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Coordination Chemistry of New Sulfur-Containing Ligands. 16.[1] Crystal and Molecular Structure of Tris(pyrrole-*N*-carbodithioato)iron(III)–Hemikis(dichloromethane), $Fe(S_2CNC_4H_4)_3 \cdot 0.5CH_2Cl_2$, a Low-Spin Dithiocarbamate Complex of Iron(III)

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Received January 26, 1979

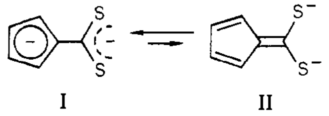
The detailed molecular structure of the low-spin iron(III) complex $Fe(S_2CNC_4H_4)_3$ has been determined from a single-crystal X-ray diffraction study. The complex crystallizes from dichloromethane/methanol in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 11.298$ (3) Å, $b = 18.095$ (3) Å, $c = 11.007$ (2) Å, $\beta = 111.32$ (2)°, and $Z = 4$. Diffraction data were collected with a Syntex $P2_1$ automated diffractometer using Mo Kα radiation. The iron and sulfur atoms were located from a Patterson synthesis, all other nonhydrogen atoms were located via difference-Fourier techniques, and hydrogen atoms were placed in calculated positions. Refinement converged with $R_F = 5.50\%$ and $R_{wF} = 4.21\%$ for all 2755 symmetry-independent reflections with $4° < 2\theta < 45°$ (none rejected). The crystals contain discrete, well-separated monomeric molecules of $Fe(S_2CNC_4H_4)_3$ and dichloromethane of solvation (which occupies positions of C_i symmetry and is disordered); the overall composition of the material is thus $Fe(S_2CNC_4H_4)_3 \cdot 0.5CH_2Cl_2$. Individual iron–sulfur distances range from 2.280 (1) to 2.314 (1) Å. The average value of 2.297 ± 0.014 Å for the iron–sulfur distance in this low-spin iron(III) complex is markedly shorter than the average iron–sulfur distance of 2.432 ± 0.009 Å for the structurally similar, *but high-spin*, iron(III) complex tris(pyrrolidine-*N*-carbodithioato)iron(III), $Fe(S_2CNC_4H_8)_3$, previously studied by Sinn. This and other geometric considerations clearly indicate that the low-spin (strong-field) dithiocarbamate complexes of iron(III) are associated with dithiocarbamate ligands in which there is a ligand structure rich in the delocalized dithio acid form $R_2NCS_2^-$ rather than in the dianionic dithio form, $R_2N^+{=}CS_2^{2-}$.

Introduction

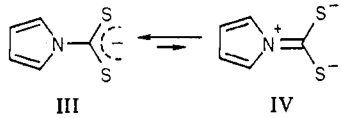
In recent years we have been interested in synthesizing new sulfur-containing ligands which promise to induce "unusual" electronic properties at the metal center.[1,3-16] With this in mind, we have recently investigated the coordination chemistry of several new dithiocarbamate ligands derived from the heterocyclic nitrogenous bases pyrrole, indole, carbazole, imidazole, and indoline. As a result of our extensive studies on the relationship between ligand resonance structure and metal bonding in the cyclopentadienedithiocarboxylate ligand[1,3,4,6-8,10] (see Scheme I), we felt confident that certain specific resonance structures of these new dithiocarbamate ligands might dominate the metal-bonding scheme. Thus, the pyrrole-*N*-carbodithioate ligand should have *little* contribution from the "normal" resonance structure proposed for dithiocarbamates (i.e., that where positive charge builds up on the nitrogen atom, IV), since this would tend to disrupt the aromaticity of the pyrrole ring (see Scheme II).

Since the early 1930's it has been known that tris bidentate chelate complexes of iron(III) can possess magnetic moments intermediate between the low-spin value ($\mu_{eff} \simeq 2.0\ \mu_B$) and the high-spin value ($\mu_{eff} \simeq 5.9\ \mu_B$).[17,18] This is particularly true of dithiocarbamate complexes and it has been assumed that variations in magnetic moment can here be attributed to differing percentage contributions from the two limiting

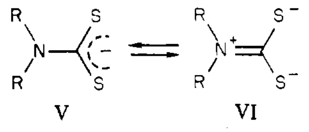
Scheme I



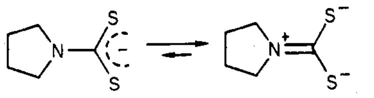
Scheme II



Scheme III



Scheme IV



VII VIII

resonance forms shown in Scheme III.[19-21] There have been few detailed comparisons of the structures of high-spin and low-spin tris(dithiocarbamato)iron(III) complexes. Noteworthy, however, is a study by Leipoldt and Coppens[22] on the temperature-dependent structure of $Fe(S_2CNEt_2)_3$. Here it was noted that the changes in bond lengths between 77 and 298 K supported the dianionic form (VI) as the principal contributor to the low-spin (strong-field) structure. As noted by the authors,[22] however, the changes in bond lengths etc. were all on the borderline of statistical significance (i.e., 2–3σ) and no corrections were made to compensate for the possible artificial shortening of bond lengths due to thermal motion, because the nature of the principal molecular modes was unknown. Spectral studies have also led to the conclusion that VI is the major contributor to the electronic structure of the dithiocarbamate ligand in low-spin (strong-field) complexes.[20,21]

Our recent spectral studies on complexes of the pyrrole-*N*-carbodithioate ligand indicate that form V (or, more strictly, III) is the predominant species present. This conclusion was based upon the following pieces of evidence: (i) a determination that a significant amount of out-of-plane copper–ligand π bonding occurred in bis(pyrrole-*N*-carbodithioato)copper(II) and (ii) the observation that the proton NMR spectrum of bis(pyrrole-*N*-carbodithioato)zinc(II) was essentially identical with that of free pyrrole.[11] In addition, we have shown that this ligand reacts smoothly with VO^{2+} to yield a simple nonoxygenated vanadium(IV) complex. This suggests that there is considerable stability to the metal–sulfur linkages, probably as a result of extensive π bonding.[14]

The complex tris(pyrrole-*N*-carbodithioato)iron(III) is of particular interest because it remains a *low-spin* species through the range 4–400 K; it is also believed to contain a dithiocarbamate ligand tending toward structure V (or III). A crystallographic study of this molecule was deemed to be of particular value because Sinn[23] had reported the results of a structural study on a closely related iron(III) complex based upon the pyrrolidine-*N*-carbodithioate ligand (see Scheme IV); this complex, tris(pyrrolidine-*N*-carbodithioate)iron(III), which is structurally very similar to tris(pyrrole-*N*-carbodithioato)iron(III), is, however, a ***high-spin*** (weak-field) complex of iron(III). Detailed comparisons of structurally similar ***high-*** and ***low-spin*** tris(dithiocarbamato)iron(III) are thus possible and are discussed below.

Experimental Section

Single crystals were prepared (with considerable difficulty) by dissolving 0.2 g of $Fe(S_2CNC_4H_4)_3{\cdot}0.5(C_4H_8O)$, prepared as previously reported,[11] in a minimal amount of 70:30 (v/v) dichloromethane/methanol and allowing the solution to evaporate slowly. Approximately 0.1 g of purple crystals, later found (vide infra) to have the composition $Fe(S_2CNC_4H_4)_3{\cdot}0.5CH_2Cl_2$, was isolated. Few, however, were of the size and quality required for an X-ray structural analysis.

The crystal used in the diffraction experiment was a regular-shaped rectangular prism measuring approximately 0.30 mm × 0.27 mm × 0.17 mm. The crystal was jammed into a 0.3-mm thin-walled glass capillary which was sealed and fixed with beeswax into an aluminum pin on a eucentric goniometer head. This was fixed to the goniostat and the crystal was centered in the X-ray beam of a Syntex $P2_1$ four-circle diffractometer under control of a Data General Nova 1200 computer with 24K of 16-bit word memory and a Diablo disk unit of 1.2×10^6 16-bit words. The relative orientation and unit cell parameters of the crystal were determined, and the X-ray data were collected by methods described previously.[24] The crystal was found to possess monoclinic symmetry. Inspection of the collected data revealed the systematic absences *h*0*l* for $l = 2n + 1$ and 0*k*0 for $k = 2n + 1$, consistent with the centrosymmetric space group $P2_1/c$.

Table I. Data for the X-ray Diffraction Study of $Fe(S_2CNC_4H_4)_3{\cdot}0.5CH_2Cl_2$

(A) Crystal Data

crystal system: monoclinic
space group: $P2_1/c$ [C_{2h}^5; No. 14]
$a = 11.298$ (3) Å
$b = 18.095$ (3) Å
$c = 11.007$ (2) Å
$\beta = 111.32$ (2)°
$V = 2096.2$ Å^3
$T = 24 \pm 1$ °C
$Z = 4$
mol wt 525.1
ρ(obsd)^a = 1.60 g/cm^3
ρ(calcd) = 1.66 g/cm^3

(B) Intensity Data

radiation: Mo Kα
monochromator: highly oriented graphite
reflctns measd: $h, k, \pm l$
max 2θ: 45°
min 2θ: 4°
scan type: θ–2θ
scan speed: 4°/min
scan range: symmetrical, $[1.8 + \Delta(\alpha_2 - \alpha_1)]°$
reflctns collected: 2755
absn coeff: 13.1 cm^{-1}; empirical absorption correction made on the basis of a series of ψ scans

[a] Measured by neutral buoyancy in *n*-butyl bromide and ethylene bromide. This measurement is prone to error due to (i) the small number of crystals of good quality and (ii) possible variation in the CH_2Cl_2 content from crystal to crystal.

Table II. Positonal Parameters and Their Esd's for $Fe(S_2CNC_4H_4)_3{\cdot}0.5CH_2Cl_2$

atom	*x*	*y*	*z*
Fe	0.060 71 (5)	0.200 61 (3)	0.221 67 (6)
S(1)	−0.080 02 (11)	0.159 87 (7)	0.311 79 (11)
S(2)	0.230 83 (10)	0.137 78 (6)	0.369 76 (10)
S(3)	0.092 20 (11)	0.308 31 (6)	0.338 66 (11)
S(11)	−0.135 52 (10)	0.233 22 (7)	0.072 05 (11)
S(22)	0.071 68 (11)	0.091 49 (6)	0.118 74 (11)
S(33)	0.188 67 (11)	0.270 61 (6)	0.143 86 (11)
C(1)	−0.193 00 (38)	0.194 91 (22)	0.178 82 (41)
N(1)	−0.320 29 (31)	0.193 38 (19)	0.161 12 (34)
C(11)	−0.368 53 (44)	0.171 51 (26)	0.255 91 (49)
C(12)	−0.497 00 (46)	0.179 19 (28)	0.200 57 (56)
C(13)	−0.528 32 (47)	0.204 99 (29)	0.072 04 (56)
C(14)	−0.420 80 (41)	0.213 89 (26)	0.049 01 (48)
C(2)	0.193 67 (38)	0.069 36 (23)	0.257 43 (40)
N(2)	0.253 05 (31)	0.002 42 (18)	0.278 27 (34)
C(21)	0.345 78 (41)	−0.020 29 (25)	0.393 96 (48)
C(22)	0.376 10 (48)	−0.090 44 (28)	0.379 64 (52)
C(23)	0.300 75 (51)	−0.113 39 (27)	0.250 83 (55)
C(24)	0.226 01 (46)	−0.056 30 (25)	0.191 32 (47)
C(3)	0.189 44 (38)	0.332 53 (23)	0.259 21 (39)
N(3)	0.263 72 (33)	0.394 04 (19)	0.289 04 (34)
C(31)	0.259 61 (47)	0.449 43 (25)	0.374 55 (46)
C(32)	0.347 86 (48)	0.499 54 (27)	0.379 68 (50)
C(33)	0.410 37 (49)	0.475 52 (29)	0.295 82 (51)
C(34)	0.358 76 (43)	0.411 51 (27)	0.241 47 (48)
H(11)	−0.320 6	0.154 8	0.341 6
H(12)	−0.555 8	0.169 0	0.241 9
H(13)	−0.611 9	0.214 2	0.012 1
H(14)	−0.413 7	0.231 1	−0.029 6
H(21)	−0.382 0	0.009 5	0.469 6
H(22)	0.436 2	−0.119 9	0.444 5
H(23)	0.303 0	−0.160 6	0.214 0
H(24)	0.165 7	−0.055 5	0.104 6
H(31)	0.203 3	0.451 0	0.420 9
H(32)	0.365 7	0.543 5	0.430 3
H(33)	0.477 7	0.500 6	0.281 0
H(34)	0.382 0	0.382 9	0.181 2
Cl	−0.045 68 (19)	0.456 58 (10)	0.086 57 (18)
C^a	0.076 64 (88)	0.011 19 (55)	0.534 02 (94)
H(1)^a	0.115 7	0.053 7	0.514 3
H(2)^a	0.136 0	−0.013 8	0.606 5

[a] Occupancy = 0.5. The CH_2Cl_2 molecule occupies a site of C_i symmetry at (0, $^1/_2$, 0). The chlorine atoms are ordered, but the CH_2 group is subject to twofold disorder.

Table III. Thermal Parameters and Their Standard Deviations for $Fe(S_2CNC_4H_4)_3 \cdot 0.5CH_2Cl_2$

A. Anisotropic Thermal Parameters[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	2.482 (28)	2.868 (30)	2.378 (28)	0.064 (23)	0.872 (21)	0.169 (23)
S(1)	2.939 (52)	4.338 (61)	3.303 (56)	0.251 (45)	1.193 (43)	1.242 (47)
S(2)	3.066 (51)	3.110 (52)	2.620 (51)	0.169 (42)	0.381 (41)	−0.308 (41)
S(3)	3.839 (56)	3.200 (53)	3.074 (52)	−0.106 (45)	1.791 (44)	−0.281 (43)
S(11)	2.867 (52)	4.470 (62)	2.964 (53)	0.216 (45)	0.840 (42)	0.912 (46)
S(22)	3.529 (55)	3.348 (55)	2.498 (51)	0.182 (44)	0.366 (42)	−0.282 (41)
S(33)	3.589 (54)	3.416 (54)	3.012 (53)	−0.353 (43)	1.808 (44)	−0.349 (42)
C(1)	2.86 (20)	2.50 (19)	3.33 (21)	0.17 (16)	1.12 (16)	−0.17 (17)
N(1)	2.64 (17)	3.23 (18)	3.61 (19)	0.03 (14)	0.97 (15)	−0.07 (15)
C(11)	4.00 (26)	4.46 (25)	4.36 (25)	−0.42 (20)	2.11 (22)	−0.42 (20)
C(12)	3.40 (25)	5.07 (29)	7.07 (37)	−0.60 (21)	2.74 (25)	−1.04 (26)
C(13)	3.10 (25)	5.64 (30)	6.00 (34)	0.08 (22)	0.93 (23)	−1.15 (26)
C(14)	3.21 (23)	4.31 (26)	4.31 (26)	0.28 (19)	0.72 (20)	−0.20 (20)
C(2)	2.55 (19)	3.10 (21)	2.71 (20)	−0.29 (16)	1.11 (16)	−0.09 (16)
N(2)	2.85 (17)	2.97 (17)	3.31 (18)	0.40 (14)	0.83 (14)	−0.26 (14)
C(21)	3.21 (22)	3.60 (23)	4.33 (25)	1.00 (18)	0.36 (20)	0.03 (20)
C(22)	4.71 (28)	4.52 (27)	4.98 (29)	1.37 (22)	1.00 (24)	0.75 (23)
C(23)	6.04 (31)	2.81 (24)	6.59 (34)	0.57 (23)	2.28 (27)	−0.56 (23)
C(24)	4.45 (25)	3.37 (23)	4.12 (25)	−0.13 (20)	1.08 (21)	−0.92 (20)
C(3)	2.63 (19)	2.99 (20)	2.42 (19)	0.43 (17)	0.49 (16)	0.15 (16)
N(3)	3.23 (18)	3.20 (18)	3.05 (18)	−0.32 (15)	0.86 (15)	−0.08 (15)
C(31)	5.01 (27)	3.54 (24)	3.81 (24)	−0.17 (21)	1.51 (21)	−0.35 (20)
C(32)	5.79 (30)	3.03 (24)	4.54 (27)	−0.87 (22)	0.54 (24)	−0.50 (20)
C(33)	4.31 (27)	4.90 (30)	5.66 (31)	−1.66 (23)	1.23 (24)	−0.00 (25)
C(34)	3.76 (24)	4.46 (26)	4.26 (25)	−1.04 (20)	1.70 (20)	−0.05 (21)
Cl	9.84 (12)	8.05 (11)	7.38 (10)	1.14 (09)	4.72 (09)	−0.72 (09)
C	4.86 (57)	4.87 (56)	4.30 (53)	−3.34 (45)	−1.34 (43)	3.21 (45)

B. Isotropic Thermal Parameters[b]

atom	B, Å^2	atom	B, Å^2	atom	B, Å^2
H(11)	5.2	H(22)	5.8	H(33)	6.2
H(12)	5.8	H(23)	6.1	H(34)	5.1
H(13)	6.1	H(24)	5.2	H(1)	6.0
H(14)	5.1	H(31)	5.2	H(2)	6.0
H(21)	4.9	H(32)	5.7		

[a] The anisotropic thermal parameters are defined by the following expression: $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^{*}b^{*} + 2B_{13}hla^{*}c^{*} + 2B_{23}klb^{*}c^{*})]$. [b] Isotropic thermal parameters are given for hydrogen atoms. These are based on the *isotropic* thermal parameters of the attached carbon atoms $B(H_i) = B(C_i) + 1.0$ (Å^2).

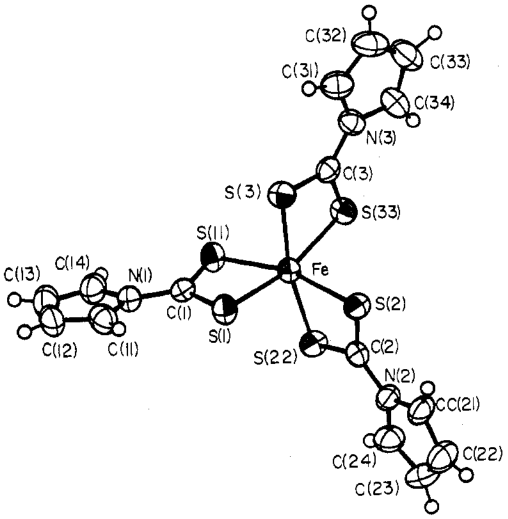


Figure 1. Molecular geometry and labeling of atoms in the $Fe(S_2CNC_4H_4)_3$ molecule (ORTEP-II diagram, 30% probability ellipsoids).

Specifics of the data collection are given in Table I.

Solution and Refinement of the Structure

Initial calculations, through the generation of a Patterson synthesis, were performed by using the Syntex XTL structure determination system, including the aforementioned computing hardware and a locally modified version of the XLT conversational crystallographic program package. Subsequent difference-Fourier syntheses and structure refinement were carried out on the CDC 6600/CYBER 173 computer at the State University of New York at Buffalo. Programs other than those in the Syntex XTL structure determination system included the following: TAPRE (reads nine-track, ASCII-character string magnetic tape created by the program CDCOUT of the XTL system and converts the tapes read to coded files); JIMDAP (Fourier synthesis, derived from A. Zalkin's FORDAP) by J. A. Ibers and co-workers; LSHF (structure factor calculations and full-matrix least-squares refinement), STAN1 (distances and angles and their esd's), and PLOD (least-squares planes) all by B. G. DeBoer; and ORTEP II (thermal ellipsoid plots) by C. K. Johnson.

Scattering factors for neutral iron, sulfur, nitrogen, and carbon were taken from the compilation of Cromer and Waber;[25] for hydrogen, the "best floated spherical H atom" values of Stewart et al.[26] were used. Both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion were included for all nonhydrogen atoms, using the values of Cromer and Liberman.[27]

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma(|F_o|)]^{-2}$. Discrepancy indices used in the text are defined in eq 1 and 2. The "goodness of fit" (GOF) is defined by eq 3, wherein NO is the number of observations and NV is the number of variables.

$$R_F = \left[\frac{\sum ||F_o| - |F_c||}{\sum |F_o|}\right] \times 100\ (\%) \qquad (1)$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}\right]^{1/2} \times 100\ (\%) \qquad (2)$$

$$\mathrm{GOF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\mathrm{NO} - \mathrm{NV}}\right]^{1/2} \qquad (3)$$

Table IV. Bond Distances (Å) for $Fe(S_2CNC_4H_4)_3 \cdot 0.5CH_2Cl_2$

(A) Iron–Sulfur Bond Lengths			
Fe–S(1)	2.280 (1)	Fe–S(11)	2.306 (1)
Fe–S(2)	2.314 (1)	Fe–S(22)	2.294 (1)
Fe–S(3)	2.284 (1)	Fe–S(33)	2.305 (1)
(B) Sulfur-Carbon Bond Lengths			
S(1)–C(1)	1.677 (4)	S(11)–C(1)	1.684 (4)
S(2)–C(2)	1.687 (4)	S(22)–C(2)	1.691 (4)
S(3)–C(3)	1.691 (4)	S(33)–C(3)	1.688 (4)
(C) (S-Bonded) Carbon–Nitrogen Bond Lengths			
C(1)–N(1)	1.380 (5)	C(3)–N(3)	1.356 (5)
C(2)–N(2)	1.358 (5)		
(D) Nitrogen–Carbon (Pyrrole) Distances			
N(1)–C(11)	1.398 (6)	N(2)–C(24)	1.384 (5)
N(1)–C(14)	1.389 (6)	N(3)–C(31)	1.384 (6)
N(2)–C(21)	1.384 (5)	N(3)–C(34)	1.391 (5)
(E) Formal C=C Distances			
C(11)–C(12)	1.362 (6)	C(23)–C(24)	1.340 (6)
C(13)–C(14)	1.338 (6)	C(31)–C(32)	1.331 (6)
C(21)–C(22)	1.333 (6)	C(33)–C(34)	1.332 (6)
(F) Formal $C(sp^2)$–$C(sp^2)$ Single Bond Distances			
C(12)–C(13)	1.407 (7)	C(32)–C(33)	1.418 (7)
C(22)–C(23)	1.424 (7)		
(G) Distances within Disordered Dichloromethane Molecule[a]			
C–Cl	1.778 (11)		

[a] This molecule lies on an inversion center. The observed image consists of two chlorine atoms, two half-carbon atoms, and four half-hydrogen atoms.

The positions of the iron atom and the six sulfur atoms were determined from a three-dimensional Patterson synthesis. Subsequent least-squares refinement and difference-Fourier maps allowed the location of all carbon and nitrogen atoms of the ligands and also indicated the presence of a (disordered) dichloromethane molecule of solvation, centered about the special position 0, $^1/_2$, 0 (of C_i symmetry). Positions of all hydrogen atoms were calculated and shifts in their positional parameters were constrained to be equal to those of the appropriate bonded carbon atom (i.e., each CH system was treated as a rigid nonrotating group). There was evidence for secondary extinction and a correction was made,[28] the final value of c being 0.758×10^{-5}. Final convergence was reached with $R_F = 5.50\%$, $R_{wF} = 4.21\%$, and GOF = 1.447. The highest feature on a final difference-Fourier synthesis was a peak of height 0.50 e $Å^{-3}$ at the position 0.123, 0, 0.468. The structural analysis is thus both correct and complete. Positional parameters are collected in Table II; thermal parameters are presented in Table III.

Results and Discussion

Interatomic distances and their estimated standard deviations (esd's) are shown in Table IV; bond angles and their esd's are given in Table V. The labeling of atoms within the $Fe(S_2CNC_4H_4)_3$ molecule is shown in Figure 1. It should be noted that there are no abnormally short contacts between the molecular iron complex and the dichloromethane of solvation. It has been previously shown by Sinn that solvent molecules can influence the spin properties of iron(III) dithiocarbamates. For example, at room temperature, tris(pyrrolidine-*N*-carbodithioate)iron(III) demonstrates an intermediate-spin state with benzene solvation and a high-spin state with dichloromethane solvation.[23] In the present case, however, the $Fe(S_2CNC_4H_4)_3$ molecule has a low-spin state at room temperature with either tetrahydrofuran or dichloromethane as solvate.

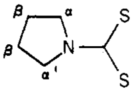
The structural results show that the gross geometry of this complex is similar of that of other tris(dithiocarbamate)iron(III) structures. That is, each of these tris(dithiocarbamato)iron(III) compounds is slightly distorted from a local octahedral field. Thus, the low-spin nature of this particular dithiocarbamate here does seem to be related to the electronic nature of the ligand as has been suggested by others.[20,21] There are a variety of ways of attempting to understand exactly the nature of the metal–ligand interaction in the structure reported here. However, perhaps the most useful is to compare this structure to that reported by Sinn for the tris(pyrrolidine-*N*-carbodithioate)iron(III) complex which is in a high-spin state at the temperature at which the structure was carried out.[23] Table VI contains average metal–sulfur bond lengths and other important dimensions within the ligand system of our unsaturated tris(pyrrole-*N*-carbodithioato)iron(III) complex and of Sinn's related, but more saturated, species tris(pyrrolidine-*N*-carbodithioato)iron(III).

The most striking contrast is the extremely short average Fe–S distance of 2.297 ± 0.014 Å in the low-spin pyrrole complex in relation to the average Fe–S distance of 2.432 ± 0.009 Å in the high-spin pyrrolidine complex. The present distance of 2.296 ± 0.014 Å is, in fact, shorter than that reported by Coppens et al.[22] for the low-spin form of Fe-

Table V. Bond Angles (deg) for $Fe(S_2CNC_4H_4)_3 \cdot 0.5CH_2Cl_2$

(A) Angles within FeS_6 Core			
S(1)–Fe–S(11)	75.60 (5)	S(1)–Fe–S(33)	165.59 (5)
S(2)–Fe–S(22)	75.46 (4)	S(2)–Fe–S(11)	164.67 (5)
S(3)–Fe–S(33)	75.80 (4)	S(3)–Fe–S(22)	168.77 (5)
S(1)–Fe–S(2)	93.91 (5)	S(11)–Fe–S(22)	94.36 (5)
S(2)–Fe–S(3)	95.67 (5)	S(22)–Fe–S(33)	97.54 (5)
S(3)–Fe–S(1)	91.05 (5)	S(33)–Fe–S(11)	99.51 (5)
S(1)–Fe–S(22)	96.35 (5)		
S(2)–Fe–S(33)	93.25 (5)		
S(3)–Fe–S(11)	95.66 (5)		
(B) Angles between Fe–S–C			
Fe–S(1)–C(1)	85.93 (15)	Fe–S(22)–C(2)	85.91 (15)
Fe–S(11)–C(1)	84.93 (15)	Fe–S(3)–C(3)	85.68 (15)
Fe–S(2)–C(2)	85.36 (15)	Fe–S(33)–C(3)	85.08 (15)
(C) Angles in Ligand 1			
S(1)–C(1)–S(11)	113.53 (24)	C(11)–N(1)–C(14)	108.87 (37)
S(1)–C(1)–N(1)	122.65 (32)	N(1)–C(11)–C(12)	106.19 (45)
S(11)–C(1)–N(1)	123,81 (33)	N(1)–C(14)–C(13)	107.76 (46)
C(1)–N(1)–C(11)	124.71 (38)	C(11)–C(12)–C(13)	108.72 (45)
C(1)–N(1)–C(14)	126.41 (39)	C(14)–C(13)–C(12)	108.45 (47)
(D) Angles in Ligand 2			
S(2)–C(2)–S(22)	113.18 (24)	C(21)–N(2)–C(24)	108.27 (36)
S(2)–C(2)–N(2)	123.27 (32)	N(2)–C(21)–C(22)	108.19 (44)
S(22)–C(2)–N(3)	123.52 (32)	N(2)–C(24)–C(23)	107.87 (44)
C(2)–N(2)–C(21)	125.43 (36)	C(21)–C(22)–C(23)	107.85 (46)
C(2)–N(2)–C(24)	126.18 (37)	C(24)–C(23)–C(22)	107.82 (45)
(E) Angles in Ligand 3			
S(3)–C(3)–S(33)	113.08 (24)	C(31)–N(3)–C(34)	108.32 (38)
S(3)–C(3)–N(3)	123.13 (32)	N(3)–C(31)–C(32)	107.93 (45)
S(33)–C(3)–N(3)	123.75 (33)	N(3)–C(34)–C(33)	107.37 (45)
C(3)–N(3)–C(31)	125.64 (39)	C(31)–C(32)–C(33)	107.95 (45)
C(3)–N(3)–C(34)	126.02 (38)	C(34)–C(33)–C(32)	108.43 (46)

Table VI. Average Bond Distances[a] in FeL_3 Systems



	dist, Å	
	pyrrolidine-*N*-carbodithioate[b]	pyrrole-*N*-carbodithioate
Fe–S	2.432 ± 0.009	2.297 ± 0.014
C–S	1.712 ± 0.009	1.686 ± 0.005
C–N	1.317 ± 0.005	1.365 ± 0.013
N–Cα(α′)	1.469 ± 0.005	1.388 ± 0.006
Cα–Cβ(Cα′–Cβ′)	1.494 ± 0.025	1.339 ± 0.012
Cβ–Cβ′	1.428 ± 0.058	1.416 ± 0.009

[a] Esd's on average value as preceded by "±" and are calculated by the formula $\sigma = [\Sigma(d_i - \bar{d})^2/(N-1)]^{1/2}$. [b] See ref 23.

Table VII. Least-Squares Planes for Metal-Ligand Systems

no.	plane[a]	*a*	*b*	*c*	*d*	dev from plane[a]	angles between planes, deg		
						Tris(pyrrole-*N*-carbodithioato)iron(III) Complex			
1	FeS(1)S(11)C(1)	−0.110	0.881	0.460	4.263	0.0035 (6), −0.0053 (12), −0.0052, 0.0070 (4)	1,1′	0.76	
1′	S(1)S(11)C(1)	−0.097	0.881	0.462	4.237		2,2′	2.59	
2	FeS(2)S(22)C(2)	0.822	0.416	−0.389	0.472	−0.0123 (6), 0.0181 (12), 0.0182 (12), −0.0241 (42)	3,3′	4.94	
2′	S(2)S(22)C(2)	0.844	0.376	−0.383	0.439		1,4	8.70	
3	FeS(3)S(33)C(3)	0.586	−0.422	0.692	−0.101	0.0235 (6), −0.0348 (12), −0.0345 (12), 0.0458 (43)	2,5	7.81	av = 9.27
3′	S(3)S(33)C(3)	0.543	−0.495	0.678	−0.582		3,6	11.29	
4	N(1)C(11)C(14)	−0.051	0.941	0.334	4.063		1′,4	8.53	
5	N(2)C(21)C(24)	0.890	0.313	−0.331	0.625		2′,5	5.40	av = 7.49
6	N(3)C(31)C(34)	0.418	−0.501	0.757	−0.565		3′,6	8.54	
						Tris(pyrrolidine-*N*-carbodithioato)iron(III) Complex[b]			
1	FeS(1)S(11)C(1)	−0.104	0.905	−0.412	1.650	0.0368 (7), −0.0578 (13), −0.0590 (14), 0.0800 (48)	1,1′	8.72	
1′	S(1)S(11)C(1)	0.048	0.905	−0.423	1.857		2,2′	0.54	
2	FeS(2)S(22)C(2)	0.748	−0.287	−0.598	1.979	−0.023 (7), 0.0037 (12), 0.0036 (13), −0.0050 (48)	3,3′	2.46	
2′	S(2)S(22)C(2)	0.751	−0.278	−0.599	2.034		1,4	14.08	
3	FeS(3)S(33)C(3)	0.745	0.573	0.341	4.216	−0.0105 (7), 0.0165 (12), 0.0166 (13), −0.0226 (48)	2,5	2.79	av = 7.32
3′	S(3)S(33)C(3)	0.771	0.540	0.336	4.335		3,6	5.28	
4	N(1)C(11)C(14)	0.141	0.896	−0.420	1.855		1′,4	5.36	
5	N(2)C(21)C(24)	0.716	−0.289	−0.635	1.790		2′,5	2.95	av = 3.81
6	N(3)C(31)C(24)	0.803	0.512	0.305	4.563		3′,6	3.02	

[a] Values in Å for respective atoms listed. [b] Calculated from data reported by Sinn.[23]

Table VIII. Structural Parameters and Magnetic Moments for Some FeS_6 Cores in Dithiocarbamate Complexes

complex	μ, μ_B	Fe-S, Å	ϕ	S-Fe-S, deg
$Fe(S_2CNC_4H_4)_3 \cdot 0.5CH_2Cl_2$	2.19	2.297 ± 0.014	44.5	75.6 ± 0.2
$Fe(S_2CNEt_2)_3$ (79 K)[a]	2.2	2.306 ± 0.004	40.5	75.9 ± 0.1
$Fe(S_2CNMePh)_3$[b]	2.9	2.312 ± 0.018	40.4	75.1 ± 0.2
$Fe(S_2CNBu_2)_3 \cdot C_6H_6$[c]	3.6	2.341 ± 0.005	40.2	74.6 ± 0.1
$Fe(S_2CNEt_2)_3$ (297 K)[a]	4.3	2.358 ± 0.005	37.6	74.3 ± 0.2
$Fe(S_2NC_4H_8O)_3 \cdot CH_2Cl_2$[d]	5.1	2.435 ± 0.015	33.4	72.7 ± 0.2
$Fe(S_2CNBu_2)_3$[e]	5.3	2.418 ± 0.006	32.0	72.7 ± 0.3
$Fe(S_2CNC_4H_8)_3$[f]	5.9	2.432 ± 0.009	38.6	73.3 ± 0.1

[a] Reference 22. [b] Reference 29. [c] Reference 30. [d] Reference 31. [e] Reference 32. [f] Reference 23.

$(S_2CNEt_2)_3$ at 79 K. If we assume that the ionic radius of low-spin iron(III) has a constant value, then the extra shortening in the Fe–S distance when compared to the case of other low-spin iron(III) dithiocarbamate complexes may well result from the increased π bonding between the iron and sulfur atoms predicted here.

Comparisons of other distances within the pyrrole-*N*-carbodithioate and pyrrolidine-*N*-carbodithioate ligands support this view. The pyrrole complex varies from the pyrrolidine in the following ways (see Table VI): (1) Its S–C linkages are significantly shorter (average values are 1.686 ± 0.005 Å vs. 1.712 ± 0.009 Å). (2) The (sulfur-bonded) C–N linkages are longer (1.365 ± 0.013 Å vs. 1.317 ± 0.005 Å). (3) The N–C(α) linkages are shorter (1.388 ± 0.006 Å vs. 1.469 ± 0.005 Å). (4) The C(α)–C(β) linkages are much shorter (1.339 ± 0.012 Å vs. 1.494 ± 0.025 Å); however, this results from unsaturation in the pyrrole ligand as compared to saturation within the pyrrolidine ligand.

Taken overall, the pyrrole ligands of the low-spin complex approximate to resonance form III and the pyrrolidine ligands of the high-spin complex approximate to resonance form VIII. These results strongly suggest that the previous assignment of formal resonance structures of dithiocarbamate ligands to high-spin and low-spin iron(III) complexes is reversed.

Least-squares planes were calculated for each S_2C and NC_2 plane in the molecule and the torsional angle in the $S_2C–NC_2$ linkage was determined. These data are presented in Table VII along with the corresponding planes employing the data of Sinn[23] for the pyrrolidine complex. A larger torsional angle exists between all pairwise comparisons for the pyrrole than for the pyrrolidine complex. The differences are, however, small and seem to be of little energetic significance. Thus the differences between the C–N bond distances in these two complexes do not seem to result from, nor be the cause of, a significant twist within the ligand itself.

Table VIII lists all of the tris(dithiocarbamate) complexes of iron(III) which have been characterized crystallographically along with some pertinent structural and magnetic data. Each of the comparisons normally made for iron(III) dithiocarbamates (e.g., S–Fe–S bond angles and ϕ, the angle of twist between the upper triangle and lower triangle of the D_3 coordination geometry) suggest that the pyrrole complex is the *most extreme example* of a low-spin iron(III) complex yet reported.

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Registry No. $Fe(S_2CNC_4H_4)_3 \cdot 0.5CH_2Cl_2$, 71214-98-7.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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Coordination Chemistry of New Sulfur-Containing Ligands. 17. Preparation, Characterization, and Crystal and Molecular Structure of [*N*,*N'*-Trimethylenebis(methyl 2-amino-1-cyclopentenedithiocarboxylato)]copper(II), a Highly Distorted CuN_2S_2 Compound[1]

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The copper(II) complex of the N_2S_2 tetradentate ligand *N*,*N'*-trimethylenebis(methyl 2-amino-1-cyclopentenedithiocarboxylate) was prepared by reaction of the neutral ligand with an equivalent amount of copper acetate in methanol. A low-energy, broad, and asymmetric absorption band at 10.5 cm^{-1} in the electronic spectrum, coupled with the observed electron spin resonance parameters ($A_{\parallel} = 160$ G, $g_{\parallel} = 2.132$, $A_0 = 67.9$ G, $g_0 = 2.060$), suggests a copper(II) coordination site intermediate between planar and pseudotetrahedral geometry. Since the recent structural results of the type I copper(II)-containing metalloenzyme plastocyanim indicates a distorted N_2S_2 coordination,[21] the further structural study of this compound is warranted. The crystal and molecular structure of the title compound was solved at 24 ± 1 °C by a single-crystal X-ray diffraction study. The complex crystallizes in the centrosymmetric monoclinic space $C2/c$ with $a = 16.7219$ (17) Å, $b = 8.4009$ (7) Å, $c = 14.5507$ (16) Å, $\beta = 108.337$ (8)°, $V = 1940.3$ Å^3, ρ(obsd) 1.54 g cm^{-3}, and ρ(calcd) = 1.53 g cm^{-3} for mol wt 448.2 and $Z = 4$. Diffraction data were collected with a Syntex $P2_1$ automated diffractometer using graphite-monochromatized Mo Kα radiation. The copper and two sulfur atoms were located in a Patterson synthesis; all other nonhydrogen atoms were located via difference Fourier techniques, and hydrogen atoms were placed in calculated positions. Final refinement resulted in discrepancy indices of $R_F = 4.31\%$ and $R_{wF} = 4.42\%$ for all 1273 symmetry-independent reflections with $4° \leq 2\theta \leq 45°$ (none rejected). The molecules are monomeric, are well separated, and lie on a C_2 axis. The copper–sulfur distance is 2.2225 (11) Å and the copper–nitrogen distance is 1.9498 (30) Å. Bond distances in the five-membered chelate ring indicate that a great deal of π delocalization exists. The plane defined by the copper and two ligand sulfur atoms intersects the plane defined by the copper and two nitrogen atoms, forming a dihedral angle of 53° (90° would be ideal for a C_{2v} inner coordination sphere geometry while 0° would be ideal for planar geometry) indicating the extent of distortion in the inner coordination sphere. The spectral properties of the copper(II) atom are discussed in terms of the geometry and the ligand atom type.

Introduction

Recent interest in our laboratories, and others, has centered on the design, preparation, and characterization of small-molecule complexes of copper(II) which offer insight into the coordination chemistry of copper(II) in metalloproteins. One of the most exciting synthetic challenges in recent years has been to prepare complexes which mimic spectral properties of the "blue" copper(II) (type I) site in proteins such as laccase, plastocyanin, stellacyanin, ceruloplasmin, and ascorbate oxidase.[3-8] Such authentic synthetic analogues would be invaluable to the understanding of the detailed stereoelectronic properties of copper(II) in this environment. Various coordination sites have been proposed for these copper(II) sites.[9-20] They have in common a geometry intermediate between tetrahedral and square planar with two nitrogen ligand atoms (imidazole nitrogen atoms from histidine residues) and at least one sulfur ligand atom (thiolate group from a cysteine residue). The recent X-ray structure of plastocyanin to 2.7-Å resolution indicates an N_2S_2 coordination for copper(II) with the second sulfur ligand atom derived from a methionine residue.[21] Other "blue" copper(II) proteins, such as stellacyanin,[22] contain no methionine residues, so other ligand atoms such as nitrogen or oxygen are still possible. Regardless, we feel that any distorted pseudotetrahedral copper(II) complex, where detailed spectral and structural data are available, is useful for providing the data base for understanding the various type I copper(II) centers.

Relatively few CuN_3S and CuN_2S_2 compounds which are severely distorted from the normally planar configuration found for copper(II) systems have been reported. Spectral data of a CuN_3S species with tris(pyrazolyl) borate serving as the nitrogen ligand and ethyl cysteinate or *p*-nitrobenzenethiolate as the sulfur ligand have been interpreted in terms of a pseudotetrahedral geometry.[23] These complexes, unfortunately, were not stable above −30 °C. Schugar and coworkers[24] have reported a nearly "tetrahedral" CoN_2S_2 complex which was valuable in the interpretation of Co(II)-substituted type I copper(II) sites.

We have exploited the utility of sulfur-containing Schiff-base ligands to prepare "distorted" copper(II) complexes.[25,26]

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