

**A novel heterometallic dinuclear compound: *rac*-pentaqua- $1\kappa^5\text{O}$ - $(\mu\text{-}2\text{-sulfidoacetato-}1:2\kappa^3\text{O:O',S})\text{-bis}(2\text{-sulfidoacetato-}2\kappa^2\text{O,S})\text{-manganese(II)tin(IV)}$**

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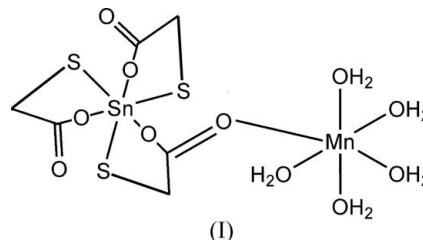
The title racemic heterometallic dinuclear compound,  $[\text{MnSn}(\text{C}_2\text{H}_2\text{O}_2\text{S})_3(\text{H}_2\text{O})_5]$ , (I), contains one main group  $\text{Sn}^{\text{IV}}$  metal centre and one transition metal  $\text{Mn}^{\text{II}}$  centre, and, by design, links the  $\text{Mn}^{\text{II}}$  centre to the building unit of the  $(\Delta/\Lambda)$   $[\text{SnL}_3]^{2-}$  complex anion ( $L$  is the 2-sulfidoacetate dianion). In this cluster, the  $\text{Sn}^{\text{IV}}$  centre of the  $(\Delta/\Lambda)$   $[\text{SnL}_3]^{2-}$  unit is coordinated by three O atoms and three S atoms from three  $L$  ligands to form an  $[\text{SnO}_3\text{S}_3]$  octahedral coordination environment. The  $\text{Mn}^{\text{II}}$  centre is in an  $[\text{MnO}_6]$  octahedral coordination environment, with five O atoms from five water molecules and the sixth from the  $\mu\text{-}L$  ligand of the  $(\Delta/\Lambda)$   $[\text{SnL}_3]^{2-}$  unit. Between adjacent dinuclear molecules, there are many hydrogen-bond interactions of  $\text{O}-\text{H}\cdots\text{O}$ ,  $\text{O}-\text{H}\cdots\text{S}$ ,  $\text{C}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{S}$  types. Of these, eight pairs of  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds fuse all the dinuclear molecules into two-dimensional supramolecular sheets along the  $bc$  plane. Adjacent supramolecular sheets are further connected through  $\text{O}-\text{H}\cdots\text{S}$  hydrogen bonds to give a three-dimensional supramolecular network.

**Comment**

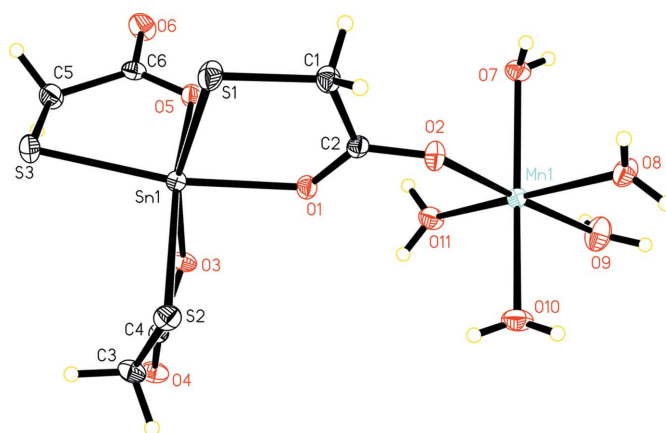
Oxygen/sulfur-bridged heterometallic coordination clusters and polymers have attracted considerable interest because of their rich structural variety and potential applications as semiconductors, nonlinear optical or luminescent materials, magnetic materials, and so on (Wang *et al.*, 2006). One synthetic route to these materials is the self-assembly technique utilizing the spontaneous reaction of an organic ligand and two or more different metallic ions. The other synthetic approach is rational stepwise assembly, in which one metallic ion reacts with one organic ligand to form a complex building unit, which then coordinates to a different metallic ion to

complete the assembly. Previously, sulfur-containing ligands and carboxylate ligands have proved to be versatile candidates which can adopt several coordination modes, for example, bidentate, tridentate *etc.* (Yang *et al.*, 2011). Additionally, the bridging S atom or carboxylate group provides an efficient pathway that couples magnetic or luminescent metal centres for ferromagnetic interaction or energy transfer (Oldham *et al.*, 1987; Faulkner & Pope, 2003).

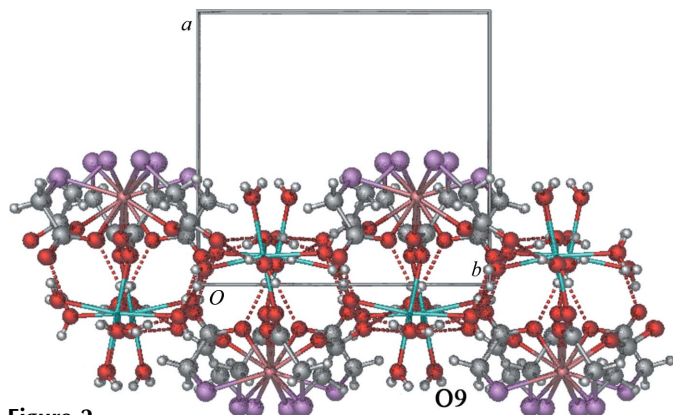
Since the establishment of Werner's coordination theory by his pioneering research on the optical resolution of chiral cobalt(III) complexes, chirality has been one of the most important and fascinating subjects in coordination chemistry (Werner, 1911, 1912; Hirotsu *et al.*, 2004). During the past few decades, a great deal of attention has been focused on the design and creation of well organized clusters or polymers, the overall structures of which can be controlled by the chirality of their building units (Leininger *et al.*, 2000; Swiegers & Malefsete, 2000). Based on these practices, we initially synthesized the optically active complex anion  $[\text{SnL}_3]^{2-}$  ( $L$  is the 2-sulfidoacetate dianion) and then utilized it as a building unit to react with heterometallic ions through the S atoms or carboxylate groups for assembling optically active heterometallic structures. In this paper, we focus on the assembly of the active  $[\text{SnL}_3]^{2-}$  complex ligand with  $\text{Mn}^{\text{II}}$  ions as the heterometallic centres. The title novel heterometallic dinuclear compound,  $[\text{MnSnL}_3(\text{H}_2\text{O})_5]$ , (I), has been synthesized and characterized, though it is found to be racemic.



The structure of (I) is a heterometallic dinuclear cluster (Fig. 1) consisting of three  $L$  ligands, five coordinated water molecules, one  $\text{Sn}^{\text{IV}}$  cation and one  $\text{Mn}^{\text{II}}$  cation. In the cluster, the  $\text{Sn}^{\text{IV}}$  centre is coordinated by three O atoms and three S



**Figure 1**  
The structure and atom labelling of the title compound, with displacement ellipsoids drawn at the 30% probability level.

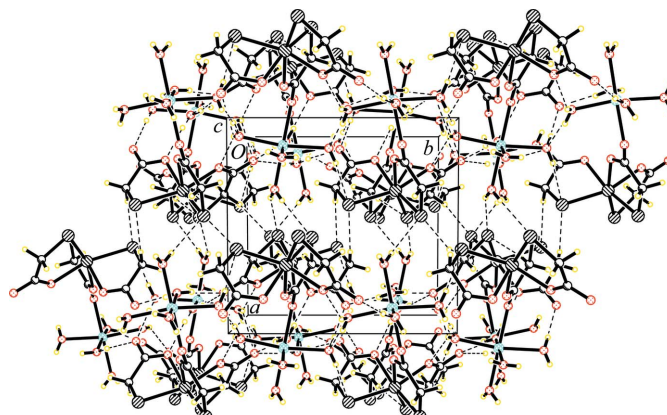
**Figure 2**

The supramolecular organic–inorganic hybrid sheet constructed by hydrogen bonds (dashed lines), viewed along the *c* direction.

atoms from three *L* ligands to form an  $[\text{SnO}_3\text{S}_3]$  octahedral coordination environment. Here, three *L* ligands chelate to the  $\text{Sn}^{\text{IV}}$  ion to give two enantiomers,  $(\Delta/\Lambda) [\text{SnL}_3]^{2-}$ . The  $\text{Mn}^{\text{II}}$  centre is composed of an  $[\text{MnO}_6]$  octahedral coordination environment, with five O atoms from five water molecules and the sixth from the  $\mu_2$ -*L* ligand of the  $(\Delta/\Lambda) [\text{SnL}_3]^{2-}$  unit. In the  $[\text{SnO}_3\text{S}_3]$  octahedron, the  $\text{Sn1}-\text{O}$  bond lengths are in the range 2.1286 (12)–2.1622 (12) Å and the  $\text{Sn1}-\text{S}$  bond lengths are in the range 2.4434 (5)–2.4484 (5) Å, with the remaining bond lengths similar to those of other reported structures (Song, 2009; Chai *et al.*, 2009; Ng *et al.*, 1996). In the  $[\text{MnO}_6]$  octahedron, the  $\text{Mn}-\text{O}$  bonds range from 2.1440 (14) to 2.2221 (15) Å, and all bond lengths are similar to those of other reported structures (Nakasuka *et al.*, 1985; Cheng *et al.*, 2000; Klištincová *et al.*, 2009; Bai *et al.*, 2008; Liu *et al.*, 2006). The bond angles of the two octahedra are near to those of an ideal octahedron, with a maximum deviation of any angle from its ideal value of 17.15 (4)° for  $\text{S2}-\text{Sn1}-\text{O5}$ .

In the crystal structure of (I), there are many hydrogen-bond interactions of  $\text{O}-\text{H}\cdots\text{O}$ ,  $\text{O}-\text{H}\cdots\text{S}$ ,  $\text{C}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{S}$  types (Table 1) between adjacent dinuclear molecules. The hydrogen-bond data are within the ranges of standard examples (Desiraju & Steiner, 1999) and have been examined using *PLATON* (Spek, 2009; van der Sluis & Spek, 1990). Along the *bc* plane, all adjacent dinuclear molecules are fused into two-dimensional supramolecular sheets (Fig. 2) by eight pairs of  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds. Neighbouring supramolecular sheets are further connected through  $\text{O9}-\text{H9A}\cdots\text{S1}^{\text{v}}$  and  $\text{O9}-\text{H9B}\cdots\text{S3}^{\text{vi}}$  hydrogen bonds to give a three-dimensional supramolecular network (symmetry codes are as in Table 1; Fig. 3).

In conclusion, the successful rational stepwise assembly of the optically active  $[\text{SnL}_3]^{2-}$  complex anion with  $\text{Mn}^{\text{II}}$  ions leads to a novel heterometallic dinuclear compound. Through the many hydrogen-bond interactions present, these dinuclear molecules fuse together to form a three-dimensional supramolecular network structure. The heterometallic dinuclear molecule is optically active, but the two enantiomers crystallize as a racemic structure. Further research into novel structures and functions, and exploration of the stepwise assembly of the active  $[\text{SnL}_3]^{2-}$  complex anion with other metallic ions,

**Figure 3**

The three-dimensional supramolecular network of (I), viewed along the *c* direction. Hydrogen bonds are indicated by dashed lines.

such as magnetic  $\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  or luminescent  $\text{Ln}^{\text{III}}$  (where Ln is rare earth metal), are ongoing.

## Experimental

All reagents were commercially available and were used without further purification. An aqueous solution of  $\text{SnL}_3$  (0.1 mol l<sup>-1</sup>) was prepared from mercaptoacetic acid (*H<sub>2</sub>L*), NaOH and  $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$  in a stoichiometric ratio in water at room temperature. To a solution of  $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$  (120 mg, 0.6 mmol) in water (5 ml) was added an aqueous solution (6 ml) of  $\text{SnL}_3$  (0.6 mmol) at room temperature. After several minutes, the solution was filtered and left to evaporate. After standing for several days at room temperature, colourless crystals of (I) were obtained in a yield of 86% (276 mg). Analysis calculated for  $\text{C}_6\text{H}_{16}\text{MnO}_{11}\text{S}_3\text{Sn}$  (%): C 13.50, H 3.02, O 32.96, S 18.01; found: C 13.24, H 3.38, O 33.26, S 18.31. IR (KBr pellet,  $\nu$ , cm<sup>-1</sup>): 3565 (*sh*), 2974 (*w*), 2903 (*w*), 2814 (*w*), 1604 (*s*), 1330 (*m*), 1222 (*m*), 993 (*ms*), 899 (*m*), 781 (*m*), 721 (*m*).

### Crystal data

$[\text{MnSn}(\text{C}_2\text{H}_3\text{O}_2\text{S})_3(\text{H}_2\text{O})_5]$	$V = 1638.2 (4) \text{ \AA}^3$
$M_r = 534.05$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.8901 (14) \text{ \AA}$	$\mu = 2.73 \text{ mm}^{-1}$
$b = 10.4992 (14) \text{ \AA}$	$T = 293 \text{ K}$
$c = 15.883 (2) \text{ \AA}$	$0.30 \times 0.25 \times 0.15 \text{ mm}$
$\beta = 96.631 (2)^\circ$	

### Data collection

Rigaku R-Axis RAPID diffractometer	12118 measured reflections
Absorption correction: multi-scan ( <i>ABSCOR</i> ; Higashi, 1995)	3738 independent reflections
$T_{\text{min}} = 0.670$ , $T_{\text{max}} = 1.000$	3504 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.015$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.044$	$\Delta\rho_{\text{max}} = 0.52 \text{ e \AA}^{-3}$
$S = 1.06$	$\Delta\rho_{\text{min}} = -0.55 \text{ e \AA}^{-3}$
3738 reflections	
239 parameters	
11 restraints	

H atoms bonded to C atoms were added at calculated positions and refined using a riding model, with  $\text{C}-\text{H} = 0.97 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) =$

**Table 1**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O7—H7A...O4 <sup>i</sup>	0.821 (18)	1.928 (18)	2.747 (2)	175 (3)
O8—H8A...O3 <sup>i</sup>	0.821 (16)	1.894 (17)	2.7055 (19)	169 (2)
O8—H8B...O6 <sup>ii</sup>	0.824 (17)	1.897 (17)	2.713 (2)	170 (3)
O10—H10A...O5 <sup>ii</sup>	0.780 (18)	2.45 (3)	3.098 (2)	141 (3)
O10—H10A...O6 <sup>i</sup>	0.780 (18)	2.52 (3)	3.024 (2)	124 (3)
O10—H10B...O7 <sup>ii</sup>	0.819 (18)	2.07 (2)	2.855 (2)	162 (3)
O11—H11A...O4 <sup>iii</sup>	0.812 (17)	1.952 (17)	2.758 (2)	173 (3)
O11—H11B...O6 <sup>iv</sup>	0.819 (17)	1.996 (17)	2.807 (2)	170 (3)
O9—H9A...S1 <sup>v</sup>	0.795 (18)	2.525 (19)	3.3038 (18)	167 (3)
O9—H9B...S3 <sup>vi</sup>	0.836 (16)	2.760 (16)	3.5251 (17)	153 (3)
O7—H7B...S2 <sup>vii</sup>	0.814 (17)	2.509 (18)	3.2928 (15)	162 (3)
C1—H1B...S3 <sup>i</sup>	0.97	2.75	3.7140 (19)	171
C3—H3B...S2 <sup>viii</sup>	0.97	2.82	3.764 (2)	164
C5—H5A...O2 <sup>ix</sup>	0.97	2.60	3.465 (2)	149

Symmetry codes: (i)  $x, -y + \frac{3}{2}, z + \frac{1}{2}$ ; (ii)  $-x, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (iii)  $-x, -y + 2, -z$ ; (iv)  $-x, -y + 1, -z$ ; (v)  $x - 1, y, z$ ; (vi)  $x - 1, -y + \frac{3}{2}, z + \frac{1}{2}$ ; (vii)  $-x, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (viii)  $-x + 1, -y + 2, -z$ ; (ix)  $x, -y + \frac{3}{2}, z - \frac{1}{2}$ .

1.2 $U_{eq}(C)$ . H atoms of coordinated water molecules were selected from peaks evident in the difference Fourier map and their positions were refined while being restrained to an O—H distance of 0.82 (2) Å. Their isotropic displacement parameters were refined freely. A restraint was applied to the intermolecular H9B...S3 distance in order to get a reasonable chemical geometry for the H9B atom.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: QS3008). Services for accessing these data are described at the back of the journal.

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