Crystal Structure of *catena*-Poly[*diaquabarium*(II)- μ -aqua- κ^2 O:O-di- μ -1-oxopyridinium-2-thioacetato- κ^4 O:O trihydrate]

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catena-Poly[*diaquabarium*(II)- μ -aqua- κ^2 O:O-di- μ -1-oxopyridinium-2-thioacetato- κ^4 O:O trihydrate], $[\text{Ba}(\text{C}_7\text{H}_6\text{O}_3\text{NS})_2(\text{H}_2\text{O})_3]_n \cdot 3n\text{H}_2\text{O}$ was synthesized and the crystal structure was determined by a single-crystal X-ray diffraction method. The title complex crystallizes in orthorhombic space group $P2_12_12_1$ with unit-cell parameters $a=7.7217(1)\text{\AA}$, $b=14.4052(2)\text{\AA}$, $c=19.9285(2)\text{\AA}$, $V=2216.70(5)\text{\AA}^3$. The final R value is 0.0143 for 3179 measured reflections. The central barium(II) metal makes coordination with ten oxygen atoms, and forms a polymeric chain by Ba-O-Ba links in the crystal.

(Received March 12, 2007; Accepted June 4, 2007; Published on web August 10, 2007)

The ligand used in the title complex, 1-oxopyridinium-2-thioacetic acid, has been found to exhibit an infinite array of a hydrogen-bond network.¹ It possesses many features: (i) it is a polydentate ligand having four donor atoms; (ii) the *N*-oxide group has been found to be more useful in the coordination mode. Using a hydrothermal technique, we synthesized² a series of transition metal (Co^{2+} , Ni^{2+} , and Zn^{2+}) coordination complexes of ligand (I) and further investigated their crystal structures and the coordination ability of the ligands around the central metal atom. Extending the above said studies with an alkaline earth metal, herein we report on a coordination polymer of barium with 1-oxopyridinium-2-thioacetic acid.

A solution of ethanol (20.0 mL) containing barium hydroxide octahydrate (0.315 g, 1 mmol) and 1-oxopyridinium-2-thioacetic acid (0.370 g, 2 mmol) was stirred at room temperature for one hour. The mixture was allowed to stand at

ambient temperature. Colorless, needle-shaped crystals of $[\text{Ba}(\text{C}_7\text{H}_6\text{O}_3\text{NS})_2(\text{H}_2\text{O})_3]_n \cdot 3n\text{H}_2\text{O}$ (Fig. 1) were obtained after three days. These crystals were washed with diethyl ether and a suitable single crystal was selected for X-ray diffraction intensity measurements.

A single crystal of the complex with approximate dimensions

Table 1 Crystal data and structure refinement details of title complex

CCDC No.	: 639407
Empirical formula:	$\text{BaC}_{14}\text{H}_{24}\text{O}_{12}\text{N}_2\text{S}_2$
Formula weight =	1227.62
Temperature =	293(2)K
Crystal system:	orthorhombic
Space group:	$P2_12_12_1$
$a =$	7.7217(1) $\text{\AA}$
$b =$	14.4052(2) $\text{\AA}$
$c =$	19.9285(2) $\text{\AA}$
$V =$	2216.70(5) $\text{\AA}^3$, $Z = 2$
$D_{\text{cal}} =$	1.839 Mg m^{-3}
$\mu =$	2.043 mm^{-1} , $\lambda(\text{Mo } K\alpha) = 0.71073\text{\AA}$
θ range for data collection:	1.02 to 23.26°
$(\Delta/\sigma)_{\text{max}} =$	0.001
$(\Delta\rho)_{\text{max}} =$	0.34 $\text{e}\text{\AA}^{-3}$
$(\Delta\rho)_{\text{min}} =$	-0.64 $\text{e}\text{\AA}^{-3}$
Crystal size =	0.3 × 0.2 × 0.12 mm
$F(0\ 0\ 0) =$	1223.8
$R_{\text{gt}} =$	0.0143 $R_{\text{all}} = 0.0156$
Goodness-of-fit =	1.06
No. of parameters =	329
Measurement:	Siemen's SMART 1K CCD area detector
Program system:	SHELXS97 and SHELXL97
Structure determination:	direct methods
Refinement:	full matrix

Fig. 1 Chemical diagram of the title complex.

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Fig. 2 ORTEP view of the title complex showing atoms with thermal ellipsoids at the 50% probability level.

of $0.3 \times 0.2 \times 0.12$ mm was mounted in air. Reflection intensity data were collected on a Siemen's SMART 1K CCD area detector using an ω scan. The structure was solved by direct methods and refined by a full-matrix least-squares method using 3123 reflections. All non-H atoms were refined with anisotropic displacement parameters, whereas H atoms were located from a difference map.

Figure 1 depicts a chemical diagram of the title complex. The molecular structure of the title complex is shown in Fig. 2. Crystal data and the details of the structure analysis are summarized in Table 1. Selected atomic distances and angles are listed in Table 2.

In $[\text{Ba}(\text{C}_7\text{H}_6\text{O}_3\text{NS})_2(\text{H}_2\text{O})_3]_n \cdot 3n\text{H}_2\text{O}$, the coordination sphere of the Ba^{2+} ion includes ten oxygen atoms (Fig. 2); six of these belong to the carboxylate group of the 1-oxypyridinium-2-thioacetic acid moiety, and the other four to the water molecules. Each barium atom is bridged to the neighboring barium by one water molecule and by two carboxylate oxygen atoms on either side of the polymeric chain in the crystal.^{3,4} Three water molecules are left uncoordinated in the crystal. The coordinated geometry of barium(II) ions can be well described as a distorted dodecahedron (Fig. 1).

The Ba...Ba distance across the chain is $4.273(1)\text{\AA}$. The Ba-O bond lengths in the complex are in the range $2.714(2) - 3.085(3)\text{\AA}$; these values are consistent with a similar reported structure.⁵ Among the Ba-O coordinations, the Ba(1)-O(3')ⁱ bond [$2.714(2)\text{\AA}$] is the shortest and the Ba(1)-O(6) bond [$3.085(3)\text{\AA}$] is the longest in the structure [symmetry code: $x-1/2, -y+1/2, -z+1$]. This difference may be attributed to the large bidentate binding. Among the carboxylate oxygen atoms [O(2), O(3), O(2') and O(3')] of the ligand, O(3) and O(3') are involved in forming bidentate interactions between two barium ions, leading to a four-membered distorted square-type chelate ring across the network. The dihedral angle between the two adjacent chelate rings is $29.2(2)^\circ$. The O(2) and O(2') are involved in a unidentate interaction with the barium(II) cations. The carboxylate groups form two four-membered chelate rings by means of coordination with barium. The dihedral angle

Table 2 Selected bond distances ($\text{\AA}$) and angles ($^\circ$)

Ba(1)-O(5)	2.779(2)
Ba(1)-O(4) ⁱ	2.856(2)
Ba(1)-O(3')	2.847(2)
Ba(1)-O(6)	3.085(3)
Ba(1)-O(2)	2.893(2)
Ba(1)-O(2')	2.963(2)
Ba(1)-O(3') ⁱ	2.714(2)
Ba(1)-O(3) ⁱ	2.749(2)
Ba(1)-O(4)	2.856(2)
Ba(1)-O(3)	2.863(2)
O(2)-C(7)	1.234(4)
O(3)-C(7)	1.250(3)
O(3')-C(7')	1.263(3)
O(2')-C(7')	1.247(3)
O(2)-C(7)-O(3)	125.2(3)
O(2')-C(7')-O(3')	123.5(2)
O(3)-Ba(1)-O(2)	45.1(1)
O(3')-Ba(1)-O(2')	44.7(1)
Ba(1)-O(4)-Ba(1) ⁱⁱ	96.8(1)

(i) $x-1/2, -y+1/2, -z+1$

(ii) $x+1/2, -y+1/2, -z+1$

between the two chelate rings is $37.4(1)^\circ$. The C-O bond length values (Table 2) range from $1.234(4)$ to $1.263(3)\text{\AA}$, indicating their partial double-bonding nature. The water molecule [O(4)] forms a bridge between the barium(II) ions (Fig. 2) in the crystal. The oxygen atoms, O(5) and O(6), from the water molecules are coordinated unidentately to the barium. The three uncoordinated water molecules interlink the neighboring $[\text{Ba}(\text{C}_7\text{H}_6\text{O}_3\text{NS})_2(\text{H}_2\text{O})_3]$ unit through O-H...O hydrogen-bond interactions. The oxygen atom of N-O group [O(1)] makes inter-molecular hydrogen-bond interactions O(7)-H(14)...O(1)ⁱ [O(7)...O(1) = $2.798(4)\text{\AA}$, $\angle\text{O(7)-H(14)...O(1)} = 151.99^\circ$] O(8)-H(16)...O(1)ⁱⁱ [O(8)...O(1) = $2.889(4)\text{\AA}$, $\angle\text{O(8)-H(16)...O(1)} = 159.45^\circ$] and O(9)-H(18)...O(1)ⁱⁱⁱ [O(9)...O(1) = $3.665(4)\text{\AA}$, $\angle\text{O(9)-H(18)...O(1)} = 159.92^\circ$] with the three uncoordinated water molecules [Symmetry codes: (i) $-x+1, y-1/2, z+1/2+1$; (ii) $-x+2, y-1/2, -z+1/2+1$; (iii) $x, y, z-1$]. These interactions stabilize the crystal packing.

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