*Bull. Chem. Soc. Jpn.*, ***74***, *731—732 (2001)*

# Isolation and Structural Characterization of New Samarium(III) Bromide–HMPA Complexes

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(Received October 24, 2000)

The crystal structures of new samarium(III) bromide–HMPA complexes were accurately determined by single crystal X-ray analysis. The Lewis acidity of samarium(III) cation is discussed based on the crystal structures of several samarium(III)–HMPA complexes.

The trivalent lanthanides are utilized as Lewis acids with characteristic reactivities in a number of organic synthetic reactions.[1] One of the reasons of the characteristic reactivities is a moderate Lewis acidity. Therefore, it is important to consider the influence of counter anions on the Lewis acidity of the central metal cation.

The structures of several trivalent lanthanide salts–hexamethylphosphoramide (HMPA) complexes have been studied: samarium(III) triflate,[2] samarium(III) iodide,[3] samarium(III) chloride.[4] The samarium(III) triflate–HMPA complex is a cationic complex owing to the weak basicity of triflate ion. The samarium(III) iodide–HMPA complex is also a cationic complex, since the interaction between soft iodide anion and hard samarium(III) ion is weak, while the samarium(III) chloride–HMPA complex is a neutral complex. Although, the bromide ion has an intermediate hardness between chloride ion and iodide ion, there has been only one report about the lanthanide bromide–HMPA complex $[LaBr_3(hmpa)_4]$.[5] However, its crystal structure has not been clarified. We prepared the HMPA coordinated anhydrous complex of samarium(III) bromide and attempted the X-ray structural analysis. Here we report the crystal structure of new samarium(III) bromide–HMPA complexes and discuss the differences in interaction between samarium and halide ions based on the crystal structures.

The anhydrous samarium(III) bromide was prepared by dehydration of samarium(III) bromide hydrate.[6] The anhydrous samarium(III) bromide was suspended in tetrahydrofuran (THF) by irradiation with ultrasound for 1 h. Then five equivalents of HMPA were added. After continuous stirring, the precipitate was removed by centrifuging and the supernatant was left for recrystallization. The colorless prismatic crystals were thus obtained. The structure of this compound was determined to be $[SmBr_2(hmpa)_4]Br{\bullet}THF$ (**1**) by X-ray crystal analysis.[7] The molecular structure of complex **1** is shown in Fig. 1. The selected bond lengths and angles are given in Table 1. The central samarium(III) ion is hexacoordinated by four HMPA molecules in the equatorial plane and two bromide ions in trans position to form an octahedral structure. One bromide ion and one THF molecule are located in the outer sphere, thus forming a monocationic complex. The structure of the complex **1** is similar to those of samarium(III) triflate–HMPA complex $[Sm(OTf)_2(hmpa)_4]OTf{\bullet}CHCl_3$ (OTf = triflate) and samarium(III) iodide–HMPA complex $[SmI_2(hmpa)_4]I{\bullet}2CHCl_3$.

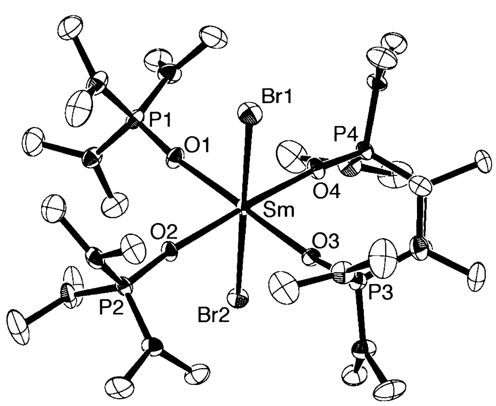

Fig. 1. Perspective ORTEP drawing of **1**. (Hydrogen atoms and not coordinated moieties are omitted for clarity; Ellipsoids are drawn at 30% probability).

Table 1. Selected Bond Lengths (Å) and Angles (°) in the Complex **1**

| | | | |
|---|---|---|---|
| Sm–Br1 | 2.854(1) | Sm–Br2 | 2.8519(9) |
| Sm–O1 | 2.271(5) | Sm–O2 | 2.301(5) |
| Sm–O3 | 2.281(4) | Sm–O4 | 2.281(5) |
| Br1–Sm–Br2 | 177.86(3) | O1–Sm–O2 | 88.6(2) |
| O1–Sm–O3 | 178.7(2) | O1–Sm–O4 | 90.8(2) |
| O2–Sm–O3 | 90.3(2) | O2–Sm–O4 | 175.4(2) |
| O3–Sm–O4 | 90.4(2) | | |

The Sm–O bond distances of 2.271(5)–2.301(5) Å are significantly longer than those of $[Sm(OTf)_2(hmpa)_4]OTf{\bullet}CHCl_3$ (2.247(4)–2.276(4) Å).[2b] This difference seems to arise from interaction between samarium(III) ion and counter anions. A strong coordination of counter anion increases the electron density on the central samarium(III) ion. This increase of electron density decreases the Lewis acidity, indicating the decrease of interaction with Lewis base, i.e., HMPA. Therefore, the bromide ion coordinates more strongly than the triflate ion, which is a conjugate base of a superacid.

Since the lanthanides are considered hard elements in Pearson's HSAB principle, the samarium(III) ion is expected to combine more strongly with a bromide ion than with a much softer iodide ion. However, Sm–O bond distances of the complex **1** are not significantly longer than those of $[SmI_2(hmpa)_4]I{\bullet}2CHCl_3$ (2.257(20)–2.301(20) Å).[3] Steric hindrance between the iodide ions and the HMPA molecules may contribute to the lengthening of Sm–O bond in $[SmI_2(hmpa)_4]I{\bullet}2CHCl_3$, because the ionic radius of iodide ion is much larger than that of bromide ion.

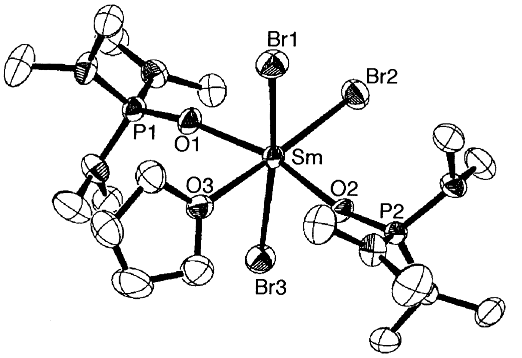

Fig. 2. Perspective ORTEP drawing of **2**. (Hydrogen atoms are omitted for clarity; Ellipsoids are drawn at 30% probability).

The Sm–O bond distances of 2.271(5)–2.301(4) Å are significantly shorter than those of [$SmCl_3(hmpa)_3$] (2.290(13)–2.388(18) Å).[4] Such a difference indicates that the chloride ions strongly combine with samarium(III) ion. Further, in contrast to samarium(III) bromide, the samarium(III) chloride is coordinated by only three molecules of HMPA. Even when an excess amount of HMPA was added, the yielded complex was always [$SmCl_3(hmpa)_3$]. The difference of interaction between samarium(III) and halide ions may be responsible for the fact that the structure of samarium(III) chloride complex is quite different from that of bromide complex. The dissociation of one halide ion seems to be necessary for coordination of the fourth large HMPA molecule. In the case of samarium(III) chloride, the Sm–Cl bond is strong enough to prevent the substitution of chloride ion with fourth HMPA, because the chloride ion is much harder than a bromide ion. Thus, the bromide ion was displaced by HMPA molecule to form the complex **1**. The samarium(III) iodide complex seems to be formed as a cationic complex in a similar manner.

Another complex was obtained when less than 2.5 equivalents of HMPA were added to samarium(III) bromide. The structure of this complex was determined to be [$SmBr_3(hmpa)_2(thf)$] (**2**) by X-ray crystal analysis.[8] The molecular structure of complex **2** is shown in Fig. 2. The selected bond lengths and angles are given in Table 2. The samarium(III) ion of this complex is surrounded by three halide ions, two HMPA molecules, and one THF molecule to form hexacoordinated octahedral structure. The Sm–Br bond distances of the complex **2** are shorter than those of complex **1**, because the electron donating property and steric hindrance of the THF molecule is much less than the HMPA molecule. Two HMPA molecules, one THF molecule, and one halide ion are located in a coplanar manner, whereas the O–Sm–O bond angle of two HMPA molecules bends to the THF molecule coordinating side. The angle of Br–Sm–Br bond, which is perpendicular to that plane is also bent to the same side. A steric hindrance of halide ion seems to be responsible for this distortion. In addition, the Sm–O bond distances of 2.280(4) and 2.280(5) Å are intermediate between those of [$SmCl_3(hmpa)_3$] and [$Sm(OTf)_2(hmpa)_4$]OTf•$CHCl_3$. This is in accord with the case of [$SmBr_2(hmpa)_4$]Br•THF.

Table 2. Selected Bond Lengths (Å) and Angles (°) in the Complex **2**

| | | | |
|---|---|---|---|
| Sm–Br1 | 2.837(1) | Sm–Br2 | 2.824(1) |
| Sm–Br3 | 2.8542(9) | Sm–O1 | 2.280(5) |
| Sm–O2 | 2.280(4) | Sm–O3 | 2.469(6) |
| Br1–Sm–Br2 | 92.89(4) | Br1–Sm–Br3 | 170.79(4) |
| Br2–Sm–Br3 | 96.31(3) | Br2–Sm–O3 | 177.7(1) |
| O1–Sm–O2 | 165.9(2) | | |

In summary, we determined the crystal structures of new HMPA complexes of samarium(III) bromide. Further, study of bond lengths and angles showed that the affinities of counter anions for samarium(III) ion are Cl $\gg$ Br > I > OTf.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 155118, 155119. The data are also deposited as Document No. 74025 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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7 Crystal Data for [$SmBr_2(hmpa)_4$]Br•(thf): formula $C_{28}H_{80}O_5Br_3N_{12}P_4Sm$, colorless prism, monoclinic, space group $P2_1/c$, $a = 15.682(2)$ Å, $b = 12.991(1)$ Å, $c = 25.136(2)$ Å, $\beta = 96.357(2)$ deg, $Z = 4$, $D_{calc} = 1.539$ g cm$^{-3}$, $R/R\mathrm{w} = 0.050/0.055$ for 7694 observed reflections.

8 Crystal Data for [$SmBr_3(hmpa)_2(thf)$]: formula $C_{16}H_{44}O_3Br_3N_6P_2Sm$, colorless prism, monoclinic, space group $P2_1/c$, $a = 10.003(2)$ Å, $b = 15.70(1)$ Å, $c = 20.06(2)$ Å, $\beta = 93.75(2)$ °, $Z = 4$, $D_{calc} = 1.734$ g cm$^{-3}$, $R/R_w = 0.062/0.093$ for 4721 observed reflections.