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Molecular Structures of *cis*-bis-Isothiocyanato bis-2,2'-bipyridyl Manganese II and Cobalt II

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The title compounds are close analogs of the extensively studied Fe(2,2'-bipyridine)$_2$(NCS)$_2$. The latter complex along with Fe(phenanthroline)$_2$(NCS)$_2$ are the original examples and archetypes of a series of ferrous α-di-imine complexes many of which exhibit a spin state transition from a ^{5}T ground term at ambient temperature to ^{1}A for T < *ca.* 200 K. The only member of this series for which there has been a single crystal X-ray structure determination is Fe(2,2'-bipyridine)$_2$(NCS)$_2$ and this was a limited film methods study. In this work, we communicate the basic features of our structure determination for the isomorphous manganous and isostructural cobaltous analogs. More complete results of this X-ray study will be published in a subsequent publication that will include detailed susceptibility (1.6 to 300 K) and ESR data.

Experimental

Single crystals of the title complexes were grown by slow evaporation from a nitromethane solution. The crystal data for these compounds are given in Table I. Three dimensional intensity data were collected by the θ–2θ scan method on a Syntex P2$_1$ automated diffractometer using monochromatized Mo-Kα radiation (λ = 0.71069 Å). Corrections for Kα_1–Kα_2 splitting and Lorentz polarization factors were applied. No corrections for absorption were made.

Structure Solutions and Refinement

The positions of the heavy atoms (Co and Mn) were determined from the corresponding three dimensional Patterson synthesis. The remaining non-hydrogen atoms were located in subsequent Fourier and difference Fourier syntheses. The structures were refined by the full matrix refinement technique using anisotropic temperature factors for non-hydrogen atoms. The positions of the bipyridyl hydrogen atoms were calculated and used with fixed isotropic temperature factors. The observed intensity data were corrected for the anomalous dispersion of molybdenum radiation by the transition metal and sulfur atoms. The final *R* factors are 0.047 and 0.045 for the cobalt and manganese structures, respectively.

Atomic scattering factors for the non-hydrogen atoms were taken from Cramer and Mann (1968) and those for hydrogen atoms from Stewart *et al.* (1965). The least-squares refinements were carried out using the X-RAY 76 crystallographic computer program system (Stewart, 1976).

Description of the Structures

The final positional parameters for the cobalt and manganese complexes are given in Table II. While

TABLE I. Crystal Data.

Molecular formula (MW)		MnS$_2$N$_6$C$_{22}$H$_{16}$ (483.48)	CoS$_2$N$_6$C$_{22}$H$_{16}$ (487.82)
Space group		Pbca	Pbca
Cell dimensions:	*a*	16.858(9) A	16.156(5) Å
	b	16.141(8)	16.940(5)
	c	16.068(5)	15.9795(5)
	v	4372.2 Å^3	4372.1 Å^3
	z	8	8
Calculated density		1.469 gm cm^{-3}	1.482 gm cm^{-3}
Range of data	$2\theta_{max}$	45°	40°
Observed (total) reflections		1780 (3240)	978 (2466)

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TABLE II. Positional Parameter of Cobalt and Manganese Complexes.

Atom	*X/a*	*Y/b*	*Z/c*	*Atom*	*X/a*	*Y/b*	*Z/c*
Co^{2+}	0.1155(1)	0.5009(1)	0.2016(1)	Mn^{2+}	0.0012(1)	0.1857(1)	0.3868(1)
N(1)	0.2163(7)	0.5820(6)	0.2220(7)	N(1)	0.0891(4)	0.2134(5)	0.2817(5)
C(2)	0.2715(9)	0.5609(7)	0.2798(8)	C(2)	0.0689(5)	0.2727(6)	0.2260(6)
C(3)	0.3437(9)	0.6056(9)	0.2936(10)	C(3)	0.1139(6)	0.2844(7)	0.1542(6)
C(4)	0.3569(9)	0.6699(10)	0.2459(12)	C(4)	0.1805(7)	0.2355(8)	0.1405(7)
C(5)	0.3019(10)	0.6928(7)	0.1850(10)	C(5)	0.2011(6)	0.1762(8)	0.1977(7)
C(6)	0.2296(8)	0.6477(9)	0.1751(8)	C(6)	0.1546(6)	0.1684(6)	0.2675(6)
N(7)	0.1909(5)	0.4449(6)	0.2989(7)	N(7)	−0.0486(4)	0.2919(5)	0.3057(5)
C(8)	0.2534(8)	0.4893(10)	0.3271(7)	C(8)	−0.0026(7)	0.3210(5)	0.2432(5)
C(9)	0.2978(10)	0.4676(9)	0.3981(9)	C(9)	−0.0211(7)	0.3935(6)	0.2008(6)
C(10)	0.2765(10)	0.3976(11)	0.4377(9)	C(10)	−0.0880(7)	0.4356(6)	0.2212(7)
C(11)	0.2136(10)	0.3501(9)	0.4063(9)	C(11)	−0.1373(6)	0.4065(6)	0.2857(8)
C(12)	0.1703(9)	0.3763(8)	0.3383(10)	C(12)	−0.1153(6)	0.3344(7)	0.3241(6)
N(13)	0.0409(6)	0.5301(6)	0.3092(7)	N(13)	0.0233(4)	0.2993(5)	0.4713(5)
C(14)	−0.0254(9)	0.4847(10)	0.3217(8)	C(14)	−0.0276(5)	0.3135(6)	0.5340(6)
C(15)	−0.0803(8)	0.4946(10)	0.3878(8)	C(15)	−0.0194(7)	0.3808(7)	0.5859(6)
C(16)	−0.0639(11)	0.5564(10)	0.4413(10)	C(16)	0.0428(8)	0.4367(7)	0.5733(8)
C(17)	0.0042(12)	0.6030(9)	0.4312(10)	C(17)	0.0934(7)	0.4223(7)	0.5095(8)
C(18)	0.0532(10)	0.5876(9)	0.3641(10)	C(18)	0.0829(7)	0.3543(7)	0.4586(7)
N(19)	0.0162(6)	0.4165(6)	0.1995(7)	N(19)	−0.0915(4)	0.1879(5)	0.4900(4)
C(20)	−0.0403(9)	0.4173(8)	0.2619(6)	C(20)	−0.0915(5)	0.2512(6)	0.5450(6)
C(21)	−0.0996(8)	0.3600(9)	0.2710(9)	C(21)	−0.1487(6)	0.2603(6)	0.6058(6)
C(22)	−0.1072(9)	0.3030(8)	0.2092(10)	C(22)	−0.2040(6)	0.1985(8)	0.6120(7)
C(23)	−0.0532(9)	0.3038(9)	0.1433(9)	C(23)	−0.2025(6)	0.1298(7)	0.5604(7)
C(24)	0.0061(9)	0.3617(8)	0.1394(10)	C(24)	−0.1452(7)	0.1289(6)	0.4998(6)
C(25)	0.2187(9)	0.3998(8)	0.0664(8)	C(25)	−0.1065(6)	0.0540(6)	0.2800(6)
N(26)	0.1809(7)	0.4427(7)	0.1084(7)	N(26)	−0.0655(5)	0.0940(5)	0.3200(5)
C(27)	0.0263(9)	0.6420(10)	0.1057(10)	C(27)	0.1495(8)	0.1015(7)	0.4758(7)
N(28)	0.0536(7)	0.5830(8)	0.1296(8)	N(28)	0.0895(6)	0.1112(6)	0.4504(6)
S(1)	0.2740(3)	0.3411(2)	0.0099(3)	S(1)	−0.1653(2)	−0.0011(2)	0.2215(2)
S(2)	−0.0119(3)	0.7255(2)	0.0756(3)	S(2)	0.2389(2)	0.0800(2)	0.5172(2)

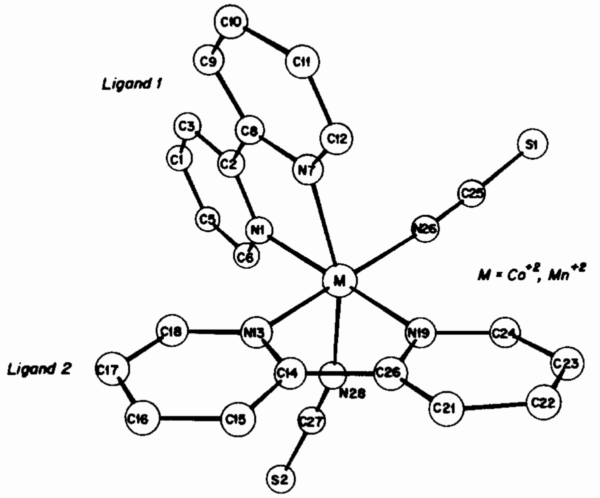

Fig. 1. Structures of the complexes.

these particular crystal samples are not isomorphous, they are essentially isostructural. Each structure consists of a central metal ion (Co^{+2} and Mn^{+2}) surrounded by two bipyridyl and two isothiocyanate ligands. The bipyridyl moieties are bidentate, coordinating through the ring nitrogen atoms, and the isothiocyanate groups are monodentate, coordinating through thy nitrogen atoms. The structures are best described as pseudo-octahedrally coordinated complexes with the isothiocyanate groups *cis* to each other (Fig. 1).

Bond lengths and bond angles involving the core atoms and the ligands are given in Table III. Distortion of the inner coordination sphere from ideal octahedral symmetry is evidenced by the deviation from 90° and 180° of the angles about the central metal ions. These distortions are in part the result of the constraints imposed by the bipyridyl moieties which do not allow for a N–M–N bite angle of 90°. In the cobalt structure the bipyridyl bite distances (N- - -N) and bite angles are 2.66 Å and 2.63 Å, and 75.5° and 75.4° for ligands 1 and 2, respectively. The corresponding values in the manganese structure are 2.72 Å and 2.63 Å, and 70.8° and 70.0°. These differences are partially attributable to the contraction of ionic radii due to the electronic configuration

TABLE III. Bond Lengths and Bond Angles Around the Central Metal Atoms.

Bond Lengths Å	*M* = Co^{+2}	*M* = Mn^{+2}
M–N(1)	2.156(11)	2.291(8)
M–N(7)	2.189(11)	2.312(8)
M–N(13)	2.156(11)	2.312(8)
M–N(19)	2.148(10)	2.280(8)
M–N(26)	2.075(12)	2.145(9)
M–N(28)	2.064(13)	2.169(10)
M–N(average)	2.13	2.25
Bond Angles °		
N(1)–M–N(7)	75.5(4)	71.0(3)
N(1)–M–N(13)	98.9(4)	100.0(3)
N(1)–M–N(19)	172.1(4)	167.7(3)
N(1)–M–N(26)	91.5(4)	96.0(3)
N(1)–M–N(28)	91.2(5)	90.7(3)
N(7)–M–N(13)	81.1(4)	78.5(3)
N(7)–M–N(19)	97.9(4)	98.6(3)
N(7)–M–N(26)	91.2(4)	92.3(3)
N(7)–M–N(28)	163.1(5)	157.8(3)
N(13)–M–(N19)	75.4(4)	70.8(3)
N(13)–M–N(26)	164.9(4)	157.7(3)
N(13)–M–N(28)	91.1(4)	93.0(3)
N(19)–M–N(26)	93.0(4)	90.0(3)
N(19)–M–N(28)	94.5(4)	97.9(3)
N(26)–M–N(28)	99.6(5)	102.3(3)

$t_{2g}^3\ e_g^2$ for Mn^{+2} and $t_{2g}^5\ e_g^2$ for Co^{+2} (Cotton-Wilkinson, 1973). The reported values of ionic radii are 0.93 Å for Mn^{+2} and 0.88 Å for Co^{+2} (Ladd, 1968).

The M^{+2}–N bond lengths *trans* to the isothiocyanate ligands show some lengthening, especially in the manganese structure. A comparison of the bond distance and bond angle values of the isothiocyanate ligands, given in Table IV, show that S–C distances are longer and the C–N distances shorter in the manganese complex than the corresponding values in the cobalt complex. In general, the dimensions of the bipyridyl ligands in both structures show no unusual features. In both complexes the crystal structures are stablized by stacking interactions involving bipyridyl ligands on adjacent molecules.

We note in the corresponding ferrous complex the Fe–N distances are 2.12 Å (average) and as expected are intermediate between the values reported here, Fe^{+2} having the electronic configuration $t_{2g}^4\ e_g^2$. However, the reported structure for $Fe(bipyridine)_2(NCS)_2$ (König and Watson, 1970) has not been fully refined (R = 21%), and thus further comparison at this juncture is unwarranted. Finally, we point out that the powders from which the present crystals were derived as well as a polycrystalline sample of $Fe(bipyridine)_2(NCS)_2$ gave *identical* Debye-Scherrer powder patterns and constitute an isomorphous series. The corresponding divalent Ni and Cu compounds gave very similar, although not identical, Debye-Scherrer powder patterns.

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TABLE IV. Bonding Parameters Involving Isothiocyanate Ligands.

Mn^{+2}–N(26)–C(25)	170.7(8)°	Co^{+2}–N(26)–C(25)	168.2(11)°
N(26)–C(25)–S(1)	178.7(10)	N(26)–C(25)–S(1)	178.0(12)
Mn^{+2}–N(28)–C(27)	152.1(9)	Co^{+2}–N(28)–C(27)	161.9(12)
N(28)–C(27)–S(2)	175.9(11)	N(28)–C(27)–S(2)	178.1(15)
N(26)–C(25)	1.144(13) A	N(26)–C(25)	1.163(18) A
C(25)–S(1)	1.630(10)	C(25)–S(1)	1.613(14)
N(28)–C(27)	1.102(16)	N(28)–C(27)	1.157(21)
C(27)–S(2)	1.683(14)	C(27)–S(2)	1.617(17)