J. Am. Chem. Soc. **2001,** *123,* 11801−11802 11801

Synthesis and Structural Properties of the First Macrocyclic Selenoether Complex of Arsenic(III): A Rare Example of Exo and Endo Coordination in a Single Species

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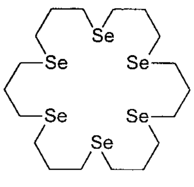
Received April 26, 2001

The coordination chemistry of the p-block elements with thio-, seleno- and telluroether ligands is of inherent interest since the p-block elements are very flexible with respect to their coordination to other ligands and therefore may reveal fundamentally new coordination modes and architectures. Volatile complexes may also provide convenient precursors for chalcogenide materials via CVD methods. We have conducted studies on a series of thio-, seleno-, and telluroether complexes of p-block metals such as Sn(IV) and Bi(III).[1,2] More recently we reported the first examples of selenoether complexes involving the metalloid Sb(III).[3] Complexes of Bi(III) and Sb(III) with thio- and selenoether ligands adopt very diverse, unusual, and often polymeric structures that are assembled through secondary Bi/Sb···S/Se interactions and a combination of primary and secondary Bi/Sb−X interactions. Subtle changes in the nature of the group 16 donor ligand (donor atom type, interdonor linkage, cyclic vs acyclic, etc.) lead to very marked differences in the structures which the complexes adopt. These results prompted us to investigate the reaction of thio- and selenoether ligands with nonmetallic species. Here we report the first example of a polydentate selenoether complex of a nonmetallic element, [$(AsCl_3)_4$([24]aneSe_6)].



[24]aneSe_6

The Lewis acid chemistry of As(III) has been very little explored,[4] and indeed there are no structural reports on any complexes of As(III) involving thio-, seleno-, or telluroether ligands. The yellow crystalline [$(AsCl_3)_4$([24]aneSe_6)] was obtained in high yield by the direct reaction of $AsCl_3$ with [24]aneSe_6 in rigorously anhydrous CH_2Cl_2 solution.[5,6] The product is poorly soluble in halogenated solvents. Selenium-77 NMR spectroscopy reveals a singlet at 153 ppm, that is, little shifted from "free" [24]aneSe_6, indicating that the complex is largely dissociated in solution. IR spectroscopy shows several relatively broad features around 310−380 cm^{-1} attributed to ν(As−Cl).

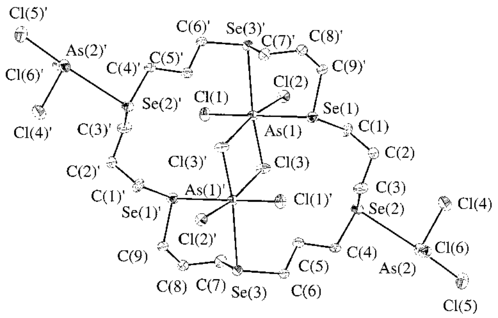


Figure 1. ORTEP drawing of [$(AsCl_3)_4$([24]aneSe_6)] with atom numbering scheme. 40% probability ellipsoids are shown. Atoms marked ′ are related by a crystallographic inversion center. Selected bond lengths: As(1)−Cl(1) = 2.292(2), As(1)−Cl(2) = 2.2100(18). As(1)−Cl(3) = 2.2862(19), As(1)−Cl(3)′ = 3.2814(21); As(1)−Se(1) = 2.9947(13), As(1)−Se(3)′ = 3.0057(14), As(2)−Cl(4) = 2.194(2), As(2)−Cl(5) = 2.250(2), As(2)−Cl(6) = 2.197(2), As(2)−Se(2) = 3.0906(15) Å.

The complex crystallizes as a discrete molecule, shown in Figure 1.[7] The structure shows a very unusual arrangement of four $AsCl_3$ units per hexaselenoether macrocycle, with two coordinated exo to the ring via a single Se atom and the other two forming a weakly associated dinuclear μ^2-chloro-bridged unit endo to the ring, with each of the As atoms coordinated to two mutually cis Se atoms from the macrocycle, giving a distorted edge-shared bioctahedral unit in the *isomer A* arrangement (according to the nomenclature of Norman and co-workers).[8] This is the first example of a discrete macrocyclic complex with both exo and endo coordination. The inclusion of a dinuclear M_2X_6 fragment within the ring is also very novel, there being no other examples involving thio- or selenoether macrocycles. The bridging As−Cl distances in the new selenoether macrocyclic complex, 2.2862(19), 3.2814(21) Å, indicate a very asymmetric, weak association of the two $AsCl_3$ units endo to the ring. Given that the sum of the van der Waals radii for As and Cl is 3.60 Å, the long As···Cl distance of 3.2814(21) Å suggests a genuine, albeit weak interaction.

The anionic $[As_2Cl_8]^{2-}$ has been identified previously and forms a weakly associated edge-shared square pyramidal arrangement, As-μ^2-Cl = 3.035(1), 3.063(1) Å,[9] however, unlike antimony(III) and bismuth(III) halide species, there are no structural reports of neutral substituted derivatives involving halide-bridged As_2 dimers and indeed the constraints of the macrocyclic ring may assist the formation of the dinuclear unit in the complex reported here. The As−Se distances are all approximately 3.0 Å, indicative of secondary interactions, akin to those which we have observed previously in antimony(III) and bismuth(III) selenoether species.[2,3] The coordination environment at As(1) (and As(1)′) is probably therefore best described as involving a facial arrangement of primary As−Cl interactions, with weaker, secondary bonding to Se(1), Se(3)′ and Cl(3)′ which occupy the opposite face of the arsenic center (cf. the structure of the parent $AsCl_3$ which shows a pyramidal molecule with three primary As−Cl interactions (ca.

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(6) Synthesis of [$(AsCl_3)_4$([24]aneSe_6)]: A solution of [24]aneSe_6 (0.036 g, 0.05 mmol) in anhydrous CH_2Cl_2 (5 cm^3) was added dropwise to a CH_2Cl_2 solution (5 cm^3) of $AsCl_3$ (0.036 g, 0.20 mmol) to give a pale yellow solution. Concentration of the solution by slow evaporation under a flow of N_2 gas afforded a yellow solid (yield 55 mg, 20%). Satisfactory microanalytical and IR spectroscopic data were obtained.

(7) Crystal data for [$(AsCl_3)_4$([24]aneSe_6)] at 150.0(1) K: $C_{18}H_{36}As_4Cl_{12}Se_6$, FW = 1451.36, monoclinic, $P2_1/n$, a = 8.227(4) Å, b = 25.66(1) Å, c = 9.808(4) Å, β = 95.71(3)°, V = 2060(1) Å^3, Z = 2. Structure solution and refinement were routine. The final R_1 was 0.0347 for 2402 reflections with $I > 2\sigma(I)$, wR_2 = 0.0969 (all data).

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10.1021/ja0110527 CCC: $20.00 © 2001 American Chemical Society
Published on Web 11/01/2001

2.17 Å); three intermolecular secondary As···Cl interactions complete a distorted octahedral environment[10]). Although it may be directed in the region of the secondary As(1)−Cl(3)′ interaction, the stereochemical activity of the lone pair of electrons on As(1) is not obvious as the angles subtended at As(1) do not show very significant deviations from the values expected for an octahedron. The location of the lone pair of electrons on the other As centers (exo to the ring) is much clearer, with As(2) and As(2)′ adopting a distorted sawhorse geometry, consistent with coordination to three terminal Cl atoms, one Se atom from the ring and the presence of a stereochemically active lone pair of electrons. There are no other As−Cl or As−Se interactions less than the sum of the van der Waals radii in the structure. The geometry of this unit contrasts with the distorted octahedral Se_2Cl_4 donor set at the As centers within the ring.

There is only one other crystallographically characterized complex of [24]aneSe_6, $[(PdCl)_2([24]aneSe_6)]^{2+}$ reported by Pinto and co-workers, which shows a square planar Se_3Cl. donor set at Pd(II), with no interaction between the $PdClSe_3$ units.[11]

Work is underway to establish whether the exceptionally unusual structural motifs identified for $[(AsCl_3)_4([24]aneSe_6)]$ are replicated in other macrocyclic complexes of arsenic trihalides. We have already established the structures of $[AsCl_3([9]aneS_3)]$ (discrete face-capped octahedron) ([9]aneS_3 = 1,4,7-trithiacyclononane) and $[(AsBr_3)_2([16]aneSe_4)]$ (polymeric with 6-coordinate As(III) through three short and one long As−Br interactions and two secondary As···Se interactions from exo coordination to two different macrocyclic rings—similar to $[(SbBr_3)_2([16]aneSe_4)]^3$) ([16]ane$Se_4$ = 1,5,9,13-tetraselenacyclohexadecane).[12]

Acknowledgment. We thank the EPSRC for support of this work.

Supporting Information Available: CIF file for the crystal structure included in this manuscript. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0110527

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