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Journal of Organometallic Chemistry 631 (2001) 94–98

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis and characterization of polynuclear half-sandwich lanthanoid complexes $[Na(THF)_6]_2[Cp^t_6Sm_6Se_{13}]$ and $[Li(THF)_4]_2[Cp_6Nd_6Se_{13}]$

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Received 15 March 2001; received in revised form 14 May 2001; accepted 29 May 2001

Dedicated to Professor Max Herberhold on the occasion of his 65th birthday

Abstract

The half-sandwich *tert*-butyl cyclopentadienyl lanthanoid complexes $\{[Cp^tLn(THF)]_2(\mu_2\text{-}Cl)_2(\mu_3\text{-}Cl)_3Na(THF)\}_n$ [$Cp^t = \eta^5\text{-}{}^tBuC_5H_4$; Ln = Nd (**1a**), Sm (**1b**), Gd (**1c**), Yb (**1d**)] are prepared by the reaction of anhydrous lanthanoid trichloride, $LnCl_3$, with $NaCp^t$ in THF solution. Complex **1b** reacts with Na_2Se_5 to give hexanuclear samarium polyselenide complexes $[Na(THF)_6]_2[Cp^t_6Sm_6(\mu_6\text{-}Se)(\mu\text{-}Se_2)_6]$ (**2**). An analogous cyclopentadienyl neodymium polyselenide complex $[Li(THF)_4]_2[Cp_6Nd_6(\mu_6\text{-}Se)(\mu\text{-}Se_2)_6]$ (**3**) is synthesized by the reaction of $[CpNdCl_2{\cdot}2LiCl{\cdot}5THF]$ with Na_2Se_5 in THF solution. The molecular structures of **1a** and **2** were determined by X-ray crystal structure analysis. Complex **2** contains an interstitial selenium atom which is coordinated with six samarium atoms. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Half-sandwich lanthanoid complexes; Samarium; Neodymium; Selenide metal complexes; Interstitial selenium

1. Introduction

Owing to their thermal stability and solubility in organic solvents, many cyclopentadienyl transition metal complexes of d-block elements with unsubstituted chalcogen ligands have been synthesized and well characterized during the last two decades [1–6]. However, the system of related organolanthanoid chalcogenide complexes is still underdeveloped [1,7]. Several organolanthanoid derivatives are known, including binuclear ytterbium complexes with bridging chalcogen ligands such as $[(Cp^*_2Yb)_2(\mu\text{-}E)]$ (E = S, Se, Te; $Cp^* = \eta^5\text{-}C_5Me_5$) [8], the binuclear samarium complexes $[(Cp^*_2Sm(THF))_2(\mu\text{-}E)]$ [9], $[(Cp^*Sm)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}E_2)]$ (E = Se, Te) [9,10], $[(Cp^*_2Sm)_2(\mu\text{-}\eta^1{:}\eta^3\text{-}E_3)]$ [9], the binuclear neodymium complex $[(Cp^*_2Nd)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Se_2)]$ [10] and the hexanuclear complex $[Cp^*_6Sm_6Se_{11}]$ [11]. 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 or by the reaction of Cp^*_3Sm with Ph_3PSe. We have investigated the reactions of the half-sandwich cyclopentadienyl lanthanoid dichloride complexes with Na_2E_5 (E = S, Se, Te) and recently described the selenium-centered hexanuclear neodymium complex $[Na(THF)_6]_2[Cp^t_6Nd_6Se_{13}]$ [12]. Herein, we report on the related samarium complex in which an interstitial selenium atom is coordinated to six samarium atoms.

2. Results and discussion

tert-Butyl-substituted cyclopentadienyl ligands are increasingly playing a role in organolanthanoid chemistry, because the resultant products are often more soluble than the parent cyclopentadienyl derivatives; *tert*-butyl-cyclopentadienyl as ligands have been successfully employed in the preparation of highly reactive organolanthanoid complexes [7].

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PII: S0022-328X(01)01023-3

The reactions of NaCp′ with one equivalent of the anhydrous $\mathrm{LnCl_3}$ (Ln = Nα, Sm, Gd, Yb) at 60 °C result in the formation of oligomeric half-sandwich complexes $\{[\mathrm{Cp'Ln(THF)}]_2(\mu_2\text{-Cl})_2(\mu_3\text{-Cl})_3\mathrm{Na(THF)}\}_n$ (L = Nd (**1a**), Sm (**1b**), Gd (**1c**), Yb (**1d**)) in moderate yields.

$$2n\mathrm{NaCp'} + 2n\mathrm{LnCl_3} \xrightarrow[60^\circ\mathrm{C}]{\mathrm{THF}} \{[\mathrm{Cp'Ln(THF)}]_2(\mu_2\text{-Cl})_2(\mu_3\text{-Cl})_3\mathrm{Na(THF)}\}_n$$

All complexes (**1a**–**1d**) are soluble in ethereal solvents (DME and THF), moderately soluble in aromatic solvents and insoluble in alkane solvents. Complexes **1a**–**1d** are very sensitive in air.

The analogous half-sandwich complexes for late lanthanide $\mathrm{Cp'LnCl_2\cdot 2THF}$ (Ln = Lu) have been previously synthesized [13]. The related iodide complex $\mathrm{Cp'SmI_2(THF)_3}$ has been determined by an X-ray crystal structure analysis [14].

The chloro-bridged half-sandwich samarium complex **1a** reacts with two equivalents of $\mathrm{Na_2Se_5}$ in THF to give a dark red diionic product $[\mathrm{Na(THF)_6}]_2[\mathrm{Cp'_6Sm_6}(\mu_6\text{-Se})(\mu\text{-Se}_2)_6]$ (**2**) in 46.1% yield

$$\{[\mathrm{Cp'Ln(THF)}]_2(\mu_2\text{-Cl})_2(\mu_3\text{-Cl})_3\mathrm{Na(THF)}\}_n + \mathrm{Na_2Se_5} \xrightarrow{\mathrm{THF}} [\mathrm{Na(THF)_6}]_2[\mathrm{Cp'_6Sm_6}(\mu_6\text{-Se})(\mu\text{-Se}_2)_6]$$

The dianion $[\mathrm{Cp'_6Sm_6}(\mu_6\text{-Se})(\mu\text{-Se}_2)_6]^{2-}$ containing six samarium, 13 selenium atoms is isostructural to the related neodymium complex $[\mathrm{Na(THF)_6}]_2[[\mathrm{Cp'_6Nd_6}(\mu_6\text{-Se})(\mu\text{-Se}_2)_6]$ [12]. Due to the voluminous ring ligands (Cp′), complex **2** is soluble in polar organic solvents such as THF and acetonitrile.

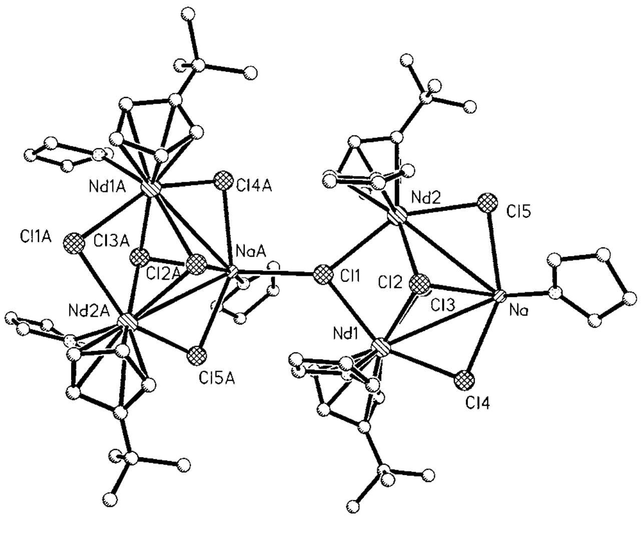

Fig. 1. Molecular structure of $[\mathrm{Cp'Nd(THF)}]_2(\mu_2\text{-Cl})_2(\mu_3\text{-Cl})_3\mathrm{Na(THF)}]_n$ (**1a**). Selected distance (Å) and angles (°): Nd(1)–Cl(1) 2.867(3), Nd(1)–Cl(2) 2.844(3), Nd(1)–Cl(3) 2.894(3), Nd(1)–Cl(4) 2.710(3), Nd(2)–Cl(1) 2.890(3), Nd(2)–Cl(2) 2.850(3), Nd(2)–Cl(3) 2.867(3), Na–Cl(3) 2.87(5), Na–Cl(2) 3.002(6), Na–Cl(4) 2.800(6), Na–Cl(5) 2.842(6); Cl(1)–Nd(1)–Cl(2) 77.3(1), Cl(1)–Nd(1)–Cl(3) 72.1(1), Cl(1)–Nd(1)–Cl(4) 147.9(1), Cl(2)–Nd(1)–Cl(3) 75.3(1), Cl(2)–Nd(1)–Cl(4) 85.2(1), Cl(3)–Nd(1)–Cl(4) 77.5(1), Cl(1)–Nd(1)–O(1) 87.5(2), Cl(2)–Nd(1)–O(1) 152.5(2), Cl(3)–Nd(1)–O(1) 78.2(2), Cl(4)–Nd(1)–O(1) 96.5(2), Nd(1)–Cl(4)–Na 90.2(1), Nd(2)–Cl(4)–Na 89.7(1).

The treatment of unsubstituted mono-cyclopentadienyl neodymium complex $\mathrm{CpNdCl_2\cdot 2LiCl\cdot 5THF}$ [15] with $\mathrm{Na_2Se_5}$ at room temperature results in the formation of hexanuclear neodymium complex $[\mathrm{Li(THF)_4}]_2[\mathrm{Cp_6Nd_6}(\mu_6\text{-Se})(\mu\text{-Se}_2)_6]$ as dark red prismatic crystals in 23.0% yield. According to a preliminary X-ray crystallographic study [16], complex **3**·2THF like **2** and $[\mathrm{Na(THF)_6}]_2[\mathrm{Cp_6Nd_6}(\mu_6\text{-Se})(\mu\text{-Se}_2)_6]$ [12] is a salt and contains an interstitial selenium atom coordinated with six neodymium atoms. However, attempts to isolate analogous sulfide and telluride complexes of **2** and **3** were not successful.

The molecular structure of both **1a** and **2** in the crystals were determined by X-ray crystal structure analyses (Figs. 1 and 2).

The molecule of **1a** is an oligomer bridged by a μ_3-Cl atom. Each Nd atom in **1a** is coordinated to one cyclopentadienyl ring of Cp′ group, one oxygen atom of THF, one μ_2-Cl atom and three μ_3-Cl atoms. The geometry around the neodymium is distorted octahedral. Two neodymium atoms and one sodium atom form an approximately equilateral triangle, with distances Nd–Na 3.929 Å and Nd(1)–Nd(2) 4.081 Å. Three chloride atoms bridge the edges of triangles with angles Nd(1)–Cl(1)–Nd(2) 90.3(1)°, Nd(1)–Cl(4)–Na 90.2(1)° and Nd(2)–Cl(5)–Na 89.7(1)°, while two additional chloride atoms cap the Nd(1)–Nd(2)–Na fragment on each side in a μ_3-fashion. A similar geometry was observed for the half-sandwich lanthanoid complexes in $[\mathrm{Na(THF)}][\mathrm{Cp^*Gd(THF)}]_2(\mu_2\text{-Cl})_3(\mu_3\text{-Cl})_2]$ [17], $\{[(\mathrm{C_5H_9C_5H_4})\mathrm{Er(THF)}]_2(\mu_2\text{-Cl})_3(\mu_3\text{-Cl})_2\mathrm{Na(THF)_2}\}$ [18], and $[\mathrm{Li(THF)_2}]_2(\mu\text{-Cl})_4[(\mathrm{MeC_5H_4})\mathrm{Nd(THF)}]$ [19].

Complex **2** is a salt containing two cations $[\mathrm{Na(THF)_6}]^+$ and the hexanuclear dianion $[\mathrm{Cp'_6Sm_6Se_{13}}]^{2-}$. The six Cp′Sm units in the dianion form a symmetrical octahedron with an interstitial selenium atom. The four Sm atoms [Sm(2)–Sm(3)–Sm(2a)–Sm(3a), Sm(1)–Sm(2)–Sm(1a)–Sm(2a) and Sm(1)–Sm(3)–Sm(1a)–Sm(3a)] and the central selenium atom (Se(1)) form almost planar arrangements. The distances of the samarium atoms from C atoms of their cyclopentadienyl ring ($d_{(\mathrm{Sm-C})}$: 2.728 Å (average)) are similar to those in other $\mathrm{Sm^{III}}$ cyclopentadienyl complexes ($d_{(\mathrm{Sm-C})}$: 2.755 Å in $[\mathrm{Cp^*Sm(THF)}]_2(\mu\text{-Se})$ [9], and 2.679 Å in $\mathrm{Cp^*_6Sm_6Se_{11}}$ [11]), but are clearly shorter than the corresponding distances in $\mathrm{Sm^{II}}$ cyclopentadienyl complexes [20]. The dianion of **2** with the central selenium atom has a highly symmetrical structure, related hexanuclear lanthanoid complexes include $[\mathrm{Cp^*_6Sm_6Se_{11}}]$ [11], $[\mathrm{Cp_6Yb_6Cl_{13}}]^-$ [21], $[\mathrm{Cp'_6Nd_6Se_{13}}]^{2-}$ [12] and $[\mathrm{Nd_6(2,4\text{-}C_7H_{11})_6Cl_{12}}](\mathrm{THF})_2$ [22] in which a centered chloride atom is absent. The structure of the

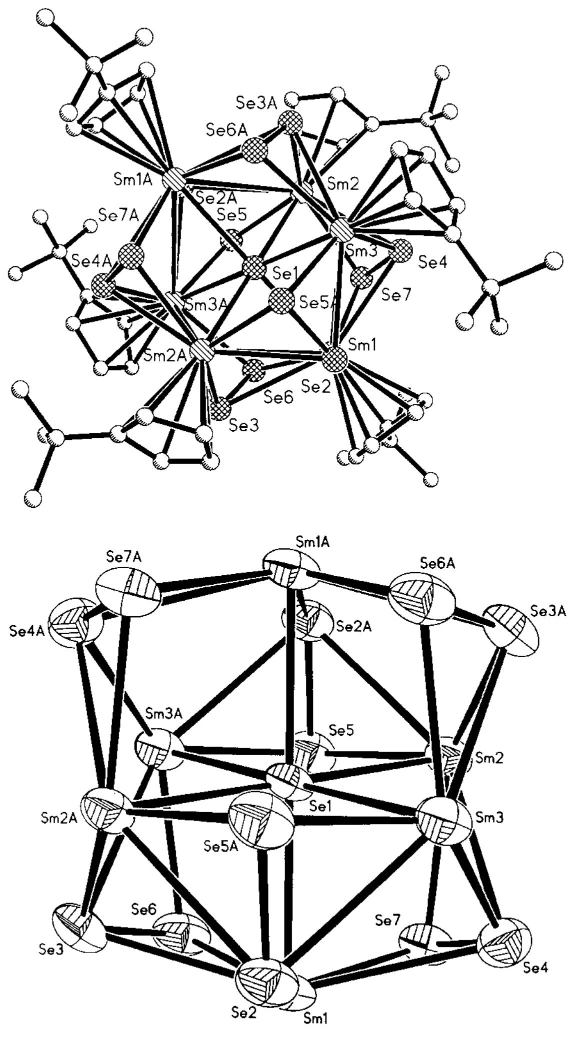

Fig. 2. Top: Molecular structure of the dianion of **2**. Bottom: Molecular structure of the central Sm_6Se_{13} core of **2**. Selected distances (Å) and angles (°): Sm(1)–Se(1) 2.9976(12), Sm(1)–Se(2) 3.068(2), Sm(1)–Se(3) 3.156(3), Sm(1)–Se(4) 3.149(3), Sm(1)–Se(6) 2.864(2), Sm(1)–Se(7) 2.906(3), Sm(2)–Se(1) 3.0123(13), Sm(2)–Se(2a) 3.152(2), Sm(2)–Se(3a) 3.031(2), Sm(2)–Se(4) 3.209(2), Sm(3)–Se(1) 3.0065(12), Sm(3)–Se(2) 3.100(2), Sm(3)–Se(3a) 3.216(2), Sm(3)–Se(5a) 2.873(3), Se(2)–Se(5a) 2.363(3), Se(3)–Se(6) 2.370(3), Se(4)–Se(7) 2.370(3), Sm(1)···Sm(4) 4.065(2); Sm(1)–Se(1)–Sm(1a) 180.0, Sm(3)–Se(1)–Sm(3a) 180.0, Sm(1)–Se(1)–Sm(3) 85.23(3), Sm(1a)–Se(1)–Sm(3) 97.77(4), Sm(1)–Se(1)–Sm(2a) 85.83(4) Sm(1a)–Se(1)–Sm(2a) 94.17(4), Se(1)–Sm(1)–Se(2a) 83.40(5), Se(1)–Sm(1)–Se(6) 82.36(5), Se(2)–Sm(1)–Se(3) 88.70(7), Se(2)–Sm(1)–Se(6) 133.74(8), Se(1)–Sm(1)–Sm(3) 47.47(2), Se(2)–Sm(1)–Sm(3) 49.10(5), Sm(1)–Se(2)–Sm(2a) 82.26(6), Sm(1)–Se(2)–Se(3) 82.46(6), Sm(3)–Se(2)–Sm(2a) 89.77(6), Sm(1)–Se(3)–Se(6) 60.45(8), Sm(3a)–Se(3)–Se(6) 59.98(7).

dianion in **2** where each Sm 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 atoms while in $[Cp^*_6Sm_6Se_{13}]$, three Sm atoms are coordinated with six Se atoms and other three Sm atoms are linked with five Se atoms, resulting in a distorted octahedral structure. The distances between the Sm and Se atoms in **2** ($d_{(Sm-Se)}$: 2.864(2)–3.216(2) Å) can be compared with other lanthanoid selenium complexes such as $[Cp^*_6Sm_6Se_{11}]$ ($d_{(Sm-Se)}$: 2.859–3.308 Å [11]), $[(Cp^*_2Sm)_2(\mu\text{-}\eta^1\text{:}\eta^3\text{-}Se_3)]$ ($d_{(Sm-Se)}$: 2.917–3.198 Å) [9], $[(THF)_3Sm(\mu_2\text{-}SePh)_3Zn(SePh)]_n$ ($d_{(Sm-Se)}$: 3.1898–3.4470 Å) [23] and $[(Cp^*_2Yb)_2(\mu\text{-}Se)]$ ($d_{(Yb-Se)}$: 2.621 Å) [8].

The 13 selenium atoms in **2** like neodymium complex $[Na(THF)_6]_2[Cp'_6Nd_6(\mu_6\text{-}Se)(\mu\text{-}Se_2)_6]$ [12] can be divided into three types: a central Se(1) atom which is coordinated to six Sm atoms ($d_{(Sm-Se)}$: 2.9976(12)–3.0123(13) Å); six pairs of bridging Se units [Se(2)–Se(5a), Se(3)–Se(6), Se(4)–Se(7)] in which one Se atom is coordinated to three Sm atoms ($d_{(Sm-Se)}$: 3.068(2)–3.216(2) Å) while the other one is connected with only two Sm atoms ($d_{(Sm-Se)}$: 2.873(3)–2.887(2) Å). The distances between two Se atoms are in the range of 2.363(3)–2.370(3) Å and can be compared with those in $[Cp^*_6Sm_6Se_{11}]$ (2.361–2.376 Å) [11], $[Na(THF)_6]_2[Cp'_6Nd_6Se_{13}]$ (2.357–2.364 Å) [12], $[Cp^*Re(Se_3)(\mu\text{-}Se_2)]_8$ (2.356–2.385 Å) [2], $[(Cp^*_2Nd)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Se_2)]$ (2.389(2) Å) [10], $[(Cp^*_2Sm)_2(\mu\text{-}\eta^1\text{:}\eta^3\text{-}Se_3)]$ (2.326–2.377 Å) [9] and $[Cp^*Ir(PMe_3)(Se_4)]$ (2.313–2.361 Å) [4].

3. Experimental

All manipulations were routinely carried out in standard Schlenk vessels under Ar. The solvents were kept free of traces of water and oxygen, and distilled in a stream of Ar before use. Anhydrous samarium trichloride [24] and $CpNaCl_2\cdot 2LiCl\cdot 5THF$ [15] were prepared according to the literature.

The IR spectra were measured on a Bio-Rad FTS 135 (as KBr pellet). Elemental analyses were performed by the Analytical Laboratory of Changchun Institute of Applied Chemistry and the Analytic Center of Fudan University.

3.1. $\{[Cp'Ln(THF)]_2(\mu_2\text{-}Cl)(\mu_3\text{-}Cl)_3Na(THF)\}_n$ [Ln = Nd (**1a**), Sm (**1b**), Gd (**1c**), Yb (**1d**)]

1a: A solution of NaCp′ (0.2651 M, 32.4 ml in THF) which was prepared by the reaction of Cp′–H with NaH, was added dropwise to a suspension of $NdCl_3$ (2.154 g, 8.59 mmol) in THF (20 ml) at −78 °C. The reaction mixture was then slowly warmed up and kept at 60 °C stirring for 6 days, filtered through a plug of sea sand. Hexane (ca. 15 ml) was added to the filtrate. The resulting solution was kept at −15 °C for several days to afforded violet prismatic crystals of **1a** (3.23 g, 80.4%), m.p. = 111 °C. Anal. Found: C, 37.84; H, 5.21; Cl, 18.47; Na, 3.03; Nd, 30.72. Calc. for $C_{30}H_{50}Cl_5NaNd_2O_3$, C, 38.03; H, 5.32; Cl, 18.71; Na, 2.43; Nd, 30.45%. IR (KBr pellet, cm^{-1}): 3068(w), 2949(s), 2895(w), 1615(m), 1570(w), 1520(m), 1460(m), 1360(m), 1276(m), 1200(m), 1158(w), 1041(m), 1018(m), 830(m), 787(s), 760(s), 570(m).

In a similar manner for **1a**, complexes **1b**, **1c** and **1d** were synthesized.

1b: Yellow crystal, yield: 71.2%. Anal. Found: C, 37.98; H, 5.55; Cl, 18.87; Sm, 31.32. Calc. for $C_{30}H_{50}Cl_5NaO_3Sm_2$: C, 37.54; H, 5.25; Cl, 18.58; Sm, 31.34%. IR (KBr pellet, cm^{-1}): 3070(w), 2949(s), 2896(w), 1615(m), 1570(m), 1521(m), 1460(m), 1360(m), 1276(m), 1200(m), 1158(w), 1040(m), 1018(m), 830(m), 786(s), 760(s), 462(m).

1c: White crystals, m.p. = 97 °C; yield: 43.13%. Anal. Found: C, 37.47; H, 6.02; Cl, 18.09; Gd, 32.25; Na, 2.34. Calc. for $C_{30}H_{50}Cl_5NaGd_2O_3$: C, 37.01; H, 5.70; Cl, 18.21; Gd, 32.31; Na, 2.36%. IR (KBr pellet, cm^{-1}): 3090(w), 2949(s), 2895(w), 1615(m), 1570(m), 1520(m), 1460(m), 1360(m), 1276(m), 1200(m), 1158(w), 1040(m), 1018(m), 830(m), 787(s), 760(s), 670(s), 450(m).

1d: Red crystal, m.p. = 118 °C; yield: 47.5%. Anal. Found: C, 36.10; H, 5.12; Cl, 17.50; Na, 2.11; Yb, 34.61. Calc. for $C_{30}H_{50}Cl_5NaYb_2O_3$: C, 35.85; H, 5.01; Cl, 17.64; Na, 2.28; Yb, 34.44%. IR (KBr pellet, cm^{-1}): 2950(s), 2895(s), 1640(m), 1460(m), 1360(m), 1274(m), 1245(m), 1178(m), 1039(m), 1010(m), 836(m), 780(m), 680(m), 450(m).

2: A suspension of Na_2Se_5 (0.800 g, 1.814 mmol) and **1b** (0.870 g, 0.907 mmol) in THF (30 ml) was stirred at room temperature (r.t.) for 2 h. The precipitate was filtered off. Hexane (ca. 5 ml) was carefully added to the top of the filtrate and allowed to stand for several days at −15 °C to isolate the dark red prismatic crystal of **2** (yield: 0.23 g, 42.2%). M.p. (dec.) = 72 °C. Anal. Found: C, 34.66; H, 5.11. Calc. for $C_{102}H_{174}Na_2O_{12}Se_{13}Sm_6$: C, 34.34; H, 4.92%. IR (KBr pellet, cm^{-1}): 3084(w), 2950(s), 2896(w), 1481(m), 1385(m), 1359(w), 1275(m), 1199(w), 1154(m), 1047(s), 894(w), 824(m), 767(s), 677(m).

3: A suspension containing $CpNdCl_2\cdot 2LiCl\cdot 5THF$ (1.07 g, 1.47 mmol) and Na_2Se_5 (0.60 g, 1.36 mmol) in THF (35 ml) was stirred at r.t. for 24 h and filtered through a plug of sea sand. The filtrate was carefully concentrated to a slightly supersaturated solution (ca. 20 ml) and kept at −15 °C for several weeks to afford red prismatic crystals of **3** (0.18 g, 23.0%). M.p. (dec.) = 81 °C. IR (KBr pellet, cm^{-1}): 3080(w), 2974(m), 2873(m), 1487(w), 1435(m), 1119(w), 1041(s), 1010(s), 911(w), 886(m), 840(w), 780(s), 763(s), 674(w).

3.2. X-ray crystal structure analyses for *1a* and *2*

Single crystals were sealed in thin-walled glass capillaries under an atmosphere of Ar. The intensity data of both compounds were collected with a Nicolet R3M/E diffractometer (**1a**) and a Siemens P4 diffractometer (**2**) using Mo–K_α radiation ($\lambda = 0.7107$ Å, graphite monochromator); the stability of the primary beam was controlled by monitoring three check reflections every 100 reflections. Corrections for Lp factors and for absorption based on ψ-scan technique were applied.

1a. $C_{30}H_{50}O_3NaNd_2Cl_5$: $M_r = 907.34$; $\rho = 1.539$ g cm^{-3}; violet prism of the dimension 0.22 × 0.14 × 0.26 mm, orthorhombic space group $P2_12_12_1$, with lattice parameters $a = 14.440(4)$, $b = 15.259(2)$, $c = 17.762(2)$ Å, $Z = 4$, unit cell volume $V = 3913.68$ Å^3. Data collection: intensity data of 6252 reflections in the range $3.0 \leq 2\theta \leq 65°$ have been measured in the ω-scan mode (measuring temperature 296 K); observed reflections: 2932 $[I \geq 3\delta(I)]$; structure solution with direct methods (SHELXTL); number of refined parameter: 370; $R = 0.047$, $wR = 0.042$.

2. $C_{102}H_{174}Na_2P_{12}Se_{13}Sm_6$, $M_r = 3567.03$; $\rho = 1.859$ g cm^{-3}, black prism of the dimension 0.44 × 0.40 × 0.36 mm, triclinic space group $P\bar{1}$, with lattice parameters $a = 14.349(3)$, $b = 15.421(3)$, $c = 16.035(3)$ Å, $\alpha = 64.590(10)$, $\beta = 81.55(2)$, $\gamma = 85.80(2)°$ and $Z = 2$; unit cell volume $V = 3169.9(11)$ Å^3, absorption coefficient $\mu = 6.521$ mm^{-1}, measured reflections: 10 038, independent reflections: 8519 ($R_{int} = 0.0298$), observed reflection: $8469(F \geq 0.0\delta(F2))$; structure solution with direct methods (SHELXTL PLUS (VMS)); refinement with 605 parameters converged at $R_1 = 0.0507$, and $wR_2 = 0.1014$ $[I > 2\delta(I)]$; max/min residual electron density was $1.324/-1.34$ e Å^{-3}.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 156405 and 156406 for compounds **1a** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Financial support by the National Natural Science Foundation of China and Special Funds for Major State Basic Research Projects is gratefully acknowledged.

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