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cis-Diisothiocyanatobis(1,10-phenanthroline)manganese(II), $[Mn(NCS)_2(C_{12}H_8N_2)_2]$

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Abstract

The crystal structure of yellow *cis*-$[Mn(phen)_2(NCS)_2]$ (phen = 1,10-phenanthroline) containing a distorted-octahedral high-spin $[Mn^{II}N_6]$ core is reported. The structure of $[Mn(phen)_2(NCS)_2]$ consists of discrete molecules of six-coordinated Mn atoms sitting on twofold rotation axes with the thiocyanates coordinating *via* their N atoms. The Mn—NCS distances are 2.139 (3) Å, while the Mn—N distances to the 1,10-phenanthrolines are 2.294 (2) and 2.301 (3) Å. The geometry is distorted from octahedral because the N—Mn—N angle formed by each 1,10-phenanthroline is only 72.2°. Four of the *cis* N—Mn—N angles are in the range 89.3 (1)-90.4 (1)°, while the remainder are 96.8 (2) and 106.0 (1)°. The thiocyanate ions are linear [179.4 (3)°] and form an angle of 166.5 (3)° with the Mn atom.

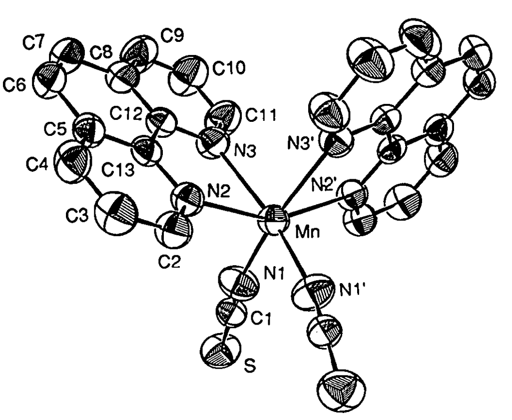


Fig. 1. *ORTEP*II (Johnson, 1976) plot of $[Mn(phen)_2(NCS)_2]$ showing the atomic numbering scheme. H atoms have been omitted.

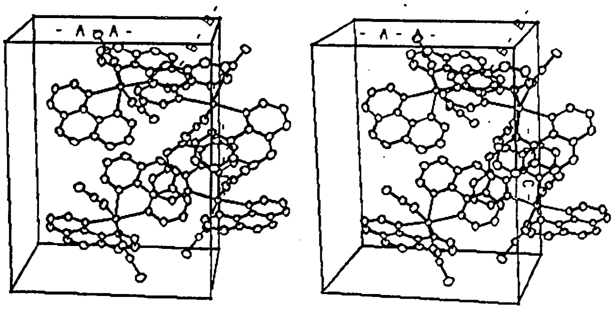
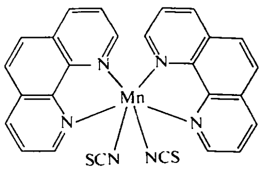


Fig. 2. Stereoscopic plot of the unit cell for $[Mn(phen)_2(NCS)_2]$.

Comment

The title compound (I) is an analog of the extensively studied $[Fe(phen)_2(NCS)_2]$ complex. The Fe complex is the archetype of a series of complexes which exhibit a spin-state crossover between the high-spin ($^5T_2$) and low-spin ($^1A_1$) states (Konig & Madeja, 1967; Konig, Madeja & Watson, 1968; Ganguli, Gàtlich & Màller, 1981). The thermal decomposition of $[Mn(phen)_2(NCS)_2]$ has been reported by Beil & Morcom (1979). We report here the crystal and molecular structure of this complex.



(I)

An *ORTEP*II (Johnson, 1976) plot of the complex with the H atoms omitted is shown in Fig. 1. The packing of the complex in the unit cell is shown as a stereoscopic plot in Fig. 2. It is interesting that an S atom of one molecule approaches one of the middle C atoms of a 1,10-phenanthroline ligand in a neighbouring molecule at a distance predicted by the sum of the two van der Waals radii (Huheey, Keiter & Keiter, 1993). The measured distance for $S\cdots C6(x-\frac{1}{2}, \frac{1}{2}-y, -z)$ is 3.349 (4) Å and the distance predicted from van der Waals radii is 3.50 Å.

The Mn—N(phen) bond distances [2.294 (2) and 2.301 (3) Å] are comparable to the corresponding bond distances in *cis*-$[Mn(bipy)_2(NCS)_2]$ (bipy = 2,2′-bipyridine) [2.286 (8) and 2.312 (8) Å (Veidis, Dockum, Charron, Reiff & Brennan, 1981)] and *cis*-$[Mn(bipy)_2(Cl)_2]$ [2.270 (3) and 2.342 (3) Å (Lumme & Lindell, 1988)]. The Mn—N(bipy) distances that are *trans* to Cl are the longer distances in *cis*-$[Mn(bipy)_2(Cl)_2]$; the same effect is observed in *cis*-$[Mn(bipy)_2(NCS)_2]$ with the longer Mn—N(bipy) distances being those *trans* to the NCS ligands. The title complex shows no significant differences in the Mn—N(phen) distances. The Mn—N(NCS) distances [2.139 (3) Å] are slightly shorter than the Mn—N(phen) distances. Shorter metal-N(NCS) distances are also observed in *cis*-$[Mn(bipy)_2(NCS)_2]$ and in *cis*-$[Co(bipy)_2(NCS)_2]$ (Veidis, Dockum, Charron, Reiff & Brennan, 1981). The reverse is observed for the metal-N-atom distances in the Cu complex $[Cu(phen)(NCS)_2]$

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(Breneman & Parker, 1993). The N(1)—C(1) and S—C(1) distances in the thiocyanate are virtually identical in *cis*-$[Mn(phen)_2(NCS)_2]$ and $[Cu(phen)(NCS)_2]$. These distances are slightly different from those found in *cis*-$[Mn(bipy)_2(NCS)_2]$ and *cis*-$[Co(bipy)_2(NCS)_2]$.

The N—Mn—N angle formed by each 1,10-phenanthroline is 72.2 (1)°, which is very close to the corresponding angles found in *cis*-$[Mn(bipy)_2(Cl)_2]$ [70.2° (Lumme & Lindell, 1988)] and *cis*-$[Mn(bipy)_2(NCS)_2]$ [70.4° (Veidis, Dockum, Charron, Reiff & Brennan, 1981)]. This is consistent with the nearly identical Mn—N(phen or bipy) distances in the three complexes.

Experimental

The title compound was prepared by adding 20 mmol of $HClO_4$ to 10 mmol (1.15 g) of $MnCO_3$. Solid KSCN (1.94 g, 20 mmol) was added with stirring and the solution filtered to remove the solid $KClO_4$. A yellow precipitate formed when a 20 ml solution of 1,10-phenanthroline (10 mmol) dissolved in ethanol was added slowly, with stirring, to the filtered solution. The pale yellow crystals were recrystallized from dimethyl sulfoxide by solvent evaporation.

Crystal data

$[Mn(NCS)_2(C_{12}H_8N_2)_2]$
$M_r = 531.51$
Orthorhombic
Pbcn
$a = 13.340$ (2) Å
$b = 10.109$ (2) Å
$c = 17.589$ (3) Å
$V = 2372.0$ (7) Å^3
$Z = 4$
$D_x = 1.49$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15.2$-$18.9°$
$\mu = 0.733$ mm^{-1}
$T = 294$ K
Prism
0.20 × 0.20 × 0.15 mm
Light yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan
$T_{\min} = 0.877$, $T_{\max} = 0.999$
2377 measured reflections
2375 independent reflections

1337 observed reflections $[I > 3\sigma(I)]$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 20$
1 standard reflection frequency: 167 min intensity variation: 0.66%

Refinement

Refinement on F
$R = 0.036$
$wR = 0.043$
$S = 1.52$
1337 reflections
191 parameters
All H-atom parameters refined

Calculated weights $w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Mn	0	0.17129 (6)	1/4	3.24 (1)
S	−0.15003 (8)	0.4808 (1)	0.07011 (6)	5.59 (2)
N1	−0.0463 (2)	0.3118 (3)	0.1661 (2)	4.78 (6)
N2	0.1644 (2)	0.1236 (2)	0.2235 (1)	3.45 (5)
N3	0.0024 (2)	0.0094 (2)	0.1581 (1)	3.80 (5)
C1	−0.0895 (2)	0.3820 (3)	0.1267 (2)	3.67 (7)
C2	0.2440 (2)	0.1795 (3)	0.2549 (2)	4.12 (6)
C3	0.3421 (2)	0.1439 (4)	0.2385 (2)	4.72 (8)
C4	0.3581 (2)	0.0472 (4)	0.1862 (2)	4.82 (8)
C5	0.2773 (2)	−0.0152 (3)	0.1509 (2)	3.94 (6)
C6	0.2877 (3)	−0.1191 (4)	0.0964 (2)	4.71 (7)
C7	0.2076 (3)	−0.1749 (3)	0.0643 (2)	5.07 (8)
C8	0.1079 (3)	−0.1339 (3)	0.0825 (2)	4.22 (7)
C9	0.0219 (3)	−0.1889 (4)	0.0503 (2)	5.8 (1)
C10	−0.0701 (3)	−0.1451 (4)	0.0708 (2)	6.09 (9)
C11	−0.0762 (3)	−0.0442 (3)	0.1245 (2)	5.17 (9)
C12	0.0938 (2)	−0.0339 (3)	0.1361 (2)	3.45 (6)
C13	0.1806 (2)	0.0270 (3)	0.1716 (2)	3.32 (6)

Table 2. *Selected geometric parameters* (Å, °)

Mn—N1	2.139 (3)	C4—C5	1.395 (5)
Mn—N2	2.294 (2)	C5—C6	1.429 (5)
Mn—N3	2.301 (3)	C5—C13	1.406 (4)
S—C1	1.625 (4)	C6—C7	1.333 (6)
N1—C1	1.148 (4)	C7—C8	1.430 (5)
N2—C2	1.324 (4)	C8—C9	1.395 (5)
N2—C13	1.354 (4)	C8—C12	1.396 (5)
N3—C11	1.320 (5)	C9—C10	1.354 (6)
N3—C12	1.353 (4)	C10—C11	1.392 (6)
C2—C3	1.388 (5)	C12—C13	1.451 (5)
C3—C4	1.359 (6)		
N1—Mn—N3	89.5 (1)	N1—Mn—N3′	162.4 (1)
N1—Mn—N2	106.0 (1)	N1—Mn—N2′	90.2 (1)
N2—Mn—N2′	155.7 (1)	N2—Mn—N3	72.2 (1)
N2—Mn—N3′	90.4 (1)	N3—Mn—N3′	89.3 (1)
N1—Mn—N1′	96.8 (2)	C7—C8—C9	124.0 (4)
Mn—N1—C1	166.5 (3)	C7—C8—C12	119.1 (3)
Mn—N2—C2	126.3 (2)	Mn—N2—C13	116.1 (2)
Mn—N3—C11	126.5 (3)	Mn—N3—C12	116.3 (2)
C2—N2—C13	117.6 (3)	C9—C8—C12	116.9 (3)
C11—N3—C12	117.1 (3)	C8—C9—C10	120.5 (4)
S—C1—N1	179.4 (3)	C9—C10—C11	118.3 (4)
N2—C2—C3	123.9 (4)	N3—C11—C10	123.9 (4)
C2—C3—C4	118.4 (4)	N3—C12—C8	123.3 (3)
C3—C4—C5	120.3 (4)	N3—C12—C13	117.3 (3)
C4—C5—C6	123.8 (3)	C8—C12—C13	119.4 (3)
C4—C5—C13	117.2 (3)	N2—C13—C5	122.6 (3)
C6—C5—C13	119.0 (3)	N2—C13—C12	118.0 (3)
C5—C6—C7	121.2 (4)	C5—C13—C12	119.5 (3)
C6—C7—C8	121.9 (4)		

Computations were performed using the *MolEN* package (Fair, 1990).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HH1078). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Synthesis and Structure of $[(\mu_3-I)(\mu_3-WSe_4)\{Ag(PMe_2Ph)\}_3]$

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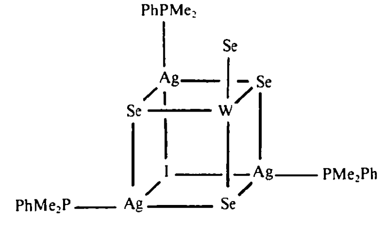
Abstract

Reaction of $[NPr_4]_2[WSe_4]$ with $[Ag(PMe_3)I]_4$ in CH_3CN followed by addition of PMe_2Ph affords the title compound, (μ_3-iodo)(μ_3-tetraselenidotungstide)tris(dimethylphenylphosphinesilver), $[(\mu_3-I)(\mu_3-WSe_4)\{AgC_8H_{11}P)\}_3]$ [systematic name: tris(dimethylphenylphosphine)-$2\kappa P,3\kappa P,4\kappa P$-$\mu_3$-iodo-$2{:}3{:}4\kappa^3 I$-tri-$\mu_3$-selenido-$1{:}2{:}3\kappa^3 Se;1{:}2{:}4\kappa^3 Se;1{:}3{:}4\kappa^3 Se$-selenido-$1\kappa Se$-trisilvertungsten], a neutral cubane cluster. The compound was characterized by a single-crystal X-ray structure determination. The molecule has crystallographically imposed symmetry 3, with the W, the I and one Se atom located on the threefold axis. The structure can be described either as three $Ag(PMe_2Ph)^+$ fragments bridged by one μ_3-WSe_4^{2-} ligand and one μ_3-I^- ligand, or as a WAg_3Se_3I cubane cluster core with an Se^{2-} ligand bound to W and a PMe_2Ph ligand bound to each Ag.

Comment

The coordination chemistry of MS_4^{2-} (M = Mo, W) has been the subject of intense investigation, primarily because of its relevance in modeling certain molybdoenzymes (Coucouvanis, 1991; Holm & Berg, 1986) and in copper-molybdenum antagonism (Sarkar & Mishra, 1984). However, the related chemistry of MSe_4^{2-} (M = Mo, W) had not been investigated until recently (Ansari & Ibers, 1990). Among the few mixed-metal selenides that have been structurally characterized are $[Ni(WSe_4)_2^{2-}]$ and $[Ni(Se_2)(WSe_4)]^{2-}$ (Ansari, Chau, Mahler & Ibers, 1989), $[(PPh_3)_3Ag_2(WSe_4)]$ (Müller *et al.*, 1989), and the cubanes $(\mu_3-Cl)(\mu_3-WSe_4)[CuL]_3$ and $(\mu_3-Cl)(\mu_3-MoOSe_3)[CuL]_3$ (Christuk, Ansari & Ibers, 1992; Müller, Wienböker & Penk, 1989). Here we summarize the synthesis and report the structural details of $[(\mu_3-I)(\mu_3-WSe_4)\{Ag(PMe_2Ph)\}_3]$, (I).



(I)

The title compound (I) is similar to the Ag/Mo/S cubane $[(\mu_3-Cl)(\mu_3-WS_4)\{Ag(PPh_3)\}_3]$ (Zhu, Wu, Du, Wu & Lu, 1992) and the Cu/W/Se cubane $[(\mu_3-Cl)(\mu_3-WSe_4)\{Cu(PPh_3)\}_3]$ (Christuk, Ansari & Ibers, 1992). In each structure the Mo or W atom is tetrahedrally coordinated by one apical and three bridging chalcogenides and the Ag or Cu atom is tetrahedrally coordinated by two bridging chalcogenides, one halide and one phosphine. Although these structures may be discussed in terms of cubanes, they may also be viewed as comprising three $Ag(PMe_2Ph)^+$ units bridged by a $(\mu_3-I)^-$ ligand and a $(\mu_3-WSe_4)^{2-}$ ligand.

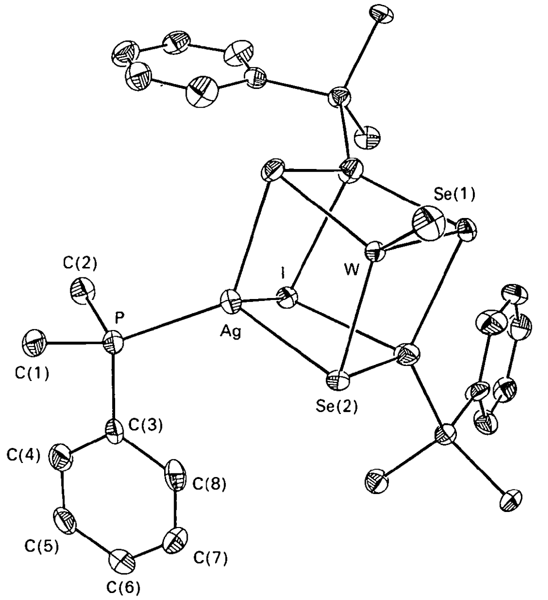


Fig. 1. A view of the title compound with 50% probability displacement ellipsoids shown. H atoms have been omitted.