Synthesis and Structure of a Novel Tetranuclear Tungsten–Bismuth–Sulfur Complex

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Reaction of $[PPh_4]_2[WS_4]$ with 1/3 equiv. of $BiCl_3$ in CH_2Cl_2 afforded a new W/Bi/S complex $[PPh_4]_3[Bi(WS_4)_3]$ (**1**). The structure of the trianion of **1** represents the first example of W/Bi/S complex which contains a central Bi coordinated by six S atoms of the three $[WS_4]^{2-}$ moieties.

The heteronuclear sulfide complexes containing both transition metals and *p*-block metals have attracted attention due to their rich chemistry,[1–5] and their potential implications such as superconductivity,[6] catalysis,[7] and non-linear optical properties.[8] Some of these compounds have been synthesized *via* reactions of transition metal sulfides (e.g. $[M_3S_4]^{4+}$, $[MS_4]^{2-}$ (M = Mo, W)) with *p*-block metals in suitable organic solvents. For instance, reactions of the preformed incomplete cubane $[M_3S_4]^{4+}$ clusters with *p*-block metals M' (e.g. M' = Sb,[9,10] Pb,[11,12]) led to the formation of a series of monocubanes $[M'M_3S_4]^{n+}$ and *spiro* dicubanes $[M_3S_4\text{-}M'\text{-}M_3S_4]^{m+}$. However, reactions of the tetrathiometallates $[MS_4]^{2-}$ with *p*-block metals are very poorly explored and only five M/M'/S (M = Mo, W, M' = Pb, Sn, Tl) complexes were reported.[8,13–15] As for bismuth (III), there was one paper describing the synthesis of $[PPh_4][(MS_4)_2Bi]$ (M = Mo, W), but so far no crystal structure of these complexes has been reported yet.[16] As an extension of our studies on the chemistry of M/M'/S compounds,[8,15] we carried out the reactions of $[PPh_4]_2[WS_4]$ with $BiCl_3$ and isolated a different W/Bi/S complex $[PPh_4]_3[Bi(WS_4)_3]$ (**1**). Herein we report its synthesis and structural characterization of **1**.

The title complex was synthesized by the reaction of $[PPh_4]_2[WS_4]$ and $BiCl_3$ under pure dinitrogen atmosphere using standard Schlenk-line techniques. To a solution of $[PPh_4]_2[WS_4]$ (0.50 g, 0.50 mmol) in 20 mL of CH_2Cl_2 was added $BiCl_3$ (0.053 g, 0.16 mmol). The yellow solution went red within minutes and the mixture was stirred for *ca.* 20 min. at ambient temperature. After filtration, the filtrate was transferred into a slender glass tube and Et_2O (20 mL) was carefully layered onto the filtrate. After standing it at 0° for two days, large orange-red prisms of $[PPh_4]_3[Bi(WS_4)_3]\cdot 5CH_2Cl_2$ ($\mathbf{1}\cdot 5CH_2Cl_2$) were produced in 63% yield.[17]

When $BiCl_3$ was contaminated with a trace amount of water or when the moisture went into the solution during the reaction, it did not give rise to **1** but a brown red precipitate $[PPh_4]_2[W_3S_9]$.[18] The reason for this may be due to the facile formation of BiO^+ and H^+ ions in the presence of moisture and the degradation of $[WS_4]^{2-}$ in the presence of H^+ ions. Compound **1** is soluble in CH_3CN and DMF, but partly soluble in CH_2Cl_2 and $CHCl_3$. Being sensitive to heat and moisture, solid **1** is gradually decomposed when it is exposed to open air. We once carried out the reaction of $[PPh_4]_2[WS_4]$ with 1/2 equiv. of $BiCl_3$ in CH_2Cl_2. However, no $[PPh_4][Bi(WS_4)_2]$ or $[PPh_4]_3[Bi(WS_4)_2BiCl_2]$ was isolated, but only the known complex $[PPh_4]_2[W_3S_9]$ along with a large amount of insoluble black materials was isolated therefrom. The black materials were confirmed by X-ray fluorescence analysis to contain Bi and S.

Crystal $\mathbf{1}\cdot 5CH_2Cl_2$ crystallizes in the triclinic space group $P\bar{1}$, and the asymmetric unit consists of one independent $[Bi(WS_4)_3]^{3-}$ trianion, three $[PPh_4]^+$ cations, and five CH_2Cl_2 crystal solvent molecules.[19] Figure 1 shows the perspective view of the $[Bi(WS_4)_3]^{3-}$ trianion of **1**. In the structure of the $[Bi(WS_4)_3]^{3-}$ trianion, the oxidation states of W and Bi remain to be +6 and +3, respectively. The central Bi is six-coordinated by six sulfur atoms of the three $[WS_4]^{2-}$ ligands. The resulting BiS_6 octahedron is severely distorted, mainly due to the stereochemical influence of the lone pair on the Bi atom. The small S–Bi–S bite angles (77.52(9)–79.32(12)°) in the three four-membered BiSWS rings may be the cause of the observed distortions of the BiS_6 octahedron, and may determine the angles between *trans* S atoms to deviate from the ideal value of 180° to 166.85(9)–173.16(8)°. The various Bi–μ–S bond lengths may also reflect the possible influence of the lone pair on Bi. The bidentate attachment of the $[W(1)S_4]^{2-}$ to Bi is almost symmetric with two comparable Bi–μ–S bond lengths while those of the other two $[WS_4]^{2-}$ ones to Bi are less symmetric with one short and one long Bi–μ–S bonds. The structure of the trianion of **1** somewhat resembles those of the previous neutral bismuth complexes containing dithio ligands, e.g. $[(Et_2PS_2)_3Bi]$,[20] $[(Et_2NCS_2)_3Bi]$,[21] and $[\{(i\text{-}PrO)_2PS_2\}_3Bi]$.[22] Except for a few examples such as $[(Et_2PS_2)_3Bi]$, the bidentate attachment of

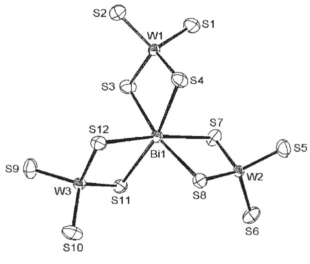

Figure 1. A perspective view of the $[Bi(WS_4)_3]^{3-}$ trianion, with the ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°) for $\mathbf{1}\cdot 5CH_2Cl_2$: Bi(1)···W(1), 3.4892(6); Bi(1)···W(2), 3.5623(7); Bi(1)···W(3), 3.5320(7); Bi(1)–μ–S(3), 2.780(3); Bi(1)–μ–S(4), 2.771(4); Bi(1)–μ–S(7), 2.821(3); Bi(1)–μ–S(8), 2.794(3); Bi(1)–μ–S(11), 2.844(4); Bi(1)–μ–S(12), 2.763(3); W–μ–S(av.), 2.233; W–S_t(av.) 2.162; S(3)–Bi(1)–S(4), 79.32(12); S(7)–Bi(1)–S(8), 77.52(9); S(11)–Bi(1)–S(12), 78.51(10), S(3)–Bi(1)–S(8), 168.10(11); S(4)–Bi(1)–S(11), 166.85(9); S(7)–Bi(1)–S(12), 173.16(8).

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the dithio ligands to Bi in most cases are asymmetric with three short and three long Bi–μ–S bonds, and therefore the coordination geometry of Bi varied from octahedron to pentagonal pyramidal.[20–22] For **1**, the average Bi–μ–S bond (av. 2.796 Å) is slightly shorter than that in [$(Et_2NCS_2)_3Bi$] (av. 2.821 Å),[21] but comparable to those found in other Bi complexes with dithio ligands such as [$(Et_2PS_2)_3Bi$] (av. 2.788 Å)[20] and [$((i\text{-}PrO)_2PS_2)_3Bi$] (av. 2.787 Å).[22] Each $[WS_4]^{2-}$ moiety acts as a bidentate ligand. The terminal W=S and W–μ–S distances are normal compared to those of the corresponding ones observed in $[PPh_4][(AgCN)WS_4]$.[23] The relatively long W···Bi contacts (av. 3.5278 Å) may preclude any significant bonding between W and Bi atoms.

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17 Anal. Found: C, 39.78; H, 2.77%. Calcd. for $C_{72}H_{60}BiP_3S_{12}W_3$ (1): C, 39.98; H, 2.80%. UV-vis (CH_2Cl_2, λ, nm, $M^{-1}cm^{-1}$): 230 (18400), 265 (8100), 385 (3300). IR (KBr pellet, cm^{-1}): $\upsilon_{\text{W-St}}$, 490 (s); $\upsilon_{\text{W-}\mu\text{-S}}$, 432 (m).

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19 Crystal data for **1**$\cdot 5CH_2Cl_2$: crystal dimensions $0.5 \times 0.6 \times 0.5\,\mathrm{mm}^3$, $C_{77}H_{70}BiCl_{10}P_3S_{12}W_3$, $M = 2588.10$, triclinic, space group $P\bar{1}$, $a = 11.7616(2)$, $b = 15.9411(2)$, $c = 27.616(1)$ Å, $\alpha = 79.20(2)$, $\beta = 81.065(2)$, $\gamma = 65.411(11)^\circ$, $V = 4611.08(3)$ Å^3, $Z = 2$, $D_c = 1.864\,\mathrm{g/cm}^3$, $\mu = 62.85\,\mathrm{cm}^{-1}$. 50230 intensity data were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo-Kα radiation at 193 K, of which 20118 ($R_{\text{int}} = 0.068$) are independent. $R(R_w) = 0.054$ (0.069) for 12020 reflections with $I > 3.00\sigma(I)$ and 980 refined parameters.

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