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Synthesis and spectroscopic characterization of tetrathiometalato complexes of bismuth(III)

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Abstract

The reaction of an alcoholic solution of $BiCl_3$ with an aqueous solution of $(NH_4)_2MS_4$ (M = Mo, W) in the presence of PPh_4Cl or Bu_4NBr results in the formation of the tetracoordinate bis(tetrathiometalato) complexes of Bi(III), $[S_2M(\mu\text{-}S)_2Bi(\mu\text{-}S)_2MS_2]^-$ in good yields (70%). Alternatively, $(Ph_4P)_2MS_4$ or $(Bu_4N)MS_4$ can react with $BiCl_3$ in CH_2Cl_2 to give the same products in slightly higher yields. The bidentate coordination of $(MS_4)^{2-}$ to Bi(III) in these complexes has been concluded based on elemental analyses, conductivity data, and infrared and electronic spectral results. This study provides the first set of examples where a main group element is bound to thiometalates in a simple tetracoordinate fashion.

Introduction

Coordination chemistry of Bi(III) is a relatively little explored area and only a handful of Bi(III) complexes have been characterized. The difficulty in isolating pure samples lies in the facile formation of BiO^+ ion in the presence of moisture. Apart from the academic curiosity, a study of the complexes of bismuth with transition metal ions like molybdenum and tungsten is important from the viewpoint of heterogeneous catalysis. Bismuth–molybdate or bismuth–tungstate compounds are used commercially in the well known SOHIO process [1, 2] for the selective oxidation and amoxidation of alkenes. This commercial utility is mostly responsible for the growth and continuing interest in bismuth–transition metal complexes.

Most studies have been carried out where bismuth ion is directly bonded to the transition metal ion(s). A few representatives of this type of complexes include carbonyls, e.g. $[Bi\{Co(CO)_4\}_3]$ [3], $[Bi\{Mn(CO)_5\}_3]$ [4], $[Ir_3(CO)_9(\mu_3\text{-}Bi)]$ [5], $[Bi_2Fe_2(CO)_8Me_2]$ [6], $[\{W(CO)_5\}_3(\mu\text{-}_3\eta^2\text{-}Bi_2)]$ [7] etc., carbonyls with cyclopentadienyls e.g. $[Cl_2BiFe(C_5H_5)(CO)_2]$ [8], $[Me_2BiFe(C_5H_5)(CO)_2]$ [9], $[\{ClBi[Mn(CO)_2(C_5H_5)]_2\}_2]$ [10], $[ClBi\{Mo(CO)_3(C_5H_5)\}_2]$ [11] etc. No compound where bismuth is linked to transition metal ion(s) via bridging sulfur or oxygen has been reported. It is to be noted that catalysts used in the SOHIO process are compounds where bismuth ion is linked to molybdenum or tungsten ions via oxygen bridging.

We have initiated systematic studies of thio- and oxo-bridged bismuth–transition metal complexes as part of the scheme to study systems for possible catalytic activities. In the present paper we describe the isolation and characterization of $[Bi(MS_4)_2]^-$ (M = Mo, W) ions utilizing the coordinating properties of tetrathiometalates [12, 13]. While a large number of transition metal ions bound to the $(MS_4)^{2-}$ anion have been characterized [13–16], to our knowledge, the present work provides the first set of examples where a main group element is bound to the tetrathiometalate anion in a simple fashion giving BiS_4 coordination. The compounds have been isolated in the solid state and characterized by elemental analysis, conductivity, IR and electronic spectra.

Experimental

Reagents were used as received. All the solvents were purified prior to use following standard methods [17]. $(NH_4)_2MS_4$, $(Ph_4P)_2MS_4$ and $(Bu_4N)_2MS_4$ (M = Mo, W) were prepared by published procedures [18]. Infrared spectra were recorded on a Perkin-

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Elmer model 580 spectrophotometer. The samples were prepared as CsI pellets and referenced to polystyrene bands. The elemental analyses were performed in the microanalytical laboratory at IIT Kanpur while the UV–Vis data were collected on a Perkin-Elmer Lambda 2 spectrophotometer. The conductivity data of the compounds in dichloromethane solutions were collected on a Elico Model CM-82T conductivity bridge.

Synthesis of $PPh_4[Bi(WS_4)_2]$ (1)

Method A

$(NH_4)_2WS_4$ (696 mg, 2 mmol) was dissolved in water (20 ml) and the solution cooled in an ice bath. Into this ice cold solution was added dropwise a methanolic solution (30 ml) containing $BiCl_3$ (315 mg, 1 mmol) and PPh_4Cl (375 mg, 1 mmol). An orange–red precipitate was thrown out of the solution immediately. The precipitate was filtered, washed with water, methanol and ether and dried in vacuum. The precipitate was dissolved in warm acetonitrile and filtered off. Addition of ether into the clear filtrate afforded orange–red microcrystals of **1** in 70% yield.

Anal. Found: C, 25.01; H, 1.92; S, 21.23. Calc. for $C_{24}H_{20}PS_8W_2Bi$: C, 24.59; H, 1.72; S, 21.88%.

Method B

$(PPh_4)_2WS_4$ (248 mg, 0.25 mmol) was dissolved in CH_2Cl_2 (10 ml). Into this yellow solution was added solid $BiCl_3$ (40 mg, 0.125 mmol). The color of the solution slowly turned red. After 30 min the reaction mixture was filtered off and ether (5 ml) was added into the clear filtrate to afford orange–red crystals. Yield 75%. The compound gave a satisfactory analysis for C, H and S.

Synthesis of $PPh_4[Bi(MoS_4)_2]$ (2)

This compound was prepared by following the same procedure as mentioned above for its tungsten analog. The use of (520 mg, 2 mmol) of $(NH_4)_2MoS_4$ instead of $(NH_4)_2WS_4$ resulted in the formation of dark red crystals of **2** in 60% yield.

Anal. Found: C, 28.26; H, 1.92; S, 25.97. Calc. for $C_{24}H_{20}PS_8Mo_2Bi$: C, 28.92; H, 2.02; S, 25.73%.

Synthesis of $Bu_4N[Bi(WS_4)_2]$ (3)

This compound was synthesized following the method used for **1**. A total of 696 mg (2 mmol) of $(NH_4)WS_4$ was allowed to react with 315 mg (1 mmol) of $BiCl_3$ and 322 mg (1 mmol) of $(C_4H_9)_4NBr$ to yield **3** as a orange–red crystalline solid in 72% yield.

Anal. Found: C, 16.63; H, 2.98; N, 1.43; S, 23.26. Calc. for $C_{16}H_{36}NS_8W_2Bi$: C, 17.87; H, 3.37; N, 1.30; S, 23.85%.

Synthesis of $Bu_4N[Bi(MoS_4)_2]$ (4)

The same procedure as for **3** was used. Yield from 1 mmol of $BiCl_3$ was 61%.

Anal. Found: C, 20.43; H, 4.21; N, 1.40; S, 27.87. Calc. for $C_{16}H_{36}NS_8Mo_2Bi$: C, 21.36; H, 4.03; N, 1.56; S, 28.50%.

Results and discussion

The reaction of an aqueous solution of $BiCl_3$ with (dtc) (dtc = dialkyldithiocarbamate or dithiocarboxylate anion) generated *in situ* in an aqueous solution results in the formation of the $Bi(dtc)_3$ complex in very high yields [19] even though it is known that BiOCl is thrown out from an aqueous solution of $BiCl_3$. Even when BiOCl is allowed to react with an excess of dtc, the $Bi(dtc)_3$ complex can be isolated [20]. The facile formation of $Bi(dtc)_3$ in an aqueous alcoholic medium and the affinity of Bi(III) for soft S-donor ligands suggested that other complexes could also be prepared by the same route [21]. This encouraged us to study the reactivity of Bi(III) with other S-donor ligands like the thiometallates. The use of an excess (3 equiv.) of $(MS_4)^{2-}$ in the above reactions does not afford the hexacoordinate complexes $[Bi(MS_4)_3]^{3-}$ but only the tetracoordinate complexes are formed indicating stability of the $[Bi(MS_4)_2]^-$ ion. In the absence of a counter cation, only insoluble species of undefined composition are formed.

The molar conductivity of the complexes lies within the range 20–26 mho cm^{-1} in dichloromethane solutions which suggests that these compounds behave as 1:1 electrolytes in that solvent [22].

Selective infrared spectral data for the complexes are given in Table 1. The uncoordinated MS_4^{2-} ion having *Td* symmetry exhibits IR active triply degenerate M–S stretching vibrations [23]. For the MoS_4^{2-} ion it occurs at 480 cm^{-1} while for the WS_4^{2-} ion it occurs at 460 cm^{-1} [18] in accordance with the expected trend. On coordination in a bidentate fashion, the symmetry of the MS_4^{2-} anion is lowered and four bands are expected in the IR, with two at higher (M–S(terminal stretch) and two at lower (M–S(bridging) stretch) frequencies. However, instead of four bands, usually only two broad bands occur for each type of vibration. For the anion, $[Bi(WS_4)_2]^-$ the broad bands that occur around 490 and 440 cm^{-1} should be due to W–S(terminal) and W–S(bridging) stretching modes, respectively. The corresponding modes for the $[Bi(MoS_4)_2]^-$ anion occur around 500 and 460 cm^{-1}, respectively. Since the M–S stretching vibrations are diagnostic and give unequivocal proof that each MS_4^{2-} ion binds a Bi(III)

TABLE 1. Selected infrared and UV–Vis spectral data of the complexes[a]

Compound	IR data (cm^{-1})	Assignment	UV–Vis data (nm) (in M^{-1} cm^{-1})	Reference
$(NH_4)_2MoS_4$	480	ν_{as}(MoS)	467 (11850) 316 (16750) 241 (24700)	18
$(NH_4)_2WS_4$	460	ν_{as}(WS)	393 (15710) 277 (24500)	18
$PPh_4[Bi(MoS_4)_2]$	530(s) 500(sb) 460(mb)	cation band $\nu(MoS_{term})$ $\nu(MoS_{br})$	450 (5500) 285 (16850)	this work
$PPh_4[Bi(WS_4)_2]$	530(s) 490(sb) 440(mb)	cation band $\nu(WS_{term})$ $\nu(WS_{br})$	385 (8700) 270 (19800)	this work
$Bu_4N[Bi(MoS_4)_2]$	505(sb) 465(mb)	$\nu(MoS_{term})$ $\nu(MoS_{br})$	445 (6100) 285 (16000)	this work
$Bu_4N[Bi(WS_4)_2]$	495(sb) 440(mb)	$\nu(WS_{term})$ $\nu(WS_{br})$	375 (8100) 280 (20600)	this work
$(Ph_4P)_2[Zn(WS_4)_2]$	489 446	$\nu(WS_{term})$ $\nu(WS_{br})$	460 395	13

[a]term = terminal, br = bridging, s = strong, m = medium, b = broad.

in bidentate fashion giving BiS_4 coordination we decided not to look for Bi–S stretching and S–Bi–S bending vibrational modes which should occur in the far-IR region.

The electronic spectra of the complexes (Table 1) show essentially ligand internal transitions corresponding to those of the free thiometallate ions. These transitions are slightly blue shifted with respect to the free anions and are similar to those obtained for $[Zn(WS_4)_2]^{2-}$ [13]. We have not been successful so far, in isolating single crystals suitable for a structural analysis. However, the Bi(III) ion has a stereochemically active lone pair and therefore the coordination geometry around Bi(III) is expected to be a distorted one.

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