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Relation between Magnetism and Structure of Iron(III) Complexes Exhibiting an $S = \frac{3}{2} \rightleftharpoons S = \frac{5}{2}$ Spin State Equilibrium. Structures of Chloroform and Water Solvated Tris(4-morpholinecarbodithioato-*S,S′*)iron(III) and -manganese(III)

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Abstract: The crystal and molecular structures of tris(1-morpholinecarbodithioato-*S,S′*)iron(III) crystallized from chloroform (FeM·$CHCl_3$) and toluene (FeM·tol) and the manganese analogue crystallized from chloroform (MnM·$CHCl_3$) were determined by single-crystal x-ray diffraction using computer techniques. Crystal data: FeM·$CHCl_3$, $Fe(S_2CNC_4H_8O)_3 \cdot CHCl_3$, $P\bar{1}$, $Z = 2$, $a = 9.209$ (4) Å, $b = 10.716$ (4) Å, $c = 14.512$ (9) Å, $\alpha = 101.40$ (6)°, $\beta = 97.02$ (6)°, $\gamma = 90.61$ (6)°, $V = 1392$ Å^3, $R = 4.0\%$, 2934 reflections; MnM·$CHCl_3$, $Mn(S_2CNC_4H_8O)_3 \cdot CHCl_3$, $P\bar{1}$, $Z = 2$, $a = 13.60$ (1) Å, $b = 11.009$ (5) Å, $c = 11.733$ (5) Å, $\alpha = 117.09$ (4)°, $\beta = 99.89$ (6)°, $\gamma = 107.72$ (5)°, $V = 1387$ Å^3, $R = 4.0\%$, 2576 reflections; FeM·tol, $Fe(S_2CNC_4H_8O)_3 \cdot H_2O$, $P\bar{1}$, $Z = 2$, $a = 9.292$ (3) Å, $b = 10.454$ (4) Å, $c = 13.646$ (8) Å, $\alpha = 100.30$ (3)°, $\beta = 95.37$ (4)°, $\gamma = 106.19$ (3)°, $V = 1238$ Å^3, $R = 3.9\%$, 3316 reflections. Like the previously studied dichloromethane solvate, FeM·$CHCl_3$ and FeM·tol exhibit a spin state equilibrium between $S = \frac{3}{2}$ and $S = \frac{5}{2}$ states. It now appears that with hydrogen bonding solvates (CH_2Cl_2 in FeM·CH_2Cl_2, $CHCl_3$ in FeM·$CHCl_3$, and H_2O in FeM·tol), the magnetic moment is raised compared to that of the desolvated FeM, and an $S = \frac{3}{2}$ ground state is produced, whereas FeM shows only $S = \frac{1}{2}$ and $S = \frac{5}{2}$ states. A possible mechanism for this, involving solvent hydrogen bonding to ligand sulfur atoms, is discussed. It is likely that $S = \frac{1}{2}$, $S = \frac{3}{2}$, and $S = \frac{5}{2}$ states are all low lying in these and related complexes. In view of this and the extreme solvent sensitivity, many of the earlier literature data for such complexes should be taken with caution. The average metal–ligand bond lengths in the iron complexes increase as the moments increase. $\langle Fe–S \rangle$ is 2.317 (1), 2.416 (1), 2.430 (4), and 2.443 (1) Å in C_6H_6, $CHCl_3$, CH_2Cl_2, and H_2O solvates, respectively, the latter being the greatest $\langle Fe–S \rangle$ distance ever observed in a ferric dithiocarbamate. The manganese environment in MnM·$CHCl_3$ exhibits strong tetragonal distortion in addition to the trigonal distortion that occurs in all tris(dithiocarbamate) complexes. Near liquid helium temperature, there is some evidence of the intermolecular antiferromagnetic interaction expected to occur in the manganese and iron complexes, via the electron spin density delocalized onto the ligands.

A large variety of N-substituted ferric dithiochelate complexes lie at or near the high spin ($^6A_1$)–low spin ($^2T_2$) crossover,[1-6] so that their magnetic properties are strongly dependent upon temperature, pressure, substituent groups remote from the metal atoms, and, to a lesser extent, the solvent when in solution. These complexes frequently crystallize with molecules of the recrystallization solvents included in the lattice. Metal–ligand bond lengths alter with variation of the high to low spin ratio, as measured by magnetic properties.[1-3,7,8]

The properties of the complexes then vary with alteration of the solvent,[9,10] thereby producing much the same effect as varying the temperature or pressure, but far easier and more convenient to accomplish for structural investigation. Moreover, the magnetism of the dichloromethane solvate[11] of tris(1-morpholinecarbodithioato-*S,S′*)iron(III), $FeM\cdot CH_2Cl_2$, is different in character—rather than in position of the high spin-low spin equilibrium—from that of the unsolvated form FeM produced by removal of the dichloromethane.[10,11] No such phenomenon can result from temperature or pressure changes. The magnetic moment for $FeM\cdot CH_2Cl_2$ levels off at $3.7\ \mu_B$ at low temperatures, appropriate for a $S = \frac{3}{2}$ ground state, while for FeM it falls off lower, to $2.3\ \mu_B$, appropriate for a normal $^2T_2$–$^6A_1$ crossover. Both compounds have a similar room temperature moment near $5\ \mu_B$. The structure of $FeM\cdot CH_2Cl_2$, and hence the $\langle Fe–S \rangle$ distance, is known, but FeM is formed as a powder by solvent removal from solvated crystals so that no structure determination has so far been reported. We report here the magnetism and structure of the chloroform solvate $FeM\cdot CHCl_3$ and of the crystals grown from toluene "FeM·tol", which, however, contains no toluene and is the closest approximation to FeM so far available. $MnM\cdot CHCl_3$, which, surprisingly, is not isomorphous with $FeM\cdot CHCl_3$, is also reported for comparison of d^5 and d^6 analogues.

A further interest in crystalline solvates is their possible relevance to the NMR splittings in many dithiocarbamates,[12-15] some of which evidence solvent interactions.[12]

Experimental Section

The complexes were prepared as previously described.[1,15-17] Crystals suitable for x-ray diffraction and samples for magnetic measurements were prepared by slow addition of ethanol to saturated solutions of tris(1-morpholinecarbodithioato-*S,S′*)iron(III) (FeM) or tris(1-morpholinecarbodithioato-*S,S′*)manganese(III) (MnM) in chloroform ($FeM\cdot CHCl_3$ and $MnM\cdot CHCl_3$), toluene (FeM·tol), or chlorobenzene (FeM·ClBz). To avoid the tendency to lose solvent molecules included in the lattice, exposure of $FeM\cdot CHCl_3$ and $MnM\cdot CHCl_3$ to the open atmosphere was minimized, and the crystals selected for x-ray study were sealed in glass capillaries.

Crystal Data for $FeM\cdot CHCl_3$. $FeCl_3S_6O_3N_3C_{16}H_{25}$, M = 662, space group $P\bar{1}$, $Z = 2$, $a = 9.209\ (4)$ Å, $b = 10.716\ (4)$ Å, $c = 14.512\ (9)$ Å, $\alpha = 101.40\ (6)°$, $\beta = 97.02\ (6)°$, $\gamma = 90.61\ (6)°$, $V = 1392$ Å^3, $\mu(Mo\ K\alpha) = 12.9\ cm^{-1}$, $\rho_c = 1.58$, $\rho_o = 1.54\ g\ cm^{-3}$, $F(000) = 678$.

Crystal Data for $MnM\cdot CHCl_3$. $MnCl_3S_6O_3N_3C_{16}H_{25}$, M = 661, space group $P\bar{1}$, $Z = 2$, $a = 13.60\ (1)$ Å, $b = 11.009\ (5)$ Å, $c = 11.733\ (5)$ Å, $\alpha = 117.09\ (4)°$, $\beta = 99.89\ (6)°$, $\gamma = 107.72\ (5)°$, $V = 1387$ Å^3, $\mu(Mo\ K\alpha) = 12.5\ cm^{-1}$, $\rho_c = 1.60$, $\rho_o = 1.61\ g\ cm^{-3}$, $F(000) = 676$.

Crystal Data for FeM·tol. $FeS_6O_4N_3C_{15}H_{26}$, M = 561, space group $P\bar{1}$, $Z = 2$, $a = 9.292\ (3)$ Å, $b = 10.454\ (4)$ Å, $c = 13.646\ (8)$ Å, $\alpha = 100.30\ (3)°$, $\beta = 95.37\ (4)°$, $\gamma = 106.19\ (3)°$, $V = 1238$ Å^3, $\mu(Mo\ K\alpha) = 11.4\ cm^{-1}$, $\rho_c = 1.50$, $\rho_o = 1.49\ g\ cm^{-3}$, $F(000) = 582$.

Crystal Data for FeM·ClBz. $FeS_6O_4N_3C_{15}H_{26}$, M = 561, space group $P\bar{1}$, $Z = 2$, $a = 9.27\ (3)$ Å, $b = 10.45\ (1)$ Å, $c = 13.64\ (2)$ Å, $\alpha = 100.5\ (1)°$, $\beta = 95.3\ (2)°$, $\gamma = 106.3\ (2)°$, $U = 1233$ Å^3.

For the crystals of $FeM\cdot CHCl_3$, $MnM\cdot CHCl_3$, and FeM·tol, the Enraf-Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then used in the program INDEX to obtain an orientation matrix for data collection and also approximate cell dimensions. The cell parameters matched those obtained from precession photographs. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of each crystal was examined by the ω-scan technique and judged to be satisfactory. For FeM·ClBz, the same procedure was followed using the 15 reflections centered initially. As FeM·ClBz is clearly isomorphous with FeM·tol, no further diffraction data were collected for the former complex.

Magnetic susceptibilities were measured using a superconducting magnetometer, as described elsewhere.[9,18,19]

Collection and Reduction of Diffraction Data. Diffraction data were collected at 292 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, using Mo $K\alpha$ radiation from a highly oriented graphite crystal monochromator. The θ-2θ scan technique was used to record the intensities for which $0° < 2\theta < 48°$. Scan widths (SW) were calculated from the formula $SW = A + B \tan \theta$ where A is estimated from the mosaicity of the crystal and B allows for the increase in width of peak due to $K\alpha_1$ and $K\alpha_2$ splitting. The values of A and B were 0.60° and 0.20°, respectively, for $FeM\cdot CHCl_3$ and $MnM\cdot CHCl_3$ and 0.90° and 0.30°, respectively, for FeM·tol. This calculated scan angle is extended at each side by 25% for background determination (BG1 and BG2). The net count (NC) is then calculated as $NC = TOT - 2(BG1 + BG2)$ where TOT is the estimated peak intensity. Reflection data were considered insignificant if intensities registered less than 10 counts above background on a rapid prescan, such reflections being rejected automatically by the computer.

The intensities of four standard reflections, monitored for each crystal at 100 reflection intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz-polarization effects, and in the case of FeM·tol, for absorption. No attempt was made to apply absorption corrections to the chloroform solvated crystals which were sealed in glass capillaries, due to the additional intensity errors due to x-ray absorption by the glass. The absence of absorption corrections should have at most a small effect on the temperature factors. After averaging the intensities of equivalent reflections, the data were reduced to 3657 independent intensities for $FeM\cdot CHCl_3$, 3415 for $MnM\cdot CHCl_3$, and 3316 for FeM·tol, of which 2934 for $FeM\cdot CHCl_3$, 2576 for $MnM\cdot CHCl_3$, and 2867 for FeM·tol had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[20] These data were used in the final refinement of the structural parameters.

Solution and Refinement of the Structures. In each case some of the heavier atoms were located from a three-dimensional Patterson synthesis: Fe and three S atoms for $FeM\cdot CHCl_3$, Mn and two S atoms for $MnM\cdot CHCl_3$, and Fe and five S atoms for FeM·tol.

Full-matrix least-squares refinement was based on F, and the function minimized as $\Sigma w(|F_o| - |F_c|)^2$. The weights w were taken as $(2F_o/\sigma(F_o^2))^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber[21] and those for hydrogen from Stewart et al.[22] The effects of anomalous dispersion for non-hydrogen atoms were included in F_c using Cromer and Ibers' values[23] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$. To minimize computer time, the initial calculations were carried out on the first 1200 reflections collected. The computing system and programs used were as described elsewhere.[24] The intensity data were phased sufficiently well by the metal and sulfur positions determined in the Patterson map to permit location of the remaining non-hydrogen atoms by difference Fourier syntheses. The chlorine atoms of the chloroform molecule in $FeM\cdot CHCl_3$ were found to be highly positionally disordered around the (undisordered) carbon atom, while in $MnM\cdot CHCl_3$ no evidence of disorder could be found. This requirement of different chloroform packing is at least one reason why the two complexes are not isomorphous. The main chlorine positions were located and the occupancy refined. The water molecule in FeM·tol was also found to be very disordered in position (Table III). After full-matrix least-squares refinement, the models converged with $R = 6.8\%$ for $FeM\cdot CHCl_3$, 7.9% for $MnM\cdot CHCl_3$, and 7.7% for FeM·tol. The remaining diffraction data were added to the calculation, anisotropic temperature factors were introduced for all non-hydrogen atoms, except for the included solvent molecules in $FeM\cdot CHCl_3$. Fourier difference maps revealed hydrogen atoms on each morpholine ring of the three complexes, and the methylene hydrogen atoms were inserted as fixed atoms at the calculated positions, with isotropic temperature factors of 5.0 Å^2, assuming C–H 1.00 Å. As no significant solvent peaks (comparable with hydrogen atom intensities) appeared on either $FeM\cdot CHCl_3$ or FeM·tol, the principal positions of the disordered atoms had been established at this stage. After convergence ($R = 4.9\%$) of the model for $FeM\cdot CHCl_3$ (including refinement of occupancies), anisotropic temperature factors were introduced for Cl(1), Cl(2), and Cl(3). The $CHCl_3$ disorder is mainly rotational, about the C–H axis, with little tilt of the C–H axes about the average positions. The C–H direction is such as to point the H atom towards the ligand sulfur atom S(22). Table Ia gives the principal Cl atom positions, Cl(1) through Cl(8), ranging in estimated occupancies from 0.61 to 0.29. Allowing for overlap or near overlap in the Cl atom positions for different $CHCl_3$ positions, the observations can be ration-

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations: $Fe(S_2CNC_4H_8O)_3 \cdot CHCl_3$

Atom	X	Y	Z	$B_{1,1}$[a] or B (Å²)	$B_{2,2}$	$B_{3,3}$	$B_{1,2}$	$B_{1,3}$	$B_{2,3}$
Fe	0.247 85 (8)	−0.003 04 (6)	0.245 74 (5)	0.009 57 (8)	0.005 66 (5)	0.004 16 (3)	0.001 9 (1)	0.002 08 (9)	0.002 66 (7)
Cl(1)	0.380 1 (4)	0.338 9 (4)	0.546 1 (2)	0.031 0 (6)	0.030 7 (5)	0.006 9 (2)	0.008 3 (10)	0.005 5 (5)	0.009 7 (5)
(Cl(2)	0.432 4 (4)	0.519 8 (4)	0.321 0 (3)	0.013 5 (5)	0.021 2 (5)	0.011 5 (3)	−0.009 2 (9)	0.000 7 (6)	0.001 2 (7)
Cl(3)	0.372 6 (4)	0.308 7 (6)	0.543 0 (3)	0.009 2 (5)	0.033 4 (8)	0.008 0 (3)	0.002 6 (11)	−0.001 8 (6)	−0.013 1 (8)
Cl(4)	0.308 7 (4)	0.341 9 (3)	0.730 4 (2)	7.42 (8)					
Cl(5)	0.305 3 (9)	0.260 7 (7)	0.702 8 (5)	7.17 (17)					
Cl(5)	0.487 7 (13)	0.489 2 (11)	0.744 9 (8)	6.76 (25)					
Cl(7)	0.323 2 (7)	0.394 4 (5)	0.744 0 (4)	6.76 (13)					
Cl(8)	0.463 9 (7)	0.500 5 (5)	0.296 2 (4)	6.48 (13)					
S(11)	0.064 7 (2)	0.072 1 (1)	0.138 60 (9)	0.014 4 (2)	0.006 0 (1)	0.004 15 (6)	−0.001 0 (2)	−0.001 2 (2)	0.001 5 (1)
S(12)	0.229 6 (1)	0.221 4 (1)	0.307 04 (9)	0.012 4 (2)	0.006 9 (1)	0.004 07 (6)	0.001 8 (2)	−0.001 2 (2)	0.001 4 (1)
S(21)	0.057 0 (1)	−0.097 4 (1)	0.314 29 (9)	0.009 7 (2)	0.007 5 (1)	0.004 54 (6)	0.000 8 (2)	0.000 5 (2)	0.002 6 (1)
S(22)	0.358 4 (1)	−0.046 6 (1)	0.394 02 (9)	0.009 3 (2)	0.010 3 (1)	0.006 18 (7)	−0.001 9 (2)	−0.001 3 (2)	0.007 3 (1)
S(31)	0.292 2 (1)	−0.192 3 (1)	0.131 74 (10)	0.010 5 (2)	0.006 8 (1)	0.006 82 (8)	−0.001 3 (2)	0.004 7 (2)	0.000 2 (2)
S(32)	0.484 2 (1)	0.031 2 (1)	0.194 94 (9)	0.012 1 (2)	0.006 6 (1)	0.005 29 (7)	−0.001 5 (2)	0.003 4 (2)	0.001 1 (1)
O(1)	−0.067 8 (4)	0.540 2 (3)	0.135 8 (2)	0.015 5 (5)	0.008 3 (3)	0.006 8 (2)	0.008 9 (7)	0.003 1 (6)	0.006 5 (4)
O(2)	0.146 5 (5)	−0.323 4 (4)	0.600 0 (3)	0.019 7 (7)	0.013 5 (4)	0.008 8 (2)	0.004 4 (9)	0.006 2 (6)	0.013 0 (4)
O(3)	0.763 9 (4)	−0.309 2 (3)	−0.022 9 (2)	0.011 5 (5)	0.010 9 (4)	0.006 9 (2)	0.004 7 (7)	0.006 0 (5)	0.001 8 (5)
N(1)	0.016 9 (4)	0.319 1 (3)	0.202 6 (3)	0.012 3 (6)	0.005 7 (3)	0.004 5 (2)	0.002 1 (7)	−0.000 1 (6)	0.003 5 (4)
N(2)	0.161 6 (5)	−0.141 4 (4)	0.485 1 (3)	0.012 4(6)	0.008 5 (4)	0.004 8 (2)	−0.003 3 (8)	−0.000 0 (6)	0.004 6 (5)
N(3)	0.542 4 (4)	−0.163 3 (4)	0.059 0 (3)	0.009 6 (5)	0.007 3 (4)	0.005 7 (2)	0.000 8 (8)	0.003 0 (6)	0.000 9 (5)
C(11)	0.093 7 (5)	0.217 9 (4)	0.214 6 (3)	0.010 7 (6)	0.005 8 (4)	0.003 6 (2)	0.000 3 (8)	0.002 6 (6)	0.002 6 (5)
C(12)	−0.107 8 (6)	0.314 2 (5)	0.128 3 (4)	0.012 3 (8)	0.009 4 (5)	0.006 2 (3)	0.001 8 (11)	−0.000 6 (8)	0.005 9 (6)
C(13)	−0.087 6 (6)	0.419 5 (5)	0.074 3 (3)	0.012 9 (7)	0.009 1 (5)	0.005 1 (3)	0.005 5 (10)	0.001 3 (7)	0.005 7 (6)
C(14)	0.044 2 (6)	0.444 9 (4)	0.263 7 (3)	0.015 5 (8)	0.006 7 (4)	0.004 9 (3)	0.004 3 (10)	0.002 7 (8)	0.001 7 (6)
C(15)	0.057 8 (6)	0.541 8 (4)	0.202 1 (4)	0.018 8 (9)	0.005 8 (4)	0.006 0 (3)	0.001 6 (11)	0.003 6 (9)	0.003 0 (6)
C(21)	0.188 2 (5)	−0.101 7 (4)	0.408 5 (3)	0.010 9 (7)	0.005 6 (4)	0.004 2 (2)	−0.000 1 (9)	0.000 9 (7)	0.002 7 (5)
C(22)	0.018 2 (6)	−0.197 3 (5)	0.495 6 (3)	0.013 8 (8)	0.010 0 (5)	0.005 0 (3)	−0.000 5 (11)	0.004 3 (8)	0.004 6 (6)
C(23)	0.042 7 (6)	−0.328 2 (5)	0.517 9 (4)	0.017 6 (8)	0.009 0 (5)	0.008 1 (3)	−0.002 0 (12)	0.010 6 (9)	0.003 9 (7)
C(24)	0.273 3 (7)	−0.140 5 (5)	0.568 0 (4)	0.017 1 (9)	0.014 5 (6)	0.005 3 (3)	−0.004 7 (13)	−0.002 5 (9)	0.008 4 (7)
C(25)	0.282 9 (7)	−0.272 4 (6)	0.587 0 (4)	0.014 8 (9)	0.017 7 (7)	0.008 3 (3)	0.003 4 (14)	0.002 3 (10)	0.013 7 (7)
C(31)	0.453 1 (5)	−0.115 2 (4)	0.121 1 (3)	0.009 0 (6)	0.006 6 (4)	0.004 9 (3)	0.001 0 (9)	0.000 9 (7)	0.002 3 (5)
C(32)	0.685 6 (6)	−0.103 4 (5)	0.054 2 (4)	0.011 9 (7)	0.008 6 (5)	0.006 0 (3)	0.000 8 (10)	0.005 4 (7)	0.003 6 (6)
C(33)	0.801 1 (6)	−0.202 9 (5)	0.052 9 (4)	0.010 8 (7)	0.010 7 (5)	0.005 9 (3)	0.001 3 (11)	0.004 0 (8)	0.003 2 (7)
C(34)	0.506 8 (6)	−0.279 6 (5)	−0.014 5 (4)	0.011 5 (7)	0.008 8 (5)	0.005 9 (3)	0.002 4 (10)	0.003 3 (8)	−0.000 5 (7)
C(35)	0.631 2 (6)	−0.368 9 (5)	−0.011 9 (4)	0.013 2 (7)	0.008 3 (5)	0.006 4 (3)	0.001 6 (11)	0.004 4 (8)	0.000 6 (7)
C	0.453 0 (6)	0.344 2 (6)	0.662 9 (4)	0.013 3 (8)	0.015 6 (7)	0.006 6 (3)	0.002 6 (13)	0.003 7 (9)	0.004 7 (8)
H(121)	−0.112 5 (7)	0.229 7 (6)	0.083 8 (4)	5.0					
H(122)	−0.200 4 (7)	0.326 1 (6)	0.157 8 (4)	5.0					
H(131)	−0.176 4 (7)	0.420 3 (5)	0.027 1 (4)	5.0					
H(132)	0.000 4 (7)	0.402 5 (5)	0.039 9 (4)	5.0					
H(141)	−0.039 5 (7)	0.466 4 (5)	0.301 5 (4)	5.0					
H(142)	0.136 6 (7)	0.445 6 (5)	0.307 6 (4)	5.0					
H(151)	0.144 3 (7)	0.521 3 (5)	0.166 6 (4)	5.0					
H(152)	0.072 7 (7)	0.628 4 (5)	0.242 8 (4)	5.0					
H(221)	−0.025 3 (7)	−0.142 0 (6)	0.548 2 (4)	5.0					
H(222)	−0.049 0 (7)	−0.205 0 (6)	0.435 1 (4)	5.0					
H(231)	0.080 0 (7)	−0.384 3 (6)	0.463 0 (5)	5.0					
H(232)	−0.052 1 (7)	−0.364 5 (6)	0.529 5 (5)	5.0					
H(241)	0.370 2 (8)	−0.112 0 (6)	0.554 3 (4)	5.0					
H(242)	0.244 0 (8)	−0.081 4 (6)	0.624 7 (4)	5.0					
H(251)	0.351 9 (8)	−0.269 1 (7)	0.646 9 (5)	5.0					
H(252)	0.321 3 (8)	−0.328 3 (7)	0.533 3 (5)	5.0					
H(321)	0.681 6 (7)	−0.067 4 (6)	−0.004 3 (4)	5.0					
H(322)	0.711 0 (7)	−0.033 2 (6)	0.111 3 (4)	5.0					
H(331)	0.809 8 (7)	−0.233 8 (6)	0.114 4 (4)	5.0					
H(332)	0.897 2 (7)	−0.164 4 (6)	0.045 8 (4)	5.0					
H(341)	0.415 7 (7)	−0.322 4 (6)	−0.002 1 (4)	5.0					
H(342)	0.489 3 (7)	−0.256 2 (6)	−0.078 2 (4)	5.0					
H(351)	0.609 2 (7)	−0.444 9 (6)	−0.064 6 (4)	5.0					
H(352)	0.643 1 (7)	−0.396 9 (6)	0.050 2 (4)	5.0					

Cl position	Occupancy	Probable chloroform positions[b]	Est occupancy
Cl(1)	0.61	(a) Cl(1) Cl(2) Cl(4)	0.23
Cl(2)	0.49	(b) Cl(1) Cl(2) Cl(7)	0.21
Cl(3)	0.39	(c) Cl(3) Cl(4) Cl(8)	0.23
Cl(4)	0.53	(d) Cl(1) Cl(5) Cl(6)	0.15
Cl(5)	0.24	(e) Cl(2) Cl(3) Cl(7)	0.07
Cl(6)	0.15	(f) Cl(1) Cl(4) Cl(8)	0.03
Cl(7)	0.30	(g) Cl(2) Cl(3) Cl(4)	0.01
Cl(8)	0.29		

[a] The form of the anisotropic thermal parameter is: $\exp[-(B_{1,1}hh + B_{2,2}kk + B_{3,3}ll + B_{1,2}hk + B_{1,3}hl + B_{2,3}kl)]$. [b] Not exhaustive, see text.

alized in terms of seven $CHCl_3$ positions, (a–g) in Table Ia, ranging in occupancy from 0.23 to 0.01. There are other Cl positions but these are of low intensity and negligible significance (vide infra). After convergence, the hydrogen atoms were inserted at their new calculated positions.

The models converged with $R = 4.0$, $R_w = 4.7\%$; $R = 4.0$, $R_w = 4.3\%$; and $R = 3.9$, $R_w = 4.9\%$ for FeM·$CHCl_3$, MnM·$CHCl_3$, and FeM·tol, respectively. The error in an observation of unit weight is 1.95, 1.25, and 2.19 for FeM·$CHCl_3$, MnM·$CHCl_3$, and FeM·tol, respectively. A structure factor calculation with all observed and

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations: $Mn(S_2CNC_4H_8O)_3 \cdot CHCl_3$

Atom	X	Y	Z	$B_{1,1}$[a] or B (Å^2)	$B_{2,2}$	$B_{3,3}$	$B_{1,2}$	$B_{1,3}$	$B_{2,3}$
Mn	0.254 64 (6)	0.484 39 (7)	0.236 45 (7)	0.005 00 (5)	0.009 18 (7)	0.008 25 (6)	0.005 71 (9)	0.006 80 (9)	0.008 6 (1)
Cl(1)	0.365 3 (2)	0.510 3 (2)	0.615 9 (2)	0.016 2 (2)	0.020 6 (2)	0.012 8 (2)	0.009 7 (4)	0.005 2 (3)	0.014 2 (3)
Cl(2)	0.585 1 (1)	0.343 6 (2)	0.096 3 (2)	0.018 2 (1)	0.035 6 (2)	0.015 5 (2)	0.035 7 (3)	0.018 5 (3)	0.030 1 (3)
Cl(3)	0.558 9 (2)	0.168 4 (2)	0.220 9 (2)	0.024 6 (2)	0.022 8 (2)	0.030 3 (2)	0.027 0 (3)	0.033 2 (4)	0.034 1 (3)
S(11)	0.141 3 (1)	0.232 4 (1)	0.019 7 (1)	0.006 37 (9)	0.010 4 (1)	0.010 4 (1)	0.007 5 (2)	0.006 5 (2)	0.011 5 (2)
S(12)	0.278 9 (1)	0.277 9 (1)	0.270 5 (1)	0.007 93 (10)	0.012 8 (1)	0.008 4 (1)	0.009 9 (2)	0.006 2 (2)	0.008 5 (2)
S(21)	0.385 1 (1)	0.525 1 (1)	0.135 0 (1)	0.005 70 (9)	0.011 7 (2)	0.007 6 (1)	0.003 4 (2)	0.006 9 (2)	0.006 5 (2)
S(22)	0.422 0 (1)	0.704 8 (2)	0.421 1 (1)	0.006 71 (9)	0.013 7 (2)	0.008 5 (1)	0.005 2 (2)	0.008 7 (2)	0.008 0 (2)
S(31)	0.141 2 (1)	0.601 3 (1)	0.168 8 (1)	0.007 85 (9)	0.013 2 (1)	0.009 8 (1)	0.011 2 (2)	0.010 7 (2)	0.014 9 (2)
S(32)	0.137 1 (1)	0.508 8 (1)	0.364 2 (1)	0.006 06 (8)	0.012 1 (1)	0.010 2 (1)	0.009 8 (2)	0.009 1 (1)	0.015 4 (2)
O(1)	0.180 1 (3)	−0.268 0 (3)	−0.118 2 (4)	0.011 3 (3)	0.010 2 (4)	0.015 9 (4)	0.010 8)5)	0.011 0 (6)	0.011 4 (6)
O(2)	0.756 9 (3)	0.995 4 (4)	0.341 8 (4)	0.008 3 (3)	0.011 1 (4)	0.018 7 (4)	0.003 0 (6)	0.012 0 (6)	0.012 8 (7)
O(3)	−0.109 2 (3)	0.798 4 (3)	0.417 1 (3)	0.008 7 (2)	0.014 1 (3)	0.012 1 (3)	0.015 6 (4)	0.011 0 (5)	0.015 1 (5)
N(1)	0.166 2 (3)	0.008 0 (4)	0.034 1 (4)	0.008 6 (3)	0.010 8 (4)	0.009 9 (4)	0.010 1 (6)	0.008 5 (6)	0.011 9 (6)
N(2)	0.580 9 (3)	0.760 7 (4)	0.320 1 (4)	0.004 8 (3)	0.010 7 (5)	0.008 2 (4)	0.003 0 (6)	0.005 6 (5)	0.005 7 (7)
N(3)	0.001 1 (3)	0.620 5 (4)	0.303 1 (3)	0.005 8 (3)	0.009 5 (4)	0.008 1 (3)	0.008 7 (5)	0.006 4 (5)	0.010 4 (5)
C(11)	0.192 6 (4)	0.155 4 (5)	0.100 5 (4)	0.005 7 (3)	0.009 8 (5)	0.009 4 (4)	0.007 5 (6)	0.008 6 (6)	0.009 8 (7)
C(12)	0.100 0 (4)	−0.097 9 (5)	−0.114 2 (5)	0.006 8 (4)	0.009 3 (5)	0.010 4 (5)	0.003 9 (8)	0.005 7 (7)	0.008 1 (8)
C(13)	0.158 0 (5)	−0.190 6 (5)	−0.180 5 (5)	0.009 2 (4)	0.010 6 (6)	0.010 9 (5)	0.006 5 (9)	0.007 8 (8)	0.007 9 (9)
C(14)	0.196 6 (5)	−0.067 5 (5)	0.100 5 (5)	0.012 0 (5)	0.014 3 (6)	0.013 5 (5)	0.014 1 (8)	0.012 5 (8)	0.018 7 (8)
C(15)	0.249 2 (5)	−0.163 5 (5)	0.021 9 (5)	0.010 3 (4)	0.015 0 (6)	0.016 0 (6)	0.014 8 (8)	0.011 8 (8)	0.020 1 (8)
C(21)	0.477 9 (4)	0.677 5 (5)	0.296 3 (4)	0.006 2 (3)	0.010 0 (5)	0.007 9 (4)	0.007 0 (7)	0.006 8 (6)	0.009 8 (7)
C(22)	0.660 6 (5)	0.890 6 (6)	0.456 0 (5)	0.006 7 (4)	0.015 1 (8)	0.009 9 (6)	0.002 3 (10)	0.005 3 (8)	0.005 9 (10)
C(23)	0.707 8 (5)	1.025 2 (6)	0.443 3 (6)	0.008 4 (5)	0.010 9 (7)	0.015 8 (8)	0.003 1 (10)	0.006 4 (10)	0.002 4 (12)
C(24)	0.627 9 (4)	0.730 5 (5)	0.211 5 (5)	0.006 2 (4)	0.010 5 (6)	0.011 3 (5)	0.004 5 (7)	0.009 6 (6)	0.010 1 (8)
C(25)	0.675 9 (5)	0.872 3 (6)	0.211 9 (5)	0.007 9 (4)	0.012 9 (7)	0.015 3 (6)	0.005 8 (9)	0.012 2 (8)	0.013 5 (9)
C(31)	0.082 0 (4)	0.581 7 (4)	0.280 4 (4)	0.005 1 (3)	0.006 6 (4)	0.006 7 (4)	0.004 2 (6)	0.004 5 (6)	0.005 2 (6)
C(32)	−0.050 4 (4)	0.605 5 (5)	0.399 7 (4)	0.007 2 (3)	0.011 2 (5)	0.011 1 (4)	0.009 9 (7)	0.011 7 (6)	0.014 8 (7)
C(33)	−0.052 9 (4)	0.753 6 (5)	0.493 1 (4)	0.007 8 (4)	0.013 9 (5)	0.009 4 (4)	0.011 5 (7)	0.009 2 (7)	0.013 4 (7)
C(34)	−0.054 1 (4)	0.672 4 (5)	0.227 2 (4)	0.006 7 (3)	0.014 1 (5)	0.008 9 (4)	0.012 1 (7)	0.006 4 (7)	0.013 5 (7)
C(35)	−0.055 1 (4)	0.818 0 (5)	0.329 0 (5)	0.008 4 (4)	0.014 7 (5)	0.013 3 (5)	0.013 5 (7)	0.009 0 (7)	0.018 2 (7)
C	0.545 6 (5)	0.323 7 (6)	0.225 7 (5)	0.011 3 (5)	0.018 4 (7)	0.012 9 (6)	0.015 4 (9)	0.012 2 (8)	0.016 4 (9)
H(121)	0.025 1 (4)	−0.166 4 (5)	−0.127 7 (5)	5.0					
H(122)	0.091 6 (4)	−0.039 3 (5)	−0.157 0 (5)	5.0					
H(131)	0.229 9 (5)	−0.121 7 (5)	−0.173 3 (5)	5.0					
H(132)	0.110 1 (5)	−0.266 9 (5)	−0.279 7 (5)	5.0					
H(141)	0.250 4 (5)	(0.010 9 (5)	0.196 8 (5)	5.0					
H(142)	0.128 5 (5)	−0.133 6 (5)	0.102 4 (5)	5.0					
H(151)	0.263 3 (5)	−0.220 7 (5)	0.063 9 (5)	5.0					
H(152)	0.321 1 (5)	−0.095 7 (5)	0.028 3 (5)	5.0					
H(221)	0.622 4 (5)	0.913 4 (6)	0.523 5 (5)	5.0					
H(222)	0.721 6 (5)	0.867 4 (6)	0.487 7 (5)	5.0					
H(231)	0.765 6 (5)	1.113 2 (6)	0.534 2 (6)	5.0					
H(232)	0.646 7 (5)	1.051 2 (6)	0.417 8 (6)	5.0					
H(241)	0.687 4 (4)	0.698 9 (5)	0.229 6 (5)	5.0					
H(242)	0.568 2 (4)	0.647 8 (5)	0.120 0 (5)	5.0					
H(251)	0.614 9 (5)	0.899 2 (6)	0.188 2 (5)	5.0					
H(252)	0.711 2 (5)	0.853 6 (6)	0.141 3 (5)	5.0					
H(321)	−0.127 7 (4)	0.522 7 (5)	0.347 0 (4)	5.0					
H(322)	−0.006 0 (4)	0.580 8 (5)	0.455 9 (4)	5.0					
H(331)	0.025 0 (4)	0.834 1 (5)	0.549 9 (4)	5.0					
H(332)	−0.091 8 (4)	0.741 6 (5)	0.554 9 (4)	5.0					
H(341)	−0.012 6 (4)	0.690 3 (5)	0.169 5 (4)	5.0					
H(342)	−0.131 9 (4)	0.593 5 (5)	0.166 6 (4)	5.0					
H(351)	−0.095 2 (4)	0.851 1 (5)	0.277 7 (5)	5.0					
H(352)	0.023 0 (4)	0.897 6 (5)	0.386 0 (5)	5.0					

[a] The form of the anisotropic thermal parameter is: $\exp[-(B_{1,1}hh + B_{2,2}kk + B_{3,3}ll + B_{1,2}hk + B_{1,3}hl + B_{2,3}kl)]$.

unobserved reflections included (no refinement) gave R 5.3, 6.0, and 4.6 for FeM·CHCl$_3$, MnM·CHCl$_3$, and FeM·tol; on this basis, it was decided that measurement of reflections rejected automatically during data collection would not significantly improve the results. A final Fourier difference map was featureless, except for rather weak chloroform H atom peaks, along the chloroform carbon to sulfur axis, in both MnM·CHCl$_3$ and FeM·CHCl$_3$ (atom S(12) in MnM·CHCl$_3$ and atom S(22) in FeM·CHCl$_3$). The chloroform H atoms were not included in the refinement. A table of the observed structure factors is available.[25]

Results and Discussion

Final positional and thermal parameters for the complexes FeM·CHCl$_3$, MnM·CHCl$_3$, and FeM·tol are given in Tables I–III. Tables IV and V contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted, and were derived from the inverse matrix in the course of least-squares refinement calculations. Figures 1 and 2 are stereoscopic pair views of FeM·CHCl$_3$ and MnM·CHCl$_3$. Only the main posi-

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations: $Fe(S_2CNC_4H_8O)_3 \cdot H_2O$ (FeM·tol)

Atom	X	Y	Z	$B_{1,1}$[a] or B (Å^2)	$B_{2,2}$	$B_{3,3}$	$B_{1,2}$	$B_{1,3}$	$B_{2,3}$
Fe	0.178 60 (6)	0.183 72 (6)	0.837 03 (5)	0.010 92 (7)	0.006 82 (5)	0.005 14 (3)	0.006 73 (9)	0.001 74 (8)	0.001 54 (7)
S(11)	0.010 5 (1)	−0.005 1 (1)	0.707 37 (9)	0.012 6 (1)	0.009 4 (1)	0.005 70 (7)	0.004 0 (2)	0.002 9 (2)	0.000 9 (2)
S(12)	0.326 4 (1)	0.130 9 (1)	0.703 52 (9)	0.011 8 (1)	0.009 7 (1)	0.007 08 (8)	0.007 0 (2)	0.004 0 (2)	−0.000 2 (2)
S(21)	0.195 6 (1)	0.030 3 (1)	0.948 95 (9)	0.011 0 (1)	0.007 8 (1)	0.007 31 (7)	0.001 8 (2)	−0.000 9 (2)	0.004 9 (1)
S(22)	0.401 1 (1)	0.300 7 (1)	0.963 90 (9)	0.013 1 (1)	0.007 1 (1)	0.005 97 (7)	0.002 8 (2)	0.001 9 (2)	0.003 2 (1)
S(31)	−0.035 7 (1)	0.244 3 (1)	0.901 30 (8)	0.012 7 (1)	0.007 5 (1)	0.006 29 (7)	0.006 5 (2)	0.005 0 (2)	0.004 1 (1)
S(32)	0.169 7 (1)	0.393 6 (1)	0.784 90 (9)	0.011 6 (1)	0.008 7 (1)	0.006 92 (7)	0.007 5 (2)	0.005 5 (2)	0.005 1 (1)
O(1)	0.178 1 (5)	−0.304 2 (4)	0.420 4 (3)	0.031 1 (7)	0.019 0 (5)	0.010 1 (3)	0.025 4 (9)	−0.001 2 (8)	−0.010 5 (6)
O(2)	0.531 3 (4)	0.160 6 (4)	1.292 6 (2)	0.022 2 (6)	0.017 5 (4)	0.005 9 (2)	0.014 0 (8)	0.000 3 (6)	0.004 3 (5)
O(3)	−0.278 9 (4)	0.590 6 (3)	0.776 1 (3)	0.016 4 (4)	0.017 5 (4)	0.011 1 (2)	0.019 7 (6)	0.008 9 (6)	0.013 9 (5)
N(1)	0.155 6 (4)	−0.077 1 (4)	0.557 1 (3)	0.017 2 (5)	0.009 5 (4)	0.005 9 (2)	0.009 2 (7)	0.004 3 (6)	−0.000 4 (5)
N(2)	0.445 6 (4)	0.137 1 (3)	1.086 0 (3)	0.011 5 (5)	0.009 1 (4)	0.005 9 (2)	0.001 7 (7)	0.000 2 (6)	0.004 7 (5)
N(3)	−0.064 5 (4)	0.470 5 (3)	0.846 7 (3)	0.011 4 (4)	0.007 8 (3)	0.007 0 (2)	0.008 5 (6)	0.005 2 (5)	0.004 0 (5)
C(11)	0.165 3 (5)	0.004 6 (4)	0.644 8 (3)	0.013 9 (5)	0.007 5 (4)	0.005 6 (3)	0.009 6 (7)	0.003 9 (6)	0.003 0 (5)
C(12)	0.019 0 (6)	−0.187 0 (5)	0.507 3 (4)	0.020 1 (8)	0.010 5 (5)	0.005 7 (3)	0.008 5 (10)	0.000 3 (8)	0.000 4 (6)
C(13)	0.061 2 (8)	−0.318 9 (5)	0.481 6 (5)	0.033 4 (12)	0.010 9 (6)	0.008 7 (4)	0.011 5 (13)	−0.006 9 (12)	−0.000 3 (8)
C(14)	0.282 1 (6)	−0.065 7 (6)	0.498 6 (4)	0.019 7 (7)	0.018 4 (7)	0.007 4 (3)	0.015 5 (11)	0.008 2 (8)	−0.003 2 (8)
C(15)	0.307 4 (7)	−0.201 5 (7)	0.471 0 (5)	0.026 5 (9)	0.025 7 (8)	0.008 5 (4)	0.031 0 (12)	0.001 6 (10)	−0.005 5 (10)
C(21)	0.359 7 (4)	0.154 9 (4)	1.010 6 (3)	0.010 0 (5)	0.007 8 (4)	0.005 4 (2)	0.005 1 (7)	0.004 7 (6)	0.002 5 (5)
C(22)	0.585 1 (5)	0.241 4 (5)	1.141 1 (4)	0.012 4 (6)	0.011 1 (5)	0.006 5 (3)	0.002 1 (9)	−0.001 5 (8)	0.003 1 (6)
C(23)	0.567 8 (6)	0.278 0 (5)	1.248 6 (4)	0.018 1 (7)	0.013 7 (6)	0.007 9 (4)	0.013 0 (10)	−0.000 8 (9)	0.001 7 (8)
C(24)	0.408 5 (5)	0.016 4 (5)	1.130 5 (4)	0.012 6 (6)	0.011 4 (5)	0.007 1 (3)	0.005 7 (9)	0.001 5 (7)	0.007 5 (6)
C(25)	0.396 8 (6)	0.062 7 (5)	1.239 5 (4)	0.019 3 (7)	0.017 4 (6)	0.009 3 (3)	0.015 4 (11)	0.009 6 (9)	0.012 6 (7)
C(31)	0.012 0 (4)	0.381 2 (4)	0.844 1 (3)	0.009 5 (5)	0.007 1 (4)	0.005 1 (2)	0.003 8 (7)	0.001 3 (6)	0.000 9 (5)
C(32)	−0.209 4 (5)	0.453 9 (4)	0.887 4 (3)	0.013 8 (5)	0.010 8 (5)	0.007 0 (3)	0.011 2 (8)	0.008 2 (7)	0.004 5 (6)
C(33)	−0.326 4 (5)	0.465 1 (5)	0.807 5 (4)	0.012 4 (5)	0.013 3 (5)	0.008 3 (3)	0.011 0 (8)	0.005 4 (7)	0.004 7 (7)
C(34)	−0.016 2 (5)	0.594 9 (4)	0.808 0 (4)	0.014 8 (6)	0.008 4 (4)	0.008 8 (3)	0.010 2 (8)	0.006 3 (8)	0.006 0 (6)
C(35)	−0.142 5 (6)	0.605 5 (5)	0.737 6 (4)	0.023 7 (9)	0.012 8 (5)	0.010 9 (4)	0.014 4 (11)	0.007 9 (10)	0.010 7 (7)
H(121)	−0.059 0 (6)	−0.197 6 (5)	0.553 4 (4)	5.0					
H(122)	−0.022 3 (6)	−0.165 3 (5)	0.444 1 (4)	5.0					
H(131)	−0.030 2 (8)	−0.394 0 (5)	0.444 5 (5)	5.0					
H(132)	0.097 2 (8)	−0.342 3 (5)	0.545 5 (5)	5.0					
H(141)	0.257 1 (6)	−0.034 4 (6)	0.435 9 (4)	5.0					
H(142)	0.375 9 (6)	0.001 7 (6)	0.540 0 (4)	5.0					
H(151)	0.342 4 (7)	−0.227 0 (7)	0.534 1 (5)	5.0					
H(152)	0.387 8 (7)	−0.194 0 (7)	0.426 6 (5)	5.0					
H(221)	0.672 9 5)	0.204 4 (5)	1.135 7 (4)	5.0					
H(222)	0.603 1 (5)	0.324 3 (5)	1.111 5 (4)	5.0					
H(231)	0.484 8 (6)	0.321 3 (5)	1.253 6 (4)	5.0					
H(232)	0.665 0 (6)	0.344 2 (5)	1.286 6 (4)	5.0					
H(241)	0.309 7 (5)	−0.049 4 (5)	1.094 6 (4)	5.0					
H(242)	0.490 0 (5)	−0.028 6 (5)	1.125 0 (4)	5.0					
H(251)	0.375 3 (6)	−0.018 1 (5)	1.271 5 (4)	5.0					
H(252)	0.311 8 (6)	0.103 5 (5)	1.243 6 (4)	5.0					
H(321)	−0.243 5 (5)	0.362 5 (4)	0.905 0 (3)	5.0					
H(322)	−0.195 4 (5)	0.526 9 (4)	0.949 1 (3)	5.0					
H(331)	−0.423 3 (5)	0.458 5 (5)	0.835 4 (4)	5.0					
H(332)	−0.343 6 (5)	0.388 4 (5)	0.747 9 (4)	5.0					
H(341)	0.014 9 (5)	0.675 9 (4)	0.865 7 (4)	5.0					
H(342)	0.071 7 (5)	0.592 8 (4)	0.771 5 (4)	5.0					
H(351)	−0.160 6 (6)	0.532 8 (5)	0.675 1 (4)	5.0					
H(352)	−0.110 7 (6)	0.697 1 (5)	0.720 1 (4)	5.0					

Disordered H_2O positions

Atom	Multiplicity	X	Y	Z	B (Å^2)
O(41)	0.26	0.427 (2)	0.437 (2)	0.499 (1)	9.3 (5)
O(42)	0.18	0.534 (3)	0.503 (4)	0.497 (3)	9.0 (6)
O(43)	0.16	0.457 (3)	0.431 (3)	0.538 (2)	9.7 (8)
O(44)	0.15	0.369 (3)	0.329 (3)	0.459 (2)	9.0 (8)
O(45)	0.13	0.694 (4)	0.530 (3)	0.500 (3)	9.3 (9)
O(46)	0.12	0.368 (4)	0.422 (4)	0.547 (3)	9.5 (10)

[a] The form of the anisotropic thermal parameter is: $\exp[-(B_{1,1}hh + B_{2,2}kk + B_{3,3}ll + B_{1,2}hk + B_{1,3}hl + B_{2,3}kl)]$.

tion (arbitrarily taken as (a) in Table I) of the disordered chloroform molecule in $FeM \cdot CHCl_3$ is shown. The single molecule view of FeM·tol does not show well the small but significant differences in geometry, and no such diagram is included for that reason. Figures 3-5 show the molecular packing in the unit cells of $FeM \cdot CHCl_3$, $MnM \cdot CHCl_3$, and FeM·tol, respectively. The closest intermolecular contacts are given in Table VI, and from these and Figures 3-5 it is evident that the complex molecules are sufficiently well separated to be considered magnetically dilute in the normal[9,19] sense. The solvent-complex contacts are all quite weak, the strongest being in the chloroform solvates, especially $FeM \cdot CHCl_3$, between the morpholyl O atoms and the chloroform Cl atoms.

As a possible model for solution interactions in chloroform, these observations are relatively unhelpful, since such interactions cannot occur in the general case, where no ligand oxygens exist and yet strong solvent interactions are apparently responsible for NMR line splittings.[12,26] Similarly, the positionally disordered water molecule in FeM·tol approaches the ligand O atoms, but neither of the close approaches (O(44)-O(2) and O(45)-O(1) at 3.379 (9) and 3.215 (15) Å) appears close enough for significant hydrogen bonding interactions between solvent and ligand. In the toluene and chlorobenzene products, the absence of these solvents indicates that this particular molecular shape precludes inclusion into the lattice. This contrasts with the observation of inclusion of such

Table IV. Bond Lengths for FeM·CHCl$_3$, MnM·CHCl$_3$, and FeM·tol (Å)

	FeM·CHCl$_3$	MnM·CHCl$_3$	FeM·tol
M-S(11)	2.407 (1)	2.483 (1)	2.446 (1)
M-S(12)	2.409 (1)	2.584 (1)	2.458 (1)
M-S(21)	2.426 (1)	2.344 (1)	2.429 (1)
M-S(22)	2.399 (1)	2.433 (1)	2.435 (1)
M-S(31)	2.424 (1)	2.527 (1)	2.443 (1)
M-S(32)	2.429 (1)	2.365 (1)	2.444 (1)
S(11)-C(11)	1.723 (3)	1.722 (5)	1.729 (3)
S(12)-C(11)	1.713 (4)	1.719 (5)	1.710 (3)
S(21)-C(21)	1.718 (4)	1.729 (4)	1.729 (3)
S(22)-C(21)	1.720 (4)	1.712 (4)	1.716 (3)
S(31)-C(31)	1.728 (4)	1.709 (4)	1.721 (3)
S(32)-C(31)	1.715 (4)	1.733 (4)	1.724 (3)
O(1)-C(13)	1.415 (5)	1.413 (6)	1.422 (6)
O(1)-C(15)	1.409 (5)	1.413 (6)	1.390 (5)
O(2)-C(23)	1.425 (5)	1.422 (6)	1.432 (4)
O(2)-C(25)	1.413 (5)	1.416 (6)	1.409 (5)
O(3)-C(33)	1.425 (5)	1.422 (5)	1.419 (4)
O(3)-C(35)	1.414 (5)	1.422 (5)	1.397 (5)
N(1)-C(11)	1.330 (4)	1.329 (5)	1.320 (4)
N(1)-C(12)	1.468 (5)	1.474 (6)	1.462 (4)
N(1)-C(14)	1.460 (4)	1.470 (6)	1.471 (4)
N(2)-C(21)	1.314 (4)	1.315 (5)	1.315 (4)
N(2)-C(22)	1.482 (5)	1.466 (6)	1.473 (4)
N(2)-C(24)	1.484 (5)	1.472 (6)	1.466 (4)
N(3)-C(31)	1.326 (4)	1.323 (5)	1.320 (3)
N(3)-C(32)	1.476 (5)	1.474 (5)	1.482 (4)
N(3)-C(34)	1.476 (5)	1.476 (5)	1.461 (4)
C(12)-C(13)	1.518 (5)	1.499 (6)	1.528 (5)
C(14)-C(15)	1.511 (5)	1.509 (7)	1.492 (6)
C(22)-C(23)	1.514 (6)	1.511 (7)	1.484 (5)
C(24)-C(25)	1.494 (6)	1.495 (6)	1.504 (5)
C(32)-C(33)	1.513 (5)	1.510 (6)	1.510 (5)
C(34)-C(35)	1.503 (5)	1.508 (6)	1.487 (5)
C-Cl(1)	1.734 (9)	1.746 (5)	
C-Cl(2)	1.751 (8)	1.775 (5)	
C-Cl(3)	1.77 (1)	1.750 (6)	
C-Cl(4)	1.748 (6)		
C-Cl(5)	1.83 (1)		
C-Cl(6)	1.76 (1)		
C-Cl(7)	1.793 (8)		
C-Cl(8)	1.78 (1)		

Table V. Bond Angles for FeM·CHCl$_3$, MnM·CHCl$_3$, and FeM·tol (Å)

	FeM·CHCl$_3$	MnM·CHCl$_3$	FeM·tol
S(11)-M-S(12)	73.66 (3)	70.72 (4)	72.32 (3)
S(11)-M-S(21)	89.98 (4)	87.72 (4)	91.09 (3)
S(11)-M-S(22)	156.74 (4)	157.32 (5)	156.05 (3)
S(11)-M-S(31)	94.05 (4)	92.48 (5)	91.94 (3)
S(11)-M-S(32)	107.42 (4)	103.92 (5)	106.60 (3)
S(12)-M-S(21)	102.76 (4)	100.40 (5)	105.38 (3)
S(12)-M-S(22)	94.12 (4)	99.57 (5)	94.22 (3)
S(12)-M-S(31)	156.84 (4)	153.72 (5)	153.88 (3)
S(12)-M-S(32)	91.59 (4)	91.36 (4)	91.51 (3)
S(21)-M-S(22)	73.17 (4)	73.63 (4)	73.08 (3)
S(21)-M-S(31)	96.66 (4)	98.89 (5)	95.40 (3)
S(21)-M-S(32)	160.11 (4)	165.72 (5)	158.71 (3)
S(22)-M-S(31)	103.57 (4)	102.88 (5)	107.06 (3)
S(22)-M-S(32)	92.35 (4)	96.59 (4)	93.16 (3)
S(31)-M-S(32)	73.09 (3)	72.73 (4)	72.73 (3)
M-S(11)-C(11)	85.9 (1)	87.7 (1)	86.5 (1)
M-S(12)-C(11)	86.0 (1)	84.6 (2)	86.5 (1)
M-S(21)-C(21)	86.2 (1)	88.1 (1)	86.1 (1)
M-S(22)-C(21)	87.0 (1)	85.6 (2)	86.2 (1)
M-S(31)-C(31)	86.3 (1)	83.8 (2)	86.4 (1)
M-S(32)-C(31)	86.4 (1)	88.4 (1)	86.3 (1)
C(13)-O(1)-C(15)	109.9 (3)	110.4 (4)	110.2 (3)
C(23)-O(2)-C(25)	110.7 (3)	109.7 (4)	110.9 (3)
C(33)-O(3)-C(35)	110.1 (3)	110.3 (3)	111.1 (3)
C(11)-N(1)-C(12)	123.2 (3)	123.2 (4)	124.1 (3)
C(11)-N(1)-C(14)	123.6 (3)	124.0 (4)	123.1 (3)
C(12)-N(1)-C(14)	113.2 (3)	112.9 (4)	112.9 (3)
C(21)-N(2)-C(22)	123.3 (3)	124.1 (4)	123.6 (3)
C(21)-N(2)-C(24)	123.7 (3)	122.8 (4)	124.3 (3)
C(22)-N(2)-C(24)	112.9 (3)	113.1 (4)	111.9 (3)
C(31)-N(3)-C(32)	123.4 (3)	123.8 (4)	123.5 (2)
C(31)-N(3)-C(34)	123.6 (3)	124.0 (4)	123.4 (2)
C(32)-N(3)-C(34)	113.0 (3)	112.1 (3)	113.1 (2)
S(11)-C(11)-S(12)	114.4 (2)	116.9 (4)	114.6 (2)
S(11)-C(11)-N(1)	122.8 (3)	121.3 (4)	121.6 (3)
S(12)-C(11)-N(1)	122.9 (3)	121.8 (4)	123.8 (2)
N(1)-C(12)-C(13)	109.2 (3)	109.2 (4)	108.4 (3)
C(12)-C(13)-O(1)	111.5 (3)	112.6 (4)	110.9 (4)
C(15)-C(14)-N(1)	108.6 (3)	110.2 (4)	109.4 (4)
O(1)-C(15)-C(14)	111.9 (3)	111.6 (4)	113.3 (4)
S(21)-C(21)-S(22)	113.6 (2)	112.6 (3)	114.5 (2)
S(21)-C(21)-N(2)	123.6 (3)	123.3 (3)	122.1 (2)
S(22)-C(21)-N(2)	122.8 (3)	124.1 (3)	123.4 (2)
N(2)-C(22)-C(23)	108.3 (3)	108.0 (4)	109.2 (3)
C(22)-C(23)-O(2)	111.8 (4)	112.2 (4)	111.7 (3)
N(2)-C(24)-C(25)	108.8 (4)	108.7 (4)	107.9 (3)
O(2)-C(25)-C(24)	112.8 (4)	111.9 (4)	112.1 (3)
S(31)-C(31)-S(32)	114.1 (2)	115.0 (2)	114.5 (2)
S(31)-C(31)-N(3)	122.8 (3)	123.0 (3)	122.8 (2)
S(32)-C(31)-N(3)	123.0 (3)	122.0 (3)	122.7 (2)
N(3)-C(32)-C(33)	109.0 (3)	108.9 (3)	108.3 (3)
C(32)-C(33)-O(3)	111.5 (3)	111.7 (4)	111.7 (3)
N(3)-C(34)-C(35)	109.7 (3)	108.9 (4)	110.3 (3)
C(34)-C(35)-O(3)	111.2 (3)	111.2 (4)	114.4 (3)
Cl(1)-C-Cl(2)	98.5	107.4	
Cl(1)-C-Cl(3)		109.7	
Cl(2)-C-Cl(3)	108.1	109.7	
Cl(1)-C-Cl(4)	108.5		
Cl(1)-C-Cl(5)	100.0		
Cl(1)-C-Cl(6)	121.9		
Cl(1)-C-Cl(7)	112.3		
Cl(1)-C-Cl(8)	105.6		
Cl(2)-C-Cl(4)	120.6		
Cl(2)-C-Cl(7)	102.3		
Cl(3)-C-Cl(4)	105.9		
Cl(3)-C-Cl(7)	113.1		
Cl(3)-C-Cl(8)	115.9		
Cl(4)-C-Cl(8)	104.3		
Cl(5)-C-Cl(6)	106.2		

solvates as CH_2Cl_2,[11,26] $CHCl_3$, C_6H_6,[10] and $(CH_3)_2CO$.[11] Clearly vacant space in the FeM·tol lattice puts strong pressure on the available small molecules to fill it. The water included in this lattice is presumably derived from the 95% ethanol used in all recrystallizations. Due to its positional disorder and weak interaction with the complex molecules, it may be considered as essentially clathrated in the lattice. From this viewpoint, FeM·tol/FeM·ClBz is the best available approximation to an unsolvated crystalline form of FeM.

A more significant complex-solvate interaction is the rather weak hydrogen-bonding indicated by the solvent carbon to ligand sulfur distance of 3.65 and 3.67 Å in FeM·CHCl$_3$ and MnM·CHCl$_3$. This places the calculated chloroform H atom at 2.73 Å from S(12) in MnM·CHCl$_3$ and a group of (disordered) hydrogens near S(22) in FeM·CHCl$_3$, the nearest being at 2.71 Å. This is analogous to the weak hydrogen-bonding interactions in FeM·CH$_2$Cl$_2$ and its analogues with Co,[11] Cr, Mn, Rh,[27] of the dichloromethane H atoms with a ligand sulfur atom. The weakly hydrogen-bonded chloroform molecules in FeM·CHCl$_3$ and MnM·CHCl$_3$ have Cl-S contacts which exceed the sum of the van der Waal's radii[28,29] but are close enough to permit some electrostatic interaction. These static interactions in the solid state must represent one of the modes of (presumably dynamic) interactions in chloroform solution, and on a short time scale, a similar but stronger complex to

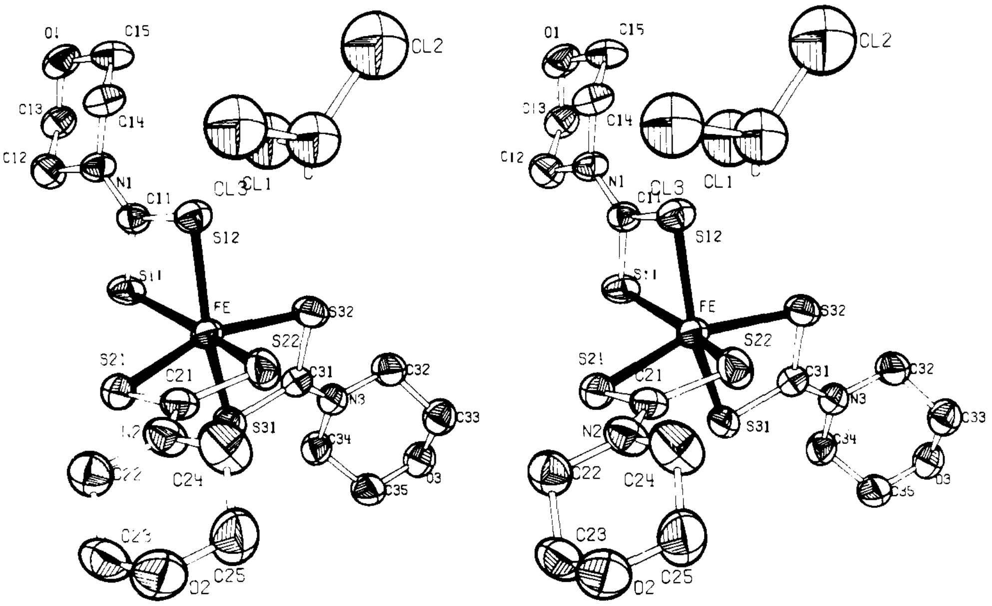

Figure 1. Stereoscopic pair view of FeM•CHCl$_3$. Disorder not shown to minimize crowding.

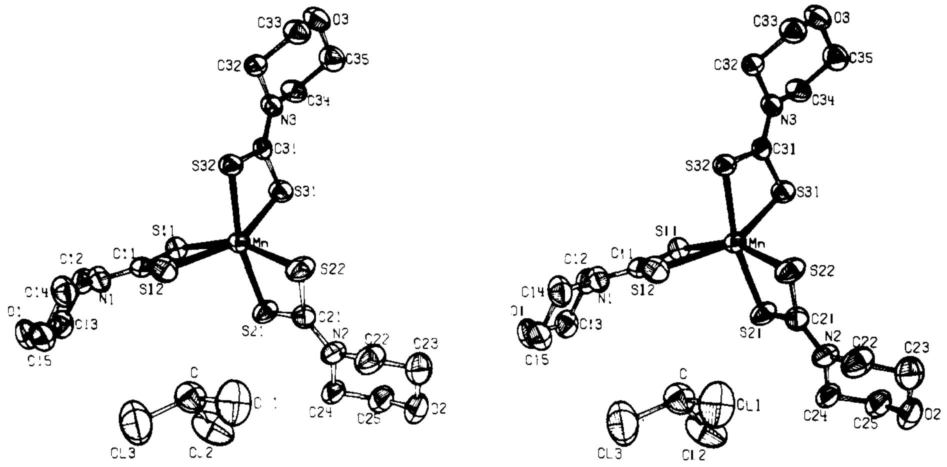

Figure 2. Stereoscopic pair view of MnM•CHCl$_3$.

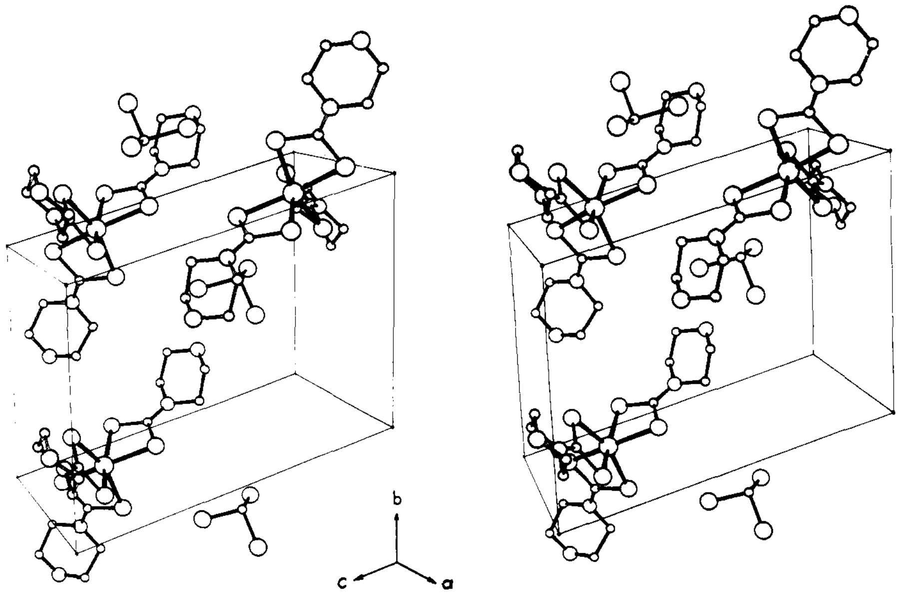

Figure 3. Molecular packing in FeM•CHCl$_3$.

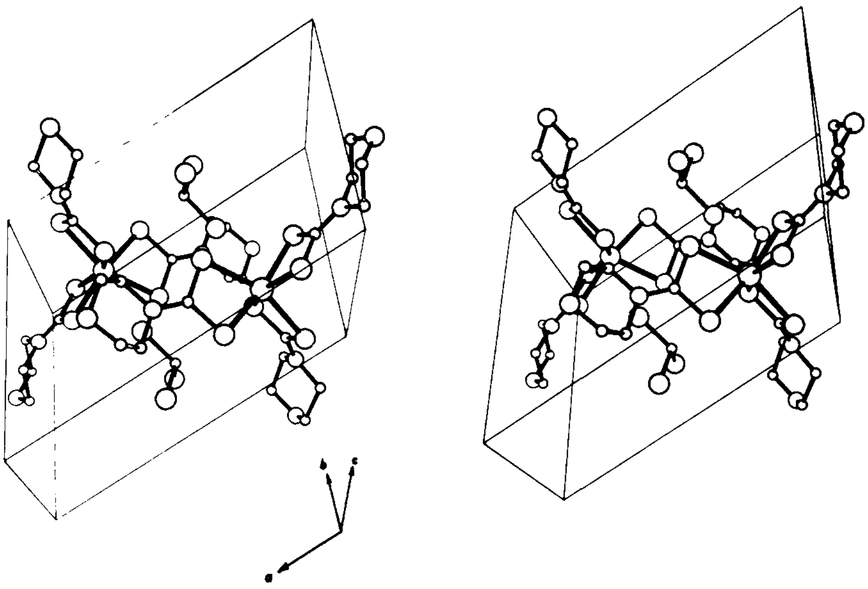

Figure 4. Molecular packing in MnM·$CHCl_3$.

solvent hydrogen-bonding interaction should be possible. Such solvent perturbation of one ligand at a time represents a mechanism for the NMR line splittings calculated for several diamagnetic dithiocarbamates,[12] but for which no physical mechanism was known at the time. It is of interest to note that in a ruthenium(III) analogue, $(RuM)_2(CHCl_3)_5$, not isomorphous with any of the present complexes, hydrogen-bonding between chloroform hydrogens and ligand sulfurs is also observed,[29] and is believed to represent the strong solvent interactions frequently proposed[12,29,30] to account for the NMR splittings. Thus ligand perturbation at the sulfurs provides a physical mechanism by which methylene proton pairs are transposed between sites of different energy,[12] thereby producing the observed multiplets. Similarly, presence of the bulky solvent molecule can hinder C–N rotation and metal-centered inversion.[26]

FeM·tol has the longest (2.443 (1) Å) average (room temperature) iron-sulfur bond length $\langle$Fe–S$\rangle$ so far observed for any ferric dithiocarbamate complex, closely followed by FeM·CH_2Cl_2,[11] with $\langle$Fe–S$\rangle$ = 2.430 (4) Å. For FeM·$CHCl_3$ it is somewhat shorter, 2.416 (1) Å, but still within the high spin range: FePDC, 2.407 (10) Å high spin;[7] FePDC·$(C_6H_6)_{0.5}$, 2.434 (1) Å, essentially high spin at room temperature.[9,19] Thus, essentially high spin behavior ($\mu > 5\ \mu_B$) is predicted for both FeM·tol and FeM·$CHCl_3$ at room temperature from the bond lengths. MnM·$CHCl_3$ exhibits strong tetragonal distortion, which can be considered as Jahn–Teller or not, depending on whether the ligands are considered nonequivalent[31] due to the solvent interaction. The two elongated bonds of the tetragonal system differ by 0.057 (1) Å, the longer one being linked to the chloroform H atom. The remaining Mn–S bonds contain two (reasonably similar) very short and two intermediate but dissimilar (by 0.040 (1) Å) bonds. This distortion is far greater than that needed to remove the orbital degeneracy and contrasts with the 0.005 (6) Å difference between the two elongated bonds. The stretch of the two longest bonds (z axis) removes the e and part of the t_2 degeneracy while the secondary distortion in the (approximate) xy plane lifts the remaining d_{xy}, d_{yz} degeneracy. By contrast, MnM·CH_2Cl_2[26] (Table VII) has the strongest solvent hydrogen to sulfur interaction (2.73 Å) at the third longest Mn–S bond (2.486 (1) Å) and the next strongest (2.85 Å) at the longest Mn–S bond. The two long bonds in MnM·CH_2Cl_2 do not differ much (0.005 (1) Å) unlike those in MnM·$CHCl_3$. Even if a significant part of the observed metal-ligand bond elongation would

Table VI. Closest Intermolecular Contacts

Molecule 1	Molecule 2	Distance	Symmetry transformation		
(a) Closest Intermolecular Contacts for FeM·$CHCl_3$					
S(11)	C(33)	3.681	$1-x$	$-y$	$-z$
O(1)	O(3)	3.311	$x-1$	$1+y$	z
O(1)	C(33)	3.393	$x-1$	$1+y$	z
O(1)	C(35)	3.557	$x-1$	$-y$	$1-z$
O(2)	C(14)	3.242	$-x$	$-y$	$1-z$
O(2)	N(1)	3.388	$-x$	$-y$	$1-z$
O(3)	C(13)	3.332	$1-x$	$-y$	$-z$
O(3)	N(1)	3.473	$1-x$	$-y$	$-z$
O(3)	C(11)	3.515	$1-x$	$-y$	$-z$
C(13)	C(13)	3.533	$-x$	$1-y$	$-z$
Solvent Contacts					
Cl(1)	S(12)	3.550	x	y	z
Cl(2)	S(12)	3.644	x	y	z
Cl(3)	S(12)	3.455	x	y	z
Cl(4)	O(1)	3.230	$-x$	$1-y$	$1-z$
Cl(7)	O(1)	3.101	$-x$	$1-y$	$1-z$
C	S(22)	3.646	$1-x$	$-y$	$1-z$
(b) Closest Intermolecular Contacts for MnM·$CHCl_3$					
O(1)	N(3)	3.242	$1-x$	$1-y$	$1-z$
O(1)	C(32)	3.264	$1-x$	$1-y$	$1-z$
O(1)	C(31)	3.529	$1-x$	$1-y$	$1-z$
O(2)	O(3)	3.521	$1+x$	y	z
O(2)	C(13)	3.533	$1-x$	$1-y$	$-z$
O(3)	C(35)	3.494	$-x$	$2-y$	$1-z$
O(3)	C(24)	3.595	$x-1$	y	z
Solvent Contacts					
Cl(1)	S(12)	3.382	$1-x$	$1-y$	$1-z$
Cl(2)	C(15)	3.496	$1-x$	$-y$	$-z$
Cl(2)	O(1)	3.534	$1-x$	$-y$	$-z$
C	S(12)	3.669	x	y	z
(c) Closest Intermolecular Contacts for FeM·tol					
S(12)	O(2)	3.651	$1-x$	$-y$	$2-z$
S(31)	C(24)	3.694	$-x$	$-y$	$2-z$
O(1)	C(35)	3.397	$-x$	$-y$	$1-z$
O(2)	C(15)	3.330	$1-x$	$-y$	$2-z$
O(3)	C(23)	3.356	$-x$	$1-y$	$2-z$
Solvent Contacts					
O(44)	O(2)	3.379	x	y	$z-1$
O(45)	O(1)	3.215	$1-x$	$-y$	$1-z$
O(45)	C(35)	3.295	$1+x$	y	z
O(45)	C(13)	3.392	$1+x$	$1+y$	z

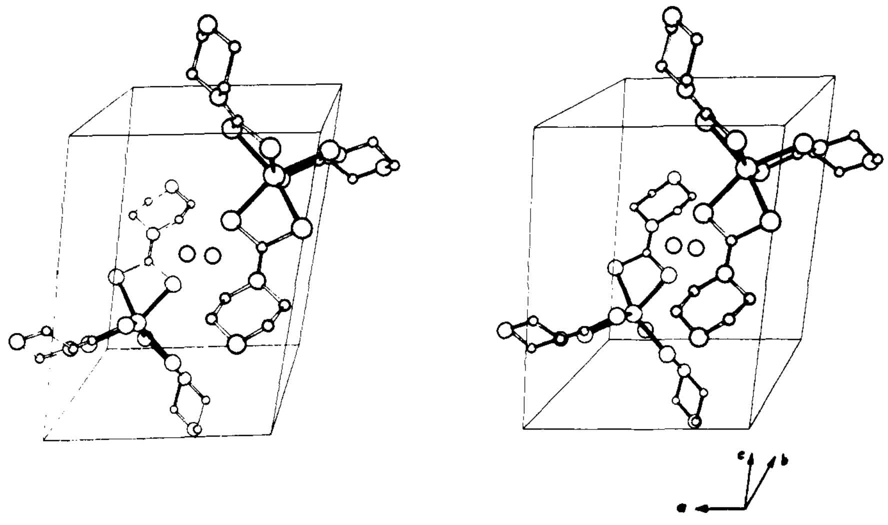

Figure 5. Molecular packing in FeM·tol.

Table VII. Coordination Sphere Data for some Dithiocarbamate Complexes

Compound	⟨M–S⟩, Å	⟨δ⟩, deg	γ	ζ	ζ′	⟨C–N⟩	Space group	*R* factor	Ref
FeM·$CHCl_3$	2.416	73.3	157.9	93.1	104.6	1.32	$P\bar{1}$	0.040	(*a*)
FeM·tol	2.443	72.7	156.2	92.9	106.4	1.32	$P\bar{1}$	0.039	(*a*)
FeM·CH_2Cl_2	2.430	72.5	157.3	93.6	104.5	1.31	$P\bar{1}$	0.063	26
FePDC	2.407	74.5	161.0	93.4	101.7	1.31	$P2_1/n$	0.13	7
FePDC$(C_6H_6)_{1/2}$[b]	2.434	73.3	160.6	94.2	101.3	1.32	$P2_1/n$	0.045	34
FeM·$(C_6H_6)_2$[b]	2.318	75.5	165.2	95.6	97.1	1.32	$C2/c$	0.047	10
MnM·$CHCl_3$	2.456	72.4	158.9	94.5	102.4	1.32	$P\bar{1}$	0.040	(*a*)
MnM·CH_2Cl_2	2.461	72.2	158.5	94.5	102.6	1.33	$P\bar{1}$	0.040	26

[a] This work. [b] Tris(1-pyrrolidinecarbodithioato-*S,S′*) complexes abbreviated as PDC.

Table VIII. Magnetic Moments

(a) FeM·$CHCl_3$												
T (°K)	5	6	7	8	9	18	20	30	40	60	80	100
μ_{eff} (μ_B)	3.51	3.65	3.76	3.80	3.86	4.11	4.13	4.27	4.33	4.42	4.55	4.68
T (°K)	150	200	240	280								
μ_{eff} (μ_B)	4.94	5.13	5.42	5.45								
(b) FeM·ClBz												
T (°K)	5.6	6.6	7.6	8.6	9.6	15.4	19.8	29.7	40.0	60.0	80.0	100
μ_{eff} (μ_B)	3.69	3.86	3.96	4.01	4.07	4.34	4.43	4.63	4.73	4.80	4.85	4.88
T (°K)	200	240	295									
μ_{eff} (μ_B)	5.32	5.52	5.61									
(c) MnM·$CHCl_3$												
T (°K)	5.6	6.6	7.6	8.6	15.4	19.7	50	60	70	80	90	100
μ_{eff} (μ_B)	4.47	4.63	4.74	4.77	5.07	5.17	5.27	5.26	5.26	5.26	5.27	5.30
T (°K)	294											
μ_{eff} (μ_B)	5.5[a]											

[a] Gouy balance measurement—lower accuracy.

have occurred in the absence of the solvent interaction (i.e., due to other lattice or intramolecular forces), the solvent determines the direction of the distortion which would have occurred anyway: elongation is consistently observed in the bonds near the solvent. However, this observation does suggest that the solvent interaction is a major cause of the distortion, at least in the ferric complexes, where the magnetic properties are also best rationalized on this basis. The strongest interactions in FeM·$CHCl_3$ are with the shortest Fe–S bond, though the range of bond lengths is negligible (0.030 (1) Å) compared with that of MnM·$CHCl_3$ (0.240 (1) Å). In FeM·CH_2Cl_2 the strongest interactions (2.76, 2.82 Å) are associated with the longest Fe–S bonds (2.432 (4), 2.452 (4) Å).

Magnetic Properties. The temperature dependence of the magnetic moments of FeM·$CHCl_3$, FeM·ClBz, FeM·tol, and MnM·$CHCl_3$ are given in Table VIII. The relative values of the moments are considered to be accurate to 0.1%, the absolute values somewhat less. FeM·tol has a consistently higher moment at the higher temperatures than FeM·$CHCl_3$, as expected from longer metal-ligand radius. The magnetic behavior of FeM·$CHCl_3$ qualitatively resembles that of FeM·CH_2Cl_2 with relatively minor numerical differences. FeM·tol/FeM·ClBz is more surprising in its large qualitative difference from the unsolvated FeM,[10] obtained by removal of FeM·CH_2Cl_2 or FeM$(C_6H_6)_2$, which ranges from low spin to essentially high spin over the same temperature range (Figure 6). Thus, in terms of magnetic behavior, the hydrated FeM·tol cannot be regarded as a crystalline model for FeM.

From the low temperature limits of their magnetic moments, it appears that both FeM·$CHCl_3$ and FeM·tol have an $S = 5/2$

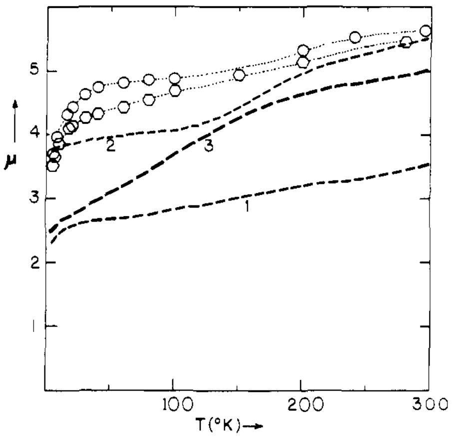

Figure 6. Temperature dependence of magnetic moments (μ_{eff}, μ_B) of: ◯, FeM·$CHCl_3$; o, FeM·tol; **1**, FeM·$(C_6H_6)_2$; **2**, FeM·CH_2Cl_2; **3**, FeM.

ground state or a low-lying $S = \frac{3}{2}$ state, like FeM·CH_2Cl_2, and this must be a distortion split T_1 state, as discussed in ref 10. At low temperature, where this state predominates, tetragonal distortion should be evident in addition to the trigonal distortion (Table VII) observed in each of the complexes. However, the magnetism may vary below 5 K, outside the available temperature range, the results do not follow normal ferric dithiocarbamate behavior and do not conform to any of the normal models for spin state crossovers.

For comparison, Figure 6 also shows the moments of FeM·$(C_6H_6)_2$[10] and FeM·CH_2Cl_2,[32] each of which differs markedly from the others. The effect of the solvent is to change the magnetic properties and simultaneously the ⟨Fe–S⟩ distance. However, the change is complex: instead of a mere shift in the equilibrium position, the nature of the equilibrium changes, and $S = \frac{3}{2}$ states appear to be produced frequently. This can only be explained if $S = \frac{1}{2}$, $S = \frac{3}{2}$, and $S = \frac{5}{2}$ states are all low lying, such that a small perturbation of the metal ligand bonds alters the balance between the states. Possibly the small perturbation produced by the solvent hydrogen interactions is sufficient to change this balance. If an Fe–S bond were thus weakened, pushing the $S = \frac{1}{2}, \frac{3}{2} \rightleftharpoons S = \frac{5}{2}$ equilibria towards the sextet state, then all the Fe–S bonds would lengthen since these must be approximately equal to $^6A_1$. The increase in μ_{eff} from unsolvated FeM, on addition of chlorinated alkanes or water, in FeM·$CHCl_3$, FeM·CH_2Cl_2, and FeM·tol is compatible with such a mechanism. The increased distortion due to solvent interaction would lower the $S = \frac{3}{2}$ state, which could then become the ground state provided it were already sufficiently low lying. However, the very low μ_{eff} observed for FeM·$(C_6H_6)_2$ is not readily explained this way. Indeed, the solvent interaction is weak and is not yet supported by sufficient data to make it more than a possible mechanism (especially when possible packing effects have not been taken into account[10]). However, the importance of the second coordination sphere in spin state equilibria, in these neutral complexes, is firmly established from our data.

It is now clear that further unraveling of the chloroform disorder in FeM·$CHCl_3$ would add nothing to the chemically significant aspects, viz., the NMR solvent effects and the magnetism. Thus restriction of the calculation to the eight most abundant chlorine position observed is justified.

In view of the extreme sensitivity to solvation, literature magnetic data on ferric dithiocarbamate complexes must now be treated with caution until the presence or absence of solvent and its effect are known. In some cases solvates are formed which lose solvent readily, and different amounts of solvent may be present when magnetic and analytical measurements are made.

The manganese complex is magnetically normal: the distortion-split ^5E ground state, with a small amount of mixing with $^5T_2$ and $^3T_1$ and configurational mixing, should have a relatively temperature independent moment.[16,33] The drop in moment at very low temperature may be partly due to the antiferromagnetic interactions expected for such a system. Tris(1-pyrrolidinecarbodithioato-*S*,*S'*)iron(III), $t_2{}^3e^2$, has extensive electron spin delocalization onto the ligand atoms and exhibits antiferromagnetic interactions between adjacent ligands on neighboring molecules, while the chromium(III) analogue, $t_2{}^3$, with negligible spin delocalization, is not significantly antiferromagnetic.[9,19] Related Mn(III) complexes, $t_2{}^3e^1$, also exhibit extensive spin delocalization,[16] though far less than in high spin iron(III). Thus significant antiferromagnetic interaction, though less than in high spin iron(III), should be apparent at low temperature. The same phenomenon is expected in the $S = \frac{3}{2}$ states, $t_2{}^4e^1$, and this may explain the slight dip moment at the lowest temperatures.

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Supplementary Material Available. A listing of observed structure factors (53 pages). Ordering information is given on any current masthead page.

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