The First Linear, Homoleptic Triple-Decker Sandwich Complex of an f-Element: A Molecular Model for Organolanthanide Nanowires†

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Received May 7, 2010

Summary: The first structurally authenticated linear, homoleptic triple-decker sandwich complex of an f-element, (Ln(COT))2[R = Me5, Ln = Sm, Yb, Eu; R = iPr5, Ln = Tb, Dy, Ho, Er, Y] (COT = C8H6(SiMe3)2-1,4), has been obtained from a one-pot synthesis that involves a reaction between anhydrous lanthanide trichlorides and a COT bridging ligand. Molecular spintronics is an exciting new and emergent subarea of spintronics that benefits from achievements in molecular electronics and molecular magnetism. During the past few years, molecular spintronics using single molecules has attracted enormous attention both experimentally and theoretically, since it holds promise for the next generation of electronic devices with enhanced functionality and improved performance, especially in high-density information storage and quantum computing. In this context, various one-dimensional organometallic sandwich molecular wires (SMW’s) have been extensively studied due to their unique electronic and magnetic properties. Among the promising examples are lanthanide-based multidecker sandwich complexes of the type Ln3(COT)3, where Ln3(COT)3 has recently been reported as a solution in toluene suspension afforded in 72% isolated yield. The most notable structural feature of 2 is the near-linear arrangement of the COT rings with anhydrous cobalt(II) chloride (molar ratio ca. 2:1) in a toluene suspension afforded in 72% isolated yield. The most notable structural feature of 2 is the near-linear arrangement of the COT rings with anhydrous cobalt(II) chloride (molar ratio ca. 2:1) in a toluene suspension afforded in 72% isolated yield. The most notable structural feature of 2 is the near-linear arrangement of the COT rings with anhydrous cobalt(II) chloride (molar ratio ca. 2:1) in a toluene suspension afforded in 72% isolated yield. The most notable structural feature of 2 is the near-linear arrangement of the COT rings with anhydrous cobalt(II) chloride (molar ratio ca. 2:1) in a toluene suspension afforded in 72% isolated yield.

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which can be synthesized via a combination of laser vaporization and molecular beam methods. This way nanowires up to 8 nm in length (Ln = Eu, n = 18) have been obtained. A major obstacle making these oligomers difficult to manipulate and to investigate is their low solubility. It has recently been pointed out by Cloke et al. that lanthanide triple-decker sandwich complexes would provide excellent molecular models for the Ln(COT) sandwich nanowires. Previously reported triple-deckers based on a COT bridging ligand include a series of lanthanide(II) complexes of the type (μ-COT)-[Ln(CpR)]2 (R = Me5, Ln = Sm, Yb, Eu; R = Pr5, Ln = Yb, Eu), as well as a number of solvated and COT-ring-substituted analogues. However, unlike the case for the nanowires, all these triple-decker sandwich complexes comprise significantly bent molecular structures. Homoleptic lanthanide triple-deckers of the type Ln3(COT)3 (Ln = Ce, Nd, Eu, Lu), for which a linear configuration is more likely, have been known since 1976, and Ce2(COT)3 has recently been re-investigated by EPR and EXAFS methods, with the latter showing consistency with a triple-decker sandwich structure. A series of ring-substituted derivatives of the type Ln2(COT)2 (Ln = Ce, Nd, Sm; COTn = C8H6(SiMe3)2-1,4)2 were reported by us in 1998.5 Thus far, unfortunately, positive proof of the linear triple-decker structure is lacking, as no X-ray diffraction data are known to exist for any of these species. We report here a novel preparation and the first structural authentication of a homoleptic, linear triple-decker sandwich complex of an f-element.

Reactions of anhydrous lanthanide trichlorides with Li2(COT)2 have been shown to strongly depend on the reaction conditions and starting material ratios. Products isolated from such reactions include not only the anionic sandwich complexes [Ln(COT)2]9 and chloro-bridged dimers ([COT]9Ln(μ-Cl)2)10 but also unusual cluster-centered


multidecker sandwich complexes as well as the bimetalics Ln₄(COT)₃. Although the latter could be isolated from LnCl₃/Li₂COT̶ reactions in a molar ratio of 2:3, all attempts to grow single crystals failed within the course of our initial investigation. In a continuation of this work we have now found a rather unexpected and novel access to the triple-decker molecules. Treatment of [Li(THF)]₄[Nd(COT)₃] (1) with anhydrous cobalt(II) chloride (molar ratio ca. 2:1) in a toluene suspension produced a dark green solution accompanied by formation of a black precipitate of metallic Co (admixed with LiCl). Crystallization of the toluene-soluble material from cyclopentane afforded dark green, prismlike crystals, which were identified as the pure triple-decker molecules. Treatment of [Li(THF)]₄[Nd(COT)₃] toluene, 25/°C, with its 1,6 isomer), which was isolated from the concentrated mother liquid and identified unambiguously by comparison of the NMR data (1H, 13C) of an authentic specimen. Apparently two important factors contribute to the success of this novel synthetic route. One is certainly the enhanced solubility of the product imparted by the use of the bulky, silyl-substituted COT ligands. The other is the heterogeneous reaction in a nonpolar solvent (toluene), which prevents the formation of solvated species. It was shown in early work by DeKock et al. that Ln₃(COT)₃-triple-deckers formed by cocondensation techniques afforded the solvated species [Ln(COT)(THF)]₄[Ln(COT)₂] upon contact with THF.

A mass spectrum of 2 showed the molecular ion of the triple-decker at m/z 1032 with 100% relative intensity. Due to the paramagnetic nature of the Nd³⁺ ions, the 1H NMR resonances are spread over a range of ca. 20 ppm. Dark green, prismlike, X-ray-quality crystals were grown by slow cooling of a saturated solution in cyclopentane. An X-ray diffraction analysis of 2₁⁴ clearly established the presence of the first homoleptic, linear triple-decker sandwich complex of an f-element (Figure 1).

All three COTₙ rings are η₅-coordinated to neodymium, with the central ring acting as a μ-η₅-η₅-bridging ligand. The

![Scheme 1](image_url)

**Figure 1.** Molecular structure of 1. Selected bond lengths (Å) and angles (deg): X_COT̶–Nd1 = 1.894, Nd1–X_COT̶–Nd3 = 2.164, X_COT̶–Nd2 = 2.156, Nd2–X_COT̶–Nd1 = 1.964, C_COT̶–Nd1 = 2.622(4)–2.688(4), Nd1–C_COT̶–Nd2 = 2.81(4)–2.91(4), C_COT̶–Nd2 = 2.80(4)–2.88(4), Nd2–C_COT̶–Nd1 = 2.62(4)–2.67(4); X_COT̶–Nd1–X_COT̶–Nd2 = 176.1, X_COT̶–Nd2–X_COT̶–Nd1 = 175.6, Nd1–X_COT̶–Nd2–Nd3 = 177.9, X_COT̶–Nd1–X_COT̶–Nd2–Nd3 = 179.3. The evaluated unit cell parameters A: a = 20.217(4), b = 21.617(4), c = 22.597(3) Å, α = 90°, β = 90°, γ = 90°. Intensities were corrected for Lorentz and polarization effects. Final R₁ = 0.0392, wR₂ = 0.0912, |F| > 2σ(|F|).


(12) Synthesis of 2: solid [Li(THF)]₄[Nd(COT)₃] (1; 2.13 mmol, 2.0 g) was added to a stirred suspension of CoCl₂ (1.16 mmol, 0.15 g) in toluene (150 mL) at room temperature. The reaction mixture was stirred for 24 h and refluxed for an additional 5 h, causing the formation of a black precipitate. After filtration the solvent was evaporated under vacuum. (72% isolated yield) in this unexpected redox process is illustrated in Scheme 1. In the course of the reaction, one of the diatomic COT ligands in 1 is oxidized to 1,4-bis(trimethylsilyl)cyclooctatetraene (admixed with its 1,6 isomer), which was isolated from the concentrated mother liquid and identified unambiguously by comparison with the NMR data (1H, 13C) of an authentic specimen. Apparently two important factors contribute to the success of this novel synthetic route. One is certainly the enhanced solubility of the product imparted by the use of the bulky, silyl-substituted COT ligands. The other is the heterogeneous reaction in a nonpolar solvent (toluene), which prevents the formation of solvated species. It was shown in early work by DeKock et al. that Ln₃(COT)₃-triple-deckers formed by cocondensation techniques afforded the solvated species [Ln(COT)(THF)]₄[Ln(COT)₂] upon contact with THF.

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(14) Crystal data for complex 2: C₆₅H₇₅Nd₂Si₆C₆H₁₆, M_r = 1104.15, monoclinic, space group P2₁/n, a = 13.2914(3) Å, b = 17.2442(1) Å, c = 24.3534(4) Å, β = 102.6801(15)°, Z = 4, T = 153(2) K, μ = 2.041 mm⁻¹, green prism. Of 45491 reflections measured, 11010 were independent (R_int = 0.0708). Final R1 = 0.0407, wR2 = 0.1017 (all data). Supplementary crystallographic data can be found in the Cambridge Crystallographic Data file CCDC-740282.
Nd–C distances to the outer rings are in the ranges of 2.622(4)–2.688(4) Å for Nd1 and 2.629(4)–2.673(4) Å for Nd2. This can be compared to average Nd–C distances of 2.660(24), 2.673(16), and 2.787(19) Å reported for the Nd–(η⁸-COT) bond lengths in [Nd(COT)(THF)₂][Nd-(COT)₂].⁶a Significantly longer Nd–C distances (2.811(4)–2.917(4) Å for Nd1 and 2.805(4)–2.885(4) Å for Nd2) are found for the bridging COT ligand. The corresponding Nd–(ring centroid) distances are 1.894 Å (Nd1) and 1.906 Å (Nd2) to the outer rings and 2.164 Å (Nd1) and 2.156 Å (Nd2) to the bridging ring. These values can be favorably compared to corresponding Nd–C(ring centroid) distances of, for example, 1.957 Å in (COT)Nd(THF)₃,¹⁵ or 1.981 and 2.027 Å in (COT)Nd(μ-η⁸:η⁸-COT)Li(THF)₃.¹⁵ The most notable structural feature of 2, however, is the near-linear arrangement of the COT⁻⁻⁻ rings with (ring centroid)–Nd–(ring centroid) angles of 176.1° (Nd1) and 175.6° (Nd2), respectively, and a Nd–(ring centroid)–Nd angle of 177.9°. The observed minor deviations from perfect linearity can be traced back to repulsive interactions between methyl groups of the ring substituents. Thus far, a comparable near-linear arrangement of rings has only been achieved in the Yb(II) quadruple-decker complex Cp*Yb(μ-η⁸:η⁸-COT)Yb(μ-η⁸:η⁸-COT)YbCp*, which contains the very bulky 1,3,6-tris-(trimethylsilyl)cyclooctatetraenyl (=COT⁻⁻⁻) bridging ligand.¹⁶ In contrast, all other triple-decker compounds containing lanthanide elements comprise bent configurations.⁴ It should be noted at this stage that the reaction was initially carried out with the intention to make a heterobimetallic Nd/Co quadruple-decker sandwich complex.

In summarizing the main results of the present study, the first linear, homoleptic triple-decker sandwich complex of an f-element, (η⁸-COT⁻⁻⁻)Nd(μ-η⁸:η⁸-COT⁻⁻⁻)Nd(η⁸-COT⁻⁻⁻) (2), has been made available through a novel high-yield synthetic route involving oxidation of the anionic sandwich complex [Li(THF)₄][Nd(COT)₂] (1) with CoCl₂. Future work in this direction will show if this method can be employed to prepare other Ln₂(COT)₃ derivatives and perhaps even the parent triple-decker sandwiches Ln₂(COT)₃. In any case the Nd complex 1 represents the first true molecular model for organolanthanide-based nanowires.

Acknowledgment. This work was generously supported by the Deutsche Forschungsgemeinschaft (SPP 1166 “Lanthanoid-spezifische Funktionalitäten in Molekül und Material”). Financial support by the Otto-von-Guericke-Universität Magdeburg is also gratefully acknowledged.

Supporting Information Available: CIF file giving X-ray structural data for 2. This material is available free of charge via the Internet at http://pubs.acs.org.