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Note

Cylindrical hexameric antimony complexes, one with an enclosed hexaaquanickel(II) ion

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ABSTRACT

The reaction of *meso*-2,3-dimercaptosuccinic acid and antimony trioxide produces an unusual hexameric cylindrical antimony complex. The cavity is large enough to accommodate the hexaaquanickel(II) cation. The crystal structures of both the parent hexamer and the Ni(II) species enclosed in the hexamer are reported. Bond valence sums were used to confirm that the antimony is +3 in both species and that the Ni ions are all +2 in the encapsulated complex.

1. Introduction

The element antimony is fascinating and important from a number of different viewpoints [1–3]. The Egyptians used antimony complexes for both cosmetic and medicinal purposes [1,2]. The coordination chemistry is of interest because of the +3 and +5 oxidation states and the question of the stereochemical activity of a lone pair in the Sb(III) [3]. Antimony complexes are also being studied for treatment of various parasitic diseases despite the question of whether Sb(III) or Sb(V) is the active form of the drug [4–8]. In addition, the use of antimony complexes in cancer chemotherapy is of current interest [9,10].

The compound *meso*-2,3-dimercaptosuccinic acid, also known as DMSA or succimer, has been proposed for the treatment of lead [11], arsenic [12], and mercury poisoning [13]. The antimony complex of DMSA has been used in the treatment of schistosomiasis [14] and the technetium complexes as radio pharmaceuticals [15]. In spite of the many possible therapeutic uses of DMSA, little is known about metal complexes of DMSA. As part of an ongoing study of complexes of Sb [16] and Bi [17], we undertook a study of the reaction of DMSA with antimony trioxide. The result has been the syntheses and characterizations of an unusual Sb(DMSA) cyclic hexamer, **1**, Figs. 1 and 2, and a $[Ni(H_2O)_6]^{2+}$ ion enclosed in the cyclic hexamer, **2**, Figs. 3 and 4.

2. Experimental

2.1. Materials

The *meso*-2,3-dimercaptosuccinic acid, henceforth DMSA, was 96% and was used as supplied by Aldrich Chemical Company. All other chemicals were reagent grade. The water was deionized and had a pH of about 6.

2.2. *meso-2,3-Dimercaptosuccinatoantimony(III) hexamer (**1**)*

DMSA (0.26 g, 1.37 mmol) was dissolved with heating in 150 mL of deionized water, and then antimony trioxide (0.20 g, 1.37 mmol Sb) was added. After 3 days the pH was 2. The mixture was stirred for 5 days at room temperature, and the cloudy yellow solution was treated with Darco and filtered. Small crystals appeared after one day. Colorless crystals from a second crop were suitable for an X-ray diffraction study. The crystals when removed from the mother liquor become opaque within 20 min at room temperature so that a chemical analysis did not seem relevant. They decompose around 212 °C when inserted into a block preheated to 130 °C.

2.3. $^{2+}Ni(H_2O)_6^{2+}$ *enclosed in the meso-2,3-dimercaptosuccinatoantimony(III) hexamer (**2**)*

DMSA (0.52 g, 2.74 mmol) was dissolved in 450 mL of water, and then antimony trioxide (0.40 g, 2.74 mmol Sb) was added. The mixture was stirred for 6 days at room temperature before

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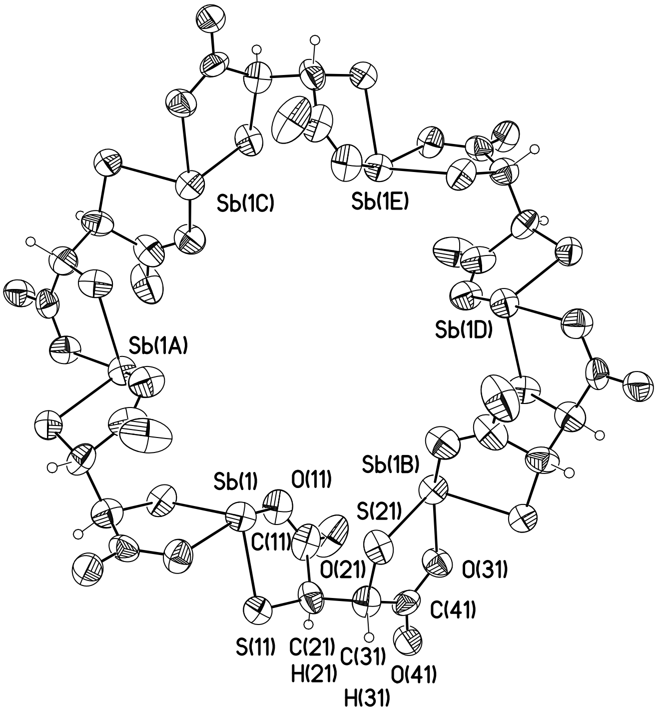

Fig. 1. A view of the cylindrical hexameric Sb(DMSA) complex with a 3-fold inversion axis of symmetry showing the atomic numbering and 40% thermal ellipsoids. The symmetry related Sb ions are Sb1A to Sb1E. The disordered water molecules within and outside of the cylinder are not shown.

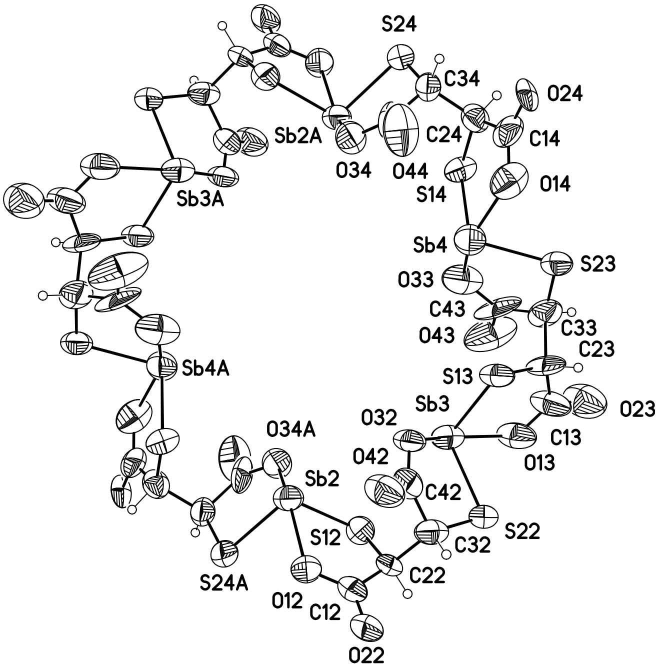

Fig. 2. A view of the cylindrical hexameric Sb(DMSA) complex with a center of symmetry showing the atomic numbering and 40% thermal ellipsoids. The symmetry related Sb ions are Sb2A, Sb3A, and Sb4A. The disordered water molecules within and outside of the cylinder are not shown.

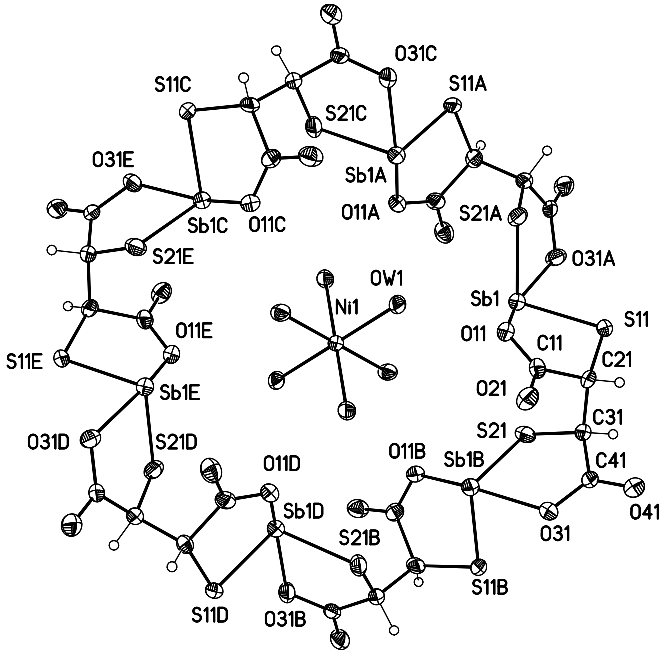

Fig. 3. A view of the cylindrical hexameric Sb(DMSA) complex with a 3-fold inversion axis of symmetry and the enclosed hexaaquanickel(II) ion showing the atomic numbering and the 40% thermal ellipsoids. The symmetry related Sb ions are Sb1A to Sb1E. The water molecules outside the cylinder are not shown.

ammonium nickel sulfate hexahydrate (1.08 g, 2.73 mmol) was added. The resulting mixture was stirred for an additional 10 days at which point the volume was about 200 mL, and the solution was filtered. Very pale green crystals, **2**, isomorphous with the Sb(DMSA) hexamer, **1**, formed after about one day. The crystals decompose rapidly if removed from the mother liquor.

2.4. X-ray structure determinations

As noted above, the crystals tend to decompose on standing so that X-ray diffraction studies were carried out as soon as possible after the crystals were removed from the solution, mounted, and covered with oil. Intensity data were measured at 173 K using a Siemens SMART PLATFORM equipped with a CCD area detector and graphite monochromator utilizing Mo Kα radiation, ($\lambda = 0.71073$ Å). A full sphere of data (1850 frames) was collected using the ω-scan method with a 0.3° frame width. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability; maximum correction on I was <1%. Absorption corrections by integration based on the measured and indexed crystal faces were applied. The structures were solved by direct methods and refined by full-matrix least squares using SHELXTL5 [18].

One problem with **1** and **2** was the difficulty in determining the number water molecules both within and between the cylindrical hexamers. The rapid and obvious water loss from the crystals when removed from the solution precluded a meaningful chemical analysis. Difference Fouriers suggested that the water molecules were disordered similar to the situation that occurs frequently in protein macromolecules [[19] and references cited therein] but is unusual in a coordination complex. Consequently, the water divining option in SHELXTL5 [18] which was developed for macromolecules was used. In addition, the program SQUEEZE [19] developed for disordered solvent molecules in X-ray structure determinations was also used. All three methods gave approximately the same answer per asymmetric unit: 18 water molecules in **1** and 12 water molecules in **2**. The refinement data given in Table 1 and the bond distances in Table 2 are from the SQUEEZE refinement. Regardless of the number of water molecules in and between the cylinders in **1**, the cylindrical nature of the hexamer has been established.