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Solvation Effects in Dithiocarbamate Complexes. Spin-State Equilibrium in Benzene- and Dichloromethane-Solvated Tris(morpholinecarbodithioato)iron(III)

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The magnetic behavior of the title solvates has been examined by means of the Mössbauer effect from room temperature down to 1.45 K. Complementary measurements of magnetic susceptibility were taken in the 300–45 K temperature range. It was found that the solvated solvent greatly influences the high–low spin-state thermal equilibrium of the complex, by shifting it toward either the $S = {}^1/_2$ (benzene solvate) or the $S = {}^5/_2$ (dichloromethane solvate) spin state. It is also shown that the previously assigned intermediate ($S = {}^3/_2$) spin ground state to the dichloromethane solvate is not supported by the experimental evidence. Infrared spectra and solution effective magnetic moments indicate that the mechanism through which the solvent affects the spin equilibrium of the complex does not involve chemical bonding, coordination, hydrogen bonding, etc. between the solute and the solvent molecules but rather lattice forces, which alter the Fe–S bond length of the complex in a way similar to the distortions arising from applied external pressure.

Octahedrally coordinated ferric compounds can exist in two distinct spin states. In the presence of strong ligand fields of O_h symmetry the term ${}^2T_{2g}$ ($g_{2g}{}^5$) lies lowest in energy and the iron ion is in the $S = {}^1/_2$ spin state ("low" spin). The room-temperature value of the effective magnetic moment is in this case close to 2.0 μ_B, somewhat higher than the spin-only value $\mu_{eff} = 1.73\ \mu_B$, due to small contributions from the nonzero value of the orbital angular momentum in the $t_{2g}{}^5$ configuration.[1,2] Under weak ligand fields of O_h symmetry, on the other hand, the ${}^6A_{1g}$ ($t_{2g}{}^3e_g{}^2$) term becomes the ground state of the system with $S = {}^5/_2$ ("high" spin) and observed moments close to the spin-only value of 5.9 μ_B. Deviations from pure high- or low-spin behavior can arise in these complexes when the ligand field strength is comparable with the mean electron-pairing energy of the d^5 configuration. In this case thermal equilibrium can be established between the two possible ground states ${}^2T_{2g}$ and ${}^6A_{1g}$, resulting in the magnetic moments varying between the limiting values of 2.0 and 5.9 μ_B. Tris(*N*,*N*-dialkyldithiocarbamato)iron(III) complexes constitute one of the most typical classes of molecules exhibiting high-spin–low-spin thermal equilibrium. Magnetic susceptibility measurements, Mössbauer spectral behavior, and NMR shifts of numerous examples of these compounds have been successfully interpreted in terms of the $S = {}^1/_2$, $S = {}^5/_2$ spin equilibrium.[2-14] Failure to observe simultaneous population of these two states by Mössbauer or NMR spectroscopy has been attributed to high-spin–low-spin crossover periods shorter than the Mössbauer or NMR time scale (10^{-7} s). Therefore the parameters obtained by these methods reflect only an average of the contributions of each ground state. Ligand field theory excludes the possibility of a ground state with three unpaired electrons and $S = {}^3/_2$ in octahedral ferric complexes, unless the symmetry of the system is considerably lowered, in which case the ${}^4A_2$ or ${}^4E$ component of the ${}^4T_1$($t_{2g}{}^4e_g$) quartet level may become the ground state.[15] This is the case with five-coordinate bis(*N*,*N*-dialkyldithiocarbamato)iron(III) halides in which the donor atoms occupy the apices of a distorted square pyramid, while the metal ion lies close to the center of gravity of the coordination polyhedron.[16-18] Although the stereochemistry of the FeS_6 core in six-coordinate ferric dithiocarbamates is that of a trigonally distorted octahedron rather than pure octahedral,[19,20] this distortion has never been considered strong enough to stabilize the "intermediate" spin state with $S = {}^3/_2$ in these complexes.

Solvent inclusion in the lattice of ferric dithiocarbamates, which takes place upon crystallization from the proper solution, is a well-established fact for both five- and six-coordinate complexes.[21-28] The solvent can be either ligated to the ferric ion whenever there is an available ligand position and the solvent is a molecule with good coordination properties[21,22] or incorporated in the lattice at crystallographic positions verified by X-ray studies.[23-28] In either case solvation is known to affect considerably the magnetic properties of the solvated complex.[21-28] Recently however a number of reports have appeared in the literature that claim the observation of an intermediate ($S = {}^3/_2$) spin ground state in dichloromethane-solvated $(morphdtc)_3Fe$[26] (morphdtc = morpholinecarbodithioato) not predicted by ligand field theory.[15] Here we present experimental evidence indicating that the assignment of a $S = {}^3/_2$ spin state to this six-coordinate ferric complex is not correct, and that despite the large effect the solvated solvent has on the spin state of iron(III), only $S = {}^1/_2$ and $S = {}^5/_2$ spin ground states exist, as predicted by theory.[15] Mössbauer spectroscopy was employed as the principal method of investigation mainly because the results obtained are rarely affected by the presence of small impurities and also because when the spectra exhibit

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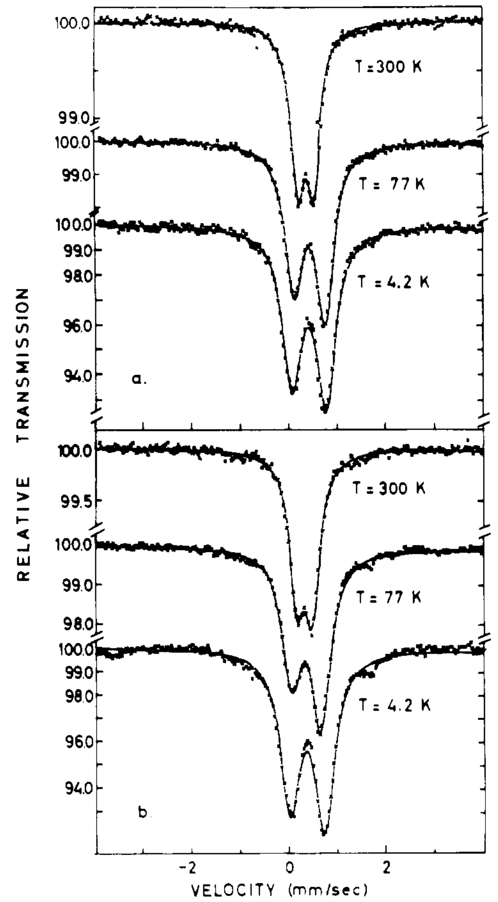

Figure 1. Mössbauer spectra of desolvated (morphdtc)$_3$Fe complex: (a) desolvated from benzene solvate; (b) desolvated from dichloromethane solvate.

hyperfine structure the spin-state assignment is unequivocal and straightforward. Magnetic susceptibility measurements were used as complementary evidence for the conclusions drawn from the analysis of the Mössbauer data. Infrared spectra were also examined for evidence of solvent–solute interactions, mainly hydrogen bonding, in solvated crystals as well as liquid solutions of the complex.

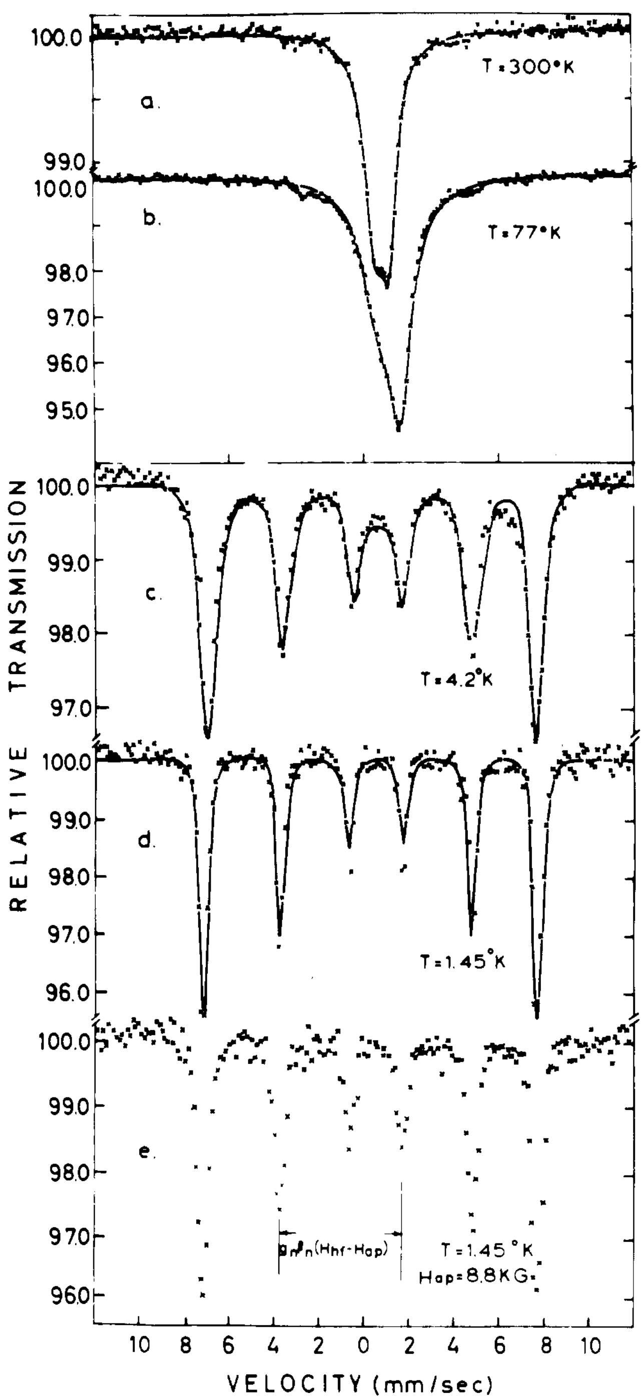

Figure 2. Mössbauer spectra of (morphdtc)$_3$Fe·CH$_2$Cl$_2$ solvate.

Experimental Section

(morphdtc)$_3$Fe was synthesized by interacting the sodium salt of the ligand with ferric chloride in ethanol.[29] The material was subsequently pumped for 48 h at 100 °C to remove any possibly solvated ethanol. This presumably desolvated complex was used for the preparation of all samples studied here. The solvated complexes were obtained by slow evaporation of solutions of (morphdtc)$_3$Fe in benzene or in 1:1 dichloromethane–cyclohexane[25] under inert atmosphere to prevent solvation by atmospheric water.[26] Also the recrystallization took place in the dark to avoid photochemical formation of the five-covalent complex (morphdtc)$_2$FeCl,[30] which is known to have spin $S = {}^3/_2$.[16-18] The solvents used were distilled and treated with the proper drying agents. Desolvated solids FeM(2PhH) and FeM(DCM) (DCM = dichloromethane) (Table I) were obtained by heating the corresponding solvates at 100 °C under vacuum for 48 h.[25] The identity and purity of the materials were confirmed by C, H, N, and Fe elemental analysis, as well as by their IR and Mössbauer spectra. Moreover, weight losses on heating the benzene and dichloromethane solvates to constant weight were consistent with (morphdtc)$_3$Fe·2C$_6$H$_6$ and (morphdtc)$_3$Fe·CH$_2$Cl$_2$ compositions respectively. Mössbauer spectra were obtained with use of a 100 mCi ^{57}Co in Rh source in conjuction with a linear velocity drive. Sub-liquid-helium temperatures were monitored and measured by helium-vapor thermometry. Since the solvated solvent can readily escape from the lattice,[25,26] Mössbauer measurements on solvates were carried out immediately after filtration of the crystals from the crystallization solution without removal of excess solvent. Solvates used for magnetic susceptibility measurements however were mildly dried with a flux of argon to remove excess of solvent possibly adsorbed on the surface of the microcrystallites. Magnetic susceptibility measurements on polycrystallites were performed on the PAR 155 vibrating-sample magnetometer. The effective moment of the complex in solution of benzene or dichloromethane was determined by the NMR method with use of the Varian HA-60 spectrometer. Infrared spectra were recorded, as either KBr pellets or solutions, on a Perkin-Elmer 257 grating spectrophotometer.

Results and Discussion

Representative Mössbauer spectra of the solvated and desolvated (morphdtc)$_3$Fe complexes obtained in the temperature range between 1.45 and 300 K are shown in Figures 1 and 2. The parameters derived from these spectra are listed in Table

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Table I. Values of Mössbauer Parameters and $\mu_{eff}(T)$ for Solvated and Desolvated $(morphdtc)_3Fe$ Complexes

complex	T, K	IS,[a] mm/s	QS, mm/s	$H_{hf}(\theta, \varphi)$,[b] kG	C, MHz	μ_{eff}, μ_B
$(morphdtc)_3Fe{\cdot}2C_6H_6$	300	0.37 ± 0.01	0.23 ± 0.02	0		2.92 ± 0.01
[FeM·2PhH]	77	0.46	0.43	0		2.14
	4.2	0.45	0.54	0		
desolvated FeM·2PhH	300	0.40	0.32	0		5.21
[FeM(2PhH)]	77	0.48	0.63	0		3.33
	4.2	0.49	0.70	0		
$(morphdtc)_3Fe{\cdot}CH_2Cl_2$	300	0.41	0.22	0		5.92
[FeM·DCM]	77	0.48	0.35	0		5.92
	4.2	0.49	0.27	460 ± 5 (0,0)	900	
	1.45	0.49	0.27	465 (0,0)		
desolvated FeM·DCM	300	0.41	0.32	0		5.20
[FeM(DCM)]	77	0.47	0.59	0		3.40
	4.2	0.49	0.71	0		

[a] IS values are expressed with respect to the metallic iron standard at room temperature. [b] θ and φ are the spherical polar coordinates of H_{hf} in the principal axis of the EFG.

I along with the corresponding values of the effective magnetic moment $\mu_{eff}(T)$. The Mössbauer parameters of FeM·DCM at 4.2 and 1.45 K were obtained by computer fitting the magnetically unperturbed spectra exhibiting hyperfine structure and relaxation effects, according to the theory described in ref 11. The same procedure at the slow relaxation limit was employed for the simulation of the magnetically perturbed spectrum, but in this case the term of the applied field was added to the spin Hamiltonian and integration was carried out over all angles between H_{ap} and $H_{hf}(T)$ since the sample was polycrystalline. All other spectra consisting of a doublet were fitted with two Lorentzian lines. The temperature dependence of the effective magnetic moment for the solvated and desolvated complexes is shown in Figure 3. It is clear from the data of Table I that removal of the solvated solvent from either solvate produces materials with identical magnetic properties, evidently the nonsolvated $(morphdtc)_3Fe$ complex.

Isomer Shift. Isomer shifts (IS) with respect to the metallic iron standard at room temperature in high-spin ferric compounds are usually about 0.5 mm/s, whereas in the low-spin complexes they are about 0.0 mm/s.[31] Unfortunately, this distinction is not so clear-cut in the case of dithiocarbamate derivatives;[9,32] it has been found however that the room-temperature value of the IS increases with increasing value of the solid-state magnetic moment in several six-coordinate ferric dithiocarbamate complexes.[33] Such a trend is evident from the data listed in Table I. The FeM·DCM solvate and the desolvated complex, which have the largest μ_{eff}(300 K) and therefore the most pronounced high-spin character, also have the largest isomer shift, whereas on the other hand FeM·2PhH, which has the smallest μ_{eff}(300 K), has the smallest IS. At lower temperatures the magnitude of the IS changes in a more complicated way. In addition to the second-order Doppler effect, which shifts the IS toward higher energies by approximately 6×10^{-4} mm/(s deg),[34] there is also a shift following the temperature dependence of the high-spin–low-spin equilibrium. The room-temperature values of the isomer shift (Table I) in conjuction with the corresponding values of μ_{eff}(300 K) suggest therefore predominance of high spin in the dichloromethane solvate and the desolvated complex at 300 K while the benzene solvate exhibits high–low character.

Quadrupole Splitting. The quadrupole splitting (QS) in ferric dithiocarbamates reflects, in principle, the spin character of the iron(III) ion. In high-spin systems the only EFG at the iron nucleus arises from charges on surrounding atoms. This so-called "lattice contribution" usually produces temperature-independent quadrupole splittings less than ~0.35 mm/s.[32] In low-spin complexes on the other hand the noncubic symmetry of the iron d electrons produces considerably larger QS, which are temperature dependent, increasing with decreasing temperature and reaching a maximum plateau at low temperature.[35] In case of high–low equilibrium, however, several factors determine the QS and its temperature dependence, the most important being the energy difference ΔE between the high- and low-spin ground states, the cubic crystal field splitting and the trigonal distortion, the spin–orbit coupling, etc. A small QS at room temperature therefore does not necessarily suggest small low-spin contribution.[32] The temperature dependence of the QS and its low-temperature magnitude however are indicative of the predominant spin state of the ferric ion. The dichloromethane-solvated complex with its small and nearly temperature-independent QS conforms to high-spin character from 1.45 through 300 K. This assignment agrees with the values of the magnetic moment measured between 45 and 300 K. The FeM·2PhH complex behaves in a manner indicative of high–low equilibrium, which shifts toward the low spin as the temperature is lowered. Magnetic moment measurements (Figure 3) corroborate this

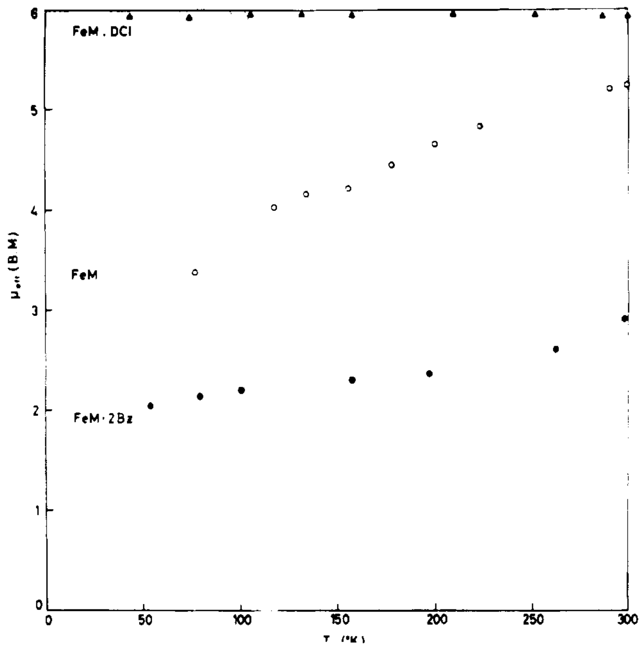

Figure 3. Temperature dependence of $\mu_{eff}(T)$ of solvated and desolvated $(morphdtc)_3Fe$ complexes.

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Table II. Values of H_c for Fe(III) in Complexes with Varying Fe-Ligand Covalency Character

complex	H_c, kG ($\langle S\rangle_{av} = 1$)	ref
FeF_3	250	40
Fe_2O_3	216	41
$FeCl_3$	195	42
$(pyrrdtc)_3Fe$	185	11
$(Et_2dtc)_2FeI$	175	43

conclusion. A similar behavior is exhibited by the desolvated complex but with larger high-spin character at room temperature as indicated by the value of $\mu_{eff}(300\ K) = 5.2\ \mu_B$.

Magnetic Hyperfine Interactions. Isotropic hyperfine magnetic fields, $H_{hf}(T)$ at the nucleus arising through the Fermi contact interaction, produce Mössbauer spectra exhibiting hyperfine structure whenever the electronic spin relaxation rate is slower than the ^{57}Fe nuclear precession frequency. The magnitude of $H_{hf}(T)$ depends on the number of unpaired 3d electrons as well as the nature of the coordination bonds.[22] It has been shown[36,37] that the contribution of each unpaired 3d electron to the total magnitude of $H_{hf}(T)$ is equal to 125 kG, and therefore the hyperfine field per unit spin is $H_c = 250$ kG. However, this value of H_c applies only for purely ionic complexes in which 3d electron density has not been removed from Fe(III) by covalency effects.[22,38] When covalency is present in the Fe–ligand bonds, H_c can become appreciably smaller than 250 kG per spin unit (Table II). The quantity $H_{hf}(T)$ therefore can be expressed in terms of H_c and the thermal average value of the spin $\langle S\rangle_{av}$ by eq 1,[39] where

$$H_{hf}(T) = \langle S\rangle_{av}H_c \qquad (1)$$

H_c is treated as a covalency-dependent parameter. At the very-low-temperature limit the saturation (or near saturation) magnitude of the effective field, in conjunction with the appropriate value of the parameter H_c, can give, by eq 1, the spin of the system. For FeM·DCM $H_{hf}(1.45\ K) = 465 \pm 5$ kG (Table I), whereas the value of H_c in this case can be taken as equal to 185 kG per spin unit—the same value as in the homologous $(pyrrdtc)_3Fe$ (pyrr = pyrrolidine), which also has six Fe–S covalent bonds (Table II)—therefore the thermal average value of the spin is $\langle S\rangle_{av} \simeq 2.5$ corresponding to five unpaired 3d electrons. Moreover, the parameter D, which determines the energy separation of the Kramers doublets, obtained from the computer fits of the low-temperature Mössbauer spectra (Figure 2), was found to be equal to −3.3 K for FeM·DCM, very close to the value of $D = -3.0$ K found in $(pyrdtc)_3Fe$.[9,11] Additional support for the rather large value of D found here is provided by the magnetically perturbed Mössbauer spectrum at 1.45 K. If D were small ($D << H_{ap}$), the application of the external field on the powder sample would split the higher doublets[44,45] and cause some population of them, resulting in considerable broadening of the absorption lines,[46] or even appearance of new lines.[47,48] This is not observed however, the only difference between the two spectra, at $H_{ap} = 0$ kG and $H_{ap} = 8.8$ kG, being a decrease in the total magnetic field acting on the ^{57}Fe nucleus by approximately 5–10 kG in the latter case. This reduction of $H_{eff}(1.45\ K, 8.8\ kG)$ compared to $H_{eff}(1.45\ K, 0\ kG)$ is expected since in ^{57}Fe the applied magnetic field acts in a direction opposite to the hyperfine field: $H_{eff}(T,H_{ap}) = H_{hf}(T) - H_{ap}$.[39] Large values of D were also found in some hemoglobin compounds and were related to the presence of excited states lying nearby.[49] In $(morphdtc)_3Fe{\cdot}CH_2Cl_2$ the source of the large D value is probably the $^2T_{2g}$ state, corresponding to the low-spin configuration, located at few hundred kelvins above the $^6A_1$ state. The parameters of the magnetic hyperfine interactions in FeM·DCM (Table I) and the preceding discussion as well as the temperature dependence of $\mu_{eff}(T)$ indicate that this solvate is in the high-spin state at all temperatures and also exhibits strong covalent character in the Fe–S bonds. A different interpretation of the experimental magnitude of the hyperfine field, $H_{hf}(1.45\ K) = 465 \pm 5$ kG, may be that it arises from a $^3/_2 \rightleftarrows {}^5/_2$ thermal spin equilibrium while the metal–ligand bonds are mainly ionic in nature. In this case the $^3/_2$ spin state would contribute, according to eq 1, $H_{hf}(T_{<<}) \simeq 375$ kG and the $^5/_2$ state $H_{hf}(T_{<<}) = 625$ kG. If this intermediate–high-spin crossover is faster than the Larmor period of the Mössbauer nucleus, a spectrum like the one shown in Figure 2b with $H_{hf}(1.45\ K) \simeq 465$ kG would be consistent with this argument. In fact a $^3/_2 \rightleftarrows {}^5/_2$ spin equilibrium has been suggested for this solvate on the basis of magnetic susceptibility measurements.[26] Closer inspection of the spectra of Figure 2, however, proves that the assumption of a spin equilibrium is contradicted by the Mössbauer data. The increase of $H_{hf}(T)$ with decreasing temperature clearly indicates that if there is a $^3/_2 \rightleftarrows {}^5/_2$ equilibrium, the state with the higher spin $S = {}^5/_2$ must lie lower in energy. However, our measurements of $\mu_{eff}(T)$ from 45 to 300 K (Figure 3) indicate that this solvate has $S = {}^5/_2$ in this temperature range. Moreover, according to the rate of the change of $H_{hf}(T)$ between $T = 4.2$ and 1.45 K the two spin states ought to be separated by an energy of the order of 10 K. Such low thermal activation is unlikely to be sufficient to induce the considerable distortion of the molecular symmetry from nearly octahedral required for stabilization of the $^4A_2$ or ^4E quartet state[1] corresponding to $S = {}^3/_2$. We conclude therefore that $(morphdtc)_3Fe{\cdot}CH_2Cl_2$ has $S = {}^5/_2$ at all temperatures as well as considerable covalent character in the Fe–ligand bonds.

Our study of the magnetic behavior of the solvated and desolvated $(morphdtc)_3Fe$ has shown that inclusion of the solvent in the crystal lattice greatly affects the high–low spin-state thermal equilibrium of Fe(III). Thus, the desolvated complex, obtained by the removal of all solvated solvent from either solvate, demonstrates mainly high-spin character at room temperature, which gradually shifts toward $S = {}^1/_2$ as the temperature is lowered to 4.2 K. The benzene-solvated complex in which two solvent molecules occupy crystallographic positions around each $(morphdtc)_3Fe$ unit exhibits high–low equilibrium at room temperature, which also shifts to predominantly low spin at 4.2 K. Finally, in the dichloromethane solvate the ferric ion is in its high-spin state at all temperatures. Furthermore, there is no evidence for a contribution from the $S = {}^3/_2$ spin state to the spin-state thermal equilibrium of any of the three systems examined here.

The solvation effects observed in these solvates are likely to arise through two alternative mechanisms: (a) by direct bonding between the solvent and the complex or (b) by dis-

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tortions imposed on the molecular configuration of the complex by the presence of the solvated molecules at crystallographic sites. The first mechanism, however, is rejected on the grounds of experimental evidence. Infrared spectra of solvates as well as solutions of (morphdtc)$_3$Fe studied in the 4000-700-cm^{-1} region showed no spectral changes indicative of solute-solvent linkages, e.g., coordination, hydrogen bonding, etc. Moreover, the solution effective magnetic moment of the complex dissolved in benzene or dichloromethane was measured by the NMR method and it was found the same, μ_{eff}(300 K) = 4.5 ± 0.1 μ_B, in both solutions. This consitutes further evidence that there are no solute-solvent interactions strong enough to induce changes in the spin-state equilibrium of the ferric ion, at least in the liquid phase. The absence of complex-solvated solvent linkages has also been suggested by X-ray studies of (Budtc)$_3$Fe·C$_6$H$_6$ monocrystals.[50] The second mechanism of the solid-state forces affecting the spin equilibrium of the paramagnetic center appears more relevant in view of the experimental data mentioned above and also from earlier studies on the pressure dependence of the solution μ_{eff}(300 K) of several Fe(III) dithiocarbamates.[3] It was found that application of external pressures up to 5000 atm on chloroform solutions of ((alkyl)$_2$dtc)$_3$Fe complexes shifts the high-spin-low-spin equilibrium toward the low-spin state. This shift has been associated with a shortening of the Fe-S bond by ca. 0.1 Å, amounting to a volume decrease of the order of 5 cm^3/mol of dithiocarbamate complex.[3] In a similar fashion the solvated solvent can be assumed to distort the complex by pure lattice forces and induce a decrease in the Fe-S bond length analogous to the decrease caused by the external pressure. In fact, in FeM·2PhH, the mean Fe-S bond length at 300 K is 2.318 Å[26] compared to Fe-S = 2.430 Å[25] in FeM·DCM. Accordingly, the former solvate exhibits high-spin-low-spin equilibrium at room temperature whereas the latter is in a predominantly high-spin state. Since the inclusion of solvent molecules at crystallographic sites seems to be very common in iron(III) dithiocarbamate crystals, combined X-ray and magnetic studies of these solvates can provide valuable information concerning the relationship between the spin state of Fe^{3+} and the exact structure of the FeS$_6$ core. The magnetic properties of several other solvated ferric dithiocarbamates are now under investigation in our laboratory along with their crystal structures at 300 and 77 K.

We conclude with a final remark concerning the previously published[26] $S = {}^3/_2$ assignment for (morphdtc)Fe·CH$_2$Cl$_2$. The temperature dependence of $\mu_{eff}(T)$ reported earlier[26], which contradicts the low-temperature Mössbauer data presented here, as well as our magnetic susceptibility measurements, probably arises from partial desolvation of the FeM·DCM and FeM·2PhH samples used in ref 26. In fact samples of dichloromethane-solvated crystals that were left at room temperature for few days produced liquid helium Mössbauer spectra consisting of two superimposed patterns, one exhibiting hyperfine structure identical with the spectrum of FeM·DCM and one exhibiting the doublet corresponding to the desolvated complex. The effective moment of those samples was indeed 5.5 μ_B at 300 K and close to 4 μ_B at 77 K. After complete removal of the solvent by heating and pumping the Mössbauer spectra demonstrated only the doublet of the desolvated complex while the magnetic susceptibility dropped to 5.2 μ_B at 300 K and 3.3 μ_B at 77 K.

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Registry No. FeM, 14285-01-9; FeM·2PhH, 59568-15-9; FeM·DCM, 53179-06-9.

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High-Pressure NMR Evidence for an Associative Interchange Mechanism, I_a, for Solvent Exchange on Iron(III)[1-3]

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Variable-pressure 60-MHz ^{1}H NMR transverse relaxation rate measurements have been made on iron(III) perchlorate solutions in dimethyl sulfoxide (Me$_2$SO), dimethylformamide (DMF), and methanol. For the two former solvents, the cation is hexasolvated whereas in methanol, even in acidic solutions, the cation is Fe(CH$_3$OH)$_5$(OCH$_3$)$^{2+}$. The derived volumes of activation (ΔV^*) for solvent exchange are interpreted in terms of an associative interchange I_a for Me$_2$SO (-3.1 ± 0.3 cm^3 mol^{-1}) and DMF (-0.9 ± 0.2 cm^3 mol^{-1}) but a dissociative interchange I_d for the hydrolyzed cation in methanol (+6.4 ± 0.2 cm^3 mol^{-1}). The reasons for the difference in mechanism between the hexasolvated and the hydrolyzed species are discussed. The results for the hexasolvated ion exchange are compared with those available for other first-row transition-metal trivalent-ion solvent exchanges and are interpreted in terms of a gradual mechanistic change from I_a to I_d on going from left to right across the periodic table. A similar trend for the divalent ions has also recently been reported.

Introduction

In a recent article,[2] the effect of pressure on the rate of water exchange on iron(III) has been studied up to 240 MPa. The pressure dependence shows marked variation with pH and yields a negative volume of activation for the water exchange with Fe(H$_2$O)$_6$$^{3+}$ and a positive volume of activation for water exchange with Fe(H$_2$O)$_5$OH^{2+}. However, the work was complicated since it was necessary to work at very high ionic strengths and acidities and to correct for changes in hydrolysis with pressure.

In a series of recent articles,[4-9] we have shown that the

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(1) This is part 14 of the series, "High-Pressure NMR Kinetics".

(2) Part 13 is to be taken as: Swaddle, T. W.; Merbach, A. E. *Inorg. Chem.* **1981**, *20*, 4212.

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