Lanthanoid Complexes of Azobenzene and Benzo[*c*]cinnoline Derived from Metallic Lanthanoids: Crystal Structures of Binuclear $[\mathrm{SmI(thf)_3}(\mu\text{-}\eta^2{:}\eta^2\text{-}trans\text{-}\mathrm{PhNNPh})\mathrm{SmI(thf)_3}]$ and Mononuclear $[\mathrm{Yb(benzo[}c\mathrm{]cinnoline)_3(thf)_2}]$

Yuushou Nakayama, Akira Nakamura,* and Kazushi Mashima*†
Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560
†Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560

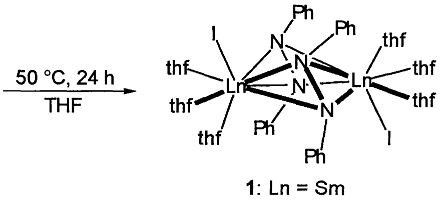
(Received April 30, 1997; CL-970317)

A binuclear samarium complex of azobenzene, $[\mathrm{SmI(thf)_3}(\mu\text{-}\eta^2{:}\eta^2\text{-}trans\text{-}\mathrm{PhNNPh})_2\mathrm{SmI(thf)_3}]$, prepared by treating metallic samarium with azobenzene in the presence of iodine was characterized crystallographically. Reaction of metallic ytterbium with benzo[*c*]cinnoline, a *cis*-azo compound, gave $\mathrm{Yb(bc)_3(thf)_2}$ (bc = benzo[*c*]cinnoline) that is monomeric and adopts distorted dodecahedral geometry, determined by X-ray analysis.

Metallic lanthanoids have been used as starting materials for preparing a variety of lanthanoid compounds such as amide[1] and organolanthanoid compounds[2-5] and are far superior to the use of anhydrous lanthanoid halides. A pertinent example is a tris(ketyl) complex of samarium prepared by the reaction of samarium metal with fluorenone.[4] Similarly, an ytterbium(II) imine complex, $[\mathrm{Yb}(\eta^2\text{-}\mathrm{Ph_2CNPh})(\mathrm{hmpa})_3]$, was reported to be derived from the direct reaction of ytterbium metal with *N*-(diphenylmethylidene)aniline.[5] Recently we have developed the direct reaction of metallic lanthanoid with organic disulfides to give a series of thiolate complexes of divalent and trivalent lanthanoids.[6-10] We were interested in an analogous approach to prepare lanthanoid complexes from metallic lanthanoids and azo compounds. Herein we report the synthesis and crystallographic characterization of lanthanoid complexes bearing azobenzene and benzo[*c*]cinnoline.

Treatment of metallic samarium with equimolar amounts of azobenzene and iodine in THF at 50 °C yielded a highly air- and moisture-sensitive binuclear complex, $[\mathrm{SmI(thf)_3}(\mu\text{-}\eta^2{:}\eta^2\text{-}trans\text{-}\mathrm{PhNNPh})_2\mathrm{SmI(thf)_3}]$ (**1**), as orange-red crystals in 23% yield (eq. 1).[11] Hydrolysis of **1** gave hydrazobenzene (94% yield), indicating the dianionic nature of the azobenzene ligand. Similarly, the corresponding ytterbium derivative **2** was also obtained as purple solids in 50% yield. Complexes **1** and **2** easily released THF and gradually became opaque in argon.

$2\ \mathrm{Ln} + 2\ \mathrm{PhNNPh} + \mathrm{I_2}$



(1)

1: Ln = Sm
2: Ln = Yb

Complex **1** crystallizes in a space group $P2_1/n$ where two binuclear molecules are crystallographically independent.[12] Figure 1 shows one of the two independent molecules. Complex **1** has two *trans*-azobenzene ligands bridging two $\mathrm{SmI(thf)_3}$ moieties; each monomer unit is related by centrosymmetry. The structural feature of **1** is quite similar to that of $[\mathrm{Cp^*Sm(thf)}(\mu\text{-}\eta^2{:}\eta^2\text{-}trans\text{-}\mathrm{PhNNPh})_2\mathrm{Cp^*Sm(thf)}]$ (**3**).[13] Each samarium atom adopts distorted doubly capped trigonal prismatic structure where two sets of atoms (O3, N1, N2) and (O2, N1*, N2*) occupy triangles of a distorted trigonal prism and the trigonal prism was capped by O1 and I1. The average distance of N-N (1.472 Å) in **1** is comparable to that (1.44 Å) found for **3**. Each azobenzene ligand is bonded to two samarium atoms by two single and two donor bonds as found in **3**.[13]

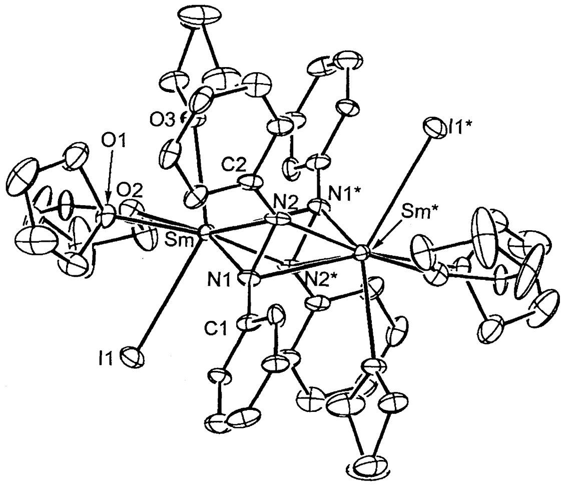
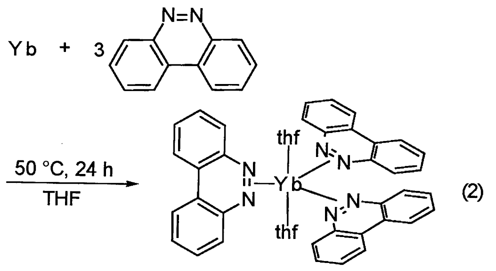


Figure 1. A drawing of **1** with a labeling scheme. Selected bond distances (Å) and angles (deg); Sm-I(1) 3.251(1), Sm-N(1) 2.311(9), Sm-N(2) 2.705(10), Sm-N(1)* 2.655(10), Sm-N(2)* 2.315(10), N(1)-N(2) 1.477(12), N(1)-Sm-N(2) 33.1(3), N(1)-Sm-N(1)* 89.7(3), N(1)-Sm-N(2)* 88.6(4), Sm-N(1)-Sm* 90.3(3), Sm-N(1)-N(2) 88.3(6), Sm*-N(1)-N(2) 60.4(5), Sm-N(1)-C(1) 151.9(8), Sm*-N(1)-C(1) 112.1(7), Sm-N(2)-C(2) 113.6(7), Sm*-N(2)-C(2) 152.6(8).

Treatment of metallic samarium and ytterbium with azobenzene in the presence of a catalytic amount of iodine presumably resulted in the formation of tris(azobenzene) adducts, $[\mathrm{Ln(azobenzene)_3(thf)_2}]_n$ (Ln = Sm (**4**), Ln = Yb(**5**)), whose characterization is hampered by their extreme air- and moisture-sensitivity. All attempts to obtain single crystals of **4** and **5** suitable for X-ray analysis have been in failure. For our purpose, we used benzo[*c*]cinnoline instead of azobenzene. Reaction of metallic ytterbium with benzo[*c*]cinnoline afforded $\mathrm{Yb(bc)_3(thf)_2}$ (**6**, bc = benzo[*c*]cinnoline) (eq. 2),[11] while the samarium derivative could not be satisfactorily characterized due to its higher air- and moisture-sensitivity.

The structure of **6** was determined by an X-ray analysis (Figure 2).[12] Complex **6** is a monomeric 8-coordinate complex having distorted dodecahedral geometry where the plane defined



6

(2)

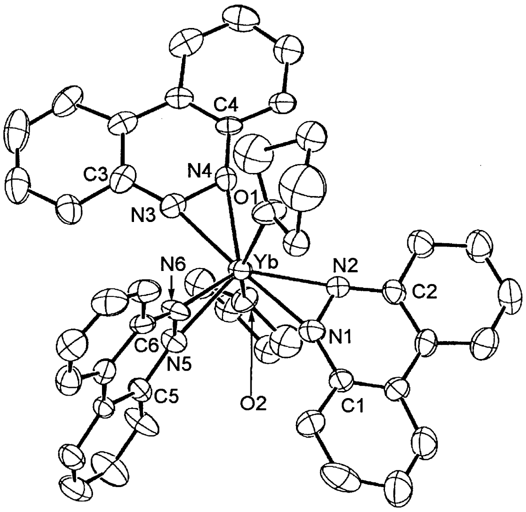


Figure 2. A drawing of **6** with a labeling scheme. Selected bond distances (Å) and angles (deg); Yb-N(1) 2.262(9), Yb-N(2) 2.309(9), Yb-N(3) 2.283(9), Yb-N(4) 2.340(9), Yb-N(5) 2.297(8), Yb-N(6) 2.296(9), Yb-O(1) 2.359(7), Yb-O(2) 2.362(6), N(1)-N(2) 1.37(1), N(3)-N(4) 1.39(1), N(5)-N(6) 1.35(1), N(1)-Yb-N(2) 34.9(3), N(3)-Yb-N(4) 34.9(2), N(5)-Yb-N(6) 34.1(3), Yb-N(1), Yb-N(1)-C(1) 161.5(7), Yb-N(2)-C(2) 166.3(7), Yb-N(3)-C(3) 165.0(8), Yb-N(4)-C(4) 168.1(7), Yb-N(5)-C(5) 165.7(7), Yb-N(6)-C(6) 165.0(8). In the two THF molecules of **6**, totally four carbons were refined as disordered form, and one set of a pair of the disordered carbons is shown.

by N1, N2, N3, and N4 is almost perpendicular (89.5°) to that of N5, N6, O1, and O2. The distances of Yb-N1 (2.262(9) Å) and Yb-N3 (2.283(9) Å) are longer by 0.05 Å than the distances of Yb-N2 (2.309(9) Å) and Yb-N4 (2.340(9) Å), while the distances of Yb-N5 (2.297(8) Å) and Yb-N6 (2.296(9) Å) are equal within a standard deviation. The average distance of Yb-N (2.298 Å) in **6** is longer by 0.06 Å than that of {Me$_2$Si(OBu^t)(NBu^t)}$_2$Yb(μ-Cl)$_2$Li(thf)$_2$ (2.236 Å)[14] and significantly shorter than the distances of typical Yb-N donor bond (2.4–2.5 Å).[8,15] The average distance of N-N (1.37 Å) in **6** is comparable to that of Cp*$_2$Sm(PhNNPh)(thf).[13] These data suggest that **6** is better formulated as a Yb^{3+} complex having three benzocinnoline radical anions rather than a Yb^0 complex.

In summary, we demonstrated that metallic lanthanoid reacted readily with azobenzene and benzo[*c*]cinnoline giving the dimeric complex **1** and the monomeric complex **6**, whose structures were revealed by X-ray analysis.

K. M. and A. N. are grateful for financial support from the Ministry of Education, Science, Sports and Culture of Japan (New Development of Rare Earth Complexes No. 08220244 and Specially Promoted Research No. 06101004).

References and Notes

1 G. B. Deacon, C. M. Forsyth, B. M. Gatehouse, and P. A. White, *Aust. J. Chem.*, **43**, 795 (1990).
2 Z. Hou, Y. Fujiwara, T. Jintoku, N. Mine, K. Yokoo, and H. Taniguchi, *J. Org. Chem.*, **52**, 3524 (1987).
3 Z. Hou, K. Takamine, H. Shiraishi, Y. Fujiwara, and H. Taniguchi, *J. Org. Chem.*, **53**, 6077 (1988).
4 Z. Hou, A. Fujita, H. Yamazaki, and Y. Wakatsuki, *J. Am. Chem. Soc.*, **118**, 7843 (1996).
5 Y. Makioka, Y. Taniguchi, Y. Fujiwara, K. Takaki, Z. Hou, and Y. Wakatsuki, *Organometallics*, **15**, 5476 (1996).
6 K. Mashima, Y. Nakayama, T. Shibahara, H. Fukumoto, and A. Nakamura, *Inorg. Chem.*, **35**, 93 (1996).
7 K. Mashima, Y. Nakayama, T. Shibahara, and A. Nakamura, *J. Organomet. Chem.*, **501**, 263 (1995).
8 K. Mashima, Y. Nakayama, H. Fukumoto, N. Kanehisa, Y. Kai, and A. Nakamura, *J. Chem. Soc., Chem. Commun.*, **1994**, 2523.
9 K. Mashima, Y. Nakayama, A. Nakamura, N. Kanehisa, Y. Kai, and H. Takaya, *J. Organomet. Chem.*, **473**, 85 (1994).
10 K. Mashima, Y. Nakayama, N. Kanehisa, Y. Kai, and A. Nakamura, *J. Chem. Soc., Chem. Commun.*, **1993**, 1847.
11 **1**: red microcrystals, yield 23%, mp 160–178 °C (dec.). Anal. Found: C, 40.46; H, 4.83; N, 4.45%; Calcd for $C_{40}H_{52}I_2N_4O_4Sm_2$: C, 39.79; H, 4.34; N, 4.64%. **2**: purple solids, yield 50%, Anal. Found: C, 36.92; H, 4.59; N, 3.96%; Calcd for $C_{36}H_{44}I_2N_4O_3Yb_2$: C, 36.62; H, 3.76; N, 4.75%. **6**: black crystals, yield 43%, mp 235–245 °C. Elemental analysis of **6** did not give a satisfactory result due to its high air- and moisture-sensitivity. UV-vis (THF): $\lambda_{max} = 423$ nm ($\varepsilon_{max} = 27000$ M^{-1}cm^{-1}), 580 nm ($\varepsilon_{max} =$ 2800 M^{-1}cm^{-1}).
12 Crystal data for **1**: formula = $C_{48}H_{68}I_2N_4O_6Sm_2$, FW = 1351.62, monoclinic space group $P2_1/n$, $a = 21.696(20)$, $b = 11.225(2)$, $c = 22.476(12)$ Å, $\beta = 111.48(3)°$, $Z = 4$, $V = 5093$ Å^3, $d_{calcd} = 1.58$ gcm^{-3}, R (R_w) = 0.045 (0.089) for 4412 diffraction data with $I > 3.0\sigma(I)$ and 627 variables. Since the intensity of X-ray diffraction of **1** was decreased rapidly within a couple of hours, the X-ray diffraction data was collected by an imaging plate instrument (MAC Science DIP3000). Crystal data for **6**: formula = $C_{44}H_{40}N_6O_2Yb$, FW = 857.88, monoclinic space group $P2_1/c$, $a = 13.764(9)$, $b = 14.362(5)$, $c = 22.834(6)$ Å, $\beta = 107.08(3)°$, $Z = 4$, $V = 4314(2)$ Å^3, $d_{calcd} = 1.321$ gcm^{-3}, R (R_w) = 0.051 (0.056) for 5468 diffraction data with $I > 3\sigma(I)$ and 454 variables. THF molecules in **6** showed disordered form, and the occupancy of the disordered atoms is fixed at 0.5.
13 W. J. Evans, D. K. Drummond, L. R. Chamberlain, R. J. Doedens, S. G. Bott, H. Zhang, and J. L. Atwood, *J. Am. Chem. Soc.*, **110**, 4983 (1988).
14 A. Recknagel, A. Steiner, S. Brooker, D. Stalke, and F. T. Edelmann, *J. Organomet. Chem.*, **415**, 315 (1991).
15 D. J. Berg, R. A. Andersen, and A. Zalkin, *Organometallics*, 7, 1858 (1988).