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# Solvated Tris(4-morpholinecarbodithioato-*S*,*S*') Complexes of Iron(III) and Cobalt(III). Direct Comparison of $d^5$ and $d^6$ Analogs and Study of Solvation Effects

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A number of tris(dithiocarbamato)iron(III) and -cobalt(III) solvate complexes have been examined. Inclusion of polar solvent molecules appears to be the common norm in crystals of these complexes. The decomposition points, at which all the solvent suddenly escapes, breaking up the crystal lattices, are well above the boiling points of the particular solvents. The iron(III) complexes retain the solvent molecules less well, and in many cases, solvent is lost on standing, a fact that may explain a number of the difficulties in earlier attempts at structural analysis. The strong trend to form solvates is the probable cause of anomalous nmr spectra observed in several of the cobalt complexes. Crystal structures of the dichloromethane solvates of the title complexes were determined from three-dimensional counter data at room temperature. Both compounds crystallize in space group $P\bar{1}$, $Z = 2$. The lattice constants are $a = 13.088$ (3) Å, $b = 10.693$ (1) Å, $c = 11.499$ (1) Å, $\alpha = 116.08$ (1)°, $\beta = 104.97$ (1)°, and $\gamma = 99.49$ (2)° for the iron complex and $a = 13.079$ (1) Å, $b = 10.682$ (1) Å, $c = 11.493$ (1) Å, $\alpha = 116.03$ (1)°, $\beta = 105.04$ (1)°, and $\gamma = 99.45$ (1)° for the cobalt complex. The data were refined by block-diagonal least squares to $R = 6.3\%$ (iron) and 4.2% (cobalt). The molecular geometry of the $CoS_6$ in the cobalt is identical with previous cobalt tris(dithio chelate) structures with $\langle Co-S \rangle = 2.27$ Å and $\langle S_{i1}-Co-S_{i2} \rangle = 76.1°$. The values of 2.44 Å and 72.5° for $\langle Fe-S \rangle$ and $\langle S_{i1}-Fe-S_{i2} \rangle$ in the iron complex are atypical and the linear relationship previously postulated for the magnetic moments and Fe–S bond length in iron tris(dithio chelate) complexes does not seem to be universally applicable. The solvent molecules are orientated so as to minimize electrostatic repulsions with the complex. However, no strong hydrogen bonding interactions exist.

## Introduction

Structures of metal(III) dithiocarbamate complexes have been of considerable interest but have presented unusual difficulty. For example, Ewald, *et al.*,[1] commented on microscopic disorder in the iron(III) complexes after observing powder X-ray patterns from apparently well-formed crystals. Bernal, *et al.*,[2] were forced to abandon attempts to collect single-crystal X-ray data on several iron(III) dithiocarbamates because of extensive changes destroying the lattices within hours of withdrawing the crystals from the mother liquor. Similar difficulties occur in the cobalt(III) complexes in addition to a tendency to form twinned crystals. Part of the problem may be the escape of solvent molecules included or adducted in the crystals. It appears that well-formed single crystals of tris(dithiocarbamates) are more likely to be produced from solvated than from unsolvated complexes. The situation is further complicated by the $^6A_1-^2T_2$ electronic equilibrium in the iron(III) complexes, so that the spin state and the metal–ligand bond lengths depend on temperature, pressure, and other external factors.[3,4]

We report here the crystal structures of two analogous solvated complexes, tris(4-morpholinecarbodithioato-*S*,*S*')iron(III)–dichloromethane and tris(4-morpholinecarbodithioato-*S*,*S*')cobalt(III)–dichloromethane. These two represent a transition from $d^5$ to $d^6$ electronic configuration in an otherwise unaltered molecule, thereby permitting observation of the structural effect of inserting a single electron. Detailed comparison of the metal–ligand distances and angles is important to an understanding of the d-electron involvement in the bonding. For dithiocarbamates, the equilibrium between high spin and low spin must also affect the metal–ligand bonding and intercomparison between ferric complexes having different proportions of high- and low-spin components is important.

Further interest in tris(dithiocarbamate) solvates stems from two other observations: the nmr spectra, particularly in deuterated chloroform, show nonequivalencies in the R groups of many $Co(S_2CNR_2)_3$ complexes;[5] lattice effects were found to be of considerable importance in determining the position of the $^6A_1-^2T_2$ crossover,[2] and such lattice-disturbing phenomena as the presence or absence of solvates must strongly influence the magnetic properties. A detailed study in the range 1–200°K on the tris(pyrrolidinecarbodithioate-*S*,*S*') has shown this to be the case; the precise magnetic properties depend dramatically on the presence or absence of a solvent molecule in the lattice.[5]

## Experimental Section

The unsolvated complexes were prepared as previously described.[6] Evaporation of an equimolar mixture of dichloromethane–cyclohexane gave well-formed crystals of the solvated complexes. Analogs with other solvents were prepared in a like manner.

Low-resolution mass spectral data for these complexes were run on a Hitachi Perkin-Elmer RMU-6E mass spectrometer. Infrared spectra were recorded as Nujol mulls between potassium bromide plates over the range 4000–400 cm$^{-1}$ on a Perkin-Elmer 521 grating ir spectrophotometer. Densities were determined by flotation in aqueous potassium iodide. Melting points were measured on a Fisher-Johns melting point apparatus.

**Collection and Treatment of X-Ray Diffraction Data.** The crystal selected for the diffraction study on the cobalt complex was mounted on a glass fiber, normal to the (100) plane and attached to a eucentric goniometer head. The crystal was a parallelepiped bound by the (100) faces, 0.24 mm apart, the (010) faces, 0.20 mm apart, and the (001) faces, 0.20 mm apart. Crystals of the iron complex deteriorated rapidly in the atmosphere and the crystal used in data collection was

**Table I**

Cobalt 4-Morpholinecarbodithioate-*S*,*S*′

| | Atomic coordinates | | | Anisotropic temperature factors (×10⁴) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Atom | *x/a* | *y/b* | *z/c* | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
| Co | 0.2354 (1) | 0.2234 (2) | 0.4782 (2) | 44 (1) | 61 (2) | 58 (2) | 16 (1) | 8 (1) | 19 (1) |
| S11 | 0.1724 (2) | 0.0031 (3) | 0.4722 (3) | 62 (2) | 75 (4) | 96 (4) | 12 (2) | 31 (3) | 27 (3) |
| S12 | 0.3512 (2) | 0.1034 (3) | 0.4072 (3) | 47 (2) | 79 (4) | 106 (4) | 21 (2) | 21 (2) | 42 (3) |
| S21 | 0.3352 (1) | 0.3449 (2) | 0.7132 (2) | 55 (1) | 71 (2) | 67 (2) | 6 (1) | 6 (1) | 36 (2) |
| S22 | 0.3428 (2) | 0.4430 (2) | 0.5177 (2) | 72 (2) | 74 (2) | 59 (2) | 22 (2) | 18 (1) | 30 (1) |
| S31 | 0.0833 (2) | 0.2901 (2) | 0.4934 (2) | 70 (2) | 108 (3) | 56 (2) | 42 (2) | 20 (1) | 18 (2) |
| S32 | 0.1347 (2) | 0.1510 (2) | 0.2528 (2) | 56 (1) | 98 (3) | 57 (2) | 39 (2) | 16 (1) | 15 (2) |
| Cl1 | 0.8262 (3) | 0.8162 (5) | 0.0954 (5) | 156 (4) | 348 (8) | 459 (10) | 27 (4) | −38 (5) | 269 (8) |
| Cl2 | 0.9481 (3) | 0.6361 (4) | 0.1360 (4) | 248 (5) | 286 (7) | 206 (5) | 147 (5) | 34 (4) | 67 (5) |
| C11 | 0.2738 (5) | 0.9586 (7) | 0.4121 (7) | 50 (6) | 80 (9) | 68 (8) | 11 (6) | 6 (6) | 31 (8) |
| N1 | 0.2899 (5) | 0.8286 (6) | 0.3718 (7) | 75 (6) | 81 (8) | 125 (9) | 38 (6) | 35 (6) | 46 (7) |
| C12 | 0.2325 (7) | 0.7145 (9) | 0.3957 (9) | 103 (8) | 121 (12) | 128 (12) | 44 (8) | 34 (8) | 73 (10) |
| C13 | 0.2065 (8) | 0.5625 (8) | 0.2725 (10) | 117 (9) | 70 (11) | 173 (14) | 26 (8) | 16 (9) | 54 (10) |
| C14 | 0.3804 (7) | 0.8020 (9) | 0.3231 (10) | 84 (8) | 115 (12) | 189 (15) | 59 (8) | 23 (8) | 65 (11) |
| C15 | 0.3455 (7) | 0.6467 (10) | 0.2054 (10) | 92 (8) | 143 (14) | 212 (16) | 81 (9) | 56 (9) | 71 (12) |
| O1 | 0.3013 (5) | 0.5427 (6) | 0.2428 (7) | 144 (7) | 101 (8) | 209 (11) | 76 (6) | 42 (7) | 69 (8) |
| C21 | 0.3976 (8) | 0.4842 (7) | 0.6887 (7) | 44 (5) | 57 (8) | 60 (8) | 20 (5) | 14 (5) | 21 (7) |
| N2 | 0.4787 (5) | 0.6077 (6) | 0.7888 (6) | 59 (5) | 70 (8) | 73 (7) | 19 (5) | 22 (5) | 29 (7) |
| C22 | 0.5187 (6) | 0.6405 (8) | 0.9388 (7) | 72 (7) | 84 (10) | 74 (9) | 20 (6) | 0 (6) | 27 (8) |
| C23 | 0.5291 (7) | 0.7990 (8) | 0.0320 (8) | 85 (7) | 92 (10) | 78 (9) | 30 (7) | 31 (7) | 20 (8) |
| C24 | 0.5382 (6) | 0.7155 (7) | 0.7595 (8) | 71 (6) | 69 (9) | 108 (10) | 13 (6) | 43 (7) | 32 (8) |
| C25 | 0.5456 (7) | 0.8694 (8) | 0.8650 (9) | 122 (9) | 70 (10) | 118 (11) | 37 (8) | 40 (8) | 41 (9) |
| O2 | 0.5943 (4) | 0.8999 (5) | 0.0053 (5) | 87 (5) | 63 (7) | 111 (7) | 9 (5) | 30 (5) | 15 (6) |
| C31 | 0.0417 (6) | 0.2219 (7) | 0.3157 (7) | 57 (6) | 86 (9) | 64 (8) | 33 (6) | 21 (6) | 26 (7) |
| N3 | −0.0492 (5) | 0.2252 (7) | 0.2363 (6) | 77 (6) | 179 (11) | 78 (8) | 88 (7) | 21 (5) | 49 (8) |
| C32 | −0.1255 (10) | 0.2881 (16) | 0.2982 (11) | 192 (14) | 576 (35) | 154 (15) | 305 (20) | 120 (12) | 183 (20) |
| C33 | −0.2062 (9) | 0.3050 (15) | 0.2160 (10) | 131 (11) | 492 (32) | 97 (13) | 200 (17) | 23 (10) | 21 (17) |
| C34 | −0.0785 (9) | 0.1625 (14) | 0.0824 (9) | 165 (12) | 463 (29) | 75 (11) | 228 (16) | 54 (9) | 125 (15) |
| C35 | −0.1597 (10) | 0.1914 (16) | 0.0130 (10) | 164 (13) | 515 (34) | 104 (13) | 231 (18) | 35 (11) | 92 (18) |
| O3 | −0.2321 (4) | 0.2480 (6) | 0.0725 (6) | 83 (5) | 182 (10) | 139 (9) | 86 (6) | 4 (5) | 44 (8) |
| C | 0.9104 (9) | 0.7909 (13) | 0.2127 (11) | 99 (10) | 314 (10) | 194 (24) | 78 (18) | 36 (13) | 118 (18) |

| Atom | *x/a* | *y/b* | *z/c* | Atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|---|---|---|---|
| H112 | 0.155 | 0.730 | 0.413 | H122 | 0.450 | 0.570 | 0.950 |
| H212 | 0.275 | 0.725 | 0.490 | H222 | 0.590 | 0.630 | 0.950 |
| H113 | 0.170 | 0.475 | 0.300 | H123 | 0.430 | 0.800 | 0.013 |
| H213 | 0.140 | 0.540 | 0.179 | H223 | 0.560 | 0.830 | 0.150 |
| H114 | 0.395 | 0.880 | 0.283 | H124 | 0.500 | 0.700 | 0.650 |
| H214 | 0.420 | 0.810 | 0.400 | H224 | 0.620 | 0.720 | 0.760 |
| H115 | 0.270 | 0.630 | 0.120 | H125 | 0.450 | 0.870 | 0.840 |
| H215 | 0.400 | 0.610 | 0.165 | H225 | 0.560 | 0.950 | 0.833 |

mounted normal to the (100) plane in a sealed glass capillary. The crystal was also a parallelepiped, bounded by the faces (110) and $(\bar{1}\bar{1}0)$, separation 0.12 mm, (101) and $(\bar{1}0\bar{1})$, separation 0.30 mm, and $(10\bar{1})$ and $(\bar{1}01)$, separation 0.24 mm.

Preliminary precession photographs gave approximate cell dimensions and indicated both compounds were triclinic and nearly isomorphous. Diffraction data was collected at 298 K on a Picker four-circle computer-controlled diffractometer using monochromated Mo K$\alpha$ radiation as described previously.[7] We are grateful to Dr. R. F. Bryan for access to the instrument. Unit cell constants and their estimated standard deviations were derived from a least-squares refinment of preliminary values against the observed values of $\pm 2\theta$ for 30 strong, general reflections measured on the diffractometer as the mean values of $2\theta$ at half-height both left and right of the peak maxima. The final cell constants were as follows: (a) for the cobalt complex, $a$ = 13.079 (1) Å, $b$ = 10.682 (1) Å, $c$ = 11.493 (1) Å, $\alpha$ = 116.03 (1)°, $\beta$ = 105.04 (1)°, $\gamma$ = 99.45 (1)°, unit cell volume $V$ = 1310 Å$^3$; (b) for the iron complex, $a$ = 13.088 (3) Å, $b$ = 10.693 (1) Å, $c$ = 11.499 (1) Å, $\alpha$ = 116.08 (1)°, $\beta$ = 104.97 (1)°, $\gamma$ = 99.49 (2)°, $V$ = 1320 Å$^3$. The observed densities, for cobalt 1.57 (1) g cm$^{-3}$ and for iron 1.55 (2) g cm$^{-3}$, suggest $Z$ = 2 for $[M(S_2CNC_4H_8O)_3][CH_2Cl_2]$ ($d_{calcd}$(cobalt) = 1.59 g cm$^{-3}$, $d_{calcd}$(iron) = 1.58 g cm$^{-3}$).

Intensity data for both crystals were collected using the $\theta$–$2\theta$ scanning technique with symmetrical scan ranges of 2.75° and a scan speed of 2°/min. Background intensities were measured as a function of $2\theta$, in 30 steps, and interpolated values were used to calculate the background for each reflection during the data collection. Reflection data were considered significant if $I > 3.0\sigma^2(I)$ where $I = N - (t_s/t_b)B$, $\sigma^2(I) = N + (t_s/t_b)^2B$, and $N$ and $B$ are the counts accumulated during $t_s$ and $t_b$, the times taken in scan and background measurements, respectively. Insignificant reflections were automatically rejected by the computer.

All independent reflections in the range $4° \leq 2\theta \leq 50°$ were examined on the cobalt complex, 2662 being found significant. A total of 1550 significant reflections were recorded for the iron complex in the range $4° \leq 2\theta \leq 45°$. For each compound, the intensities of two standard reflections, monitored at 50 reflection intervals, showed no greater fluctuations than those expected from Poisson statistics during the data collections.

The intensity data were corrected for Lorentz and polarization effects and then for absorption.[8] Grid sizes of 8 × 8 × 8 and 8 × 6 × 8 were used for the cobalt ($\mu$ = 13.61) and iron ($\mu$ = 12.62) complexes, respectively. Transmission coefficient ranges were as follows: cobalt, 0.78–0.85; iron, 0.77–0.88.

**Structure Determination and Refinement.** Analysis of a standard Patterson map calculated from the data collected on the cobalt complex showed the ($2x$, $2y$, $2z$) coordinates of the Co–Co vector to be face centered at (0.5, 0.5, 0.0), corresponding to a cobalt position of (0.25, 0.25, 0.0) with the Co–S vectors lying approximately parallel to the molecular axes. As in the solution of the manganese diethyldithiocarbamate,[9] this configuration resulted in ambiguous phasing with several molecular configurations possible. Solution by direct methods was attempted using the FAME-MAGIC programming package.[10] Normalized structure factor amplitudes ("$|E|$ values") were calculated and tested for large $\Sigma_2$ interactions by FAME. Symbols were assigned to nine reflections having large $|E|$ values, six different parities, and many $\Sigma_2$ interactions. Application of the symbolic addition procedure by MAGIC assigned symbolic signs to 361 reflections. Three assignments of real (+ or −) signs to symbols had

Iron 4-Morpholinecarbodithioate-*S*,*S*'

| | Atomic coordinates | | | Anisotropic temperature factors ($\times 10^4$) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Atom | *x*/*a* | *y*/*b* | *z*/*c* | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
| Fe | 0.2471 (2) | 0.2166 (2) | 0.4854 (2) | 63 (2) | 92 (2) | 74 (3) | 17 (3) | 15 (2) | 23 (2) |
| S11 | 0.2073 (4) | −0.0082 (5) | 0.4982 (5) | 105 (5) | 120 (6) | 136 (6) | 15 (4) | 68 (4) | 45 (5) |
| S12 | 0.3627 (3) | 0.0776 (4) | 0.3876 (4) | 79 (4) | 123 (6) | 125 (6) | 34 (4) | 41 (4) | 63 (5) |
| S21 | 0.3504 (3) | 0.3625 (4) | 0.7353 (4) | 71 (6) | 104 (5) | 84 (4) | 12 (3) | 15 (4) | 48 (5) |
| S22 | 0.3643 (3) | 0.4473 (4) | 0.5330 (4) | 83 (4) | 102 (6) | 87 (5) | 15 (4) | 24 (4) | 37 (5) |
| S31 | 0.0744 (4) | 0.2709 (5) | 0.4898 (4) | 91 (4) | 171 (7) | 77 (5) | 46 (4) | 32 (4) | 31 (5) |
| S32 | 0.1356 (3) | 0.1486 (4) | 0.2502 (4) | 71 (4) | 150 (7) | 70 (5) | 40 (4) | 27 (4) | 30 (5) |
| Cl1 | 0.8408 (5) | 0.8406 (7) | 0.1334 (8) | 151 (8) | 282 (13) | 446 (17) | 27 (8) | −20 (9) | 165 (12) |
| Cl2 | 0.9639 (6) | 0.6486 (7) | 0.1415 (7) | 233 (9) | 306 (13) | 298 (12) | 142 (9) | 28 (9) | 63 (11) |
| C | 0.933 (2) | 0.816 (2) | 0.236 (2) | 18 (2) | 37 (5) | 15 (3) | 10 (3) | 6 (2) | 15 (3) |
| C11 | 0.300 (1) | 0.945 (1) | 0.412 (1) | 6 (1) | 11 (2) | 9 (2) | 3 (1) | 2 (1) | 4 (2) |
| N1 | 0.316 (1) | 0.816 (1) | 0.369 (1) | 10 (1) | 9 (2) | 14 (2) | 4 (1) | 4 (1) | 6 (2) |
| C12 | 0.271 (2) | 0.710 (2) | 0.409 (2) | 19 (2) | 10 (2) | 17 (3) | 3 (2) | 7 (2) | 7 (2) |
| C13 | 0.221 (1) | 0.552 (2) | 0.276 (2) | 13 (2) | 9 (2) | 18 (3) | 4 (2) | 6 (2) | 4 (2) |
| C14 | 0.391 (1) | 0.777 (2) | 0.292 (2) | 8 (2) | 15 (3) | 17 (3) | 5 (2) | 5 (2) | 2 (2) |
| C15 | 0.329 (2) | 0.623 (2) | 0.160 (2) | 18 (2) | 10 (3) | 15 (3) | 6 (2) | 7 (2) | 7 (2) |
| O1 | 0.299 (1) | 0.522 (1) | 0.211 (1) | 14 (1) | 15 (1) | 17 (2) | 7 (1) | 4 (1) | 4 (2) |
| C21 | 0.411 (1) | 0.491 (1) | 0.704 (1) | 5 (1) | 10 (2) | 4 (2) | 3 (1) | 2 (1) | 2 (2) |
| N2 | 0.490 (1) | 0.616 (1) | 0.804 (1) | 6 (1) | 10 (2) | 9 (2) | 2 (1) | 3 (1) | 3 (1) |
| C22 | 0.5346 (1) | 0.656 (2) | 0.953 (1) | 11 (2) | 11 (2) | 5 (2) | 1 (2) | 0 (1) | 2 (2) |
| C23 | 0.538 (1) | 0.815 (1) | 0.041 (1) | 14 (2) | 10 (2) | 5 (2) | 2 (2) | 4 (2) | 0 (2) |
| C24 | 0.553 (1) | 0.722 (1) | 0.773 (1) | 11 (2) | 5 (2) | 10 (2) | −1 (1) | 5 (2) | 3 (2) |
| C25 | 0.554 (1) | 0.876 (1) | 0.873 (2) | 15 (2) | 7 (2) | 14 (3) | 2 (2) | 6 (2) | 3 (2) |
| O2 | 0.604 (1) | 0.913 (1) | 0.017 (1) | 7 (1) | 2 (1) | 7 (1) | 0 (1) | 3 (1) | 0 (1) |
| C31 | 0.037 (1) | 0.213 (2) | 0.315 (1) | 5 (1) | 16 (2) | 8 (2) | 4 (2) | 2 (1) | 2 (2) |
| N3 | −0.053 (1) | 0.218 (2) | 0.239 (1) | 9 (1) | 30 (3) | 12 (2) | 13 (2) | 5 (1) | 8 (2) |
| C32 | −0.135 (2) | 0.272 (3) | 0.297 (2) | 22 (3) | 80 (8) | 19 (3) | 37 (4) | 15 (3) | 28 (5) |
| C33 | −0.201 (2) | 0.315 (3) | 0.226 (2) | 15 (3) | 52 (6) | 11 (3) | 20 (3) | 2 (2) | 9 (3) |
| C34 | −0.080 (2) | 0.160 (3) | 0.084 (2) | 21 (2) | 67 (7) | 10 (3) | 29 (4) | 5 (2) | 19 (4) |
| C35 | −0.151 (2) | 0.206 (3) | 0.030 (2) | 13 (2) | 49 (6) | 13 (2) | 19 (3) | 4 (2) | 10 (3) |
| O3 | −0.233 (1) | 0.255 (1) | 0.081 (1) | 11 (1) | 22 (2) | 17 (2) | 9 (1) | 0(1) | 8 (2) |

much greater internal consistency than any of the others. One of these assignments resulted in an *E* map which defined the $Co(S_2CNC_2)_3$ core of the molecule,[7] consistent with the Patterson map. A Fourier map in space group $P\bar{1}$ revealed the remainder of the ligand atoms, and isotropic block-diagonal least-squares refinement gave $R = 0.18$. Three large peaks still remained in the difference map, and from the relative peak heights, the geometry, and past history of the recrystallization process, the presence of dichloromethane of solvation was assumed. This was confirmed by subsequent measurement of other physical properties of the system and by the decrease in *R* (0.11). Introduction of anisotropic thermal parameters and a weighting scheme based on counting statistics with $p = 0.007$ gave $R = 0.049$.[7] The hydrogen atoms attached to ligands 1 and 2 were found in a further difference Fourier. However, the thermal parameters of the carbon atoms on ligand 3 were excessively large, and no hydrogen atoms were observed.

The apparent disorder in this ligand may be related to the breakdown of the crystalline lattice as the solvent escapes, the solvent–molecule contact distances being closest for the ligand (Table II). The solvent perturbation may cause random disorder, cause the two morpholyl rings in the unit cell to crystallize in independent conformations, or allow each ring to assume both conformations with 50% occupancy. To attempt to distinguish between these possibilities, a difference Fourier without the ligand 3 morpholyl ring was calculated. No distinct conformers were resolved. These atoms were thus reincluded in the atom list and the structure refined to convergence; the final $R = 0.042$ with $R_w = 0.044$. A final difference map was featureless, the maximum electron density being in the region of the morpholyl ring on ligand 3 and of the order of 0.6 of the hydrogen atom peaks.

The atomic positions for the iron structure were taken directly from the cobalt complex. From an initial *R* of 0.46, refinement with anisotropic temperature factors, and, in the final stages, a weighting scheme based on counting statistics with the final *p* being 0.006, the structure converged at $R = 0.063$ and $R_w = 0.061$. A difference map showed only diffuse electron density at the magnitude expected for hydrogen atoms, and hydrogen atoms were not included in the atomic model.

Scattering curve factors were derived from ref 11a for neutral Fe, Co, Cl, S, O, N, and C atoms, those for Co, Fe, Cl, and S being corrected for anomalous dispersion according to the values of ref 12. Scattering curve factors for the H atoms were taken from ref 11b.

The final atomic coordinates and anisotropic thermal parameters are given in Table I. The digits in parentheses are standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of normal least-squares refinement calculations. Tables of the observed structure factors are available.[13]

## Results and Discussion

A stereoscopic diagram of the molecular geometry of both structures is given in Figure 1 and includes the atomic numbering scheme used in the text. Interatomic distances and angles for the dithiocarbamate complex are detailed in Table II. Table II also contains the interatomic bond lengths and angles for the dichloromethane molecule and selected contact distances with the dithiocarbamate. Figure 2 indicates the molecular packing.

The geometry of the $CoS_6$ core can be compared to the two other reported structures of this type[14,15] (Table III). In spite

**Table II**

Interatomic Distances (Å) within the MS$_6$ Polyhedron

| | M = Co | M = Fe | | M = Co | M = Fe |
|---|---|---|---|---|---|
| M-S11 | 2.285 (2) | 2.452 (4) | M-S22 | 2.277 (2) | 2.423 (4) |
| M-S12 | 2.259 (2) | 2.431 (4) | M-S31 | 2.287 (2) | 2.432 (4) |
| M-S21 | 2.276 (2) | 2.424 (4) | M-S32 | 2.264 (2) | 2.420 (4) |
| S11-S12 | 2.802 (2) | 2.888 (6) | S22-S32 | 3.329 (2) | 3.524 (5) |
| S21-S22 | 2.806 (2) | 2.879 (5) | S11-S32 | 3.418 (2) | 3.896 (6) |
| S31-S32 | 2.805 (2) | 2.874 (5) | S12-S21 | 3.399 (2) | 3.883 (5) |
| S11-S21 | 3.320 (3) | 3.474 (5) | S22-S31 | 3.414 (3) | 3.747 (6) |
| S11-S31 | 3.397 (2) | 3.719 (6) | S11-S22 | 4.519 (2) | 4.762 (5) |
| S21-S31 | 3.421 (2) | 3.621 (6) | S21-S32 | 4.514 (2) | 4.776 (5) |
| S12-S22 | 3.300 (2) | 3.544 (5) | S12-S31 | 4.502 (2) | 4.755 (5) |
| S12-S32 | 3.228 (2) | 3.359 (5) | | | |
| ⟨M-S⟩ | 2.27 (2) | 2.44 (2) | $\langle S_{i1}-S_{j1}\rangle$ | 3.38 (6) | 3.6 (2) |
| $\langle S_{i1}-S_{i2}\rangle$ | 2.804 (2) | 2.88 (1) | $\langle S_{i2}-S_{j2}\rangle$ | 3.28 (6) | 3.5 (2) |

Interatomic Angles (deg) within the MS$_6$ Polyhedron

| | M = Co | M = Fe |
|---|---|---|
| S11-M-S12 | 76.1 (1) | 72.5 (1) |
| S21-M-S22 | 76.1 (1) | 72.9 (1) |
| S31-M-S32 | 76.1 (1) | 72.6 (1) |
| S11-M-S21 | 93.5 (1) | 90.9 (1) |
| S11-M-S31 | 96.0 (1) | 99.2 (2) |
| S21-M-S31 | 97.1 (1) | 96.4 (2) |
| S12-M-S22 | 93.4 (1) | 93.8 (1) |
| S12-M-S32 | 91.1 (1) | 87.6 (1) |
| S22-M-S32 | 94.3 (1) | 93.4 (1) |
| S11-M-S32 | 97.4 (1) | 106.2 (2) |
| S12-M-S21 | 97.1 (1) | 106.2 (1) |
| S22-M-S31 | 96.9 (1) | 101.0 (2) |
| S11-M-S22 | 164.3 (1) | 155.3 (2) |
| S21-M-S32 | 167.7 (1) | 160.8 (2) |
| S12-M-S31 | 164.1 (1) | 155.8 (2) |
| $\langle\zeta\rangle$ | 94.2 | 93.6 |
| $\langle\delta\rangle$ | 76.1 | 72.6 |
| $\phi$ | 57.8 | 57.3 |
| $\theta$ | 42.8 | 33.4 |

Interatomic Distances (Å) within the Ligands

| | Ligand 1 | | Ligand 2 | | Ligand 3 | |
|---|---|---|---|---|---|---|
| | M = Co | M = Fe | M = Co | M = Fe | M = Co | M = Fe |
| S1-C1 | 1.707 (6) | 1.75 (1) | 1.707 (6) | 1.70 (1) | 1.706 (6) | 1.72 (1) |
| S2-C2 | 1.703 (6) | 1.70 (1) | 1.703 (6) | 1.71 (1) | 1.708 (7) | 1.75 (1) |
| C1-N | 1.33 (1) | 1.32 (2) | 1.33 (1) | 1.32 (2) | 1.33 (1) | 1.28 (2) |
| N-C2 | 1.46 (1) | 1.49 (2) | 1.47 (1) | 1.50 (2) | 1.47 (1) | 1.48 (3) |
| N-C4 | 1.46 (1) | 1.47 (2) | 1.46 (1) | 1.51 (2) | 1.48 (1) | 1.52 (2) |
| C2-C3 | 1.52 (1) | 1.58 (2) | 1.52 (1) | 1.54 (2) | 1.33 (2) | 1.31 (3) |
| C4-C5 | 1.50 (1) | 1.54 (2) | 1.52 (1) | 1.54 (2) | 1.35 (2) | 1.27 (3) |
| C3-O | 1.41 (1) | 1.41 (2) | 1.42 (1) | 1.41 (2) | 1.38 (1) | 1.41 (2) |
| C5-O | 1.41 (1) | 1.46 (2) | 1.41 (1) | 1.45 (2) | 1.38 (1) | 1.42 (2) |

Interatomic Angles (deg) within the Ligands

| | Ligand 1 | | Ligand 2 | | Ligand 3 | |
|---|---|---|---|---|---|---|
| | M = Co | M = Fe | M = Co | M = Fe | M = Co | M = Fe |
| M-S1-C1 | 86.2 (2) | 85.6 (4) | 86.5 (2) | 85.9 (4) | 86.4 (2) | 87.7 (5) |
| M-S2-C1 | 87.1 (2) | 87.5 (5) | 86.6 (2) | 85.8 (4) | 87.1 (2) | 87.6 (5) |
| S1-C1-S2 | 110.5 (4) | 114.0 (7) | 110.7 (3) | 115.4 (7) | 110.4 (4) | 111.9 (7) |
| S1-C1-N | 125.4 (5) | 122.5 (10) | 124.8 (5) | 122.4 (9) | 125.3 (5) | 125.1 (11) |
| S2-C1-N | 124.1 (5) | 123.4 (10) | 124.5 (4) | 122.2 (9) | 124.2 (5) | 123.0 (10) |
| C1-N-C2 | 122.6 (6) | 121.7 (12) | 121.8 (5) | 123.5 (10) | 121.2 (6) | 121.9 (13) |
| C1-N-C4 | 121.1 (6) | 122.0 (11) | 122.8 (5) | 122.2 (10) | 121.4 (7) | 121.0 (14) |
| C2-N-C4 | 115.5 (6) | 116.0 (11) | 115.3 (5) | 113.9 (10) | 117.4 (7) | 117.1 (14) |
| N-C2-C3 | 110.2 (6) | 108.0 (12) | 109.1 (5) | 107.0 (10) | 117.5 (8) | 115.6 (17) |
| N-C4-C5 | 110.4 (6) | 109.1 (12) | 108.6 (6) | 106.8 (11) | 118.0 (9) | 114.9 (18) |
| C2-C3-O | 111.3 (7) | 110.1 (13) | 111.6 (5) | 112.4 (11) | 123.7 (10) | 122.7 (20) |
| C4-C5-O | 111.7 (7) | 106.1 (12) | 111.5 (6) | 111.0 (11) | 121.5 (8) | 124.8 (16) |
| C3-O-C5 | 110.8 (6) | 113.8 (11) | 110.4 (5) | 109.4 (10) | 119.4 (7) | 114.0 (13) |

**Table II** *(Continued)*

Closest Contact Distances (Å) between the Morpholyl Complex and Dichloromethane

| Atoms | | $x$ | $y$ | $z$ | Sym | M = Co | M = Fe |
|---|---|---|---|---|---|---|---|
| S11 | HC2 | −1 | −1 | 0 | | 2.63 | 2.82 |
| C11 | HC2 | −1 | 0 | 0 | | 3.65 | 3.65 |
| C12 | Cl2 | −1 | 0 | 0 | | 3.86 | 4.13 |
| C13 | Cl2 | −1 | 0 | 0 | | 3.77 | 3.82 |
| H213 | Cl2 | 0 | 0 | −1 | $\bar{1}$ | 3.00 | 3.37 |
| H112 | Cl2 | 1 | 0 | 0 | | 3.23 | 3.73 |
| C22 | Cl1 | 0 | 0 | 1 | | 3.76 | 3.70 |
| C23 | Cl1 | 0 | 0 | 0 | | 3.80 | 3.74 |
| H222 | Cl1 | 0 | 0 | 1 | | 2.98 | 3.34 |
| H223 | Cl1 | 0 | 0 | 1 | | 3.76 | 3.61 |
| S31 | HC1 | 0 | 0 | 0 | $\bar{1}$ | 2.91 | 2.76 |
| S32 | HC2 | −1 | −1 | 0 | | 3.30 | 3.13 |
| C31 | HC2 | −1 | −1 | 0 | | 3.32 | 3.14 |
| C31 | Cl1 | −1 | −1 | 0 | | 3.96 | 3.65 |
| N3 | Cl1 | 0 | −1 | 0 | | 3.77 | 3.56 |
| N3 | HC2 | 0 | −1 | 0 | | 3.88 | 3.79 |
| C34 | Cl1 | 0 | −1 | 0 | | 3.71 | 3.73 |
| H134 | Cl1 | 0 | 1 | 0 | | 2.85 | 3.02 |

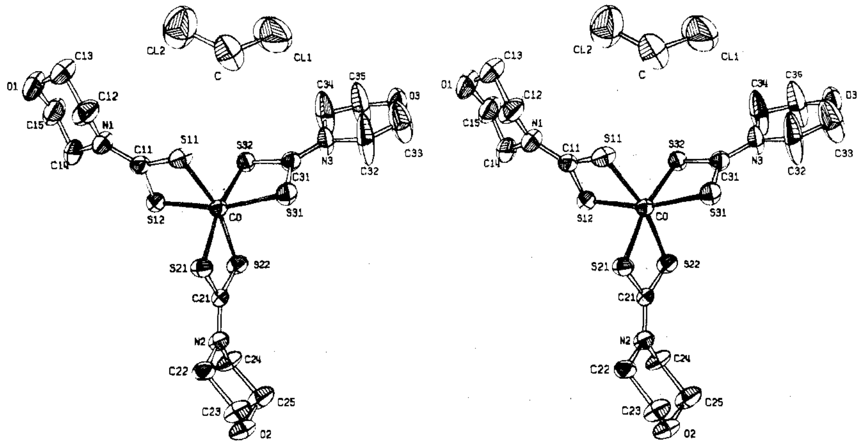

**Figure 1.**

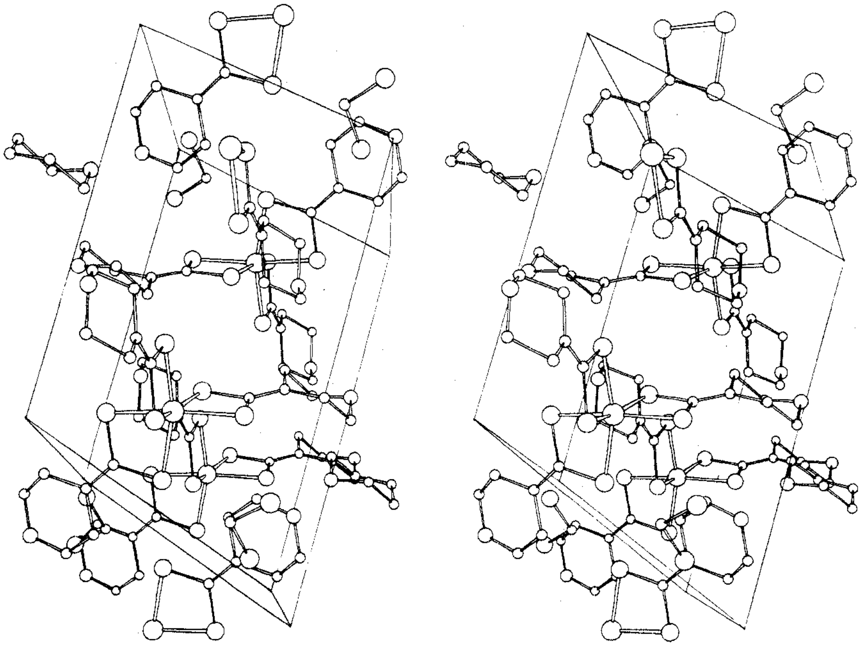

**Figure 2.**

of the wide range of ligand field strengths[16a] and the perturbing effects of the solvent molecule in the morpholyl complexes, the geometries are identical.[16b] These complexes provide a convenient reference standard with which to compare the iron

**Table III.** Comparison of $CoS_6$ and $FeS_6$ Structural and Magnetic Parameters

| Compd[a] | | Space group | $R$ factor | ⟨M–S⟩, Å | ⟨δ⟩, deg | ⟨ζ⟩, deg | 2θ, deg | ⟨C–N⟩, Å | μ, BM | Ref |
|---|---|---|---|---|---|---|---|---|---|---|
| CoEtXan | | $R\bar{3}$ | 0.090 | 2.28 | 76.1 | 94.3 | 42.4 | | | 14 |
| $CoEt_2dtc$ | | $C2/c$ | 0.062 | 2.26 | 76.2 | 94.2 | 43.0 | 1.32 | | 15 |
| Co(morph)cdt | | $P\bar{1}$ | 0.044 | 2.27 | 76.1 | 94.2 | 42.8 | 1.33 | | *b* |
| FeEtXan | | $R\bar{3}$ | 0.067 | 2.32 | 75.5 | 94.3 | 41.2 | | 2.1 | 18 |
| $FeEt_2dtc$ | 79 K | $C2/n$ | 0.068 | 2.31 | 75.0 | 93.4 | 40.5 | 1.32 | 2.2 | 17 |
| | 297 K | $P2_1/c$ | 0.054 | 2.36 | 74.3 | 93.8 | 37.6 | 1.33 | 4.2 | 17 |
| Fe(morph)cdt | | $P\bar{1}$ | 0.063 | 2.44 | 72.6 | 93.6 | 33.4 | 1.31 | 5.1 | *b* |
| Fe(*n*-Bu)$_2$dtc | | $C2/c$ | 0.10 | 2.42 | 72.8 | 93.5 | 33.2 | 1.41 | 5.3 | 19 |
| Fe(pyr)cdt | | $P2_1/n$ | 0.13 | 2.41 | 74.5 | 93.5 | 38.6 | 1.31 | 5.9 | 4 |
| FeMe(Ph)dtc | | $P2_1/a$ | 0.09 | 2.32 | 75.1 | 94.1 | 40.4 | 1.37 | 2.9 | 4 |

[a] Abbreviations: Xan, xanthate; dtc, dithiocarbamate; cdt, carbodithioate. [b] This work.

complexes, which are nearly structurally isomorphous for each ligand type. The removal of one d electron in passing from the $d^6$ Co(III) complexes to $d^5$ Fe(III) complexes has a dramatic effect on the $MS_6$ molecular configuration, the M–S bond length increasing from about 0.05 Å for low-spin $d^5$ with one unpaired electron to 0.17 Å for high-spin $d^5$ configurations.

High-pressue studies[1,3] have shown that change from low- to high-spin $d^5$ is accompanied by a volume decrease of about 6 cm$^3$/mol, corresponding to an average 0.1 Å Fe–S bond length increase in all the dithiocarbamates. It appeared possible to produce a linear relation between the Fe–S bond lengths in ferric dithio chelates, in general, and their magnetic moments, $\mu_{eff}$. This expected trend is observed in the diethyl complex, whose structure has been determined at two temperatures,[17] and more approximately in the structures of low-spin complexes.[4,17,18] However, of the two known high-spin structures,[4,19] the pyrrolidinecarbodithioate-*S,S'* fits poorly to the line relating ⟨Fe–S⟩ and $\mu_{eff}$, and the di-*n*-butyl complex gives even poorer agreement. A less pronounced trend in the average angular values has similar exceptions. As in the di-*n*-butyl complex, ⟨δ⟩ for the iron morpholyl is some 3.0° less than the normal values, and ⟨Fe–S⟩, at 2.44 Å is longer than ⟨Fe–S⟩ in the purely high spin pyrrolidyl complex in spite of the lower $\mu_{eff}$.

It is noteworthy that the solid-state magnetic moments for both the di-*n*-butyl and morpholyl complexes are ~1.0 BM higher than the solution values. It has been postulated earlier that lattice forces may play an important role in determining the properties of the complexes,[3] and very high sensitivity measurements on the solvated complex to determine the sensitivity of the magnetic moment to the nature of the solvate have been commenced.

In these complexes, the lattice interactions and packing modes are determined by the configuration of the peripheral substituent groups R and R', attached to the nitrogen, and in the 4-morpholinecarboditthioate-*S,S'*, there are two atypical features. These are the presence of the dichloromethane molecule and the chair conformation of the morpholyl ring resulting in the β carbons being directed out of the ligand plane on the same side. Unlike the trans configuration assumed by the tris(diethyldithiocarbamate) complexes,[4,14,17] steric protection on both sides of the conjugated ligand plane by the β-methyl groups does not exist, and strong static interaction of one side of the plane with the solvent is possible.

A similar situation may occur in the di-*n*-butyl complex with one pair of ligands assuming a cis configuration and the terminal carbon atoms interacting with adjacent molecules. Certainly, the carbon chains in bis(di-*n*-butyldithiocarbamato)copper(II) interact in this manner.[20]

Although stable solid-state adducts are confined to molecules of this type, it is likely that rotation about the N–C bond in solution allows a dynamic interaction of the dithiocarbamate ligand and the solvent, giving rise to the temperature-dependent effects observed in the proton nmr spectra.[6]

**Table IV.** Density Measurements on Cobalt Tris(4-morpholinecarbodithioate-*S,S'*) Solvate

| | Density,[a] cm$^{-3}$ | |
|---|---|---|
| Solvent of crystallizn | Found | Calcd[b] |
| $CH_2Cl_2$ | 1.57 (13.9) | 1.60 (13.5) |
| Unsolvated | 1.37 | 1.38 |
| Benzene | 1.36 | 1.38 |
| $CHCl_3$ | 1.51 (17.0) | 1.68 (17.9) |

[a] Weight loss (%) in parentheses. [b] Assuming $V = 1310$ Å$^3$ in each case.

These structural results suggested that adduct formation should occur with polar molecules. This was confirmed experimentally from melting point behavior, density measurements, and infrared and low-resolution mass spectra. Nonsolvated complex only was formed from solution in benzene, carbon tetrachloride, and carbon disulfide.

Melting point behavior provided the most rapid and convenient method of determining the presence of solvent. Breakdown of the crystalline lattice with concomitant escape of solvent was observed in the temperature range 80–90° for the iron complex and 120–130° for cobalt, the higher values applying to samples that were visibly crystalline rather than finely powdered. The melting point of the remaining solid was that of the unsolvated complex (cobalt, 305°; iron, >300° dec). Low-resolution mass spectra provided further direct evidence of solvation, the ionization fragment peaks due to the solvent appearing to the detector first, followed at higher temperatures by ionization of the main complex. Dichloromethane and chloroform were recognized by their characteristic ion current peaks, the most prominent of which are $CH_2Cl^+$ and $CH_2Cl_2^+$ for dichloromethane and $CHCl_2^+$ and $CCl_2^+$ for chloroform. At higher temperaures, typical dithiocarbamate peaks are observed including the molecular ion and other characteristic peaks such as $M(S_2CNC_4H_8O)_2(SCNC_4H_8O)^+$, $M(S_2CNC_4H_8O)_2^+$, $M(S_2CNC_4H_8O)(SCNC_4H_8)^+$, $M(SCNC_4H_8O)_2^+$, $(S_2CNC_4H_8O)_2^+$, $(SCNC_4H_8O)(S_2CNC_4H_8O)$, $(SCNC_4H_8O)_2^+$, $M(S_2CNC_4H_8OH)^+$, $HS_2CNC_4H_8O$, $SCNC_4H_8O$, $NC_4H_8O$, and $CS_2$.

Comparison of the measured densities of the dichloromethane solvate and the unsolvated species with values calculated assuming $V = 1320$ Å$^3$ (Table IV) indicates the solvent volume remains unoccupied in the unsolvated compound. Clearly crystallization from benzene produces unsolvated complex, and the "dichloromethane volume" is again unoccupied. Differences in the observed and calculated values for the chloroform solvate suggest either an increase in unit cell volume or perhaps less than 100% occupancy. Weight losses on heating the dichloromethane and chloroform solvates at 100° to constant weight (overnight), suggest 1:1 solvation.

Infrared spectra were recorded for the unsolvated iron and cobalt 4-morpholinecarbodithioates-*S,S'* and for the adducts of dichloromethane, chloroform, and acetone with cobalt 4-morpholinecarbodithioates-*S,S'*. The presence of the dichloromethane and chloroform could not be ascertained from the spectra as the characteristic bands for these compounds coincided with strong bands due to the complex. In the acetone solvate, however, an isolated band at 1707 $cm^{-1}$ and a shoulder at 530 $cm^{-1}$ indicated the presence of acetone.

Within experimental error (2 $cm^{-1}$), the ligand vibrational frequencies contained in the region 1500–500 $cm^{-1}$ were unchanged, either by the presence of the included solvent or by substituting iron for cobalt. Such results are consistent with the structural data where the ligand geometry of the system is relatively unchanged, and no strong bonding interactions occur between the complex molecule and the solvent included in the lattice.

**Registry No.** Co[(morph)cdt]$_3$·$CH_2Cl_2$, 53179-05-8; Fe[(morph)cdt]$_3$·$CH_2Cl_2$, 53179-06-9.

**Supplementary Material Available.** Listings of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers of this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number AIC40400+.

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