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Lanthanoid Complexes with Hexamethylphosphoramide (HMPA) Ligand. Preparation and Crystal Structure of Ytterbium Complexes of HMPA, $[Yb(H_2O)_5(HMPA)_2]Cl_3 \cdot H_2O \cdot HMPA$ and $YbCl_3(HMPA)_3$

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Reaction of $YbCl_3$ with hexamethylphosphoramide (HMPA) in THF under air gave $[Yb(H_2O)_5(HMPA)_2]Cl_3 \cdot H_2O \cdot HMPA$ and $YbCl_3(HMPA)_3$ respectively, depending on the recrystallization conditions. Both complexes have been structurally characterized by X-ray crystallography.

Hexamethylphosphoramide (HMPA) usually plays a significant role in lanthanoid mediated reactions.1,2) For example, addition of some HMPA to the LnI_2 (Ln = Sm,Yb)-mediated reaction system dramatically accelerates the electron transfer process.2) Explanation on this HMPA effect with sound evidence has not appeared.2b) So far, a lot of lanthanoid complexes containing HMPA ligand have been synthesized,3,4) but relatively few of them have been structurally characterized.4) X-ray structural data on lanthanoid HMPA complex and on HMPA molecule are thought to be helpful for us to understand the role played by HMPA in lanthanoid mediated reactions. In the lanthanoid and other metal HMPA complexes which have been structurally characterized so far, the HMPA ligands are all bonded directly to the central metal.4,5) Structural data on free HMPA and on HMPA unbonded to the central metal atom are not currently available. We report here an ytterbium HMPA complex, $[Yb(H_2O)_5(HMPA)_2]Cl_3 \cdot H_2O \cdot HMPA$ (**1**), which constitutes the first example of metal complex with HMPA ligands both bonded and unbonded to the central metal. This complex enables us to compare the metal-bonded HMPA with the nearly free HMPA, and to gain some knowledge of the nature and real structure of HMPA molecule. Preparation and crystal structure of the corresponding H_2O free complex, $YbCl_3(HMPA)_3$ (**2**),3a) are also described.

Complex **1** was first obtained from the reaction of Yb-benzophenone1) with $Cp^*{}_2TiCl_2$ (Cp^*: pentamethylcyclopentadienyl) in THF/HMPA.6) It was later found that it could also be isolated from the reaction of $YbCl_3$ with HMPA in THF under air. Thus, after 1 mmol of $YbCl_3$ was stirred for 1 h in THF (5 cm^3) and HMPA (1 cm^3) under air, the solvent was evaporated to give white powders wetted with HMPA. The product was washed three times with hexane and then dissolved in CH_2Cl_2/toluene. Natural evaporation of the solvents at room temperature under air for a few days gave colorless prismatic crystals of $[Yb(H_2O)_5(HMPA)_2]Cl_3 \cdot H_2O \cdot HMPA$ (**1**) in which no Yb-Cl bond was present. Interestingly, vacuum evaporation of the above solution gave a viscous liquid, from which the corresponding H_2O free rhombic colorless crystals of $YbCl_3(HMPA)_3$ (**2**) were obtained almost quantitatively. Recrystallization of **1** from CH_2Cl_2/toluene also gave **2**. Obviously, simple recrystallization resulted in ligand exchange between inner- and outer-sphere. As expected, complex **1** is quite stable to moisture, while **2** is very hygroscopic.

The molecular structures of complexes **1** and **2** have been determined by X-ray analysis and are shown in Fig. 1 and Fig. 2, respectively.[7,8] In the case of complex **1**, although there are two molecules in one unit cell, only one mlecule is given in Fig. 1, since both molecules in the unit cell have the same structure. Complex **2** consists of an Yb(III) ion coordinated in mer type by three HMPA groups via the oxygen atoms and three chloride ions, as shown in Fig. 2. The six ligands form a distorted octahedron in similar manner to that in $PrCl_3(HMPA)_3$.[4a] The overall structure of complex **1** is formally determined by replacement of three Cl^- ions and their coplanar HMPA in complex **2** with five water ligands. The central Yb(III) ion is seven-coordinated by five H_2O ligands and two HMPA groups, which form a distorted pentagonal bipyramid (Fig. 1). Three Cl^- anions, one HMPA, and one H_2O are located in the outer-sphere, with no bond to the central ytterbium atom but having interaction with the coordinated H_2O groups through hydrogen bonds. Maybe due to this interaction, the chloride ions, the oxygen atoms (O(15) and O(17)) of HMPA and H_2O in the outer-sphere, and the oxygen atoms (O(3-7)) of the five Yb-coordinated H_2O ligands are almost in the same plane.

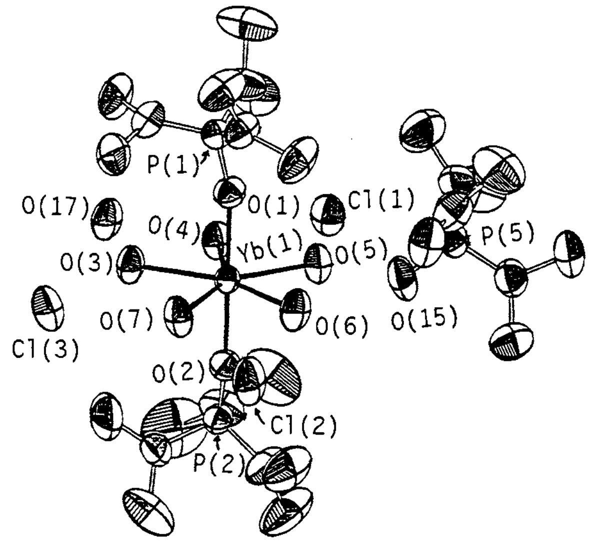


Fig. 1. ORTEP drawing of 1. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Yb(1)-O(1): 2.180(7), Yb(1)-O(2): 2.176(7), Yb(1)-O(3): 2.330(8), Yb(1)-O(4): 2.338(8), Yb(1)-O(5): 2.305(9), Yb(1)-O(6): 2.323(8), Yb(1)-O(7): 2.307(9), P(1)-O(1): 1.492(7), P(2)-O(2): 1.475(7), P(5)-O(15): 1.498(9), P(1)-N(av.): 1.63, P(2)-N(av.): 1.62, P(15)-N(av.): 1.63, Cl(1)···O(4): 3.074(10), Cl(1)···O(5): 3.029(9), Cl(2)···O(3): 3.056(10), Cl(2)···O(7): 3.077(9), Cl(3)···O(6): 3.005(10), Cl(3)···O(7): 3.003(8), O(15)···O(5): 2.628(11), O(15)···O(6): 2.664(14), O(17)···O(3): 2.691(11), O(17)···O(4): 2.697(11).

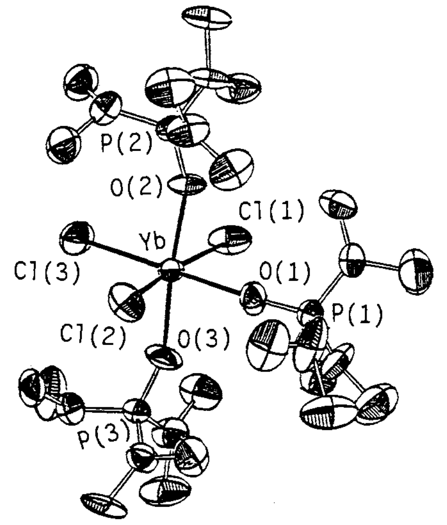
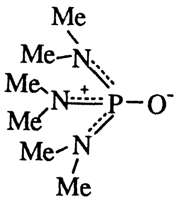


Fig. 2. ORTEP drawing of 2. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Yb-O(1): 2.217(10), Yb-O(2): 2.227(9), Yb-O(3): 2.228(8), Yb-Cl(1): 2.592(4), Yb-Cl(2): 2.589(4), Yb-Cl(3): 2.582(5), P(1)-O(1): 1.48(1), P(2)-O(2): 1.47(1), P(3)-O(3): 1.48(1), P(1)-N(av.): 1.61, P(2)-N(av.): 1.62, P(15)-N(av.): 1.64.



A

The average bond distance (2.178 Å) of Yb-O(HMPA) in complex **1** is slightly but significantly shorter than that (2.224 Å) in complex **2**. This shortness may result from location of the counter chloride anions in the outer-sphere, which increases the electrophilicity of the central Yb(III) and thus results in formation of stronger Yb-O(HMPA) bonds in complex **1**. It is also worthy to note that Yb-O(HMPA) bonds in both complexes are much shorter than Yb-O(H$_2$O) bonds (av. 2.321 Å) in complex **1**. The latter is comparable with the Yb-O(H$_2$O) bond (2.336 Å) found in Yb(acac)$_3$(H$_2$O)9) and is a reasonable value for coordinate bonds between neutral oxygen containing ligands and Yb(III). The unusual shortness of the Yb-O(HMPA) bonds suggests that the HMPA ligand does not act as a neutral one in these complexes, and the Yb-O(HMPA) bonds can be considered to some extent as ionic ones. In fact, similar values have been found for bonds between ytterbium ion and oxygen anion ligands, e.g., Yb(III)-O(acac): 2.233,9) 2.22 Å;10) Yb(II)-OAr: 2.14-2.20 Å.11) Another characteristic of HMPA ligand is that its P-O bond distances are almost the same in both complexes with an average value of 1.48 which is comparable with that found in other HMPA complexes.4a,5b-f) More surprisingly, the P-O bond distance (1.498(9) Å) and other structural data of the HMPA in the outer-sphere in complex **1** do not have significant difference compared with those found for the HMPA's coordinated to a central metal atom.4a,5b-f) In other words, coordination of HMPA to a metal ion via the oxygen atom does not lengthen its P-O bond. This means that the P-O bond in HMPA behaves as a single bond rather than a double one, since a double bond usually becomes longer when coordinated to a metal atom. The overall neutral HMPA can therefore be considered as an anionic oxygen containing ligand, with the plus charge being delocalized to the three amino groups as shown in **A**.5c,12) The average sum of the angles around the nitrogen atoms, 357 and 355°, respectively for coordinated and uncoordinated HMPA, indicates that they have essentially planar configuration and is consistent with the delocalization scheme.

The anionic property of HMPA must be one of the reasons why it greatly accelerates the electron transfer from divalent lanthanoid species LnI$_2$.2) Because of its strong electron donating ability (as strong as an anion), coordination of HMPA to the lanthanoid ion makes the divalent lanthanoid species Ln(II) easier to release an electron and makes the resulting trivalent species Ln(III) more stable (less reducible), and thus enables the electron transfer process, Ln(II) + OX $\longrightarrow$ Ln(III) + OX$^-$, to be more rapid.

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6) The deoxygenated coupling product of benzophenone, tetraphenylethylene, was also formed besides **1**. Details on this reaction will be reported elsewhere.

7) Crystallographic data for $\{[Yb(H_2O)_5(HMPA)_2]Cl_3 \cdot H_2O \cdot HMPA\}_2$: FW = 1850.19, monoclinic, $P2_1/a$, λ = 0.7107 Å, a = 19.793(5), b = 38.558(10), c = 11.385(4) Å, β = 102.30(3)°, V = 8532(50) Å^3, Z = 4, Dc = 1.44 g cm^{-3}, R/Rw = 0.052/0.058 for 11534 independent reflections.

8) Crystallographic data for $YbCl_3(HMPA)_3$: FW = 817.00, monoclinic, $P2_1/n$, λ = 0.7107 Å, a = 14.760(8), b = 22.866(5), c = 11.526(4) Å, β = 108.78(3)°, V = 3683(40) Å^3, Z = 4, Dc = 1.47 g cm^{-3}, R/Rw = 0.063/0.075 for 5300 independent reflections.

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