Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Diaquabis(1,10-phenanthroline-κ^2N,N')manganese(II) thiodiglycolate bis(1,10-phenanthroline-κ^2N,N')(thiodiglycolato-κ^2O,O')manganese(II) tridecahydrate

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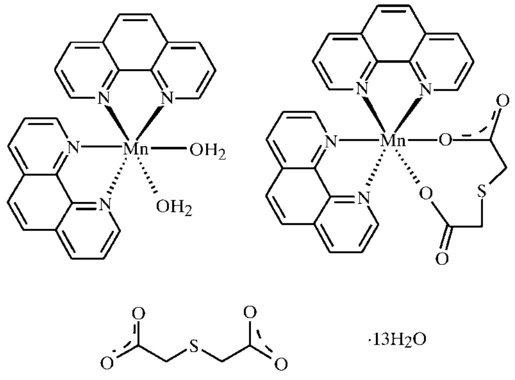
Received 26 August 2003
Accepted 11 September 2003
Online 11 October 2003

The title compound, $[Mn(C_{12}H_8N_2)_2(H_2O)_2](C_4H_4O_4S)\cdot$-$[Mn(C_4H_4O_4S)(C_{12}H_8N_2)_2]\cdot 13H_2O$, contains one dianion of thiodiglycolic acid ($tdga^{2-}$) and two independent manganese(II) moieties, *viz*. $[Mn(phen)_2(H_2O)_2]^{2+}$ and [Mn(tdga)-(phen)$_2$], where phen is 1,10-phenanthroline. The Mn^{II} atoms are octahedrally coordinated by four N atoms of two bidentate phen ligands [Mn—N = 2.240 (2)–2.3222 (19) Å] and either two water O atoms or two tdga carboxyl O atoms [Mn—O = 2.1214 (17)–2.1512 (17) Å]. The tdga ligand chelates as an *O*,*O*′-bidentate ligand, forming an eight-membered ring with one Mn atom. The free $tdga^{2-}$ dianion is hydrogen bonded to an $[Mn(phen)_2(H_2O)_2]^{2+}$ ion, with O$\cdots$O distances of 2.606 (2) and 2.649 (2) Å. The crystal structure is further stabilized by an extensive network of hydrogen bonds involving 13 water molecules.

Comment

Metal complexes involving carboxylate groups are of interest not only as compounds that can potentially be used for the preparation of precursors applicable in materials chemistry (Devereux *et al.*, 2002), and for their potential biological activity (Geraghty *et al.*, 1999), but also from a structural point of view. Thiodiglycolic acid ($tdgaH_2$) is a dicarboxylic acid containing four O atoms and one S atom, These atoms cause coordination variability of $tdga^{2-}$ to metal centers. It has been found that $tdga^{2-}$ coordinates preferentially as an *O*,*S*,*O*′-tridentate ligand (Drew *et al.*, 1975; Delaunay *et al.*, 1976, 1978; Bonomo *et al.*, 1982). Moreover, it can also chelate as an *O*,*S*-bidentate ligand (Efimenko *et al.*, 1991) and it can form bridges in binuclear complexes (Baggio *et al.*, 1999). Apart from the formation of mononuclear or binuclear compounds, transition metal complexes with $tdgaH_2$ in the form of polymeric chains (Bonomo *et al.*, 1982) or three-dimensional structures (Kepert *et al.*, 1999; Zhang *et al.*, 2002; Grirrane *et al.*, 2003) have been prepared. Recently, we have prepared and structurally characterized two mixed-ligand binuclear Cu^{II} complexes in which the $tdga^{2-}$ dianion acts as a bridge (Kopel *et al.*, 2003). We report here the structure of the title compound, (I), which contains the $tdga^{2-}$ dianion chelated as an *O*,*O*′-bidentate ligand, thus forming an eight-membered ring with one Mn atom.



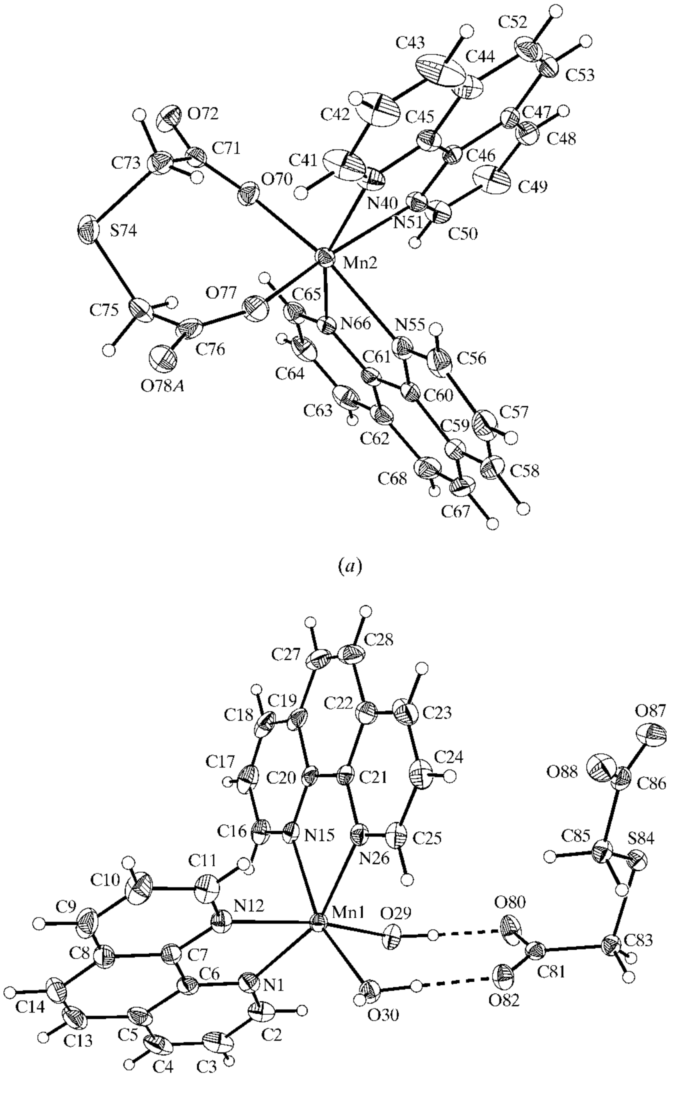
(I)

The crystal structure of (I) consists of [Mn(tdga)(phen)$_2$] complex molecules (Fig. 1*a*), $[Mn(phen)_2(H_2O)_2]^{2+}$ complex cations (Fig. 1*b*), $tdga^{2-}$ anions (Fig. 1*b*) and water molecules (phen is 1,10-phenanthroline).

The Mn^{II} ion in the complex molecule adopts a substantially distorted octahedral geometry, defined by four N atoms of two phen ligands and two carboxyl O atoms of a tdga ligand in a *cis* configuration. While the first bidentate chelating phen ligand (containing atoms N40 and C53) is almost perfectly planar (the angles between its individual six-membered rings are not greater than 0.8°), the second phen ligand (containing atoms N55 and C68) is significantly deformed from planarity (the angles between its six-membered rings vary from 3.5 to 5.3°). The tdga ligand is chelated as an *O*,*O*′-bidentate ligand and forms an eight-membered ring with an Mn atom. The Mn—N and Mn—O distances in this complex are in the ranges 2.240–2.322 and 2.123–2.151 Å, respectively. These lengths are comparable to the mean Mn—N and Mn—O distances (2.270 and 2.112 Å) found in related complexes (Cambridge Structural Database, Version 5.24.3; Allen, 2002).

The structure of the $[Mn(phen)_2(H_2O)_2]^{2+}$ complex cation is similar to those of Mn^{II} complex ions determined previously (McCann *et al.*, 1997; Geraghty *et al.*, 1998; Devereux *et al.*, 2000*a*,*b*, 2002; Zheng *et al.*, 2001). The Mn atom is surrounded by four N atoms of two phen ligands and two O atoms of two water molecules. Like the [Mn(tdga)(phen)$_2$] complex molecule, the cation displays a *cis* configuration and the Mn atom has a substantially distorted octahedral coordination. The Mn—N and Mn—O distances in the cation are in the ranges 2.2517 (19)–2.284 (2) and 2.1214 (17)–2.1302 (16) Å, respectively (Table 1).

DOI: 10.1107/S0108270103020249



(*a*)

(*b*)

Figure 1

*ORTEP*III (Johnson & Burnett, 1996) plot of (*a*) the [Mn(tdga)(phen)$_2$] complex moiety and (*b*) the [Mn(phen)$_2$(H$_2$O)$_2$]$^{2+}$ complex cation with the hydrogen-bonded tdga^{2-} dianion. Non-H atoms are drawn with displacement ellipsoids at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

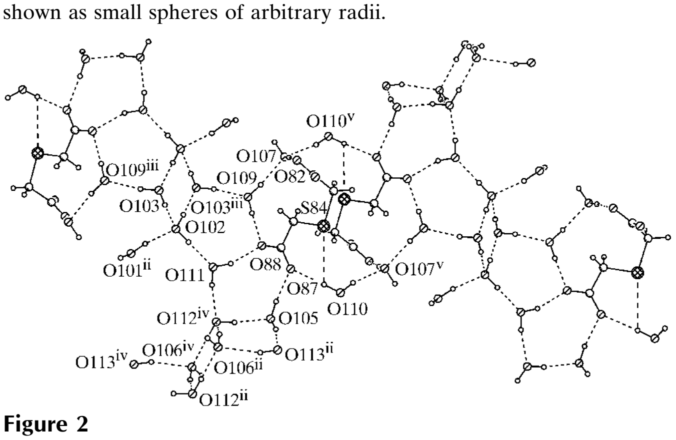


Figure 2

Part of the crystal structure of (I), showing the formation of a layer of hydrogen-bonded tdga^{2-} dianions and water molecules. [Mn(tdga)(phen)$_2$] and [Mn(phen)$_2$(H$_2$O)$_2$]$^{2+}$ moieties and the disordered O99 water molecule have been omitted for clarity. [Symmetry codes: (ii) $1 - x, -y, -z$; (iii) $-x, -y, -z$; (v) $-x, 1 - y, -z$; (vi) $x, y, z - 1$.]

The positive charge of the cation is compensated by the negative charge of the tdga^{2-} dianion, which is connected to the [Mn(phen)$_2$(H$_2$O)$_2$]$^{2+}$ ion *via* O—H···O hydrogen bonds (Fig. 1*b* and Table 2). The tdga^{2-} dianion is further hydrogen bonded to five water molecules. In the crystal lattice of (I), anions and water molecules are linked by an extensive network of hydrogen bonds, thus forming two-dimensional (101) layers (Fig. 2 and Table 2).

Experimental

TdgaNa$_2$ (0.19 g), dissolved in distilled water (10 ml), was added to a solution of MnSO$_4$·4H$_2$O (0.22 g) in an ethanol–water (1:1) mixture (30 ml). The reaction mixture was stirred for 30 min at room temperature and then phen·H$_2$O (0.2 g), dissolved in ethanol (20 ml), was added to the solution with stirring. The color changed to yellow and the solution was stirred for a further 1 h and then left to crystallize. Yellow crystals suitable for single-crystal X-ray analysis were obtained after several days.

Crystal data

[Mn(C$_{12}$H$_8$N$_2$)$_2$(H$_2$O)$_2$]-
(C$_4$H$_4$O$_4$S)·[Mn(C$_4$H$_4$O$_4$S)-
(C$_{12}$H$_8$N$_2$)$_2$]·13H$_2$O
M_r = 1393.17
Triclinic, $P\bar{1}$
a = 15.0347 (7) Å
b = 15.9870 (7) Å
c = 16.4562 (8) Å
α = 83.501 (4)°
β = 66.004 (5)°
γ = 61.981 (5)°

V = 3175.1 (3) Å^3
Z = 2
D_x = 1.457 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7031 reflections
θ = 5.3–56.5°
μ = 0.55 mm^{-1}
T = 120 (2) K
Prism, yellow
0.55 × 0.55 × 0.40 mm

Table 1

Selected geometric parameters (Å, °).

Mn1—O29	2.1214 (17)	C73—S74	1.814 (2)
Mn1—O30	2.1302 (16)	S74—C75	1.811 (3)
Mn1—N1	2.2517 (19)	C75—C76	1.520 (5)
Mn1—N26	2.2817 (19)	C76—O78*B*	1.189 (8)
Mn1—N15	2.2823 (19)	C76—O77	1.257 (3)
Mn1—N12	2.284 (2)	C76—O78*A*	1.320 (4)
Mn2—O70	2.1232 (16)	O80—C81	1.247 (3)
Mn2—O77	2.1512 (17)	C81—O82	1.257 (3)
Mn2—N66	2.2403 (19)	C81—C83	1.520 (3)
Mn2—N40	2.240 (2)	C83—S84	1.811 (2)
Mn2—N55	2.286 (2)	S84—C85	1.803 (2)
Mn2—N51	2.3222 (19)	C85—C86	1.522 (3)
O70—C71	1.260 (3)	C86—O87	1.245 (3)
C71—O72	1.254 (3)	C86—O88	1.260 (3)
C71—C73	1.521 (3)		
O29—Mn1—O30	87.17 (6)	N66—Mn2—N40	156.80 (7)
O29—Mn1—N1	94.00 (7)	O70—Mn2—N55	165.15 (7)
O30—Mn1—N1	104.28 (7)	O77—Mn2—N55	84.55 (7)
O29—Mn1—N26	101.59 (7)	N66—Mn2—N55	73.50 (7)
O30—Mn1—N26	90.19 (7)	N40—Mn2—N55	95.38 (7)
N1—Mn1—N26	159.27 (7)	O70—Mn2—N51	95.22 (6)
O29—Mn1—N15	89.62 (7)	O77—Mn2—N51	162.05 (7)
O30—Mn1—N15	161.96 (7)	N66—Mn2—N51	85.85 (7)
N1—Mn1—N15	93.65 (7)	N40—Mn2—N51	73.08 (7)
N26—Mn1—N15	73.07 (7)	N55—Mn2—N51	87.12 (7)
O29—Mn1—N12	167.67 (7)	C71—O70—Mn2	139.78 (15)
O30—Mn1—N12	95.03 (7)	O70—C71—C73	118.6 (2)
N1—Mn1—N12	73.69 (7)	C71—C73—S74	110.25 (17)
N26—Mn1—N12	90.55 (7)	C75—S74—C73	100.71 (12)
N15—Mn1—N12	91.89 (7)	C76—C75—S74	110.5 (2)
O70—Mn2—O77	96.90 (7)	O77—C76—C75	117.9 (2)
O70—Mn2—N66	92.01 (7)	C76—O77—Mn2	139.8 (2)
O77—Mn2—N66	106.85 (7)	C81—C83—S84	111.41 (15)
O70—Mn2—N40	99.33 (7)	C85—S84—C83	98.80 (11)
O77—Mn2—N40	91.89 (7)	C86—C85—S84	111.76 (16)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O29—H29*V*···O72	0.90 (4)	1.78 (2)	2.680 (2)	168 (3)
O29—H29*W*···O80	0.92 (3)	1.69 (3)	2.606 (2)	178 (3)
O30—H30*W*···O101$^{\rm i}$	0.94 (4)	1.71 (4)	2.645 (2)	178 (3)
O30—H30*V*···O82	0.93 (3)	1.72 (3)	2.649 (2)	174 (3)
O101—H01*V*···O78*A*	0.93 (3)	1.84 (2)	2.759 (3)	170 (4)
O101—H01*V*···O78*B*	0.93 (3)	1.85 (2)	2.761 (8)	166 (4)
O101—H01*W*···O102$^{\rm ii}$	0.93 (3)	1.82 (4)	2.743 (3)	171 (4)
O102—H02*V*···O111	0.93 (4)	1.77 (3)	2.698 (3)	177 (4)
O102—H02*W*···O103$^{\rm iii}$	0.95 (3)	1.85 (3)	2.793 (3)	176 (4)
O103—H03*W*···O102	0.93 (3)	1.93 (2)	2.846 (3)	168 (3)
O103—H03*V*···O109$^{\rm iii}$	0.91 (3)	1.84 (2)	2.736 (3)	168 (4)
O105—H5*V*···O113$^{\rm ii}$	0.92 (4)	1.92 (2)	2.816 (3)	165 (4)
O105—H5*W*···O87	0.91 (2)	1.89 (2)	2.779 (2)	166 (4)
O106—H6*V*···O112$^{\rm iv}$	0.91 (4)	1.90 (2)	2.763 (3)	155 (4)
O106—H6*W*···O72	0.93 (2)	1.83 (2)	2.742 (2)	167 (4)
O107—H7*V*···O82	0.92 (4)	1.88 (4)	2.797 (2)	177 (4)
O107—H7*W*···O78*B*$^{\rm i}$	0.91 (4)	1.86 (3)	2.690 (8)	150 (3)
O107—H7*W*···O78*A*$^{\rm i}$	0.91 (4)	2.03 (2)	2.922 (4)	165 (3)
O108—H8*V*···O78*A*	0.89 (3)	2.29 (2)	3.173 (5)	174 (4)
O108—H8*V*···O77	0.89 (3)	2.38 (4)	2.975 (3)	125 (3)
O109—H9*V*···O88	0.92 (4)	1.84 (3)	2.759 (3)	177 (4)
O109—H9*W*···O107	0.93 (3)	1.97 (2)	2.891 (3)	168 (4)
O110—H10*V*···O87	0.92 (4)	2.02 (5)	2.930 (3)	169 (3)
O110—H10*V*···S84	0.92 (4)	2.91 (4)	3.404 (2)	115 (3)
O110—H10*W*···O107$^{\rm v}$	0.94 (3)	1.95 (2)	2.866 (3)	167 (4)
O111—H11*V*···O88	0.93 (3)	1.84 (2)	2.730 (3)	160 (4)
O111—H11*W*···O112$^{\rm vi}$	0.93 (3)	1.90 (2)	2.822 (3)	170 (4)
O112—H12*W*···O105$^{\rm vii}$	0.93 (2)	1.83 (2)	2.740 (3)	163 (4)
O112—H12*V*···O106	0.93 (3)	1.87 (3)	2.794 (3)	175 (4)
O113—H13*W*···O106	0.88 (3)	2.07 (2)	2.917 (4)	162 (4)

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

Data collection

Kuma KM-4-Plus CCD diffractometer
ω scans
16 741 measured reflections
10 803 independent reflections
9798 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.032$
$\theta_{\rm max} = 25.0°$
$h = -17 \rightarrow 14$
$k = -19 \rightarrow 18$
$l = -19 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.099$
$S = 1.05$
10 803 reflections
901 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 4P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.87$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.73$ e Å^{-3}

Disordered water molecule O99 (atoms O99*A*–O99*C*) was refined isotropically. The large value (14.6) of the $U_{\rm eq}({\rm max})/U_{\rm eq}({\rm min})$ ratio for O78 and the fact that the highest peak in the electron-density map was close to this atom led us to refine atom O78 as disordered, with two possible positions. The O78*A*—C76 [1.320 (4) Å] and O78*B*—C76 [1.189 (8) Å] bond lengths indicate a localization of electron density in the carboxyl moiety instead of an electron delocalization, such as was found around atoms C71, C81 and C86. H atoms attached to C atoms were positioned geometrically, with $U_{\rm iso}$ values derived from the $U_{\rm eq}$ values of the corresponding C atoms. H atoms attached to O atoms were refined with a DFIX (*SHELXL*97; Sheldrick, 1997) restraint of 0.95 (2) Å on all O—H distances and two free variables were used to describe the $U_{\rm iso}$(H) values. The first free variable describes the $U_{\rm iso}$ values of the four H atoms attached to atoms O29 and O30, and the second describes the $U_{\rm iso}$ values of H atoms attached to uncoordinated water O atoms.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Johnson & Burnett, 1996); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

The financial support of this work by the Ministry of Education of the Czech Republic (MŠMT) (grant No. J07/98:143100008) and the Grant Agency of the Czech Republic (GAČR) (grant No. 203/02/0436) is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1182). Services for accessing these data are described at the back of the journal.

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