Ligand Fragmentation Promoted by a Transient Low-Valent Thulium

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Summary: Dipyrrolide dianions were formed by a transient divalent Tm complex via fragmentation of the (Et_8-calix[4]tetrapyrrole)[K(DME)]$_4$ ligand during the reaction with $TmI_2(DME)_3$.

The preparation of stable and well-characterized divalent $LnI_2(DME)_3$ (Ln = Tm, Dy) salts,[1] as recently reported by Bocharev and Schumann, has provided new perspectives and fascinating possibilities for exploring the unique reactivity of strongly reducing low-valent lanthanides. These expectations are further corroborated by the recent findings of dinitrogen reduction[2] and ether cleavage[3] as obtained by Evans upon halide replacement reactions by cyclopentadienyl-based ligands on the above divalent salts. This high reactivity is particularly promising in view of the fact that these metals possess a reduction potential that is even stronger than that of divalent samarium[4] and for which a unique wealth of redox chemistry has been already discovered.

The calix[4]tetrapyrrole tetraanion has proven to be a versatile ligand in the chemistry of low-valent Sm[5] and U,[6] having provided low-valent stable complexes with which a few aspects of molecular activation have been studied. A general characteristic of this ligand system seems to be a remarkable ability not only to stabilize a variety of low-valent species but also to increase the reactivity of the metal center with respect to the Cp counterparts. This is well reiterated by the behavior of its low-valent Sm derivatives, whose higher reactivity has allowed four-electron reduction of dinitrogen[7] and reversible fixation of ethylene.[8] Finally, pyrrolide-based ligands promote cooperative interaction of several metal centers on the same substrate,[9] thus making possible multielectron redox processes and overcoming the limitation arising from the fact that each low-valent lanthanide may exclusively work as a one-electron reductant.

Given the above scenario, we became interested in probing the possibility of preparing low-valent thulium calix[4]tetrapyrrolide complexes with the aim of isolating species sufficiently stable to enable further reactivity studies. Although at this stage we could not isolate a low-valent Tm complex, here we report some unusual transformations resulting from the attack of a transient divalent Tm species on the ligand system that reiterates the presence of a high reactivity distinctively different from that of Sm(II).

The ligand Et_8-calix[4]tetrapyrrole was prepared according to published procedures[10] and its purity carefully and systematically tested via conventional analytical techniques, including NMR, TLC, and high-resolution MS. The corresponding crystalline tetrapotassium salt[6b] was also carefully inspected, via both NMR spectroscopy and hydrolytic degradation followed by TLC, for possible ligand cleavage and isomerization. The reaction of $TmI_2(DME)_2$ with (Et_8-calix[4]tetrapyrrole)[K(DME)]$_4$ was carried out in DME and under an N_2 atmosphere.[11] After suitable workup two different trivalent compounds, [(Et_8-calix[4]tetrapyrrole)Tm][K(DME)] (**1**) and [$Et_2C(C_4H_3N)_2]_3$Tm][K(toluene)]$_3$ (**2**), were isolated in analytically pure and crystalline form in 61% and 16% yields, respectively (Scheme 1). The magnetic moments of both species were as expected for trivalent Tm derivatives. Complex **1** was also prepared in 39% yield via direct reaction of $TmCl_3$ with an equivalent amount of (Et_8-calix[4]tetrapyrrole)[K(DME)]$_4$.

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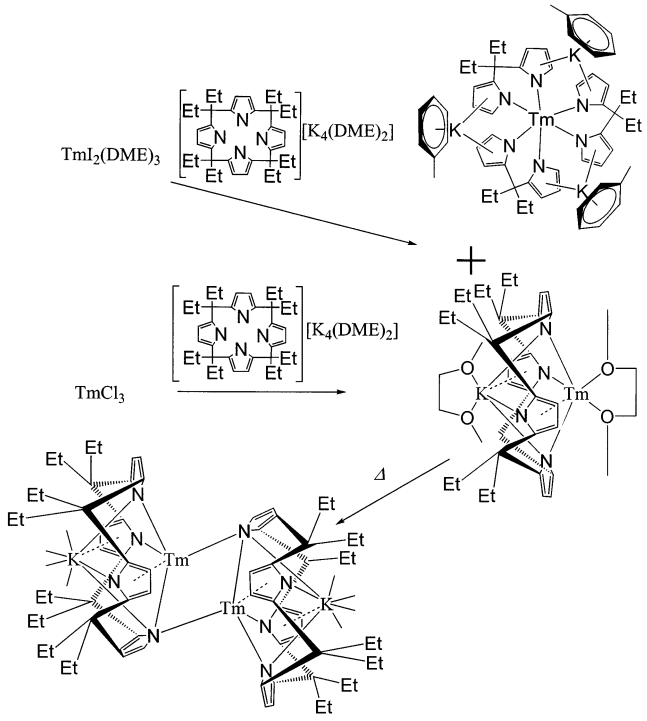
Scheme 1



The connectivity of both compounds was yielded by X-ray crystal structures.[12] Compound **1** is mononuclear and contains a DME-solvated trivalent Tm σ-bonded to the N atoms of three of the four rings of the ligand and π-bonded to the fourth (Figure 1). A K atom, also solvated by one molecule of DME and placed on the other side of the ligand plane, is both π- and σ-bonded to each couple of pyrrolide rings.

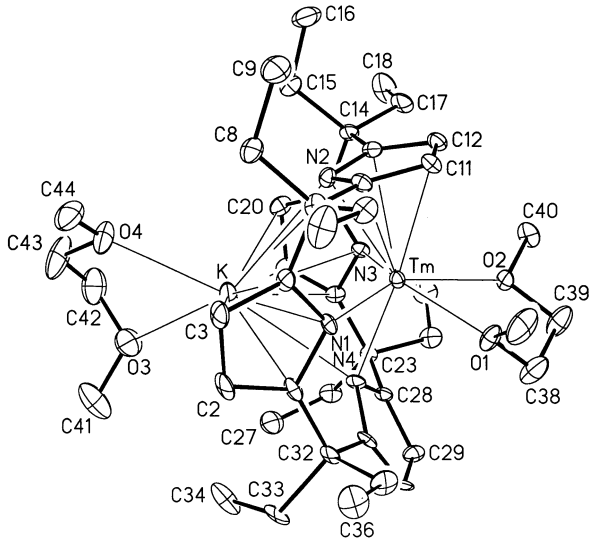


Figure 1. Thermal ellipsoid plot of **1**. Relevant bond distances (Å): Tm−N(1) = 2.366(6), Tm−N(2) = 2.491(6), Tm−N(3) = 2.377(5), Tm−N(4) = 2.373(6), Tm−O(1) = 2.437(5), Tm−O(2) = 2.447(5), Tm−C(10) = 2.631(7), Tm−C(11) = 2.803(7), Tm−C(12) = 2.826(8), Tm−C(13) = 2.647-(6), K−N(1) = 3.125(6), K−C(1) = 3.196(8), K−C(2) = 3.399(9), K−C(4) = 3.337(7), K−N(2) = 3.228(7), K−N(3) = 3.227(6), K−N(4) = 3.107(6).

The formation of **2** implies that an unprecedented ligand fragmentation has taken place in parallel to the formation of **1**. The crystal structure (Figure 2) showed the molecule formed by one trivalent Tm atom surrounded by three σ-bonded $Et_2C(C_4H_3N)_2$ dianions that provide the metal with a trigonal-antiprismatic coordination geometry. Three atoms of potassium, each π-coordinated to one molecule of toluene, complete the structure. The alkali-metal cations are connected to the ligand system exclusively, forming π-bonds to two pyrrolide rings from two ligand units.

Both complexes contain the Tm atom in the formal trivalent state. The cleavage of the macrocycle to form dipyrrolide units in **2** requires replacement of two Et_2C units by four hydrogen atoms. The nature of the organic byproduct is the factor determining whether this process is a redox reaction. Unfortunately, reiterated attempts to identify other species in the reaction mixture and to clarify the reaction pathway did not provide a clear answer. Furthermore, complex **2** contains *three* rather than two dipyrrolide units, thus indicating that the cleavage of the macrocycle was accompanied by ligand scrambling. However, the fact that **1** and **2** are both trivalent and that together they account for at least 77% of the Tm atom strongly suggests that the cleavage indeed is the result of a reductive attack.

A possible hint to understand the ligand cleavage is indirectly offered by the thermal instability of **1**. A

(11) Complex **1**. Method A. $TmI_2(DME)_3$ (2.1 g, 3.1 mmol) and $K_4(C_{36}H_{48}N_4)(DME)_2$ (2.7 g, 3.1 mmol) were placed together in a flask to which 75 mL of DME was added under an N_2 atmosphere. The solution immediately became dark cherry red. The reaction mixture was stirred for 4 h at room temperature, KI was separated by centrifugation, and the solution was concentrated to 20 mL and allowed to stand overnight at −37 °C. Colorless prisms of **1** separated (yield 1.7 g, 61%). Method B. Solid $K_4(C_{36}H_{48}N_4)(DME)_2$ (2.2 g, 2.2 mmol) was added to a suspension of $TmCl_3$ (0.6 g, 2.2 mmol) in 100 mL of DME at room temperature. A slow reaction was observed, during which the solution changed from colorless to light green. The solution was stirred for an additional 24 h, centrifuged to remove KCl, and then concentrated to about 20 mL. Colorless crystals of **1** (0.8 g, 0.9 mmmol, 39%) were obtained upon standing 72 h at 4 °C. Anal. Calcd (found) for $C_{44}H_{68}KN_4O_4Tm$: C, 57.13 (57.56); H, 7.41 (7.62); N, 6.06 (5.97). IR (Nujol mull, cm^{-1}): ν 1600 (w), 1325 (w), 1315 (w), 1302 (w), 1291 (w), 1272 (m), 1263 (s), 1243 (s), 1209 (m), 1190 (w), 1155 (m), 1116 (s), 1093 (s), 1076 (m), 1050 (s), 1017 (s), 989 (m), 968 (m), 925 (m), 885 (m), 866 (s), 848 (m), 832 (w), 788 (s), 747 (s), 677 (s), 591 (w), 571 (w), 548 (w). μ_{eff} = 7.84 μ_B/mol, room temperature, solid state. Complex **2**. The mother liquor from the preparation of **1** (method A) was evaporated in vacuo at 40 °C. The residual solid was redissoved in 30 mL of toluene at 60 °C. The resulting pale pink solution was filtered and allowed to stand at −37 °C. After 24 h light-pink needles of **2** separated (0.6 g, 16%). Anal. Calcd (found) for $C_{60}H_{72}N_6K_3Tm$: C, 61.94 (61.88); H, 6.24 (6.23); N, 7.22 (7.15). IR (Nujol mull, cm^{-1}): ν 1603 (m), 1323 (m), 1261 (s), 1210 (m), 1194 (w), 1093 (s, br), 1027 (s, br), 978 (w), 921 (s), 887 (m), 790 (s, br), 746 (m), 731 (m), 694 (s), 679 (m), 665 (m), 593 (w). μ_{eff} = 8.63 μ_B/mol, room temperature, solid state. Complex **3**. Solid $K_4(C_{36}H_{48}N_4)(DME)_2$ (2.4 g, 2.8 mmol) was added at room temperature to a suspension of $TmCl_3$ (0.8 g, 2.8 mmol) in 100 mL of DME under an N_2 atmosphere. The solution was refluxed overnight (16 h) at 100 °C, during which the solution turned light yellow. The solution was centrifuged to remove KCl and then concentrated to 20 mL and stored at 4 °C. Colorless crystals of **3** (1.0 g, 0.5 mmmol, 39%) were obtained upon standing 72 h. Anal. Calcd (found) for $C_{44}H_{68}KN_4O_4Tm$: C, 57.13 (57.48); H, 7.41 (7.55); N, 6.06 (5.93). IR (Nujol mull, cm^{-1}): ν 1601 (w), 1324 (w), 1315 (w), 1301 (w), 1288 (w), 1273 (m), 1261 (m), 1243 (s), 1208 (m), 1188 (m), 1156 (m), 1117 (s), 1093 (s), 1074 (m), 1048 (s), 1016 (m), 989 (m), 967 (m), 925 (m), 884 (m), 866 (s), 846 (m), 829 (w), 787 (s), 746 (s), 676 (m), 666 (w). [μ_{eff} = 11.54 μ_B/mol, room temperature, solid state.

(12) Crystal data are as follows. **1**: $C_{44}H_{68}KN_4O_4Tm$, M_w = 925.05, monoclinic, $P2_1/n$, a = 10.9275(9) Å, b = 37.087(3) Å, c = 11.5591(12) Å, β = 108.90(2)°, V = 4431.9(7) Å^3, Z = 4, T = 203 K, F_{000} = 1920, R1 = 0.0485, wR2 = 0.0877, GOF = 1.074. **2**: $C_{60}H_{72}N_6K_3Tm$, M_w = 1163.47, hexagonal, $P6_3$, a = 16.1671(8) Å, c = 13.9841(10) Å, V = 3165.4(3) Å^3, Z = 2, T = 203 K, F_{000} = 1200, R1 = 0.0333, wR2 = 0.0819, GOF = 1.036. **3**: $C_{44}H_{68}KN_4O_4Tm$, M_w = 925.05, monoclinic, $P2_1/n$, a = 15.5465(9) Å, b = 14.4079(9) Å, c = 21.3084(12) Å, β = 108.9160(10)°, V = 4515.2(5) Å^3, Z = 4, T = 203 K, F_{000} = 1920, R1 = 0.0327, wR2 = 0.0814, GOF = 1.077.

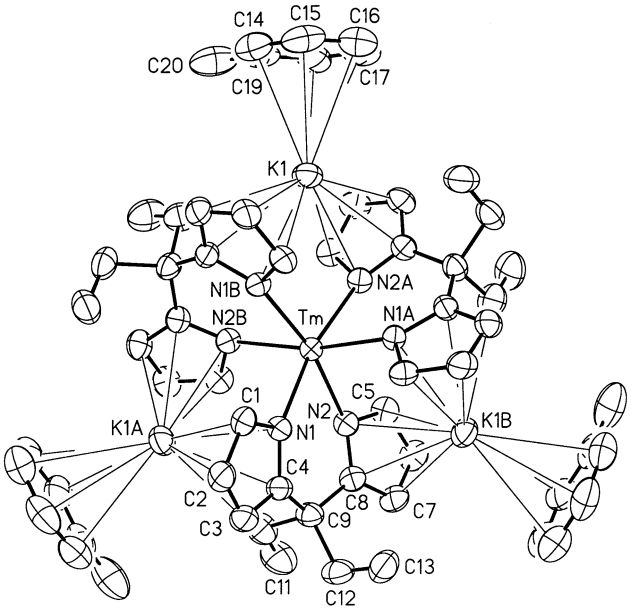


Figure 2. Thermal ellipsoid plot of **2**. Relevant bond distances (Å): Tm−N(1) = 2.332(3), Tm−N(2) = 2.39(4), K(1)−C(1B) = 2.921(5), K(1)−C(2B) = 3.053(5), K(1)−C(3B) = 3.123(6), K(1)−C(4B) = 3.066(5), K(1)−C(5A) = 3.078(5), K(1)−C(6A) = 3.020(6), K(1)−C(7A) = 3.017(6), K(1)−C(8A) = 3.104(5), K(1)−N(1B) = 2.947(4), K(1)−N(2A) = 3.166(4), K(1)−C(14) = 3.249(4), K(1)−C(15) = 3.24(6).

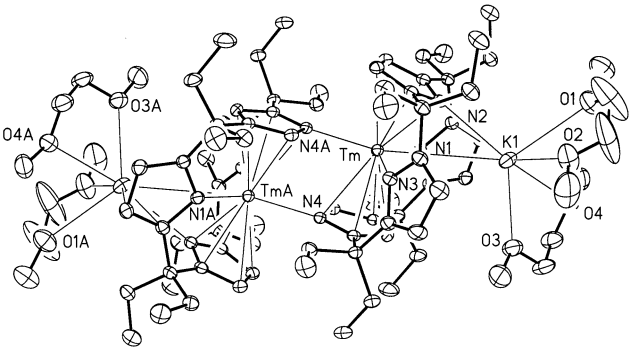


Figure 3. Thermal ellipsoid plot of **3**. Relevant bond distances (Å): Tm−N(1) = 2.385(3), Tm−N(2) = 2.552(3), Tm−N(3) = 2.380(3), Tm−N(4) = 2.838(2), Tm−N(4A) = 2.380(2), Tm−C(28) = 2.828(3), Tm−C(29) = 2.778(3), Tm−C(30) = 2.824(3), Tm−C(31) = 2.815(3), Tm−C(10) = 2.706(3), Tm−C(13) = 2.692(3), K(1)−N(2) = 2.885(3), K(1)−C(3) = 3.376(4), K(1)−C(4) = 3.190(3).

simple reflux of **1** in toluene or more simply carrying out the preparation of **1** from $TmCl_3$ in boiling DME afforded the new dimeric compound $\{[(Et_8\text{-calix-[4]-tetrapyrrole*}\}TmK(DME)_2]_2$ (**3**; the asterisk indicates an isomerized ligand (N-confused)) in 39% yield.[11]

The molecular connectivity, as clarified by an X-ray crystal structure,[12] indicated a dinuclear compound where the ligand has undergone ring isomerization by shifting the attachment of the chain of one of the four pyrrole rings from the α- to the *β*-position (Figure 3). Nevertheless, the ligand adopted the usual conformation with the thulium center. The isomerized pyrrolyl ring, as well as the other one on the opposite side of the macrocycle, are both *π*-bonded to thulium with the two centroids forming an almost linear array with the metal center. The nitrogen atoms of the other two rings *π*-bonded to the K, placed on the opposite side of the ligand, are *σ*-bonded to Tm. The N atom of the N-confused ring (containing N(4)) is *σ*-bonded to the Tm atom of a second identical unit, thus holding together the dinuclear structure.

The "N-confused"[5a,13] or isomerized polypyrrolides are often encountered in the chemistry of polypyrroles and porphyrins, where they play an important role in the biochemistry of these systems.[14] Variable amounts of the N-confused isomers may also be present as byproducts of the preparation of calix[4]tetrapyrroles and dipyrroles, usually requiring chromatographic purifications.[13a] In the case of **3**, the ligand used for the preparation was isomer-free, as indicated by its ^{13}C NMR spectrum, which did not show the resonance in the region around 112.8 ppm characteristic of an N-confused ring.[13a] Therefore, there is no doubt that, similar to the case of the Sm[5a] and U[6b] analogues, the ligand isomerization was mediated by the Tm center.

The shifting of the chain from the α- to the *β*-position of the pyrrole ring is not a redox process but does require cleavage and re-forming of the C−C bond. Thus, we speculate about the possible presence of a dissociation/association equilibrium where the stability of the N-confused ligand system is likely to provide the thermodynamic driving force for the formation of **3**. Somehow, this process *is* mediated by the Tm metal, since the free ligand and its tetrapotassium salt are both thermally robust. Therefore, it is possible that a transient divalent Tm derivative, generated during the formation of **1** and **2**, engages in a redox process, making the C−C cleavage "irreversible" and eliminating some organic fragment.

In conclusion, attempts to isolate a Tm(II) calix[4]-tetrapyrrole compound so far did not afford the expected complex but yielded instead ligand reorganization and cleavage. This is substantially different from what was observed in the chemistry of divalent Sm with the same ligand system and gives the reasonable expectation that divalent Tm will provide in the end versatile reagents for C−C and C−H bond activation. Further work is in progress.

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Supporting Information Available: Complete listings of structural parameters for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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