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A one-dimensional coordination polymer with metal–metal interactions: *catena*-poly[[triaquabarium(II)]-μ-aqua-κ^2O:O-di-μ-thiosalicylato-κ^4O:O]

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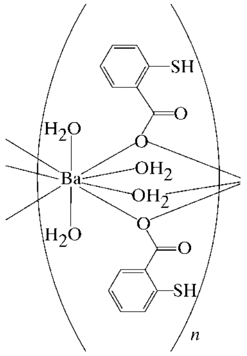
In the title compound, $[Ba(C_7H_5O_2S)_2(H_2O)_4]_n$, the Ba^{II} atom lies on a mirror plane and is nine-coordinated by four bridging carboxylate O atoms of the thiosalicylate ligands, two bridging water molecules and three terminal water molecules. There is an intramolecular $S—H\cdots O$ hydrogen bond between the S and O atoms in the thiosalicylate ligand. A one-dimensional coordination polymer is formed *via* weak metal–metal interactions along polymeric zigzag chains.

Comment

The contamination of water and soil by metals such as barium, chromium, copper, cadmium, lead, mercury and zinc may cause a great deal of harm to the biosphere (Code of Federal Regulations, 1993). When barium compounds, which are frequently used in fireworks, paints, rat poisons and heat stabilizers in plastics, are ingested, barium is known to alter muscle and nerve cells by disrupting the flow of potassium. Eventually, barium behaves like calcium in living organisms and becomes potentially hazardous by accumulating in bone (Harte *et al.*, 1991). There are many technologies and products for remediation of heavy-metal contaminants, including activated carbon adsorption, chemical precipitation, electrolytic treatment, *in situ* vitrification, and biological treatment with plants, fungi and bacteria. Chemical precipitation is one of the more popular and economical methods for removing heavy metals from water.

Thiolate ligands such as cysteamine and thiosalicylic acid are known to be useful for chemical precipitation owing to their coordination character (Kuehn & Isied, 1980). Because they combine hard amine and soft thiolate donors, or hard carboxylate and soft thiolate donors, thiolate ligands could potentially form novel complexes with a wide range of metal centers, such as mercury (Kim *et al.*, 2002), platinum, palladium, nickel (McCaffrey *et al.*, 1997), rhodium, iridium, ruthenium (Henderson *et al.*, 2001), bismuth (Burford *et al.*, 2002) and lanthanides (Bo & Hongzhu, 2000). In our group, research has been focused on the development of new heavy-metal remediation agents containing thiolate groups and supplementary hard donor atoms, such as oxygen and nitrogen. In this paper, we report the preparation and crystal structure of the title compound, (I), which is a new barium(II) complex containing the thiosalicylate (tsa) ligand.



(I)

The coordination environment around the central barium ion is shown in Fig. 1. The Ba atom lies on a mirror plane and is nine-coordinated by four bridging O atoms (O8) from different carboxylate groups of the tsa ligands, two bridging water O atoms (O11) and three terminal water O atoms (O12 and O13). The bridging O11 and terminal O12 atoms lie on a

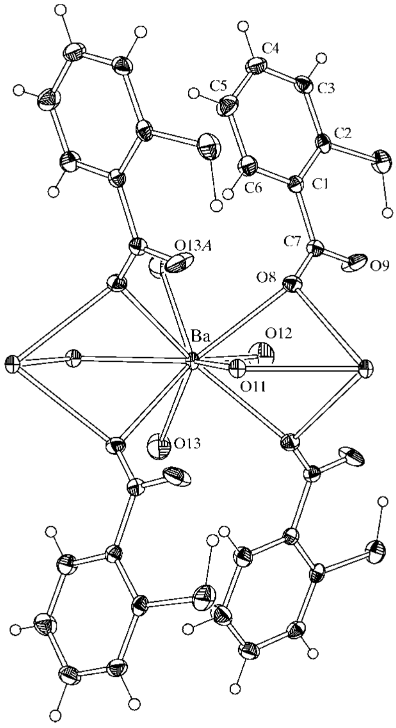


Figure 1
The coordination environment around the Ba^{II} atom in (I), showing displacement ellipsoids at the 30% probability level.

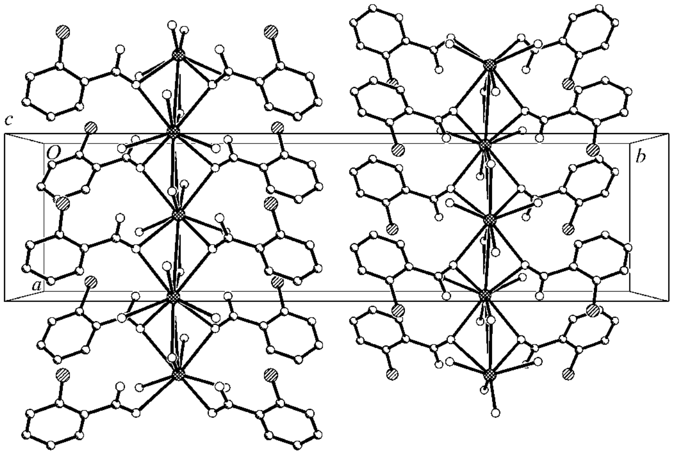


Figure 2
The crystal-packing diagram of (I), showing polymeric chains, viewed along the *c* axis.

mirror plane. Atom O12 is coordinated to only one Ba atom; the distance from O12 to the adjacent Ba^{ii} atom [symmetry code: (ii) $\frac{1}{2}+x, y, \frac{1}{2}-z$] is 5.04 (1) Å and the $Ba^{ii}\cdots O12-Ba$ angle is 59.2 (1)°. The Ba—O(carboxylate) bond distances of 2.842 (3)–2.946 (3) Å, the Ba—O(water) distances of 2.768 (4)–2.817 (6) Å and the Ba$\cdots$Ba interaction distances of 4.3355 (13) Å are comparable to those reported for the barium–2,2′-dithiobis(benzoate) (Murugavel *et al.*, 2001) and barium–2-aminobenzoate (Murugavel *et al.*, 2000) complexes. The bond angles around the Ba atom are in the range 64.74 (9)–142.34 (7)° (Table 1). The bond distances and angles of the tsa ligands are consistent with previously reported results (Henderson *et al.*, 2001).

The crystal-packing diagram of this complex reveals a one-dimensional coordination polymer, as shown in Fig. 2. The two carboxylate O8 atoms and the water O11 atom bridge the two adjacent Ba atoms, with Ba—O8—Ba and Ba—O11—Ba angles of 96.99 (9) and 102.41 (13)°, respectively. Furthermore, the central Ba atom is engaged in a weak metal–metal interaction with two neighboring Ba atoms. The Ba$\cdots$Ba$\cdots$Ba interaction angle of 121.44 (2)° in the *ac* plane gives polymeric zigzag chains. The S and O atoms in the tsa ligand are linked by an intramolecular S10—H10*A*$\cdots$O9 hydrogen bond (Table 2). However, there is no direct bonding between the Ba and S10 atoms. In other complexes, tsa is able to adopt a variety of coordination modes, ranging from monodentate S-bonded through to bridging (Henderson *et al.*, 2001). For example, the Ag atom of $[Ag(tsa)(PPh_3)_3]$ and the Au atom of $[Au(tsa)(PPh_3)]$ are coordinated by the monodentate S atom of the tsa ligand (Nomiya *et al.*, 1998), the Cu atom of $[\{Cu(PPh_3)_2\}_2\{Cu(tsa)_2\}]\cdot MeCN$ is bridged by the S and O atoms of the tsa ligand (Bott *et al.*, 1998), and the Cu atom of $[Cu(tsa)_2(py)]_2$ is chelated by the two O atoms of the tsa ligand (Ferrer & Williams, 1997). Therefore, the present barium–tsa complex, containing only one bridged O atom of the tsa ligand, is different in structure from the previously reported silver–, gold– and copper–tsa complexes.

Experimental

An ethanol–water (1:1) solution (10 ml) of thiosalicylic acid (1.54 g, 10 mmol) was added slowly to an aqueous solution (10 ml) of $BaCl_2\cdot 2H_2O$ (1.22 g, 5 mmol) with continuous stirring. The reaction mixture was neutralized with an aqueous solution containing KOH (0.56 g, 10 mmol) and then filtered. Pale-yellow block crystals of (I) suitable for X-ray analysis were obtained after a week at room temperature (yield 73%). Analysis found: C 32.68, H 3.20, O 22.95, S 12.05, Ba 26.30%; calculated for $C_{14}H_{18}BaO_8S_2$: C 32.60, H 3.52, O 24.82, S 12.43, Ba 26.63%.

Crystal data

$[Ba(C_7H_5O_2S)_2(H_2O)_4]$
$M_r = 515.74$
Orthorhombic, *Pnma*
$a = 7.563$ (3) Å
$b = 29.885$ (3) Å
$c = 8.2254$ (9) Å
$V = 1859.2$ (7) Å^3
$Z = 4$
$D_x = 1.843$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 41 reflections
$\theta = 5.0$–12.5°
$\mu = 2.40$ mm^{-1}
$T = 295$ (2) K
Block, pale yellow
0.40 × 0.38 × 0.20 mm

Data collection

Bruker *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (North *et al.*, 1968)
$T_{min} = 0.383$, $T_{max} = 0.619$
2650 measured reflections
1957 independent reflections
1794 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$

$\theta_{max} = 26.5°$
$h = -1 \rightarrow 9$
$k = -1 \rightarrow 37$
$l = -1 \rightarrow 10$
3 standard reflections every 97 reflections intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.113$
$S = 1.13$
1957 reflections
118 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0664P)^2 + 3.6403P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.12$ e Å^{-3}
$\Delta\rho_{min} = -1.75$ e Å^{-3}

The H atoms of the thiosalicylate ligand were refined using a riding model [HFIX 43 for the aromatic H atoms and HFIX 83 for the H atom of the thiol group; *SHELXTL* (Sheldrick, 1997)]. The H atoms

Table 1
Selected geometric parameters (Å, °).

$Ba-O11^i$	2.768 (4)	$Ba-O8^{ii}$	2.842 (3)
$Ba-O11$	2.794 (4)	$Ba-O8$	2.946 (3)
$Ba-O13$	2.799 (4)	$Ba-Ba^i$	4.3355 (13)
$Ba-O12$	2.817 (6)		
$O11^i-Ba-O11$	121.87 (11)	$O13^{iii}-Ba-O8$	129.87 (12)
$O11^i-Ba-O13$	66.79 (12)	$O13-Ba-O8$	75.41 (14)
$O11-Ba-O13$	131.40 (13)	$O12-Ba-O8$	142.34 (7)
$O13^{iii}-Ba-O13$	96.9 (3)	$O8^{ii}-Ba-O8$	88.32 (8)
$O11^i-Ba-O12$	112.68 (17)	$O8^{iv}-Ba-O8$	135.14 (5)
$O11-Ba-O12$	125.45 (17)	$O8^{iii}-Ba-O8$	73.26 (12)
$O13^{iii}-Ba-O12$	70.09 (14)	$O11-Ba-Ba^{ii}$	38.58 (9)
$O11^i-Ba-O8^{iv}$	141.79 (6)	$O12-Ba-Ba^{ii}$	86.87 (14)
$O13^{iii}-Ba-O8^{iv}$	80.98 (13)	$Ba^i-Ba-Ba^{ii}$	121.44 (2)
$O13-Ba-O8^{iv}$	140.26 (13)	$Ba^{ii}-O11-Ba$	102.41 (13)
$O12-Ba-O8^{iv}$	72.01 (13)	$C7-O8-Ba$	123.9 (3)
$O11^i-Ba-O8$	64.74 (9)	$Ba^i-O8-Ba$	96.99 (9)
$O11-Ba-O8$	69.40 (9)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
S10—H10*A*···O9	1.20	1.79	2.658 (4)	124

of the water molecules were not introduced as they could not be located in difference electron-density maps.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1109). Services for accessing these data are described at the back of the journal.

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