The First Example of a Structurally Characterized Monomeric Bismuth Selenolate

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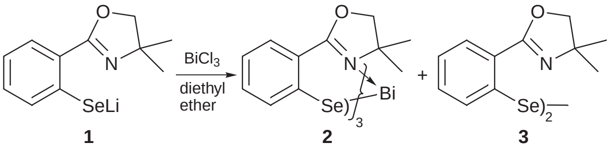
The reaction of intramolecularly coordinating 2-(4,4-dimethyloxazolino)phenyl selenolate ligand with anhydrous $BiCl_3$ (3:1 equivalents) produces the monomeric, air stable, homoleptic bismuth(III) selenolate complex.

The chemistry of main group metal chalcogenolate complexes is a growing area of current interest because of their potential use as single source precursors for the low temperature synthesis of semiconductor materials.[1] To avoid the formation of oligomeric or polymeric complexes and to enhance the compound solubility and volatility, several methods such as the use of sterically bulky organic substituents[3] and bifunctional chalcogenolate ligands having an additional donor atom[4] have been used. The chalcogenolates of Group 15 are particularly important since their solid state chalcogenides possess desired thermoelectric and optoelectronic properties.[5] Here, we report the synthesis and first structural characterization of a monomeric, air stable, homoleptic bismuth selenolate.



Scheme 1

Synthesis of the selenolate complex was approached by the metathesis reaction of the lithium areneselenolate with anhydrous $BiCl_3$ in diethyl ether (Scheme 1). Reaction of the lithium areneselenolate, $OxSe^-Li^+$ **1**,[9] with $BiCl_3$ gave the desired selenolate **2** along with the diselenide **3** in moderate yield. The crude product was crystallized repeatedly from chloroform–methanol to obtain the pure red air stable crystals of the bismuth selenolate **2**. The compound was found to be quite soluble in common organic solvents and stable in solution for extended periods without any noticeable decomposition. The compound melts sharply without decomposition to give a clear liquid.

The room temperature ^{77}Se NMR spectrum of **2** shows a sharp singlet which indicates that the three selenium atoms present in the complex are equivalent. The ^{77}Se chemical shift for the complex is observed at $\delta 261.6$ which is much lower than the value observed for the diselenide **3** ($\delta 454.8$)[10] thus indicating shielding of the selenium nuclei.

The crystal structure of **2** is shown in Fig. 1. The compound crystallizes as a monomer with no close intermolecular contacts. The Se–Bi bond lengths (2.691–2.745 Å) are comparable to the sum of the single bond covalent radii of the two atoms (2.69 Å).[11] This contrasts with the bismuth–sulfur distances reported for bis(diethyldithiocarbomato)[2-(2′-pyridyl)phenyl]bismuth(III) in which the Bi–S distances are longer than the expected values.[12] As expected, the N···Bi distances, N(1)···Bi 2.952(6), N(2)···Bi 2.827(7), N(3)···Bi 2.884(6) Å, are much longer than the sum of the single bond covalent radii of nitrogen and bismuth (2.22 Å) but are well within the van der Waals distance.[11] These distances are also significantly longer than the N···Bi distance reported for bis(diethyldithiocarbomato)[2-(2′-pyridyl)phenyl]bismuth(III)[12] and lie at the upper end of the range reported for the same interactions in other bismuth compounds[13] which lie in the range 2.56–2.86 Å. The N···Bi interactions are, therefore, considered as secondary in nature. The unequal Se–Bi–N bond angles result in the complex being distorted octahedral.

The most interesting feature in the structure is the observation of a stereochemically active lone pair of electrons at the bismuth. There is an approximate three-fold axis passing through the Bi with the three Se donor atoms above and the three nitrogen donor atoms below the Bi (Fig. 1). The lone pair is aligned along this axis pointing down between the three nitrogens which are mutually displaced away from the pseudo three-fold axis to accommodate the lone pair.

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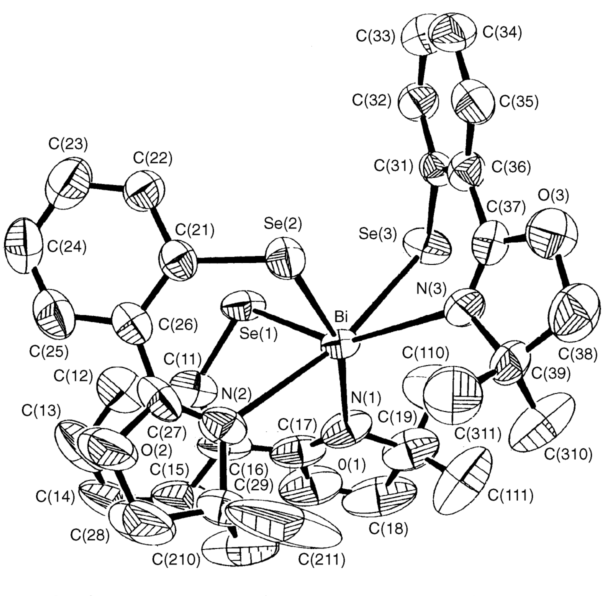

Fig. 1 Crystal structure of monomeric bismuth(III) complex **2**; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Bi–N(1) 2.952(6), Bi–N(2) 2.827(7), Bi–N(3) 2.884(6), Bi–Se(1) 2.7049(9), Bi–Se(2) 2.6910(8),Bi–Se(3) 2.7454(9); N(1)–Bi–N(2) 95.1(2), N(1)–Bi–N(3) 127.4(2), N(2)–Bi–N(3) 113.5(2), N(1)–Bi–Se(1) 68.63(14), N(1)–Bi–Se(2) 161.4(2), N(1)–Bi–Se(3) 91.4(2), N(2)–Bi–Se(1) 86.46(14), N(2)–Bi–Se(2) 73.65(14), N(2)–Bi–Se(3) 167.4(2), N(3)–Bi–Se(1) 150.20(12), N(3)–Bi–Se(2) 71.22(13), N(3)–Bi–Se(3) 70.13(13) Se(1)–Bi–Se(2) 95.39(3), Se(1)–Bi–Se(3) 85.92(3) Se(2)–Bi–Se(3) 97.14(3)

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Techniques used: NMR, X-ray diffraction

References: 15

Table 1: Crystal and Structure Refinement Data for **2**

Table 2: Significant bond lengths and angles for **2**

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