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

$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Sb	0.23245 (2)	0.30718 (1)	0.35402 (2)	0.01728 (8)
Cl1	0.36868 (7)	0.40978 (4)	0.47591 (10)	0.0277 (2)
Cl2	0.10910 (7)	0.39965 (5)	0.16334 (11)	0.0337 (2)
Cl3	0.08650 (7)	0.32835 (5)	0.59127 (10)	0.0280 (2)
Cl4	0.39272 (7)	0.29377 (4)	0.11523 (10)	0.0262 (2)
Fe	0.27396 (4)	0.59740 (2)	−0.04572 (5)	0.01836 (10)
C1	0.2915 (4)	0.6018 (2)	0.2292 (4)	0.0396 (8)
C2	0.3805 (3)	0.6514 (2)	0.1665 (4)	0.0345 (8)
C3	0.3170 (4)	0.7077 (2)	0.0576 (5)	0.0350 (8)
C4	0.1879 (4)	0.6943 (2)	0.0516 (6)	0.0429 (10)
C5	0.1705 (4)	0.6289 (3)	0.1566 (5)	0.0453 (10)
C6	0.3008 (3)	0.4828 (2)	−0.1349 (4)	0.0241 (6)
C7	0.3930 (3)	0.5340 (2)	−0.1860 (4)	0.0231 (6)
C8	0.3307 (3)	0.5934 (2)	−0.2934 (4)	0.0250 (6)
C9	0.1995 (3)	0.5788 (2)	−0.3069 (4)	0.0282 (6)
C10	0.1822 (3)	0.5105 (2)	−0.2086 (4)	0.0273 (6)

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

Sb—Cl1	2.3888 (7)	C2—C3	1.391 (5)
Sb—Cl2	2.4226 (8)	C3—C4	1.399 (6)
Sb—Cl3	2.5788 (8)	C4—C5	1.402 (6)
Sb—Cl4	2.6832 (8)	C6—C10	1.406 (4)
Sb—Cl3^{i}	3.3202 (8)	C6—C7	1.413 (4)
Sb—Cl4^{ii}	3.0063 (8)	C7—C8	1.416 (4)
C1—C2	1.406 (6)	C8—C9	1.421 (4)
C1—C5	1.422 (6)	C9—C10	1.411 (5)
Cl1—Sb—Cl2	91.18 (3)	Cl4—Sb—Cl4^{ii}	92.6 (1)
Cl1—Sb—Cl3	91.03 (3)	Cl3^{i}—Sb—Cl4^{ii}	101.1 (1)
Cl2—Sb—Cl3	90.13 (3)	C2—C1—C5	107.3 (3)
Cl1—Sb—Cl4	85.18 (3)	C3—C2—C1	108.6 (3)
Cl2—Sb—Cl4	89.44 (3)	C2—C3—C4	108.2 (3)
Cl3—Sb—Cl4	176.18 (2)	C3—C4—C5	108.4 (3)
Cl1—Sb—Cl3^{i}	164.2 (1)	C4—C5—C1	107.4 (3)
Cl2—Sb—Cl3^{i}	84.6 (1)	C10—C6—C7	108.1 (3)
Cl3—Sb—Cl3^{i}	104.2 (1)	C6—C7—C8	107.9 (3)
Cl4—Sb—Cl3^{i}	79.6 (1)	C7—C8—C9	107.8 (3)
Cl1—Sb—Cl4^{ii}	83.6 (1)	C10—C9—C8	107.7 (3)
Cl2—Sb—Cl4^{ii}	174.2 (1)	C6—C10—C9	108.5 (3)
Cl3—Sb—Cl4^{ii}	87.4 (1)		

Symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

The determination of the cell parameters and intensity-data collection were carried out at 173 K. The structure was solved by heavy-atom methods and refined by a full-matrix least-squares technique. All H atoms were located from difference maps and refined isotropically.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93. Geometric calculations: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1201). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diaqua[2,6-diacetylpyridine bis(thiosemicarbazone)]manganese(II) Diperchlorate

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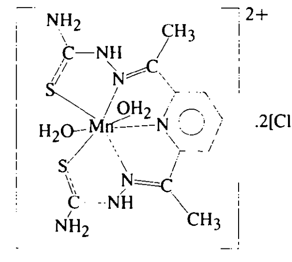
Abstract

The Mn atom in $[Mn(C_{11}H_{15}N_7S_2)(H_2O)_2](ClO_4)_2$ is in a distorted pentagonal bipyramidal environment with three N and two S atoms of the open-chain ligand forming the pentagonal girdle and O atoms of the water molecules occupying the apical positions. The ClO_4^- ions are involved in hydrogen bonding with the H_2O molecules and with the terminal amino groups of the ligand [3.002 (5) and 2.962 (8) Å].

Comment

Although N-heterocyclic thiosemicarbazones, including those formed from 2-formylpyridine and 2-acetylpyridine, have received much attention, little is known about their metal complexes (West *et al.*, 1993) or their structures (Mohan, Sharma, Kumar & Jha, 1986). Accordingly we have undertaken the preparation and structure analysis of diaqua[2,6-diacetylpyridine bis(thiosemicarbazone)]manganese(II) diperchlorate, (I), to further the study of the effect of metal ions in the template synthesis of seven-coordinate complexes (Othman & Ng, 1995).



(I)

The Mn atom in (I) is in a distorted pentagonal bipyramidal environment with three N and two S atoms of the open-chain macrocyclic ligand forming the pentagonal girdle and the O atoms of the water molecules occupying the apical positions. The cationic complex lies approximately parallel to the *ab* plane and has exact twofold symmetry, with atoms Mn, N1 and C3 lying on the twofold axis parallel to *b*. The N2 and N2*A* atoms lie 0.14 Å above and below the MnN_3S_2 least-squares plane. The Mn—N(py) bond [2.268 (3) Å] is shorter than both the Mn—N(imino) bond [2.364 (3) Å] in (I) and the Mn—N(py) distance [2.328 (4) Å] in aquachloro[2,6-diacetylpyridine bis(semicarbazone)]manganese(II) chloride dihydrate, (II) (Capparelli, De Meester, Goodgame, Gunn & Skapski, 1985). In (I) the Mn atom is thus displaced towards the pyridine N atom along the C_2 axis. Similar displacements have been observed in diphenyl[2,6-diacetylpyridine bis(thiosemicarbazonato)]tin(IV) bis(dimethylformamide), (III) (Casas *et al.*, 1994), but not in (II) or in a similar complex reported by Palenik & Wester (1978). However, the Mn—S bond [2.6073 (10) Å] in (I) is comparable with the Sn—S bonds [2.603 (1) and 2.593 (1) Å] in (III) (Casas *et al.*, 1994) and the Fe—S bond [2.639 (4) Å] in bis(isothiocyanato)[2,6-diacetylpyridine bis(thiosemicarbazone)]iron(II) dihydrate (Dessy & Fares, 1981).

There are a number of close contacts in (I) suggestive of hydrogen bonds; those involving the ClO_4^- anion with an H_2O molecule and the terminal amino group of the ligand are considered significant [O1*W*···O4^{i} 3.002 (5) Å, O1*W*—H1*W*···O4^{i} 161 (6)° and N4···O1^{ii} 2.962 (8) Å, N4—H4*NA*···O1^{ii} 178 (6)°; symmetry codes: (i) $-x$, $-y + 2$, $-z$; (ii) $-x + \frac{1}{2}$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$]. The crystal structure is stabilized by these hydrogen bonds and numerous close intermolecular contacts shorter than 3.5 Å.

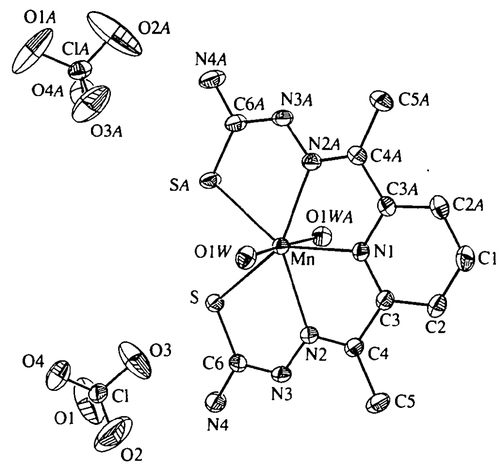


Fig. 1. *ORTEP*II (Johnson, 1976) plot of (I) with the numbering scheme, showing 50% probability displacement ellipsoids.

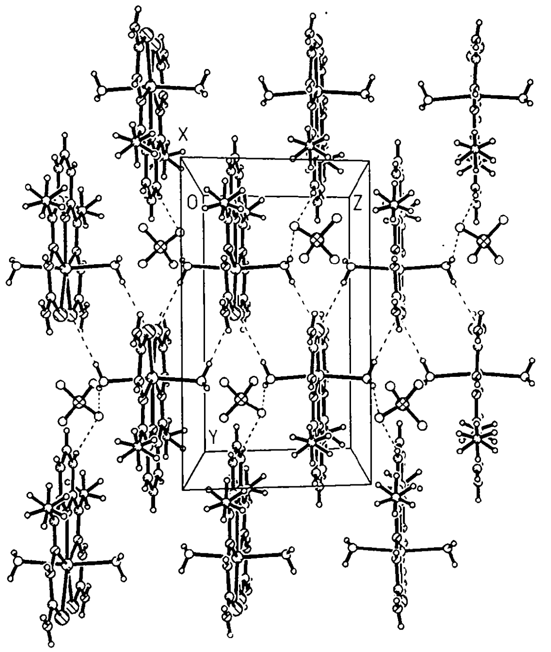


Fig. 2. Packing diagram viewed down the *a* axis showing the hydrogen bonds.

Experimental

The title compound was synthesized by the template reaction between 2,6-diacetylpyridine, thiosemicarbazide and manganese perchlorate in refluxing methanol. Orange crystals of the product were obtained on cooling to room temperature.

Crystal data

$[Mn(C_{11}H_{15}N_7S_2)(H_2O)_2]$-
$(ClO_4)_2$
$M_r = 599.29$
Monoclinic
$C2/c$
$a = 23.6801\,(9)$ Å
$b = 12.9415\,(9)$ Å
$c = 7.8455\,(5)$ Å
$\beta = 106.069\,(4)°$
$V = 2310.4\,(2)$ Å^3
$Z = 4$
$D_x = 1.723$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 5$–$12.5°$
$\mu = 1.046$ mm^{-1}
$T = 293\,(2)$ K
Needle
$0.70 \times 0.44 \times 0.40$ mm
Orange

Data collection

Siemens *P*4 diffractometer
θ–2θ scans
Absorption correction:
ψ scan (Siemens, 1994)
$T_{\min} = 0.667$, $T_{\max} = 0.756$
3090 measured reflections
2649 independent reflections
2341 observed reflections
$[I > 2\sigma(I)]$

$R_{\rm int} = 0.0154$
$\theta_{\max} = 27.49°$
$h = -1 \rightarrow 30$
$k = -1 \rightarrow 16$
$l = -10 \rightarrow 9$
3 standard reflections
monitored every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0531$
$wR(F^2) = 0.1552$
$S = 1.064$
2649 reflections
178 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0826P)^2 + 5.5115P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.75$ e Å^{-3}
$\Delta\rho_{\min} = -0.66$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0027 (5)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Mn	0	0.81352 (5)	1/4	0.0345 (2)
S	0.06806 (4)	0.97074 (7)	0.24189 (15)	0.0538 (3)
N1	0	0.6383 (3)	1/4	0.0362 (7)
N2	0.08889 (11)	0.7470 (2)	0.2133 (3)	0.0380 (5)
N3	0.13372 (13)	0.8105 (2)	0.2010 (4)	0.0467 (7)
N4	0.1744 (2)	0.9674 (3)	0.1992 (7)	0.0724 (12)
C1	0	0.4247 (4)	1/4	0.0570 (13)
C2	0.0480 (2)	0.4784 (3)	0.2291 (5)	0.0507 (8)
C3	0.04666 (14)	0.5858 (2)	0.2308 (4)	0.0383 (6)
C4	0.09697 (14)	0.6491 (3)	0.2110 (4)	0.0408 (6)
C5	0.1523 (2)	0.5983 (3)	0.1962 (7)	0.0680 (11)
C6	0.12854 (14)	0.9136 (3)	0.2115 (5)	0.0464 (7)
Cl	0.18869 (4)	1.27680 (8)	0.23319 (14)	0.0569 (3)
O1	0.2239 (3)	1.3479 (6)	0.3451 (8)	0.186 (4)
O2	0.2193 (5)	1.2135 (8)	0.1548 (13)	0.271 (7)
O3	0.1642 (3)	1.2132 (5)	0.3363 (7)	0.156 (3)
O4	0.1451 (2)	1.3258 (3)	0.1031 (5)	0.0940 (12)
O1*W*	−0.03561 (13)	0.8020 (2)	−0.0437 (4)	0.0492 (6)

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

Mn—O1*W*	2.229 (3)	N4—C6	1.315 (5)
Mn—N1	2.268 (3)	C1—C2	1.379 (5)
Mn—N2	2.364 (2)	C2—C3	1.390 (5)
Mn—S	2.6073 (10)	C3—C4	1.490 (4)
S—C6	1.686 (3)	C4—C5	1.499 (5)
N1—C3	1.341 (3)	Cl—O2	1.350 (7)
N2—C4	1.282 (4)	Cl—O1	1.381 (5)
N2—N3	1.367 (4)	Cl—O4	1.388 (3)
N3—C6	1.344 (5)	Cl—O3	1.388 (5)
O1*W*—Mn—O1*W*$^{\rm i}$	172.3 (2)	C4—N2—N3	118.1 (3)
O1*W*—Mn—N1	86.16 (8)	C4—N2—Mn	120.2 (2)
O1*W*—Mn—N2	86.82 (10)	N3—N2—Mn	121.7 (2)
O1*W*$^{\rm i}$—Mn—N2	90.39 (11)	C6—N3—N2	120.4 (3)
N1—Mn—N2	68.66 (7)	C2—C1—C2$^{\rm i}$	119.5 (5)
N2—Mn—N2$^{\rm i}$	137.32 (13)	C1—C2—C3	118.7 (3)
O1*W*—Mn—S	94.96 (9)	N1—C3—C2	122.0 (3)
O1*W*$^{\rm i}$—Mn—S	91.03 (8)	N1—C3—C4	116.1 (3)
N1—Mn—S	141.30 (2)	C2—C3—C4	121.9 (3)
N2—Mn—S	72.77 (7)	N2—C4—C3	114.6 (3)
N2$^{\rm i}$—Mn—S	149.78 (7)	N2—C4—C5	124.9 (3)
S—Mn—S$^{\rm i}$	77.41 (4)	C3—C4—C5	120.5 (3)
C6—S—Mn	102.48 (12)	N4—C6—N3	115.4 (3)
C3$^{\rm i}$—N1—C3	119.1 (4)	N4—C6—S	121.9 (3)
C3—N1—Mn	120.5 (2)	N3—C6—S	122.6 (3)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

The structure was solved by direct methods and refined by full-matrix least-squares methods. All H atoms were located from difference Fourier maps except those of the methyl group (C5) which were found to be disordered over two sites (each with an occupancy of 0.5), one site being rotated 60° from the other. The located H atoms were refined isotropically, whereas the disordered H atoms were refined using a riding model (*AFIX*123; Sheldrick, 1993).

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990), *ORTEP*II (Johnson, 1976). Geometric calculations: *PARST* (Nardelli, 1983). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1217). (00 pp.). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Mixed-Ligand Complexes of Technetium. XIV. Structure of *trans*-[TcCl$_2$(NCS)(Me$_2$PhP)$_3$]

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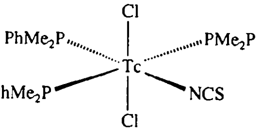
Abstract

mer-[TcCl$_3$(Me$_2$PhP)$_3$] reacts with potassium thiocyanate with the replacement of only one Cl$^-$ ligand by NCS$^-$ and forms selectively (*OC*-6-12)-dichlorotris(dimethylphenylphosphine)(thiocyanato-κN)-technetium(III) {*mer,trans*-[TcCl$_2$(NCS)(Me$_2$PhP)$_3$]}. No evidence could be found for the formation of the *cis* analogue. The title compound crystallizes in monomeric units. The Tc atom is coordinated in a distorted octahedral manner with the two Cl ligands in *trans* positions to each other. The NCS$^-$ ligand is N-bonded with a Tc—N bond length of 2.104 (3) Å.

Comment

Coordination compounds of technetium with the metastable γ-emitting ^{99m}Tc (E_γ = 140 keV, half-life $t_{1/2}$ = 6 h) are frequently used in diagnostic nuclear medicine (Clarke & Podbielski, 1987). This has also encouraged the development of the basic coordination chemistry of the artificial element (Baldas, 1994). Most chemical studies are carried out with the long-lived β-emitting isotope ^{99}Tc ($E_{\max}$ = 0.29 MeV, $t_{1/2}$ = 2.12 × 10^5 years) which is available from fission products in macroscopic amounts.

In the course of our systematic studies on mixed-ligand complexes of technetium, we studied the ligand-exchange behaviour of trichlorotris(dimethylphenylphosphine)technetium(III). *mer,trans*-[TcCl$_2$(NCS)(Me$_2$PhP)$_3$], (I), is formed by refluxing *mer*-[TcCl$_3$(Me$_2$PhP)$_3$] with an excess of KSCN in methanol. No products with larger NCS$^-$ contents could be isolated in crystalline form (even using a larger excess of KSCN). Significantly longer refluxing periods result in the decomposition of the technetium(III) complex and the formation of dark oily products that could not be structurally characterized.



(I)

The title compound is readily soluble in organic solvents such as CH$_2$Cl$_2$ or CHCl$_3$ and moderately soluble in alcohols. It is indefinitely stable in air as a solid and in solution. The IR spectrum of the compound shows an intense band for the ν(NCS) vibration at 2076 cm^{-1}. This is in good agreement with the spectrum of the rhenium analogue *mer,trans*-[ReCl$_2$(NCS)(Me$_2$PhP)$_3$] which has recently been structurally characterized (Hübener, Ortner, Strähle& Abram, 1995). Interestingly, the rhenium compound undergoes an isomerization to the *cis* isomer when refluxed in CH$_2$Cl$_2$/methanol for a longer period. This could not be observed for *mer,trans*-[TcCl$_2$(NCS)(Me$_2$PhP)$_3$].

Crystals of *mer,trans*-[TcCl$_2$(NCS)(Me$_2$PhP)$_3$] were obtained from a CH$_2$Cl$_2$/methanol solution. The structure consists of neutral monomeric technetium(III) complexes with N-bonded NCS$^-$ ligands. The reorientation matrix $\bar{1}00/\bar{1}0\bar{2}/0\bar{1}0$ gives a metrically *C*-centred orthorhombic cell with a = 14.997, b = 35.263, c = 10.840 Å, but the $R_{\rm int}$ value (0.59) for this Laue symmetry is too high. Fig. 1 shows a representation of the structure of the molecule together with the atom-numbering scheme.

The Tc atom is octahedrally coordinated with the phosphine ligands in meridional positions, but distortions from the idealized octahedral geometry are evident. Angles P1—Tc—P2 and P2—Tc—P3 of 94.79 (4) and 99.14 (4)°, respectively, are much larger than the N1—Tc—P1 [82.09 (9)°] and N1—Tc—P3 [84.14 (9)°] angles. The geometry of *mer,trans*-[TcCl$_2$(NCS)(Me$_2$PhP)$_3$] is thus similar to that of the analogous rhenium complex *mer,trans*-[ReCl$_2$(NCS)(Me$_2$PhP)$_3$] (Hübener *et al.*, 1995) and that of [TcNCl$_2$(Me$_2$PhP)$_3$] (Batsanov, Struchkov, Lorentz & Olk, 1988). The linear NCS$^-$ ligand [N—C—S 179.1 (4)°] is coordinated in the *trans* position to Me$_2$PhP. In accordance with all other struc-