Inorg. Chem. **1986**, *25*, 1481–1484 **1481**

arguments presented above, we are reasonably confident that the enthalpy of reaction 12 is close to −50 kcal mol^{-1}. This enthalpy for substitution of NO^+(aq) onto $[(NH_3)_5RuOH_2]^{2+}$ is much more exothermic than the corresponding −38.2 ± 1.4 kcal mol^{-1} for CO(aq) as a ligand. Such a large exothermicity is consistent with the view that when NO^+ combines with $(NH_3)_5RuOH_2{}^{2+}$, there is an enormous redistribution of electronic charge. The high acidities of $[(NH_3)_4Ru(NO)OH_2]^{2+}$ (pK_a = 4.1 and 1.4 for cis and trans forms,[21] especially in the case of the trans isomer, which is even more acidic than $[(NH_3)_5RuOH_2]^{3+}$ (pK_a = 4.1)[22] suggests that the nitrosyl group bears a net negative charge in this case.

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Registry No. $[(NH_3)_5RuNO]^{3+}$, 37874-79-6; $[(NH_3)_5RuOH_2]^{2+}$, 21393-88-4; NO^+, 14452-93-8.

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Partial Molal Volumes of Spin-Equilibrium Metal Complexes

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The partial molal volumes of spin-equilibrium complexes of iron(II), iron(III), and cobalt(II) have been measured and compared with known crystal volumes. In each case close agreement within several cubic centimeters per mole is found, indicating that crystal packing and solvation contacts are similar. The volume difference between the high-spin and low-spin isomers of the iron complexes was obtained previously by ultrasonic absorption measurements and for the cobalt complex is calculated from the temperature dependence of the magnetic moment and the electronic absorption spectrum and the pressure dependence of the absorption spectrum. The difference in the complex ion radii is calculated and a minimum value obtained for the change in the metal–ligand bond lengths between the spin isomers. By a comparison of these with differences observed in crystal structures, an indication of the solvation of the complexes is obtained.

Introduction

The partial molal volumes of many ions have been determined,[1] but there are few measurements for metal complexes.[2] The necessary data are obtained from precise measurements of the densities of solutions of the complexes as a function of concentration, measurements which are considerably simplified with currently available commercial technology. We have made such measurements in conjunction with ultrasonic relaxation studies of the dynamics of the spin equilibrium that exists in some metal complexes between low-spin and high-spin d-electron configurations.[3-5] The transition from the low-spin to the high-spin state results in lengthening of the metal–ligand bonds and a consequent increase in the volume of the complex. The magnitude of the volume change can be obtained from the amplitude of the ultrasonic absorption.

The change in the metal complex radius accompanying the spin-state transition can be calculated from the partial molal volume and the volume difference between the spin isomers. Comparisons can then be made with known bond length differences obtained from crystal structures. In this paper we report results for four spin-equilibrium complexes for which all of the necessary data are available.

Experimental Section

The iron compounds were prepared as described previously.[3-5] Bis(terpyridine)cobalt(II) chloride dihydrate was prepared by adding dropwise a solution of 2.38 g (10 mmol) of $CoCl_2{\cdot}6H_2O$ in 40 mL of distilled water to a stirred suspension of 5.00 g (21.4 mmol) of terpyridine in 75 mL of distilled water. The resulting dark brown reaction mixture was stirred for 45 min and then filtered to remove excess terpyridine and a trace of the green impurity, $[Co(terpy)Cl_2]$.[6] The solution was concentrated to 35 mL by rotary evaporation and filtered again, removing a further trace of terpyridine but no further green impurity, and then taken to dryness by rotary evaporation. The brown solid was dissolved in a minimum volume of methanol and filtered to remove any trace of green impurity (none was detected), and the filtrate was taken to dryness by rotary evaporation. The purified brown solid was dissolved in a minimum volume of water and filtered and the solution concentrated to 20 mL by rotary evaporation. After the solution was cooked in an ice bath, the dark brown crystals that were formed were collected by filtration, air-dried, and then dried for 48 h in vacuum at room temperature over P_2O_5. The brown crystalline product was free of any green impurity and gave satisfactory elemental analyses.

Density difference measurements were made by using an Anton Parr (Graz, Austria) DMA-02C precision density meter. The temperature of 25.0 °C was maintained by using a locally constructed precision temperature bath controlled to ±0.0005 °C with a Bayley Instruments Co. (Danville, CA) Model 121 precision temperature controller. With the room temperature controlled to 25.0 ± 0.5 °C by air conditioning, temperature fluctuations of ±0.01 °C were obtained in the density meter, resulting in density difference measurements precise to $\pm 3 \times 10^{-6}$ g cm^{-3} for aqueous solutions and to $\pm 3 \times 10^{-5}$ g cm^{-3} for tetrahydrofuran solutions.

From the density difference measurements the apparent molal volume (Φ_V) of the solutes were calculated by using eq 1, where m is the molal

$$\Phi_V = \frac{1000}{m d_0 d_s}(d_0 - d_s) + \frac{MW}{d_s} \qquad (1)$$

concentration, d_s and d_0 are the densities of the solution and solvent, respectively, and MW is the molecular weight of the solute.[1] The partial molal volume of the solute, $\bar{V}^\circ_s$, is determined from the concentration dependence of the apparent molal volume by extrapolating Φ_V to infinite dilution where Φ°_V is equal to $\bar{V}^\circ_s$.

Variable-temperature electronic spectra were recorded with a Varian Techtron Model 635 spectrophotometer and jacketed quartz cells in conjunction with a Colora WK-5 refrigerated constant-temperature bath. The data were corrected for changes in solvent density, and hence sample concentration, with temperature.[7]

Variable pressure electronic spectral measurements were obtained at the University of Melbourne on a Varian Techtron 635D spectrophotometer fitted with a thermostated, high-pressure cell in the sample beam.[8,9] Single-wavelength absorbance measurements were recorded at

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Table I. Concentration Dependence of Apparent Molal Volumes at 25.0 °C

compd	m, mol kg^{-1}	d_s, g cm^{-3}	Φ_V, cm^3 mol^{-1}
[Fe(HB(pz)$_3$)$_2$]	0.117 90	0.900 35	340.6
	0.058 53	0.891 35	340.0
	0.022 76	0.885 71	342.1
[Fe((acac)$_2$trien)]NO$_3$	0.104 45	1.009 84	300.7
	0.026 064	1.000 30	301.9
	0.010 947	0.998 45	300.3
	0.005 100	0.997 71	301.1
[Fe((sal)$_2$trien)]NO$_3$	0.025 958	1.001 081	314.5
	0.016 732	0.999 679	313.2
	0.009 401	0.998 538	312.7
	0.004 075	0.997 713	309.5
[Co(terpy)$_2$]Cl$_2$	0.117 40	1.016 992	419.1
	0.061 137	1.007 684	419.0
	0.031 794	1.002 653	419.2
	0.015 109	0.999 749	418.4

Table II. Temperature Dependence of ϵ_{obsd} at 445 nm for [Co(terpy)$_2$]Cl$_2$·2H$_2$O in H$_2$O

T, K	ϵ_{obsd}, M^{-1} cm^{-1}	K_{24}(NMR)[a]	K_{24}(calcd)[b]
278	1665	0.604	0.638
298	1542	0.973	0.939
318	1406	1.476	1.433
338	1281	2.131	2.177
358	1157	2.954	3.560

[a] Equilibrium constants obtained by NMR method. [b] Equilibrium constants calculated from eq 3, excluding the datum at 358 K.

25 °C over the pressure range 1–1367 atm. The data were corrected for changes in solvent density, and hence sample concentration, with pressure.[10]

Results

Partial Molal Volumes. For [Fe(HB(pz)$_3$)$_2$] measurements were made in tetrahydrofuran solutions. The results are given in Table I. The density of tetrahydrofuran at 25.0 °C was found to be 0.882 12 (3) g cm^{-3}, in good agreement with the value of 0.8819 g cm^{-3} previously reported.[11] For three concentrations between 0.02 and 0.10 M there is no significant concentration dependence, so the average value of the apparent molal volumes, 340.9 ± 1.1 cm^3 mol^{-1}, is taken as the partial molal volume.

For [Fe(acac)$_2$trien)]NO$_3$ measurements made in distilled water were independent of concentration in the range from 0.005 to 0.10 M. The partial molal volume is taken as the average value of the apparent molal volumes given in Table I, 301.1 ± 0.7 cm^3 mol^{-1}.

For Fe((sal)$_2$trien)](NO$_3$) in distilled water the data shown in Table I are concentration-dependent and were extrapolated to infinite dilution by using the Redlich–Meyer equation for a 1:1 electrolyte[1]

$$\Phi_V = \Phi^\circ_V + 1.868C^{1/2} + b_V C \qquad (2)$$

where C is the molal concentration and b_V is an empirical factor determined from the experimental results. The data were fitted by least-squares as ($\Phi_V - 1.868C^{1/2}$) against C and yielded a value of 309.4 ± 1.5 cm^3 mol^{-1} for Φ°_V.

For [Co(terpy)$_2$]Cl$_2$ measurements made in distilled water were independent of concentration and gave an average value of 419.0 ± 0.2 cm^3 mol^{-1} for the partial molal volume.

Volume Differences. The volume differences between the high-spin and low-spin isomers of the iron complexes are available from previous ultrasonic absorption measurements.[3-5] For [Co(terpy)$_2$]$^{2+}$, however, the doublet–quartet relaxation is too rapid to be observed in the ultrasonic experiment. The volume difference between the spin isomers was therefore obtained from the variable-pressure electronic spectrum of the complex. First the temperature dependence of the spin-equilibrium constant (Figure 1) was obtained from a variable-temperature Evans' NMR experiment, as previously described.[5] Then the temperature dependence of the electronic absorption spectrum (Figure 2) at 445 nm (Table II) was fitted by linear least-squares methods with eq 3 to give

$$(K + 1)\epsilon_{obsd} = \epsilon_{LS} + K\epsilon_{HS} \qquad (3)$$

values of 2170 and 870 M^{-1} cm^{-1} for the molar absorptivities of the low-spin and high-spin isomers, respectively. Finally, the pressure dependence of the absorbance at 445 nm was measured. Assuming that the molar absorptivities are independent of pressure, the pressure dependence of the equilibrium constant was calculated. A plot of ln K vs. P was non-linear, indicating that the

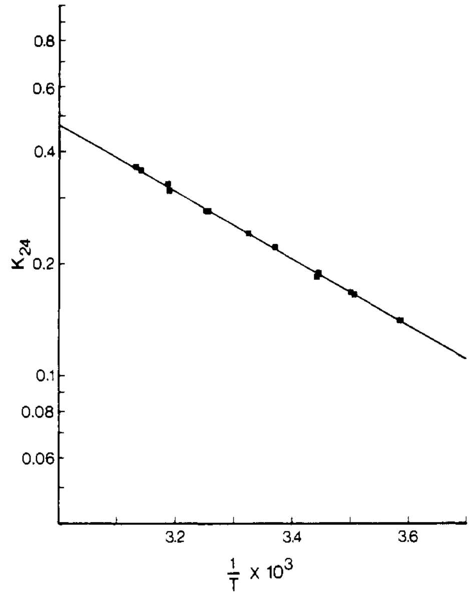

Figure 1. Temperature dependence of the spin-equilibrium constant for [Co(terpy)$_2$]Cl$_2$·2H$_2$O in distilled water.

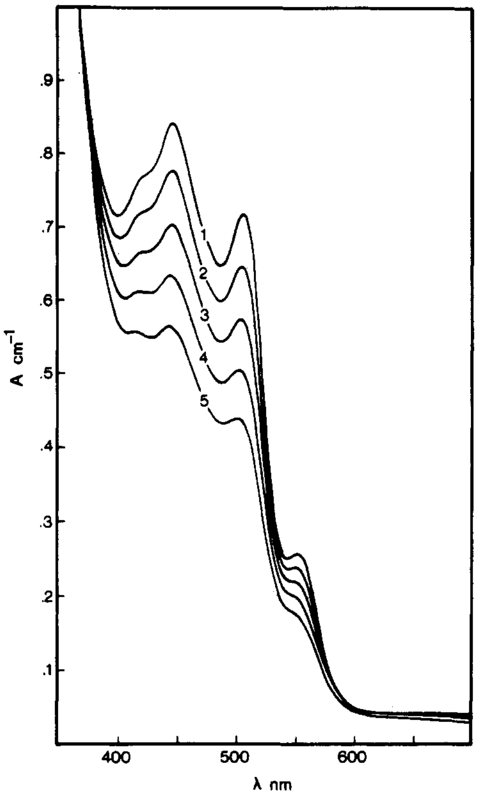

Figure 2. Temperature dependence of the electronic absorption sectrum of a 5 × 10^{-4} M solution of [Co(terpy)$_2$]Cl$_2$·2H$_2$O in distilled water: (1) 278 K; (2) 298 K; (3) 318 K; (4) 338 K; (5) 358 K.

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Table III. Pressure Dependence of ϵ_{obsd} at 445 nm for $[Co(terpy)_2]Cl_2 \cdot 2H_2O$ in H_2O at 298 K

P, atm	ϵ_{obsd}, M^{-1} cm^{-1}	K_{24}[a]
1	1542	0.940
340	1597	0.793
680	1664	0.640
1021	1752	0.477
1381	1845	0.335

[a] Equilibrium constants calculated according to eq 4.

volume difference is pressure-dependent, probably due to a compressibility difference, $\Delta\kappa^\circ_1$, between the two isomers. Consequently, the data were fitted by least squares using eq 4[12] (Table III). This gave a value for ΔV° at atmospheric pressure of 10.1 ± 0.4 cm^3 mol^{-1}.

$$[-RT/(P-1)] \ln (K_p/K_1) = \Delta V^\circ_1 - \tfrac{1}{2}\Delta\kappa^\circ_1(P-1) \quad (4)$$

Discussion

The partial molal volumes measured in solution can be compared with the volumes of the complexes in the solid state, where crystal structures are available. Solid $[Fe(HB(pz)_3)_2]$ is entirely low spin and occupies a volume of 337.3 cm^3 mol^{-1}.[13] In tetrahydrofuran solution at 25 °C the complex exists in an equilibrium of 86% low-spin and 14% high-spin isomers.[3] Using the volume difference between the two spin isomers, ΔV°, of 23.6 cm^3 mol^{-1} obtained from the amplitude of the ultrasonic relaxation of the spin equilibrium,[3] the volume of the low-spin isomer in solution can be calculated to be 337.6 cm^3 mol^{-1}. The close agreement between the volumes in solution and the solid indicates that the intermolecular contacts in the two states are similar. Apparently the tetrahydrofuran solvent molecules do not have any greater access to spaces between the planes of the pyrazolyl ligands than the intermolecular contacts in the crystal, and the complex behaves in solution as a nearly spherical ellipsoid.

The partial molal volumes of the complex salts $[Fe((acac)_2trien)](NO_3)$ and $[Fe((sal)_2trien)](NO_3)$ include the volume of the nitrate anion. The conventional partial molal volume of the nitrate anion is 29.0 cm^3 mol^{-1}, referred to H^+.[1] The absolute partial molal volume of H^+ has been estimated[1] to be −5 ± 2 cm^3 mol^{-1}; hence the absolute partial molal volume of the nitrate anion is 34 ± 2 cm^3 mol^{-1}. The absolute partial molal volumes of the complex cations $[Fe((acac)_2trien)]^+$ and $[Fe((sal)_2trien)]^+$ in aqueous solution at 25 °C are therefore 267 ± 3 and 275 ± 3 cm^3 mol^{-1}, respectively.

Both complexes exist in solution as equilibrium mixtures of 67% low-spin and 33% high-spin isomers.[4,5] The absolute partial molal volumes of the low-spin and high-spin isomers can be calculated from the volume differences between the spin states, ΔV°, obtained from the amplitudes of the ultrasonic relaxation of the spin equilibria.[4] For $[Fe((acac)_2trien)]^+$ this volume difference is 10.3 cm^3 mol^{-1}, giving a partial molal volume of 264 ± 3 cm^3 mol^{-1} for the low-spin isomer and 274 ± 3 cm^3 mol^{-1} for the high-spin isomer. The crystal structure has been determined of the high-spin hexafluorophosphate salt, which possesses a molal volume of 341.4 cm^3 mol^{-1}.[14] The partial molal volume of the hexafluorophosphate anion in solution is 67 cm^3 mol^{-1}.[15] The crystal volume of the hexafluorophosphate anion was not given in a recent tabulation[1] but can be calculated from the cell volumes of the KPF_6, NH_4PF_6, and $CsPF_6$ crystals[16] and the crystal volumes of the cations.[1] These give values of 62, 66, and 71 cm^3 mol^{-1}, respectively. Subtracting the average value of 66 cm^3 mol^{-1} from the solid-state volume of the complex salt gives a solid-state volume of 275 cm^3 mol^{-1} for the high-spin complex cation, again in excellent agreement with the solution value. This implies that the interionic contacts between the complex cation and the disordered hexafluorophosphate anion are similar to the solvation of the cation in aqueous solution.

The crystal structures of low-spin (1.94 μ_B) $[Fe((sal)_2trien)]Cl \cdot 2H_2O$ and low-spin (2.47 μ_B) $[Fe((sal)_2trien)]NO_3 \cdot H_2O$ have been determined[14] to have molal volumes of 329.2 and 328.5 cm^3 mol^{-1}, respectively. Subtracting a crystal volume of 14.9 cm^3 mol^{-1} for the chloride anion[1] and 19.6 cm^3 mol^{-1} for each of the two hydrogen-bonded water molecules gives a molal volume for the low-spin complex cation of 275 cm^3 mol^{-1}. This again is in good agreement with the partial molal volume of 272 ± 3 cm^3 mol^{-1} obtained from the solution density measurements and the volume difference of 11.9 cm^3 mol^{-1} between the spin states. For the nitrate salt, subtracting a crystal volume of 21.1 cm^3 mol^{-1} for the nitrate anion and 19.6 cm^3 mol^{-1} for one water molecule give a volume of 288 cm^3 mol^{-1} for the cation, in poorer agreement with the solution value. In this structure, however, the nitrate anion is disordered, principally by rotation about one N–O bond, and thus apparently occupies more volume than the conventional crystal volume.

The partial molal volume of 419.0 ± 0.2 cm^3 mol^{-1} for $[Co(terpy)_2]Cl_2$ contains the volume of the hydrated chloride ions, 23.2 cm^3 mol^{-1} each.[1] Subtracting these gives a partial molal volume of 372.6 cm^3 mol^{-1} for the complex cation, which is in spin equilibrium in solution with an intermediate magnetic moment of 3.88 μ_B. This corresponds to an equilibrium constant of 1.0. The volume of the low-spin cation is then calculated to be 368 cm^3 mol^{-1} from the spin-equilibrium volume difference of 10 cm^3 mol^{-1} obtained from the pressure dependence of the electronic absorption spectrum as described above. The crystal structure of the iodide salt, $[Co(terpy)_2]I_2 \cdot 2H_2O$, has recently been determined.[17] Subtracting from the volume of the formula unit (464.6 cm^3 mol^{-1}) the crystal volume of two iodide ions (2 × 25.4 cm^3 mol^{-1}) and two hydrogen-bonded water molecules gives a volume for the complex cation of 374.6 cm^3 mol^{-1}. In the crystal the complex also displays an intermediate magnetic moment of 3.2 (1) μ_B. The crystal volume of the low-spin isomer is then calculated to be 372 cm^3 mol^{-1}, in reasonable agreement with the value of 368 cm^3 mol^{-1} obtained from the solution measurements.

Thus for each of the complexes studied there is close agreement between the volume occupied in the crystal and the partial molal volume in solution.

Metal–Ligand Bond Length Changes. The effective spherical radius of each complex can be calculated from its partial molal volume. Then from the volume difference between the low-spin and high-spin isomers the change in spherical radius due to the spin-state change can be calculated. For the neutral iron(II) complex $[Fe(HB(pz)_3)_2]$ the volume of 337.6 cm^3 mol^{-1} for the low-spin isomer corresponds to a spherical radius of 511.5 pm. From the volume difference between the isomers of 23.6 cm^3 mol^{-1}, the spherical radius of the high-spin isomer is calculated to be 523.2 pm, 12 pm larger. Since the complex is not a perfect sphere and the expansion of the coordination sphere is directed mainly along the metal–ligand bonds, this value of 12 pm is a minimum estimate of the change in metal–ligand distance between the spin states. A difference of 19.9 pm has been observed between the iron–nitrogen distances in the crystal structures of $[Fe(HB(pz)_3)_2]$, which is low spin in the solid state, and its dimethyl derivative, which is high spin.[13] The crystal structures also reveal that the complexes are ellipsoidal, rather than spherical, suggesting that the change in volume occurs mainly along the 3-fold, long axis of the ellipsoid.

For the iron(III) complexes $[Fe((acac)_2trien)]^+$ and $[Fe((sal)_2trien)]^+$ the partial molal volumes of 263.6 and 271.5 cm^3 mol^{-1} correspond to spherical radii of the low-spin complexes of 471.0 and 475.7 pm, respectively. From the volume differences of 10.3 and 11.9 cm^3 mol^{-1} between the spin states obtained from the ultrasonic measurements, differences in the effective spherical radii of the isomers are calculated to be 6.1 and 6.9 pm, re-

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Table IV. Summary of Results

	vol, cm^3 mol^{-1}			dist, pm		
complex[d]	V°_{xst}	V°_s	ΔV°	Δr^a	$\Delta r(M-L)^b$	$\Delta r(xst)$
$Fe(HB(pz)_3)_2$	337.3	337.6	23.6	12		19.9
$Fe((acac)_2trien)^+$	265	264	10.3	6.1	11.4	12.6
$Fe((sal)_2trien)^+$	275	272	11.9	6.9	13.1	
$Co(terpy)_2^{2+}$	372	368	10.1	4.8		12[c]

[a] Minimum value calculated from V°_s and ΔV, assuming spherical complexes. [b] Calculated from radius of coordination sphere. [c] Average value of two nitrogen atoms at 21 pm and four at 7 pm. [d] Low-spin isomer.

spectively. From the open nature of the complexes revealed in the crystal structures, it is likely that most of the ligand remains solvated in the same way in the two spin states. The effective solvated radius of the metal–ligand core may be taken as the average metal–ligand distance of 193.9 pm plus the average van der Waals radius of the coordinated atoms of 146.7 pm. With this value of 340.6 pm for the solvated radius of the low-spin isomer in solution, the volume differences correspond to metal–ligand bond length changes of 11.4 and 13.1 pm, respectively. These values are in excellent agreement with the difference of 12.6 pm found in the solid state between low-spin $[Fe((sal)_2trien)]Cl_2 \cdot 2H_2O$ and high-spin $[Fe((acac)_2trien)]PF_6$.[14] This suggests that the atoms of the first coordination sphere are solvated and that the solvation of the remainder of the ligand is not significantly altered between the spin states. This interpretation is consistent with previous observations[18] of the solvent dependence of the spin equilibrium. This solvent dependence was ascribed to specific hydrogen bonding between the solvent molecules and the N–H protons of the trien ligand, which is manifest in a correlation between the magnetic moment and the N–H stretching frequency.

For $[Co(terpy)_2]^{2+}$ the partial molal volume of 368 cm^3 mol^{-1} corresponds to a spherical radius of 526.4 pm. From the volume difference between the spin states obtained from the pressure measurements, the difference in spherical radii is calculated to be only 4.8 pm. Again this represents a lower limit to the difference in metal–ligand bond lengths. A comparison among a series of $[Co(terpy)_2]^{2+}$ structures indicates that the spin-state change results in a lengthening of the bond to the central nitrogen of each ligand by as much as 21 pm, but a lengthening of only 7 pm in the bonds to the two distal nitrogens of each ligand.[19] Thus the expansion is concentrated along one axis of the complex. Comparison of the absolute values of the bond length changes suggests solvation of the ligand in both spin states, consistent with the intermolecular overlap of the ligands observed in the crystal structures.

Conclusions

The principal conclusions are summarized in Table IV. The partial molal volumes found for these relatively large metal complexes in solution are very close to the volumes occupied in crystals of the compounds. Analysis of the volume difference between the high-spin and low-spin isomers of these spin-equilibrium complexes provides information about the solvation of the complexes that is not available from the partial molal volumes alone. The larger complexes display larger volume differences between their low-spin and high-spin isomers, consistent with a larger excluded volume. (Note that the iron complexes undergo a change of two-electrons in the antibonding e_g^* orbitals while the cobalt(II) complex undergoes a one-electron change. Hence the volume difference for the cobalt complex is intrinsically smaller.) The changes in metal complex radius between spin states calculated for a spherical complex are much smaller than those observed in crystal structures. This implies that much of the ligand remains solvated to the same extent in both spin states. For the ligands derived from triethylenetetramine in which the coordinated atoms are accessible to hydrogen bonding with the solvent, good agreement is obtained between the calculated and observed metal–ligand bond length changes, assuming solvation of the first coordination sphere of the complex, consistent with previous observations of a correlation between the spin equilibrium and amine–hydrogen stretching frequencies.[18]

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Registry No. $Fe(HB(pz)_3)_2$, 16949-45-4; $[Fe((acac)_2trien)]NO_3$, 68108-57-6; $[Fe((sal)_2trien)]NO_3$, 67225-84-7; $[Co(terpy)_2]Cl_2$, 26096-47-9; tetrahydrofuran, 109-99-9.

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Low-Temperature IR MCD Using Modified PTFE Films and Applications to the Creutz–Taube Complex

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We report the use of a PTFE polymer with ion-exchange properties (Nafion), to prepare very thin films containing a high concentration of a cationic species under study. These films are remarkably transparent throughout the near- and mid-IR regions and have the particular advantages (for MCD measurements) of being both optically isotropic and transparent. We present MCD spectra of the Creutz–Taube mixed-valence ion, which exhibit both vibrational and electronic MCD spectral features in the IR region. Spectra of related monomeric materials dispersed in KCl disks are also presented. The presence of an electronic transition near 2000 cm^{-1} in the Creutz–Taube complex, predicted by a previous theoretical analysis, is confirmed. The reported spectra appear to be the first low-temperature IR MCD spectra in the range from 1800 to 2500 cm^{-1}.

1. Introduction

Spectral transmission measurements made in the IR region are usually made on gases, solutions, mulls, and pressed disks. Single crystals of suitable size and thickness can seldom be prepared. Furthermore, in crystals, there are problems in accounting for reflectivity dispersions arising from changes in the real part of the dielectric constant. The magnetic circular dichroism (MCD) technique[1] has recently been extended to the IR region,[2,3] but

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