agreement should not be expected, since τ is not as good a measure of tetrahedral distortion in this case and because there is a perturbing influence from the apical Cu–O bond. However, ignoring the effect of the Cu–O–Cu bridging angle[16] and the limitations of τ as a measure of tetrahedral distortion, the effect of the weak apical Cu–O bond is seen to be in the same direction as increasing τ: the bond reduces the superexchange overlap. The effect of such apical bonds cannot be specified more precisely in the absence of data on any other complexes of this type. The Cu–O–Cu bridging angle does not differ sufficiently from the others in Table V to attribute to it any effect upon *J*.

The use of $Ni(etsal)_2$ in place of $Cu(etsal)_2$ to form crystals of $[Cu(etsal)NO_3]_2$ (identical, from infrared spectroscopy, with the conventionally prepared complex[5]) follows the observation of ligand exchange in this type of synthesis. The analogous nickel dimer, also formed in the reaction, remains in solution unless some solvent is evaporated.

$$2Cu(NO_3)_2 + 2Ni(etsal)_2 + 2(solvent) \rightarrow [Cu(etsal)NO_3]_2 + [Ni(etsal)NO_3(solvent)]_2$$

Acknowledgment. Support recieved for instrumentation under NSF Grant GP-41679 is gratefully acknowledged.

Registry No. $[Cu(etsal)NO_3]_2$, 57428-26-9; $Ni(etsal)_2$, 13987-25-2.

Supplementary Material Available: Listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

References and Notes

(1) E. Sinn and C. M. Harris, *Coord. Chem. Rev.*, **4**, 391 (1968), and references cited therein.
(2) E. Sinn and W. T. Robinson, *J. Chem. Soc., Chem. Commun.*, 359 (1972).
(3) R. M. Countryman, W. T. Robinson, and E. Sinn, *Inorg. Chem.*, **13**, 2013 (1974).
(4) P. Gluvchinsky, G. M. Mockler, P. C. Healy, and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 1156 (1974).
(5) J. O. Miners, E. Sinn, R. B. Coles, and C. M. Harris, *J. Chem. Soc., Dalton Trans.*, 1149 (1972).
(6) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(7) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 511 (1965).
(8) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(9) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(10) Supplementary material.
(11) A. H. Ewald and E. Sinn, *Inorg. Chem.*, **8**, 537 (1969).
(12) P. C. Healy, G. M. Mockler, D. P. Freyberg, and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 691 (1975).
(13) R. J. Majeste and L. M. Trefonas, *Inorg. Chem.*, **13**, 1062 (1974).
(14) R. J. Butcher and E. Sinn, *J. Chem. Soc., Chem. Commun.*, 832 (1975).
(15) E. Sinn, *J. Chem. Soc., Chem. Commun.*, 665 (1975); *Inorg. Chem.*, preceding paper in this issue.
(16) D. J. Hodgson, *Prog. Inorg. Chem.*, **19**, 173 (1975).

Contribution from the Chemistry Department,
University of Virginia, Charlottesville, Virginia 22901

Solvent Effects in Dithiocarbamate Complexes. Structures of Tris(1-pyrrolidinecarbodithioato)iron(III)–, -chromium(III)–, and -iridium(III)–Hemibenzene. Direct Comparison of $3d^5$, $3d^3$, and $5d^6$ Coordinations

EKK SINN

Received August 11, 1975 AIC50603D

The crystal and molecular structures of the title complexes were solved by single-crystal x-ray diffraction using computer techniques. Crystal data: $Fe(S_2CNC_4H_8)_3 \cdot 0.5C_6H_6$ space group $P2_1/n$, $Z = 4$, $a = 16.356$ (3) Å, $b = 14.933$ (2) Å, $c = 10.191$ (2) Å, $\beta = 90.3$ (1)°, $V = 2489$ Å^3, $R = 4.5\%$, 3276 reflections; $Cr(S_2CNC_4H_8)_3 \cdot 0.5C_6H_6$, space group $P2_1/n$, $Z = 4$, $a = 16.490$ (5) Å, $b = 15.071$ (7) Å, $c = 9.909$ (6) Å, $\beta = 91.01$ (3)°, $V = 2462$ Å^3, $R = 4.4\%$, 1599 reflections; $Ir(S_2CNC_4H_8)_3 \cdot 0.5C_6H_6$, space group $P2_1/n$, $Z = 4$, $a = 16.72$ (1) Å, $b = 15.272$ (5) Å, $c = 9.602$ (2) Å, $\beta = 91.54$ (3)°, $V = 2451$ Å^3, $R = 6.4\%$, 1646 reflections. The complex molecules are monomeric and well separated, but the solvating benzene molecule lies on a center of symmetry. The benzene-solvated Fe complex has a slightly greater (0.03 Å) average metal–ligand bond length than the previously studied, unsolvated, complex. This is unexpected, since the former compound exhibits a high-spin–low-spin equilibrium at low temperatures, while the latter is purely high spin. Qualitatively only, this complex conforms with the expectation that increased population of the high-spin state in a series of complexes with slight structural differences corresponds to increased metal–ligand bond length. The Ir complex is closest to having an octahedral ligand environment, but all are trigonally distorted from octahedral symmetry. The average metal–ligand distance increases with increasing number of unpaired electrons, and this effect overrides that of increasing atomic number vertically downward in the periodic table: $\langle Fe–S \rangle = 2.434$ Å ($t_2{}^3e^2$), $\langle Cr–S \rangle = 2.404$ Å ($t_2{}^3$), $\langle Ir–S \rangle = 2.38$ Å ($t_2{}^6$).

Introduction

Tris(1-pyrrolidinecarbodithioato-*S*,*S*')iron(III), FePDC, when obtained in chloroform, exhibits intermolecular antiferromagnetic interactions which are presumed to act via unpaired electron spin density delocalized onto the ligand atoms.[1,2] The ground state is $^6A_1$, and there is no sign of a spin-state crossover as observed in related ferric dithiocarbamates.[3] Formed from benzene, the same complex does show evidence of a spin-state crossover, though the equilibrium is toward the high-spin side over most of the temperature range,[2] and it is effectively high spin ($^6A_1$) at room temperature.

The crystal structure of one form of the complex, from chloroform–ethanol, has been determined.[4] However, high accuracy was not obtainable at that time ($R = 13\%$) because a composite film data set from two crystals had to be used. No molecules of solvent were observed in the crystals, though only solvated molecules were obtained in the present study immediately after removal of crystals from several solvents. The magnetic properties of the chloroform solvate $FePDC \cdot CHCl_3$, I, and the unsolvated FePDC, II, formed by removal of the solvent, are the same.[1,2] The benzene solvate $2FePDC \cdot C_6H_6$, III, differs in not losing the solvent readily, in addition to the magnetic properties. The structure of this

Table I. Positional and Thermal Parameters[a] and Their Estimated Standard Deviations

(a) FePDC·0.5C_6H_6

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	0.22746 (4)	0.15953 (4)	0.01992 (7)	0.00430 (3)	0.00517 (3)	0.01345 (8)	0.00151 (6)	−0.00205 (8)	−0.00079 (9)
S(11)	0.10286 (9)	0.10351 (9)	−0.0876 (1)	0.00530 (7)	0.00612 (7)	0.0149 (2)	0.0003 (1)	−0.0008 (2)	−0.0037 (2)
S(12)	0.11529 (9)	0.18518 (11)	0.1708 (1)	0.00535 (7)	0.00994 (9)	0.0121 (1)	0.0028 (1)	−0.0015 (2)	−0.0023 (2)
S(21)	0.21476 (9)	0.29827 (8)	−0.1035 (1)	0.00531 (6)	0.00565 (6)	0.0144 (1)	0.0010 (1)	−0.0040 (2)	0.0002 (2)
S(22)	0.31866 (9)	0.26757 (9)	0.1253 (1)	0.00541 (6)	0.00585 (6)	0.0169 (2)	0.0017 (1)	−0.0069 (2)	−0.0009 (2)
S(31)	0.32215 (9)	0.08854 (8)	−0.1311 (1)	0.00568 (6)	0.00527 (6)	0.0128 (1)	0.0019 (1)	−0.0001 (2)	0.0014 (2)
S(32)	0.28670 (9)	0.03187 (9)	0.1359 (1)	0.00552 (6)	0.00658 (7)	0.0131 (1)	0.0019 (1)	0.0006 (2)	0.0017 (2)
N(1)	−0.0264 (3)	0.1589 (3)	0.0491 (4)	0.0050 (2)	0.0064 (2)	0.0136 (5)	−0.0000 (4)	0.0004 (5)	0.0019 (6)
N(2)	0.3094 (3)	0.4245 (3)	0.0001 (4)	0.0049 (2)	0.0055 (2)	0.0158 (5)	−0.0005 (3)	−0.0007 (5)	−0.0011 (5)
N(3)	0.3865 (2)	−0.0579 (2)	−0.0235 (4)	0.0040 (2)	0.0046 (2)	0.0134 (4)	0.0001 (3)	−0.0006 (5)	−0.0003 (5)
C(11)	0.0535 (3)	0.1490 (3)	0.0461 (5)	0.0050 (2)	0.0053 (2)	0.0127 (5)	0.0007 (4)	0.0004 (6)	0.0022 (6)
C(12)	−0.0821 (3)	0.1339 (3)	−0.0588 (5)	0.0050 (3)	0.0067 (3)	0.0180 (7)	−0.0024 (5)	−0.0028 (7)	−0.0002 (8)
C(13)	−0.1648 (4)	0.1639 (5)	−0.0039 (8)	0.0043 (3)	0.0114 (4)	0.0419 (13)	0.0002 (6)	−0.0086 (10)	−0.0158 (13)
C(14)	−0.1527 (4)	0.2232 (6)	0.0989 (7)	0.0068 (4)	0.0194 (7)	0.0224 (10)	0.0064 (9)	0.0050 (10)	−0.0025 (15)
C(15)	−0.0719 (4)	0.2014 (5)	0.1572 (5)	0.0051 (3)	0.0131 (5)	0.0144 (6)	0.0015 (6)	0.0038 (7)	0.0015 (9)
C(21)	0.2839 (3)	0.3404 (3)	0.0065 (5)	0.0038 (2)	0.0056 (2)	0.0145 (6)	0.0015 (4)	−0.0010 (6)	−0.0011 (6)
C(22)	0.3724 (4)	0.4638 (4)	0.0874 (6)	0.0056 (3)	0.0072 (3)	0.0189 (7)	−0.0010 (5)	−0.0015 (8)	−0.0034 (8)
C(23)	0.3942 (4)	0.5494 (4)	0.0159 (7)	0.0074 (3)	0.0078 (3)	0.0253 (9)	−0.0043 (6)	0.0001 (10)	−0.0048 (9)
C(24)	0.3160 (4)	0.5772 (4)	−0.0492 (7)	0.0087 (4)	0.0060 (3)	0.0261 (10)	−0.0014 (6)	0.0035 (10)	0.0021 (9)
C(25)	0.2800 (4)	0.4900 (3)	−0.0963 (5)	0.0064 (3)	0.0061 (3)	0.0177 (7)	−0.0001 (5)	0.0004 (8)	0.0016 (7)
C(31)	0.3379 (3)	0.0119 (3)	−0.0073 (5)	0.0039 (2)	0.0044 (2)	0.0137 (5)	−0.0004 (4)	−0.0024 (6)	−0.0003 (6)
C(32)	0.4278 (3)	−0.0791 (3)	−0.1475 (5)	0.0051 (2)	0.0058 (2)	0.0154 (6)	0.0007 (4)	−0.0007 (7)	−0.0018 (7)
C(33)	0.4626 (4)	−0.1699 (4)	−0.1254 (6)	0.0083 (3)	0.0102 (4)	0.0205 (8)	0.0107 (5)	−0.0034 (9)	−0.0026 (10)
C(34)	0.4525 (5)	−0.1925 (4)	0.0081 (7)	0.0122 (5)	0.0065 (3)	0.0269 (10)	0.0071 (6)	0.0073 (12)	0.0035 (10)
C(35)	0.4028 (3)	−0.1263 (3)	0.0770 (5)	0.0045 (2)	0.0051 (2)	0.0177 (7)	0.0007 (4)	−0.0024 (7)	0.0035 (7)
C(1)	0.0121 (4)	0.4105 (4)	−0.0143 (6)	0.0077 (3)	0.0076 (3)	0.0203 (8)	0.0045 (6)	0.0044 (9)	0.0021 (9)
C(2)	0.0652 (4)	0.4591 (4)	0.0593 (5)	0.0065 (3)	0.0104 (4)	0.0156 (7)	0.0056 (6)	0.0031 (8)	0.0062 (9)
C(3)	0.0531 (4)	0.5486 (4)	0.0738 (6)	0.0064 (3)	0.0102 (4)	0.0180 (8)	0.0002 (6)	0.0001 (8)	−0.0014 (10)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(12A)	−0.0807 (11)	0.0667 (11)	−0.081 (2)	5.0	H(25A)	0.2955 (7)	0.4746 (7)	−0.187 (1)	5.0
H(12B)	−0.0694 (11)	0.1664 (11)	−0.145 (2)	5.0	H(25B)	0.2165 (7)	0.4953 (7)	−0.094 (1)	5.0
H(13A)	−0.1986 (14)	0.1049 (14)	0.018 (2)	5.0	H(32A)	0.4738 (7)	−0.0363 (7)	−0.164 (1)	5.0
H(13B)	−0.2004 (14)	0.1893 (14)	−0.085 (2)	5.0	H(32B)	0.3893 (7)	−0.0792 (7)	−0.223 (1)	5.0
H(14A)	−0.2016 (18)	0.2172 (20)	0.172 (3)	5.0	H(33A)	0.5206 (8)	−0.1728 (9)	−0.147 (1)	5.0
H(14B)	−0.1591 (18)	0.2900 (20)	0.074 (3)	5.0	H(33B)	0.4306 (8)	−0.2150 (9)	−0.181 (1)	5.0
H(15A)	−0.0763 (11)	0.1604 (13)	0.239 (2)	5.0	H(34A)	0.5072 (10)	−0.2014 (9)	0.046 (2)	5.0
H(15B)	−0.0418 (11)	0.2582 (13)	0.193 (2)	5.0	H(34B)	0.4224 (10)	−0.2541 (9)	0.008 (2)	5.0
H(22A)	0.4249 (11)	0.4258 (12)	0.092 (2)	5.0	H(35A)	0.4362 (6)	−0.0996 (7)	0.153 (1)	5.0
H(22B)	0.3547 (11)	0.4750 (12)	0.181 (2)	5.0	H(35B)	0.3513 (6)	−0.1522 (7)	0.115 (1)	5.0
H(23A)	0.4363 (9)	0.5412 (9)	−0.044 (1)	5.0	H(1)	0.0255 (8)	0.3448 (8)	−0.035 (1)	5.0
H(23B)	0.4064 (9)	0.5969 (9)	0.085 (1)	5.0	H(2)	0.1112 (7)	0.4271 (9)	0.103 (1)	5.0
H(24A)	0.3335 (8)	0.6170 (8)	−0.126 (1)	5.0	H(3)	0.0927 (9)	0.5842 (10)	0.127 (1)	5.0
H(24B)	0.2811 (8)	0.6124 (8)	0.010 (1)	5.0					

(b) CrPDC·0.5C_6H_6

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	0.2315 (1)	0.1676 (1)	0.0191 (2)	0.00338 (7)	0.00392 (9)	0.0134 (2)	0.0010 (2)	−0.0018 (2)	−0.00121 (3)
S(11)	0.1100 (2)	0.1080 (2)	−0.0853 (3)	0.0039 (1)	0.0046 (2)	0.0143 (4)	0.0002 (3)	−0.0005 (4)	−0.0040 (5)
S(12)	0.1245 (2)	0.1985 (2)	0.1729 (3)	0.0042 (1)	0.0065 (2)	0.0121 (4)	0.0013 (3)	−0.0013 (4)	−0.0042 (5)
S(21)	0.2160 (2)	0.3037 (2)	−0.1029 (3)	0.0040 (1)	0.0044 (2)	0.0144 (4)	0.0009 (3)	−0.0034 (4)	−0.0004 (5)
S(22)	0.3258 (2)	0.2707 (2)	0.1233 (3)	0.0040 (1)	0.0038 (2)	0.0179 (4)	0.0011 (3)	−0.0061 (4)	−0.0007 (5)
S(31)	0.3250 (2)	0.1000 (2)	−0.1330 (3)	0.0041 (1)	0.0038 (2)	0.0137 (4)	0.0013 (3)	0.0007 (4)	0.0017 (5)
S(32)	0.2828 (2)	0.0380 (2)	0.1340 (3)	0.0039 (1)	0.0051 (2)	0.0135 (4)	0.0015 (3)	0.0005 (4)	0.0014 (5)
N(1)	−0.0170 (4)	0.1602 (5)	0.0553 (7)	0.0046 (4)	0.0046 (5)	0.0116 (1)	0.0000 (8)	0.0005 (1)	−0.0048 (1)
N(2)	0.3125 (4)	0.4288 (5)	0.0025 (8)	0.0034 (4)	0.0053 (5)	0.0175 (1)	0.0005 (8)	−0.0016 (1)	0.0016 (1)
N(3)	0.3821 (4)	−0.0500 (5)	−0.0274 (7)	0.0031 (4)	0.0043 (5)	0.0122 (1)	−0.0010 (7)	0.0009 (1)	0.0022 (1)
C(11)	0.0634 (5)	0.1543 (7)	0.0488 (9)	0.0028 (4)	0.0065 (7)	0.0129 (1)	0.0008 (10)	0.0017 (1)	−0.0014 (2)
C(12)	−0.0723 (5)	0.1313 (6)	−0.0548 (10)	0.0034 (5)	0.0055 (7)	0.0171 (2)	−0.0002 (11)	−0.0005 (2)	−0.0059 (2)
C(13)	−0.1553 (6)	0.1544 (8)	−0.0016 (12)	0.0039 (5)	0.0099 (9)	0.0350 (2)	−0.0009 (11)	−0.0054 (2)	−0.0146 (3)
C(14)	−0.1442 (6)	0.2221 (8)	0.0964 (13)	0.0036 (5)	0.0116 (10)	0.0287 (2)	0.0004 (11)	0.0054 (2)	−0.0043 (3)
C(15)	−0.0625 (6)	0.2038 (7)	0.1645 (11)	0.0039 (5)	0.0083 (8)	0.0184 (2)	−0.0011 (11)	0.0017 (2)	−0.0010 (2)
C(21)	0.2872 (5)	0.3447 (6)	0.0083 (9)	0.0029 (4)	0.0050 (6)	0.0122 (1)	0.0038 (9)	−0.0016 (1)	0.0005 (2)
C(22)	0.3753 (6)	0.4675 (7)	0.0903 (10)	0.0032 (5)	0.0057 (7)	0.0185 (2)	−0.0004 (11)	−0.0014 (1)	−0.0051 (2)
C(23)	0.3956 (6)	0.5528 (7)	0.0171 (11)	0.0056 (6)	0.0043 (7)	0.0256 (2)	−0.0036 (10)	0.0017 (2)	−0.0010 (2)
C(24)	0.3166 (6)	0.5815 (7)	−0.0427 (11)	0.0059 (6)	0.0038 (7)	0.0236 (2)	−0.0006 (10)	0.0010 (2)	0.0039 (2)
C(25)	0.2790 (6)	0.4949 (6)	−0.0923 (10)	0.0040 (5)	0.0046 (7)	0.0193 (2)	−0.0016 (11)	0.0015 (2)	0.0025 (2)
C(31)	0.3342 (5)	0.0221 (6)	−0.0091 (9)	0.0029 (4)	0.0035 (6)	0.0117 (1)	−0.0021 (9)	−0.0016 (1)	−0.0010 (2)
C(32)	0.4255 (5)	−0.0679 (6)	−0.1524 (10)	0.0034 (5)	0.0042 (6)	0.0151 (2)	−0.0005 (10)	−0.0017 (1)	0.0004 (2)
C(33)	0.4625 (6)	−0.1567 (7)	−0.1294 (11)	0.0062 (6)	0.0076 (7)	0.0206 (2)	0.0079 (11)	−0.0030 (2)	−0.0024 (2)
C(34)	0.4409 (7)	−0.1897 (7)	−0.0015 (12)	0.0112 (8)	0.0058 (8)	0.0285 (2)	0.0066 (10)	0.0105 (2)	0.0034 (2)
C(35)	0.3948 (5)	−0.1213 (6)	0.0718 (10)	0.0034 (5)	0.0044 (6)	0.0177 (2)	0.0004 (11)	−0.0018 (1)	0.0036 (2)
C(1)	0.0108 (7)	0.4113 (7)	−0.0123 (12)	0.0071 (6)	0.0037 (7)	0.0255 (2)	0.0010 (12)	0.0024 (2)	0.0007 (2)
C(2)	0.0664 (6)	0.4601 (8)	0.0567 (11)	0.0053 (5)	0.0089 (8)	0.0172 (2)	0.0088 (11)	0.0059 (2)	0.0034 (2)
C(3)	0.0548 (6)	0.5479 (8)	0.0717 (11)	0.0053 (6)	0.0091 (8)	0.0168 (2)	0.0009 (11)	−0.0008 (2)	−0.0034 (2)

Table I (*Continued*)

(b) CrPDC·0.5C_6H_6 (*continued*)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(12A)	−0.0675 (7)	0.0648 (9)	−0.070 (1)	5.0	H(25A)	0.2954 (8)	0.4813 (8)	−0.187 (1)	5.0
H(12B)	−0.0617 (7)	0.1625 (9)	−0.140 (1)	5.0	H(25B)	0.2185 (8)	0.4972 (8)	−0.088 (1)	5.0
H(13A)	−0.1800 (8)	0.1005 (10)	0.043 (2)	5.0	H(32A)	0.3873 (7)	−0.0696 (8)	−0.232 (1)	5.0
H(13B)	−0.1915 (8)	0.1750 (10)	−0.075 (2)	5.0	H(32B)	0.4684 (7)	−0.0223 (8)	−0.168 (1)	5.0
H(14A)	−0.1890 (9)	0.2195 (11)	0.164 (2)	5.0	H(33A)	0.5232 (9)	−0.1515 (10)	−0.133 (1)	5.0
H(14B)	−0.1446 (9)	0.2809 (11)	0.051 (2)	5.0	H(33B)	0.4432 (9)	−0.1987 (10)	−0.201 (1)	5.0
H(15A)	−0.0363 (8)	0.2607 (10)	0.194 (1)	5.0	H(34A)	0.4898 (10)	−0.2041 (10)	0.054 (2)	5.0
H(15B)	−0.0687 (8)	0.1642 (10)	0.244 (1)	5.0	H(34B)	0.4055 (10)	−0.2430 (10)	−0.011 (2)	5.0
H(22A)	0.4237 (7)	0.4270 (9)	0.098 (1)	5.0	H(35A)	0.4260 (7)	−0.0994 (8)	0.152 (1)	5.0
H(22B)	0.3544 (7)	0.4794 (9)	0.183 (1)	5.0	H(35B)	0.3412 (7)	−0.1456 (8)	0.101 (1)	5.0
H(23A)	0.4376 (8)	0.5410 (9)	−0.052 (2)	5.0	H(1)	0.0163 (9)	0.3443 (9)	−0.017 (2)	5.0
H(23B)	0.4175 (8)	0.5973 (9)	0.084 (2)	5.0	H(2)	0.1160 (8)	0.4309 (10)	0.098 (1)	5.0
H(24A)	0.3253 (8)	0.6224 (9)	−0.121 (2)	5.0	H(3)	0.0947 (8)	0.5848 (11)	0.126 (1)	5.0
H(24B)	0.2816 (8)	0.6101 (9)	0.025 (2)	5.0					

(c) IrPDC·0.5C_6H_6

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ir	0.23437 (9)	0.17409 (9)	0.0183 (2)	0.00434 (5)	0.00333 (5)	0.01380 (2)	0.00068 (2)	−0.0048 (2)	−0.00067 (3)
S(11)	0.1148 (6)	0.1111 (6)	−0.0801 (11)	0.0053 (5)	0.0037 (4)	0.0183 (1)	0.0000 (8)	−0.0058 (1)	−0.0033 (1)
S(12)	0.1319 (6)	0.2084 (6)	0.1682 (10)	0.0074 (5)	0.0044 (5)	0.0176 (1)	−0.0004 (9)	−0.0137 (1)	−0.0010 (1)
S(21)	0.2152 (6)	0.3097 (5)	−0.1000 (10)	0.0066 (5)	0.0032 (5)	0.0192 (1)	0.0006 (8)	−0.0100 (1)	0.0025 (1)
S(22)	0.3322 (6)	0.2725 (6)	0.1174 (11)	0.0053 (5)	0.0035 (4)	0.0210 (2)	0.0014 (8)	−0.0099 (1)	−0.0020 (1)
S(31)	0.3279 (6)	0.1097 (5)	−0.1311 (9)	0.0053 (5)	0.0038 (4)	0.0127 (1)	−0.0003 (8)	−0.0047 (1)	0.0037 (1)
S(32)	0.2804 (6)	0.0423 (6)	0.1298 (11)	0.0059 (5)	0.0041 (5)	0.0183 (2)	0.0010 (9)	−0.0067 (1)	0.0033 (2)
N(1)	−0.011 (2)	0.158 (2)	0.068 (2)	0.006 (1)	0.004 (1)	0.007 (3)	−0.000 (3)	0.006 (4)	−0.005 (4)
N(2)	0.321 (2)	0.433 (2)	0.007 (3)	0.008 (2)	0.003 (1)	0.032 (6)	0.000 (3)	−0.019 (5)	0.006 (5)
N(3)	0.385 (1)	−0.046 (2)	−0.034 (3)	0.003 (1)	0.004 (1)	0.019 (5)	0.000 (2)	0.001 (4)	−0.004 (4)
C(11)	0.067 (2)	0.160 (2)	0.053 (2)	0.006 (1)	0.002 (1)	0.004 (3)	0.002 (3)	0.007 (4)	0.005 (4)
C(12)	−0.067 (2)	0.125 (2)	−0.049 (4)	0.007 (2)	0.003 (2)	0.015 (5)	−0.003 (3)	0.008 (6)	−0.007 (5)
C(13)	−0.147 (2)	0.148 (2)	0.008 (4)	0.003 (2)	0.007 (2)	0.029 (8)	−0.002 (3)	−0.003 (6)	−0.002 (7)
C(14)	−0.117 (4)	0.214 (3)	0.122 (5)	0.021 (4)	0.005 (2)	0.039 (8)	−0.003 (6)	0.043 (9)	−0.008 (8)
C(15)	−0.047 (2)	0.198 (3)	0.171 (5)	0.006 (2)	0.011 (3)	0.030 (8)	0.001 (5)	−0.013 (7)	0.004 (9)
C(21)	0.293 (2)	0.352 (2)	0.009 (3)	0.003 (1)	0.004 (2)	0.015 (5)	0.001 (2)	−0.008 (4)	0.006 (4)
C(22)	0.383 (2)	0.473 (3)	0.094 (4)	0.005 (2)	0.008 (2)	0.027 (7)	−0.001 (4)	−0.014 (6)	−0.001 (7)
C(23)	0.400 (2)	0.557 (2)	0.014 (4)	0.004 (2)	0.005 (2)	0.024 (7)	−0.002 (3)	−0.003 (6)	0.002 (6)
C(24)	0.323 (2)	0.586 (2)	−0.039 (4)	0.010 (2)	0.003 (2)	0.020 (6)	−0.003 (4)	−0.012 (7)	0.002 (6)
C(25)	0.283 (2)	0.499 (2)	−0.078 (3)	0.001 (1)	0.011 (3)	0.013 (4)	−0.003 (3)	0.014 (3)	−0.004 (6)
C(31)	0.339 (2)	0.022 (2)	−0.008 (4)	0.001 (1)	0.007 (2)	0.020 (6)	−0.003 (3)	−0.003 (4)	−0.006 (6)
C(32)	0.428 (2)	−0.060 (2)	−0.155 (4)	0.004 (2)	0.005 (2)	0.019 (6)	0.001 (3)	0.004 (5)	−0.005 (6)
C(33)	0.463 (2)	−0.151 (2)	−0.131 (4)	0.006 (2)	0.006 (2)	0.028 (7)	0.007 (3)	−0.009 (6)	−0.006 (7)
C(34)	0.433 (3)	−0.183 (3)	−0.008 (4)	0.019 (3)	0.006 (2)	0.026 (6)	0.009 (6)	0.031 (7)	0.018 (7)
C(35)	0.388 (2)	−0.121 (2)	0.071 (3)	0.004 (2)	0.004 (2)	0.014 (5)	0.001 (3)	0.003 (5)	0.012 (4)
C(1)	0.004 (3)	0.406 (3)	−0.005 (5)	0.011 (3)	0.011 (3)	0.019 (6)	0.000 (5)	−0.014 (7)	0.003 (8)
C(2)	0.060 (3)	0.456 (3)	0.056 (4)	0.009 (2)	0.011 (3)	0.019 (6)	0.013 (4)	−0.003 (7)	0.013 (7)
C(3)	0.058 (3)	0.553 (3)	0.066 (5)	0.008 (2)	0.009 (3)	0.029 (8)	0.002 (5)	−0.009 (7)	−0.002 (8)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(12A)	−0.0567 (23)	0.1570 (21)	−0.139 (4)	5.0	H(25A)	0.2924 (23)	0.4931 (23)	−0.188 (4)	5.0
H(12B)	−0.0588 (23)	0.0603 (21)	−0.067 (4)	5.0	H(25B)	0.2222 (23)	0.5059 (23)	−0.075 (4)	5.0
H(13A)	−0.1867 (23)	0.1673 (24)	−0.066 (4)	5.0	H(32A)	0.3955 (21)	−0.0552 (23)	−0.244 (4)	5.0
H(13B)	−0.1725 (23)	0.0925 (24)	0.053 (4)	5.0	H(32B)	0.4749 (21)	−0.0147 (23)	−0.165 (4)	5.0
H(14A)	−0.1736 (29)	0.2128 (29)	0.187 (6)	5.0	H(33A)	0.5239 (23)	−0.1519 (23)	−0.130 (5)	5.0
H(14B)	−0.1341 (29)	0.2735 (29)	0.067 (6)	5.0	H(33B)	0.4457 (23)	−0.1922 (23)	−0.213 (5)	5.0
H(15A)	−0.0541 (21)	0.1688 (25)	0.270 (4)	5.0	H(34A)	0.4817 (28)	−0.2051 (26)	0.052 (4)	5.0
H(15B)	−0.0258 (21)	0.2622 (25)	0.205 (4)	5.0	H(34B)	0.3998 (28)	−0.2376 (26)	−0.029 (4)	5.0
H(22A)	0.3669 (24)	0.4863 (28)	0.196 (5)	5.0	H(35A)	0.4154 (22)	−0.1037 (20)	0.163 (4)	5.0
H(22B)	0.4336 (24)	0.4334 (28)	0.107 (5)	5.0	H(35B)	0.3326 (22)	−0.1429 (20)	0.094 (4)	5.0
H(23A)	0.4369 (22)	0.5462 (23)	−0.071 (5)	5.0	H(1)	0.0255 (8)	0.3448 (8)	−0.035 (1)	5.0
H(23B)	0.4293 (22)	0.6058 (23)	0.070 (5)	5.0	H(2)	0.1112 (7)	0.4271 (9)	0.103 (1)	5.0
H(24A)	0.3234 (25)	0.6325 (23)	−0.117 (4)	5.0	H(3)	0.0927 (9)	0.5842 (10)	0.127 (1)	5.0
H(24B)	0.2900 (25)	0.6160 (23)	0.040 (4)	5.0					

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

complex is therefore of special interest. A further interest in FePDC stems from the relation between the metal–ligand bond length and the proportions of high-spin and low-spin species in various ferric dithiocarbamates,[3-5] which FePDC fits rather poorly. In fact, it has been suggested that this relationship may hold well only for a given compound as the spin-state proportions are varied and poorly from one compound to another.[6]

The formation of solvated forms of FePDC appears to have gone essentially unnoticed, despite extensive studies on this complex,[1-4,7-14] and the effect of the included solvent molecules, unstudied. This paper reports a study of this solvent inclusion and the crystal and molecular structure determination by x-ray diffraction of 2FePDC·C_6H_6 (III), 2CrPDC·C_6H_6 (IV), and 2IrPDC·C_6H_6 (V). Complexes III, IV, and V are nearly isomorphous and permit direct comparisons of the effect of altering the d-electron population or the d shell in the central transition metal. The analogous complexes with Co(III) and Mn(III) would have been of interest here but could not be studied because no suitable crystals of the Co(III) complex could be obtained and the Mn(III) analogue was found to be too unstable for us to attempt recrystallization.

Experimental Section

Low-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer. Densities were determined by flotation in aqueous potassium iodide and in bromoform–acetone.

Potassium 1-pyrrolidinecarbodithioate (KPDC) was prepared by the slow addition of excess carbon disulfide to a stirred solution of potassium hydroxide (0.3 mol) and pyrrolidine (0.3 mol) in ethanol (100 ml) at 0°C. Reduction of the volume at low pressure produced white crystals of the potassium salt, which was recrystallized from ethanol. Solutions of KPDC and ferric nitrate in aqueous ethanol were mixed in a 3:1 ratio and the resulting ferric dithiocarbamate was extracted into dichloromethane and precipitated with ethanol. Recrystallization from chloroform–ethanol produced **FePDC·$CHCl_3$** (weight loss on warming 16.1%; calculated for one molecule of $CHCl_3$ 19.4%). **CoPDC·$CHCl_3$** was formed by the same method, using cobalt(II) chloride, the oxidation to cobalt(III) being performed by atmospheric oxygen (weight loss on heating 18.3%; calculated 19.3%). **CrPDC·$CHCl_3$** was formed similarly to the cobalt complex, using chromium(II) acetate (weight loss on heating 19.2%; calculated 19.6%). Mass spectra of MPDC·$CHCl_3$ (M = Fe, Co, Cr) showed the characteristic fragmentation pattern of $CHCl_3$ in addition to the molecular ion MPDC; the remainder of the spectra exhibit stepwise loss of ligand sulfurs and then the remainder of the ligand, very like the morpholyl carbodithioate complexes.[6]

RhPDC was formed as above, using $RhCl_3$. The initial transparent orange crystals, presumably RhPDC·$CHCl_3$, rapidly became cloudy on removal from the mother liquor, with simultaneous loss of the single-crystal diffraction pattern within minutes. **IrPDC** was formed as above using $KIrCl_6$ with excess KPDC. As with RhPDC, an unstable chloroform solvate was formed initially. The fragmentation pattern under electron impact of RhPDC and IrPDC closely resembles those of the other three complexes.

The benzene solvates, 2MPDC·C_6H_6, were formed by recrystallization of MPDC·$CHCl_3$ or MPDC from benzene–ethanol. For three of the compounds, suitable crystals were obtained and selected for single-crystal diffraction studies (M = Fe, Cr, Ir). No suitable crystals were found for M = Co, Rh, Mn.

Crystal data for III: $FeS_6N_3C_{18}H_{27}$, mol wt 534, space group $P2_1/n$, $Z = 4$, $a = 16.356$ (3) Å, $b = 14.933$ (2) Å, $c = 10.191$ (2) Å, $\beta = 90.3$ (1)°, $V = 2489$ Å^3, μ(Mo Kα) = 11.2 cm^{-1}, $d_c = 1.44$ g cm^{-3} and $d_o = 1.42$ g cm^{-3}, where d_c and d_o are the calculated and observed densities, respectively. Crystal data for IV: $CrS_6N_3C_{18}H_{27}$, mol wt 530, space group $P2_1/n$, $Z = 4$, $a = 16.490$ (5) Å, $b = 15.071$ (7) Å, $c = 9.909$ (6) Å, $\beta = 91.01$ (3)°, $V = 2462$ Å^3, μ(Mo Kα) = 9.8 cm^{-1}, $d_c = 1.43$ g cm^{-3}, $d_o = 1.44$ g cm^{-3}. Crystal data for V: $IrS_6N_3C_{18}H_{27}$, mol wt 670, space group $P2_1/n$, $Z = 4$, $a = 16.72$ (1) Å, $b = 15.272$ (5) Å, $c = 9.602$ (2) Å, $\beta = 91.54$ (3)°, $V = 2451$ Å^3, μ(Mo Kα) = 62.1 cm^{-1}, $d_c = 1.80$ g cm^{-3}, $d_o = 1.73$ g cm^{-3}.

For each crystal, 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 to approximate cell dimensions. 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 scan technique and judged to be satisfactory. Transformations to space group $P2_1/n$ were calculated for the cells, in order to correspond to the cell of FePDC reported by Healy and White[4] ($a = 16.23$ (4) Å, $b = 14.53$ (2) Å, $c = 10.22$ (3) Å, $\beta = 90.3$ (4)°, $V = 2410$ Å^3, space group $P2_1/n$), which differs from that of 2FePDC·C_6H_6 only in the b axis. It is also apparent that complexes 2MPDC·C_6H_6 with M = Fe, Cr, and Ir are almost isomorphous, since their cell parameters are reasonably close to one another. $P2_1/n$ is an alternative setting of the conventional space group $P2_1/c$ and has the general equivalent positions x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$; $^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$. The transformation matrix for conversion of the present setting to the conventional one is

$$\begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 1 \end{pmatrix}$$

Thus the cell parameters in $P2_1/c$ (a_c, b_c, c_c, β_c) derived from those given for $P2_1/n$ (a_n, b_n, c_n, β_n), have $a_c = c_n$ and $b_c = b_n$ in each case. The values of c_c, β_c are 19.32 Å, 122.1° for III, 19.31 Å, 121.4° for IV, and 19.66 Å, 121.8° for V.

Collection and Reduction of the 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 Kα radiation from a highly oriented graphite crystal monochromator. The θ–2θ scan technique was used to record the intensities for all reflections for which $1° < 2\theta < 52°$ for III, $1° < 2\theta < 50°$ for IV and $1° < 2\theta < 50.0°$ for V. 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 Kα_1 and Kα_2 splitting. The values of A and B were 0.6° and 0.2°, respectively, for III and were 1.0° and 0.3° for both IV and V. 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 then for absorption, spherical absorption corrections being applied to IV and V, due to absence of well-defined crystal faces. After averaging of the intensities of equivalent reflections, the data were reduced to 4051 independent intensities for III, 3260 for IV, and 3412 for V, of which 3276 for III, 1599 for IV, and 1646 for V had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[15] These data were used in the final refinement of the structural parameters.

Refinement of the Structure

Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. 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[16] and those for hydrogen from Stewart.[17] The effects of anomalous dispersion were included in F_c using Cromer's values[18] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum \| F_o| - |F_c\| / \sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$.

The solution of III was attempted by least-squares refinement of the atomic parameters from the known form of FePDC.[4] This failed, and the model converged with $R = 58.6\%$ using all 3σ data. Use of just the iron atomic parameters and those of the iron and some of the sulfur atoms also failed, and structure IV was therefore solved by standard heavy-atom methods. To minimize computer time, the initial calculations were carried out on the first 1000 reflections collected for each crystal. The positions of chromium and two sulfur atoms were determined from a three-dimensional Patterson function, and the remaining nonhydrogen atoms were located from Fourier difference maps. For compound III the metal and sulfur atoms were inserted at the calculated positions of the corresponding atoms in IV, while for V, the metal atom alone was initially inserted, the sulfur atoms being added after two cycles of least-squares refinement. Then the remaining nonhydrogen atoms were inserted, and two cycles of full-matrix least-squares refinement produced $R = 7.6, 7.6, 8.3\%$ for III, IV, and V, respectively. The remaining diffraction data were added to the calculation, anisotropic temperature factors were introduced, and nonmethyl hydrogen atoms were inserted as fixed atoms at the calculated positions, with isotropic temperature factors of 5.0, assuming C–H = 1.00 Å. After convergence the hydrogen atoms were inserted at their new calculated positions. The models converged with $R = 4.5$, $R_w = 4.8\%$ for III, $R = 4.4$, $R_w = 4.3\%$ for IV, and $R = 6.4$, $R_w = 7.7\%$ for V. The error in an observation of unit weight is 2.01, 3.41, and 1.85 for III, IV, and V, respectively. The possibility of disorder in the positions of some of the pyrrolidyl ring carbons (C(13), C(14), C(33), and C(34)) was checked for three compounds but found not to be statistically significant.[19] A structure factor calculation with all observed and unobserved reflections included (no refinement) gave $R = 6.0$, 7.5, and 9.5 for III, IV, and V; on this basis, it was decided that careful measurement of reflections rejected automatically during

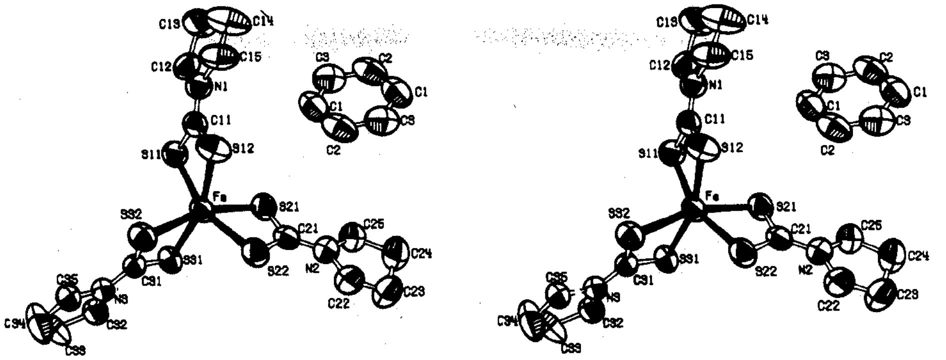

Figure 1. Stereoscopic view of IV, $CrPDC\cdot 0.5C_6H_6$.

data collection would not significantly improve the results. A final Fourier difference map was featureless. A table of the observed structure factors is available.[20]

Results and Discussion

Final positional and thermal parameters for complexes III, IV, and V are given in Table I. Tables II and III 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. Figure 1 is a stereoscopic pair view of complex IV, shown with a complete benzene molecule, while Figure 2 shows the molecular packing of IV in the unit cell. As is evident from the packing diagram and the closest intermolecular distances (Table IV), the complex molecules are well separated from one another, with no evidence of extraordinarily close contacts. Similarly, the solvating benzene molecule is well separated in each of the three complexes, being closest to "ligand 3" in each case. (See Table V.)

The closest approaches of metal atoms to one another are 8.82, 8.83, and 9.29 Å in $2FePDC\cdot C_6H_6$. The corresponding distances in the Cr(III) analogue are 8.83, 9.16, and 9.26 Å, while in the Ir(III) complex they are 8.85, 9.23, and 9.47 Å. This compares with 8.69, 8.69, and 8,78 Å in the previously studied unsolvated complex FePDC.[4]

The unstable $FePDC\cdot CHCl_3$, I, failed to produce crystals and was therefore not studied, but, since its magnetic properties are the same as those of II, from which the solvent was removed,[1,2] the solvent is unimportant to the properties unlike the benzene in complexes III, IV, and V. A possible explanation for this behavior may be that the solvent in I is merely adsorbed on microcrystallites, rather than clathrated at the molecular level. This is supported by the observation that I loses its solvent spontaneously while all of the benzene solvates appear to be stable indefinitely at room temperature. Complexes I and II have the same magnetic properties within experimental error as those of the previously studied complex FePDC,[4] and therefore the structure is presumably the same, especially for II. Complexes II and III are significantly different in their structural as well as in their magnetic properties: the atomic coordinates of II could not be used to solve III.

Table II. Bond Distances (Å)

(a) $FePDC\cdot 0.5C_6H_6$

Fe–S(11)	2.449 (1)	N(2)–C(25)	1.463 (4)
Fe–S(12)	2.422 (1)	N(3)–C(31)	1.319 (3)
Fe–S(21)	2.427 (1)	N(3)–C(32)	1.467 (3)
Fe–S(22)	2.436 (1)	N(3)–C(35)	1.467 (3)
Fe–S(31)	2.425 (1)	C(12)–C(13)	1.528 (5)
Fe–S(32)	2.435 (1)	C(13)–C(14)	1.382 (5)
S(11)–C(11)	1.722 (3)	C(14)–C(15)	1.478 (9)
S(12)–C(11)	1.703 (3)	C(22)–C(23)	1.511 (5)
S(21)–C(21)	1.705 (3)	C(23)–C(24)	1.493 (5)
S(22)–C(21)	1.719 (3)	C(24)–C(25)	1.502 (4)
S(31)–C(31)	1.718 (3)	C(32)–C(33)	1.484 (4)
S(32)–C(31)	1.707 (3)	C(33)–C(34)	1.409 (5)
N(1)–C(11)	1.312 (4)	C(34)–C(35)	1.458 (4)
N(1)–C(12)	1.469 (4)	C(1)–C(2)	1.352 (5)
N(1)–C(15)	1.472 (4)	C(2)–C(3)	1.356 (5)
N(2)–C(21)	1.321 (3)	C(1)–C(3′)	1.364 (5)
N(2)–C(22)	1.476 (4)		

(b) $CrPDC\cdot 0.5C_6H_6$

Cr–S(11)	2.413 (3)	N(2)–C(25)	1.471 (10)
Cr–S(12)	2.398 (3)	N(3)–C(31)	1.357 (9)
Cr–S(21)	2.392 (3)	N(3)–C(32)	1.467 (9)
Cr–S(22)	2.416 (3)	N(3)–C(35)	1.469 (10)
Cr–S(31)	2.402 (3)	C(12)–C(13)	1.516 (12)
Cr–S(32)	2.407 (3)	C(13)–C(14)	1.418 (13)
S(11)–C(11)	1.696 (8)	C(14)–C(15)	1.521 (12)
S(12)–C(11)	1.711 (8)	C(22)–C(23)	1.516 (12)
S(21)–C(21)	1.711 (8)	C(23)–C(24)	1.485 (12)
S(22)–C(21)	1.710 (8)	C(24)–C(25)	1.522 (11)
S(31)–C(31)	1.704 (8)	C(32)–C(33)	1.486 (11)
S(32)–C(31)	1.682 (8)	C(33)–C(34)	1.414 (12)
N(1)–C(11)	1.332 (8)	C(34)–C(35)	1.479 (12)
N(1)–C(12)	1.475 (9)	C(1)–C(2)	1.351 (13)
N(1)–C(15)	1.481 (10)	C(2)–C(3)	1.346 (14)
N(2)–C(21)	1.335 (9)	C(1)–C(3′)	1.368 (14)
N(2)–C(22)	1.463 (10)		

(c) $IrPDC\cdot 0.5C_6H_6$

Ir–S(11)	2.390 (7)	N(2)–C(25)	1.44 (3)
Ir–S(12)	2.327 (9)	N(3)–C(31)	1.33 (3)
Ir–S(21)	2.380 (7)	N(3)–C(32)	1.39 (3)
Ir–S(22)	2.399 (7)	N(3)–C(35)	1.52 (3)
Ir–S(31)	2.364 (8)	C(12)–C(13)	1.50 (4)
Ir–S(32)	2.397 (7)	C(13)–C(14)	1.57 (6)
S(11)–C(11)	1.71 (2)	C(14)–C(15)	1.27 (7)
S(12)–C(11)	1.70 (3)	C(22)–C(23)	1.53 (4)
S(21)–C(21)	1.77 (2)	C(23)–C(24)	1.44 (4)
S(22)–C(21)	1.72 (2)	C(24)–C(25)	1.53 (3)
S(31)–C(31)	1.80 (3)	C(32)–C(33)	1.52 (4)
S(32)–C(31)	1.69 (3)	C(33)–C(34)	1.38 (4)
N(1)–C(11)	1.31 (3)	C(34)–C(35)	1.44 (4)
N(1)–C(12)	1.53 (4)	C(1)–C(2)	1.34 (5)
N(1)–C(15)	1.32 (5)	C(2)–C(3)	1.48 (6)
N(2)–C(21)	1.32 (3)	C(1)–C(3′)	1.34 (5)
N(2)–C(22)	1.46 (3)		

Measurements at low temperatures have demonstrated the existence of antiferromagnetic interaction in II, which is carried by unpaired spin density delocalized onto ligand atoms, principally from the metal e orbitals: the interaction is gradually removed by increasing dilution of the ferric $(t_2{}^3e^2)$ complex, while the chromic $(t_2{}^3)$ analogue lacks both the magnetic interaction and the spin delocalization.[1,2] Complex III exhibits a high-spin–low-spin equilibrium, which depopulates the e orbitals at low temperatures, thereby removing the antiferromagnetic interactions. Despite these dramatic differences at low temperatures, the magnetic properties of the complexes become more similar as temperature rises, and both complexes are effectively high spin at temperatures approaching room temperature. Thus the metal–ligand bond lengths should be approximately the same, with those of II

Table III. Bond Angles (deg)

			(a) FePDC·0.5C_6H_6				
S(11)-Fe-S(12)	73.16 (3)	C(11)-N(1)-C(15)	124.7 (3)	S(31)-Fe-S(32)	73.38 (3)	C(14)-C(15)-N(1)	104.2 (3)
S(11)-Fe-S(21)	89.47 (3)	C(12)-N(1)-C(15)	110.9 (3)	Fe-S(11)-C(11)	84.4 (1)	S(21)-C(21)-S(22)	116.3 (2)
S(11)-Fe-S(22)	157.64 (3)	C(21)-N(2)-C(22)	124.4 (3)	Fe-S(12)-C(11)	85.6 (1)	S(21)-C(21)-N(2)	121.6 (2)
S(11)-Fe-S(31)	95.56 (3)	C(21)-N(2)-C(25)	124.4 (3)	Fe-S(21)-C(21)	85.4 (1)	S(22)-C(21)-N(2)	122.1 (2)
S(11)-Fe-S(32)	106.03 (3)	C(22)-N(2)-C(25)	111.3 (2)	Fe-S(22)-C(21)	84.8 (1)	N(2)-C(22)-C(23)	102.2 (3)
S(12)-Fe-S(21)	97.50 (3)	C(31)-N(3)-C(32)	123.8 (2)	Fe-S(31)-C(31)	85.3 (1)	C(22)-C(23)-C(24)	104.2 (3)
S(12)-Fe-S(22)	94.44 (3)	C(31)-N(3)-C(35)	124.6 (2)	Fe-S(32)-C(31)	85.3 (1)	C(23)-C(24)-C(25)	103.5 (3)
S(12)-Fe-S(31)	162.60 (3)	C(32)-N(3)-C(35)	111.6 (2)	S(31)-C(31)-S(32)	116.0 (2)	C(24)-C(25)-N(2)	103.8 (3)
S(12)-Fe-S(32)	96.61 (3)	S(11)-C(11)-S(12)	115.9 (2)	S(31)-C(31)-N(3)	121.4 (2)	C(32)-C(33)-C(34)	108.5 (3)
S(21)-Fe-S(22)	73.45 (3)	S(11)-C(11)-N(1)	122.0 (2)	S(32)-C(31)-N(3)	122.7 (2)	C(33)-C(34)-C(35)	111.7 (3)
S(21)-Fe-S(31)	95.57 (3)	S(12)-C(11)-N(1)	122.1 (2)	N(3)-C(32)-C(33)	104.0 (3)	C(34)-C(35)-N(3)	103.5 (3)
S(21)-Fe-S(32)	161.54 (3)	N(1)-C(12)-C(13)	101.3 (3)	C(1)-C(2)-C(3)	119.6 (4)	C(2)-C(1)-C(3′)	120.1 (4)
S(22)-Fe-S(31)	100.28 (3)	C(12)-C(13)-C(14)	109.9 (3)	C(11)-N(1)-C(12)	124.4 (3)	C(2)-C(3)-C(1′)	120.3 (4)
S(22)-Fe-S(32)	93.64 (3)	C(13)-C(14)-C(15)	106.7 (4)				
			(b) CrPDC·0.5C_6H_6				
S(11)-Cr-S(12)	74.3 (1)	C(11)-N(1)-C(12)	123.2 (8)	S(31)-Cr-S(32)	74.2 (1)	C(13)-C(14)-C(15)	106.0 (9)
S(11)-Cr-S(21)	91.3 (1)	C(11)-N(1)-C(15)	125.6 (8)	Cr-S(11)-C(11)	84.0 (3)	C(14)-C(15)-N(1)	102.2 (8)
S(11)-Cr-S(22)	161.1 (1)	C(12)-N(1)-C(15)	111.0 (7)	Cr-S(12)-C(11)	84.1 (3)	S(21)-C(21)-S(22)	115.9 (6)
S(11)-Cr-S(31)	96.3 (1)	C(21)-N(2)-C(22)	124.9 (9)	Cr-S(21)-C(21)	85.3 (3)	S(21)-C(21)-N(2)	121.7 (7)
S(11)-Cr-S(32)	100.5 (1)	C(21)-N(2)-C(25)	123.9 (8)	Cr-S(22)-C(21)	84.6 (3)	S(22)-C(21)-N(2)	122.4 (7)
S(12)-Cr-S(21)	94.7 (1)	C(22)-N(2)-C(25)	111.3 (8)	Cr-S(31)-C(31)	83.7 (3)	N(2)-C(22)-C(23)	102.3 (8)
S(12)-Cr-S(22)	94.5 (1)	C(31)-N(3)-C(32)	123.7 (8)	Cr-S(32)-C(31)	84.0 (3)	C(22)-C(23)-C(24)	103.8 (8)
S(12)-Cr-S(31)	165.7 (1)	C(31)-N(3)-C(35)	124.9 (8)	C(23)-C(24)-C(25)	103.3 (8)	N(3)-C(32)-C(33)	104.0 (8)
S(12)-Cr-S(32)	96.5 (1)	C(32)-N(3)-C(35)	111.4 (7)	C(24)-C(25)-N(2)	103.2 (8)	C(32)-C(33)-C(34)	110.2 (9)
S(21)-Cr-S(22)	74.2 (1)	S(11)-C(11)-S(12)	117.0 (5)	S(31)-C(31)-S(32)	117.9 (5)	C(33)-C(34)-C(35)	109.6 (10)
S(21)-Cr-S(31)	96.4 (1)	S(12)-C(11)-N(1)	120.9 (7)	S(31)-C(31)-N(3)	120.0 (7)	C(34)-C(35)-N(3)	104.5 (9)
S(21)-Cr-S(32)	165.6 (1)	S(11)-C(11)-N(1)	122.0 (7)	S(32)-C(31)-N(3)	122.0 (7)	C(2)-C(1)-C(3′)	120 (1)
S(22)-Cr-S(31)	97.2 (1)	N(1)-C(12)-C(13)	103.0 (7)	C(1)-C(2)-C(3)	120 (1)	C(2)-C(3)-C(1′)	120 (1)
S(22)-Cr-S(32)	95.8 (1)	C(12)-C(13)-C(14)	107.3 (9)				
			(c) IrPDC·0.5C_6H_6				
S(11)-Ir-S(12)	73.4 (3)	Ir-S(22)-C(21)	87.5 (8)	S(31)-Ir-S(32)	73.3 (3)	S(11)-C(11)-N(1)	124 (2)
S(11)-Ir-S(21)	93.5 (3)	Ir-S(31)-C(31)	88.2 (10)	Ir-S(11)-C(11)	86.2 (10)	N(1)-C(12)-C(13)	101 (2)
S(11)-Ir-S(22)	164.3 (2)	Ir-S(32)-C(31)	89.5 (11)	Ir-S(12)-C(11)	88.4 (9)	C(12)-C(13)-C(14)	97 (3)
S(11)-Ir-S(31)	98.8 (3)	C(11)-N(1)-C(12)	121 (2)	Ir-S(21)-C(21)	87.1 (8)	C(13)-C(14)-C(15)	114 (4)
S(11)-Ir-S(32)	95.4 (3)	C(11)-N(1)-C(15)	123 (3)	C(14)-C(15)-N(1)	104 (5)	S(31)-C(31)-S(32)	109 (2)
S(12)-Ir-S(21)	90.4 (3)	C(12)-N(1)-C(15)	115 (3)	S(21)-C(21)-S(22)	111 (1)	S(31)-C(31)-N(3)	121 (2)
S(12)-Ir-S(22)	96.8 (3)	C(21)-N(2)-C(22)	130 (3)	S(21)-C(21)-N(2)	126 (2)	S(32)-C(31)-N(3)	130 (2)
S(12)-Ir-S(31)	168.2 (2)	C(21)-N(2)-C(25)	121 (2)	S(22)-C(21)-N(2)	122 (2)	N(3)-C(32)-C(33)	102 (3)
S(12)-Ir-S(32)	98.4 (3)	C(22)-N(2)-C(25)	109 (2)	N(2)-C(22)-C(23)	102 (2)	C(32)-C(33)-C(34)	108 (3)
S(21)-Ir-S(22)	74.1 (3)	C(31)-N(3)-C(32)	127.(3)	C(22)-C(23)-C(24)	105 (2)	C(33)-C(34)-C(35)	115 (3)
S(21)-Ir-S(31)	99.0 (3)	C(31)-N(3)-C(35)	118 (3)	C(23)-C(24)-C(25)	102 (2)	C(34)-C(35)-N(3)	99 (2)
S(21)-Ir-S(32)	169.0 (3)	C(32)-N(3)-C(35)	115 (2)	C(24)-C(25)-N(2)	107 (2)	C(2)-C(1)-C(3′)	116 (4)
S(22)-Ir-S(31)	92.7 (3)	S(11)-C(11)-S(12)	112 (2)	C(1)-C(2)-C(3)	125 (4)	C(2)-C(3)-C(1′)	118 (4)
S(22)-Ir-S(32)	98.2 (3)	S(12)-C(11)-N(1)	124 (2)				

Table IV. Intermolecular Contacts

Molecule 1	Molecule 2	Distance, Å			Symmetry transformation
		Fe	Cr	Ir	
S(11)	C(12)	3.855	3.918	3.903	$-x, -y, -z$
S(11)	C(24)	3.948	3.921	3.849	$0.5 - x, -0.5 + y, -0.5 - z$
S(12)	C(23)	3.778	3.795	3.872	$0.5 - x, -0.5 + y, 0.5 - z$
S(12)	C(35)	3.816	3.728	3.638	$0.5 - x, 0.5 + y, 0.5 - z$
S(12)	C(34)	3.904	3.837	3.842	$0.5 - x, 0.5 + y, 0.5 - z$
S(21)	C(14)	3.740	3.820	3.941	$0.5 + x, 0.5 - y, -0.5 + z$
S(21)	C(32)	3.885	3.856	3.863	$0.5 - x, 0.5 + y, -0.5 - z$
S(22)	C(12)	3.879	3.872	3.904	$0.5 + x, 0.5 - y, 0.5 + z$
S(22)	C(33)	3.850	3.890	3.896	$1 - x, -y, -z$
S(22)	C(13)	3.915	3.892	3.948	$0.5 + x, 0.5 + y, -0.5 - z$
S(31)	C(25)	3.546	3.563	3.714	$0.5 - x, -0.5 + y, -0.5 - z$
S(31)	C(14)	3.949	3.832	3.720	$0.5 + x, 0.5 - y, -0.5 + z$
S(32)	C(13)	3.773	3.801	3.868	$-x, -y, -z$
S(32)	C(22)	3.967	3.954	3.998	$0.5 - x, -0.5 + y, 0.5 - z$
C(12)	C(22)	3.950	3.901	3.811	$-0.5 + x, 0.5 - y, -0.5 + z$
C(22)	C(23)	3.955	3.954	3.830	$1 - x, 1 - y, -z$
C(23)	C(23)	3.764	3.814	3.795	$1 - x, 1 - y, -z$

Table V. Benzene Contacts

Molecule 1	Molecule 2	Distance, Å		
		Fe	Cr	Ir
C(1)	C(32)	3.584	3.516	3.528
	C(33)	3.879	3.729	3.663
	C(15)	3.827	3.792	3.706
	N(1)	3.857	3.872	3.861
	S(21)	3.815	3.873	3.951
	C(14)		3.990	3.779
C(2)	S(21)	3.803	3.779	3.762
	C(25)	3.876	3.863	
	C(35)	3.944	3.923	3.848
	C(32)			3.873
C(3)	C(32)	3.530	3.509	3.495
	C(33)	3.853	3.733	3.679
	S(32)	3.941	3.928	3.934

possibly being slightly larger. Just the opposite is the case, however, ⟨Fe–S⟩ being almost 0.03 Å smaller for II than for III (Table VI). Complex III would fit slightly better than II, but still poorly, to the ⟨Fe–S⟩ vs. magnetic moment plot, and this correlation now has too many exceptions to be applied other than *very approximately between different* complexes (though not within a given complex).

It is not certain how the solvent molecule produces the difference in properties between II and III, but the solvent itself is not close enough to cause significant molecular perturbations itself. The ligand ("3") nearest the benzene does have a shorter average Fe–S distance than the other two, but this difference is very slight. A more significant effect is molecular packing, which is strongly affected by the benzene. This in turn affects the lattice forces and hence the magnetism, which is known to be very sensitive to very subtle changes in ferric dithiocarbamates.[3-7] A more detailed analysis would require more precise structural data for II.

The metal–ligand coordination sphere MS_6, in each of the

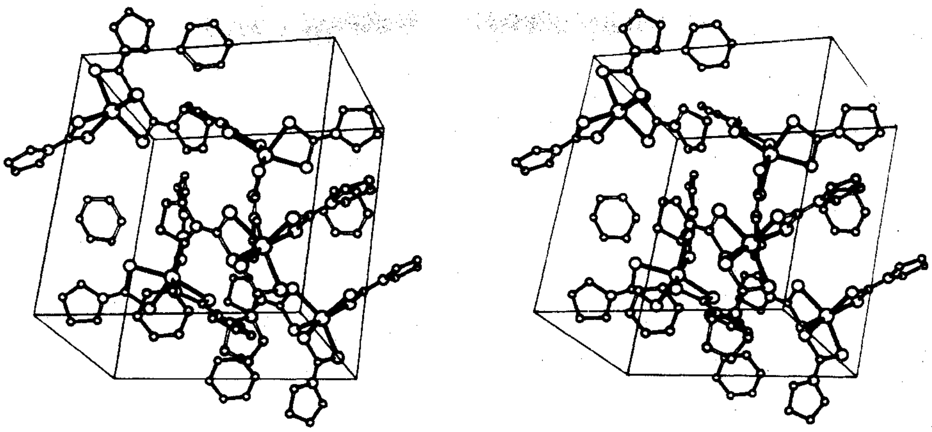

Figure 2. Molecular packing in complex IV.

Table VI. Comparison of Average Structural Parameters

	⟨M-S⟩, Å	⟨C-N⟩, Å	δ, deg	ζ, deg	γ, deg	ζ', deg	Ref
CrPDC·$^1/_2$Bz (IV)	2.404	1.341	74.2	95.1	164.1	97.5	*a*
CrMC·CH_2Cl_2[b]	2.406	1.348	72.2	94.6	162.0	99.6	21
CoMC·CH_2Cl_2[b]	2.275	1.33	76.1	94.2	165.4	97.1	6
IrPDC·$^1/_2$Bz (V)	2.376	1.32	73.3	97.4	167.2	92.8	*a*
FePDC (II)	2.407	1.31	74.5	93.4	161.0	101.7	4
FePDC·$^1/_2$Bz (III)	2.434	1.317	73.3	94.2	160.6	101.3	*a*

[a] Present work. [b] MC = 4-morpholinecarbodithioato-*S,S'*.

complexes III, IV, and V, approximates a trigonally distorted octahedron. The average values of the interatomic angles in the MS_6 coordination sphere define the trigonality of the complexes and are given in Table VI, where $\delta = \langle S_{i1}\text{–M–}S_{i2}\rangle$, $\zeta = \langle S_{i1}\text{–M–}S_{j1}\rangle$ and $\langle S_{i2}\text{–M–}S_{j2}\rangle$, $\zeta' = \langle S_{i1}\text{–M–}S_{j2}\rangle$, and $\gamma = \langle S_{i1}\text{–M–}S_{j2}\rangle$; δ is the ligand "bite", ζ and ζ' are the angles between cis pairs of metal–ligand bonds, and γ is the angle between trans bonds. In an ideal octahedron, $\delta = \zeta = \zeta' = 90°$ and $\gamma = 180°$. Relevant data for related complexes are included in the table for comparison. Of the three complexes, that of iridium is closest to octahedral in its metal environment. The average metal–ligand (M–L) bond length increases vertically downward in the periodic table as expected, when comparing d^6 configurations for different ligands: ⟨Co–S⟩ = 2.275 Å for CoMC·CH_2Cl_2; ⟨Ir–S⟩ = 2.38 Å in V. Within the same transition series, the M–L distance decreases with decreasing unpaired electron density in the d shell: ⟨Fe–S⟩ = 2.43 Å in III; ⟨Cr–S⟩ = 2.40 Å in IV (and ⟨Co–S⟩ = 2.275 Å for CoMC·CH_2Cl_2). The half-filled $t_2{}^3$ subshell in the chromium complex dramatically lengthens the M–L distance over that for the filled $t_2{}^6$ configurations: ⟨Cr–S⟩ in IV is not only greater than ⟨Co–S⟩ in a typical and similar cobalt dithiocarbamate but it is even greater than ⟨Ir–S⟩ in V, a $t_2{}^6$ case involving a third series transition metal. The "bite" angle, δ, of these and related dithiocarbamate ligands appears to correlate approximately with the M–L distance and seems to be quite independent of other factors such as trigonal distortion other than within the ligands, tetragonal distortion, or packing effects as far as can be determined from data so far in the literature.[4-6,21]

Acknowledgment. Support for instrumentation received under NSF Grant GP41679 is gratefully acknowledged.

Registry No. FePDC·$^1/_2$Bz, 57428-48-5; CrPDC·$^1/_2$Bz, 57428-49-6; IrPDC·$^1/_2$Bz, 57428-50-9.

Supplementary Material Available: Listings of structure factor amplitudes (42 pages). Ordering information is given on any current masthead page.

References and Notes

(1) E. J. Cukauskas, B. S. Deaver, Jr., and E. Sinn, *J. Chem. Soc., Chem. Commun.*, 698 (1974).
(2) E. J. Cukauskas, B. S. Deaver, Jr., and E. Sinn, to be submitted for publication.
(3) A. H. Ewald, R. L. Martin, E. Sinn, and A. H. White, *Inorg. Chem.*, **8**, 1837 (1969).
(4) P. C. Healy and A. H. White, *Chem. Commun.*, 1446 (1971); *J. Chem. Soc., Dalton Trans.*, 1163 (1972).
(5) J. G. Leipoldt and P. Coppens, *Inorg. Chem.*, **12**, 2269 (1973).
(6) P. C. Healy and E. Sinn, *Inorg. Chem.*, **14**, 109 (1975).
(7) A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, *Proc. R. Soc. London, Ser. A*, **280**, 235 (1964).
(8) A. H. White, R. Roper, E. Kokot, H. Waterman, and R. L. Martin, *Aust. J. Chem.*, **17**, 294 (1964).
(9) R. M. Golding, W. C. Tennant, C. R. Kanekar, R. L. Martin, and A. H. White, *J. Chem. Phys.*, **45**, 2688 (1966).
(10) B. N. Figgis and G. E. Toogood, *J. Chem. Soc., Dalton Trans.*, 2177 (1972).
(11) R. M. Golding and H. J. Whitfield, *Trans. Faraday Soc.*, **62**, 1713 (1966).
(12) R. Rickards, C. E. Johnson, and H. A. O. Hill, *J. Chem. Phys.*, **48**, 5231 (1968).
(13) R. Rickards, C. E. Johnson, and H. A. O. Hill, *J. Chem. Phys.*, **51**, 846 (1969).
(14) H. H. Wickman and C. F. Wagner, *J. Chem. Phys.*, **51**, 435 (1969).
(15) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(16) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 511 (1965).
(17) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(18) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965); D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(19) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).
(20) Supplementary material.
(21) R. J. Butcher and E. Sinn, *J. Chem. Soc., Dalton Trans.*, in press.