Hydroxylaminato yttrate and samarate complexes

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Received 18th May 2007, Accepted 31st May 2007
First published as an Advance Article on the web 13th June 2007
DOI: 10.1039/B707575H

The first homoleptic anions of hydroxylaminato ate-complexes of yttrium and samarium of the formulae K[M(ONPr2)i] (M = Y, Sm) have been prepared and structurally characterised featuring variations of the hapticity of their ONPr2 ligands leading to different chain connectivities in their solid state aggregates.

The recent rapid development of alkoxide and aryloxide chemistry of the rare earth elements1 was mainly focused on generating new molecular precursors metal oxide materials2 and for applications in catalytic processes including polymerization and ring opening reactions.3 The use of small alkoxide ligands generally leads to the formation of large clusters with complicated stoichiometries and difficult accessibility of the metal atoms.4 Moreover, obtaining simple chloride-free alkoxides has always been a challenge. We realized that the anions of N,N-dialkylated hydroxylamines could prove to be ideal ligands for achieving accessible metal atoms in their rare earth complexes, since they possess an extra N-donor function directly adjacent to the O-atom, binding to the metal centre. This leads to a saturation of the metal ion’s demand for electron density by a minimum of atoms and steric bulk in their coordination sphere. Up to now, there is only one report by Evans et al. of a hydroxylamine-related complex in rare earth chemistry, the compound [(C5H6Me4NO)2Sm(eq)Pr2] containing ligands introduced by the stable radical TMPO in a redox process.5 Only this year Batten, Deacon et al. have reported homoleptic 12-coordinate lanthanoid complexes with loosely related π-nitroso ligands, which can alternatively be seen as oximates [La(ON=C(OMe)2)]6.7 Herein we report two compounds with sterically more flexible hydroxylamine ligands than the TMPO anion, demonstrating the principle of hemilabile N–O ligands with two directly adjacent donor sites to be successfully applicable to the chemistry of the rare earth elements.

Our recent studies on hydroxylamine compounds of group 127 and 13 metals8 have given access to a wealth of new structural motifs [e.g. flexible coordination motif in (MeAl)(MeAl2)[(ON(Me)CH2)]9] and featured the N–O ligands to be unique in their flexibility of binding modes. Hydroxylamide complexes of the highly charged group 4 metal ions are monomeric compared to their alkoxide analogues.1 Hydroxylamine based ligands have been employed to achieve coordination numbers up to eight for M(ONR2) where M = Ti, Zr, Hf [R = Me, Et]10 with a minimum of organic substituent mass leading to relatively volatile compounds, even suitable for MOCVD applications.11

Resemblance of rare earth ions to those of group 4 metals in their hardness motivated us to pursue achieving monomeric lanthanide complexes.

Complexes of the type KM(ONPr2)i [M = Y (1), Sm (2)] were prepared† by the reaction of anhydrous MCl3 (M = Y, Sm) with an excess of KONPr2 in THF. Exploring these types of reactions for a long time we always experienced the formation of gels accompanied by incomplete transformations. Only after application of ultrasound did the reactions proceed further and lead to suspensions from which 1 and 2 can be isolated.

\[ \text{MCi} + 4 \text{KONPr} \rightarrow [\text{K}[\text{M(ONPr)}]_3] + 3 \text{KCl} \]

\[ \text{M} = \text{Y (1), Sm (2)} \]

The compounds were characterised by elemental analyses, by NMR spectroscopy and crystal structure determination. The 1H and 13C NMR spectra of 1 and 2 in THF-d8 solutions at RT show one set of peaks for the methine and methyl groups of the isopropyl substituent at the hydroxylamine backbone, indicating a symmetric distribution about the central metal atom in solution on the timescale of the NMR experiment. Upon cooling, the signal for the methyl groups splits into two signals, while the resonance for the methine unit stays a singlet (Fig. 1). This indicates a dynamic situation at ambient temperature and a frozen \( S_i \) symmetric situation at low temperatures with four \( n \) bonded ONPr2 groups, i.e. a total coordination number of eight at the metal centre. The exchange of the CH3 positions is then due to cleavage of the M–N bond, rotation about N–O and N inversion. Consequently, the potassium atoms would have to be independently THF solvated or highly dynamically bonded to the ligand sphere.

![Fig. 1](image-url) Variable temperature 1H (upper part) and 13C NMR (lower part) of KSm(ONPr3)3 (2) in THF-d8; * denotes signals of the solvent.

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Dalton Trans., 2007, 3124–3126
This is in contrast to the situation in the solid state, as the crystal structures$^4$ of both, 1 and 2, consist of endless chains as depicted in Fig. 2 and 3. In both cases there are two independent units of the formula K[M(ON$^\text{Pr}_2$)$_4$].

The insets in Fig. 2 and 3 show the coordination environments of one K atom and one of the Y or Sm atoms in 1 or 2 in more detail. The yttrium atom in 1 has the coordination number six, while the larger samarium atom in 2 is coordinated by seven O and N atoms. In the case of 1 two of the four ON$^\text{Pr}_2$ ligands are $\eta^1$-coordinated and the two others are linked only by their oxygen atoms. The Y–O bond lengths are between 2.099(4) and 2.114(4) Å, compare with the data of the mentioned TMPO derivative (average values: 2.203 Å$^5$) vs. 2.257(9) and 2.290(10) Å in compound 2. Surprisingly similar are the Y–N bonds with lengths between 2.463(5) and 2.478(5) Å.

In compound 2 three of the four ON$^\text{Pr}_2$ ligands are $\eta^1$-coordinate and only one is attached solely through its oxygen atom. This $\eta^1$ vs. $\eta^2$ coordination was also observed in the compound [(C$_5$H$_6$Me$_4$NO)$_2$Sm(ON$^\text{Pr}_2$)$_4$]$^i_n$, but in this compound only one of the TMPO ligands is $\eta^2$-coordinate and simultaneously $\mu^1$-O-bridging two Sm atoms leading to a total coordination number of five in this case. The higher flexibility of the alkyl groups in ON$^\text{Pr}_2$ allows obviously more of these ligands to bind more closely in a $\eta^2$ mode to the Sm atom.

The Sm–O bonds of $\eta^2$-bonded ligands are between 2.257(9) and 2.290(10) Å and those to $\eta^1$-bonded ligands 2.203 Å$^6$ on average. This parallels the situation in 1 and is consistent with the data of the mentioned TMPO derivative (average values: $\eta^1$ Sm–O 2.117, $\eta^2$ Sm–O 2.325 Å)$^6$. The Sm–N distances, which fall in a range between about 2.512(14) and 2.589(11) Å, compare

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**Fig. 2** A: Part of the crystal structure of a dimeric unit of K[Y(ON$^\text{Pr}_2$)$_4$] in 1. Shown is the asymmetric unit (in black) within an endless chain aggregate. Representation of the displacement ellipsoids is at the 50% level, C atoms are shown as circles for clarity. B and C: Coordination environments of yttrium (B) and potassium atoms (C) in K[Y(ON$^\text{Pr}_2$)$_4$] (1). Only one of each of the two Y and K atoms are shown, as the structures are similar. Selected bond lengths (Å) and angles (°): Y1–O1 2.102(4), Y1–O2 2.185(4), Y1–N2 2.463(5), Y1–O3 2.211(4), Y1–N3 2.474(5), Y1–O4a 2.103(4), K1–O1 2.846(4), K1–O2 2.703(4), K1–O6 2.945(4), K1–O7 2.702(4), K1–N1 2.752(5), K1–N6 2.979(5), O1–N1 1.435(5), Y2–O1 2.099(4), Y2–O6 2.114(4), Y2–O7 2.184(4), Y2–N7 2.478(5), Y2–O8 2.179(4), Y2–N8 2.468(5), K2–O3b 2.660(4), K2–O4 2.938(4), K2–O5 2.821(4), K2–O8 2.677(4), K2–N5 2.478(5), K2–N4 2.474(5), K2–O7 2.478(5), K2–N7 2.478(5), K2–N8 2.478(5).

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**Fig. 3** A: Part of the crystal structure of a dimeric unit of K[Sm(ON$^\text{Pr}_2$)$_4$] in 2. Shown is the repetitive unit (in black) within an endless chain aggregate. Representation of the displacement ellipsoids is at the 50% level, C atoms are shown as circles for clarity. B and C: Coordination environments of samarium (B) and potassium atoms (C) in K[Sm(ON$^\text{Pr}_2$)$_4$] (1). Only one of each of the two Sm and K atoms are shown, as the structures are similar. Selected bond lengths (Å) and angles (°): Sm1–O1 2.206(9), Sm1–O2 2.257(9), Sm1–N2 2.512(14), Sm1–O3 2.278(9), Sm1–O4 2.288(8), Sm1–N4 2.589(11), K1–O3 2.658(8), K1–O4 2.547(9), K1–O5 2.716(9), K1–O6 2.807(9), K1–N6 2.806(12), O1–N1 1.419(14), Sm2–O1 2.287(9), Sm2–O2 2.288(8), Sm2–O3 2.288(8), Sm2–O4 2.288(8), Sm2–O5 2.515(11), Sm2–O6 2.200(9), Sm2–O7 2.290(10), Sm2–N7 2.587(12), Sm2–O8 2.268(10), Sm2–N8 2.558(11), K2–O1b 2.681(9), K2–O2b 2.660(9), K2–O3b 2.660(9), K2–O4b 2.660(9), K2–O5b 2.660(9), K2–O6b 2.660(9), K2–O7b 2.660(9), K2–O8b 2.660(9), K2–O9b 2.660(9).
well with the data for the TMPO complex (2.537(6) Å) but are slightly shorter than that of a related hydrazine complex 
(Cp*Cp*Sm(HNNHPh)2)(thf), 2.610(5) Å.13

The different demand of the rare earth atoms for coordinative saturation in 1 and 2 leaves six donor contacts for coordination of the potassium atom in the case of 1, while in 2 only five such contacts are observed. Consequently the situation of the K atoms in 1 can be described as approximately symmetrically coordinated by two Y(ONPr2)3 units, each exerting η1 coordination from one and η1 coordination from the other ONPr2 ligand of the Y(ONPr2)3 unit. This unit itself is also approximately symmetrically involved in its connectivity within the chain aggregate. The K–O distances in 1 vary much more than the Y–O distances do. They cover a range from 2.677(4) to 2.945(4) Å and again the distances are shorter to the η1-coordinate ligand O atoms than to those involved in η1-coordination.

The K atoms in 2 are non-symmetrically coordinated. They receive three contacts from one Sm(ONPr2)3 unit (one η1 and one η1 coordination) and only two contacts from the other Sm(ONPr2)3 unit (two η1 coordination contacts). The distribution of K–O distances is similar to that of 1, but the contact K2–O1b is much shorter (2.681(9) Å) than the other K–O distances of η1-coordination contacts.

In essence we have demonstrated that anionic hydroxylamine ligands can be introduced into rare earth metal chemistry employing the potassium salts of these ligands, thus without the involvement of a redox process, which limited the application so far to derivatives of the stable radical TMPO and rare earth precursor compounds easily undergoing redox chemistry in their ligand periphery (Cp*). The resulting complexes contain the flexibly binding hemilabile hydroxylamine ligands.

We are grateful for support to Fonds der Chemischen Industrie, Deutsche Forschungsgemeinschaft and to the NRW International Graduate School of Chemistry, Münster (stipend to A. V.). We thank Prof. P. W. Roesky, Freie Universität Berlin, for fruitful advice and discussions.

Notes and references


