

catena-Poly[[diaqua(1,10-phenanthroline-*N,N'*)manganese(II)]- μ -(thiosulfato-*O:S*)] and bis(2,2'-bipyridyl-*N,N'*)(tetrathionato-*O,O'*)-manganese(II)

Eleonora Freire,^a Sergio Baggio,^a Ricardo Baggio^{b*} and Alvaro Mombrú^c

^aUniversidad Nacional de la Patagonia, Sede Puerto Madryn and CenPat, CONICET, 9120 Puerto Madryn, Chubut, Argentina, ^bDepartamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina, and ^cCSSC Lab., Facultad de Química, Universidad de la República, Montevideo, Uruguay

Correspondence e-mail: baggio@cnea.gov.ar

Received 5 July 2000

Accepted 29 September 2000

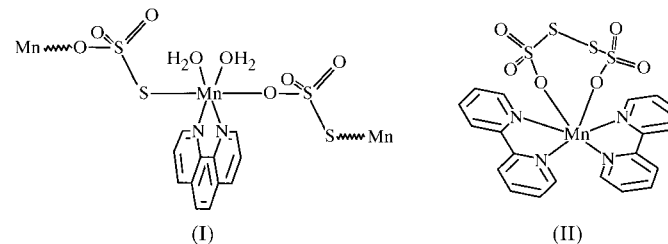
The structures of $[\text{Mn}(\text{S}_2\text{O}_3)_2(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_2]$ and $[\text{Mn}(\text{S}_4\text{O}_6)(\text{C}_{10}\text{H}_8\text{N}_2)_2]$ are presented. The former consists of pairs of polymeric chains formed by manganese polyhedra bridged by bidentate thiosulfate anions, which are in turn related to each other by a pseudo-twofold screw axis. The latter has crystallographic twofold symmetry and consists of monomers in which manganese displays its typical octahedral coordination provided by the bidentate bites of two bipyridine bases and a tetrathionate anion, which is, to our knowledge, the first chelating tetrathionate to be reported in the literature.

Comment

In the last few years, the study of complexes of transition metals with sulfur oxoanions and *N,N'*-bidentate organic ligands has been the subject of our interest. The thiosulfate ion has been one of the ligands most frequently used and has proved to be very versatile in coordination compounds of transition metals, with a geometry quite dependent on the type of coordination present. As a rule, we have tried to centre our attention on thiosulfate 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 metallic ions are expected to bind to the hard (O) as well as to the soft (S) end of thiosulfate, resulting in a variety of coordination modes depending on other concurrent factors, such as crystal-field stabilization, shapes of accompanying ligands and intermolecular forces, such as van der Waals and hydrogen bonding, *etc.*

Manganese(II), although a hard acid according to the Pearson classification, is borderline to the cations that behave

as intermediate, and so is an interesting species to study in conjunction with the thiosulfate ligand. Furthermore, no structures have been reported which contain thiosulfate coordinated to manganese. With these ideas in mind, we attempted the syntheses of manganese thiosulfate complexes with phenanthroline and bipyridine. While in the first case, the expected complex was readily obtained, an oxidation of S_2O_3^- took place in the second case and the tetrathionate ion was formed '*in situ*', coordinating to manganese. Thus, in this paper, we report the structures of $[\text{Mn}(\text{phen})(\text{S}_2\text{O}_3)_2(\text{H}_2\text{O})_2]$, (I), and $[\text{Mn}(\text{bipy})_2(\text{S}_4\text{O}_6)]$, (II).



The structure of (I) includes two independent Mn^{2+} ions (labelled *A* and *B* in Fig. 1), having very similar environments in which they are octahedrally surrounded by a bidentate phenanthroline [range of Mn–N distances 2.269 (8)–2.289 (6) Å], two aqua ligands [range of Mn–OW distances 2.122 (6)–2.173 (6) Å], and one oxygen [Mn–O distances 2.176 (8) and 2.177 (8) Å] and one sulfur [Mn–S distances 2.642 (3) and 2.656 (3) Å] from thiosulfate groups related by a whole unit-cell translation along *b*. Both independent coordination polyhedra are distorted, as expected from the restraints imposed by the chelate character of the ligands, the most notable departures from ideal values being the angles N1A–Mn1A–O1WA 167.0 (3), N1A–Mn1A–N2A 73.6 (3), N2B–Mn1B–O2WB 166.1 (3) and N1B–Mn1B–N2B 73.5 (2)°.

The thiosulfate groups in (I) act as bridging ligands between neighbouring cations through S and O atoms, in a way reported before only in bis(ethylenethiourea)zinc(II) thiosulfate (Baggio *et al.*, 1974). The structure includes two different types of linear chains (Fig. 2) parallel to each other and to the crystallographic *b* axis. These linear arrangements, in turn, are very nearly related to each other through a frustrated 2_1 symmetry axis at roughly 0.506 (16), 0.248 (6), with a 0.53 (2) translation along *b*. The application of such a pseudo-operation to bring the two chains into coincidence results in an average deviation of 0.27 Å and maximum departures of ~0.56 Å for C5 and C6 of the phen groups. Although the quality of the data prevented the location of the water H atoms in the final difference Fourier maps, there are a number of short $\text{O}_{\text{water}} \cdots \text{O}_{\text{thiosulfate}}$ contacts (<3.00 Å) clearly attributable to hydrogen bonding (Table 2 and Fig. 2). Some are of the intra-chain type (those involving the pairs O3···O1W and O2···O2W in each chain) which define the spatial arrangement of the thiosulfate group; the remaining ones, involving atoms from different chains, provide stabilization by joining chains together into a three-dimensional structure.

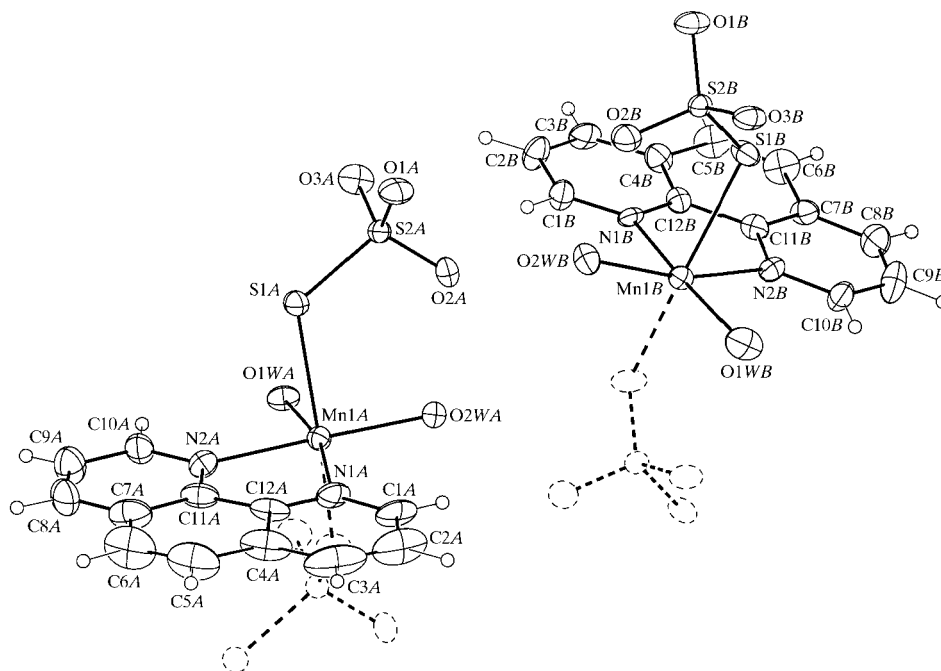


Figure 1
View of the two independent Mn coordination polyhedra in (I). Displacement ellipsoids are drawn at the 50% probability level.

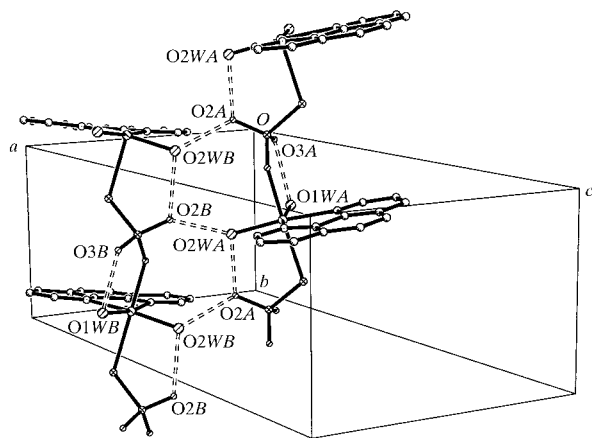


Figure 2
Schematic packing view of (I), showing both types of chains, A and B, and the way in which they interact *via* intra- as well as intermolecular hydrogen bonds. Interactions to symmetry-related chains have been omitted for clarity.

The structure of (II) consists of monomers in which the Mn atom is octahedrally coordinated by four N atoms from two bidentate bipyridines [Mn—N 2.249 (2) Å], and two O atoms from a bidentate tetrathionate [Mn—O 2.122 (3) Å]. Only half of the molecule is independent, however, as a twofold axis bisects the cation and the S2—S2($-x, y, \frac{1}{2} - z$) bond (Fig. 3). As a result of the restrictions imposed by the chelate bites, the Mn octahedron departs somewhat from ideality, most notably in the angles N1—Mn—N2 72.11 (14)° and N2—Mn—N2($-x, y, \frac{1}{2} - z$) 160.9 (2)°. The individual pyridinic groups are strictly planar within resolution, and are rotated around the C5—C6 bond by 1.8 (1)°. The monomers interact with each other *via* a

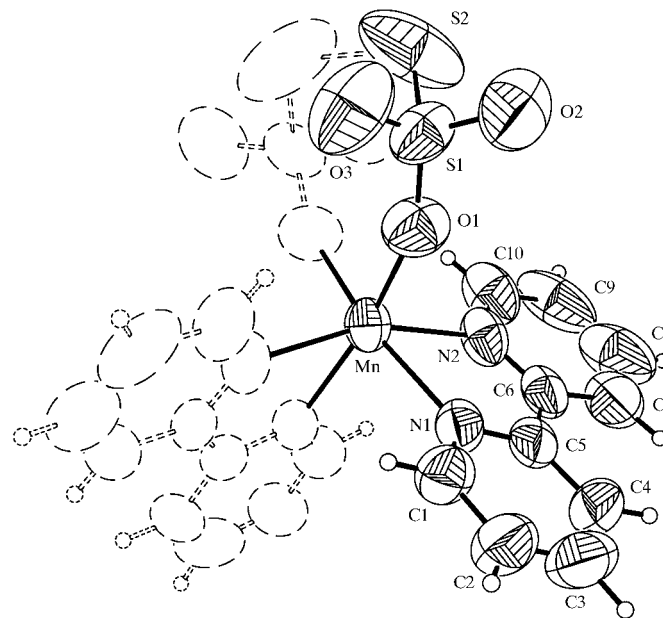


Figure 3
Monomeric unit in (II). Note the twofold axis through the cation and the midpoint of the tetrathionate anion. The symmetry-related part of the molecule is depicted in broken lines. Displacement ellipsoids are shown at the 30% probability level.

number of O···H—C contacts (Table 4) which are distributed more or less evenly in space with no obvious preferred orientation. These interactions correlate fairly well with the S—O bond lengths observed in the oxoanion, in the sense that the stronger the interaction in which one oxygen takes part, the shorter the bond length to sulfur observed. To our

knowledge, this is the first structure ever reported with a chelating $S_4O_6^{2-}$ group. A survey in the Cambridge Structural Database (Allen & Kennard, 1993) shows only five structures containing the anion, in three of which the group is not coordinated at all to the metal centre, acting merely as a counter-ion [bis(ethylenediamine)ammoniumbromocobalt tetrathionate (Bernal *et al.*, 1993); tris(1,10-phenanthroline)-copper(II) tetrathionate pentahydrate (Freire *et al.*, 1998); and tetraammine(oxalato-*O,O'*)cobalt tetrathionate monohydrate (Bernal *et al.*, 1996)]. In the remaining two structures [bis(2,2'-bipyridyl)copper(II) tetrathionate (Harrison & Hathaway, 1978) and bis(1,10-phenanthroline)copper(II) tetrathionate (Freire *et al.*, 1998); which in fact ought to be considered just as one and the same structure, since they are very nearly isostructural], the anion binds very loosely through two opposite O atoms acting as a bridge between adjacent cations, to define infinite one-dimensional polymers. Comparison of the tetrathionate molecule herein presented with those found in the literature shows that the S—S bond lengths lie on the short side of the ranges found for the reported structures: S1—S2 2.085 (8) Å (range reported 2.09–2.13 Å); S2—S2' 1.963 (5) Å (range reported 1.98–2.02 Å). These differences, however, might not be too meaningful due to the slightly disordered character of S2 (see *Experimental*).

Experimental

Compound (I) was obtained by mixing manganese chloride, sodium thiosulfate and phenanthroline in a (1:3:1) ratio. A few hours after mixing, crystals suitable for X-ray diffraction were already present in the solution. A similar procedure using bipy did not, however, produce similar results. All trials with bipy were unsuccessful, the solutions becoming dark as a result of some (presumed) oxidation processes. As indirect evidence of this, in one of the many attempts to generate the bipy thiosulfate, crystals of the tetrathionate (II) were fortuitously obtained when a solution left unattended for months was finally checked for crystals.

Compound (I)

Crystal data

$[Mn(S_2O_3)(C_{12}H_8N_2)(H_2O)_2]$	$D_x = 1.695 \text{ Mg m}^{-3}$
$M_r = 383.30$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 25 reflections
$a = 10.371$ (2) Å	$\theta = 7.5\text{--}15^\circ$
$b = 7.1020$ (14) Å	$\mu = 1.180 \text{ mm}^{-1}$
$c = 20.446$ (4) Å	$T = 293$ (2) K
$\beta = 94.07$ (3)°	Plate, pale yellow
$V = 1502.1$ (5) Å ³	$0.38 \times 0.28 \times 0.14 \text{ mm}$
$Z = 4$	

Data collection

Rigaku AFC-7S diffractometer	3935 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$R_{\text{int}} = 0.087$
Absorption correction: ψ scan	$\theta_{\text{max}} = 27.46^\circ$
(Molecular Structure Corporation, 1988)	$h = -13 \rightarrow 13$
$T_{\text{min}} = 0.61$, $T_{\text{max}} = 0.85$	$k = -1 \rightarrow 9$
4432 measured reflections	$l = 0 \rightarrow 26$
3723 independent reflections (plus 523 Friedel-related reflections)	3 standard reflections every 150 reflections
	intensity decay: <3%

Table 1

Selected bond lengths (Å) for (I).

Mn1A—O2WA	2.122 (6)	Mn1B—O2WB	2.1489 (6)
Mn1A—O1WA	2.173 (6)	Mn1B—O1WB	2.150 (6)
Mn1A—O1A ⁱ	2.176 (8)	Mn1B—O1B ⁱ	2.177 (8)
Mn1A—N1A	2.269 (8)	Mn1B—N2B	2.270 (7)
Mn1A—N2A	2.270 (8)	Mn1B—N1B	2.289 (6)
Mn1A—S1A	2.656 (3)	Mn1B—S1B	2.642 (3)
S1A—S2A	2.005 (3)	S1B—S2B	2.007 (3)
S2A—O3A	1.470 (7)	S2B—O3B	1.465 (6)
S2A—O2A	1.469 (7)	S2B—O2B	1.466 (7)
S2A—O1A	1.475 (8)	S2B—O1B	1.494 (7)

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

Table 2

Hydrogen-bonding interactions (Å) in (I).

$D \cdots A$		$D \cdots A$	
O2WA \cdots O2A	2.65 (1)	O2WA \cdots O1A ⁱ	3.05 (1)
O2WB \cdots O2A	2.73 (1)	O2WA \cdots O1B ⁱ	3.57 (1)
O2WB \cdots O2B	2.69 (1)	O2WA \cdots O2B ⁱ	2.74 (1)
O2WA \cdots O1WA	3.17 (1)	O1WB \cdots O3A ⁱⁱⁱ	2.76 (1)
O2WB \cdots O1WB	3.21 (1)	O1WB \cdots O1B ⁱ	2.93 (1)
O1WA \cdots O1A ⁱ	3.00 (1)	O1WB \cdots O3B ⁱ	2.66 (1)
O1WA \cdots O3A ⁱ	2.76 (1)	O2WB \cdots O1B ⁱ	3.00 (1)
O1WA \cdots O3B ⁱⁱ	2.79 (1)		

Symmetry codes: (i) $x, y - 1, z$; (ii) $x - 1, y - 1, z$; (iii) $1 + x, y, z$.

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.062$	$\Delta\rho_{\text{max}} = 1.28 \text{ e \AA}^{-3}$
$wR(F^2) = 0.193$	$\Delta\rho_{\text{min}} = -0.68 \text{ e \AA}^{-3}$
$S = 1.188$	Absolute structure: Flack (1983)
4255 reflections	Flack parameter = 0.06 (5)
397 parameters	
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.067P)^2 + 9.528P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Compound (II)

Crystal data

$[Mn(S_4O_6)(C_{10}H_8N_2)_2]$	Mo $K\alpha$ radiation
$M_r = 591.55$	Cell parameters from 25 reflections
Orthorhombic, $Pbcn$	$\theta = 7.5\text{--}15^\circ$
$a = 15.330$ (3) Å	$\mu = 0.930 \text{ mm}^{-1}$
$b = 9.889$ (2) Å	$T = 293$ (2) K
$c = 16.061$ (3) Å	Irregular block, pale yellow
$V = 2434.8$ (8) Å ³	$0.26 \times 0.24 \times 0.24 \text{ mm}$
$Z = 4$	
$D_x = 1.614 \text{ Mg m}^{-3}$	

Data collection

Rigaku AFC-7S diffractometer	$R_{\text{int}} = 0.062$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 27.51^\circ$
Absorption correction: ψ scan	$h = 0 \rightarrow 19$
(Molecular Structure Corporation, 1988)	$k = 0 \rightarrow 12$
$T_{\text{min}} = 0.75$, $T_{\text{max}} = 0.80$	$l = 0 \rightarrow 20$
3002 measured reflections	3 standard reflections every 150 reflections
2804 independent reflections	intensity decay: <3%
1247 reflections with $I > 2\sigma(I)$	

Table 3
Selected bond lengths (Å) for (II).

Mn—O1 ⁱ	2.122 (3)	S1—O3	1.382 (5)
Mn—O1	2.122 (3)	S1—O2	1.429 (4)
Mn—N2 ⁱ	2.249 (4)	S1—O1	1.466 (3)
Mn—N2	2.249 (4)	S1—S2	2.086 (3)
Mn—N1	2.249 (4)	S2—S2 ⁱ	1.963 (5)
Mn—N1 ⁱ	2.249 (4)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.**Table 4**
Hydrogen-bonding geometry (Å, °) for (II).

D—H...A	D—H	H...A	D...A	D—H...A
C1—H1A...O3 ⁱ	0.93	2.50	3.24 (1)	136
C10—H10A...O3 ⁱⁱⁱ	0.93	2.69	3.57 (1)	157
C4—H4A...O2 ⁱⁱⁱ	0.93	2.43	3.26 (1)	148
C8—H8A...O2 ^{iv}	0.93	2.35	3.14 (1)	142

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

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.183$
 $S = 1.014$
 2804 reflections
 159 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.093P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.01$
 $\Delta\rho_{\max} = 0.59 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.42 \text{ e } \text{Å}^{-3}$

H atoms attached to carbon were added at their expected positions and not refined, but allowed to ride (C—H = 0.96 Å). Those pertaining to the water molecules were not found in the difference Fourier map, and were ignored. Crystals of (I) were of poor quality, and this was reflected in the refinement results; the final agreement factor was rather high, as was the residual electron-density ripple (ca 1.3 e Å⁻³), uniformly distributed. The inner S2 atom in the tetra-thionate group in (II) was surrounded by a number of small residual electron-density peaks and exhibited a conspicuously large displacement ellipsoid, suggesting some kind of disorder. Although the splitting of the model into two halves tended to diminish the discrepancy index $R1$, this was achieved at the cost of a deterioration of the overall geometry of the group, both in bond lengths and in

interatomic angles. It was then decided to keep the model unsplit, and to leave to the anisotropic displacement factor of S2 the whole representation of this anomalous situation. With this final model, the residual electron-density ripple around S2 consisted of a large number of peaks below 0.70 e Å⁻³, at distances of less than 1 Å.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *PARST* (Nardelli, 1983) and *CSD* (Allen & Kennard, 1993).

This work was partially supported by a CONICET grant, PIP 0470/98. We thank the Spanish Research Council (CSIC) for providing us with a free-of-charge license to the CSD system. EF is a grateful recipient of a scholarship from CONICET.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1146). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
 Baggio, S., Baggio, R. F. & de Perazzo, P. K. (1974). *Acta Cryst.* **B30**, 2166–2172.
 Bernal, I., Cetrullo, J. & Jackson, W. G. (1993). *Inorg. Chem.* **32**, 4098–4101.
 Bernal, I., Cetrullo, J. & Somoza, F. (1996). *J. Coord. Chem.* **40**, 57–69.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Freire, E., Baggio, S., Baggio, R. & Garland, M. T. (1998). *Acta Cryst.* **C54**, 464–468.
 Harrison, W. D. & Hathaway, B. J. (1978). *Acta Cryst.* **B34**, 2843–2845.
 Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
 Pearson, G. R. (1973). In *Hard and Soft Acids and Bases*. Stroudsburg, Pennsylvania: Dowden, Hutchinson and Ross.
 Sheldrick, G. M. (1994). *SHELXTL/PC*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.