CHEMISTRY LETTERS, pp. 2123-2126, 1994.

Synthesis and Structural Characterization of a Unique Octanuclear Bismuth(III) Thiosalicylate Complex with a Disk-like Cluster Core

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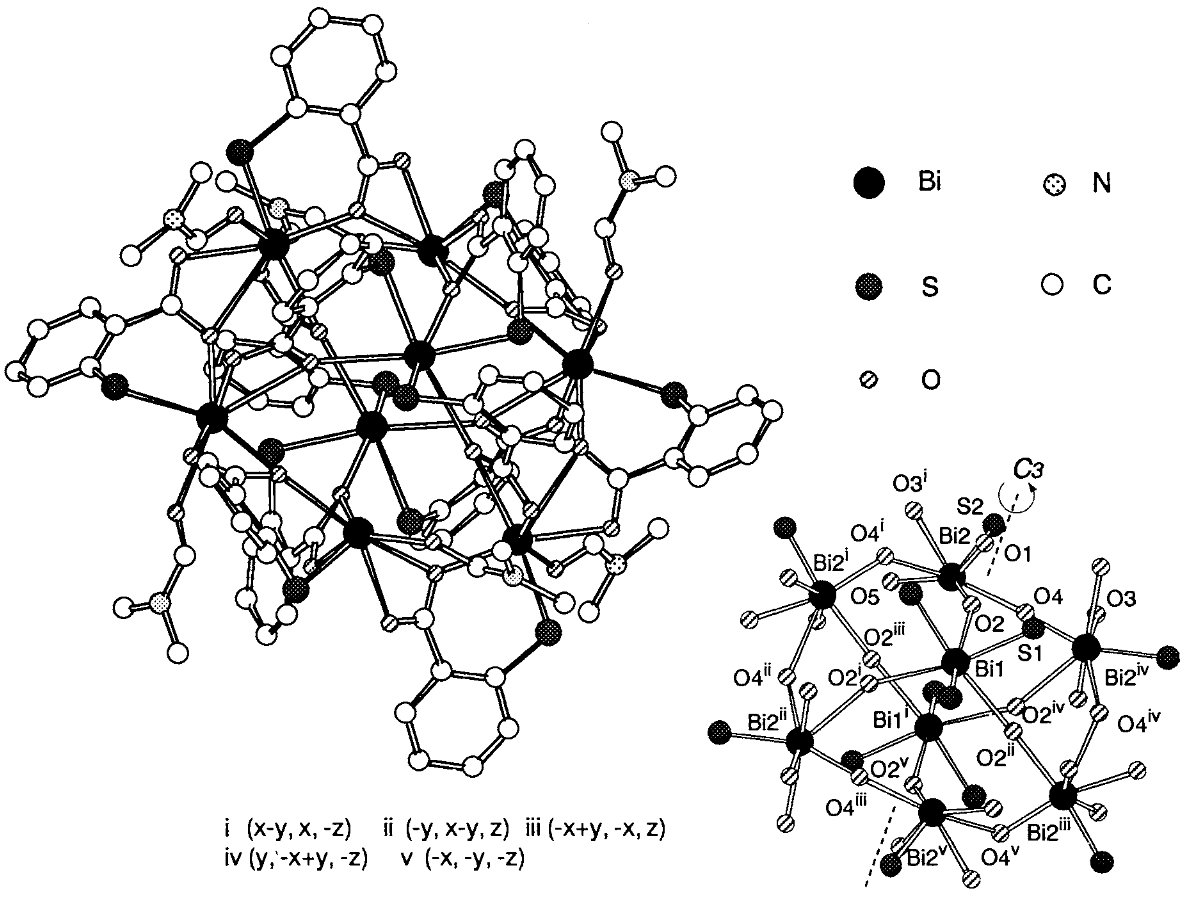
The octanuclear bismuth(III) thiosalicylate complex, $[Bi_8(tsal)_{12}(DMF)_6](DMF)_6$ (H_2tsal = thiosalicylic acid, DMF = N,N'-dimethylformamide), has been prepared and structurally characterized. The single crystal X-ray structure analysis has demonstrated that the eight Bi atoms form a disk-like cluster core and that each lone pair of two Bi atoms as the asymmetric unit is stereochemically activated.

Most bismuth salts are usually insoluble in organic solvents and will undergo hydrolysis in water to form insoluble bismuth-oxy salts. This chemical property is responsible for the difficulty in preparing the complexes and has retarded the development of the structural chemistry, compared to other metal complexes. However, since a recent renewed interest has risen in the Bi alkoxides1) as potential precursors for new superconductor with high T_c, the structural data of Bi-O interactions is now rapidly increasing. In contrast, despite of current interest of bismuth thiolates in potential utility as antitumor agents,2) fungicides,3) analytical reagents,4) and vulcanization catalysts,5) structural data on Bi-thiolate interaction remains scare. Our interest6) of bismuth citrate compounds in medical application as a ulcer healing agent caused us to start investigation of Bi-thiolate chemistry, since thiol-containing chelators such as *D,L*-2,3-dimercapto-propane-1-sulfonic acid and *meso*-2,3-dimercaptosuccinic acid7) have been reported to be effective intoxication agents for Bi overdose *in vitro* and *in vivo* experiments. In the course of investigating the chemistry, we have isolated a unique octanuclear bismuth thiosalicylate complex with a disk-like cluster core. We herein report the preparation and structural characterization of the complex $[Bi_8(tsal)_{12}(DMF)_6](DMF)_6$ (**1**).

The octanuclear complex **1** was isolated as follows. To a suspension of $Bi(NO_3)_3{\cdot}5H_2O$ (1.0 g, 2.1 mmol) in ethanol (80 cm^3) was added thiosalicylic acid (0.64 g, 4.2 mmol) with stirring, giving a clear yellow solution. Addition of a 25% ammonia solution (1 cm^3) to the reaction mixture immediately gave a yellow precipitate. The precipitate was collected on a glass-filter, washed with methanol, air-dried, and then dissolved in DMF (30 cm^3). On standing at room temperature for several days, orange cubic crystals **1** deposited (yield 0.32 g). Since the crystals very easily loose the lattice solvent DMF, the single crystal for X-ray crystallography was mounted into a capillary with a small amount of DMF solvent.

X-ray structure analysis8) of **1** revealed that this compound has a unique octanuclear structure (Fig. 1), characterized by the Bi_8O_{12} cluster core, in which the oxygen atoms used to bridge Bi(III) ions are coming from carboxylate in thiosalicylate (Fig. 2). The asymmetric unit is two Bi atoms, two thiosalicylate anions, one coordinated and one lattice DMF molecules, which are located around the three-fold axis on the two apical Bi1



i (x-y, x, -z) ii (-y, x-y, z) iii (-x+y, -x, z)
iv (y, -x+y, -z) v (-x, -y, -z)

Fig. 1. Molecular structure of **1** and its Bi_8O_{12} cluster core with some additional donors.

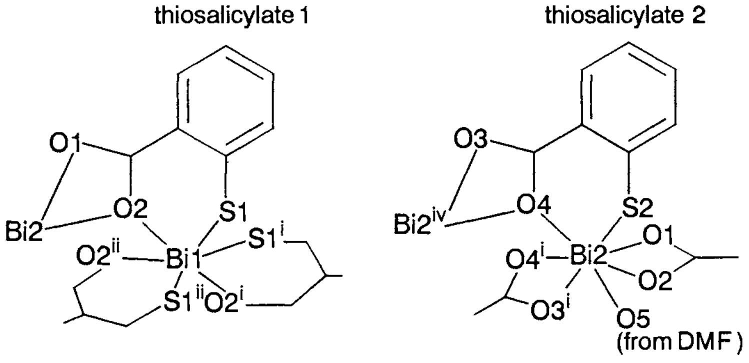
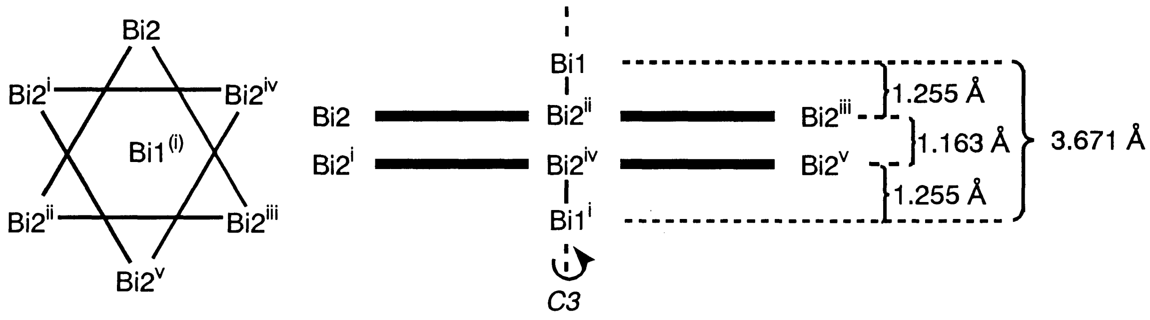


Fig. 2. Chelation and bridging modes of thiosalicylate units.

and Bi1$^{\text{i}}$ atoms. Two regular triangles formed by two sets of three Bi atoms, all of which are crystallographically equivalent, are parallel with a distance of 1.163 Å and twisted by 60 ° each other. Each Bi atom in the apical sites (Bi1 and Bi1$^{\text{i}}$) is situated in the position(s) 1.255 Å above (or below) the closer trigonal plane. Spatial arrangement of the all Bi atoms is schematically drawn in Fig. 3, indicating that the cluster core is compressed along the three fold axis and in a disk-like form.



Bi1 - Bi2 = 4.909 Å, Bi2 - Bi2^{ii} = 8.220 Å, Bi2 - Bi2^v = 9.562 Å, Bi2 - Bi2^{iv} = 4.885 Å

Fig. 3. Schematic drawing of 8 Bi atoms' spatial arrangement in **1**.

The coordination geometries around Bi1 and Bi2 are shown in Fig. 4. The Bi1 geometry with a S_3O_3 donor set is a strictly compressed octahedron along with the C_3 axis. Bi1-S1 distance 2.596(8) Å and S1-Bi1-$S1^i$ (or $S1^{ii}$) angle 96.6(2)° are comparable with those of $Bi(SAr')_3$ (Ar' = 2,4,6-t-$Bu_3C_6H_2$),9) which is a sole complex structurally characterized by X-ray analysis for $Bi(SR)_3$ type compounds. The location of O2 is significantly deviated from that expected for the ideal S_3O_3 octahedron geometry, *e.g.* S1-Bi1-O2 = 70.8(4)° and S1-Bi1-$O2^i$ = 162.7(4)°, to leave the vacant space for the Bi-6s electron pair, suggesting that the lone pair density is stereochemically activated. Nontransition elements are well known to have a stereochemically active lone pair on complexation with certain ligands. In general, when these metals form complex with 'hard' donor such as alkoxide with strong covalency,7,10) the lone pair of the metal is activated onto the trans position to the covalent bond. Concerning the Bi1 lone pair, it is activated by the three 'soft' sulfur atoms onto the trans position. As a result, the two active lone pairs from Bi1 and $Bi1^i$ locate on the C_3 axis with facing each other. Therefore, Bi1 appears likely to be expressed as seven coordination with a BiS_3O_3E geometry, where E is the active lone pair. The most striking characteristic of Bi2 geometry is a rather irregular polyhedron with a SO_6 donor set and the absence of donor atom in the space surrounded by O2, O4, $O4^i$, and O5 atoms, suggesting the active lone pair being at the space. It is strongly supported by the fact that the three strongest bonds are

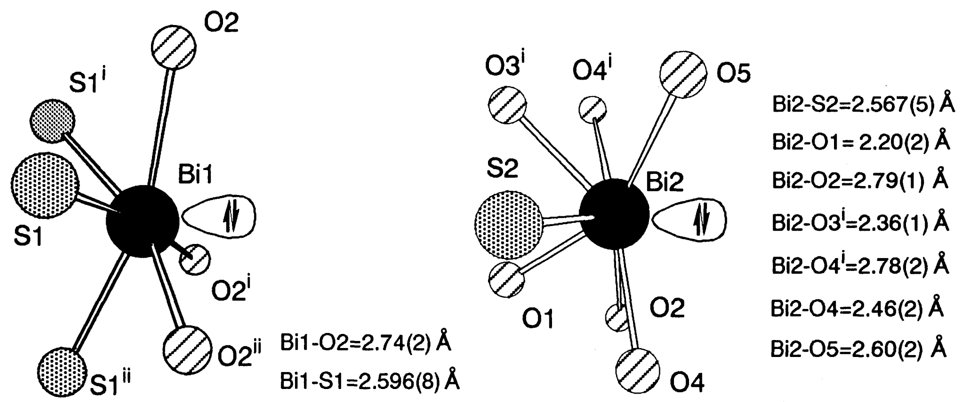


Fig. 4. Coordination geometry of Bi1 and Bi2. Stereochemically active lone pairs are also located in their expected position.

observed in the trans position, *i.e.* Bi2-O1 = 2.20(2) Å, Bi2-O3^{i} = 2.36(1) Å, and Bi2-S2 = 2.567(5) Å, which have almost covalent character.11) That is, Bi2 can be formulated as a $BiSO_6E$ geometry with the coordination number of 8.

In spite of departure from well known structural requisites for a donor set to activate a lone pair, *i.e.* 'hard' donor atoms and/or four-membered chelate ligands such as dithiocarbamates12) and pyridine-2-thiolate,13) the 6s lone pair of Bi1 is significantly activated. To our best knowledge, it is the first example of lone pair activation on Bi complex by 'soft' donor atoms from large bite six-membered chelate ring. Although the distance between the two facing lone pairs (from Bi1 and Bi1^{i}) is expected to be short, it is unlikely to occur some interaction between the two metals, when considered the metal-metal separation and the ionic radii.14) In order to see whether the activation is due to the covalent character of Bi-S bonds or a seeming phenomenon resulted from two Bi atoms' interaction, a structural study of mononuclear Bi complex with the same chelate ligand is now in progress.

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(Received August 15, 1994)