Preparation and Properties of Hexamethylphosphoramide-Coordinated Complexes of Samarium(III) Iodide

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(Received June 22, 1995)

Samarium(III) iodide complexes with hexamethylphosphoramide ligand, $[SmI_3(hmpa)_2(H_2O)_5]\cdot 2hmpa$ and $SmI_3(hmpa)_3(H_2O)_4$, have been isolated and structurally characterized by X-ray diffraction analyses. The dehydrated complex, $SmI_3(hmpa)_4$, was less reactive toward *n*-butyllithium or samarium metal than SmI_3.

It is well-known that the reducing ability of samarium(II) iodide (SmI_2) is dramatically increased by the addition of hexamethylphosphoramide (HMPA).[1,2] This HMPA effect is responsible for the coordination of HMPA to the samarium atom.[3,4] Thus, HMPA coordinates to the Sm(II) atom with increase of the electron density at the samarium atom to promote the electron transfer process. The great stabilization of the resulting Sm(III) species by the strong coordination is another driving force for the process. Hou and Wakatsuki revealed a direct evidence of the coordination of the oxygen atom of HMPA to SmI_2 by X-ray crystallographic study.[5] On the other hand, no reports dealing with SmI_3–HMPA complexes have appeared hitherto, although many HMPA-coordinated lanthanide(III) salts have been reported so far.[6] We have studied preparation, structural characterization, and reactivities of SmI_3–HMPA complexes in order to obtain some knowledges on the HMPA-enhanced reducing ability of SmI_2.

A SmI_3–HMPA complex was readily prepared by the following procedure: Diiodomethane (1.3 mL, 16 mmol) was added with stirring to a mixture of samarium powder (ca. 50 mesh, 1.50 g, 10 mmol), HMPA (8.7 mL, 50 mmol), and dry THF (30 mL) under argon atmosphere. After the initial exothermic reaction was subsided, the mixture was refluxed for 1 h. The solvent was removed under reduced pressure, and most of the residual solid material was dissolved in hot ethyl acetate–chloroform (1/1) (180 mL). The mixture was filtered and the filtrate was stood at room temperature overnight. The resulting pale yellow needles were collected, washed with ethyl acetate–chloroform (1/1), and dried in vacuo at 100 °C for 5 h to give moisture-sensitive white powder (8.64 g, 69%). The composition of the dried complex was found to be $SmI_3(hmpa)_4$ by elemental analysis and FAB mass spectroscopy.[7]

In order to obtain good crystals for single crystal X-ray analysis, the complex was recrystallized from 3-pentanone to give cubes and irregular prisms. The molecular structures of both crystals were determined by X-ray diffraction analyses.

Figure 1 shows an ORTEP drawing of the cubic crystal.[8] It is apparent that the complex consists of one Sm(III) atom, three iodide anions, four HMPA, and five H_2O molecules. The central samarium atom is hepta-coordinated by two HMPA oxygen atoms and five H_2O molecules to form a pentagonal bipyramid structure.[9] It is noted that the other two HMPA molecules are not directly bonded to the Sm(III) atom.[10] Judging from the atomic distances of O5–O9 (2.64Å), O6–O9 (2.66Å), O6–O8 (2.56Å), and O7–O8 (2.66Å), these HMPA oxygen atoms are interacted with the coordinated H_2O molecules through hydrogen bonds.

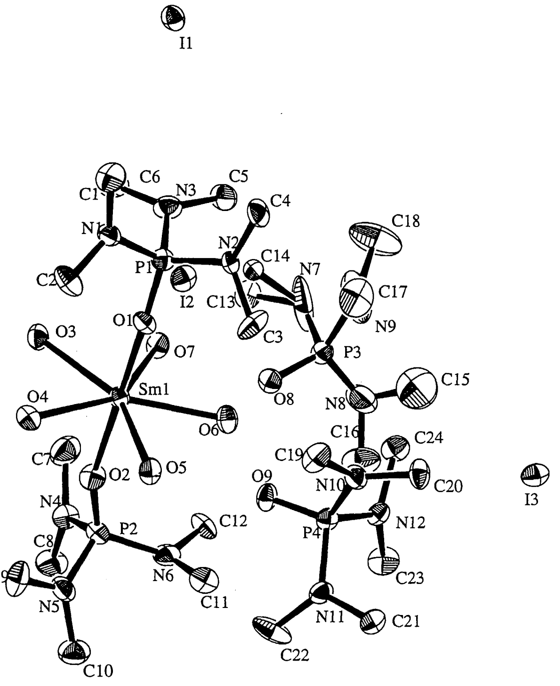

Figure 1. ORTEP drawing of $[SmI_3(hmpa)_2(H_2O)_5]\cdot 2hmpa$. Selected bond distances (Å) and angles (deg): Sm–O1 2.222(5), Sm–O2 2.283(5), Sm–O3 2.395(9), Sm–O5 2.451(8), Sm–O6 2.430(5), P1–O1 1.510(3), O1–Sm–O2 177.6(9), O1–Sm–O3 91.0(9), O3–Sm–O4 74.6(3), O3–Sm–O7 71.2(1).

The molecular structure of the irregular prismatic crystal is shown in Figure 2.[11] The central samarium atom is coordinated by three HMPA oxygen atoms and four H_2O molecules to form a distorted pentagonal bipyramid structure.[9] The three iodide anions are not directly bonded to the Sm(III) atom.

The reactivities of the dried SmI_3–HMPA complex $[SmI_3(hmpa)_4]$ were examined in comparison with those of SmI_3 itself.[12,13] In contrast to SmI_3, this trivalent complex was not reduced to low-valent samarium species by *n*-butyllithium or *sec*-butyllithium. The proportionation reaction between this complex and samarium metal to form divalent samarium species did not

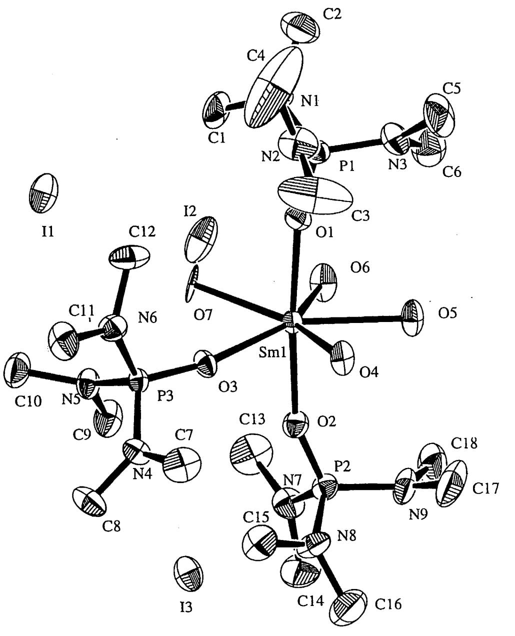

Figure 2. ORTEP drawing of $SmI_3(hmpa)_3(H_2O)_4$. Selected bond distances (Å) and angles (deg): Sm–O1 2.263(7), Sm–O2 2.293(7), Sm–O3 2.335(6), Sm–O5 2.442(6), P1–O1 1.50(4), O1–Sm–O2 175.2(3), O1–Sm–O3 100.5(3), O2–Sm–O3 83.6(3), O3–Sm–O4 75.4(3), O3–Sm–O7 75.0(3), O5–Sm–O6 71.2(3).

take place even at reflux in THF. These results are reasonably interpreted by considering that this complex is well stabilized by the coordination of HMPA.

In summary, we have studied preparation, structural characterization, and reactivities of SmI_3–HMPA complexes. The results support the consideration that the great stabilization of trivalent samarium species by complexation with HMPA and/or H_2O is one of the driving forces for the facile electron transfer of SmI_2.[1–4]

The present work was supported by a Grant-in Aid for Scientific Research on Priority Area "New Development of Rare Earth Complexes" No. 06241108 from the Ministry of Education, Science and Culture.

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7 Mp > 250 °C; IR (KBr) 2890, 1300, 1190, 1105, 990 cm^{-1}; MS (FAB) 1122 {$[SmI_2(hmpa)_4]^+$} (8%), 943 {$[SmI_2(hmpa)_3]^+$} (98%), 764 {$[SmI_2(hmpa)_2]^+$} (100%). Anal. Calcd for $SmI_3C_{24}H_{72}O_4N_{12}P_4$: C, 23.31; H, 5.87; N, 13.56. Found: C, 23.26; H, 5.84; N, 13.38.

8 X-ray crystallographic data for $[SmI_3(hmpa)_2(H_2O)_5]\cdot 2hmpa$: FW = 1375.91, monoclinic, Cc (#9), a = 14.054(6), b = 19.163(2), c = 20.531(3)Å, β = 100.90(2)°, V = 5429.6Å^3, Z = 4, D_{calc} = 1.683 g/cm^3, R = 0.062, R_w = 0.067, temperature of data collection 173 K, 2906 unique reflections with $I > 3.00\sigma(I)$.

9 The coordinated H_2O molecules might be incorporated from water contaminated in 3-pentanone.

10 Hou *et al.* observed that one of the HMPA molecules in $[Yb(H_2O)_5(hmpa)_2]Cl_3\cdot H_2O\cdot hmpa$ was not directly bonded to the ytterbium atom. See reference 2.

11 X-ray crystallographic data for $SmI_3(hmpa)_3(H_2O)_4$: FW = 1140.78, monoclinic, $P2_1/c$ (#14), a = 15.853(5),b = 14.495(3), c = 19.158(4)Å, β = 95.57(2)°, V = 4381(1)Å^3, Z = 4, D_{calc} = 1.717 g/cm^3, R = 0.048, R_w = 0.076, temperature of data collection 296 K, 4162 unique reflections with $I > 3.00\sigma(I)$.

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