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Synthesis and X-ray Structure of a Highly Symmetrical Selenium-Centered Hexanuclear Neodymium Complex, $[Cp^t{}_6Nd_6Se_{13}]^-$ ($Cp^t = \eta^5$-$Bu^tC_5H_4$)[†]

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*Summary: The half-sandwich tert-butylcyclopentadienyl neodymium complex $[Cp^tNdCl_2(THF)_2]_2$ (**1**) reacts with Na_2Se_5 to give organoneodymium polyselenide complex $[Na(THF)_6][Cp^t{}_6Nd_6(\mu_6\text{-}Se)(\mu_2\text{-}Se_2)_6]$ (**2**), which has been characterized by X-ray crystallography.*

Although many cyclopentadienyl transition metal complexes of the d-block elements with unsubstituted chalcogen ligands have been synthesized during the last two decades,[1–5] the system of the related organolanthanoid chalcogenide complexes is still underdeveloped.[1,6] Only a few organolanthanoid derivatives are known, including binuclear ytterbium complexes with bridging chalcogen ligands such as $[(Cp^*{}_2Yb)_2(\mu\text{-}E)]$ (E = S, Se, Te),[7] the binuclear samarium complexes $[(Cp^*{}_2Sm(THF))_2(\mu\text{-}E)]$, $[(Cp^*{}_2Sm)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Te_2)]$, and $[(Cp^*{}_2Sm)_2(\mu\text{-}\eta^1{:}\eta^3\text{-}E_3)]$,[8] and the hexanuclear complex $[Cp^*{}_6Sm_6Se_{11}]$.[9] These complexes were generally prepared by the reactions of the low-valent lanthanoid bis(pentamethylcyclopentadienyl) complexes $[Cp^*{}_2Ln(THF)_n]$ (Ln = Yb, $n = 0$; Ln = Sm, $n = 2$) with elemental chalcogen. We have investigated the reactions between the half-sandwich cyclopentadienyl lanthanoide dichloride complexes and Na_2E_5 (E = S, Se, Te) and report on the novel neodymium polyselenide complex in which a central selenium atom is coordinated to six neodymium atoms.

The chloro-bridged half-sandwich neodymium compound $[Cp^tNdCl_2(THF)_2]_2$[10] (**1**) reacts with 2 equiv of

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[†] Dedicated to Prof. Dr. Dr. h.c. mult. E. O. Fischer on the occasion of his 80th birthday.

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Na_2Se_5 in THF to give a red ionic crystal product, $[Na(THF)_6][Cp^t{}_6Nd_6Se_{13}]$ (**2**) in 37% yield.[11]

$$\underset{\mathbf{1}}{3[Cp^tNdCl_2(THF)_2]_2} + 6Na_2Se_5 \xrightarrow{THF} \underset{\mathbf{2}}{[Na(THF)_6][Cp^t{}_6Nd_6Se_{13}]}$$

The anion $[Cp^t{}_6Nd_6(\mu_6\text{-}Se)(\mu\text{-}Se_2)_6]^-$ containing six neodymium and 13 selenium atoms represents a new class of polynuclear lanthanoid chalcogenide complexes. Due to the voluminous ring ligand $Bu^tC_5H_4$, complex **2** is soluble in polar organic solvents such as THF, acetonitrile, and toluene. Attempts to isolate analogous sulfide and telluride complexes were not particularly successful; the reactions between **1** and Na_2E_5 (E = S, Te) in THF solution led to red precipitates which could not be identified due to their extreme air-sensitivity. Complex **2** was characterized by an X-ray structure analysis.[12]

2 is a salt containing the cation $[Na(THF)_6]^+$ and the hexanuclear anion $[Cp^t{}_6Nd_6Se_{13}]^-$ (Figure 1). The six Cp^tNd units in the anion form a symmetrical octahedron with a selenium atom in the center. The four Nd atoms (Nd(2)−Nd(3)−Nd(2a)−Nd(3a)) and the interstitial selenium atom (Se(1)) form an almost planar arrangement. The distances of the Nd atoms from the center of their cyclopentadienyl ligand ($d_{(Nd-Cptcent)}$: 2.495−2.500 Å) are similar to those in other Nd^{III} cyclopentadienyl complexes ($d_{(Nd-Cptcent)}$: 2.507−2.540 Å in $[(Bu^tC_5H_4)_3Nd(THF)]$[13] and 2.487 Å in $[((Bu^t{}_2C_5H_3)_2Nd)_2(\mu\text{-}Cl)_2]$[14]), but are clearly shorter than the corresponding distances in Ln^{II} (Ln = Sm, Yb) cyclopentadienyl complexes.[15] The anion of **2** with the central selenium atom has a highly symmetrical structure; related hexanuclear lanthanoid complexes include $[Cp^*{}_6Sm_6Se_{11}]$[9], $[Cp_6Yb_6Cl_{13}]^-$,[16] and $[Nd_6(2,4\text{-}C_7H_{11})_6Cl_{12}](THF)_2$,[17] in which a centered chloride atom is absent. The structure of the anion in **2**, where each Nd atom is coordinated with six Se atoms, differs from that of the complexes of $[Cp^*{}_6Sm_6Se_{11}]$ and $[Cp_6Yb_6Cl_{13}]^-$; in $[Cp_6Yb_6Cl_{13}]^-$, each Yb atom is bound to five chloride ligands, while in $[Cp^*{}_6Sm_6Se_{11}]$ three Sm atoms are coordinated with six Se atoms and the other three Sm atoms are linked with five Se atoms, resulting in a distorted octahedral structure. The distances between the Nd and Se atoms in **2** ($d_{(Nd-Se)}$: 2.888−3.214 Å) can be compared with other lanthanoid selenide complexes such as $[Cp^*{}_6Sm_6Se_{11}]$ ($d_{(Sm-Se)}$: 2.859−3.308 Å),[9] $[(Cp^*{}_2Sm)_2(\mu\text{-}\eta^1{:}\eta^3\text{-}Se_3)(THF)]$ ($d_{(Sm-Se)}$: 2.917−3.198 Å),[8] and $[(Cp^*{}_2Yb)_2(\mu\text{-}Se)]$ ($d_{(Yb-Se)}$: 2.621 Å).[7]

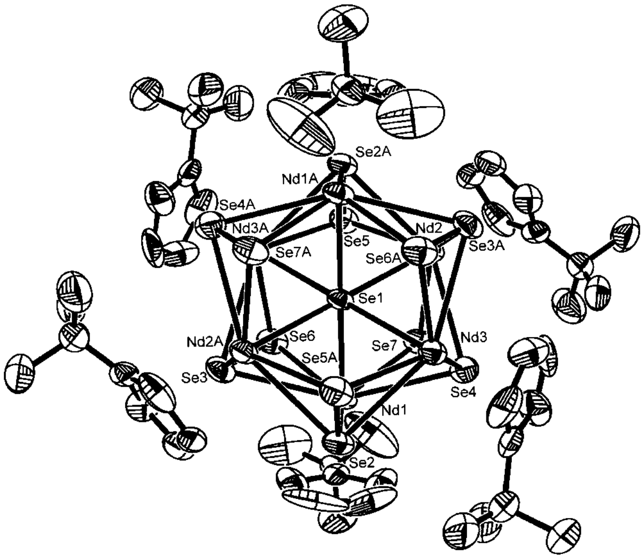

Figure 1. Molecular structure of the anion of $[Na(THF)_6][Cp^t{}_6Nd_6Se_{13}]$ (**2**) (a) and molecular structure of Nd_6Se_{13}−core in **2** (b). Selected distances [Å] and angles [°]: Nd(1)−Se(1) 3.0240(12), Nd(1)−Se(2) 3.1005(18), Nd(1)−Se(3) 3.157(2), Nd(1)−Se(4) 3.163, Nd(1)−Se(6) 2.8881(18), Nd(1)−Se(7) 2.9380(19), Nd(2)−Se(1) 3.0346(10), Nd−Se(2a) 3.158(2), Nd(2)−Se(3a) 3.0798(19), Nd(2)−Se(4) 3.214(2), Nd(2)−Se(5) 2.9492(19), Nd(2)−Se(7) 2.9269(19), Nd(3)−Se(1) 3.0293(12), Nd(3)−Se(2) 3.1285(17), Nd(3)−Se(3a) 3.2218(18), Nd(3)−Se(4) 3.080(2), Nd(3)−Se(5a) 2.9078(18), Nd(3)−Se(6a) 2.912(2), Se(2)−Se(5a) 2.364(2), Se(3)−Se(6) 2.357(2), Se(4)−Se(7) 2.359(2), Nd(1)−$Cp^t{}_{cent}$ 2.495, Nd(2)−$Cp^t{}_{cent}$ 2.500, Nd(3)−$Cp^t{}_{cent}$ 2.493, Nd(1)···Nd(3) 4.1034(16), Nd(1)−Se(1)−Nd(1a) 180.00, Nd(2)−Se(1)−Nd(2a) 180.0, Nd(1)−Se(1)−Nd(2) 94.19(3), Nd(1)−Se(1)−Nd(3) 85.36(4), Se(1)−Nd(1)−Se(3) 75.19(5), Se(2)−Nd(1)−Se(4) 88.88(5), Se(2)−Nd(1)−Se(7) 133.40(5), Se(3)−Nd(1)−Se(6) 45.62(5), Se(3)−Nd(1)−Se(4) 150.16(5), Se(3)−Nd(1)−Se(7) 86.29(4), Nd(1)−Se(2)−Nd(3) 82.41(4), Nd(1)−Se(2)−Nd(2a) 82.45(4), Nd(1)−Se(2)−Se(5a) 128.31(7), Nd(1)−Se(3)−Se(6) 61.15(6), Se(2a)−Se(5)−Nd(2) 71.98(6), Nd(2)−Se(5)−Nd(3a) 98.66(5).

The 13 Se atoms in **2** can be divided into three types: a central Se(1) atom which is coordinated to six Nd atoms ($d_{(Nd-Se)}$: 3.024−3.035 Å); six pairs of bridging Se_2 units (Se(2)−Se(5), Se(3)−Se(6), Se(4)−Se(7)) in which one Se atom is coordinated to three Nd atoms

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[10] $[Cp^tNdCl_2(THF)_2]_2$, which has been characterized by X-ray structure analysis, was prepared from the reaction between Cp^tNa and $NdCl_3$ in a 1:1 mole ratio in THF solution; see: Y. X. Cheng, Q. Shen, Y. H. Lin, Abstract on 6th Chinese Organometallic Meeting, Changchun, China, A − 71 (1990).

[11] Synthesis and spectral data of **2**: A suspension of **1**[10] (0.283 g, 0.348 mmol) and Na_2Se_5 (0.315 g, 0.715 mmol) in THF (40 mL) was stirred for 4 days and filtered through a plug of sea sand, and hexane (ca. 15 mL) was added to the filtrate. The resulting solution was kept at −15 °C for several weeks to give red prismatic crystals of **2** (0.13 g, 36.6%), mp 64 °C (dec); ^1H NMR (400 MHz, $[D_8]THF$, 25 °C, TMS): δ −3.27 (s, 54H, Bu^t), −6.92 (br, 12H, C_5H_4), 5.25 (br, 12H, C_5H_4); IR (CsI, BIO-RAD, FIS-7) $\nu[cm^{-1}]$ 3082, 2950, 2895, 1360, 1049, 893, 820, 764, 676. Anal. Calcd for $C_{78}H_{126}NaNd_6O_6Se_{13}$: C, 30.45; H, 4.13; Nd, 28.15. Found: C, 30.17; H, 3.98; Nd, 27.79.

[12] Crystal structure analysis of **2**: $C_{78}H_{126}Na_1Nd_6O_6Se_{13}$, $M = 3074.7$, triclinic, space group $P1$, $a = 14.392(3)$ Å, $b = 15.412(3)$ Å, $c = 16.003(3)$ Å, $\alpha = 64.75(3)°$, $\beta = 81.21(3)°$, $\gamma = 85.73(3)°$; $V = 3172.6(11)$ Å^3, $Z = 2$; $D_c = 3.301$ g cm^{-3}, $F(000) = 2978$; red prismatic crystal, dimensions 0.20 × 0.20 × 0.40 mm. Diffractometer: Siemens P4, Mo Kα radiation ($\lambda = 0.710\,73$ Å), 293 K, 2θ range 3.1−45.0°, index ranges $-1 \le h \le 15$, $-15 \le k \le 15$, $-17 \le l \le 17$; measured reflections 10053, independent reflections 8547 ($R_{int} = 0.0404$), observed reflection 8547 ($F \ge 0.0\sigma(F^2)$); structure solution with direct methods (SHELXTL PLUS (VMS)); number of refined parameters 605; $R = 0.0534$, $wR = 0.1260$, $w^{-1} = [\sigma^2(F_o{}^2) + (0.0794P)^2 + 0.0000P]$, $P = (F_o{}^2 + 2F_c{}^2)/3$; maximun/minimum residual electron density 1.338/−0.982 e Å^{-3}.

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($d_{(\mathrm{Nd-Se})}$: 3.080−3.220 Å); and the other one is connected with only two Nd atoms ($d_{(\mathrm{Nd-Se})}$: 2.888−2.912 Å). The distances between two Se atoms are in the range 2.357(2)−2.364(2) Å and can be compared with those in [$\mathrm{Cp^*_6Sm_6Se_{11}}$] (2.361−2.376 Å),[9] [$\mathrm{Cp^*Ir(PMe_3)(Se_4)}$] (2.313−2.361 Å),[4] and [$\mathrm{(Cp^*_2Se)_2(\mu\text{-}\eta^1{:}\eta^3\text{-}Se_3)(THF)}$] (2.326−2.377 Å).[8]

The hexanuclear complex **2**, which was synthesized by the reaction of a half-sandwich lanthanoid dichloride with $\mathrm{Na_2Se_5}$, is unique in the organolanthanoid chalcogenide chemistry. Apparently, the substituted cyclopentadienyl ligands shield the outer hemisphere of the lanthanoid metals effectively and facilitate the incorporation of a larger number of chalcogens into the polynuclear framework. The reactions of half-sandwich cyclopentadienyl lanthanoid complexes, such as [$\mathrm{Cp^tLnCl_2(THF)}$]$_n$ ($n = 1, 2$), with chalcogen sources are under investigation.

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Supporting Information Available: Tables giving crystal data and refinement detail, positional and thermal parameters, and bond distances and angles for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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