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Carbon Dioxide Fixation by Organolanthanides and Thermal Degradation into Amorphous and Higher Condensed Ln/O/C/N Solids

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Ammine[tris(cyclopentadienyl)]-, amido[bis(cyclopentadienyl)]lanthanides, and tris[bis(trimethylsilylamido)]cerium have been studied with respect to CO_2 absorption under various reaction conditions. Subsequent thermal treatment of these complexes under gaseous and supercritical CO_2 yielded new higher condensed lanthanide Ln/O/C/N solids. IR spectroscopic studies of the CO_2-activated species reveal the formation of various oxonitridocarbonates, in particular carbamates ($O_2CNH_2^-$), imidocarbonates (O_2CNH^{2-}), isocyanates (OCN^-), and carbonates (CO_3^{2-}), which function as multidentate linkers between the lanthanide ions. Thereby, inorganic polymers are formed, which represent single-source precursors for application in various deposition methods and can therefore be utilized as pre-organized reagents in solid-state chemistry. In this context, we report on the structural characterization of one of the molecular precursors [Cp_3YbNH_3] [reticular pseudomerohedral twin, $P2_1/c$, a = 826.8(2), b = 1103.8(2), c = 1482.0(3) pm, β = 101.60(3)°, Z = 4, V = 1309.0(5)·10^6 pm^3]. Crystals of [Cp_3YbNH_3] appear red, orange, yellow, and dark green depending on the orientation under plane-polarized light (pleochroism).

Introduction

Carbon dioxide (CO_2) is an interesting reagent for various synthetic approaches in the chemistry of catalysis and represents a reagent of growing interest in other fields of chemistry.[1–6] Novel methods to sufficiently activate CO_2 for an application in organic and inorganic solvent reactions have been reported emphasizing the potential of this compound in various processes.[7–12] We have discovered a novel approach for this "green" reagent as a pre-organized C/O donor in solid-state reactions for the synthesis of novel mixed N-containing lanthanide derivatives of carbonato compounds, which can be described as oxonitridocarbonates (i.e. $O_2CNH_2^-$, O_2CNH^{2-}, $O_3C_3N_3H^{2-}$, OCN^-). These groups can be envisaged to function as bidentate or multidentate linkers between the Ln ions (Ln = lanthanide = La–Lu) resulting in crosslinked inorganic polymers.

The present study revealed that several kinds of oxonitridocarbonates were formed by the reaction of CO_2 with N-containing inorganic complexes and it was therefore intended to investigate these CO_2 absorbants for the use as single-source precursors and potential Ln/O/C/N-dopants for applications in solid-state reactions. (Nitrido)lanthanide materials are of particular interest in materials chemistry of optically active or semiconducting compounds. Research previously carried out in our laboratory revealed that the introduction of oxygen into Ln nitridosilicates results in interesting luminescent properties.[13–17] The CO_2 reactivity studies of these precursor compounds reported herein enlarge the potential of amorphous O/C/N-containing solids as future reagents for materials science.

In this context we have focused on the study of the solid-state reactivity of activated ammine- and amidolanthanide compounds towards carbon dioxide under various reaction conditions. In particular we report the use of tris[bis(trimethylsilyl)amido]cerium (Ce-BTMSA) as well as ammine-[tris(cyclopentadienyl)]lanthanides (Ln-NH_3, cyclopentadienyl = Cp) and amido[bis(cyclopentadienyl)]lanthanides (Ln-NH_2) as reactive complexes for the absorption and insertion of CO_2 in the solid state.

[Ce{N(SiMe$_3$)$_2$}$_3$] (Ce-BTMSA) has been used as a dopant in materials chemistry yielding SrS:Ce.[18] Because of the sterically demanding nature of the BTMSA moiety, the central atom exhibits free coordination sites above and below the cerium atom, and – caused by the electron deficiency at the Ce center – these complexes can be considered to be highly reactive with respect to a variety of O-containing reagents and in particular against CO_2.

Lanthanide metallocenes have been shown to be interesting molecular reagents in materials chemistry.[19] Recently, the synthesis of aggregated nanocrystalline lanthanide nitride materials was reported to be successful using [Cp_3LnNH_3] and [{Cp_2LnNH_2}$_2$] as precursors.[20] These amido- and ammine(cyclopentadienyl)lanthanide com-

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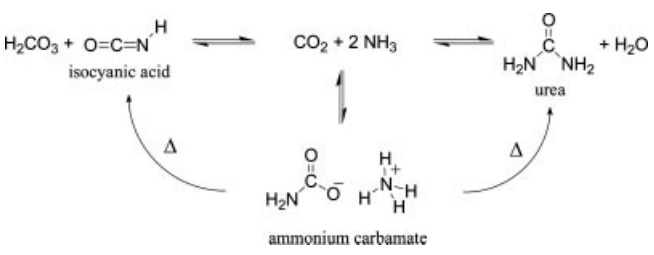
plexes are volatile under vacuum (10^{-3} mbar) and at temperatures as low as 150–250 °C, which makes them potentially relevant for chemical vapor deposition (CVD) processes.[21,22]

These complexes have been described in the literature;[23–27] however, neither further applications nor crystal structure determinations have been reported for $[Cp_3YbNH_3]$. In the course of our work the crystal structure of $[Cp_3YbNH_3]$ (Yb-NH_3) has been determined successfully. Pleochroic behavior was observed viewing the crystals under plane-polarized light. Yb-NH_3 can therefore be considered as an interesting material for optical applications.

For further degradation processes, the Cp rings can be removed easily by thermal treatment or using inorganic bases like $LiNH_2$ or CaH_2.[20] The mild-temperature conditions, under which supercritical carbon dioxide is used, are of special interest for these precursor compounds.[2,5,10] In this manner, Yb-NH_3 can be carboxylated before thermal degradation of the Cp ligands occurs. Thus, this CO_2-activated compound represents a molecular single-source precursor.

The absorption of CO_2 and the resulting amorphous products have been studied by IR spectroscopy, elemental analysis, and temperature-dependent in-situ mass spectrometry (MS) studies. The higher condensed O/C/N materials obtained are rather difficult to characterize. Solid-state NMR studies can be considered to be rather inappropriate, because of the anisotropic environment around the metal ions resulting in very large quadrupole moments. Furthermore, most Ln^{III} complexes exhibit unpaired electrons (paramagnetism).

As an important reference substance for IR spectroscopy, ammonium carbamate was used and re-characterized[28] more accurately by IR spectroscopy and X-ray structure analysis. This compound was synthesized by the reaction of liquid ammonia with gaseous CO_2. Whereas the reaction of these gases under normal conditions (pressure, temperature) always yields ammonium carbamate, amido and ammine metal complexes react with carbon dioxide in a different way.[7,29–35] Scheme 1 shows possible species formed by the nonstoichiometric reaction of CO_2 with NH_3. Apparently, some of these products are not stable in the protonated form, but are known as anionic ligands in inorganic chemistry.



Scheme 1. Protonated species formed by the reaction of CO_2 and NH_3.

Results and Discussion

Characterization and Reactivity of $[Cp_3YbNH_3]$ and $[\{Cp_2YbNH_2\}_2]$

The molecular structure of $[Cp_3YbNH_3]$ (Yb-NH_3) has been determined by X-ray diffraction analysis and is illustrated in Figure 1. The Yb^{III} ion shows a coordination number CN = 10 taking into account only the binding electron pairs of the Cp and NH_3 ligands. The centroids (Ctr) of the Cp rings and the coordinated NH_3 ligand form a distorted tetrahedral environment around the Yb center. Selected bond lengths and angles are given in Table 1.

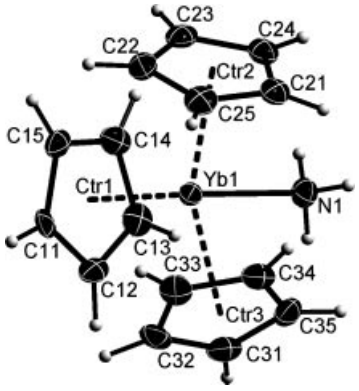


Figure 1. Molecular structure of $[Cp_3YbNH_3]$ at 130 K (50% probability ellipsoids). The hydrogen atoms were calculated and refined using a riding model with fixed isotropic thermal parameters.

Table 1. Selected bond lengths [pm] and angles [°] for $[Cp_3YbNH_3]$.

$[Cp_3YbNH_3]$	
Yb–N	242.0(4)
Yb–Ctr(1)	241.1(3)
Yb–Ctr(2)	242.2(3)
Yb–Ctr(3)	240.0(3)
N–Yb–Ctr(1)	97.23(2)
N–Yb–Ctr(2)	98.65(2)
N–Yb–Ctr(3)	98.55(2)
Ctr(1)–Yb–Ctr(2)	117.98(2)
Ctr(1)–Yb–Ctr(3)	118.04(2)
Ctr(2)–Yb–Ctr(3)	118.06(2)

The three Cp ligands are η^5-coordinated to the central ion and the Yb–Ctr bond lengths lay within the expected ranges from 240.0(3) to 242.2(3) pm. The Yb–N bond is only slightly shorter [242.0(4) pm] compared with other reported structures of $[Cp_3LnNH_3]$ (Ln = Gd, Dy, Ho, Er).[20] Additional intermolecular interaction was observed for one Cp ring (Ctr1) to a neighboring ammonia ligand of another complex molecule. Intermolecular distances Yb–Ctr1 of 319.6(4) and 263.5(4) pm for C(15)–H(1N) were observed. The formation of a weak N–H–C interaction is probable as one proton of the coordinated ammonia is slightly acidic (Figure 2).

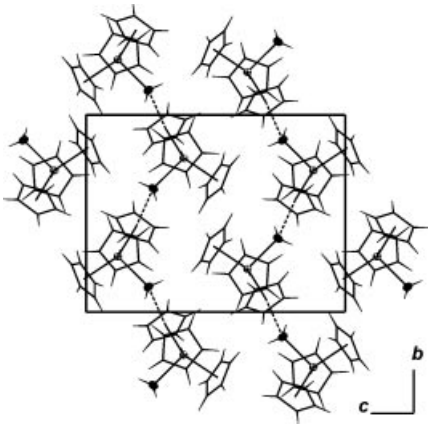


Figure 2. Projection of the unit cell of [Cp_3YbNH_3], view along axis *a*. Intermolecular interactions are depicted with dotted lines.

Crystals of Yb–NH_3 appear in different colors depending on the orientation of plane-polarized light under which they are viewed (pleochroism). In the literature, Cp-containing ytterbium complexes have been discussed controversially towards their colors. Often, explanations for this discrepancy were given taking into account also the presence of Yb^{II}. In the case of Yb-NH_3 all colors given elsewhere have been described correctly.[24,26,27] Along the crystal faces the crystallites appear red, orange, yellow, and dark green. Figure 3 displays two crystals at different orientations towards the light source. The emerald green powder of Yb-NH_3 sealed in an ampule is shown as well.

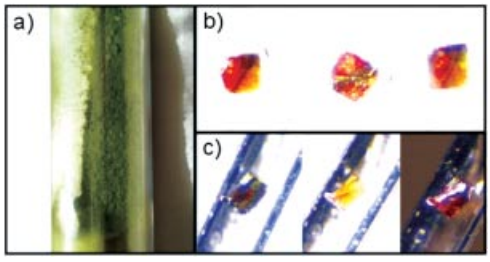


Figure 3. a) Yb–NH_3 sealed in an ampule under argon. b, c) Two crystals of Yb-NH_3 viewed under plane-polarized light and in three different orientations towards the light source.

Thermal treatment of Yb-NH_3 under argon (250 °C) causes deprotonation of the coordinated NH_3 ligand and abstraction of one cyclopentadiene molecule (C_5H_6) forming the more stable and sublimable dinuclear complex [{Cp_2YbNH_2}$_2$] (Yb-NH_2). The crystal structure of this complex has been determined recently.[20] The Yb–Ctr and Yb–N distances of 234.3(6)–234.6(7) pm and 229(1) and 233(1) pm, respectively, were observed to be significantly shorter than in the ammonia-coordinated derivative.

Yb-NH_3 has been characterized by IR spectroscopy (Figure 4). The coordinated ammonia can be identified by the strong N–H stretching vibrations at 3365, 3330, and 3250 cm^{-1} and by the intense asymmetric and symmetrical N–H deformation and reticular vibrations at 1600, 1225, and 500 cm^{-1}. The vibrations differ only slightly within a range of ±7 cm^{-1} from the corresponding ammine complexes of Sm, Gd, Dy, Ho, and Er.[20] The seven typical stretching [2 $\nu_{(CH)}$, 2 $\nu_{(CC)}$] and deformation vibrations [1 $\delta_{(CH)}$ parallel, 2 $\delta_{(CH)}$ perpendicular] of the cyclopentadienyl rings at 3090, 3070, 1440, 1360, 1010, 790, and 775 cm^{-1} were also observed.[36]

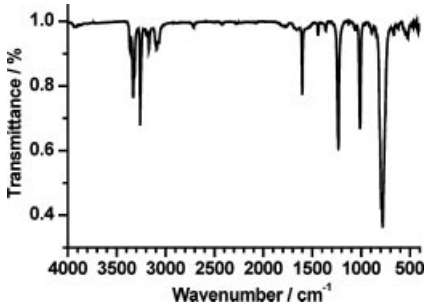


Figure 4. IR spectrum of Yb-NH_3.

In contrast to Ln-NH_3, the amido complexes (Ln-NH_2) are stable up to 360 °C until melting and decomposition to LnN occurs. Thus, the ammonia complex can be considered as a reactive reagent for low-temperature carboxylation reactions whereas the Ln-NH_2 compounds are interesting for solid-state reactions up to 350 °C under normal pressure. Both species (Ln = Ho, Yb) were used for decomposition reactions utilizing gaseous and supercritical carbon dioxide.

Characterization of Ammonium Carbamate $[NH_4]^+[O_2CNH_2]^-$

The solid-state structure of thin colorless plate-like crystals was re-determined by X-ray diffraction analysis. The crystal parameters reported in older literature data were confirmed and the bond lengths and angles of the ammonium ion and the amido moiety were determined more accurately.[28] Ammonium carbamate crystallizes in the orthorhombic space group *Pbca*, with a = 653.5(2), b = 675.4(2), c = 1711.9(4) pm, V = 755.73(3)·10^6 pm^3.

The compound is stable in closed vessels or under CO_2. The IR spectrum was used as an important reference for further investigations, as it shows vibrations of an oxonitridocarbonate without any metal interaction (Figure 5).

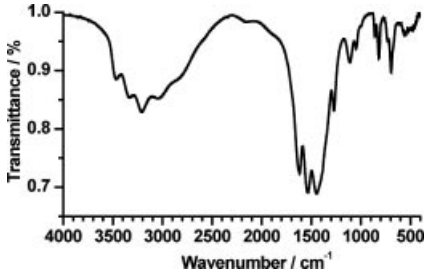


Figure 5. IR spectrum of ammonium carbamate.

Broad N–H and O–H stretching vibrations between 3500 and 2500 cm^{-1} indicate the presence of N···H···O-bridging ligands of the carbonyl and the ammonium moiety. Three intense signals are attributed to the O=C and N=C valences of the carbamate ligand at 1615, 1535, and 1445 cm^{-1}.[29,32]

Additionally, the deformation vibrations of N–H and O–C–N can be located at 1272, 1112, 859, and 695 cm^{-1}.[29,32]

Heterogeneous Solid-Gas Reactivity of $[Ce\{N(SiMe_3)_2\}_3]$ Towards CO_2

The structure of Ce-BTMSA has been determined elsewhere[18] and revealed a mononuclear species with the Ce^{III} ion in the center of the three BTMSA ligands (CN = 3). It has been shown that the central atom displays a disorder in the *z* direction, occupying two sites positioned above and below the plane formed by the ligand nitrogen atoms. The compound has been described to be isostructural with other Ln derivatives.

Crystalline Ce-BTMSA was heated under argon to 150 °C and then brought into reaction with a slow stream of pure gaseous CO_2. The beige solid (Ce-1a) was analyzed by IR spectroscopy and showed 40.3% loss of weight. Subsequent thermal treatment of the reaction product under NH_3 to 650 °C resulted in the formation of a brown amorphous solid (Ce-1b). Further loss of weight was observed and IR spectroscopic measurements and elemental analysis were carried out. The product showed a composition of Ce/O/C/N = 4:14:7:4. Figure 6 represents the vibrational spectra of the reagent Ce-BTMSA and also includes the carboxylation product after thermal treatment at 150 °C and 650 °C.

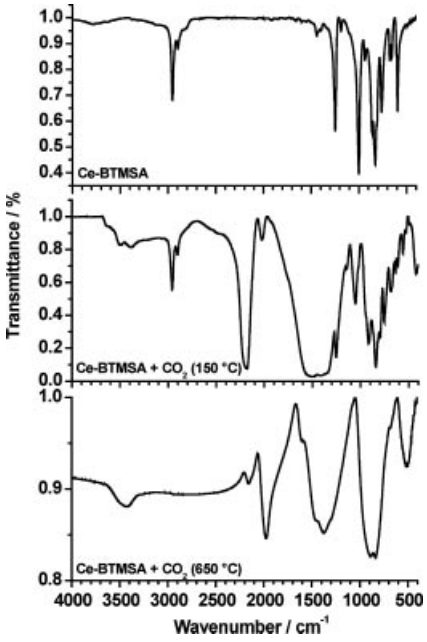


Figure 6. IR spectra of Ce-BTMSA (top) and the carboxylation products after annealing at 150 °C under CO_2 (center) and 650 °C (bottom).

Ce-1a heated to 150 °C still shows sharp signals at 2960, 1250, 1055, and 840 cm^{-1}, indicating the presence of stretching and deformation vibrations of Si–C and Si–N moieties.[37] A broad and intense absorption between 1700 and 1300 cm^{-1} is characteristic of both carbonate and carbamate groups.[29,38] Additionally, an intensive large and a weak vibration are located between 2150 and 2250 and at 2015 cm^{-1}. They can be assigned to several kinds of molecular fragments: Strong absorptions can be observed in the region 2250–1950 cm^{-1} if isocyanates are present.[38,39] Signals of weak and strong intensities have been reported upon occurrence of agostic Si–H or CO_2 adducts.[37,40] The formation of OCN groups can be regarded as improbable due to the low reaction temperature and the specific energy necessary for the conversion of a carbamic ligand into carbonate and isocyanate moieties according to Scheme 1.

The ammonolysis reaction of Ce-1a at 650 °C yielded a product (Ce-1b) with a largely different IR spectrum (Figure 6). Less-resolved vibrations typical of amorphous, more condensed solid-state compounds are present, thus proving further decomposition into an O/C/N-containing material. Considering the thermal conditions and peak profiles, this spectrum closely corresponds to typical isocyanato vibrations reported in the literature.[39] N–C–O stretching and deformation modes can be attributed to the signals at 2160 and 1975 as well as 887 and 837 cm^{-1}, respectively. Absorptions at 1595, 1455, and 1375 are situated in the characteristic region for both carbamato and carbonato ligands.[29,38]

A formula for the amorphous compound (Ce-1b) with composition $Ce_4O_{14}C_7N_4$ (according to elemental analysis) can be formulated as $[Ce_4(OCN)_3(O_3C)(O_2CN)]$. Further decomposition of the compounds at higher temperatures resulted in the formation of Ce_2O_3. The overall thermal treatment of Ce-BTMSA under CO_2 can by summarized as Equations (1) and (2).

$$4\ Ce\{N(SiMe_3)_2\}_3 + 7\ CO_2 \xrightarrow{150\ °C} "Ce_4\{N(SiMe_3)_2\}_{12}(CO_2)_7" + 4\ NH_3 \quad (1)$$

$$"Ce_4\{N(SiMe_3)_2\}_{12}(CO_2)_7" \xrightarrow{650\ °C} Ce_4O_{14}C_7N_4 + 12\ HN(SiMe_3)_2 \quad (2)$$

Heterogeneous Solid-Gas Reactivity of $[\{Cp_2HoNH_2\}_2]$ Towards CO_2

Crystalline Ho-NH_2 was heated under purified gaseous CO_2, H_2, and N_2 ($CO_2/H_2/N_2$ = 1:1:1). The pink crystallites of Ho-NH_2 did not show reaction with the gases below a temperature of 200 °C. During the reaction, the compound decolorized forming a beige solid (Ho-1a). Subsequent heating to a temperature of 350 °C was carried out to achieve a complete thermal degradation of the Cp ligands. A brownish reaction product (Ho-1b) was isolated and analyzed by X-ray diffraction, elemental analysis, and IR spectroscopy. The solid was observed to be amorphous and showed a composition of Ho/O/C/N/H = 2:8:12:1:11. The vibrational spectra of the starting material Ho-NH_2 and the carboxylation product after thermal treatment at 200 °C and 350 °C are depicted in Figure 7.

Compared with Ho-NH_2 the N–H valence vibrations at 3504 cm^{-1} are broadened in the spectrum of Ho-1a. Similar signals were observed in the IR spectrum of ammonium carbamate (vide supra) and indicate the formation of

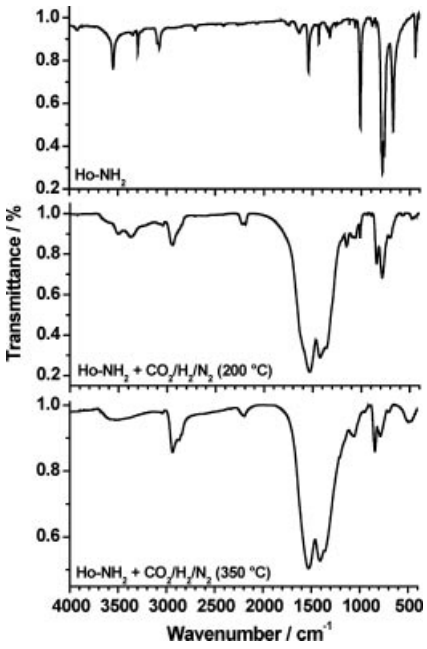


Figure 7. IR spectra of Ho-NH_2 (top) and the carboxylation products after annealing under $CO_2/H_2/N_2$ at 200 °C (center) and 350 °C (bottom).

N···H···N-bridged molecular units in the solid. Absorptions around 2950 and 2850 cm^{-1} indicate the occurrence of C_5H_6 formed by degradation of the Cp ligands under H_2.[26]

Intense broad vibrations at 1620, 1598, and 1530 cm^{-1} are characteristic of CO and CN moieties in carbamato derivatives.[38] Together with additional strong signals between 1480 and 1290 cm^{-1} these absorptions confirm the formation of carbamates or carbonates.[29,32,38] Especially the shoulders at 1620, 1598, and 1290 cm^{-1} are in accordance with vibrations observed for other lanthanide carbamates and ammonium carbamate. The C–O deformations can be attributed to the 950–750 cm^{-1} region.

Only weak intensities were observed between 2250 and 2100 cm^{-1}. The presence of isocyanato moieties can therefore be excluded, but signals of similar shape and intensity in this region were described for several adduct complexes of CO_2 and H_2. The temperature conditions (200 °C) could still justify the occurrence of these species. As a matter of fact, the spectrum of Ho-1b clearly shows that the stretching vibrations for the CO_2 and NCO_2 fragments in the region 2250–1550 cm^{-1} are diminished and thus a further thermal degradation apparently occurred.

For Ho-1a a possible formula can be formulated as $[Ho_2(CO_3)_2(O_2CNH)]_n$. A further thermal treatment of this compound at higher temperatures resulted in the formation of holmium carbonate, confirmed by X-ray powder diffraction. Therefore, the thermal treatment of Ho-NH_2 with $CO_2/H_2/N_2$ at temperatures between 200 and 350 °C can be written as Equation (3).

$$(Cp_2HoNH_2)_2 + 4\ CO_2 + 2\ H_2 \xrightarrow{200\ °C} Ho_2(CO_3)_2(O_2CNH) + 4\ C_5H_6 + NH_3 \quad (3)$$

In order to detect volatile species being potentially evolved during the degradation process of Ho-1a, mass spectra were acquired while heating an evacuated sample in a furnace up to 300 °C. Until 160 °C, a peak of relatively low intensity with m/z = 18 dominates the spectra, which can be attributed to water adsorbed on the sample and adhering to the inside wall of the spectrometer and glass tube. A peak at m/z = 44 shows increasing intensity between 80 and 180 °C; at 200 °C it dominates the spectra. Ammonia (m/z = 17) simultaneously appears in the diagram between 140 and 260 °C, the associated intensity, however, being orders of magnitude smaller as compared to that of CO_2. The degradation of cyclopentadiene (C_5H_6, m/z = 66) was detected beyond 200 °C. At temperatures above 220 °C the relative intensity of CO_2 (m/z = 44) decreases, while the m/z = 66 peak was observed to be the dominating species in the defragmentation pattern until the final temperature of 300 °C was reached. The MS measurement of Ho-1a proved the insertion of CO_2 into the N–H bond and showed that C_5H_6 was built during the degradation process. N–H moieties must have been present in the carboxylation product, otherwise a formation of NH_3 would not be observable.

Heterogeneous Solid-Gas Reaction of $[Cp_3YbNH_3]$ in Supercritical CO_2

Yb-NH_3 shows high reactivity against supercritical CO_2 at 40–50 °C and at a pressure of 250–280 bar. The emerald green amido complex adsorbed CO_2 forming an orange-yellow solid (Yb-1). During the carboxylation process, Yb-NH_3 was transformed into Yb-NH_2. Under normal pressure conditions this reaction was observed to require temperatures between 200 and 290 °C. Yb-NH_2 formed in the first reaction stage as well as the reaction product Yb-1 and both were analyzed by IR spectroscopy. The spectra are depicted in Figure 8.

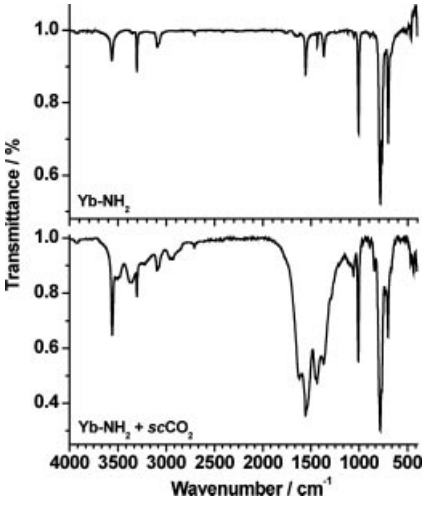


Figure 8. IR spectra of Yb-NH_2 (top) and the carboxylation product (bottom) after the reaction in supercritical CO_2 (T = 50 °C, p = 250–280 bar).

The μ_2-bridged amido ligands of the dinuclear complex Yb-NH_2 can be identified by the intense N–H stretching

vibrations around 3350 and 3290 cm^{-1}, and the asymmetric and symmetric N–H deformation modes around 1540, 670, and 440 cm^{-1}.[20] An intense vibration mode at 3500 cm^{-1}, probably due to a combination of two lower signals, is typical of these amido compounds.[20]

The characteristic stretching and deformation vibrations of Yb-NH_2 are observed in both spectra. Therefore, a degradation of the Cp ring did not occur, probably due to the mild thermal conditions under which the experiment was carried out. Additionally, broad N–H stretching vibrations can be identified in the 3500–3000 cm^{-1} region and can be interpreted as N–H-bridging moieties (vide infra). Signals at 2950 cm^{-1} indicate the occurrence of C_5H_6 formed by the decomposition process of Yb-NH_3 to Yb-NH_2. The most characteristic vibrations in the spectra of Yb-1 are the intense absorptions at 1640, 1540, 1450, and 1379 cm^{-1}. They fit well in the expected ranges of CO and CN stretching vibrations of carbamato complexes.[29] The deformation modes for these kinds of carbamato ligands can be observed at 841 and 670 cm^{-1}. Therefore, the formation of an isolated or higher condensed carbamato complex with the formula [{CpYb}$_2$O$_2$CNH] is very probable.

The synthesized oxonitridocarbonates were observed to be amorphous and not soluble in any common polar and nonpolar solvent. Attempts to crystallize these products by thermal treatment resulted in the decomposition of these precursors to the corresponding oxides or oxide cyanamides.

Conclusions

Ce-BTMSA, Ln-NH_3, and Ln-NH_2 have been shown to be considerable molecular precursor compounds for thermal degradation reactions resulting in novel highly condensed lanthanide O/C/N materials. The carbonato, imidocarbonato, and carbamato species were synthesized using different kinds of heterogeneous solid-gas reactions.

The Ce-BTMSA precursor absorbs CO_2, leading to the formation of a mixed carbamato(carbonato)isocyanato compound. The IR spectra of the products differ significantly from the results reported for carboxylation reactions in solution or in sealed ampules.[35,41] The cerium precursor Ce-BTMSA is activated with CO_2 in the first step. According to the results of the elemental analysis two molecules of CO_2 are absorbed by one molecule of Ce-BTMSA. Subsequently, the CO_2 inserts into the Ce–N bond yielding a carbamato species. According to Scheme 1 further ammonolysis of the compound at higher temperatures results in the formation of an carbonato(isocyanato)cerium compound. The flowing gas stream provides for a better degradation of the Me_3Si groups.

Lanthanide metallocenes were observed to be quite stable against thermal treatment under an inert gas, but they represent a highly reactive molecular precursor species under CO_2 at temperatures above 200 °C. The use of both a reducing (H_2) and oxidizing agent (CO_2) with N_2 as the carrier gas gave satisfying results forming a polymeric (imidocarbonato)holmium complex. The Cp ligands can be split off easily by the presence of H_2 with CO_2 occupying the free coordination sites of the lanthanide ion. The activation or doping of the surface of various materials with lanthanide carbonates or carbamates could therefore be achieved in this way.

The carboxylation reaction of Yb-NH_3 in supercritical carbon dioxide showed, that the temperature necessary for the CO_2 insertion into the Yb–N bond can be lowered significantly. The complex molecule reacted with CO_2 without simultaneous degradation of the Cp ligands. Thus, a molecular single-source precursor with the tentative formula [{CpYb}$_2$O$_2$CNH] has been synthesized. It represents an adequate compound for the deposition of predefined Ln/O/C/N material on various surfaces in materials chemistry.[19]

Furthermore, the observed pleochroism of [Cp_3YbNH_3] is a promising optical property for further applications of this compound as a future dopant in solid-state sciences. Thus, small amounts of this compound introduced during the synthesis of materials could change significantly the optical properties of the final products. The high volatility of [Cp_3YbNH_3] facilitates significantly the doping process using CVD techniques at very convenient conditions (180 °C, 10^{-3} mbar).

Experimental Section

General Procedures: All manipulations described below were performed with rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware or tubes of silica glass, interfaced to a vacuum (10^{-3} mbar) line. Argon was purified by passage through columns of silica gel, molecular sieve, KOH, P_4O_{10}, titanium sponge (650 °C), hydrogen and nitrogen by passage through columns of silica gel, molecular sieve, KOH, P_4O_{10}, BTS,[42] and Cr^{II} oxide catalyst.[43] Carbon dioxide was purified by passage through columns of P_4O_{10} and BTS catalyst.[42] Anhydrous lanthanide(III) chlorides were purchased from Alfa Aesar (99.99%, ultra dry) and were used without any further purification. The complexes [Cp_3YbNH_3] (Ln-NH_3) and [{Cp_2LnNH_2}$_2$] (Ln-NH_2, with Ln = Ho, Yb) as well as [Ce{N(SiMe$_3$)$_2$}$_3$] were prepared according to known procedures[20,25,44] and sublimed twice before use (10^{-3} mbar, 120–250 °C). For thermal degradation experiments a Reetz collapsible tube furnace (LK-1100-45-250) handled by an Omron (RE.LB.1.P16) temperature controller was used. For CO_2 experiments under supercritical conditions a Parr high-pressure vessel (Type 4740) with a Parr gage block (Type 4316) was used. FT-IR spectra were recorded with a Bruker IFS 66v/S spectrometer with DTGS detector. The samples were thoroughly mixed with dried KBr and the preparation procedures were performed in a glovebox under dried argon. The spectra were collected in a range from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1}. During the measurement, the sample chamber was evacuated. Elemental analysis was performed by Mikroanalytisches Labor Pascher, Remagen, Germany. Each element of the sample was analyzed twice. Temperature-dependent mass spectra were recorded using DEI+ (70 eV) with the sample contained in an evacuated (10^{-4} mbar) Schlenk tube (length 330 mm, diameter 10 mm) connected with the gas inlet system of the spectrometer by glass tubes of about 200 mm total length, thus providing dynamic vacuum conditions. The Schlenk tube was placed horizontally in a Carbolite furnace

equipped with a Eurotherm temperature controller (Type 2132). The sample was heated up to 573 K in steps of 5 K min^{-1} and mass spectra of the volatile decomposition products were acquired successively at intervals of 20 K.

X-ray Crystallography: Reflection data were collected with a STOE IPDS diffractometer. The Stoe IPDS software package was used for the determination of the unit-cell parameters, the data collection, and to transform the raw data into the reflection data file. Subsequent calculations after the determination of the unit-cell parameters and data reduction to the *hkl* format were carried out using the SHELXS[45] and SHELXL[46] program. The analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms were either treated isotropically, if found in the Fourier maps, or were otherwise included manually using a riding model. Absorption correction was carried out using the Stoe IPDS program package. All non-hydrogen atoms were refined anisotropically. X-ray diffraction experiments on powder samples at room temperature were conducted with a STOE Stadi P diffractometer with Ge(111)-monochromated Cu-$K_{\alpha1}$ radiation (λ = 154.06 pm). **[Cp_3YbNH_3]:** The structure of Yb-NH_3 was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Intrinsic reticular pseudo-merohedral twinning was observed for each of the isolated crystals.[47] The compound crystallizes as emerald-green or ruby (depending on the viewing direction and lighting) brick-shaped crystals. An appropriate extracted crystal was used and two data sets for each twin domain were extracted from the diffraction data. Yb-NH_3 showed pseudo-orthorhombic symmetry, but X-ray powder diffraction experiments (XRD) confirmed a monoclinic cell setting. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/c$. The reflections were isolated unifying all of the overlapping reflections of the two domains to one reflection set of the most appropriate individual. Subsequent determination of the twin law and refinement of the data resulted in a satisfying crystal structure refinement, taking into account the problems encountered during the isolation and weighting of the overlapping reflections in the reciprocal space. Tables 1 and 2 show the crystallographic data as well as bond lengths and angles, and Figure 1 the molecular structure of Yb–NH_3. CCDC-603950 (for [Cp_3YbNH_3]) and -603951 (for $[NH_4]^+$-$[O_2CNH_2]^-$) 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.

Table 2. Summary of crystallographic data for [Cp_3YbNH_3].

	[Cp_3YbNH_3]
Empirical formula	$C_{15}H_{15}NYb$
Formula mass [g mol^{-1}]	385.34
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14); reticular pseudo-merohedral twinning
Diffractometer device	Stoe IPDS
Crystal size [mm]	0.20 × 0.14 × 0.06
Wavelength λ [pm]	71.073 (Mo-K_α)
Temperature T [K]	120
Twin law	$\begin{pmatrix} -0.12 & 0 & -0.565 \\ 0 & -1 & 0 \\ -1.745 & 0 & 0.12 \end{pmatrix}$
Twin ratio	0.027(2)
Lattice constants [pm, °]	a = 826.8(2) b = 1103.8(2) c = 1482.0(3) β = 101.60(3)
Cell volume [10^6 pm^3]	1309.0(5)
Formula units/cell	4
$\rho_{calcd.}$ [g cm^{-3}]	1.955
μ [mm^{-1}]	7.12
F(000)	740
2θ range [°]	2.53–30.61
Measured refl.	15421
Independent refl.	3952
Refl. with $F_o^2 = 2\sigma(F_o^2)$	12103
No. of refined parameters	155
Max. peak/min. hole [e·Å^{-3}]	1.684/–1.485
R_{int}/R_σ	0.0459/0.0342
R_1 [$I > 2\sigma(I)$]	0.0457
wR_2	0.1224
GooF	1.152

Synthesis. Ce-1: Ce-BTMSA was ground in a mortar, placed in an alumina boat and transferred into a silica tube situated in a tube furnace. First, the solid was heated under flowing argon to 150 °C and than predried CO_2 was added to the gas stream. Melting of the yellow Ce-BTMSA was observed immediately after the first contact with CO_2 and the yellow fluid solidified within 30 min yielding a beige product (Ce-1a). The solid was cooled slowly to room temperature and a small part of the solid was used for IR spectroscopic analysis. The residue was re-introduced into the silica tube and heated to 650 °C under flowing predried ammonia. Ammonia was dried by passage over KOH pellets, Cr^{II} catalyst and condensed over Na and K before use. A dark-brown solid (Ce-1b) was isolated after the sample was cooled to room temperature (4 h) and analyzed by elemental analysis, IR spectroscopy, and X-ray powder diffraction. Ce-1b (0.0615 g) was isolated after the reaction process using an argon-filled glovebox. **Ho-1:** Ho-NH_2 was ground in a mortar, placed in an alumina boat and transferred into a silica tube situated in a tube furnace. The solid was heated under a flowing gas stream of a mixture of $CO_2/H_2/N_2$ = 1:1:1 and heated slowly to 200 °C. The temperature was maintained for 4 h. Cooling of the sample to room temperature yielded a beige solid (Ho-1a). A small part of the solid was used for IR spectroscopic analysis and the residue was re-introduced into the silica tube and heated to 350 °C (4 h) under the same conditions as described above. A dark-brown solid (Ho-1b) was isolated after the sample was cooled to room temperature (2 h) and analyzed by elemental analysis, IR spectroscopy, and X-ray powder diffraction. **Yb-1:** Yb-NH_3 was introduced into a high-pressure vessel and connected with a gas vacuum line. Purified carbon dioxide was desublimated by cooling the vessel to –80 °C until sufficient solid CO_2 was present. The reaction vessel was closed and warmed slowly to 50 °C. A pressure of 250–280 bar was observed during the reaction. After 1 d, the pressure was reduced carefully by opening the valve of the unit and the vessel was opened in an argon-filled glovebox. A yellow-orange powder (Yb-1) was isolated and analyzed by X-ray diffraction methods, IR spectroscopy, and elemental analysis.

Supporting Information (see footnote on the first page of this article): Tables of crystal data, structure solution and refinement, bond lengths and angles for $[NH_4]^+[O_2CNH_2]^-$ as well as figures of the crystal structure.

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