A one-dimensional double-chain coordination polymer: [Mn(C$_{12}$H$_{13}$NO$_6$S)(C$_{10}$H$_8$N$_2$)]$_n$

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In the title compound, poly[[(2,2′-bipyridine-$\kappa^2 N,N'$)manganese(II)]-μ_3-N-tosyl-L-glutamato-$\kappa^4 O,O':O'':O'''$], [Mn(tsgluo)(bipy)]$_n$, where tsgluo is N-tosyl-L-glutamate (C$_{12}$H$_{13}$NO$_6$S) and bipy is 2,2′-bipyridine (C$_{10}$H$_8$N$_2$), the Mn atoms are octahedrally coordinated by two N atoms of one bipy ligand and by four O atoms of three tsgluo^{2-} anions. The γ-carboxyl group coordinates to the Mn^{II} atom in a chelating mode, while the α-carboxyl group coordinates in a bidentate–bridging mode. The complex displays a one-dimensional double-chain structure.

Comment

In recent years, there has been considerable interest in the design and synthesis of manganese(II) complexes with carboxylate ligands (Yu *et al.*, 1992; Zheng *et al.*, 2002; Tangoulis *et al.*, 1996; Zhang *et al.*, 2003). The main reason may be that these complexes can be used for investigation of the exchange coupling interactions between metal ions, as well as for a new variety of molecular-based magnetic materials (Cano *et al.*, 1994; Ma *et al.*, 2003; Sain *et al.*, 2003). Furthermore, polymanganese complexes have been used as models for the study of the photosynthetic oxygen-evolving complexes (OEC) of photosystem II in green plants (Wieghardt, 1989). On the other hand, N-protected amino acids, being biologically important compounds derived from naturally occurring amino acids, have been studied extensively in the coordination chemistry of metal ions (Bonamartini Corradi, 1992). However, N-p-tolylsulfonyl-L-glutamic acid (H$_2$tsglu), which may act as a polydentate ligand and present a variety of coordination modes because of the presence of two carboxyl functions and a sulfonamide group, has been studied only in a limited number of systems (Bonamartini Corradi *et al.*, 1999) so far, and the manganese complex of H$_2$tsglu has not yet been reported. We present here the crystal structure of a manganese complex with mixed ligands of bipy and H$_2$tsglu,

[Mn(C$_{12}$H$_{15}$NO$_6$S)(C$_{10}$H$_8$N$_2$)]$_n$, (I). The complex has a one-dimensional double-chain structure.

(I)
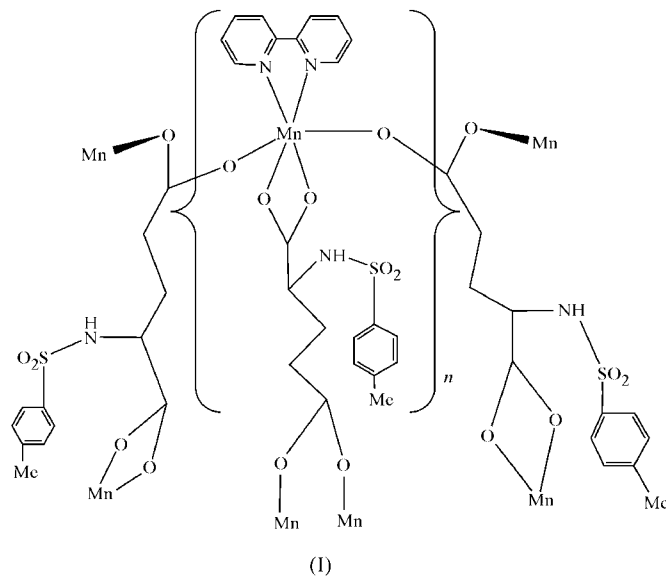
The molecular structure of (I) and the dimeric [Mn-(C$_{12}$H$_{15}$NO$_6$S)(C$_{10}$H$_8$N$_2$)]$_2$ unit are shown in Figs. 1 and 2, respectively. The crystal structure consists of an infinite one-dimensional double chain. Each Mn ion is six-coordinated by two N atoms of one 2,2′-bipyridine (bipy) group, two O atoms of the γ-carboxyl group of one tsgluo^{2-} ligand and two O atoms from two α-carboxyl groups of two other tsgluo^{2-} ligands. The two carboxylate groups display different coordination modes. The γ-carboxyl group coordinates to the Mn^{II} atom in a chelating mode, while the α-carboxyl group coordinates in a bidentate–bridging mode. The bridging of the α-carboxyl O atoms of a ligand between every two adjacent manganese ions gives rise to an infinite chain. The alternate disposition of the α- and γ-carboxylate terminals of the ligands along the *a* axis results in a one-dimensional double-chain structure. The Mn site exhibits a distorted octahedral coordination sphere, with bond angles ranging from 163.10 (6) to 176.54 (6)° for *trans* angles and from 71.58 (6) to 137.25 (6)° for the other angles (Table 1). The Mn—O bond distances range from 2.1268 (13) to 2.3010 (16) Å. The Mn1—O6 bond length [2.3010 (16) Å] is slightly longer than those of the other Mn1—O bonds (Table 1), indicating a weaker interaction of the axially coordinated O atom (O6) as a result of the
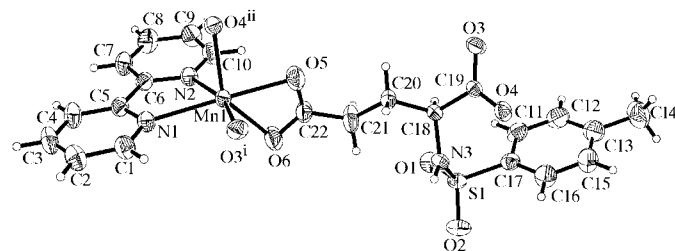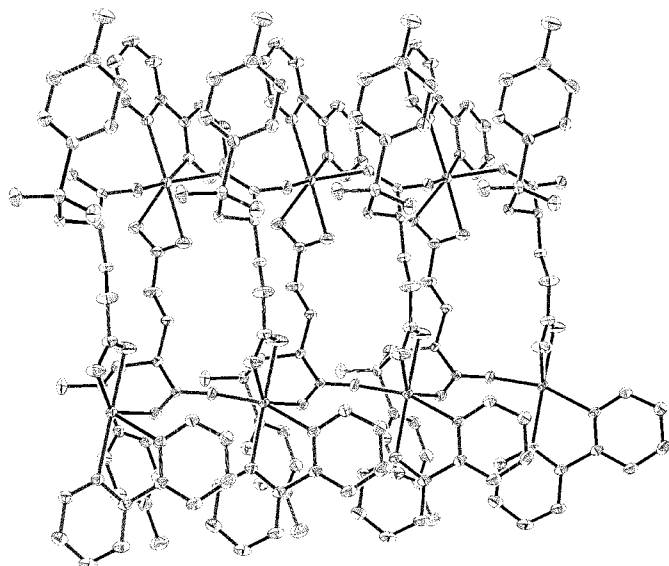

Figure 1
The [Mn(tsgluo)(bipy)] molecule in (I). Displacement ellipsoids are drawn at the 50% probability level. The symmetry codes are as in Table 1.

Figure 2
A projection showing the polymeric ribbon of (I).

instability of the four-membered ring formed by the chelating action of the γ-carboxyl group. The Mn—N bond distances range from 2.2397 (15) to 2.2910 (15) Å and the C—O bond lengths are in the range 1.235 (2)–1.273 (2) Å; these values are in good agreement with the corresponding bond lengths reported for manganese–carboxylic acid–phen complexes (phen is 1,10-phenanthroline) (Shen, 2003).

Experimental

An ethanol solution (10 ml) of 2,2′-bipyridine (0.156 g, 1 mmol) was added dropwise with continuous stirring to an aqueous solution (10 ml) of N-p-tolylsulfonyl-L-glutamic acid (0.301 g, 1 mmol), NaOH (0.080 g, 2 mmol) and MnSO$_4$·H$_2$O (0.175 g, 1 mmol). The resulting yellow solution was stirred for 4 h at room temperature and then filtered. Crystals of the title complex suitable for X-ray analysis were obtained by slow evaporation of the filtrate after 20 d. Analysis calculated for C$_{22}$H$_{21}$MnN$_3$O$_6$S: C 51.72, H 4.11, N 8.22, S 6.27%; found: C 51.76, H 4.15, N 8.23, S 6.28%.

Crystal data

[Mn(C$_{12}$H$_{13}$NO$_6$S)(C$_{10}$H$_8$N$_2$)]	Mo $K\alpha$ radiation
$M_r = 510.42$	Cell parameters from 924
Orthorhombic, $P2_12_12_1$	reflections
$a = 5.3131 (6)$ Å	$\theta = 3.6–27.0°$
$b = 17.727 (2)$ Å	$\mu = 0.74$ mm^{-1}
$c = 23.382 (3)$ Å	$T = 293 (2)$ K
$V = 2202.2 (4)$ Å^3	Block, yellow
$Z = 4$	$0.43 \times 0.40 \times 0.40$ mm
$D_x = 1.539$ Mg m^{-3}	

Data collection

Bruker SMART CCD area-detector diffractometer	4789 independent reflections
	4406 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.019$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 27.0°$
	$h = -6 \rightarrow 5$
$T_{min} = 0.742$, $T_{max} = 0.756$	$k = -22 \rightarrow 19$
13 798 measured reflections	$l = -29 \rightarrow 29$

Table 1
Selected geometric parameters (Å, °).

Mn1—O3^i	2.1268 (13)	Mn1—O6	2.3010 (16)
Mn1—O4^{ii}	2.1745 (13)	C19—O4	1.235 (2)
Mn1—O5	2.1874 (15)	C19—O3	1.273 (2)
Mn1—N2	2.2397 (15)	C22—O6	1.242 (2)
Mn1—N1	2.2910 (15)	C22—O5	1.248 (3)
O3^i—Mn1—O4^{ii}	98.12 (5)	N2—Mn1—N1	71.58 (6)
O3^i—Mn1—O5	90.80 (7)	O3^i—Mn1—O6	99.88 (6)
O4^{ii}—Mn1—O5	84.00 (6)	O4^{ii}—Mn1—O6	137.25 (6)
O3^i—Mn1—N2	163.10 (6)	O5—Mn1—O6	57.40 (5)
O4^{ii}—Mn1—N2	84.93 (5)	N2—Mn1—O6	88.70 (6)
O5—Mn1—N2	106.07 (7)	N1—Mn1—O6	119.62 (5)
O3^i—Mn1—N1	91.52 (5)	O4—C19—O3	124.68 (16)
O4^{ii}—Mn1—N1	98.21 (6)	O6—C22—O5	120.08 (18)
O5—Mn1—N1	176.54 (6)		

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

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0428P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.025$	$+ 0.0383P]$
$wR(F^2) = 0.067$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.002$
4789 reflections	$\Delta\rho_{max} = 0.32$ e Å^{-3}
298 parameters	$\Delta\rho_{min} = -0.40$ e Å^{-3}
H-atom parameters constrained	Absolute structure: Flack (1983), 2002 Friedel pairs
	Flack parameter = 0.003 (12)

The H atoms on atom C14 were positioned geometrically, with C—H distances of 0.96 Å, and included in the refinement with U_{iso}(H) values of 1.5U_{eq}(C). All other H atoms were placed at idealized positions and refined using a riding model, with C—H distances of 0.93–0.98 Å, an N—H distance of 0.86 Å and U_{iso}(H) values of 1.2U_{eq}(C,N). The U_{eq} values of atoms O5 and C21 [0.0657 (6) and 0.0518 (7) Å^2] are greater than those of atoms C22 and C20 [0.0372 (5) and 0.0295 (4) Å^2]; this difference can be ascribed to the slight disorder of atoms O5 and C21.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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