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Easy Access to Bismuth Catecholates

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ABSTRACT

*The reaction of catechols with bismuth (III) acetate in acetic acid solution provides an easy access to the polymeric bismuth catecholate acetate (**1**), 4-*tert*·butylcatecholate hydroxide (**2**), and 3,5-*di*-tert·butylcatecholate hydroxide (**3**).*

Bismuth holds a special position in the periodic table as the heaviest stable element, and bismuth compounds often show special behavior, both electronically and sterically. Thus, as illustrated in this paper, bismuth differs markedly from its predecessors in group V.

The direct reaction of phosphorus, arsenic or antimony trihalides with alcohols and, in particular with catechols, in the presence of a tertiary amine as HCl acceptor, constitutes an easy, long-known route to the haloalkoxides $EX_2(OR)$ or $EX(OR)_2$ where E = P, As, Sb, and, in particular, to the catecholates (Cat)EX [1]. In our attempts to prepare bismuth catecholates, we first tested this synthetic approach, but found that the major compounds formed were amine adducts of bismuth trichloride, while only very poor yields of bismuth catecholates (<10%) were obtained.

In view of the above, we considered the preparation reported in 1957 [2] where, starting with bismuth nitrate in acetic acid solutions, the authors claimed they had synthesized $(CatH)_2Bi(OH)$. However, the only evidence they presented to support their formulation was bismuth analysis. We found that the compound which in fact is formed under their conditions is CatBiOAc, **1**, and we report here a modified procedure which gives easy access to the molecular bismuth catecholates CatBiOAc, **1**, TBCatBiOH, **2**, and DTBCatBiOH, **3**. The following abbreviations will be used throughout this report: Cat = catecholate; TBCat = 4-*tert*·butylcatecholate; DTBCat = 3,5-*di-tert*·butylcatecholate.

RESULTS AND DISCUSSION

The reaction of catechols with bismuth triacetate, generated in situ through dissolution of bismuth trinitrate in acetic acid [3], is easy and rapid. The catecholates precipitate from the reaction mixture on addition of aqueous NaOH (1 N). The yellow microcrystalline compounds **1**, **2**, and orange **3** that formed with $CatH_2$, $TBCatH_2$, and $DTBCatH_2$, respectively, are insoluble in all common solvents, including dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).

Compound **1**, which already starts to precipitate at pH = 1, analyzes as (Cat)Bi(OAc). The infrared (IR) spectra (KBr pellets) measured on **1** show evidence for the bidentate coordination of catechol (1250 and 1480 cm^{-1}) [4] while coordination of the OAc moiety can be accounted for by two weak CO vibrations at 1570 and 1448 cm^{-1}; these two ν(CO), with a 122 cm^{-1} separation, i.e., close to that found in the free ion (144 cm^{-1}), can be taken to indicate a bridging behavior for the acetate group [5]: the separation between the two ν(CO) is much larger in unidentate complexes (>200 cm^{-1}) and smaller in the bidentate chelate structure (<80 cm^{-1}). Polymerization of **1** through acetato bridges is likely to be responsible for the insolubility of compound **1**, to which we assign the structure shown in Formula 1.

Further support for this formulation of **1** is found in its mass spectra: in the EI spectrum the molecular peak shows clearly, while in the IC (NH_3)

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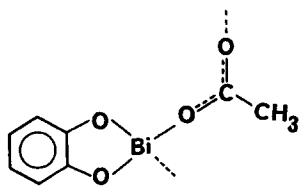


FORMULA 1

spectrum, the associated structure of **1** is evidenced by the presence of the CatBi(OAc)Bi(Cat) fragment as the parent peak.

The ^1H nuclear magnetic resonance (NMR) spectra (in CF_3COOD) recorded for **1** show, at δ = 7.44 the multiplet characteristic of the aromatic protons of catechol and a singlet at δ = 2.47 assignable to the acetate protons.

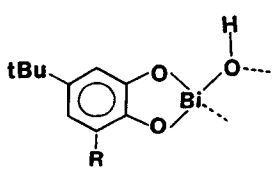
The presence of one acetate group per bismuth in **1** was confirmed through mineralization by HCl followed by neutralization by NaOH, which afforded BiOCl, catechol, and sodium acetate in a 1 : 1 : 1 ratio.

Compounds **2** and **3** analyze as (TBCat)Bi(OH), **2**, and (DTBCat)Bi(OH), **3**. They precipitate from the reaction mixture at the acetate buffer (pH = 4.8) where the analogues of **1** are most likely to be hydrolyzed into oxy species [6]. In agreement with a polymeric structure for **2** and **3**, their mass spectra show almost exclusively the catechol ligand indicating that **2** and **3** are nonvolatile compounds.

Their infrared spectra (KBr pellets) show bidentate coordination of catecholate. The vibrations that we assigned to the OAc moiety in **1** are no longer detected in the spectra of **2** and **3**. On the other hand, new bands can be assigned to the Bi-O(H)-Bi vibrator through comparison with the data in the literature [7]. The ^1H NMR spectra (in CF_3COOD) show only the signals arising from the catechols (**2:** δ = 7.68; m, 3 H, aromatic C**H**, δ = 1.57, s, 9 H, $C(CH_3)_3$; **3:** δ = 7.89, d, 1 H, aromatic ortho C**H**, δ = 7.58, d, 1 H, aromatic meta C**H**, δ = 1.64 and 1.60, s, 18 H , $C(CH_3)_3$). These data led us to assign the structure shown in Formula 2 to compounds **2**, R = H and **3**, R = tBu:

Compounds **1**, **2**, and **3** add to the only example reported so far of a molecular catecholato bismuth complex [8], i.e., CatBiMe, which was prepared from $MeBi(OEt)_2$ by interchange reaction with catechol.

FORMULA 2



EXPERIMENTAL

All the chemical reagents were of commercial grade; the catechols $TBCatH_2$ and $DTBCatH_2$ were recrystallized from petroleum ether, $CatH_2$ from water, before use. Elemental analyses were performed by the Service Central de Microanalyses du CNRS. Infrared (IR) spectra were recorded as KBr pellets on a Bruker IFS 45 spectrometer; ^1H NMR spectra were measured on a Bruker WH-90 spectrometer. Mass spectra (MS) were obtained on an R10 RIBERMAG L10 spectrometer.

Bi(Cat)(OAc)

1. $Bi(NO_3)_3$ 5 H_2O (4.85 g, 10 mmol) was dissolved in 30 mL acetic acid. The resulting solution was slowly added to a solution of 1.10 g of catechol (10 mmol) in 20 mL water, to yield a yellow solution which was cooled to 0°C. NaOH (1 N) was slowly added until a bright yellow precipitate formed (pH = 1–2). This was collected by filtration, washed with water, acetone, and ether and dried under vacuum (3.42 *g*; 91% yield). *Anal.* Calcd for $C_8H_7BiO_4$ (376.1): C, 25.55; H, 1.87; Bi, 55.56; O, 17.02. Found: C, 25.52; H, 1.91; Bi, 54.63; O, 17.09. IR (KBr pellets, cm^{-1}): ν(COO) 1570 and 1448, ν(CO) 1480 and 1250. MS: 376 (M^+, 9%), 317 (M^+-OAc, 6%), 268 (M^+-Cat), 12%); MS(NH_3): 693 ($2M^+$-OAc, 5%), 376 (M^+, 15%), 334 (M^+-OAc + NH_3, 65%), 317 (M^+-OAc, 93%).

Bi(TBCat)(OH)

2. To a solution of 2.425 g (5 mmol) of $Bi(NO_3)_3.5H_2O$ in 30 mL acetic acid, a solution of $TBCatH_2$ (0.83 g; 5 mmol) in acetone (30 mL) was slowly added. After 30 min stirring, the yellow solution was neutralized by NaOH (1 N) thus yielding a yellow precipitate which was rapidly filtered off. The yellow, microcrystalline compound was washed with water, acetone, and ether, and dried under vacuum (1.33 *g*; 68% yield). *Anal.* Calcd for $C_{10}H_{13}BiO_3$ (390.2): C, 30.78; H, 3.36; Bi, 53.56. Found: C, 30.60; H, 3.25; Bi, 53.03. IR (KBr pellets, cm^{-1}): ν(CO)1485 and 1258, ν(Bi-O) 550 and 334.

Bi(DTBCat)(OH)

3. The same procedure as for **2** was applied to 2.43 g (5 mmol) of $Bi(NO_3)_3 \cdot 5H_2O$ in 30 mL acetic acid and 1.12 g (5 mmol) $DTBCatH_2$ in acetone (30 mL) to give 1.65 g (74% yield) of the orange microcrystalline **3.** *Anal.* Calcd for $C_{14}H_{21}BiO_3$ (446.3): C, 37.67; H, 4.74; Bi, 46.83. Found: C, 38.11; H, 4.77; Bi, 47.24. IR (KBr pellets, cm^{-1}): ν (CO) 1410 and 1242, ν(Bi-O) 582 and 357.

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