π-Bonding encapsulation in aryl-substituted lanthanide selenolates: monomeric compounds with apparent low-coordinate metal atoms

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Reaction of $LnCl_3$ with KSeAr* in thf afforded the unsolvated, alkane-soluble complexes $LnCl(SeAr^*)_2$ (Ln = Nd, Pr; Ar* = 2,6-$Trip_2C_6H_3$; Trip = 2,4,6-$i$$Pr_3C_6H_2$) in which the rare-earth metal cations show additional η^6-π-coordination by two flanking arene rings.

Lanthanide (Ln) based materials are increasingly important in photonic or magnetic applications such as lasers, electroluminescent devices, light emitting phosphors, optical fibers, scintillator detectors, spintronics and high-density optical or magnetic data storage.[1] Among these materials lanthanide chalcogenides, either in stoichiometric or doped form, have gained considerable attraction. Molecular compounds with bonds between rare-earth metals and the heavier group 16 elements are potential precursors for the synthesis of bulk or nano-scale LnE and Ln_2E_3 (E = S, Se, Te). Suitable candidates for this purpose are homoleptic, mononuclear complexes with the composition $Ln(ER)_2$ or $Ln(ER)_3$ (R = bulky organyl group), that are very rare, however. Structurally authenticated examples are currently restricted to a couple of Ln^{III} and Ln^{II} thiophenolates.[2,3]

In order to prepare homoleptic lanthanide selenophenolates, we have now examined reactions between rare-earth metal trichlorides and potassium selenolates containing sterically crowded aryl substituents.[4a] Thus, an excess of $NdCl_3$ or $PrCl_3$ was reacted with KSeAr* (Ar* = 2,6-$Trip_2C_6H_3$ with Trip = 2,4,6-$i$$Pr_3C_6H_2$) in tetrahydrofuran as the solvent.‡ Removal of the solvent followed by extraction with *n*-heptane and crystallization at −20 °C gave donor-free $LnCl(SeAr^*)_2$ (Ln = Nd {**1**}, Pr {**2**}) as air sensitive pale green (**1**) or pale yellow (**2**) crystalline material in good yield.§ The selective formation of the bis SeAr* complexes is explained by ligand redistribution reactions, favoured by the low solubility of $LnCl_3(thf)_x$ in alkanes and the size of the Ar* groups. Obviously, the selenophenolate ligands are too bulky to be accommodated more than twice around the Ln centers.

As with the related Ln^{II} compounds $Ln(SAr^*)_2$ (Ln = Eu, Sm, Yb),[3] **1** and **2** also exhibit a remarkably low tendency to coordinate σ-donor solvents such as tetrahydrofuran, which was used in their synthesis. This unusual behavior is in contrast to the preparation of other unsolvated lanthanide compounds, *e.g.* $Ln(OAr)_3$, in the presence of coordinating solvents, that normally requires repeated sublimations at elevated temperatures.[5]

In the solid state,¶ complexes **1** and **2** crystallize as monomers in which the metal atoms show a slightly distorted trigonal planar coordination by two selenium atoms of the terminal selenolate ligands and the chlorine atom, respectively. Because of their very similar features, only the solid-state structure of **1** (Fig. 1) will be discussed in detail in the following.

The most striking structural features are the additional Ln···η^6-π-interactions to two *ortho*-2,4-6-triisopropylphenyl rings of the terphenyl groups (Fig. 2), which are unprecedented for structurally authenticated Ln^{III} compounds.[6] Both terphenyl selenolate ligands are orientated in such a way that the most favorable η^6-π-arene bonding is maximized. In effect, the interplanar angles between the Ln–Se–C planes and the central 2,6-substituted C_6H_3 rings are small, as indicated by the Nd–Se1–C11–C12 and Nd–Se2–C41–C42 torsion angles of 9.1° and 10.5°, respectively. Together with the perpendicular arrangement of the *ortho*-Trip groups (A/B, A/C, D/E, D/F = 82.4–89.3°; for the definition of the least-square planes see Fig. 1) an almost parallel orientation of the interacting

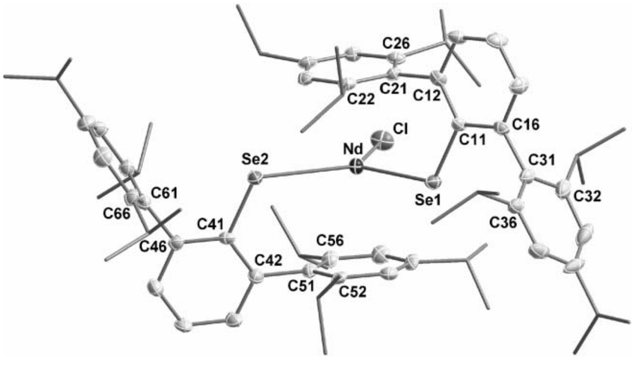

Fig. 1 Molecular structure of **1** with thermal ellipsoids set to 30% probability. Hydrogen atoms have been omitted and carbon atoms of *iso*-propyl groups are shown as lines for clarity. Selected bond lengths (Å), angles (°) and interplanar angles (°) for **1** and **2** (in brackets): M–Cl 2.629(2) {2.652(3)}, M–Se1 2.8805(11) {2.8963(14)}, M–Se2 2.8863(10) {2.9059(13)}, M···C21 3.167(6) {3.176(9)}, M···C22 3.176(6) {3.199(9)}, M···C23 3.131(6) {3.156(10)}, M···C24 3.133(7) {3.140(9)}, M···C25 3.104(6) {3.109(9)}, M···C26 3.160(6) {3.179(9)}, M···C51 3.187(7) {3.195(9)}, M···C52 3.164(7) {3.177(9)}, M···C53 3.108(7) {3.132(9)}, M···C54 3.125(7) {3.123(10)}, M···C55 3.125(7) {3.139(10)}, M···C56 3.195(7) {3.183(10)}, M···X6 2.816 {2.831}, M···X6′ 2.822 {2.822}, Cl–M–Se1 117.55(5) {117.89(7)}, Cl–M–Se2 119.88(5) {120.07(7)}, Se1–M–Se2 122.56(3) {122.05(4)}, X6···M···X6′ 174.6, {173.9}. A/B 82.9, A/C 88.2, D/E 82.4, D/F 89.3, B/G 2.2, E/G 3.2, B/E 4.6. X6 and X6′ define the centroids of the coordinated C21 → C26 and C51 → C56 arene rings, respectively. Least square planes defined by the following atoms: A: C11 → C16; B: C21 → C26; C: C31 → C36; D: C41 → C46; E: C51 → C56; F: C61 → C66; G: M, Se1, Se2, Cl.

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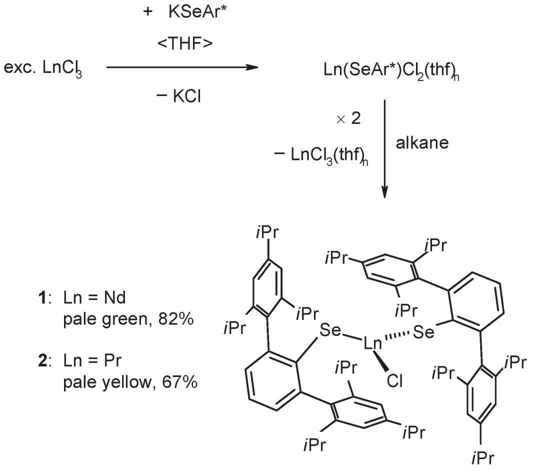

$C21 \rightarrow C26$ and $C51 \rightarrow C56$ rings to the central $NdClSe_2$ plane is achieved (B/G = 2.2°, E/G = 3.2°).

Taking into account the additional π-contacts, a formal coordination number of nine is calculated. However, the observed Nd–Se distances (av. 2.883 Å) are surprisingly short. In fact, they are approx. 0.09–0.25 Å shorter than the corresponding values reported for the polymer $[Nd(\mu\text{-}SeTrip)_3(thf)]_\infty$ that contains seven-coordinate neodymium atoms and represents the only neodymium selenolate available for comparison.[7a] Moreover, significantly longer or comparable mean distances are found in the compounds $[Sm(Me_2pzBH)_2(SePh)]$ (cn = 7, Sm–Se 2.948 Å)[7b] and $[Er(SePh)_3(thf)_3]$ (cn = 6, Er–Se 2.776 Å).[7a] Allowing for the larger size of Nd^{3+} than Sm^{3+} or Er^{3+} (difference +0.025 Å and +0.093 Å for cn = 6, respectively)[8] Nd–Se distances of 2.973 Å and 2.869 Å are extrapolated for seven- and six-coordinate metal atoms, respectively.

From these data a lower effective coordination number of approximately 5 may be estimated for complex **1** (and **2**), assuming that every η^6-bonded arene ring occupies only one coordination site. In **1**, the neodymium cation interacts essentially equally with both Trip rings with Nd–C distances in the relatively narrow range 3.104(6)–3.176(6) Å for $C21 \rightarrow C26$ and 3.108(7)–3.195(7) Å for $C51 \rightarrow C56$ with average values of 3.145 Å and 3.151 Å, respectively. The metal–centroid distances average to 2.819 Å, whereas the X6–Sm–X6′ angle, where X6 and X6′ define the centroids of the coordinated arene rings, is 174.6°. Significantly shorter metal···centroid distances of 2.696 Å and 2.714 Å, have been reported for the phenolates $[\{Nd(ODip)_3\}_2]$[9a] (Dip = 2,6-$i$$Pr_2C_6H_3$) and $[Nd(ODpp)_3]$[9b] (Dpp = 2,6-$Ph_2C_6H_3$), respectively. Even shorter metal···centroid distances within the narrow range 2.57 to 2.61 Å were observed for a number of tetrachloroaluminate complexes of the composition $[Nd(\eta^6\text{-arene})(AlCl_4)_3]$.[10] Taking into account the different ionic radii for Eu^{2+} (+0.187 Å) and Yb^{2+} (+0.037 Å)[8] much stronger Ln···η^6-arene interactions are found in the thiophenolates $[Eu(SAr^*)_2]$ (av. Eu···X6 2.728 Å) and $[Yb(SAr^*)_2]$ (av. Yb···X6 2.637 Å).[3a]

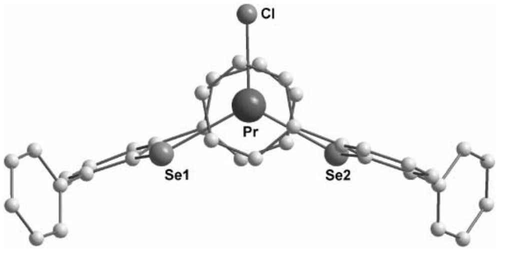

Fig. 2 Molecular structure of **2**, showing a view perpendicular to the $PrClSe_2$ plane. Hydrogen atoms and carbon atoms of *iso*-propyl groups have been omitted for clarity.

The considerably weaker Ln···η^6-arene interactions in complexes **1** and **2** compared to the $[Ln(SAr^*)_2]$ compounds are somewhat surprising. Since the bonding between a η^6-coordinated arene ring and a Ln^{2+} or Ln^{3+} cation is dominated by polar contributions (ion–quadrupol interaction) stronger interactions and shorter Ln···C contacts would be expected for the Ln^{III} compounds.[11] The weaker Ln···C interactions are most probably a result of increased steric crowding due to the replacement of S by Se and the introduction of a third substituent. However, additional experimental data such as the preparation and characterization of $Ln(SeAr^*)_2$ or $LnCl(SAr^*)_2$ derivatives is needed to prove this fact.

It is know from studies on lanthanide amide, phenolate and thiophenolate complexes that infrared spectroscopy is a valuable tool for the identification of intra-[3] or intermolecular[9a,12] Ln···η^6-arene interactions. IR spectroscopy shows distinct differences in aromatic C=C vibrational modes for π-bound and non-coordinating arene rings in these compounds.

Table 1 shows the IR vibration frequencies for the aromatic stretching modes in the Ln^{III} compounds **1**, **2**, in the Ln^{II} complexes $Eu(SAr^*)_2$, $Yb(SAr^*)_2$ and in the thiol Ar*SH or the selenol Ar*SeH, recorded as Nujol mulls. There are two bands in the regions 1602–1606 cm^{-1} and 1563–1569 cm^{-1} which are visible in all spectra. Additional stretching modes in the range 1591–1592 cm^{-1} and 1541–1545 cm^{-1} are observed only in the IR spectra of the metal complexes. They clearly indicate a weakening of the aromatic C=C bonds, consistent with the presence of metal···π-arene interactions as observed by X-ray crystallography.

In conclusion, the following features of **1** and **2** are remarkable: (i) The compounds contain apparent low coordinated metal atoms. (ii) The observation of two additional metal···η^6-π-arene interactions is unprecedented for structurally authenticated Ln^{III} compounds. These interactions are responsible for the low tendency of **1** and **2** to coordinate σ-donor solvents such as tetrahydrofuran. (iii) **1** and **2** are the first monomeric unsolvated bis(organylselenato) lanthanide compounds. (iv) Both compounds are also the first examples of monomeric halogeno-functionalized lanthanide chalcogenolates of the heavier group 16 elements that are stable with respect to ligand redistribution. (v) Finally, it is notable that both complexes crystallize in isomorphous cells to the previously reported $Eu(SAr^*)_2$,[13] thus allowing in principle doping experiments with lanthanide ions in different oxidation states.

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Table 1 Infrared vibrational wavenumbers [cm^{-1}] for the ν(C=C) stretching modes in Ln complexes with Ar*-substituted thiolato and selenolato ligands

1	1606	1592	1568	1541	this work
2	1606	1592	1568	1541	this work
Ar*SeH	1602		1563		4*a*
$Eu(SAr^*)_2$	1606	1591	1569	1545	3*a*
$Yb(SAr^*)_2$	1606	1592	1568	1544	3*a*
Ar*SH	1605		1567		4*b*

Notes and references

‡ The use of an excess of $LnCl_3$ is based on the earlier observation (see ref. 3) that heteroleptic complexes of the composition $Ln(SAr^*)I(thf)_x$ cleanly rearrange in alkanes as solvent to homoleptic $Ln(SAr^*)_2$ with elimination of $LnI_2(thf)_x$.

§ **1**: A mixture of $NdCl_3$ (1.81 g, 7.22 mmol) and $KSeAr^*\cdot(C_7H_8)$ (1.66 g, 2.77 mmol) in thf (40 ml) was stirred for 64 h, after which the solvent was removed under reduced pressure. The residue solid was extracted with 40 ml of *n*-heptane and solid by-products were separated by centrifugation. The solution was concentrated and stored overnight at −16 °C to give pale green crystals (1.48 g, 1.14 mmol, 82%). Mp: 208 °C. Anal.: Calc. for $C_{72}H_{98}ClNdSe_2$: C, 66.6; H, 7.6%. Found: C, 66.4; H, 7.7%. EI-MS: *m*/*z* (%) 1300 (M^+, 20), 1265 [$(M - Cl)^+$, 2], 740 [$(M - Trip_2C_6H_3Se)^+$, 57], 562 [$(Trip_2C_6H_3Se)^+$, 100]. IR (CsBr, Nujol, cm^{-1}): 1606s, 1592m, 1568s, 1541w, 1336m, 1316s, 1252m, 1169m, 1104s, 1082m, 1070m, 1052m, 1028s, 939s, 927m, 898s, 875s, 795s, 739s, 713m, 650m. **2**: The synthesis was accomplished in a similar manner to that of **1**. Pale yellow crystals. Yield: 67%. Mp: 195 °C. Anal.: Calc. for $C_{72}H_{98}ClPrSe_2$: C, 66.6; H, 7.6%. Found: C, 66.7; H, 7.6%. EI-MS: *m*/*z* (%) 1297 (M^+, 8), 1262 [$(M - Cl)^+$, 1], 737 [$(M - Trip_2C_6H_3Se)^+$, 57], 562 [$(Trip_2C_6H_3Se)^+$, 84]. IR (CsBr, Nujol, cm^{-1}): 1607s, 1591s, 1568s, 1541m, 1335m, 1317s, 1252m, 1189m, 1169s, 1151m, 1104s, 1082m, 1070m, 1053m, 1028s, 939s, 927m, 897s, 875s, 793s, 773m, 755m, 739s, 713m, 658m, 650m, 507m.

¶ *Crystallographic data*. **1**: $C_{72}H_{98}ClNdSe_2$, $M = 1301.1$, crystal size 0.40 × 0.20 × 0.06 mm^3, triclinic, space group $P\bar{1}$, $a = 13.423(3)$, $b = 14.363(3)$, $c = 18.700(4)$ Å, $\alpha = 103.421(17)$, $\beta = 93.755(18)$, $\gamma = 99.332(17)°$, $V = 3440.4(13)$ Å^3, $Z = 2$, $D_{calc} = 1.256$ g cm^{-3}, μ(Mo Kα) = 1.89 mm^{-1}, $T = 173(2)$ K, 14143 collected ($3 \leqslant 2\Theta \leqslant 50°$) and 12097 unique reflections ($R_{int} = 0.061$), 712 parameters, 8 restraints, $R_1 = 0.065$ for 7925 reflections with $I > 2\sigma(I)$, w$R_2 = 0.117$ (all data), GOF = 1.20. **2**: $C_{72}H_{98}ClPrSe_2$, $M = 1297.8$, crystal size 0.20 × 0.20 × 0.05 mm^3, triclinic, space group $P\bar{1}$, $a = 13.439(3)$, $b = 14.392(3)$, $c = 18.751(4)$ Å, $\alpha = 103.497(17)$, $\beta = 93.751(19)$, $\gamma = 99.288(17)°$, $V = 3460.2(13)$ Å^3, $Z = 2$, $D_{calc} = 1.246$ g cm^{-3}, μ(Mo Kα) = 1.83 mm^{-1}, $T = 173(2)$ K, 11404 collected ($3 \leqslant 2\Theta \leqslant 48°$) and 10864 unique reflections ($R_{int} = 0.075$), 712 parameters, 8 restraints, $R_1 = 0.079$ for 6132 reflections with $I > 2\sigma(I)$, w$R_2 = 0.137$ (all data), GOF = 1.10. CCDC 619008 and 619009. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612182a.

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11 According to quantum-chemical calculations and low-temperature NMR experiments, metal–π-arene interactions to flanking arene rings in some Ln^{II} compounds or related complexes of the heavier alkaline-earth metals Ca and Sr are in the range 40–55 kJ mol^{-1}. See ref. 3*a* and: (*a*) S.-O. Hauber and M. Niemeyer, *Inorg. Chem.*, 2005, **44**, 8644; (*b*) S.-O. Hauber, F. Lissner, G. B. Deacon and M. Niemeyer, *Angew. Chem., Int. Ed.*, 2005, **44**, 5871.

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13 Cell parameters for $Eu(SAr^*)_2$: $a = 13.371(3)$, $b = 14.372(4)$, $c = 18.535(5)$ Å, $\alpha = 104.17(2)$, $\beta = 94.08(2)$, $\gamma = 98.99(2)°$, $V = 3388.7(15)$ Å^3. These parameters are close to those reported earlier[3a] for the packing complex $Eu(SAr^*)_2\cdot(thf)_{0.5}$.