Molecular Neodymium and Yttrium Cations with the *N*,*N*-Bis[2-(pyrid-2-yl)ethyl]hydroxylaminato Ligand

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The three component reaction of $LnCp_3$, $LnCp_2Cl$ (Ln = Nd, Y) and *N*,*N*-bis[2-(pyrid-2-yl)ethyl]hydroxylamine $[HON(C_2H_4\text{-}o\text{-}py)_2]$ results in the formation of the $[Nd(ON(C_2H_4\text{-}o\text{-}py)_2)_2]^+[NdCp_3Cl]^-$ salt in the case of neodymium and the $[Y(ON(C_2H_4\text{-}o\text{-}py)_2)_2]^+[YCp_2Cl_2]^-$ salt if yttrium is used in the synthesis. The *N*,*N*-bis[2-(pyrid-2-yl)ethyl]hydroxylaminato ligand is able to coordinate doubly to the metal atoms resulting in the formation of a cationic species. The compounds were characterised by X-ray diffraction experiments and additionally by CHN analyses in the case of the neodymium salt.

Key words: Lanthanides, Hydroxylamines, N-O Ligands, X-Ray Diffraction

Introduction

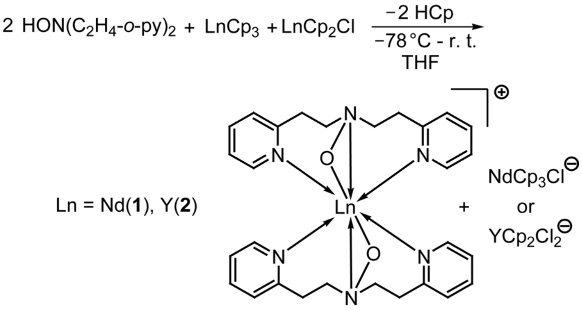
The large variety of hydroxylaminato compounds of the metal ions of groups 4 [1], 12 [2], and 13 [3] shows the high flexibility of $[R_2NO^-]$ ligands in coordination chemistry. These ligands are capable of complexing metal atoms *e. g.* by end-on, side-on, μ-O-end-on, or μ-O-side-on coordination modes, to exemplify only four of the explored binding motifs. The special binding characteristics of hydroxylamines to act as side-on coordinating ligands was even demonstrated for the main-group elements silicon and germanium, where they lead to the formerly unexpected formation of SiON [4] and GeON [5] three-membered ring systems.

The principle of achieving unusually high coordination numbers in rare earth metal complexes with the related nitroso ligands has impressively been demonstrated by Batten and Deacon *et al.* [6]. We have shown that combining cyclopentadienide substituents with hydroxylaminato ligands leads to a variety of complexes with different binding and aggregation modes in rare earth metal chemistry. With larger *N*-substituents like the benzyl group, we have found compounds like $[Cp_2Y(ONBn_2)]_2$ and $[Cp_2Sm(ONBn_2)]_2$ to form dimers with side-on binding of hydroxylaminato ligands and four-membered M_2O_2 ring systems [7].

Recently we reported the possibility to generate the first monomeric hydroxylaminato rare earth metal complexes $[Cp_2Ln\{\eta^2\text{-}ON(C_2H_4\text{-}\eta^1\text{-}o\text{-}Py)(C_2H_4\text{-}o\text{-}Py)\}]$ with the *N*,*N*-bis[2-(pyrid-2-yl)ethyl]hydroxylaminato ligand $[HON(C_2H_4\text{-}o\text{-}py)_2]$ [8]. This ligand system disfavours the dimerisation *via* an Ln_2O_2 linkage by coordination of one pyridine donor site. Moreover, the molecular structures, ligand coordination modes and aggregation types of these complexes depend strongly on the ionic radii of the involved rare earth metal ions. In the case of ionic radii larger than that of Sm^{3+}, the molecular structures reveal the well known dimeric μ-O-bridging motif without coordination of a pyridine donor, as previously observed *e. g.* in $[Cp_2Y(ONBn_2)]_2$ [7]. If lanthanum is utilised, the coordination number of the metal ion increases by one upon coordination of a pyridine donor atom. The donor-stabilised complexes are hemilabile and rapidly change their coordination in solution.

It is also possible to generate heterobimetalic and even heterotrimetalic complexes by reacting the compounds $[LnCp_2ON(C_2H_4\text{-}o\text{-}Py)_2]$ (Ln = Y, Sm) with the Lewis acids $AlMe_3$, $GaMe_3$ and $InMe_3$. The coordinated EMe_3 units block some of the donor sites of these complexes and thus inhibit further aggregation as observed in some of the underlying EMe_3-free complexes [9].

Herein we report the synthesis of homoleptic yttrium and neodymium cations with only two *N*,*N*-bis[2-(pyrid-2-yl)ethyl]hydroxylaminato ligands.



Scheme 1. Synthetic route to the compounds **1** and **2**.

Results and Discussion

The reaction of a mixture of *Ln*Cp_3 and *Ln*Cp_2Cl (*Ln* = Nd (**1**), Y (**2**)) with two equivalents of *N*,*N*-bis[2-(pyrid-2-yl)ethyl]hydroxylamine [$HON(C_2H_4$-*o*-$py)_2$] yielded the rare earth metal salts [$Nd(ON(C_2H_4$-*o*-$py)_2)_2]^+[NdCp_3Cl]^-$ (**1**) and [$Y(ON(C_2H_4$-*o*-$py)_2)_2]^+[YCp_2Cl_2]^-$ (**2**) (Scheme 1). Starting materials and products in these syntheses decompose upon contact with oxygen and/or moisture. This dictates preparative protocols under rigorous exclusion of such traces from the atmosphere.

The equation shown in Scheme 1 is balanced for the neodymium-containing salt **1**. However, as the anion in compound **2** contains two chloride atoms, we propose the existence of an equilibrium between anions with mixed Cp and Cl^- ligands. $[YCp_2Cl_2]^-$ seems to be the preferred partner in crystallisation and is found to be the partner anion in salt **2**. Besides **1** and **2**, we also found traces of the previously described complexes [$YCp_2ON(C_2H_4$-*o*-$py)_2$] and [$NdCp_2ON(C_2H_4$-*o*-$py)_2$] as side products, which could be separated by fractionated crystallisation. The anion equilibrium and the side products are obvious explanations for the low yield of 10 % for **2**. The yield of compound **1** with 58 % is clearly higher.

*Molecular structures of the compounds **1** and **2***

The structures of both compounds, **1** and **2**, reveal mononuclear cations coordinated by two *N*,*N*-bis[2-(pyrid-2-yl)ethyl]hydroxylaminato ligands. The structure of the anion in compound **1** $[NdCp_3Cl]^-$ has been previously reported in the case of the praseodymium salt [$Na(phen)_4][PrCp_3Cl]$ [10]. The $[YCp_2Cl_2]^-$ anion in yttrium salt **2** is so far unknown, but Cp* [11, 12] and [$C_5H_3(SiMe_3)_2$] [13] derivatives have earlier been reported for the elements ytterbium and erbium. Therefore we will only describe the cationic species in more detail. As the structure of the yttrium cation does not reveal substantial differences in coordination and aggregation, the structure of the cation in **1** is discussed first, followed by pointing out the differences to the cation in **2**.

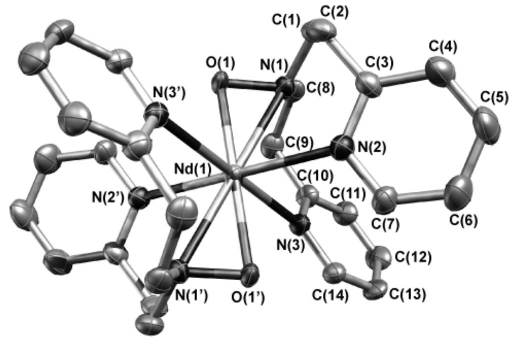


Fig. 1. Molecular structure of the cation [$Nd(ON(C_2H_4$-*o*-$py)_2)_2]^+$ of **1** in the crystal. Ellipsoids are drawn at the 50 % probability level, and hydrogen atoms have been omitted for clarity. Selected distances (Å): O(1)–Nd(1) 2.280(3), N(1)–Nd(1) 2.521(3), N(2)–Nd(1) 2.623(4), N(3)–Nd(1) 2.601(4). Symmetry transformation used to generate equivalent atoms: $2-x$, $1-y$, $-z$.

The two hydroxylaminato functions coordinate in a side-on manner towards the neodymium atom in the cationic species of compound **1** (Fig. 1). This coordination can be characterised by the O(1)–Nd(1) and the N(1)–Nd(1) bonds with lengths of 2.280(3) and 2.521(3) Å, respectively. The O(1)–Nd(1) value is comparable to that of the cation in [Nd(12-crown-4)$Cl_3 \cdot 5H_2O$] with O–Nd distances of 2.580 Å [14]. The side-on coordination can also be compared to that in the compound [$NdCp_2ON(C_2H_4$-*o*-$py)_2]_2$ with O(1)–Nd(1) and N(1)–Nd(1) bond lengths of 2.361(2) and 2.563(2) Å [8]. The occurrence of shorter O(1)–Nd(1) bonds in the cation of **1** can be explained by the presence of a bridging atom O(1) in the dinuclear [$NdCp_2ON(C_2H_4$-*o*-$py)_2]_2$ complex. Furthermore, the O(1)–Nd(1)–N(1) angle of 34.5(1)° is almost identical to that in [$NdCp_2ON(C_2H_4$-*o*-$py)_2]_2$ (33.7(1)°). As the structure of the cation exhibits an centre of inversion at Nd(1), the two N-O functions are arranged exactly parallel to each other.

In addition to the two N-O functions the neodymium atom is coordinated by four nitrogen atoms of the pyridyl groups. The N(2)–Nd(1) and the N(3)–Nd(1) bonds exhibit lengths of 2.623(4) and 2.601(4) Å, respectively. These lengths are shorter if compared to the complex [$NdCp_2ON(C_2H_4$-*o*-$Py)_2 \cdot InMe_3$], which

Table 1. Bond lengths (Å) and angles (deg) of compounds **1** and **2**.

1		**2**	
Nd(1)–O(1)	2.280(3)	Y(1)–O(1)	2.199(4)
–	–	Y(1)–O(2)	2.210(4)
Nd(1)–N(1)	2.521(3)	Y(1)–N(1)	2.459(5)
–	–	Y(1)–N(4)	2.449(5)
Nd(1)–N(2)	2.623(4)	Y(1)–N(2)	2.524(5)
–	–	Y(1)–N(5)	2.515(5)
Nd(1)–N(3)	2.601(4)	Y(1)–N(3)	2.518(5)
–	–	Y(1)–N(6)	2.536(6)
O(1)–N(1)	1.443(4)	O(1)–N(1)	1.437(6)
–	–	O(2)–N(4)	1.439(6)
Nd(2)–Cl(1)	2.736(2)	Y(2)–Cl(1)	2.586(2)
–	–	Y(2)–Cl(2)	2.592(2)
Nd(2)–C(15–29)	$2.813_{\text{av.}}$	Y(2)–C(29–38)	$2.665_{\text{av.}}$
O(1)–Nd(1)–N(1)	34.5(1)	O(1)–Y(1)–N(1)	35.4(2)
O(1)–Nd(1)–N(2)	98.8(2)	O(1)–Y(1)–N(2)	98.6(2)
O(1)–Nd(1)–N(3)	99.9(1)	O(1)–Y(1)–N(3)	100.7(2)
N(1)–Nd(1)–N(2)	75.3(1)	N(1)–Y(1)–N(2)	75.6(2)
N(1)–Nd(1)–N(3)	74.8(1)	N(1)–Y(1)–N(3)	74.4(2)
N(2)–Nd(1)–N(3)	89.3(2)	N(2)–Y(1)–N(3)	90.6(2)
N(3)–Nd(1)–N(2′)	90.7(2)	N(3)–Y(1)–N(6)	88.6(2)
–	–	N(5)–Y(1)–N(6)	95.0(2)
N(2′)–Nd(1)–N(2)	180	N(5)–Y(1)–N(2)	85.9(2)
–	–	O(1)–Y(1)–O(2)	177.7(2)
O(1)–Nd(1)–O(1′)	180	N(1)–Y(1)–N(4)	177.3(2)
N(1)–Nd(1)–N(1′)	180	Cl(1)–Y(2)–Cl(2)	96.4(2)

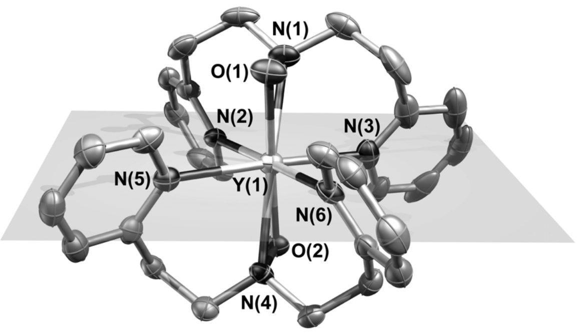


Fig. 2. Molecular structure of the cation $[Y(ON(C_2H_4\text{-}o\text{-}py)_2)_2]^+$ of **2** in the crystal. Ellipsoids are drawn at the 50 % probability level, and hydrogen atoms have been omitted for clarity. The plane includes the atoms N(2), N(3), N(5), N(6).

also contains N(2)–Nd(1) and N(3)–Nd(1) bonds with distances of 2.696(2) and 2.729(2) Å. This indicates a larger space requirement of two cyclopentadienyl rings compared to one further *N*,*N*-bis[2-(pyrid-2-yl)ethyl]hydroxylaminato ligand.

The intra-ligand chelate angle N(2)–Nd(1)–N(3) of 89.3(2)° is slightly smaller than its counterpart N(2)–Nd(1)–N(3′) of 90.7(2)°. The anion $[NdCp_3Cl]^-$ in **1** exhibits a bond length Cl(1)–Nd(2) of 2.736(2) Å. The average distance of the carbon atoms to Nd(2) is 2.813 Å – as long as in $NdCp_3\cdot THF$ with an average distance of 2.805(13) Å [15].

Structure analysis of the cation in compound **2** reveals a similar coordination of the ligands. But as the ionic radius of yttrium is 0.09 Å smaller than that of neodymium the ideal angles between the pyridyl donor atoms of 90° cannot be accomplished. The angles N(5)–Y(1)–N(6) and N(5)–Y(1)–N(2) are 95.0(2)° and 85.9(2)°, respectively. The four nitrogen atoms of the pyridyl groups are located in a square-planar arrangement about Y(1) (max. dev. 0.0221 Å) as is displayed in Fig. 2.

The two Y–Cl bonds in the anion of **2** exhibit distances of 2.586(2) Å for Y(2)–Cl(1) and 2.592(2) Å for Y(2)–Cl(2). The carbon atoms have an average distance of 2.665 Å to atom Y(2). Further selected bond lengths and angles are collected in Table 1.

Conclusions

We have generated homoleptic molecular neodymium and yttrium cations with two *N*,*N*-bis[2-(pyrid-2-yl)ethyl]hydroxylaminato ligands. The cationic charge is balanced by the anions $[NdCp_3Cl]^-$ and $[YCp_2Cl_2]$, respectively. The cations are octa-coordinate by two N-O functions and four pyridyl nitrogen atoms in both cases. Despite using organometallic starting materials, this coordination leads to cationic species without any metal-carbon bonds.

Experimental Section

General methods

All manipulations were performed under a rigorously dry inert atmosphere of argon using standard Schlenk and glove-box techniques. THF and *n*-pentane, dried over Na/benzophenone, were freshly condensed from $LiAlH_4$ before being employed in reactions. $[D_8]$THF was dried over Na/K alloy and degassed. $Ln\text{Cp}_3$ [16], $Ln\text{Cp}_2\text{Cl}$ [17] and *N*,*N*-bis[2-(pyrid-2-yl)ethyl]hydroxylamine [18] were synthesised according to literature procedures. Elemental analysis was performed by using a Leco CHNS 932 instrument.

*$[Nd(ON(C_2H_4\text{-}o\text{-}py)_2)_2]^+[NdCp_3Cl]^-$ (**1**)*

$HON(C_2H_4\text{-}o\text{-}py)_2$ (243 mg, 1 mmol), $NdCp_3$ (170 mg, 0.5 mmol) and $NdCp_2Cl$ (155 mg, 0.5 mmol) were mixed as solids under an inert atmosphere in a glove box. Afterwards 20 mL of thf was condensed onto the reaction mixture at −78 °C, and the solution stirred for 12 h at r. t. After filtration, the solution was concentrated to half of its volume, and the salt was crystallised by carefully layering hexane onto the

Table 2. Crystal structure data for **1** and **2**.

	1	**2**
Formula	$C_{43}H_{47}N_6Nd_2O_2Cl$, 2.5(C_4H_8O) 0.125(C_6H_{14})	$C_{38}H_{42}Cl_2N_6O_2Y_2$
M_r	1194.83	863.50
Colour	blue	colourless
T [K]	100(2)	100(2)
Crystal size, mm^3	0.22 × 0.19 × 0.14	0.10 × 0.04 × 0.02
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a, Å	15.223(1)	9.603(1)
b, Å	15.584(1)	25.766(1)
c, Å	25.272(1)	15.829(1)
α, deg	92.929(1)	90
β, deg	90.910(1)	102.784(3)
γ, deg	117.386(1)	90
V, Å^3	5311.3(1)	3819.5(3)
Z	4	4
ρ_{calcd}, g cm^{-3}	1.49	1.50
μ, mm^{-1}	2.0	3.2
$F(000)$	2425	1760
Θ range, deg	2.91 – 27.47	3.08 to 25.00
Reflns. collected / unique	136527 / 24228	39911 / 6698
Reflns. with $I \geq 2\sigma(I)/R_{\text{int}}$	17103 / 0.068	4006 / 0.142
Data / restraints / param.	24228 / 150 / 1210	6698 / 0 / 433
R_1/wR_2 [$I \geq 2\sigma(I)$]	0.0406 / 0.0953	0.0617 / 0.1097
R_1/wR_2 (all data)	0.0713 / 0.1066	0.1302 / 0.1317
GoF (F^2)	1.033	1.019
Largest diff. peak / hole, e Å^{-3}	2.169 / −0.983	0.704 / −0.396
Remarks	Largest diff. peak near Nd(5) (1.21 Å); Disorder of solvent molecules	–
CCDC number	776758	776759

thf solution. Crystals were obtained after 12 h. Yield 287 mg (0.29 mmol, 58 %). This yield refers to the amount obtained after a second recrystallisation. For $NdCp_2Cl$ a mixture out of two eq. $NdCp_3$ and one eq. $NdCl_3$ was used in synthesis. Anal. for $C_{43}H_{47}N_6Nd_2O_2Cl \cdot C_4H_8O$: calcd. C 52.47, H 5.15, N 7.81; found C 52.64, H 5.29, N 7.72.

*[Y(ON(C_2H_4-o-py)$_2$)$_2$]$^+$[YCp$_2$Cl$_2$]$^-$ (**2**)*

HON(C_2H_4-*o*-py)$_2$ (243 mg, 1 mmol), YCp_3 (142 mg, 0.5 mmol) and YCp_2Cl (127 mg, 0.5 mmol) were mixed as solids under an inert atmosphere. Afterwards 20 mL of thf was condensed onto the reaction mixture at −78 °C, and the solution was stirred for 12 h at r. t. After filtration, the solvent was removed *in vacuo*. The residue was dissolved in hot toluene and directly filtered. This solution was allowed to cool down slowly to r. t. Crystals were obtained after 12 h. Yield 43 mg (0.05 mmol, 10 %). This yield refers to the amount obtained after the first crystallisation.

Crystallographic structure determinations

Single crystals suitable for X-ray diffraction measurement were picked inside a glove box, suspended in a Paratone-N/paraffin oil mixture, mounted on a glass fibre and transferred onto the goniometer of the Nonius Kappa CCD diffractometer. The measurements were carried out with MoK_α radiation (λ = 0.71073 Å). The structures were solved by Direct Methods and refined by full-matrix least-squares cycles (programs SHELXS-97 and SHELXL-97 [19]) (Table 2). The structure plots in this article were generated using the program DIAMOND 3.2 [20].

CCDC 776758 (**1**) and 776759 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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