Isolation and X-Ray Structures of the Hexamethylphosphoramide (hmpa)-coordinated Lanthanide(II) Diiodide Complexes $[SmI_2(hmpa)_4]$ and $[Yb(hmpa)_4(thf)_2]I_2$

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Reaction of samarium diiodide (SmI_2) with hexamethylphosphoramide (hmpa) in tetrahydrofuran (thf) gave $[SmI_2(hmpa)_4]$ **1** after recrystallization from toluene, while in the case of YbI_2, crystals of $[Yb(hmpa)_4(thf)_2]I_2$ **2** were obtained from thf; both **1** and **2** have been structurally characterized and the influence of hmpa on the reactivity of SmI_2 is discussed.

Lanthanide diiodides LnI_2 (Ln = Sm, Yb), synthesized first by Kagan and coworkers in 1977,[1] have now become useful one-electron transfer agents in organic synthesis.[2] Of particular interest is the fact that addition of hexamethylphosphoramide (hmpa) to SmI_2 in tetrahydrofuran (thf) solution greatly increases its reducing power[3] and often dramatically changes the regio- and stereo-selectivity of its reactions.[4] Although the coordination of hmpa to the Sm^{II} ion was thought to be responsible for this effect, the lack of structural information hampered further understanding of the role played by hmpa.[4,5] The isolation and structural characterization of new SmI_2–hmpa complexes are required to clarify this problem. By use of hmpa as a coordination ligand, we have recently prepared a few divalent[6,7] and trivalent[5,7] ytterbium complexes, showing that hmpa is a good ligand for lanthanides. In this paper, we report the successful isolation and structural characterization of the first hmpa complexes of lanthanide diiodides, $[SmI_2(hmpa)_4]$ **1** and $[Yb(hmpa)_4(thf)_2]I_2$ **2**.

Hexamethylphosphoramide (0.8 ml, *ca.* 4.5 mmol) was added to a blue solution of SmI_2 (1 mmol) in thf at room temperature and stirred for 30 min.† After reduction of the solution volume *in vacuo*, toluene was added and the mixture was further concentrated. After addition of toluene, the purple solution darkened a little. After a few days at room temperature, black-purple blocks of $[SmI_2(hmpa)_4]$ **1** were deposited in *ca.* 90% yield (Fig. 1).‡ The Sm^{II} ion sits on an inversion centre and is bonded by two I^- anions and four hmpa ligands in a distorted octahedron. Owing to this crystallographic symmetry, the central Sm^{II} ion and the oxygen atoms O(1), O(2), O(1′) and O(2′) of the four hmpa ligands are exactly coplanar, and the two iodide anions are mutually *trans*. The bond distance between the Sm^{II} ion and hmpa [Sm–O(hmpa): av. 2.500(6) Å] in **1** is much shorter than those between Sm^{II} and other oxygen-donor ligands, *e.g.* Sm–O(diglyme), av. 2.699(4) Å in $[SmI_2\{O(CH_2CH_2OMe)_2\}_2]$;[8] Sm–O(thf), av. 2.592(6) Å and Sm–O(dme), av. 2.685(8) Å in $[\{(Me_3Si)_2N\}Sm(\mu\text{-}I)(dme)(thf)]_2$,[9] reflecting the unusually strong electron donating ability of hmpa.[5]

On the other hand, owing to this strong coordination of the four polar hmpa ligands, the Sm–I bond [3.390(2) Å] in **1** is significantly longer than those found in other divalent samarium iodide complexes such as: $[Sm(\mu\text{-}I)_2(NCCMe_3)_2]_\infty$ 3.260(1) and 3.225(1) Å;[8] *trans*-$[SmI_2\{O(CH_2CH_2OMe)_2\}_2]$, 3.265(1) Å;[8] *cis*-$[SmI_2\{O(CH_2CH_2OMe)_2\}_2]$, 3.332(1) and 3.333(1) Å;[10] and $[\{(Me_3Si)_2N\}Sm(\mu\text{-}I)(dme)(thf)]_2$, 3.3414(9) and 3.3553(9) Å,[9] suggesting that the Sm–I bond in complex **1** is rather weak.

The reaction of YbI_2 with hmpa was carried out as in the case of SmI_2. The colour change was not as obvious as for SmI_2, although the yellow colour of the solution became a little deeper after addition of hmpa. Yellow $[Yb(hmpa)_4(thf)_2]I_2$ **2** crystallized from concentrated thf solution. An X-ray crystallographic study revealed that in complex **2** the central Yb^{II} was coordinated by four hmpa and two *trans*-thf ligands in distorted octahedral form, whereas the two iodide anions were located in the outer sphere (Fig. 2).‡ The Yb atom lies on a twofold axis that also passes through the oxygen atoms [O(3) and O(4)] of both thf ligands. As required by the crystallographic symmetry of the molecule, the Yb and the oxygen atoms [O(1), O(2), O(1′) and O(2′)] of the hmpa ligands are in the same plane. Interestingly, the two iodide anions are also located within this plane [d = 0.02(3) Å]. The bond distance of Yb–O(hmpa) [av. 2.357(6) Å] in **2** is slightly longer than those reported for other divalent ytterbium–hmpa complexes, *e.g.* $[Yb(\mu\text{-}OCPh_2)(hmpa)_2]_2$, 2.28(3) Å;[6] $[Yb(OC_6H_2Bu^t_2\text{-}2,4\text{-}Me\text{-}4)_2(hmpa)_2]$, 2.298(7) Å,[6] and *cis*-$[Yb(\{\mu\text{-}OCMo(CO)_2(C_5H_5)\})_2(hmpa)_4]$, 2.33(1) Å,[7] possibly owing to the planar orientation of the four bulky hmpa ligands. The Yb–O(hmpa) bond in **2** is much shorter than the Yb–O(thf) bond [av. 2.46(1) Å], reflecting the stronger electron-donating ability of hmpa.

It is interesting that complex **2** is formally formed by replacement of the inner-sphere-bonded I^- anions in **1** with two thf ligands. The isolation of **2** from thf strongly suggests

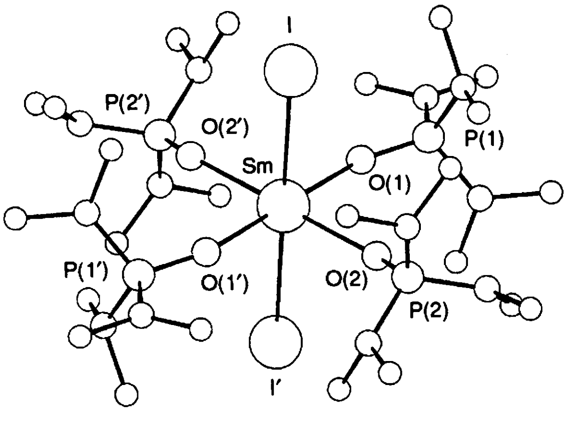

Fig. 1 ORTEP drawing of **1**. Selected bond lengths (Å) and angles (°): Sm–I 3.390(2), Sm–O(1) 2.515(6), Sm–O(2) 2.484(5), P(1)–O(1) 1.496(7), P(2)–O(2) 1.493(5), I–Sm–O(1) 92.2(1), I–Sm–O(2) 89.1(1), O(1)–Sm–O(2) 89.9(2).

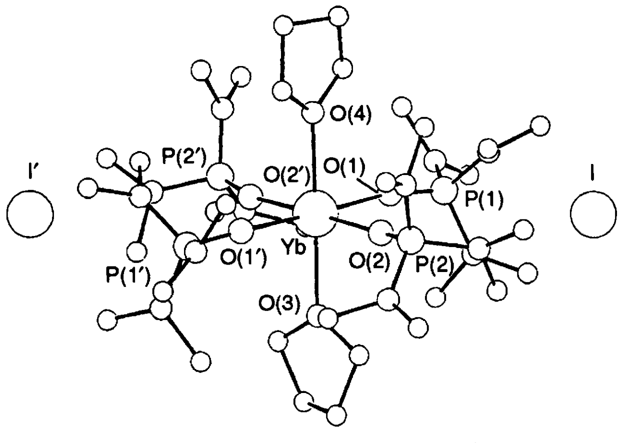

Fig. 2 ORTEP drawing of **2**. Selected bond lengths (Å) and angles (°): Yb···I 8.116(1), Yb–O(1) 2.347(6), Yb–O(2) 2.366(6), Yb–O(3) 2.454(12), Yb–O(4) 2.470(10), P(1)–O(1) 1.489(7), P(2)–O(2) 1.474(7), O(1)–Yb–O(2) 90.1(2), O(1)–Yb–O(3) 89.3(2), O(1)–Yb–O(4) 90.7(2), O(2)–Yb–O(3) 90.9(2), O(2)–Yb–O(4) 89.1(2).

that **1** in thf might have a similar structure as **2**. The colour change observed on addition of toluene to the solution of SmI_2–hmpa in thf might be due to the exchange between I^- and thf at the coordination spheres of samarium. Such exchange of ligands between inner and outer spheres has previously been observed in trivalent ytterbium chloride hmpa complexes.[5]

The results presented in this paper and others[5–7] show that hmpa is a unique ligand for lanthanide complexes. The coordination of four strong electron donating hmpa ligands to the Sm^{II} ion must explain why the reducing power of SmI_2 is greatly enhanced upon addition of hmpa. It is reasonable to suppose that, during the reactions, substrates will approach the central metal from either below or above the square plane formed by the hmpa ligands. The steric repulsion between the substrates and these strongly coordinated bulky hmpa ligands will change the regio- and stereo-selectivity of the reactions as compared to the non-hmpa system. The structures of **1** and **2** quantitatively explain why the hmpa effect was best demonstrated when 4 to 5 equivalents of hmpa per SmI_2 were used.[4,11]

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Footnotes

† All manipulations were done under dry and oxygen-free Ar or N_2 by using Schlenk technique or in an MBRAUN glove box.

‡ *Crystal data* for **1**: $C_{24}H_{72}I_2N_{12}O_4P_4Sm$, $M = 1121.02$, monoclinic, space group $P2_1/n$ (no. 14), $a = 12.644(3)$, $b = 14.763(8)$, $c = 13.312(3)$ Å, $\beta = 107.82(2)°$, $U = 2365(14)$ Å^3, $Z = 2$, $D_c = 1.574$ g cm^{-3}, μ(Mo-Kα) = 27.088 cm^{-1}, $R = 0.0430$ ($R_w = 0.0602$) for 4550 unique data with $F_o > 5\sigma(F_o)$ and 215 variables. For **2**: $C_{32}H_{88}I_2N_{12}O_6P_4Yb$, $M = 1287.32$, orthorhombic, space group *Ibca* (no. 73), $a = 26.145(10)$, $b = 20.842(3)$, $c = 20.839(3)$ Å, $U = 11356(5)$ Å^3, $Z = 8$, $D_c = 1.507$ g cm^{-3}, μ(Mo-Kα) = 28.728 cm^{-1}, $R = 0.0491$ ($R_w = 0.0472$) for 3126 unique data with $F_o > 5\sigma(F_o)$ and 260 variables. Crystals for X-ray analyses were sealed in thin-walled glass capillaries under N_2, with, in the case of **2**, a small amount of mother liquor. Data were collected on an Enraf-Nonius CAD4 diffractometer (20 °C, Mo-Kα radiation, $\lambda = 0.71069$ Å, ω-scan, $2 \leq \theta \leq 27.5°$) and were corrected for absorption. The metal atoms were located by MULTAN[12] and the remaining non-hydrogen atoms were found from subsequent difference Fourier syntheses. No attempts were made to locate the hydrogen atoms. Refinements were performed by the block-diagonal least-squares method.[13] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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