Carbon dioxide reduction by lanthanide(III) complexes supported by redox-active Schiff base ligands

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Here we have explored the ability of Schiff bases to act as electron reservoirs and to enable the multi-electron reduction of small molecules by lanthanide complexes. We report the reductive chemistry of the Ln(III) complexes of the tripodal heptadentate Schiff base H2trensal (2,2',2''-tris(salicylideneimino)triethylamine), [Ln(III)(trensal)], 1-Ln (Ln = Sm, Nd, Eu). We show that the reduction of the [Eu(III)(trensal)] complex leads to the first example of a Eu(II) Schiff base complex [K(µ-THF)THF2]Eu(III)(trensal)]2, 3-Eu. In contrast the one- and two-electron reduction of the [Nd(III)(trensal)] and [Sm(III)(trensal)] leads to the intramolecular reductive coupling of the imino groups of the trensal ligand and to the formation of one and two C–C bonds leaving the metal center in the +3 oxidation state. The resulting one- and two-electron reduced complexes [(K(THF)2)2Ln2(bis-trensal)], 2-Ln, and [(K(THF)2)2Ln2(cyclo-trensal)], 4-Ln (Ln = Sm, Nd) are able to effect the reductive disproportionation of carbon dioxide by transferring the electrons stored in the C–C bonds to CO2 to selectively afford carbonate and CO. The selectivity of the reaction contrasts with the formation of multiple CO2 reduction products previously reported for a U(IV)-trensal system.

Introduction

The redox-chemistry of lanthanide complexes has attracted increasing attention in recent years because of the unique reactivity of Ln(s) ions in small molecule activation and in particular their ability to reduce N2, CO2 or CO.1 However, lanthanides can only undergo one-electron transfer processes and therefore reduction of CO2 or other small molecules (N2, CO) can only occur by simultaneous electron transfer by several mononuclear complexes2 or by suitably designed polynuclear compounds.3

A novel alternative approach for implementing multielectron transfer in lanthanide complexes takes advantage of redox-active ligands for the storage and release of electrons. Redox-active ligands are increasingly used across the periodic table to facilitate metal-based multielectron transfer reactivity and catalytic activity.4 Redox-active ligands can either directly store electrons during reactivity by forming stable radicals or through the formation of new reversible C–C bonds in the ligand backbone.5

Recently it has been shown that multiple redox states can become accessible to lanthanides when associated to redox active ligands.4c,d,5a,c,e,6 However, only two systems were reported that show that the electrons stored in lanthanide complexes supported by redox active ligands can be used for the reductive transformation of substrates such as S8, Se or 9,10-phenanthrenquinone.7

Redox active ligands were also found to enable redox-switchable catalysis in rare-earth promoted polymerization chemistry.8 However, the use of redox-active ligands to implement multi-electron transfer in f elements chemistry remains significantly rarer compared to the d block. Moreover, there are so far no examples of the ability of such systems to reduce less reactive molecules such as carbon dioxide.

The ability of Schiff bases to act as electron reservoirs and to enable the multi-electron reduction of small molecules such as carbon dioxide has been identified in complexes of d block metals9 and more recently in complexes of uranium.5d,10

In contrast, the use of Schiff base ligands in lanthanide chemistry has been essentially limited to Ce(IV)11 and Ln(III) complexes that have found application as efficient Near-IR and visible luminescence emitters12,13 and have shown attractive physical properties.14
The reductive chemistry of lanthanide Schiff base complexes remains so far largely unexplored.6,7b,15

Our group demonstrated that the tetradeinate salophen Schiff base salophen (N,N′-disalicylidene-o-phenylenediaminate) acts as redox active ligand also when combined to lanthanide ions.6b Notably we showed that the reduction of monoligand and bis-ligand Ln(III) complexes of salophen results in the reduction of the imino groups of the ligand followed by formation of intermolecular or intramolecular C–C bonds (Scheme 1). The electrons stored in the C–C bonds could be used in the reduction of I₂ or 9,10-phenanthrenequinone but could not effect the reduction of less reactive substrates such as carbon dioxide.

Here we report the reductive chemistry of the Ln(III) complexes of the tripodal heptadentate Schiff base H₄trensal (2,2′,2″-tris(salicylideneimino)triethylamine), [LnIII(trensal)], 1-Ln (Ln = Sm, Nd, Eu). [LnIII(trensal)] complexes have been previously synthesised and crystallographically characterized for a wide range of ions.16 These complexes have attracted significant interest for their magnetic properties14 but their reductive chemistry was never explored. Here we show that the reduction of the [EuIII(trensal)] leads to the Eu(II) analogue. In contrast the one- and two-electron reduction of the [NdIII(trensal)] and [SmIII(trensal)] leads to the intermolecular reductive coupling of the imino groups of the trensal ligand and to the formation of one and two C–C bonds leaving the metal center in the +3 oxidation state. The resulting reduced complexes are able to effect the reductive disproportionation of carbon dioxide by transferring the electrons stored in the C–C bonds to CO₂ to selectively afford carbonate and CO. The selectivity of the reaction contrasts with the formation of multiple CO₂ reduction products previously reported for a U(IV)-trensal system.10c

**Experimental section**

**Materials and methods**

**General considerations.** Unless otherwise noted, all manipulations were carried out at ambient temperature under an inert argon atmosphere using Schlenk techniques and an MBraun glovebox equipped with a purifier unit. The water and oxygen levels were always kept at less than 1 ppm. Glassware was dried overnight at 150 °C before use.

**NMR experiments.** NMR experiments were carried out using NMR tubes adapted with J. Young valves. 1H and 13C{1H} NMR spectra were recorded on a Bruker 400 MHz spectrometer. NMR chemical shifts are reported in ppm with solvent residual signal as internal reference.

**Elemental analyses.** Elemental analyses were performed using a Thermo Scientific Flash 2000 Organic Elemental Analyzer at the Institute of Chemistry and Chemical Engineering at EPFL.

**Starting materials.** Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. The solvents were purchased from Aldrich or Cortecnet (deuterated solvents) in their anhydrous form, conditioned under argon and vacuum distilled from K/benzophenone (toluene, hexane, pyridine and THF). The ligand H₄trensal18 and the K₃trensal19 ligand salt were prepared according to published procedures. 13CO₂ (93.13% 13C) was purchased from Sigma Aldrich and used without purification. [SmL₃(THF)₂] was prepared according to a published procedure20 and the number of coordinated solvent molecules was determined via quantitative 1H NMR spectroscopy.

**Synthetic procedures**

1-Ln were prepared by reacting 1 equiv. of K₂trensal salt with the anhydrous [LnX₃] (Ln = Sm, Nd; X = OTf, I) precursors in THF. Because of the low solubility of the 1-Ln complexes in THF we did not attempt the separation of the potassium salts and the resulting crude mixture was used as such for further reduction. The 1-Ln complexes were characterized by 1H NMR spectroscopy.

![Scheme 1](Image)

**Scheme 1** The two-electron reduction of mono- (top) and bis- (bottom) Schiff base complexes of Nd(III) with alkali metals leads to intermolecular (top) or intramolecular C–C bond formation (bottom).

1-Nd. 1H NMR (pyr-d₅, 400 MHz, 298 K) δ = 27.20 (s, 3H), 11.28 (s, 3H), 9.29 (s, 3H), 8.14 (s, 3H), 7.28 (s, 3H), 4.15 (s, 6H) and −5.28 (s, 6H).

1-Sm. 1H NMR (pyr-d₅, 400 MHz, 298 K) δ = 8.81 (d, 3H), 8.76 (s, 3H), 7.13 (t, 3H), 6.83 (t, 3H), 6.79 (d, 3H), 3.02 (s, 6H) and −0.42 (s, 6H).

1-Eu. 1H NMR (pyr-d₅, 400 MHz, 298 K) δ = 9.12 (s, 6H), 7.18 (s, 3H), 5.68 (s, 3H), 3.84 (s, 3H), 3.09 (s, 3H), 1.36 (s, 6H) and −23.78 (s, 3H).

**Synthesis** [(K(THF)₃)₂Nd₂(bis-trensal)]. 2-Nd. An off-white suspension of trensalK₂ (86.0 mg, 0.150 mmol, 1 equiv.) in THF (2.0 mL) was added to the light blue solid [NdL₃(THF)₃] (78.9 mg, 0.150 mmol, 1 equiv.) and the resulting suspension was stirred for 3 h at room temperature affording an off-white
A bronze suspension of KC₈ (20.2 mg, 0.150 mmol, 1 equiv.) in THF (1.0 mL) was added and the reaction mixture was stirred at room temperature for 3 h. The resulting dark grey suspension was filtered at room temperature to remove the graphite and the KI formed, yielding a yellow-orange solution. The solution was concentrated until approx. 1.5 mL. Slow diffusion of n-hexane into the solution resulted in the formation after 3 days of yellow colored X-ray quality crystals in 52.1% yield (49.5 mg). ¹H NMR (THF-d₈, 400 MHz, 298 K) δ = 25.76 (2H), 24.44 (2H), 20.85 (2H), 18.69 (2H), 14.13 (2H), 13.92 (2H), 13.18 (2H), 12.67 (2H), 11.89 (2H), 11.83 (2H), 9.33 (2H), 8.78 (4H), 7.25 (4H), 5.92 (2H), 5.00 (2H), 4.86 (2H), −2.50 (2H), −4.34 (2H), −6.12 (2H), −6.61 (2H), −12.50 (2H), −13.89 (2H), −18.19 (2H), −22.26 (2H), −27.35 (2H). Elem. anal. calc. (%) for [K₂Nd₂(bis-trensal)] : C, 50.76%; H, 4.26%; N, 8.77%. Found: C, 50.38%; H, 4.26%; N, 8.36%.

Synthesis [K(THF)₃]₂Sm₂[bi-s(trensal)], 2-Sm. An off-white suspension of trensalK₃ (43.4 mg, 0.0753 mmol, 1 equiv.) in THF (2.5 mL) was added to a suspension of [SmI₃] (40 mg, 0.0753 mmol, 1 equiv.) in THF (2.5 mL). The resulting off-white suspension was stirred at room temperature for 4 h affording a pale yellow suspension. Then a bronze suspension of KC₈ (10.1 mg, 0.0753 mmol, 1 equiv.) in THF (1.0 mL) was added and the reaction mixture was stirred at room temperature for 4 h. The resulting dark grey suspension was filtered to remove the graphite and the KI formed during the reaction, yielding a pale orange solution. Slow diffusion of hexane into the solution afforded 38 mg of compound (70% yield). ¹H NMR (THF-d₈, 400 MHz, 298 K) δ = 8.78 (d, 2H), 8.04 (d, 2H), 7.86 (m, 4H), 7.68 (br, 2H), 7.64 (d, 2H), 7.06 (m, 4H), 6.53 (t, 2H), 6.39 (d, 2H), 5.97 (br, 2H), 5.82 (t, 2H), 5.42 (m, 6H), 4.44 (m, 4H), 2.51 (br, 2H), 2.43 (br, 4H), 1.05 (d, 2H), 0.92 (d, 2H), 0.10 (d, 2H) −0.58 (br, 2H), −1.27 (d, 2H), −2.63 (br, 2H), −9.32 (br, 2H). Elem. anal. calc. (%) for [K₂Sm₂(bis-trensal)] (THF)₂: C, 52.28%; H, 5.07%; N, 7.62%. Found: C, 52.18%; H, 4.73%; N, 7.24%. Crystals of 2-Sm suitable for X-ray diffraction were obtained by storing a concentrated solution of the compound in THF at −40 °C.

Synthesis [(K[µ-THF](THF)]₃[Eu(THF)(trensal)]], 3-Eu. An off-white suspension of trensalK₃ (50.1 mg, 0.0843 mmol, 1 equiv.) in THF (2.5 mL) was added to a suspension of [Eu(OTf)₃] (50.5 mg, 0.0843 mmol, 1 equiv.) in THF (2.5 mL). The resulting off-white suspension was stirred at room temperature for 4 h affording an off-white suspension. Afterwards a bronze suspension of KC₈ (11.4 mg, 0.0843 mmol, 1 equiv.) in THF (1 mL) was added and the reaction mixture was stirred at room temperature for 4 h. The resulting deep purple suspension was filtered, affording a deep purple solution. Slow diffusion of hexane into a THF solution of the complex afforded 44.3 mg of compound (75% yield). Elem. anal. calc. (%) for [KEu(trensal)] (THF)₀.₇₅: C, 51.43%; H, 4.75%; N, 8.00%. Found: C, 51.16%; H, 4.83%; N, 7.71%. Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a THF solution of 3-Eu.

Synthesis [(K(THF)]₃[(K(THF)]₃)[Sm_2(cyclo-trensal)], 4-Sm. A suspension of trensalK₃ (43.4 mg, 0.0753 mmol 1 equiv.) in THF (2.5 mL) was added to a suspension of [SmI₃] (40 mg, 0.0753 mmol 1 equiv.) in THF (2.5 mL) and left to react at room temperature overnight. A bronze suspension of KC₈ (93.2 mg, 0.689 mmol, 3 equiv.) in THF (2.0 mL) was added and the mixture was stirred at room temperature for 5 h affording a dark orange suspension. The mixture was filtered at room temperature to remove the graphite and the KI formed during the reaction, affording a dark orange solution. Slow diffusion of n-hexane into the THF solution afforded after one night 45 mg of compound (77% yield). ¹H NMR (THF-d₈, 400 MHz, 298 K) δ = 9.23 (4H), 8.88 (2H), 8.70 (2H), 8.30 (4H), 8.11 (2H), 7.19 (8H), 6.45 (8H), 5.22 (4H), −0.63 (s, 2H), −1.13 (4H), −4.06 (4H), −5.06 (2H), −6.19 (4H), −9.12 (4H). Elem. anal. calc. (%) for [K₂Sm₂(cyclo-trensal)](THF)₂: C, 49.64%; H, 4.82%; N, 7.24%. Found: C, 49.81%; H, 4.55%; N, 7.11%. Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a THF solution of 4-Sm.

Reactivity with CO₂

Reaction of 2-Ln with 2 equiv. of ¹³CO₂. Complexes 2-Ln were prepared in situ as described above. After removal of KI and graphite, the resulting yellow solution of 2-Ln was degassed by freeze–pump–thawing and 2 equiv. of ¹³CO₂ were added. Upon addition of CO₂ the solution turned immediately from yellow to colorless and a pale yellow precipitate formed. The characterization of the product was prevented by its low solubility in organic solvents.

Upon removal of the solvent in vacuo and after dissolution in basic D₂O (pD = 13.4), quantitative ¹³C{¹H} NMR experiments were performed (¹³C-labelled sodium acetate as reference). The yields in carbonate correspond to 96% and 98% for Nd and Sm, respectively.

Reaction of 4-Ln with 4 equiv. of ¹³CO₂. Complexes 4-Ln were prepared in situ as described above. After removal of KI and graphite, the resulting dark orange solution of 4-Ln was degassed by freeze–pump–thawing and 4 eq. of ¹³CO₂ were added.
added. Upon addition of CO₂ the solution turned immediately from yellow to colorless and a pale yellow precipitate formed.

The characterization of the product was prevented by its low solubility in organic solvents. The ¹H NMR spectrum of the reaction mixture taken immediately after addition of 4 equiv. of ¹³CO₂ showed only signals assigned to complex 1. The ¹³C{¹H} NMR spectrum of the reaction mixtures (THF-d₈, 100 MHz, 298 K) showed a signal at δ = 181.30 ppm of ¹³CO₂.

Upon removal of the solvent in vacuo and after dissolution in basic D₂O (pD = 13.4), quantitative ¹³C{¹H} NMR experiments were performed (¹³C-labelled sodium acetate as reference).

The yields in carbonate correspond to 100% and 97% for Nd and Sm, respectively.

X-ray crystallography

The diffraction data for the analysed crystal structures were collected at low temperature using Cu (2-Nd, 3-Eu) or Mo (2-Nd, 4-Sm, 4-Nd) Kα radiation on a Rigaku SuperNova dual system in combination with Atlas type CCD detector. The data reduction and correction were carried out by CrysAlisPro.²¹

The solutions and refinements were performed by SHELXT²² and SHELXL,²³ respectively. The crystal structures were refined using full-matrix least-squares based on F² with all non-H atoms defined in anisotropic manner. Hydrogen atoms were placed in calculated positions by means of the "riding" model.

Compound 2-Nd displayed 2 disordered THF molecules. Their treatment was carried out by the split method; some similarity restraints (SADI and SIMU cards) were applied to bond distances and to the ADPs. Compound 2-Sm showed a quite similar disorder but the entire K(THF)₃⁺ moiety was involved; it was rather easy to identify two different positions of K but the splitting of the THFs did not work and this explains why their occupancies is less than 1 and why some restraints were used (ISOR, DFIX and RIGU cards). The crystal structure of 3-Eu showed the disorder of one THF. DFIX and SIMU restraints were used to get reasonable parameters. The crystal structures of 4-Sm and 4-Nd were also affected by the same kind of disorder, e.g. 2 and 3 disordered THF molecules; some similarity restraints were imposed on the bond distances (SADI and DFIX commands), some were used for the ADPs (SIMU and RIGU commands).

Owing to the high degree of displayed disorder, the free solvent molecules (about 1 THF) were removed by applying the SQUEEZE algorithm of PLATON.²⁴

Electrochemical methods

Cyclic voltammetry data were carried out at room temperature in an argon-filled glovebox described above. Data were collected using a Biologic SP-300 potentiostat connected to a personal computer. All samples were saturated in complex with 0.1 M [Bu₄N][PF₆] supporting electrolyte in THF solution. The experiments were carried out with a platinum disk (d = 5 mm) working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. The experiments were repeated on independently synthesized samples to assess the reproducibility of the measurement. Potential calibration was performed at the end of each data collection cycle using the ferrocene/ferrocenium ([C₆H₅]₂Fe)⁺⁻⁻ couple as an internal standard.

Results and discussion

Reduction of [Ln(trensal)] complexes

The previously reported 1-Ln complexes were prepared "in situ" using a salt metathesis procedure previously used in the synthesis of the [U⁴⁺(trensal)] complex.²⁹

This procedure avoids the presence of protic solvent or residual water in the final product that would be difficult to remove. The addition of one equivalent of KC₈ to the 1-Ln complexes in THF afforded the complexes [[K(THF)₃]₂Ln₂(bis-trensal)], 2-Ln in 70% (Ln = Sm) and 53% (Ln = Nd) yield (Scheme 2). Alternatively, 2-Sm can also be obtained from the reaction of the divalent [SmI₂] with one equiv. of the trensalK₃ ligand salt (Fig. S3†). The ¹H NMR spectra of 2-Nd and 2-Sm (Fig. S1 and S2† respectively) in THF-d₈ show the presence of 27 overlapping signals in the paramagnetic range, consistent with the presence of fully asymmetric solution species and in agreement with the solid state structure.

The two dinuclear 2-Nd and 2-Sm complexes crystallize in the C2/c group and are isostructural. Their solid-state molecular structure shows respectively the presence of two neodymium(m) (Fig. 1) and samarium(m) (Fig. S12†) cations coordinated by the octa-anionic bis-trensal ligand, formed by C–C coupling of two imino groups of the original trensal ligands. The formation of the bis-trensal ligand was previously observed by our group during the reduction of the trensal ligand by UI₃ yielding the [UIV(trensal)] complex.¹⁰ The resulting dianucleating ligand in 2-Ln holds the two metal centres in close proximity (Nd–Nd distance = 3.8922(3) Å and Sm–Sm distance = 3.8389(4) Å (Table 1).
The 2-Ln complexes present two equivalent Ln centers octa-coordinated by two imino nitrogen (avg Ln–N_{im} = 2.67(4) Å for Nd and 2.63(5) Å for Sm), one amino nitrogen (Ln–N_{am} = 2.782 (2) Å for Nd and 2.745(4) Å for Sm), two bridging amido nitrogen atoms (Ln–N_{amido} = 2.478(2) Å for Nd and 2.50(7) Å for Sm) and three phenoxide oxygen atoms (avg Ln–O = 2.38(4) Å for Nd and 2.36(4) Å of the bis-trensal ligand. Two of the phenoxide oxygen atoms (O1 and O3) coordinate a potassium cation, which is also bound to three molecules of THF.

The structural parameters of 2-Ln, as summarized in Table 1, clearly show that the reduction has occurred on the imino groups of the ligands rather than on the metal ions. The values of the C–C bond distance (1.573(6) Å for 2-Nd and 1.586(7) Å for 2-Sm) compare well with the intermolecular C–C bonds found in the previously reported [Na₂U(bis-salophen)] (1.59(7) Å),

\[ \text{Nd} - \text{N}_{\text{amido}} = 2.478(2) \text{ Å} \]

and \[ \text{U}_{2}\text{bis}^4\text{BuTrensal}] (1.59(2) Å) for the 9c complexes. The C–N_{amido} bond distances in 2-Nd (1.487(4) Å) and in 2-Sm (1.485(5) Å) are longer than the C–N_{amino} bond distances (1.287(2) Å in 2-Nd and 1.288(6) Å in 2-Sm) which remain similar to those reported\(^{16a,b}\) for 1-Nd (1.280(6) Å) and 1-Sm (1.274(8) Å), respectively. The Ln–N_{amido} bond distances for 2-Nd (2.48(7) Å) and 2-Sm (2.50(7) Å) are shorter than the Ln–N_{amino} distances (2.57(4) Å for 1-Nd and 2.531(4) Å for 1-Sm) found in the 1-Ln complexes. These values are in agreement with the presence of the bis-amido, tetra-imino, hexaphenolate bis-trensal ligand resulting from the reductive coupling of two imino moieties from two different trensal units. These distances also compare well with the values reported\(^{7b}\) for the complex [Nd(bis-salophen)]\(^{3−}\) (Nd–N_{am} (2.45(2) Å) and Nd–N_{am} (2.64(4) Å) which also presents a reduced Schiff base ligand.

In contrast with what observed with Nd and Sm the reduction of 1-Eu did not afford the Eu(u) bis-trensal complex, but led instead to the reduction of the metal center and formation of the Eu(u) complex of the trensal ligand, \([\text{[K(µ-THF)}\text{(THF)}_2\text{Eu}^\text{II(trensal)}]_2]\), 3-Eu (Scheme 3). No \(^1\text{H}\) NMR spectrum was observed as expected for the 4f\(^7\) configuration of Eu(u).

The molecular structure of 3-Eu (Fig. 2) shows two potassium-bound Eu(u)(trensal) complexes bridged by a THF molecule. Each Eu(u)(trensal) moiety binds a potassium counterion through three phenoxide oxygen atoms, the latter being also coordinated by one terminal THF molecule and one bridging THF.

The europium centers are heptacoordinated by the amino nitrogen atoms (Eu–N_{am} = 2.826(4) Å), the three imino nitrogen atoms (avg Eu–N_{im} = 2.66(4) Å) and the three phenoxide oxygen atoms (avg Eu–O = 2.45(1) Å) from the trensal ligand. The average Eu–N and Eu–O distances are consistent with the formation of a divalent europium complex,\(^{21}\) and the C–N distances (1.272(6) Å) remain unchanged compared to those

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**Table 1** Mean values of selected bond lengths (Å) in 2-Nd, 2-Sm, 3-Eu, 4-Nd and 4-Sm compared to the values reported for 1-Ln,\(^{16a,b}\) and for the [Nd(bis-salophen)]\(^{3−}\) and [Nd₂(cyclo-salophen)]\(^{2−}\) complexes\(^{7b}\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>C–C</th>
<th>C–N_{im}</th>
<th>C–N_{am}</th>
<th>M–N_{im}</th>
<th>M–N_{am}</th>
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<td>2.535(7)</td>
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<td>—</td>
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<td>2.679(9)</td>
<td>2.61(12)</td>
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found in the crystal structure of the H3trensal ligand (average 1.266(3) Å). The Eu–N distances in 3-Eu are longer compared to those reported for the [Eu(H3trensal)] complex (Eu–Naminino = 2.761(9) Å, Eu–Nimino = 2.535(7) Å, Eu–O = 2.233(6) Å), as expected due to the larger radius of the reduced metal center. The structural parameters show that the reduction occurred at the metal center rather than in the ligand like in 2-Nd and 2-Sm.

These results indicate that while for 1-Nd and 1-Sm the reduction of the ligand occurs before the reduction of the metal center, in the case of 1-Eu reduction occurs first on the metal center probably due to its lower redox potential (Eu3+/Eu2+ = −0.35 V, Sm3+/Sm2+ = −1.55 V, Nd3+/Nd2+ = −2.6 V, referenced vs. NHE). This result differs significantly from what was observed with the Eu(III) complex of the salophen Schiff base K[Eu(salophen)], where the reduction following the addition of alkali metal occurs on the ligand scaffold.7b These results indicate that the trensal ligand is better suited than the salophen ligand to stabilize the divalent oxidation state in europium compounds.

Complex 3-Eu is the first example of a divalent europium complex supported by a Schiff base ligand. Only one complex of a divalent lanthanide (Sm(III)) supported by a Schiff base ligand had been reported so far.6f

Complexes 2-Nd and 2-Sm can be further reduced in a controlled fashion by the addition of excess KC8 (three equiv.) to a white suspension of [Ln(trensal)], 1-Ln in THF affording the complexes [(K(THF))3Ln2(cyclo-trensal)], 4-Ln in 77% (Ln = Sm) and 78% (Ln = Nd) yield (Scheme 4). When the reduction was conducted with only 2 equiv. of KC8 it yielded a mixture of 2-Ln and 4-Ln. The 1H NMR spectrum of 4-Nd (Fig. S4†) shows rather broad signals suggesting the presence of fluxional solution species. In contrast the 1H NMR spectrum of 4-Sm (Fig. S5†) show only one set of 14 well resolved signals suggesting the presence of D2h symmetric solution species in agreement with the observed D2h pseudo-symmetry of the solid state structure.

The two complexes 4-Nd and 4-Sm crystallize in the P21/n group and are isostructural. The molecular structure of the 4-Ln complexes shows the presence of two Nd(III) (Fig. 3) or Sm(III) cations (Fig. S13†) bound by the dodecadentate deca-anionic amidophenolate macrocyclic ligand cyclo-trensal produced in the reductive coupling of two imino groups of the trensal ligand. The dinucleating cyclo-trensal ligand in 4-Ln holds the two Ln centers in close proximity, at Ln–Ln distances (3.42619(19) Å for Nd and 3.4077(4) Å for Sm) shorter than those found in 2-Ln (3.8922(3) Å for Nd and 3.8389(4) Å for Sm) or in the macrocyclic complex in [Nd2(cyclo-salophen)]4− (Nd–Nd = 3.54(1) Å)7b (Table 1).

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Fig. 2 Molecular structure of complex 3-Eu (50% probability ellipsoids). Hydrogen atoms were omitted for clarity.

Scheme 4 Synthesis of [(K(THF))2K(THF)Ln2(cyclo-trensal)], 4-Ln, Ln = Nd, Sm.

Fig. 3 Molecular structure of complex 4-Nd (C–C bonds between imine highlighted in yellow, 50% probability ellipsoids Hydrogen atoms, potassium atoms and THF molecules were omitted for clarity.)
The 4-Ln complexes present two equivalent Ln(n) centers in a tricapped trigonal prismatic geometry nonacoordinated by four amido nitrogens (avg Ln–N amid = 2.6 (1) Å for Nd and 2.61(12) Å for Sm), one imino nitrogen atom (Ln–N imino = 2.6895(16) Å for Nd and 2.679(9) Å for Sm), one amino nitrogen atoms (Ln–N amino = 2.7209(15) Å for Nd and 2.706(3) Å) and three phenoxy oxygen atoms (avg Ln–O = 2.47(1) Å for Nd and 2.45(1) Å for Sm). The six phenoxy oxygen atoms coordinate also four potassium counterions, whose coordination sphere is completed by THF molecules.

When comparing the selected bond distances shown in Table 1, the C–N amid bond distances (mean C–N amid = 1.472(4) Å for Nd and 1.470(3) Å for Sm) of the ligand backbone are much longer than those of the remaining imino group (C–N imino = 1.273(3) Å for Nd and 1.263(6) Å for Sm) or the values observed for the free ligand (avg. C–N amid = 1.266(3) Å). These data are in agreement with the presence of four amido groups. The value of the C–C bond distances (1.558(3) Å for Nd and 1.560(3) Å for Sm) fall in the range of those reported for the previously observed for the free ligand (avg C–N amid = 1.472(4) Å for Nd and 1.470(3) Å for Sm). The presence of carbonate indicated that the electrons released in the reduction process were stored in the C–C bonds of the cyclo-trensal ligand similarly to the previously reported K3[Ln(bis-Rsalophen)] complexes. The reactivity of the 2-Ln complexes also differs from that of the recently reported U(IV) analogue, [U2(bis-trensal)]10− that only undergoes insertion of the CO2 into the U–N amid bond. In spite of the presence of the same binucleating bis-trensal ligand the molecular structure of the 2-Ln complexes differs significantly from that of the U(IV) complex [U2(bis-trensal)]. Notably in the structure of [U2(bis-trensal)] the amid nitrogen atoms do not bridge the two metal centers as found in the 2-Ln complexes resulting in a large U−U separation at 7.311(2) Å. Such difference is probably originating from the smaller size of the U(IV) cation which prevents amido bridging to occur.

The difference in reactivity between the 2-Ln complexes and the U(IV) complex [U2(bis-trensal)] is probably due to both structural and electronic differences. The bridging mode adopted by the amido nitrogen in 2-Ln probably results in a less basic character compared to the non-bridging amido nitrogen in [U2(bis-trensal)] preventing the insertion of CO2 into the Ln–N amid bond. Moreover, the close proximity of the Ln centers in the 2-Ln should promote CO2 activation via cooperative binding to the two metal centers.

The 4-Ln complexes contain four electrons stored in the two C–C bonds of the cyclo-trensal ligand similarly to the pre-
Previously reported cyclo-salophen complexes $K_2[\text{Nd}_2(\text{cyclo-salophen})]$ and $[\text{U}_2(\text{cyclo-salophen})]$ isolated from the reduction of salophen complexes. The cyclo-salophen complexes were found able to transfer the four electrons stored in the two C–C bonds to strongly oxidizing substrates but were not able to reduce CO$_2$ or CS$_2$. In contrast we found that the cyclo-trensal complexes 4-Ln display a dramatically different reactivity towards CO$_2$. Notably, the addition of 4 equiv. of $^{13}$CO$_2$ to a solution of 4-Ln in THF leads to an immediate color change of the solution from red/orange to pale yellow with concomitant formation of a precipitate. The $^1$H NMR spectra recorded after formation of the solid products showed the disappearance of the signals assigned to 4-Ln. The $^{13}$C{1H} NMR spectra recorded after one day showed the formation of $^{13}$CO (181 ppm) as only visible product in THF solution (Fig. S6†). The low solubility of the reduction product prevented its structural characterization.

However, the removal of the solvent under vacuum and the dissolution of the residue in basic D$_2$O (pD = 13.4) allowed the identification of the water soluble products. The quantitative $^{13}$C{1H} NMR spectra recorded in presence of $^{13}$AcO$^-$ as internal standard showed the formation of $^{13}$CO$_3^{−}$ in 97% (Ln = Sm) and 100% yield (Ln = Nd) (yields given with respect to the value expected from the conversion of 4 $^{13}$CO$_2$ molecules into 2 $^{13}$CO$_3^{−}$ and 2 $^{13}$CO) (Scheme 5 bottom).

These results show that the four electrons stored in the two C–C bonds of the cyclo-trensal ligands are quantitatively used for the reductive disproportionation of CO$_2$. The clean quantitative reductive disproportionation observed for the 4-Ln complexes contrasts remarkably with the multiple reaction pathways previously reported for the reaction of the analogue U(IV) complex $[\text{K(THF)}_2\text{U}_2(\text{cyclo-trensal})]$ with CO$_2$. Such pathways included reductive disproportionation of CO$_2$, insertion of CO$_2$ in the U–N$_{amido}$ bonds, CO$_2$ cleavage and further addition of the formed CO to the U–N$_{amido}$ bonds.

**Electrochemistry**

Cyclic voltammetry data were measured for complexes 1-Ln in $\sim$0.1 M THF solution of $[\text{Bu}_4\text{N}]\text{[PF}_6]$ and are presented in Fig. 4. All redox potentials are referenced against the $[(\text{C}_6\text{H}_5)_2\text{Fe}]^{10}$ redox couple. Complexes 1-Nd and 1-Sm showed similar behavior, but the voltammogram of 1-Eu did not show any clear reduction event at any scan rates (see Fig. S22†).

The voltammograms of complexes 1-Nd and 1-Sm show two distinct irreversible reduction events at $E_{\text{pc}} = −2.91$ V and $−3.58$ V (Fig. S16–S18†) and $E_{\text{pc}} = −2.96$ V and $−3.82$ V (Fig. S19–S21†), respectively associated with a series of irreversible redox processes in the range $−0.55$ to 0.3 V. The irreversible reduction events observed for 1-Sm and 1-Nd can be assigned to ligand based redox processes resulting in formation of the first C–C bond in 2-Ln and to the formation of a second C–C bond in 4-Ln. However, the voltammograms of 2-Ln and 4-Ln complexes measured in the same conditions (in the presence or absence of cryptand) did not show clear redox events probably due to the strong interaction with potassium cations.

Previously reported electrochemistry studies$^{10c}$ of the analogous U(iv) complex $[\text{U(Trensal)}][\text{OTf}]$, showed two similar irreversible ligand-based reduction events occurring at higher potentials ($E_{\text{pc}} = −2.03$ V and $−2.50$ V for the formation of the first and the second C–C bond, respectively).

The ability of complex 2-Ln to reduce CO$_2$ compared to the lack of reductivity towards CO$_2$ reduction reported for the analogous mono-reduced U(iv) complex is probably due to its lower redox potential associated to a higher accessibility to the electrons stored in the ligand framework.

**Conclusions**

In summary we have reported the reductive chemistry of Ln(mm) complexes of the tripodal heptadentate trensal$^{−}$ ligand. We showed that, depending on the metal, the reduction can occur at the metal center affording a stable Eu(mm)-trensal complex or can lead to the reductive coupling of two imino groups of two trensal ligands and to the formation of an intermolecular C–C bond where two electrons are stored. In the case of the Nd and Sm trensal complexes the one-electron reduction leads to the isolation of dinuclear Ln(mm) complexes of the bis-trensal ligand. Further reduction results in the formation of a second C–C bond from the intramolecular reductive coupling of two imino groups of the bis-trensal ligand to afford a dinuclear macrocyclic complex of the cyclo-trensal ligand where two Ln(mm) ions are held together in close proximity. These results show that the reductive chemistry of Ln(mm) Schiff bases provide an attractive tool for the synthesis of polynuclear Ln(mm) complexes.Remarkably the electrons stored in the C–C bonds of the bis-trensal and cyclo-trensal complexes become available for the reduction of carbon dioxide to selective afford CO and carbonate.

![Fig. 4](Image)  
**Fig. 4** Cyclic voltammogram of complexes 1-Nd (grey), 1-Sm (orange) and 1-U (yellow) from ref. 10c in $−0.1$ M $[\text{Bu}_4\text{N}]\text{[PF}_6]$ THF solution at a 100 mV s$^{−1}$ scan rate.
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Conflicts of interest

There are no conflicts to declare.

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Notes and references


