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Preparation and Characterization of Two Mixed-Valence Samarium Octameric Clusters

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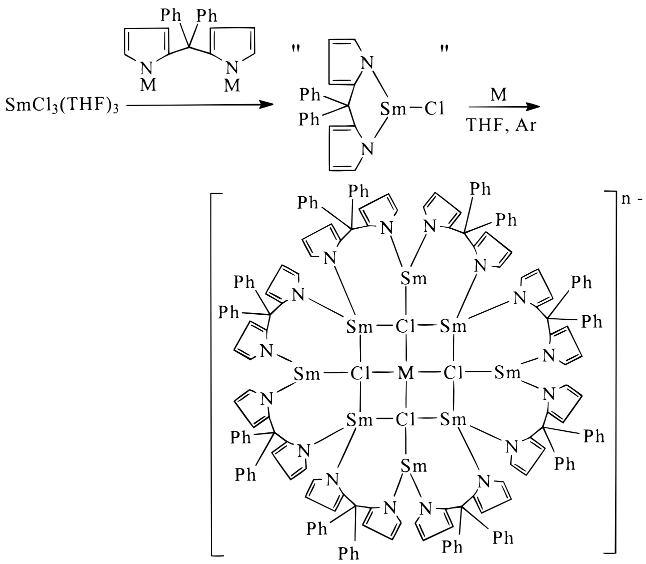
Summary: Reduction of the [$Ph_2C(C_4H_3N)$]SmCl precursor with either Li or Na afforded a similar octameric cluster where the valence is apparently determined by the nature of the alkali-metal cation.

One of the most attractive characteristics of cluster complexes resides in the ability of these systems to perform cooperative attack of two or more metals on the same substrate. Despite the great potential offered by lanthanides for reactivity purposes and in particular by their low-valent complexes, their cluster chemistry remains remarkably underdeveloped. Aside from a few recently reported examples of chalcogenide derivatives,[1] only a few clusters involving cyclopentadienyl ligands[2] have been reported so far. Cases of mixed-valence or Ln(II) clusters remain extremely rare.[3]

In an attempt to model dinitrogen activation processes, we have recently reacted a dipyrrolide dianion ligand with $SmI_2(THF)_2$, obtaining a tetrametallic cluster where a molecule of dinitrogen located in the center of the tetrametallic core had undergone a four-electron reduction.[4] In an effort to identify the reactive divalent species responsible for interacting with dinitrogen, we have now attempted the reduction of a trivalent precursor of the same ligand system under Ar and obtained two unprecedented mixed-valence octameric clusters. Herein, we describe our findings.

Scheme 1



M = Li, n = 2 (**1**)
M = Na, n = 1 (**2**)

Treatment of a solution of the dilithium salt of the diphenyldipyrromethanyl dianion in THF with an equivalent amount of $SmCl_3(THF)_3$ followed by reduction with metallic lithium under Ar produced the dark brown $\{[Ph_2C(C_4H_3N)_2Sm]_8(LiCl_4)\}^{2-}[Li_2Cl(THF)_4]^+[Li(THF)_4]^+$ (**1**) in good yield (Scheme 1).[5] An X-ray crystal structure[6] revealed an octameric dianionic complex consisting of eight $\{[Ph_2C(C_4H_3N)_2Sm\}$ units with the samarium atoms arranged in an overall bowl conformation (Figure 1). Each set of adjacent samarium atoms is bridged by one ligand with the pyrrole rings being in turn π-bonded to one samarium and σ-bonded to a second. The overall

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(1) (a) Freedman, D.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **1997**, *119*, 11112. (b) Melman, J. H.; Emge, T. J.; Brennan, J. G. *J. Chem. Soc., Chem. Commun.* **1997**, 2269. (c) Cary, D.; Ball, G.; Arnold, J. *J. Am. Chem. Soc.* **1995**, *117*, 3492. (d) Evans, W.; Rabe, G.; Ziller, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2110.

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(5) Synthesis of **1**: A solution of diphenyldipyrromethane (1.1 g, 3.7 mmol) in THF (75 mL) under Ar was treated at room temperature with a solution of MeLi in ether (5.2 mL, 1.4 M, 7.3 mmol). Stirring proceeded for 30 min followed by addition of $SmCl_3(THF)_3$ (1.7 g, 3.6 mmol). A rapid reaction resulted in an immediate color change to bright orange. After the mixture was stirred for 30 min, an excess of metallic lithium (0.03 g, 4.0 mmol) was introduced in the flask. After 16 h of further stirring under Ar, the reaction mixture was dark brown. The small amount of unreacted lithium was filtered off, and the solution was concentrated to 50 mL. Layering with 50 mL of toluene and standing at room temperature for 2 days produced dark brown crystals of **1** (1.5 g, 0.3 mmol, 72%). Anal. Calcd (found) for $C_{216}H_{224}N_{16}O_{12}Cl_5Li_4Sm_8$: C, 55.86 (55.72); H, 4.86 (4.72); N, 4.83 (4.39); Cl, 3.82 (3.77). IR (Nujol mull, cm^{-1}): ν 3081 (w), 3051 (w), 1946 (w), 1809 (w), 1651 (w), 1597 (m), 1491 (s), 1464 (vs), 1417 (m), 1377 (s), 1259 (w), 1236 (w), 1182 (w), 1155 (s), 1038 (vs), 980 (w), 964 (w), 893 (m), 850 (m), 796 (w), 758 (vs), 751 (vs), 700 (vs), 660 (m), 636 (s).

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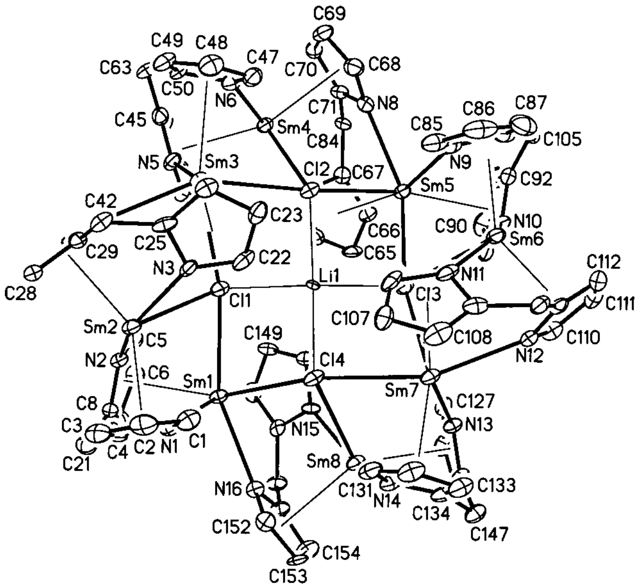

Figure 1. ORTEP drawing of **1**. Phenyl rings have been removed for clarity reasons. Thermal ellipsoids are drawn at the 30% probability level. Bond distances (Å) and angles (deg): Sm(1)–N(1) = 2.713(10), Sm(1)–N(16) = 2.655(8), Sm(1)–N(2) = 2.825(8), Sm(1)–C(8) = 2.898(10), Sm(1)–N(15) = 2.863(8), Sm(1)···Sm(2) = 3.980(7), Li(1)–Cl(1) = 2.444(15), Li(1)–Cl(2) = 2.482(14), Li(1)–Cl(3) = 2.421(15), Li(1)–Cl(4) = 2.477(14), Sm(2)–Cl(1) = 2.916(3), Sm(3)–Cl(2) = 3.099(3), Sm(4)–Cl(2) = 2.937(3), Sm(6)–Cl(3) = 2.919(3), Sm(8)–Cl(4) = 2.920(3); Sm(3)–Cl(2)–Sm(5) = 165.44(9), Cl(4)–Li(1)–Cl(2) = 166.5(4) Cl(1)–Li(1)–Cl(2) = 90.0(3), Sm(1)–Cl(1)–Sm(3) = 167.0(4).

effect is the establishment of a samarocene-type environment about each samarium atom which is defined by two π-bonded and two σ-bonded pyrrole rings from two ligand molecules. Four chlorine atoms are arranged within the cavity formed by the eight samarium atoms such that each chloride bridges three adjacent samariums. The four chlorides are, in turn, bridged by a single lithium atom which is located in the center of the cluster and is nearly coplanar with the four chlorine atoms. The two negative charges of the octamer are balanced by separated $Li(THF)_4$ and $[Li_2Cl(THF)_4]$ cations.

The chemical connectivity as indicated by the X-ray crystal structure clearly indicates that complex **1** is a mixed-valence species, *formally* composed of seven divalent samarium atoms and one trivalent metal. Surprisingly, complete reduction of this particular system could not be obtained, even when using large excesses of lithium, increasing reaction times, employing elevated temperatures, or adding catalytic amounts of naphthalene. The apparent critical role of lithium in assembling and stabilizing the cluster structure of **1**, as well as the fact that **1** is a mixed-valence species, prompted us to explore the effect of other alkali metals as reducing agents.

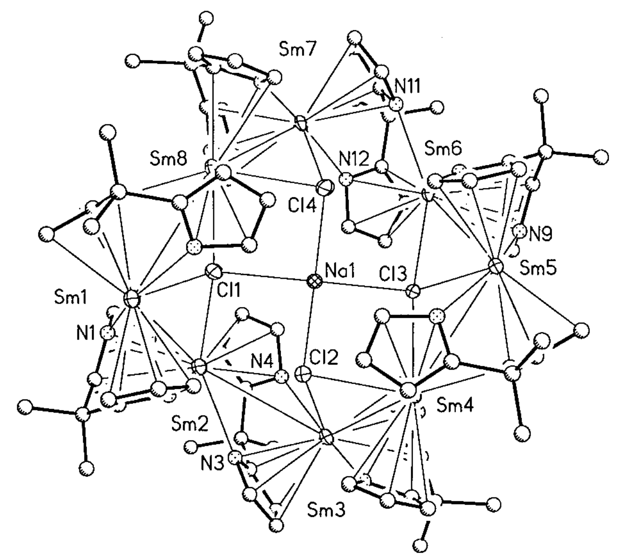

Figure 2. ORTEP drawing of **2**. Phenyl rings have been removed for clarity reasons. Thermal ellipsoids are drawn at the 30% probability level. Bond distances (Å) and angles (deg): Sm(1)–N(1) = 2.61(2), Sm(1)–Cl(1) = 2.882(12), Sm(1)···Sm(2) = 3.991(7), Sm(2)–Cl(1) = 2.990(12), Sm(2)–N(4) = 2.91(2), Sm(2)···Sm(3) = 4.097(5), Sm(3)–Cl(2) = 2.703(12), Sm(5)–Cl(3) = 2.859(11), Sm(6)–Cl(3) = 3.009(11), Sm(7)–Cl(4) = 2.713(10), Sm(8)–Cl(1) = 3.105(12), Sm(8)–Cl(4) = 3.209(14), Na(1)–Cl(2) = 2.57(3), Na(1)–Cl(3) = 2.74(3), Na(1)–Cl(1) = 2.78(3); Cl(1)–Na(1)–Cl(4) = 90.1(5), Cl(1)–Na(1)–Cl(3) = 165.5(6).

A very similar reduction under Ar but using Na instead of Li yielded a deep green solution from which dark green crystals of the new species $\{[Ph_2C(C_4H_3N)_2Sm]_8(NaCl_4)\}^-[Na(THF)_5]^+$ (**2**) were isolated in modest yield (Scheme 1).[7] An X-ray crystal structure determination[6] revealed an octameric cluster with structural parameters rather similar to those of **1** (Figure 2). The only differences consist of the presence of a sodium atom instead of lithium in the center of the cluster and of the fact that the octameric structure in this case is monoanionic. Thus, despite the close structural similarity between **2** and **1**, a lower extent of reduction has occurred during the formation of **2**, since this cluster contains *two* samarium atoms which have retained their trivalent state. Similar to the case of **1** and despite the low yield in which **2** may be obtained, the reaction

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[6] Crystal data for **1**: $C_{216}H_{224}Cl_5Li_4N_{16}O_{12}Sm_8$, M_w = 4643.92, triclinic, $P\bar{1}$, a = 20.066(5) Å, b = 21.437(5) Å, c = 27.865(7) Å, α = 79.451(4)°, β = 78.407(4)°, γ = 86.683(4)°, V = 12369(5) Å^3, Z = 2, D_{calcd} = 1.247 Mg/m^3, absorption coefficient 1.972 mm^{-1}, F(000) = 4642, 93 120 reflections collected, 37 901 independent reflections, GOF = 1.039, R1 = 0.0734, wR2 = 0.2128. Crystal data for **2**: $C_{188}H_{168}Cl_4N_{16}Na_2O_5Sm_8$, M_w = 4121.96, triclinic, $P1$, a = 17.718(9) Å, b = 18.274(9) Å, c = 34.526(9) Å, α = 78.06(5)°, β = 82.45(4)°, γ = 65.09(4)°, V = 9908(2) Å^3, Z = 2, D_{calcd} = 1.382 Mg/m^3, absorption coefficient 2.440 mm^{-1}, F(000) = 4068, 44 742 reflections collected, 13 605 independent reflections, GOF = 1.111, R1 = 0.0991, wR2 = 0.2621.

[7] Synthesis of **2**: A clear solution of diphenyldipyrromethane (2.3 g, 7.7 mmol) under Ar and in THF (100 mL) was treated with NaH (0.35 g, 15 mmol). Stirring was continued at room temperature for 2 h, after which time $SmCl_3(THF)_3$ (3.6 g, 7.6 mmol) was added to the resulting suspension. Heating to 60 °C for 30 min produced a golden yellow suspension. An excess of metallic sodium (0.28 g, 12 mmol) was introduced, as well as a catalytic amount of naphthalene (0.01 g, 78 μmol). After the mixture was stirred for 16 h at room temperature under Ar, the solution assumed a dark green color. After filtration and addition of toluene (75 mL), the solution was concentrated to small volume under reduced pressure and was allowed to stand at room temperature overnight, during which time an appreciable amount of dark green solid accumulated. The solid was collected and recrystallized at room temperature from a 90:10 mixture of THF and hexane to produce plates of **2** (1.5 g, 0.36 mmol, 38%). Anal. Calcd (found) for $C_{188}H_{168}Cl_4N_{16}Na_2O_5Sm_8$: C, 54.77 (54.12); H, 4.11 (4.24); N, 5.44 (5.20); Cl, 3.44 (3.38). IR (Nujol mull, cm^{-1}): ν 3082 (w), 3051 (w), 1597 (w), 1464 (vs), 1377 (s), 1261 (w), 1234 (w), 1182 (w), 1149 (s), 1078 (w), 1038 (s), 893 (w), 850 (w), 795 (s), 758 (s), 741 (s), 704 (s), 658 (m), 635 (m).

leading to **2** is perfectly reproducible and displays the same robustness features observed for **1**.

Complexes **1** and **2** are formed when the reduction reactions are carried out under an Ar atmosphere. Once formed, the two complexes per se do not react with dinitrogen. Since interaction with bridging dinitrogen appears to occur exclusively at the level of divalent samarium,[8] we have attempted to reduce the trivalent centers of **1** and **2** via reaction with excess KH. Reaction of **1** with KH resulted in the collapse of the octameric framework to release the $[Ph_2C(C_4H_3N)_2Sm]_4$ unit, which readily reacts with N_2 to form the dinitrogen complex $[\{[\mu\text{-}Ph_2C(\eta^1{:}\eta^5\text{-}C_4H_3N)_2]Sm\}_4(\mu\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}N_2)]$, previously obtained via direct reaction of $SmI_2(THF)_2$ with the dipyrrolyl dianion under a nitrogen atmosphere (the same reaction under Ar gave instead a divalent samarium pentameric cluster).[4] Similar treatment of **2** with either KH or NaH led instead to intractable materials.

In conclusion, the reductions of the trivalent "dipyrrole-SmCl" precursor with Li and Na follow very similar trends in the sense that similar octameric structures resulted. However, the nature of the alkali-metal cation seems to control the extent of reduction and to play a surprising role in determining the stability of the cluster overall oxidation state.

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Supporting Information Available: Crystallographic data (excluding structure factors), including extensive tables of bond distances and angles, for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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