

Adducts of Cp_3Ln with $\text{LGa}(\text{Me})\text{OH}$, Syntheses and X-ray Crystal Structures of $\text{LGa}(\text{Me})\text{HO} \rightarrow \text{LnCp}_3$ $\{\text{Ln} = \text{Sm}, \text{Nd}, \text{Yb}; \text{L} = \text{HC}[\text{C}(\text{Me})\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)]_2\}$

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Keywords: Adducts / Hydroxides / Gallium / Heterodimetallic compounds / Lanthanides

Various heterodimetallic (gallium-lanthanide) compounds have been prepared by the reaction of $\text{LGa}(\text{Me})\text{OH}$ (**2**) with Cp_3Ln . Thus, the adducts $\text{LGa}(\text{Me})\text{HO} \rightarrow \text{LnCp}_3$ ($\text{Ln} = \text{Sm}$, **3**; Nd , **4**; Yb , **5**) were obtained and characterized by IR spec-

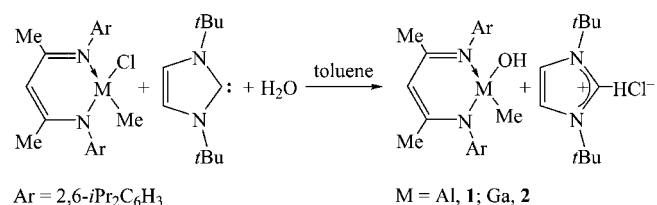
troscopy and elemental analyses. The single-crystal X-ray structures of **3** and **4** are also reported.

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Introduction

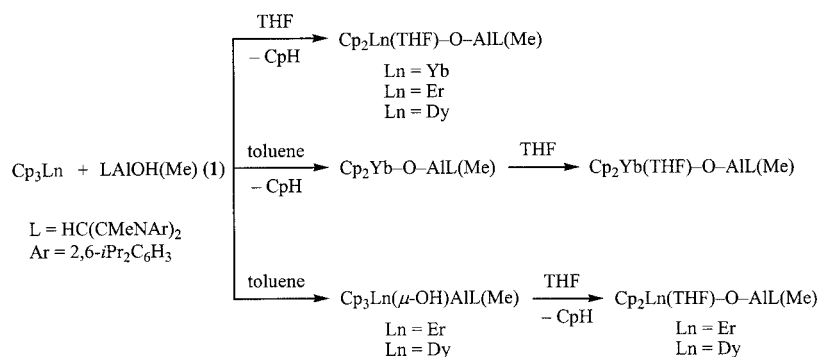
Due to our long-standing interest in the syntheses of molecular main group hydroxides, we have successfully assembled several novel hydroxido complexes.^[1–4] Among these, soluble group 13 hydroxides of aluminum^[5] are of special interest in view of their utilization in the syntheses of alumoxanes^[6] and other heterodimetallic compounds of potential applications.^[7–10] The toluene/liquid ammonia two-phase hydrolysis^[5] or the hydrolysis in the presence of N-heterocyclic carbenes, as an HCl scavenger,^[8] are genuine routes to prepare these molecules. According to the latter method, we have assembled the methylgallium hydroxide (Scheme 1) and have also utilized it as a synthon to prepare new heterodimetallic compounds. Thus, the reaction of the gallium hydroxide $\text{LGa}(\text{Me})\text{OH}$ (**2**) with Cp_2ZrMe_2 gave

the Ga–Zr mixed oxide $\text{LGa}(\text{Me})\text{–O–Zr}(\text{Me})\text{Cp}_2$.^[11] Also, the reaction of $\text{LAl}(\text{Me})\text{OH}$ (**1**) with Cp_3Ln ($\text{Ln} = \text{Yb}$, Er, Dy) led to the formation of various aluminum–lanthanide mixed oxides (Scheme 2).^[9]



Scheme 1.

This new area of research that combines both main group and lanthanide elements to constitute a novel class



Scheme 2.

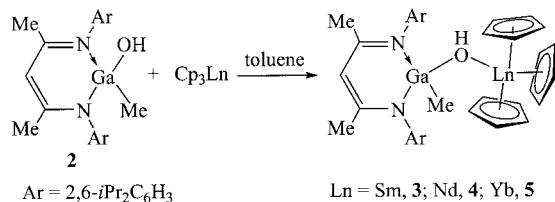
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of heterodimetallic species started with the work of Mehrotra and co-workers who reported in the late 1970s the isopropoxides of gallium and lanthanides (La, Pr, Nd, Sm, Gd, Ho and Er), $[\text{Ln}\{\text{Ga}(\text{O}i\text{Pr})_4\}_3]$, by the reaction of either

lanthanide chlorides with potassium gallium isopropoxides or by the reaction of lanthanide isopropoxides with gallium isopropoxides.^[12,13] However, none of these compounds were structurally characterized and to the best of our knowledge there has been no other attempt to prepare mixed metal oxides or hydroxides of gallium with lanthanide atoms. It is to be noted that heterodimetallic compounds containing aluminum and lanthanides are well known but the corresponding gallium compounds are very rare. Our main aim in this area is to prepare mixed metal gallium–lanthanide compounds connected by an oxygen atom. Therefore, we report herein the synthesis and structural characterization of various Ga–Ln metal hydroxides by the reaction of LGa(Me)OH with Cp₃Ln (Ln = Sm, Nd, Yb). Moreover, the reactivity of LGa(Me)OH is also compared with its aluminum analogue LAl(Me)OH.

Results and Discussion

Reaction of LGa(Me)OH (**2**) with 1 equiv. of Cp₃Ln was carried out in toluene at room temperature to afford the adducts LGa(Me)(μ-OH)LnCp₃ (Ln = Sm, **3**; Nd, **4**; Yb, **5**) (Scheme 3) in good yields. Compounds **3** and **5** are stable yellow solids and **3** melts at 275 °C whereas **5** melts with decomposition at 275 °C. Compound **4** is a blue-green solid that melts with decomposition at 254 °C. As observed in the IR spectrum of the adducts **3**, **4** and **5**, elimination of CpH did not occur and the (μ-OH) stretching frequency was observed at 3592, 3591, and 3609 cm⁻¹ respectively. These frequencies are redshifted when compared to that of LGa(Me)OH (**2**) observed at 3676 cm⁻¹, which also confirms that the hydroxide group bridges between the Ga and Ln atom. This is in contrast to the reaction of the corresponding aluminum hydroxide LAl(Me)OH (**1**) with Cp₃Ln where the elimination of CpH occurred (Scheme 2). This indicates that the proton of LGa(Me)OH (**2**) is less acidic than that of LAl(Me)OH (**1**).^[9]



Scheme 3.

Single crystals of **3** and **4** were obtained from a toluene solution. Figures 1 and 2 show the structures of **3** and **4**, respectively. Both **3** and **4** are isomorphous and crystallize in the monoclinic space group *P*₂₁/*m* with half of a molecule in the asymmetric unit. The lanthanide ions possess a pseudotetrahedral geometry surrounded by three cyclopentadienyl rings and an oxygen atom. The Ga atom forms a distorted tetrahedron with two nitrogen atoms of the β-diketiminato ligand, one carbon atom of the methyl group and an oxygen atom of the hydroxy bridge. The hydrogen atom of the bridging hydroxido group [O(1)] in compound

3 cannot be located in the electron density map, probably due to the refinement against non-merohedrally twinned data. However, its presence was confirmed by the infrared spectrum and also due to the presence of three cyclopentadienyl rings connected to the samarium atom.

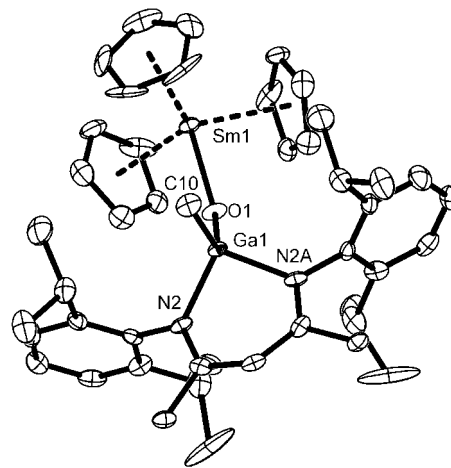


Figure 1. Molecular structure of LGa(Me)(μ-OH)SmCp₃ (**3**). Thermal ellipsoids are shown at 50% probabilities. Hydrogen atoms are omitted for clarity.

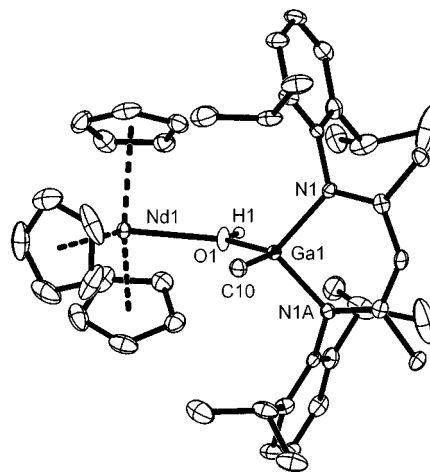


Figure 2. Molecular structure of LGa(Me)(μ-OH)NdCp₃ (**4**). Thermal ellipsoids are shown at 50% probabilities. Hydrogen atoms (except that at the oxygen atom) are omitted for clarity.

The Ga(1)–O(1) bond in compounds **3** [1.862(7) Å] and **4** [1.851(3) Å] is longer than that found in LGa(Me)OH [1.831(1) Å]. This elongation is expected due to coordination of the hydroxy group to the other metal atoms in **3** and **4**. The Sm(1)–O(1) bond of 2.465(7) Å is significantly shorter than that of the corresponding aluminum compound LAl(Me)(μ-OH)SmCp₃ [2.500(4) Å]^[9] but longer than that of [Cp*₂Sm(μ-O₂CSPH)]₂ [2.328(2) Å].^[14] The Nd(1)–O(1) bond of 2.479(3) Å is longer than the bridging Nd–O bond in Nd₅O(O⁺Pr)₁₃ [2.304(12)–2.345(11) Å] and significantly longer than the terminal Nd–O bonds [2.082(11)–2.123(11) Å].^[15] The Ga(1)–O(1)–Sm(1)/Nd(1) core is bent with an angle of 149.3(4)° (**3**)/149.7(2)° (**4**)

which is comparable to that of $\text{LaAl}(\text{Me})(\mu\text{-OH})\text{SmCp}_3$ [151.9(2)°] (Table 1).

Table 1. Selected bond lengths [Å] and angles [°] of **3** and **4**.

3		4	
Ga(1)–C(10)	1.971(2)	Ga(1)–C(10)	1.961(5)
Ga(1)–O(1)	1.862(7)	Ga(1)–O(1)	1.851(3)
Ga(1)–N(2)	1.963(7)	Ga(1)–N(1)	1.956(3)
Sm(1)–O(1)	2.465(7)	Nd(1)–O(1)	2.479(3)
Ga(1)–O(1)–Sm(1)	149.3(4)	Ga(1)–O(1)–Nd(1)	149.7(2)
O(1)–Ga(1)–N(2)	108.1(2)	O(1)–Ga(1)–N(1)	108.4(2)
N(2A)–Ga(1)–N(2)	95.4(4)	N(1)–Ga(1)–N(1A)	95.68(2)
N(2)–Ga(1)–C(10)	114.0(3)	N(1)–Ga(1)–C(10)	114.1(2)

Conclusion

We have attempted to synthesize heterodimetallic compounds containing gallium and lanthanide elements. The adducts thus obtained represent rare examples for such a system. We anticipate that further reaction of $\text{LGa}(\text{Me})\text{OH}$ with other suitable lanthanide precursors may allow the formation of heterodimetallic gallium–lanthanide oxides. Such studies are underway in our laboratory.

Experimental Section

General: All manipulations were performed under dry and oxygen-free N_2 or Ar using Schlenk-line and glove-box techniques. Solvents were purified according to conventional procedures and were freshly distilled prior to use. $\text{LGa}(\text{Me})\text{OH}$,^[11] Cp_3Yb ,^[16] and Cp_3Nd ^[16] were synthesized according to literature procedures.

Cp_3Sm was purchased from Aldrich and used without further purification.

Synthesis of $\text{LGa}(\text{Me})(\mu\text{-OH})\text{SmCp}_3$ (3**):** Toluene (40 mL) was added to a mixture of $\text{LGa}(\text{Me})\text{OH}$ (0.52 g, 1.00 mmol) and Cp_3Sm (0.35 g, 1.00 mmol) at room temperature. The mixture was stirred overnight when the color of the mixture slowly turned to yellow from orange. After removal of all volatiles in vacuo, toluene (60 mL) was added and the mixture was heated to 80 °C and filtered while hot. The clear yellow filtrate was kept at room temperature to afford yellow crystals of **3** (0.58 g), another crop of yellow crystals was obtained from the mother liquor (0.17 g). Total crystal yield (0.75 g, 87%). M.p. 275 °C. $\text{C}_{45}\text{H}_{60}\text{GaN}_2\text{OSm}$ (865.05): calcd. C 62.48, H 6.99, N 3.24; found C 62.17, H 6.80, N 3.22. EI-MS: m/z (%) = 504 (72) [$\text{M}^+ - \text{Me} - \text{Cp}_3\text{Sm}$]. IR (Nujol): $\tilde{\nu}$ = 3592, 1521, 1442, 1384, 1311, 1255, 1204, 1176, 1105, 1013, 967, 941, 867, 801, 772, 755, 725, 587, 557, 442 cm^{-1} .

Synthesis of $\text{LGa}(\text{Me})(\mu\text{-OH})\text{NdCp}_3$ (4**):** Toluene (45 mL) was added to a mixture of $\text{LGa}(\text{Me})\text{OH}$ (0.26 g, 0.50 mmol) and Cp_3Nd (0.17 g, 0.50 mmol) at room temperature. The mixture was stirred overnight when the color of the mixture slowly turned to light blue-green. After removal of all volatiles in vacuo, toluene (40 mL) was added to the residue. The mixture was heated to 90 °C and filtered while hot. The clear light blue-green filtrate was kept at room temperature to afford greenish crystals of **4**. Crystal yield (0.38 g, 88%). M.p. 254 °C (decomp.). $\text{C}_{45}\text{H}_{60}\text{GaN}_2\text{NdO}$ (858.93): calcd. C 62.92, H 7.04, N 3.26; found C 62.69, H 7.13, N 3.22. EI-MS: m/z (%) = 792 (2) [$\text{M}^+ - \text{CpH}$], 503 (24) [$\text{M}^+ - \text{Me} - \text{Cp}_3\text{Nd}$]. IR (Nujol): $\tilde{\nu}$ = 3591, 1553, 1521, 1463, 1440, 1378, 1311, 1258, 1204, 1177, 1106, 963, 942, 868, 801, 784, 770, 953, 725, 587, 557, 442 cm^{-1} .

Synthesis of $\text{LGa}(\text{Me})(\mu\text{-OH})\text{YbCp}_3$ (5**):** Toluene (40 mL) was added to a mixture of $\text{LGa}(\text{Me})\text{OH}$ (0.26 g, 0.50 mmol) and Cp_3Yb (0.18 g, 0.50 mmol) at room temperature. The mixture was stirred overnight when the color of the mixture slowly turned to orange-

Table 2. Crystallographic data for the structural analyses of compounds **3** and **4**.

Compound	3	4
Empirical formula	$\text{C}_{45}\text{H}_{60}\text{GaN}_2\text{OSm}$	$\text{C}_{45}\text{H}_{60}\text{GaN}_2\text{NdO}$
Formula mass	865.01	858.91
<i>T</i> [K]	100(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/m$	$P2_1/m$
<i>a</i> [Å]	10.219(2)	10.223(3)
<i>b</i> [Å]	19.616(3)	19.588(3)
<i>c</i> [Å]	10.586(2)	10.594(2)
β [°]	109.23(3)	109.26(2)
<i>V</i> [Å ³]	2003.6(6)	2002.7(6)
<i>Z</i>	2	2
<i>D</i> (calcd.) [g·cm ^{−3}]	1.434(2)	1.424(2)
μ (Cu- <i>K</i> α) [mm ^{−1}]	11.971	10.858
<i>F</i> (000)	890	886
θ range [°]	4.42 to 59.05	4.42 to 58.98
Index range	$-11 \leq h \leq 10$ $0 \leq k \leq 21$ $0 \leq l \leq 11$	$-11 \leq h \leq 10$ $0 \leq k \leq 21$ $0 \leq l \leq 11$
Reflections collected	18619	18407
Independent reflections	2951	3414
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
Data/restraints/parameters	2951/0/241	3414/2/248
R_1 , wR_2 [$I > 2\sigma(I)$] ^[a]	0.0521, 0.1192	0.0234, 0.0591
R_1 , wR_2 (all data) ^[a]	0.0528, 0.1197	0.0236, 0.0592
<i>S</i>	1.077	1.147
$\Delta\rho$ (min), $\Delta\rho$ (max) [e·Å ^{−3}]	1.141, −1.077	0.651, −0.414

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2]^{1/2}$.

yellow from green. After removal of all volatiles in vacuo, toluene (45 mL) was added and the mixture was heated to 90 °C and filtered while hot. The clear orange-yellow filtrate was kept at room temperature to afford yellow crystals of **5**. Crystal yield (0.37 g, 91%). M.p. 275 °C (decomp.). $C_{45}H_{60}GaN_2OYb$ (887.73): calcd. C 60.88, H 6.81, N 3.16; found C 60.79, H 6.86, N 3.20. EI-MS: m/z (%) = 726 (50) [$M^+ - 2\text{ Cp} - 2\text{ Me}$], 711 (60) [$M^+ - 2\text{ Cp} - 3\text{ Me}$]. IR (Nujol): $\tilde{\nu}$ = 3609, 1552, 1524, 1440, 1398, 1315, 1261, 1177, 1106, 1015, 940, 832, 817, 797, 760, 643, 555, 444 cm^{-1} .

X-ray Structure Determination of 3 and 4: A suitable crystal of **3** and **4** was mounted on a glass fibre and coated with paraffin oil. Data for **3** and **4** were obtained with a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector using mirror-monochromated $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178\text{ \AA}$). Data of both structures were non-merohedrally twinned. The twin operation in both cases is a twofold axis along the reciprocal axis 001. The fractional contribution of the minor domain refined to 0.475(2) (**3**) and 0.495(1) (**4**). The structures were solved by direct methods using SHELXS-97^[17] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.^[18] All non-hydrogen atoms were refined anisotropically. Atom scattering factors (including anomalous scattering) were taken from the "International Tables for X-ray Crystallography".^[19] Hydrogen atoms connected to carbon atoms were included at geometrically calculated positions and refined using a riding model. The hydrogen atom of the OH group could be located in **4** in the electron density map and was refined with distance restraints (Table 2). CCDC-614180 (**3**) and -614181 (**4**) 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.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and the Göttinger Akademie der Wissenschaften. S. S. thanks the Graduiertenkolleg 782 for a fellowship.

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Received: July 11, 2006

Published Online: September 5, 2006