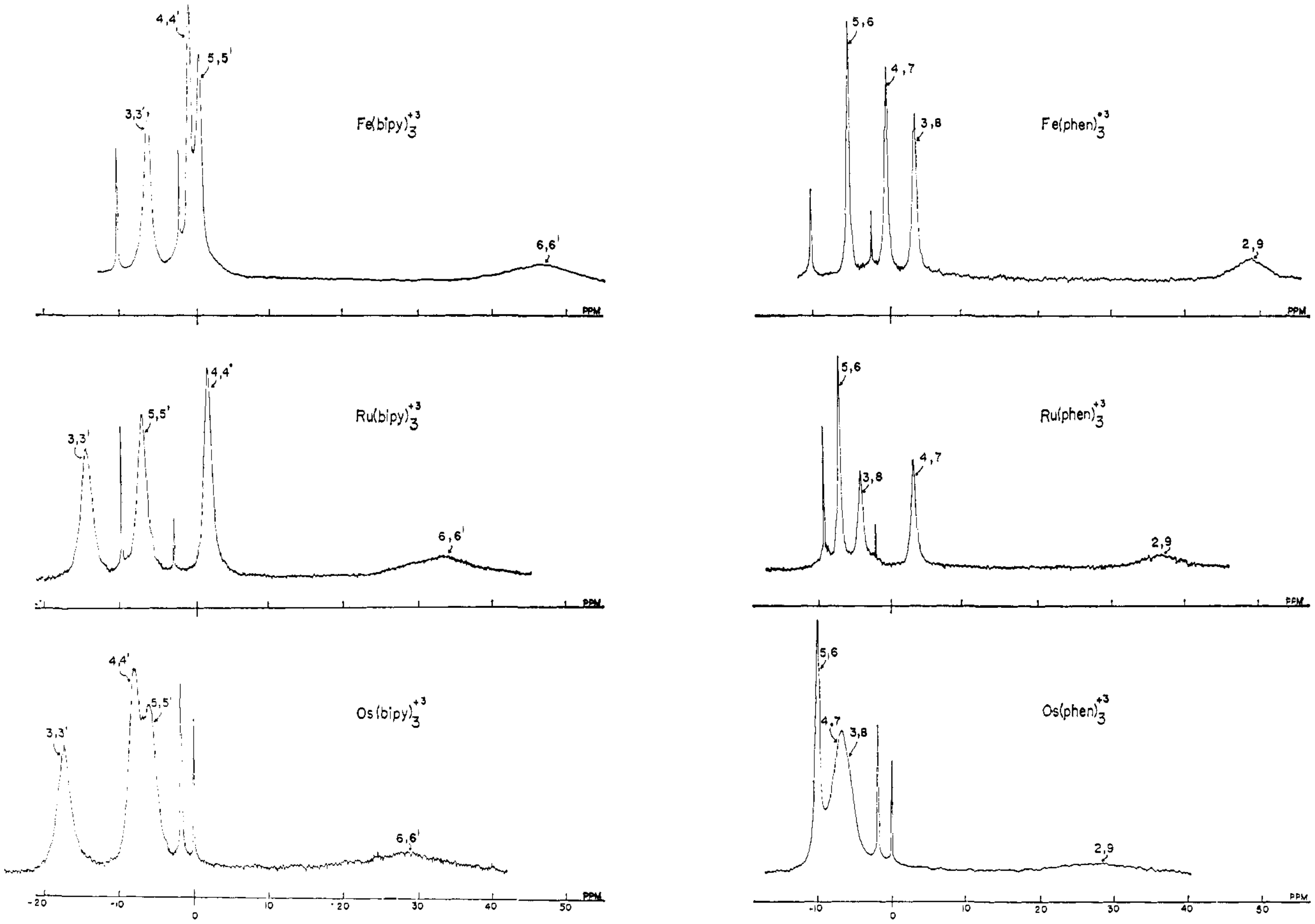

Figure 1. Nmr spectra of unsubstituted bipyridines and phenanthrolines. Scale at bottom is for all spectra.

changes in the solutions after more than 1 week. Protonation of the ligand in H_2SO_4 has been considered[11b] and we feel that the bulk of evidence does not support a protonated species.[11b] In addition, there is considerable evidence for formation of high-spin Fe(III) phenanthroline dimers in aqueous Cl_2 solution.[11c] Spectra of the diamagnetic cobalt(III) and rhodium(III) analogs were run in the same solvent with no apparent destruction of the complexes. The osmium(III) complexes, those which are most stable to reduction, were found to be destroyed by concentrated sulfuric acid. Other than slightly acidic D_2O in which solubility was poor, the only satisfactory solvent was acetonitrile in which the complex was stable for several hours. After longer periods, the red solution darkened slightly due to small amounts of the intensely green osmium(II) complex, but this appeared to have no effect on the peak position of the paramagnetic species. Comparison with $Os(bipy)_3{}^{2+}$ in CH_3CN showed no resonances from the diamagnetic compound. As a further check to see that exchange between osmium(II) and osmium(III) was not yielding false contact shifts, Cl_2 was bubbled through the solution and the spectrum was rerecorded. There appeared to be a broadening and loss of resolution of the resonances, but positions remained exactly the same. It is conceivable that in this case catalytic amounts of osmium(II) present in the solution resulted in an exchange narrowing of the resonance lines *via* an electron-transfer process. A difficulty in referencing the osmium(III) complexes arises since the corresponding diamagnetic iridium(III) salts are not known to exist.[12] Since the particular diamagnetic complex used as reference is not especially critical, we have chosen to reference osmium(III) to rhodium(III). In making this decision, we have noted the similar charge and size of the ions. It is most important that the reference not be made to the free ligand, which for bipyridine has a *trans* configuration and whose nmr spectrum is considerably different[13] from any diamagnetic complex. Errors up to 100 Hz have been incurred in this way.[4] In addition, we have found that the diamagnetic compounds yield spectra which are markedly solvent dependent. This is further reason to reference paramagnetic shifts to a *complex* in the same solvent.

The results of our nmr spectral measurements are presented in Tables I and II and representative spectra are shown in Figure 1. It is believed that these are the first published Ru(III) and Os(III) spectra which have been completely assigned, although a few Ru(III) spectra have been reported.[14] Peak assignments have been made on the basis of methyl substitution wherever possible. Relative line widths have also been useful since, for all complexes, it has been found that resonances are broader the closer the proton is to the metal, indicating that the dipolar interaction is predominantly responsible for line widths.

We have obtained spectra of the iron(III) compounds over a 70° temperature range and a "Curie plot" extrap-

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Table I. Nmr Spectral Data[a-c]

Complex	$\nu_{6,6'}$	$\nu_{5,5'}$	$\nu_{4,4'}$	$\nu_{3,3'}$	$\nu_{4\text{-CH}_3}$	$\nu_{5\text{-CH}_3}$
Fe(bipy)$_3$(PF$_6$)$_3$	+2656	+4	−82	−426		
Fe(4,4'-dmb)$_3$(PF$_6$)$_3$	+2716	+34		−450	−963	
Fe(5,5'-dmb)$_3$(PF$_6$)$_3$	+2650		−30	−360		−30
Co(bipy)$_3$(PF$_6$)$_3$	−440	−474	−514	−523		
Co(4,4'-dmb)$_3$(PF$_6$)$_3$	−423	−453		−504	−159	
Co(5,5'-dmb)$_3$(PF$_6$)$_3$	−411		−488	−500		−139
Ru(bipy)$_3$(PF$_6$)$_3$	+1882	−501	+36	−954		
Ru(4,4'-dmb)$_3$(PF$_6$)$_3$	+1860	−419		−900	−1460	
Ru(5,5'-dmb)$_3$(PF$_6$)$_3$	+1900		+114	−912		−78
Rh(bipy)$_3$(PF$_6$)$_3$	−460	−467	−506	−515		
Os(bipy)$_3$(PF$_6$)$_3$	+1610	−376	−491	−1049		
Os(4,4'-dmb)$_3$(PF$_6$)$_3$	+1600	−415		−1050	−1050	
	$\nu_{2,9}$	$\nu_{3,8}$	$\nu_{4,7}$	$\nu_{5,6}$	$\nu_{4,7\text{-CH}_3}$	
Fe(phen)$_3$(PF$_6$)$_3$	+2849	+179	−60	−372		
Fe(4,7-dmp)$_3$(PF$_6$)$_3$	+2860	+186		−357	−1014	
Co(phen)$_3$(PF$_6$)$_3$	−444	−475	−535	−509		
Ru(phen)$_3$(PF$_6$)$_3$	+2084	−366	+69	−542		
Rh(phen)$_3$(PF$_6$)$_3$	−479	−484	−540	−508		
Os(phen)$_3$(PF$_6$)$_3$	+1675	−390	−420	−603		

[a] At 30° in D_2SO_4 with $N(CH_3)_4Cl$ as internal standard or in CD_3CN with TMS internal standard. [b] Estimated error limits ±50 cps for 6,6' and 2,9 protons, ±6 cps for all others. [c] dmb = dimethylbipyridine; dmp = dimethylphenanthroline.

Table II. Nmr Contact Shifts[a]

	$\Delta\nu_{6,6'}$	$\Delta\nu_{5,5'}$	$\Delta\nu_{4,4'}$	$\Delta\nu_{3,3'}$	$\Delta\nu_{4\text{-CH}_4}$	$\Delta\nu_{5\text{-CH}_3}$
Fe(bipy)$_3$(PF$_6$)$_3$	+3096	478	432	97		
Fe(4,4'dmb)$_3$(PF$_6$)$_3$	−3139	487		54	−804	
Fe(5,5'dmb)$_3$(PF$_6$)$_3$	+3091		458	40		+109
Ru(bipy)$_3$(PF$_6$)$_3$	+2342	−34	542	−439		
Os(bipy)$_3$(PF$_6$)$_3$	+2072	+91	+16	−526		
Ru(5,5'dmb)$_3$(PF$_6$)$_3$	*b*	*b*	*b*	*b*		∼+60
Os(4,4'dmb)$_3$(PF$_6$)$_3$	*b*	*b*	*b*	*b*	∼−900	*b*
Ru(4,4'dmb)$_3$(PF$_6$)$_3$	*b*	*b*	*b*	*b*	∼−1300	*b*
	$\Delta\nu_{2,9}$	$\Delta\nu_{3,8}$	$\Delta\nu_{4,7}$	$\Delta\nu_{5,6}$	$\Delta\nu_{4,7\text{-CH}_3}$	
Fe(phen)$_3$(PF$_6$)$_3$	+3293	+654	+475	+137		
Fe(4,7-dmp)$_3$(PF$_6$)$_3$	*b*	*b*	*b*	*b*	∼−850	
Ru(phen)$_3$(PF$_6$)$_3$	+2563	+118	+609	−34		
Os(phen)$_3$(PF$_6$)$_3$	+2156	+93	+89	−61		

[a] In cps relative to appropriate diamagnetic complex. [b] Only Δν for methyl groups reported here.

olates to zero within 10 Hz, which is better than for many reported systems in which Curie-law behavior is assumed. This indicates the probable absence of other effects (from ion-pairing, geometry change, etc.) contributing to the observed shifts.

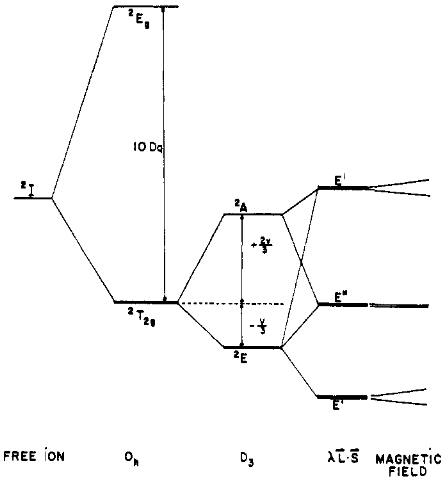

Figure 2. Energy level diagram for a low-spin d^5 system with a negative trigonal field. Primed representations are of the D_3 double group.

Epr. In order to aid in unraveling the pseudo-contact shift problem, we have obtained epr spectra of all compounds studied, both in the solid state and in frozen solutions. Data are complete and consistent for all iron(III) complexes. For ruthenium(III) and osmium(III), there is uncertainty surrounding the value of $g_{||}$, the effects of which will be discussed following a short diversion into the theory required to interpret the spectra.

The theory of the $t_{2g}{}^5$ configuration under the combined action of spin–orbit coupling and low-symmetry ligand field components was first presented by Stevens[15] and then Bleany and O'Brien;[16] only aspects necessary to interpretation of the spectra are presented here. The pertinent energy level diagram is given in Figure 2.

Following the usual conventions, we take the value of the spin–orbit coupling constant, ξ, to be negative for the more than half-full t_{2g} set. The quantity v is defined as the splitting of the $^2T_{2g}$ term created by the

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(15) K. W. H. Stevens, *Proc. Roy. Soc., Ser. A*, **219**, 542 (1953).

(16) B. Bleany and M. C. M. O'Brien, *Proc. Phys. Soc., London, Sect. B*, **69**, 1215 (1956).

Table III. Electron Spin Resonance Data[a,b]

	$g_\perp$	$g_\parallel$	k	v/ξ
$Fe(bipy)_3(PF_6)_3$	−2.61 ± 0.02	1.61 ± 0.01	1.068	3.03
$Fe(4,4'\text{-dmb})_3(PF_6)_3$	−2.64 ± 0.02	1.38 ± 0.01	0.982	2.33
$Fe(5,5'\text{-dmb})_3(PF_6)_3$	−2.60 ± 0.02	1.60 ± 0.01	1.044	2.97
$Fe(phen)_3(PF_6)_3$[c]	−2.69 ± 0.02	1.19 ± 0.01	0.933	2.00
$Ru(bipy)_3(PF_6)_3$	−2.64 ± 0.02	1.14 ± 0.03[d]	0.932	1.91
$Ru(phen)_3(PF_6)_3$[c]	−2.63 ± 0.02	1.00 ± 0.03[d]	0.912	1.73
$Os(bipy)_3(PF_6)_3$[e]	−2.49 ± 0.02	(0.40 to −0.40)	(0.82 to 0.94)	(1.16 to 0.74)
$Os(phen)_3(PF_6)_3$[c,e]	−2.43 ± 0.02	(0.40 to −0.40)	(0.78 to 0.90)	(1.18 to 0.76)

[a] Measured at X-band frequencies at 77°K. [b] Doped into the suitable diamagnetic host. [c] Small rhombic splitting detected but ignored in calculations of k and v/ξ. [d] Even in view of the uncertainties expressed in the text, ±0.03 in $g_\parallel$ corresponds to a relatively large error in field strength. [e] Range of k and v/ξ given corresponds to the range of $g_\parallel$ indicated.

axial ligand field component and is positive by definition if the orbital singlet lies lowest.[17] The other trigonal field parameter, v', is unnecessary since we do not include configuration interaction *via* matrix elements of the sort $\langle t_{2g}|v'|e_g\rangle$. The matrix of the trigonal field and spin–orbit coupling is given elsewhere together with the basis functions.[17] Upon diagonalization, three Kramers' doublets result with energies

$$E'' = -(v/3 + \xi/2) \qquad (1)$$

$$E'(\pm) = {}^1\!/_2[v/3 + \xi/2 \pm (v^2 - v\xi + {}^9\!/_4\xi^2)^{1/2}] \qquad (2)$$

where the primes correspond to representations of the double group. E'' is not split by a magnetic field. For a negative v and/or ξ, a magnetic doublet lies lowest and it is the transition within this doublet which we observe in the epr experiment. In the absence of nuclear hyperfine interactions (which we do not expect to see even for Ru(III) and Os(III) at 77°K) and no zero-field splittings, the analysis of the epr spectrum becomes extremely simple. Under axial symmetry the Hamiltonian containing only the Zeeman term is simply

$$H = g_\parallel \beta H_z S_z + g_\perp \beta (H_x S_x + H_y S_y) \qquad (3)$$

and evaluation of the matrix elements of the magnetic moment operator $(k\vec{L} + 2\vec{S})$ between the two states of the lowest Kramers' doublet

$$|+\rangle = \sin\alpha|0^+\rangle + \cos\alpha\,[\sqrt{2/3}|-2^-\rangle + \sqrt{1/3}|1^-\rangle] \qquad (4)$$

$$|-\rangle = \sin\alpha|0^-\rangle + \cos\alpha\,[\sqrt{2/3}|2^+\rangle - \sqrt{1/3}|-1^+\rangle] \qquad (5)$$

yields the g values. General expressions for these were given by Bleany and O'Brien[16] in a convenient form, relating $g_\parallel$, $g_\perp$, k, v, and ξ.

$$g_\parallel = 2[\sin^2\alpha - (1 + k)\cos^2\alpha] \qquad (6)$$

$$g_\perp = -2[\sqrt{2}k\cos\alpha\sin\alpha + \sin^2\alpha] \qquad (7)$$

where

$$\tan 2\alpha = \frac{\sqrt{2}}{(1/2 - v/\xi)}$$

with $0 < 2\alpha < \pi$, and k, the "orbital reduction factor," is defined as[15]

$$k = \frac{\langle\phi|\mathbf{L}|\phi\rangle}{\langle d|\mathbf{L}|d\rangle} \qquad (8)$$

where ϕ represents the real molecular orbitals and d the pure d orbitals of the metal. The orbital reduction factor is defined so as to take into account modifications of the d orbital not inherent in the crystal field model. Considering delocalization to be a reality, $\langle\phi|\mathbf{L}|\phi\rangle$ should be less than $\langle d|\mathbf{L}|d\rangle$ thus making $k \leq 1.0$. Attempts have been made to establish k on a molecular orbital foundation, but at our present level of understanding, it is best treated as an empirical parameter to be derived from experimental data rather than calculated from molecular wave functions.

We have found it vastly preferable in this work to examine spectra of powders or frozen solutions (glasses). Most of the compounds proved too unstable to dope into any crystals and indeed not enough structural information is available on any host lattice to make single crystal work possible. Since we have $S = {}^1\!/_2$ systems, we can extract the required g values from powder spectra quite readily.[18] We have followed the method of Ibers and Swalen[19] who present a relatively lucid account of the principles and procedures involved.

An experimental spectrum is reproduced in Figure 3 along with the g values calculated by the line shape program. From the experimental spectrum, it is apparent that the line shape is what might be called a "Gaussian broadened" Lorentzian function—due to dipolar and exchange effects—and not a simple Lorentzian function as the calculation assumes. While the fit, point by point along the curve, is thus not as good as it could be with the proper choice of the line shape function, the g values do not appear very sensitive to the goodness of fit which is mainly determined by line width. We have also chosen to set larger error limits on the results than those determined by a least-squares analysis in the fitting program.

Results of epr experiments are presented in Table III. Several points need to be made regarding the values of parameters in this table. First of all, it will be noted that the orbital reduction factor for some of the iron(III) complexes is calculated to be greater than 1.0. There are several possibilities to explain this effect. The most obvious and in this case probably the correct one is that we have neglected all configuration interaction. (To include it would result in more parameters than observables.) The fact that values greater than one are only observed for iron and not for ruthenium and osmium would be consistent with the smaller Dq found for first-row metals, which would enable mix-

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(17) B. N. Figgis, *Trans. Faraday Soc.*, 57, 198 (1961).

(18) F. K. Kneübuhl, *J. Chem. Phys.*, 33, 1074 (1960).

(19) J. A. Ibers and J. D. Swalen, *Phys. Rev.*, 127, 1914 (1962); we thank Professor Ibers for a copy of the line shape program.

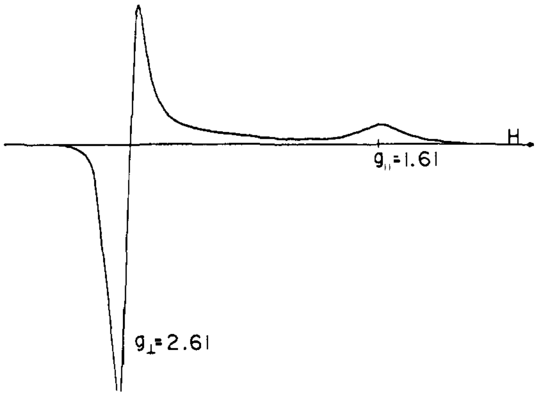

Figure 3. Epr spectrum of polycrystalline $Fe(bipy)_3(PF_6)_3$ in $Co(bipy)_3(PF_6)_3$ at 77°K.

ing—which is $\alpha(1/\Delta E)$—to occur more easily. The larger *Dq* found for phenanthroline as compared with bipyridyl may account for the lower *k* found for $Fe(phen)_3{}^{3+}$. Other possibilities for anomalous *k* values are contribution of orbital angular momentum to the t_{2g} electrons from the ligand itself, and the fact that we have assumed an isotropic *k* in the theory outlined above. A point to bear in mind is that interpretation of *k* is quite difficult and the tendency is for it to become a catch-all for all effects not inherent in a point-charge model.[20]

The next point to be noted is the sign of the *g* values. It is of course impossible without the use of circularly polarized radiation to determine the signs of the *g* tensor components.[21] It is necessary then to resort to elimination of signs giving unreasonable values of derived parameters. Using eq 6 and 7, we can fix *k* and calculate the $g_{\parallel}$ values corresponding to various $g_{\perp}$ values. To illustrate, Figure 4 is a plot of $g_{\parallel}$ *vs.* $g_{\perp}$ for various values of *k*. Using $Fe(bipy)_3{}^{3+}$ as an example, with $g_{\parallel} = -1.61$ and $g_{\perp} = -2.61$, a value of $k = 1.23$ is interpolated from Figure 4. This is unreasonable even considering the limitations in the theory for *k* discussed above. Furthermore, such an assignment yields a value of v/ξ of 0.33 as opposed to 3.0 for the alternate assignment of $g_{\parallel} = 1.61$, $g_{\perp} = -2.61$, for which $k = 1.06$ is calculated. For $Fe(phen)_3{}^{3+}$ if both *g* values are negative, we obtain $v/\xi = 0.6$, and if $g_{\perp}$ is negative and $g_{\parallel}$ positive, we obtain $v/\xi = 2.3$. Both Mössbauer[22] and X-ray[23] absorption experiments lead one to predict a greater axial distortion for bipyridyl complexes than for phenanthroline complexes. This is supported by our choice of sign for $g_{\parallel}$.

The above result of a negative *v* for the iron complexes lead us to postulate an E ground state. This is contrary to the conclusion of an A ground state reached by Figgis[24] through powder susceptibility data and a curve-fitting procedure. In a recent publication,[25] however, the same author shows that such powder susceptibility data are not reliable in choosing between alternative fits. We also find a considerably larger trigonal distortion than previously indicated[24] although that might be expected with the different ground state predicted from our work.

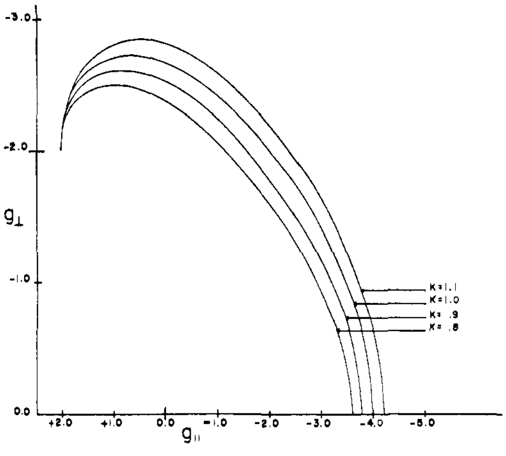

Figure 4. Plot of $g_{\parallel}$ *vs.* $g_{\perp}$ for $t_{2g}{}^5$ configuration for various values of the orbital reduction parameter, *k*. Points on a line of constant *k* correspond to different values of v/ξ.

We now return to the problem of the $g_{\parallel}$ resonance in the Ru(III) and Os(III) complexes. In contrast to the iron(III) complexes, where frozen solutions, dilute powders, and concentrated powders yielded identical results, results for $g_{\parallel}$ in the ruthenium(III) complexes were not consistent. Very weak absorption was noticeable at about $g = 1.14$ in $Ru{:}Rh(bipy)_3(PF_6)_3$ and at about $g = 1.00$ in $Ru{:}Rh(phen)_3(PF_6)_3$. Undiluted $Ru(bipy)_3(PF_6)_3$ gave an even broader absorption in this same region which was not reproducible to our satisfaction. In H_2SO_4 glasses, the situation was equally uncertain. Curiously enough, $g_{\perp}$ always remained the same. For $Ru(bipy)_3{}^{3+}$, calculation of *k* and v/ξ assuming a $g_{\parallel}$ value of 1.14 yielded values of 0.93 and 1.91, respectively, which are quite reasonable.[26] The alternative assumption, that $g_{\parallel}$ is <0.45 and out of the range of our magnet system yields $v/\xi = 1.0$ or less and *k* values considerably higher than expected, and for $g_{\parallel} < 0.0$, greater even than 1.0. In view of the expected value of $v \cong 2000$ cm^{-1},[26] we feel that the values of $g_{\parallel} = 1.14$ for $Ru(bipy)_3{}^{3+}$ and $g_{\parallel} = 1.00$ for $Ru(phen)_3{}^{3+}$ are the most reasonable of those we have any reason to accept. Further work in this area would be most desirable. As for the osmium(III) complexes, no trace whatsoever of $g_{\parallel}$ was to be found leading us to conclude that for these complexes $g_{\parallel}$ lies between +0.45 and −0.45. The effect of the assumptions made here on the pseudo-contact shift calculations will be discussed below.

It might also be mentioned here that epr signals were relatively easy to observe for all compounds at 77°K contrary to what might be expected for a $t_{2g}{}^5$ configuration and in view of the paucity of experimental data on these systems. This is most likely due to the magnitude of the axial distortion splitting the $^2T_{2g}$ term. Dilution in a diamagnetic host of course reduces the line width dramatically. It is the extreme sharpness of the $g_{\perp}$ resonance of $Os{:}Rh(bipy)_3{}^{3+}$, for example, which leads us to conclude that the $g_{\parallel}$ resonance is not broadened beyond recognition but is out of the range of our

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[20] M. Gerloch and J. R. Miller, *Progr. Inorg. Chem.*, **10**, 1 (1968).

[21] C. Poole, Jr., "Electron Spin Resonance," Wiley-Interscience, New York, N. Y., 1967, p 321.

[22] R. L. Collins, R. Pettit, and W. A. Baker, Jr., *J. Inorg. Nucl. Chem.*, **28**, 1001 (1966).

[23] W. Seka and H. P. Hanson, *J. Chem. Phys.*, **50**, 344 (1969).

[24] B. N. Figgis, *Trans. Faraday Soc.*, **57**, 204 (1961).

[25] B. N. Figgis, M. Gerloch, and R. Mason, *Proc. Roy. Soc., Ser. A*, **309**, 91 (1969).

[26] R. A. Palmer and T. S. Piper, *Inorg. Chem.*, **5**, 864 (1966); these authors estimated *v* for $Ru(bipy)_3{}^{2+}$ to be about 2000 cm^{-1}. Such a value along with $\xi \approx -1000$ cm^{-1} is in agreement with our calculated value of v/ξ.

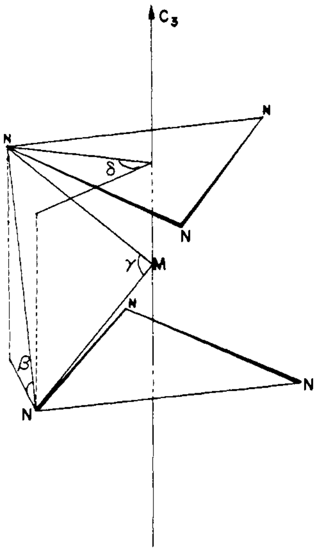

Figure 5. Representation of complex showing angles involved in geometric factor calculations: γ = NMN angle, δ = projection of γ on a plane perpendicular to C_3, β = polar angle.

magnet and that going to lower temperatures would not help locate it.

Opposite to what is found in the nmr spectra where iron(III) gives the sharpest lines and osmium(III) the broadest, we find that similar concentrations of these paramagnetic ions in a diamagnetic host show that the narrowest epr lines occur for osmium(III), with the broadest lines occurring in the iron(III) complexes. The sharp lines and hence longer excited state lifetimes may be explained by considering the effect of the larger axial distortion. The electron relaxation time is directly proportional to the energy separation of the ground and nearby excited states, and will be shortest for iron(III) where the trigonal distortion is smallest.

Geometric Factors

The remaining obstacle to proper evaluation of the pseudo-contact shift is determination of the geometric factor, enclosed in square brackets in eq 9. θ_i is the

$$\Delta\nu_i = K\cdot f(g)\left[\frac{(3\cos^2\theta_i - 1)}{r_i^3}\right] \quad (9)$$

angle between the ith atom and the highest-fold symmetry axis in the molecule and r_i is the distance from that atom to the paramagnetic center. f(g) in eq 9 is a function of the g-tensor components, which is discussed below, and K is a composite constant. The calculation of geometric factors in ion-pairing systems[27] has been treated in detail, but little concern about this aspect of the pseudo-contact problem is evident among workers interested in the Fermi contact interaction. Along with other erroneous assumptions made[3a] about the pseudo-contact shift, there seems to be little awareness of how sensitive the dipolar shift is to small changes in bond lengths and angles. We shall show that uncertainty surrounding geometry in solution prevents an accurate determination of the dipolar shift even though g-tensor anisotropies are accurately known.

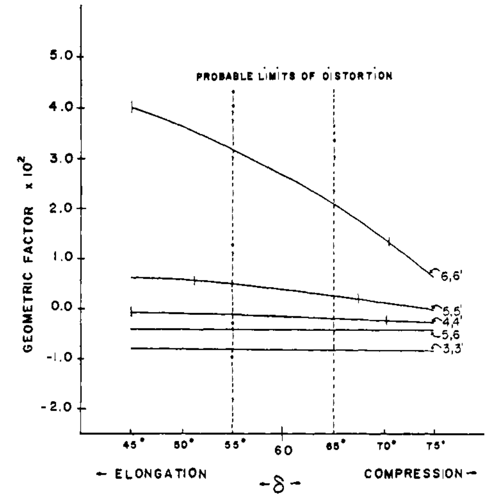

Figure 6. Variation of geometric factors for bipy + phen as a function of compression or elongation of the octahedron. δ = 60° corresponds to a pure octahedron. Vertical bars on the curves correspond to ±50% of the δ = 60° value.

In the absence of a crystal structure, we must make the best use of what little structural information is available. In our calculations, we have used an Fe–N bond length of 1.97 Å which has been reported for $Fe(phen)_3^{2+}$.[28] Ru–N and Os–N bond lengths were taken as 2.05 Å to account for the difference in atomic radii. Since we do not know by how much the octahedron is compressed or elongated—although axial elongation would be expected to result in the observed E ground state—we have undertaken a calculation to assess the sensitivity of the geometric factors to this type of distortion. Figure 5 is a representation of the complex showing the angles involved in our calculations. δ is the projection of the N–M–N angle γ on a plane perpendicular to the C_3 axis. A change in δ may be brought about by compression or elongation of the octahedron which also changes the polar angle β. Mathematically, it proved easier to vary δ than β; thus we have varied δ for a given bond length and made calculations of $3(\cos^2\theta - 1)/r^3$ for all protons in bipyridine and phenanthroline. Our results are given in Figure 6. For a regular octahedron, δ = 60°. Since our available structural information indicates that γ is almost 90°, δ should be close to 60°. We have therefore arbitrarily adopted that value in our calculation. True D_3 symmetry would require $\delta \neq 60°$ as it undoubtedly is. Note the large possible error (±250 cycles associated with a ±5° distortion) at the 6,6′ (or 2,9) proton. However, as indicated on Figure 6, the 5,5′ proton is the most sensitive, with 3,3′ and 5,6 on phen being most insensitive. Suspecting axial elongation, our estimate of the geometric factor based on δ = 60° is most probably low and the calculated pseudo-contact shifts may be a bit smaller than they really are. However, the X-ray structure indicates the six nitrogens form an almost perfect octahedron around iron(II) so δ must be very close to 60°. We have also calculated changes in the geometric factor as a function of bond distance from 1.93 to 2.07 Å, and over this range we find uncertainties comparable to those associated with a ±5° change in δ.

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[27] I. M. Walker and R. S. Drago, *J. Amer. Chem. Soc.*, 90, 6951 (1968); G. N. LaMar, R. H. Fischer, and W. D. Horrocks, Jr., *Inorg. Chem.*, 6, 1798 (1967).

[28] D. H. Templeton, A. Zalkin, and T. Ueki, *Acta Crystallogr.*, 21, A154 (1966).

Table IV. Geometric Factors[a]

	$G_{6,6'}$	$G_{5,5'}$	$G_{4,4'}$	$G_{3,3'}$	$G_{4\text{-CH}_3}$	$G_{5\text{-CH}_3}$
Fe(bipy)$_3$(PF$_6$)$_3$	0.026277	0.003654	−0.001680	−0.008312		
Fe(4,4′dmb)$_3$(PF$_6$)$_3$	0.026277	0.003654		−0.008312	−0.001216	
Fe(5,5′dmb)$_3$(PF$_6$)$_3$	0.026277		−0.001680	−0.008312		0.002917
Ru(bipy)$_3$(PF$_6$)$_3$[b]	0.021452	0.002579	−0.001945	−0.007857		
Os(bipy)$_3$(PF$_6$)$_3$[b]	0.021452	0.002579	−0.001945	−0.007857		
	$G_{2,9}$	$G_{3,8}$	$G_{4,7}$	$G_{5,6}$		
Fe(phen)$_3$(PF$_6$)$_3$	0.026277	0.003654	−0.001680	−0.004175		
Ru(phen)$_3$(PF$_6$)$_3$[b]	0.021452	0.002579	−0.001945	−0.003998		
Os(phen)$_3$(PF$_6$)$_3$[b]	0.021452	0.002579	−0.001945	−0.003998		

[a] Values are $\times 10^{24}$ Å^3. [b] Osmium and ruthenium numbers are the same since we have assumed the same M–N bond length.

Table V. Pseudo-Contact Shifts[a]

	$\Delta\nu_{6,6'}$	$\Delta\nu_{5,5'}$	$\Delta\nu_{4,4'}$	$\Delta\nu_{3,3'}$	$\Delta\nu_{4\text{-CH}_3}$	$\Delta\nu_{5\text{-CH}_3}$
Fe(bipy)$_3$(PF$_6$)$_3$	+1282	+178	−82	−406		
Fe(4,4′dmb)$_3$(PF$_6$)$_3$	+1398	+194		−442	−65	
Fe(5,5′dmb)$_3$(PF$_6$)$_3$	+1274		−81	−403		+141
Ru(bipy)$_3$(PF$_6$)$_3$	+1190	+143	−107	−436		
Os(bipy)$_3$(PF$_6$)$_3$	+1074	+129	−97	−393		
	$\Delta\nu_{2,9}$	$\Delta\nu_{3,8}$	$\Delta\nu_{4,7}$	$\Delta\nu_{5,6}$		
Fe(phen)$_3$(PF$_6$)$_3$	+1511	+210	−97	−240		
Ru(phen)$_3$(PF$_6$)$_3$	+1204	+145	−109	−224		
Os(phen)$_3$(PF$_6$)$_3$	+1023	+123	−93	−190		

[a] In cps, at 60 MHz.

We emphasize, however, that we feel our chosen bond length of 1.97 Å is quite good and, since this fixes the N–M–N angle in a planar chelate, errors from assuming $\delta = 60°$ are not unduly large.

One further problem arises in the bipyridyl complexes which does not present itself with phenanthrolines; that is ring tipping. We have done all calculations, including extended Hückel calculations assuming coplanar pyridyl rings. There is solid state evidence[29] that the rings may indeed be tipped as much as 10°. However, due to no evidence of proton nonequivalence—which is expected for all but the 5,5′ proton for a tipped conformation—in the nmr spectra, it appears that in solution there is no locked-in distortion and that the barrier to interconversion of "twistomers" is relatively low. Geometric factors appear in Table IV.

Contact Shifts and Coupling Constants

The values of the pseudo-contact shift at various protons in the molecule were calculated from the following equation[30]

$$\Delta\nu_i = -\frac{(3\cos^2\theta_i - 1)}{r^3}\left[\frac{(g_\parallel - g_\perp)(3g_\parallel + 4g_\perp)}{45kT}\beta^2 S(S+1)\nu\right] \qquad (10)$$

which is appropriate for the case where $\tau_c \gg T_1$, where τ_c and T_1 are the molecular correlation and electron spin relaxation times, respectively. For the cases of Ru(III) and Os(III) where $g_\parallel$ is not accurately known, the expression in square brackets in eq 10 was evaluated for the known value of $g_\perp$ and for $g_\parallel$ values from 0.45 to −0.45. Within this range of $g_\parallel$ values, there is only a 10% difference in the maximum and minimum value of this "g-anisotropy factor." By choosing for Os(III) complexes an arbitrary value halfway between the two extremes, we will probably be off by no more than ±5%. In the case of the Ru(III) complexes where there is a lingering doubt about $g_\parallel$, we find an approximate spread of 8% in the g-anisotropy factor. Significantly, for $g_\parallel = 1.14$ as we have chosen, the g-anisotropy factor falls within this range so that here again we expect to find at most about a ±5% error introduced by our uncertainty of $g_\parallel$. Compared to errors due to geometric factor uncertainty, which may be three–four times as large, this poses no serious limitation on our final result. Pseudo-contact shifts calculated from eq 10 appear in Table V, and Fermi contact shifts appear in Table VI. Note that the pseudo-contact shift (Table VI) is indeed significant and that neglect of this interaction could lead to gross errors in interpretation of the Fermi contact shifts.

Coupling constants were calculated from the standard Fermi contact shift equation

$$\frac{\Delta\nu_i}{\nu} = \frac{A_i g_{av}^2\beta_e^2}{g_N\beta_N}\,\frac{S(S+1)}{3kT} \qquad (11)$$

where A_i, the electron-nuclear hyperfine coupling constant, is defined as

$$A_i = \frac{8\pi}{6S} g_N\beta_N|\psi_i(0)|^2 \qquad (12)$$

and is expressed in gauss.

Equation 11 presupposes Curie-law behavior and in view of the magnetic studies of Figgis, the large axial field distortions we find, and our ΔH *vs.* $1/T$ plots which pass through zero, we feel Curie behavior is indicated well enough to justify its use. In calculating coupling constants, g_{av}^2 was obtained from the

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(29) I. M. Proctor and F. S. Stephens, *J. Chem. Soc.*, *A*, 1248 (1969).
(30) J. P. Jesson, *J. Chem. Phys.*, 47, 579 (1967).

Table VI. Fermi Contact Shifts[a,b]

	$\Delta\nu_{6,6'}$	$\Delta\nu_{5,5'}$	$\Delta\nu_{4,4'}$	$\Delta\nu_{3,3'}$	$\Delta\nu_{4\text{-}CH_3}$	$\Delta\nu_{5\text{-}CH_3}$
$Fe(bipy)_3(PF_6)_3$	+1814	+300	+514	+503		
$Fe(4,4'dmb)_3(PF_6)_3$	+1741	+293		+496	−739	
$Fe(5,5'dmb)_3(PF_6)_3$	+1817		+539	+543		−32
$Ru(bipy)_3(PF_6)_3$	+1152	−143	+649	−3		
$Os(bipy)_3(PF_6)_3$	+998	−38	+113	−113		
	$\Delta\nu_{2,9}$	$\Delta\nu_{3,8}$	$\Delta\nu_{4,7}$	$\Delta\nu_{5,6}$		
$Fe(phen)_3(PF_6)_3$	+1781	+444	+572	+377		
$Ru(phen)_3(PF_6)_3$	+1359	−27	+718	+190		
$Os(phen)_3(PF_6)_3$	+1133	−30	+182	+129		

[a] In cps, at 60 MHz. [b] Numbers for Ru and Os are to be regarded as approximate due to restrictions mentioned in the text.

Table VII. Fermi Contact Coupling Constants[a,b]

	$A_{6,6'}$	$A_{5,5'}$	$A_{4,4'}$	$A_{3,3'}$	$A_{4\text{-}CH_3}$	$A_{5\text{-}CH_3}$
$Fe(bipy)_3(PF_6)_3$	−0.3071	−0.0508	−0.0870	−0.0852		
$Fe(4,4'dmb)_3(PF_6)_3$	−0.3017	−0.0508		−0.0860	+0.1280	
$Fe(5,5'dmb)_3(PF_6)_3$	−0.3101		−0.0920	−0.0927		+0.0055
$Ru(bipy)_3(PF_6)_3$	−0.2075	+0.0257	−0.1169	+0.0005		
$Os(bipy)_3(PF_6)_3$	−0.2211	+0.0084	−0.0250	+0.0294		
	$A_{2,9}$	$A_{3,8}$	$A_{4,7}$	$A_{5,6}$		
$Fe(phen)_3(PF_6)_3$	−0.3079	−0.0768	−0.0989	−0.0652		
$Ru(phen)_3(PF_6)_3$	−0.2517	+0.0050	−0.1330	−0.0352		
$Os(phen)_3(PF_6)_3$	−0.2631	+0.0069	−0.0423	−0.0300		

[a] In gauss, ±0.01 at 6,6′ and 2,9 positions, ±0.003 at other protons. [b] Numbers for Ru and Os are to be regarded with less certainty due to restrictions mentioned in text.

geometric mean of $g_{\parallel}$ and $g_{\perp}$ and the value is in reasonable agreement with results from susceptibility measurements. In view of the extremely large spin–orbit coupling in Os(III), one is forced to wonder whether eq 11 is at all applicable. For the cases of iron(III) and ruthenium(III) where weak to moderate *LS* coupling prevails, quenching of the orbital angular momentum by the low symmetry field probably results in *S* remaining a fairly good quantum number when used in conjunction with g_{av}. Curie-law behavior would tend to support this view. For osmium(III), however, we are approaching, if not already in, the region of *j–j* coupling, and the validity of *S* as a good quantum number even in the presence of low-symmetry fields which quench the orbital moment is highly questionable. This uncertainty should be borne in mind with regard to all osmium(III) coupling constants presented here. Coupling constants are tabulated in Table VII.

Discussion

Examination of Tables II and VII and comparison of these results with those for Ni(II)[3b] make it apparent that what we find in these complexes is an extensive amount of π delocalization. For all complexes studied, we find the largest shifts at the 4,4′ and 6,6′ positions of bipyridyl and the 4,7 and 2,9 positions of phenanthroline. This, coupled with the fact that all methyl groups substituted for ring protons show shifts opposite in direction and, in several cases, much larger than the ring protons they replace, leaves no doubt that a π delocalization mechanism *is dominant* in these complexes.

The conclusion reached by LaMar and Van Hecke[4] that a σ mechanism is dominant in the iron(III) complexes is the result of several incorrect and incomplete pieces of experimental data, which enable the authors to explain away the pseudo-contact shift problem when, in fact, it is of utmost importance that the effects of this interaction be taken into account. Even upon neglect of the pseudo-contact shift, it still requires a rather improbable stretch of the imagination to accept the comparison made with $Ni(bipy)_3^{2+}$ and to conclude on the basis of the ratios given that σ delocalization is predominant in these d^5 systems. Needless to say, the conclusion[4] that the shifts in these complexes represent "the first conclusive evidence for the existence of the exchange polarization delocalization mechanism" is entirely unwarranted.

It has previously been shown that the mode of delocalization does not necessarily imply a similar mode of metal–ligand bonding.[1d] Consequently, previous studies have provided little evidence of metal–ligand π-type interactions. Comparison of the nickel and iron shifts enables us to draw such conclusions. Nickel(II) has its two unpaired electrons in e_g orbitals. Even though strict σ–π separability is lost in symmetry lower than cubic, the molecular orbitals retain much of their original character, and we shall use the terms "σ" and "π" to imply this in our discussion. With nickel(II), one might expect mainly a σ interaction with the ligand and a small π contribution arising from previously described mechanisms.[3b] In iron(III), the unpaired electron is in a metal π-type orbital of a_1 symmetry. Since this orbital does not mix with the upper e_σ set (to first order approximation at least), metal–ligand π-type interactions should predominate and lead one to expect mainly π delocalization in the ligand with a smaller σ contribution. Since this is observed, extensive mixing of metal and ligand π-type orbitals is conclusively demonstrated. That the delocalization mechanism is indeed radically different for iron(III) and nickel(II) is further supported by comparison of the ratios of the coupling constants for the bipyridyl complexes. With the iron(III) shifts normalized to 1.0, the corresponding nickel(II)/iron(III) shift ratios are $H_{6,6'} = -1.96$, $H_{5,5'} = -5.77$, $H_{4,4'} = -0.32$, and $H_{3,3'} = -2.91$. As well as being of opposite sign, the numbers are nowhere near similar as has been contended.[4]

As pointed out by LaMar and Van Hecke, it does seem that the relatively large upfield shift at the 6,6′ (or 2,9) protons will result in some difficulty when trying to fit the observed shifts to a pure π mechanism—at least for iron(III) and osmium(III). However, there is also reason to suspect that some other effect may be operative at the 6,6′ (2,9) position, which would not be detected in the nickel(II) complex owing to the large amount of spin density at this position, the breadth of this peak, and also to the small amount of unpaired spin in the π system. Examination of a model of the complex shows that the 6,6′ (2,9) proton approaches very closely to the ring of another ligand molecule; close enough, indeed, to result in a shift in the diamagnetic complexes of as much as 100 cycles. One sees this most clearly in the *cis*-bisbipyridyl complexes,[12] where there are two different 6,6′ (2,9) protons, one separated from the other by quite a large amount. With a diamagnetic shielding difference as large as this, one might expect this 6,6′ (2,9) proton to be in a very favorable position to interact strongly with the π system of another ring containing unpaired spin. Where in the π system this interaction is taking place would of course determine whether up or down spin is transmitted to the 6,6′ (2,9) proton. Further study of this possibility is in progress along with detailed molecular orbital calculations to determine whether the observed contact shifts can be satisfactorily explained within our present capability to calculate such complicated systems.

For the present we can attempt only a simplified treatment of the shifts encountered in this series. The alternation of signs of A_i around the rings for both osmium and ruthenium complexes demonstrates that we have here, even more convincingly than in the iron complexes, cases of predominantly π delocalization. Perhaps the best place to look for comparisons is the 4-methyl proton where any σ effect would be very small and where the pseudo-contact shift contributes only slightly. We find at this position shifts of -800 and -900 cps for iron(III) and osmium(III), respectively, but a shift of ~ -1300 cps in the ruthenium(III) complex. This indicates that the amount of π delocalization is significantly larger in the ruthenium(III) complex. The actual coupling constants at the 4-methyl protons would probably be closer in iron(III) and osmium(III) than is indicated by the $\Delta\nu$'s above since g_{av}^2 is smaller for $Os(bipy)_3^{3+}$ than for $Fe(bipy)_3^{3+}$. Thus we cannot within the limit of accuracy of this experiment say whether π interaction is stronger in Fe(III) than Os(III) or *vice versa*. Quite certainly, however, we can write for π-unpaired spin delocalization: Ru(III) > Fe(III) $\sim$ Os(III). Comparison of the σ interaction is a bit more difficult. If the very small downfield shifts at the 5-methyl position in Fe(III) were due to cancellation of σ and π contributions, one would be forced to conclude that a σ shift at any proton must be an upfield shift. A downfield σ shift can in no way explain the observed shifts at any position. A relatively small upfield σ shift at the 3 and 5 positions could reverse the downfield π shifts expected here and lead to the observed upfield shifts in the iron(III) complexes. For ruthenium(III) and osmium(III), where both 3 and 5 protons show the expected downfield shifts, albeit small, we can conclude that the σ delocalization is smaller. This could also explain the difference of $\sim$0.1 G in A at the 6,6′ position between Fe(III) and Ru(III) and Os(III), although all of the A values at this position may be large due to the effect mentioned above. Again, we feel that it is impossible to distinguish the difference in σ delocalization between Ru(III) and Os(III) since they appear so similar. We feel reasonably sure that we are correct in writing for the σ-unpaired spin delocalization: Fe(III) > Ru(III) $\sim$ Os(III).

It should be borne in mind that the above discussion of unpaired spin delocalization cannot be directly related to the ability of the metals to form π and σ bonds to the ligands. In the contact-shift experiment we are obtaining information about mixing of metal and ligand atomic orbitals only by looking at molecular orbitals containing the unpaired spin, *i.e.*, by looking at nonbonding or antibonding orbitals. Questions of covalency and σ and π bond strengths are in most cases more appropriately answered by examining the filled bonding molecular orbitals. In nickel(II) complexes with O_h symmetry, for example, there is no reason to expect the contact-shift experiment to tell us anything about π bonding since the unpaired electrons which we "observe" are in σ orbitals. The metal t_{2g} electrons which may be taking part in extensive π bonding with certain of the ligands are all paired and inaccessible to this experiment. By comparing the contact shifts in a nickel complex with those in a metal complex containing unpaired spin in the t_{2g} set, some evidence for π bonding can be obtained, but assessment of the relative magnitude of this effect in a series of complexes is extremely difficult on the basis of the limited information so obtained. One can at best hope that in a series of closely related complexes of the same symmetry containing the same ligand and with the same d-electron configuration, the relative changes in the extent of metal–ligand mixing in the orbitals containing unpaired spin parallel the overall mixing of ligand and metal orbitals. Interpretation of any magnetic resonance parameters (nmr or epr) in terms of covalency and type of bonding must be carried out with these facts in mind.

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