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Bis(1,10-phenanthroline)(thiosulfato)-manganese(II) methanol solvate and *catena*-poly[[diaqua(2,9-dimethyl-1,10-phenanthroline)manganese(II)]-μ-thiosulfato]

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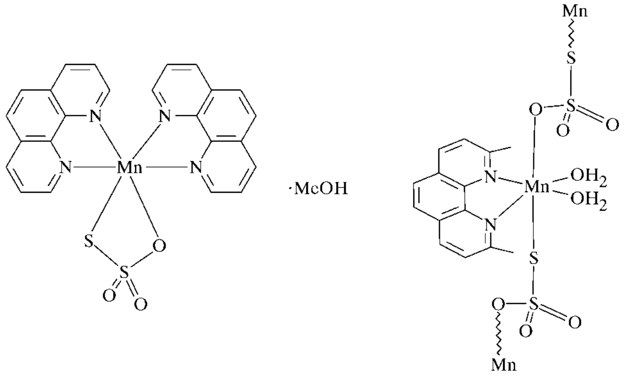
The structure of bis(1,10-phenanthroline-κ^2N,N')(thiosulfato-κ^2O:S)manganese(II) methanol solvate, $[Mn(S_2O_3)(C_{12}H_8N_2)_2]\cdot CH_3OH$, is made up of Mn^{2+} centers coordinated to two bidentate phenanthroline (phen) groups and an *S*,*O*-chelating thiosulfate anion, forming monomeric entities. The structure of *catena*-poly[[diaqua(2,9-dimethyl-1,10-phenanthroline-κ^2N,N')manganese(II)]-μ-thiosulfato-κ^2O:S], $[Mn(S_2O_3)(C_{14}H_{12}N_2)(H_2O)_2]_n$, is polymeric, consisting of Mn(dmph)$(H_2O)_2$ units (dmph is 2,9-dimethyl-1,10-phenanthroline) linked by thiosulfate anions acting in an *S*,*O*-chelating manner.

Comment

In recent years, a large amount of structural work on the complexing properties of the thiosulfate ion has been published (Brezeanu *et al.*, 1998; Carter & Drew, 1999; Freire *et al.*, 1999, 2001; Freire, Baggio, Baggio & Mariezcurrena, 2000; Freire, Baggio, Suescun & Baggio, 2000). From these results, it is clear that the anion behaves as a very versatile ligand in coordination compounds involving transition metals, displaying an internal geometry very dependent on the type of coordination present. A preferred target of the studies have been those complexes of cations which behave as borderline acids between the '*a*' and '*b*' classes in the Pearson classification scale (Pearson, 1973); in these cases, the thiosulfate group is expected to bind to the metal ions both through its hard (O) and soft (S) ends, with a resulting variety of coordination modes depending on other factors, *viz*. the shapes of accompanying ligands, crystal field stabilization, hydrogen bonding, van der Waals interactions, *etc*. Table 1 summarizes the effect that the simpler coordination modes seem to have on the thiosulfate geometry, through the statistics of relevant interatomic distances and angles in the thiosulfate structures present in the October 2001 Release of the Cambridge Structural Database (CSD; Allen & Kennard, 1993). A trend is observed in *S*-monodentate complexes towards a lengthening of the S—S bond, and a similar effect is observed in *S*,*O*-chelate compounds for the S—O$_{coord}$ bonds. In the latter case, the S—O$_{uncoord}$ bonds shorten to maintain the bond valence around the central S atom (Brown & Altermatt, 1985). The differences in the angles are explained by the predominant effect of non-bonded repulsion, as discussed by McDonald & Cruickshank (1967), when analysing tetrahedral distortions in sulfates.



(I) (II)

Although manganese(II) is a hard acid according to the Pearson classification and it is thus expected to bind preferentially to hard bases or to the hard end when multiple coordination sites are available, there are examples of Mn^{II}–thiosulfate complexes where the cation behaves as an intermediate acid, binding both to the hard as well as the soft end (O and S, respectively; see, for example, Freire *et al.*, 2001). Therefore, it is of interest to explore the bonding character-

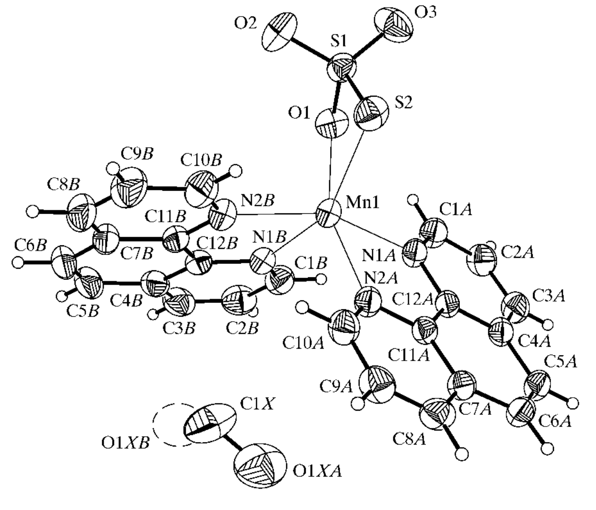


Figure 1
A view of the monomeric manganese(II) coordination polyhedron in (I). Displacement ellipsoids are drawn at the 40% probability level.

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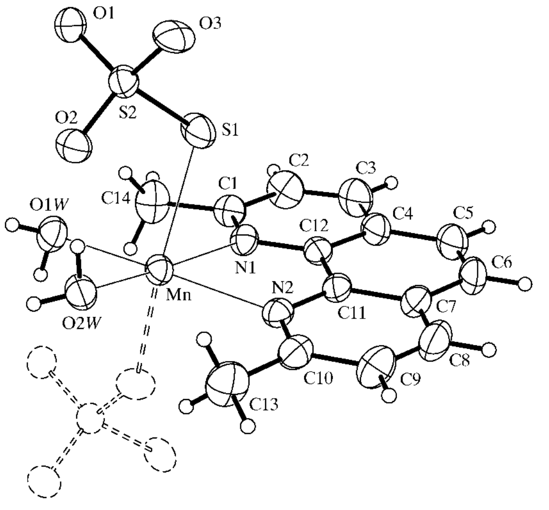

Figure 2
A view of the manganese(II) coordination polyhedron in (II), suggesting the way in which chains are formed. Displacement ellipsoids are drawn at the 40% probability level.

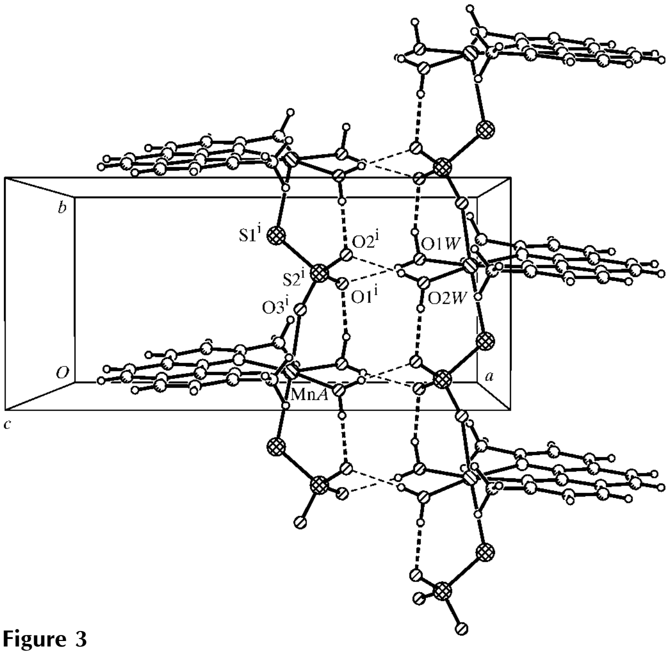

Figure 3
Packing view of (II), showing the hydrogen-bonding interactions. Intrachain hydrogen bonds are drawn as thick dashed lines, while those connecting different chains are presented as thin dashed lines. [Symmetry code: (i) $\frac{3}{2} - x, -\frac{1}{2} + y, z$.]

istics of other Mn–thiosulfate compounds in the light of this rather unpredictable behavior. In addition, our experience with the thiosulfate anion complexed to a variety of different metal centers suggests that substantially different structures can be obtained through the introduction of small differences in the coordinating organic ligands used or even by using the same ligands but working under slightly different ambient conditions (Freire *et al.*, 1999; Freire, Baggio, Baggio & Mariezcurrena, 2000; Freire, Baggio, Suescun & Baggio, 2000).

With these ideas in mind, we have been attempting to synthesize Mn–thiosulfate complexes, our only successful outcome so far being a polymeric phenanthroline complex, $[Mn(S_2O_3)(phen)(H_2O)_2]_n$, of which two independent structure determinations are now available (Brezeanu *et al.*, 1998; Freire *et al.*, 2001). In this paper, we report our most recent advances in this area, namely $[Mn(S_2O_3)(phen)_2]\cdot CH_3OH$, (I), a new monomeric phenanthroline (phen) structure, and a 2,9-dimethyl-1,10-phenanthroline (dmph) polymer, $[Mn(S_2O_3)(dmph)(H_2O)_2]_n$, (II).

Compound (I) is monomeric, with two bidentate phen groups [Mn—N 2.246 (2)–2.302 (2) Å] and an *S,O*-chelating thiosulfate [Mn—O 2.1637 (18) Å and Mn—S 2.6131 (8) Å] providing a quite distorted octahedral coordination of manganese (Fig. 1 and Table 2). Due to the restraints imposed by the chelate character of the ligands present, there are many important geometrical departures from ideal values, the most obvious being for the angles S2—Mn—O1 [70.44 (5)°] and S2—Mn—N1*B* [155.95 (5)°]. The bidentate thiosulfate anion presents the usual lengthening of the S—O bond, corresponding to the coordinated O atom, of about 3% of its total length [$S—O_{coord}$ 1.4893 (18) Å and mean $S—O_{uncoord}$ 1.448 (2) Å], as well as the usual narrowing of the corresponding S—S—O angle by *ca* 7% [$S—S—O_{coord}$ 103.82 (8)° and mean $S—S—O_{uncoord}$ 110.4 (1)°]. On the other hand, the S—S bond length matches almost exactly the corresponding mean value in Table 1. The two independent phenanthroline groups are planar (maximum deviations from their mean planes are 0.025 and 0.011 Å for units *A* and *B*, respectively) and their bond distances and angles are as expected.

The structure of (II) presents a manganese ion octahedrally surrounded by a bidentate 2,9-dimethyl-1,10-phenanthroline ligand [Mn—N 2.279 (2) and 2.296 (2) Å], two aqua molecules [Mn—O*W* 2.184 (2) and 2.206 (2) Å], and one O [Mn—O 2.1655 (19) Å] and one S atom [Mn—S 2.6306 (9) Å] from thiosulfate groups related by a whole unit-cell translation along *b* (Fig. 2 and Table 3). The coordination polyhedron is irregular, as expected from the restraints imposed by the bidentate dmph ligand, but less distorted than in (I). The most significant departures from ideal values are again associated with the bite angle, *viz*. N1—Mn—N2 [74.20 (8)°] and N2—Mn—O1*W* [173.24 (9)°].

The thiosulfate group acts as a bridging ligand between neighboring cations (through

Table 1
Mean values of selected distances and angles (Å, °) for selected parameters in the S_2O_3 geometry according to the type of coordination.

Coordination type	S—S	$S—O_{coord}$	$S—O_{uncoord}$	$S—S—O_{coord}$	$S—S—O_{uncoord}$	CSD†
S-Monodentate	2.05 (4)		1.453 (16)		107 (2)	19
S,O-Chelating	2.02 (2)	1.51 (2)	1.447 (6)	101 (3)	110.6 (11)	7
S,O-Bridging	2.009 (8)	1.479 (15)	1.467 (12)	108.5 (10)	108.9 (12)	5
Ionic	1.992 (13)		1.466 (12)		109.1 (13)	7

† Number of cases found in the CSD (Allen & Kennard, 1993). No entries for *O*-monodentate, *O,O*-chelating or *O,O*-bridging were found. Mixed coordination types have not been included in the survey.

S and O) in a rather uncommon disposition for the anion, only reported previously in a zinc(II) bis(ethylenethiourea) thiosulfate complex (Baggio *et al.*, 1974) and the previously mentioned manganese(II) phenanthroline complex, to which (II) is closely related. The molecular geometry matches fairly well the mean values in the reported structures, where it displays a similar coordination, except perhaps for a slight shortening of the S—S bond [1.9719 (11) Å *versus* a mean of 2.009 (8) Å]. This type of connectivity leads to the configuration of linear chains (Fig. 3) parallel to each other and to the crystallographic *b* axis. All the H atoms of the aqua molecules are involved in hydrogen bonding (Table 4 and Fig. 3). Two such contacts are of the 'intra-chain' type, which add to the chain cohesion (thick dashed lines in Fig. 3). The other two contacts (thin dashed lines in Fig. 3) link pairs of chains into a strip-like structure.

In both structures, there are π–π-stacking interactions between adjacent planar organic ligands. In (I), this effect seems to be stronger than in (II), as inferred from the larger stacking overlap between the expected parallel interleaved groups (33 *versus* 12%), as well as from the smaller angle between them [3.9 (2) *versus* 9.2 (2)°] and the shorter contact in the overlapping region [3.28 (1) *versus* 3.37 (1) Å].

The results of this work confirm Mn^{II} to behave in thiosulfate complexes as a medium strength acid, in spite of its classification in the Pearson scale. They also corroborate the fact that the structure of thiosulfate complexes can not be predicted on stoichiometric grounds alone; slight variations both in the geometry of the ligands involved and in the conditions of synthesis can result in important structural differences. Sometimes these variations reside directly in the environment around the metal atom [*viz*. structures (I) and (II) in this work] or, in the case where the environments are similar, in the way in which these entities pack. A clear example can be found by comparison of the dmph structure reported herein with the phen analog reported in Freire *et al.* (2001); in spite of the fact that both structures are built up by almost indistinguishable chains, the resulting crystal packings show significant differences, *viz*. in the latter structure, adjacent phen groups are far from parallel and present no staking overlap whatsoever.

Experimental

Small yellow blocks of (I) were obtained as a minor component in the synthesis of the polymer form of the phenanthroline complex, which has already been reported (Freire *et al.*, 2001). After mixing aqueous solutions of manganese chloride and sodium thiosulfate with a methanol solution of phenanthroline, in a 1:3:1 molar ratio, crystals of the dominant polymer form appeared readily, while only a few individual crystals of (I) were found. On the other hand, pale-yellow plates of (II) suitable for X-ray diffraction analysis appeared in a reasonable quantity after diffusion of a methanol solution of dmph into an aqueous solution of manganese chloride and sodium thiosulfate, in a similar ratio to that used for the preparation of (I). In both cases, crystals were used as obtained in the synthesis, without further recrystallization.

Compound (I)

Crystal data

$[Mn(S_2O_3)(C_{12}H_8N_2)_2]\cdot CH_4O$
$M_r = 559.51$
Monoclinic, $P2_1/n$
$a = 12.924$ (1) Å
$b = 11.412$ (1) Å
$c = 17.084$ (1) Å
$\beta = 109.18$ (1)°
$V = 2379.9$ (3) Å^3
$Z = 4$
$D_x = 1.562$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 84 reflections
$\theta = 1.7$–28.0°
$\mu = 0.77$ mm^{-1}
$T = 293$ (2) K
Block, yellow
0.18 × 0.14 × 0.12 mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: refined from ΔF (*SADABS* in *SAINT–NT*; Bruker, 2000)
$T_{min} = 0.88$, $T_{max} = 0.91$
11 546 measured reflections
5302 independent reflections
3942 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 28.0°$
$h = -8 \rightarrow 16$
$k = -14 \rightarrow 14$
$l = -22 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.125$
$S = 1.00$
5302 reflections
330 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0728P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.011$
$\Delta\rho_{max} = 0.68$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (I).

Mn—O1	2.1637 (18)	Mn—S2	2.6131 (8)
Mn—N1*A*	2.246 (2)	S1—O2	1.4466 (18)
Mn—N2*B*	2.258 (2)	S1—O3	1.449 (2)
Mn—N2*A*	2.261 (2)	S1—O1	1.4893 (18)
Mn—N1*B*	2.302 (2)	S1—S2	2.0175 (9)
O1—Mn—N1*A*	92.71 (7)	N1*A*—Mn—S2	108.42 (5)
O1—Mn—N2*B*	103.93 (8)	N2*B*—Mn—S2	93.31 (6)
N1*A*—Mn—N2*B*	156.20 (8)	N2*A*—Mn—S2	96.45 (5)
O1—Mn—N2*A*	157.67 (7)	N1*B*—Mn—S2	155.95 (5)
N1A—Mn—N2*A*	73.92 (7)	O2—S1—O3	111.79 (14)
N2*B*—Mn—N2*A*	94.57 (8)	O2—S1—O1	109.98 (12)
O1—Mn—N1*B*	93.40 (7)	O3—S1—O1	110.15 (12)
N1*A*—Mn—N1*B*	89.49 (7)	O2—S1—S2	110.39 (8)
N2*B*—Mn—N1*B*	72.88 (8)	O3—S1—S2	110.43 (10)
N2*A*—Mn—N1*B*	104.06 (8)	O1—S1—S2	103.82 (8)
O1—Mn—S2	70.44 (5)		

Compound (II)

Crystal data

$[Mn(S_2O_3)(C_{14}H_{12}N_2)(H_2O)_2]$
$M_r = 411.35$
Orthorhombic, *Pbca*
$a = 15.3800$ (12) Å
$b = 7.0779$ (5) Å
$c = 30.148$ (2) Å
$V = 3281.9$ (4) Å^3
$Z = 8$
$D_x = 1.665$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 108 reflections
$\theta = 1.4$–28.1°
$\mu = 1.09$ mm^{-1}
$T = 293$ (2) K
Plate, light yellow
0.26 × 0.20 × 0.10 mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: refined from ΔF (*SADABS* in *SAINT–NT*; Bruker, 2000)
$T_{\min} = 0.82$, $T_{\max} = 0.90$
18 352 measured reflections
3810 independent reflections
2341 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.061$
$\theta_{\max} = 28.1^\circ$
$h = -20 \rightarrow 19$
$k = -9 \rightarrow 8$
$l = -38 \rightarrow 36$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.087$
$S = 0.85$
3810 reflections
235 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0342P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.009$
$\Delta\rho_{\max} = 0.52$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

Mn—O3$^{\rm i}$	2.1655 (19)	Mn—S1	2.6306 (9)
Mn—O2*W*	2.184 (2)	S1—S2	1.9719 (11)
Mn—O1*W*	2.206 (2)	S2—O1	1.4648 (19)
Mn—N2	2.279 (2)	S2—O2	1.4663 (19)
Mn—N1	2.296 (2)	S2—O3	1.4763 (19)
O3$^{\rm i}$—Mn—O2*W*	89.76 (9)	O2*W*—Mn—S1	90.62 (7)
O3$^{\rm i}$—Mn—O1*W*	87.11 (9)	O1*W*—Mn—S1	97.08 (8)
O2W—Mn—O1W	83.61 (9)	N2—Mn—S1	86.53 (6)
O3$^{\rm i}$—Mn—N2	89.31 (8)	N1—Mn—S1	83.76 (6)
O2*W*—Mn—N2	102.11 (9)	O1—S2—O2	109.60 (12)
O1*W*—Mn—N2	173.24 (9)	O1—S2—O3	110.13 (12)
O3$^{\rm i}$—Mn—N1	95.60 (8)	O2—S2—O3	109.89 (12)
O2*W*—Mn—N1	173.42 (9)	O1—S2—S1	109.86 (9)
O1*W*—Mn—N1	100.44 (9)	O2—S2—S1	109.85 (9)
N2—Mn—N1	74.20 (8)	O3—S2—S1	107.48 (10)
O3$^{\rm i}$—Mn—S1	175.80 (6)		

Symmetry code: (i) $x, y-1, z$.

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O1$^{\rm i}$	0.93 (4)	1.81 (4)	2.714 (3)	164 (3)
O1*W*—H1*WB*···O1$^{\rm ii}$	0.79 (3)	1.96 (3)	2.747 (3)	173 (3)
O2*W*—H2*WA*···O2	0.84 (4)	1.83 (4)	2.662 (3)	173 (4)
O2*W*—H2*WB*···O2$^{\rm ii}$	0.83 (3)	1.93 (3)	2.752 (3)	175 (3)

Symmetry code: (i) $x, y-1, z$; (ii) $\frac{3}{2}-x, y-\frac{1}{2}, z$.

H atoms attached to C atoms were added at calculated positions and allowed for as riding atoms. Terminal methyl H atoms of the dmph ligand were additionally allowed to rotate. For (II), water H atoms were found in difference Fourier maps and were refined with restrained O—H (0.80 Å) and H···H (1.66 times O—H) distances. Compound (I) contains a methanol solvate molecule, which has a disordered O atom, split into two sites with occupancies of 0.65 and 0.35. The corresponding H atoms were not included in the model.

For both compounds, data collection: *SMART–NT* (Bruker, 2001); cell refinement: *SMART–NT*; data reduction: *SAINT–NT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL*/*PC* (Sheldrick, 1994).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1070). Services for accessing these data are described at the back of the journal.

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