
This is an electronic reprint of the original article.
This reprint may differ from the original in pagination and typographic detail.

Rudel, Stefan S.; Graubner, Tim; Karttunen, Antti J.; Kraus, Florian

Reactions in Anhydrous Liquid Ammonia : Syntheses and Crystal Structures of $[M(\text{NH}_3)_8]I_2$ (M = Eu, Yb) with Bicapped Trigonal-Prismatic Octaammine Lanthanoid(II) Cations

Published in:
Zeitschrift für Anorganische und Allgemeine Chemie

DOI:
[10.1002/zaac.202000181](https://doi.org/10.1002/zaac.202000181)

Published: 31/08/2020

Document Version
Publisher's PDF, also known as Version of record

Published under the following license:
CC BY

Please cite the original version:
Rudel, S. S., Graubner, T., Karttunen, A. J., & Kraus, F. (2020). Reactions in Anhydrous Liquid Ammonia : Syntheses and Crystal Structures of $[M(\text{NH}_3)_8]I_2$ (M = Eu, Yb) with Bicapped Trigonal-Prismatic Octaammine Lanthanoid(II) Cations. *Zeitschrift für Anorganische und Allgemeine Chemie*, 646(16), 1396-1402.
<https://doi.org/10.1002/zaac.202000181>

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

Reactions in Anhydrous Liquid Ammonia: Syntheses and Crystal Structures of $[M(\text{NH}_3)_8]\text{I}_2$ ($M = \text{Eu}, \text{Yb}$) with Bicapped Trigonal-Prismatic Octaammine Lanthanoid(II) Cations

Stefan S. Rudel,^[a] Tim Graubner,^[a] Antti J. Karttunen,^[b] and Florian Kraus*^[a]

Dedicated to Prof. Dr. Christian Robl on the Occasion of his 65th Birthday

Abstract. The compounds $[M(\text{NH}_3)_8]\text{I}_2$ ($M = \text{Eu}, \text{Yb}$) were obtained from reactions in anhydrous liquid ammonia solutions as side products. They were characterized by single-crystal X-ray diffraction and found to be isotypic to the compounds $[\text{Ca}(\text{NH}_3)_8]\text{X}_2$ ($X = \text{Cl}, \text{Br}, \text{I}$). The coordination sphere of the lanthanoid(II) cations is not square-antiprismatic but much better described as bicapped trigonal-prismatic. In contrast, quantum-chemical gas-phase calculations show the square-anti-

prismatic coordination polyhedron (point group S_8) to be energetically favored over the bicapped trigonal prism and the latter is not even a true local minimum. Obviously, hydrogen bonding and eventually other weak interactions have an impact on the observed bicapped trigonal-prismatic coordination sphere of the $[M(\text{NH}_3)_8]^{2+}$ cations in the solid state.

Introduction

Liquid ammonia under ambient pressure is able to dissolve the alkali and alkaline earth metals as well as Eu and Yb, and can form, depending on the metal concentration, deep blue solutions of solvated electrons.^[1–5] The reaction of a solution of europium in ammonia with NH_4I was previously used for the preparation of EuI_2 . However, the intermediate formed inside the liquid ammonia solution remained unclear.^[6] It has been reported that the solutions of Eu and Yb likely contain hexaammine complexes $[M(\text{NH}_3)_6]^{2+} \cdot 2e^-$ ($M = \text{Eu}, \text{Yb}$).^[7] From the reactions of these two metals with AgN_3 as an oxidant in liquid ammonia, we obtained octaammine complexes of Eu^{II} and Yb^{II} as the azides $[M(\text{NH}_3)_8](\text{N}_3)_2$ and $[M(\text{NH}_3)_8](\text{N}_3)_2 \cdot 2\text{NH}_3$. We characterized them structurally by X-ray diffraction on single crystals.^[8] Thus, it was for the first time that compounds of Eu^{II} and Yb^{II} were reported with coordination numbers larger than six at the metal atoms with simple ammine ligands.^[8] We now have obtained analogous iodides of Eu^{II} and Yb^{II} that also show coordination number eight

for the metal atoms and present their syntheses and crystal structures here.

Results and Discussion

The title compounds were obtained as products from reactions of UI_4 with $\text{Eu}(\text{NH}_2)_2$ or of NH_4I with $\text{Yb}(\text{NH}_2)_2$, respectively. In the context of our exploration of the chemistry of uranium halides in liquid ammonia, we investigated the effect of reducing agents on solutions of U^{IV} cations. The rare earth amides $\text{Eu}(\text{NH}_2)_2$ and $\text{Yb}(\text{NH}_2)_2$ are powerful one-electron reducing agents and the latter was reported to even reduce potassium amide to a potassium electride solution in liquid ammonia.^[9] So we expected these compounds to reduce complexes of U^{IV} to U^{III} in liquid ammonia. So far, we were not able to crystallize any uranium compounds from these reactions. However, the byproduct $[\text{Eu}(\text{NH}_3)_8]\text{I}_2$, which we describe here, speaks for the absence of the desired redox reaction under the applied conditions.

Instead, a simple acid-base reaction seems to occur. UI_4 forms a decaammine complex in neutral liquid ammonia which reacts acidic due to the polarization of the N–H bonds of the ammine ligands by the Lewis acidic metal cation.^[10] Reactions of uranium tetrahalides with alkali metal amides in liquid ammonia yielded a variety of amide complexes. Notably, once started, such deprotonation reactions can start an ammonolysis reaction which proceeds further to practically insoluble amides, imides or nitrides, which appear in the form of amorphous brown precipitates. This releases excessive protons, so that we observed the formation of ammono acids, namely the respective ammonium halides, after starting from ammonobasic solutions.^[10]

Here we reacted UI_4 and $\text{Eu}(\text{NH}_2)_2$ in a stoichiometric 1:1 ratio in liquid ammonia and observed formation of the octa-

* Prof. Dr. F. Kraus
E-Mail: f.kraus@uni-marburg.de

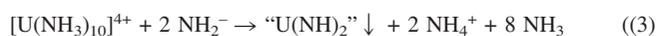
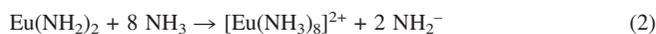
[a] Fluorchemie, Anorganische Chemie, Fachbereich Chemie
Philipps-Universität Marburg,
Hans-Meerwein-Str. 4
35032 Marburg, Germany

[b] Department of Chemistry and Materials Science
Aalto University
00076 Aalto, Finland

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/zaac.202000181> or from the author.

© 2020 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

ammine Eu^{II} complex [Eu(NH₃)₈]²⁺ besides some brown precipitate. Based on our previous findings in the chemistry of uranium in ammonia, we can describe the reactions with the following, simplified Equation (1), Equation (2), and Equation (3).^[10] We deem the brown precipitate to be an uranium imide or amide nitride which we address based on previous reports as “U(NH)₂”.^[11] However, we have no actual knowledge on the dissolved species.



A more detailed investigation of the reaction with different ratios of the starting materials is ongoing.

In case of the reaction of Yb(NH₂)₂ with an equimolar amount of NH₄I, we have evidence that protolysis occurs as we observe the formation of the octaammine complex [Yb(NH₃)₈]²⁺. However, besides the compound [Yb(NH₃)₈]I₂, we encountered an ammoniate of a dinuclear, NH₂-bridged complex [Yb₂(μ-NH₂)₃(NH₃)₁₀](N₃)₃·xNH₃ after short reaction time and likely due to the substoichiometric amount of NH₄I with regard to the NH₂⁻/NH₄⁺ ratio. Unfortunately, we did not succeed in obtaining single crystals of a quality that would allow for an unambiguous crystal-structure determination. However, it is clear from lattice parameters and the heavy-atom positions that the compound is structurally closely related to [Ho₂(μ-NH₂)₃(NH₃)₁₀](N₃)₃·1.25NH₃.^[12] Yb(NH₂)₂ is known to be easily oxidized by liquid ammonia to form Yb(NH₂)₃,^[9] so the formation of trivalent byproducts is not surprising. Further investigations under different stoichiometric ratios are ongoing.

For these reasons, we give a simplified equation for the stoichiometric reaction leading to the octaammine complexes described in this work Equation (4). Despite the equation being plausible, further evidence has to be gained on how the reaction proceeds under different conditions and if intermediates are formed.



The compounds [M(NH₃)₈]I₂ (M = Eu, Yb) crystallize isotopic to the compounds [Ca(NH₃)₈]X₂ (X = Br, I)^[13] in the orthorhombic crystal system, space group *Pnma* (Wyckoff sequence 62, *d*³*c*⁵) and therefore belong to the [Ca(NH₃)₈]Cl₂ or [Sr(NH₃)₈]Cl₂ structure type.^[14,15] As a side comment, [Ca(NH₃)₈]Cl₂ was likely erroneously reported as [Ca(NH₃)₆]Cl₂·2NH₃ in the original work,^[14] while for [Sr(NH₃)₈]Cl₂ the space group choice was not unambiguous.^[15] In contrast, the crystal structures of [Ca(NH₃)₈]X₂ (X = Br, I) are firmly established.^[13] We will therefore limit the structural discussion to the necessary minimum. Crystallographic data and details of the structure determinations are available from Table 1 and Table 2 holds atomic coordinates and equivalent isotropic displacement parameters.

Table 1. Selected crystallographic data and details of the structure determinations.

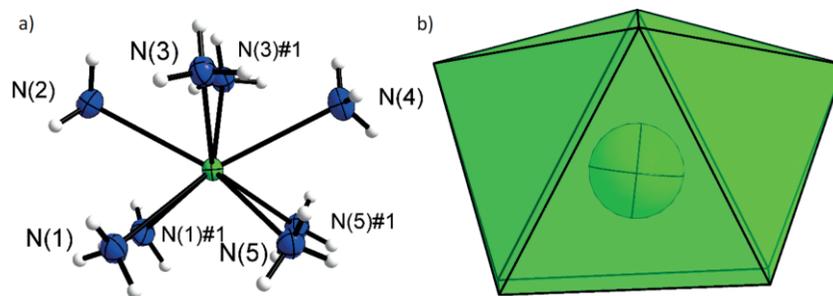
	[Eu(NH ₃) ₈]I ₂	[Yb(NH ₃) ₈]I ₂
Molar mass /g·mol ⁻¹	542.03	563.11
Space group (no.)		<i>Pnma</i> (62)
<i>a</i> /Å	12.363(2)	12.125(2)
<i>b</i> /Å	7.8410(16)	7.7762(16)
<i>c</i> /Å	16.751(3)	16.700(3)
<i>V</i> /Å ³	1623.8(6)	1574.5(5)
<i>Z</i>		4
Pearson symbol		<i>oP</i> 44 (without H atoms), <i>oP</i> 140
$\rho_{\text{calcd.}}$ /g·cm ⁻³	2.22	2.38
μ /mm ⁻¹	7.64	9.84
Color	yellow	orange
Crystal morphology		needle
Crystal size /mm ³	0.9 × 0.2 × 0.15	0.13 × 0.05 × 0.03
<i>T</i> /K		100
λ /Å		0.71073 (Mo- <i>K</i> _α)
No. of reflections	16350	8178
θ range /°	3.51–30.50	3.57–30.51
Range of Miller indices	–17 ≤ <i>h</i> ≤ 17 –11 ≤ <i>k</i> ≤ 11 –22 ≤ <i>l</i> ≤ 23	–17 ≤ <i>h</i> ≤ 14 –11 ≤ <i>k</i> ≤ 10 –23 ≤ <i>l</i> ≤ 19
Absorption correction	numerical	numerical
<i>T</i> _{max} , <i>T</i> _{min}	0.2094, 0.6985	0.4525, 0.7408
<i>R</i> _{int} , <i>R</i> _σ	0.026, 0.013	0.043, 0.032
Completeness of the data set	0.997	0.997
No. of unique reflections	2630	2563
No. of parameters	64	63
No. of restraints	0	0
No. of constrains	0	0
<i>S</i> (all data)	1.11	1.09
<i>R</i> (<i>F</i>) (<i>I</i> ≥ 2σ(<i>I</i>), all data)	0.015, 0.017	0.027, 0.038
<i>wR</i> (<i>F</i> ²) (<i>I</i> ≥ 2σ(<i>I</i>), all data)	0.031, 0.031	0.049, 0.051
Extinction coefficient	0.00039(7)	–
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ /e·Å ⁻³	0.52, –0.66	1.11, –0.92

The coordination polyhedra of [Ca(NH₃)₈]²⁺ were better described with bicapped trigonal prisms instead of square antiprisms, and we find this to be the case also here. The Eu–N bond lengths within the trigonal prism are 2 × 2.7132(15), 2 × 2.7478(15), and 2 × 2.7521(15) Å, and for the Yb compound 2 × 2.602(3), 2 × 2.639(3), and 2 × 2.644(3) Å are observed. The capping ammine ligands show distances of 2.768(2) and 2.823(2) Å for the Eu, and 2.675(5) and 2.743(5) Å for the Yb compound. So, the atomic distances between the central atoms and the ammine ligands follow the lanthanoid contraction. Figure 1 shows the [M(NH₃)₈]²⁺ complex cation (M = Eu, Yb) from the crystal structures of the title compounds and the coordination sphere of the *M* atoms highlighting the difference to a square antiprismatic coordination sphere.

The Yb–N bond lengths in the compound [Yb(NH₃)₈](N₃)₂ were observed from 2.599(12) to 2.660(15) Å within the trigonal prism, and from 2.697(10) to 2.758(17) Å for the capping ammine ligands.^[8] Thus, the bond lengths are well in agreement with those of [Yb(NH₃)₈]I₂ presented here. To the best of our knowledge only very little structural research has been conducted on NH₃ complexes of divalent Eu and Yb complexes. Crystal structures of divalent ytterbium compounds where the central atom carries only one ammine

Table 2. Atomic coordinates and equivalent isotropic displacement parameters U_{iso} for the title compounds. Hydrogen atoms are omitted for clarity. Numbers separated by a “/” are for the Eu / Yb compound, respectively.

Atom	Pos.	x	y	z	$U_{\text{iso}} / \text{\AA}^2$
Eu / Yb	4c	0.23821(2) / 0.23845(2)	¼	0.64057(2) / 0.63941(2)	0.01207(4) / 0.01179(5)
I(1)	4c	0.42042(2) / 0.41612(3)	¼	0.33547(2) / 0.33494(2)	0.01479(4) / 0.01427(7)
I(2)	4c	0.34341(2) / 0.33911(3)	¼	0.94196(2) / 0.94145(2)	0.01718(4) / 0.01652(7)
N(1)	8d	0.36516(13) / 0.3652(3)	0.0357(2) / 0.0439(5)	0.55030(9) / 0.5535(2)	0.0212(3) / 0.0203(6)
N(2)	4c	0.15489(18) / 0.1551(4)	¼	0.48718(13) / 0.4911(3)	0.0196(4) / 0.0191(9)
N(3)	8d	0.09085(12) / 0.0965(3)	−0.00551(19) / 0.0000(4)	0.63048(9) / 0.6299(2)	0.0186(3) / 0.0181(6)
N(4)	4c	0.11445(19) / 0.1135(4)	¼	0.78220(14) / 0.7763(3)	0.0218(4) / 0.0189(9)
N(5)	8d	0.32697(12) / 0.3280(3)	0.01650(19) / 0.0284(4)	0.74387(9) / 0.7399(2)	0.0197(3) / 0.0177(6)

**Figure 1.** (a) The cationic complex $[\text{M}(\text{NH}_3)_8]^{2+}$ ($\text{M} = \text{Eu}, \text{Yb}$) shown as central projection. Displacement ellipsoids at 70% probability at 100 K, hydrogen atoms isotropic with arbitrary radius. Only one set of hydrogen atoms is shown for the ammine ligands with N(2) and N(4) nitrogen atoms. Symmetry operation for the generation of equivalent atoms: #1 $x, \frac{1}{2} - y, z$. (b) Coordination polyhedron around the central atom showing the deviation from a square antiprismatic coordination sphere and the closer relation to a bicapped trigonal prism.

ligand, namely $[\text{Yb}(\text{C}_{10}\text{H}_{15})_2(\text{NH}_3)(\text{THF})]$ and $[\text{Yb}(\text{C}_{10}\text{H}_{15})_2(\text{C}_6\text{H}_5\text{S})(\text{NH}_3)]$, are known.^[16,17] These Yb–N distances are slightly shorter with 2.56(2) and 2.423(8) Å, respectively, compared to those of the Yb title compound, which may be due to the very different coordination sphere in these heteroleptic complexes. Besides these few Yb complexes with oxidation number +II, the octaammine Yb^{III} cation has been observed in the compounds $[\text{Yb}(\text{NH}_3)_8][\text{Cu}(\text{S}_4)_2] \cdot \text{NH}_3$ and $[\text{Yb}(\text{NH}_3)_8][\text{Ag}(\text{S}_4)_2] \cdot 2\text{NH}_3$. The compounds were prepared from supercritical ammonia at 170 °C.^[18] The reported Yb^{III}–N bond lengths of these square-antiprismatic $[\text{Yb}(\text{NH}_3)_8]^{3+}$ cations range from 2.470(14) to 2.459(13) Å, and are thus shorter due to the higher oxidation state of the central metal atoms. Müller-Buschbaum, who also worked on heteroleptic ammine complexes,^[19] states Yb^{III}–N distances of 2.446(2)–2.504(2) Å for the Yb^{III} compound $[\text{Yb}(\text{NH}_3)_8][\text{Yb}(\text{Pyr})_6]$ (Pyr = pyrrolate), which was crystallized from liquid ammonia at –35 °C.^[20] Again, the coordination polyhedron was described as square-antiprismatic with bond lengths shorter than in our compound. As we observed a bicapped trigonal-prismatic coordination sphere for the Yb cations of the compound $[\text{Yb}(\text{NH}_3)_8](\text{N}_3)_2$, but a square antiprismatic one for its ammoniate $[\text{Yb}(\text{NH}_3)_8](\text{N}_3)_2 \cdot 2\text{NH}_3$, it seems that the energy barrier between the two isomers is quite small.^[8] The small energy difference has been reported and previously discussed in some detail.^[21–24]

Comparing the Eu^{II}–N atom distances with other compounds is not simple as mononuclear complexes of Eu^{II} in coordination number eight are not frequent.^[25] Even in the cryptate complexes of [2.2.2]cryptand and its derivatives, which one would expect to be eight-coordinate, Eu^{II} is mostly

coordinated by additional solvent molecules leading to higher coordination numbers.^[26–28] Only in the aza-cryptate in reference^[29] coordination number eight is unambiguous. However, this multidentate aza-cryptand complex is quite unsuitable for comparison to our system as a bicapped trigonal antiprism with much larger Eu–N distances has been reported. The compound $[\text{Eu}(\text{NH}_3)_8](\text{N}_3)_2$ is certainly isotopic to $[\text{Yb}(\text{NH}_3)_8](\text{N}_3)_2$. Unfortunately, the detailed crystal structure of $[\text{Eu}(\text{NH}_3)_8](\text{N}_3)_2$ is unknown.^[8]

Other Eu^{II} complexes like $[\text{Eu}(\text{C}_{12}\text{H}_8\text{N}_2)_2]$, which forms one-dimensional infinite chains with a coordination number of six for the metal atom, show Eu^{II}–N distances in the range of 2.53 to 2.68 Å.^[30] In our case the Eu^{II}–N distances are $2 \times 2.7132(15)$, $2 \times 2.7478(15)$, and $2 \times 2.7521(15)$ Å within the trigonal prism and 2.768(2) and 2.823(2) Å for the two capping ammine ligands. We therefore see the Pauling rule fulfilled that the higher coordination number should show increased atom distances between central atom and ligand. Comparing the complex cation to octaammine complexes of Sr²⁺ may therefore be helpful: In the compound $[\text{Sr}(\text{NH}_3)_8]_3(\text{C}_{70})_2 \cdot 19\text{NH}_3$ three independent $[\text{Sr}(\text{NH}_3)_8]^{2+}$ complexes are present. Two of them are slightly distorted square-antiprismatic with Sr–N distances of 2.703(5) to 2.777(6) Å and 2.727(6) to 2.800(7) Å, while the third is clearly better described as distorted bicapped trigonal-prismatic with Sr–N distances from 2.683(5) to 2.778(5) Å.^[31] Unfortunately, the structural studies carried out on $[\text{Sr}(\text{NH}_3)_8]\text{Cl}_2$ were “only” done by Rietveld refinement and the authors report disorder for the capping NH₃ ligands. Thus, the Sr–N distances span from 2.714(2) to long 2.950(7) Å. The authors therefore state “distorted tetragonal antiprisms or double-

capped trigonal prisms” for the shape of the complex cations.^[32] Be it as it may, the $\text{Eu}^{\text{II}}\text{-N}$ distances observed by us agree with the Sr-N distances reported by *Jansen* and co-workers.^[31]

Müller-Buschbaum and co-workers noticed that the homoleptic ammine complexes of Eu^{II} and Yb^{II} were described with coordination number six,^[7,33] despite that Eu^{II} and Yb^{II} have larger ionic radii^[34] than the trivalent lanthanoid cations for which the octa- and nonaammine complexes $[\text{Yb}(\text{NH}_3)_8]^{3+}$, $[\text{La}(\text{NH}_3)_9]^{3+}$ and $[\text{Sm}(\text{NH}_3)_9]^{3+}$ have been reported.^[18,20,35] One would therefore expect Eu^{II} and Yb^{II} to also show larger coordination numbers like those we observe in the title compounds. From our experiences in the CaX_2/NH_3 system ($X = \text{Br}, \text{I}$), we know that both octaammine and hexaammine complexes can exist.^[13] It is therefore not unlikely that also hexaammine complexes of Eu^{II} and Yb^{II} exist, despite structural evidence for these species is so far not direct under different conditions, however quite likely: (i) *Thompson, Stone* and *Waugh* reported: “We have investigated the composition dependence of the vapor pressure of ammonia over solutions of both europium and ytterbium metals in liquid ammonia at -75.9° . We find that these two metals do behave in a manner similar to that of the alkaline earths in that both europium and ytterbium appear to form hexaammoniates.”^[7] (ii) *Oesterreicher, Mammano*, and *Sienko* have shown in 1969 that the lattice parameters of golden crystals obtained from solutions of Yb and Eu in ammonia at -173°C have similar lattice parameters as $\text{Sr}(\text{NH}_3)_6$.^[33] Our investigations are ongoing and we will attempt to obtain hexaammine Eu^{II} and Yb^{II} salts.

Quantum-chemical calculations (for more details see Experimental Section and the Supporting Information) were carried out on the complex cations $[\text{M}(\text{NH}_3)_8]^{2+}$ ($M = \text{Eu}, \text{Yb}$) in the gas-phase for two possible coordination spheres, the bicapped trigonal prism (C_{2v}) and the square antiprism (S_8). In the case of the $[\text{Eu}(\text{NH}_3)_8]^{2+}$ cation the geometry optimization for the square antiprism had to be carried out in the Abelian subgroup C_2 as the complex irreducible representations of the S_8 point group resulted in major numerical problems. The geometry optimizations for the $[\text{Eu}(\text{NH}_3)_8]^{2+}$ cation showed that the square-antiprismatic coordination sphere (calculated in C_2), but the structure remained S_8) is $32\text{ kJ}\cdot\text{mol}^{-1}$ lower in energy than the bicapped trigonal-prismatic one. A subsequent harmonic frequency analysis confirmed that the bicapped trigonal-prismatic coordination sphere is not a true local minimum on the potential energy surface, as three imaginary frequencies of $111i\text{ cm}^{-1}$, $71i\text{ cm}^{-1}$ and $7i\text{ cm}^{-1}$ were obtained. They all represent movement of the ammine ligands towards the more favored square-antiprismatic coordination sphere.

The optimization for the $[\text{Yb}(\text{NH}_3)_8]^{2+}$ cation showed similar results. The S_8 -symmetric molecule with square-antiprismatic coordination sphere was $13\text{ kJ}\cdot\text{mol}^{-1}$ lower in energy than the bicapped trigonal-prismatic coordination sphere. Furthermore, the subsequent harmonic frequency analysis showed for the latter four imaginary frequencies at $169i\text{ cm}^{-1}$, $142.5i\text{ cm}^{-1}$, $142.0i\text{ cm}^{-1}$ and $111i\text{ cm}^{-1}$. All vibration modes correspond to a movement towards the more preferred S_8 -symmetric coordination sphere.

In conclusion, the favored gas-phase structure of the $[\text{M}(\text{NH}_3)_8]^{2+}$ cations ($M = \text{Eu}, \text{Yb}$) is the square antiprism. This matches with results previously reported for the $[\text{Ca}(\text{NH}_3)_8]^{2+}$ cation, where the difference between the square-antiprismatic coordination sphere was favored over the bicapped trigonal-prismatic coordination sphere by $15\text{ kJ}\cdot\text{mol}^{-1}$.^[13] The discrepancy between the experimentally observed solid-state and the calculated gas-phase structures is likely a result of hydrogen bonding and possibly of other weak interactions.

Conclusions

The compound $[\text{Eu}(\text{NH}_3)_8]\text{I}_2$ was obtained from the reaction of UI_4 with $\text{Eu}(\text{NH}_2)_2$ in liquid ammonia, while $[\text{Yb}(\text{NH}_3)_8]\text{I}_2$ was synthesized from NH_4I and $\text{Yb}(\text{NH}_2)_2$ in the same solvent. Both compounds are side products but could be characterized using single-crystal X-ray diffraction. The compounds are isotopic to $[\text{Ca}(\text{NH}_3)_8]\text{X}_2$ ($X = \text{Cl}, \text{Br}, \text{I}$). The coordination polyhedra of the lanthanoid(II) cations are best described as bicapped trigonal-prismatic instead of square-antiprismatic. Our study shows that coordination numbers for Eu^{II} and Yb^{II} larger than six with monodentate ligands are not unusual. Quantum-chemical calculations at the DFT-PBE0/def2-TZVP level of theory displayed that the square-antiprismatic coordination polyhedron is favored over the bicapped trigonal-prismatic one for both the $[\text{Eu}(\text{NH}_3)_8]^{2+}$ and the $[\text{Yb}(\text{NH}_3)_8]^{2+}$ cation in the gas phase, with $32\text{ kJ}\cdot\text{mol}^{-1}$ and $13\text{ kJ}\cdot\text{mol}^{-1}$, respectively. Additionally, the bicapped trigonal-prismatic coordination polyhedron is not a true local minimum in the gas phase. We conclude that for the solid-state compounds, hydrogen bonding and other weak interactions lead to the observed bicapped trigonal-prismatic coordination polyhedra. In the past we observed a bicapped trigonal-prismatic coordination sphere for the Yb cations of the compound $[\text{Yb}(\text{NH}_3)_8](\text{N}_3)_2$, but a square antiprismatic one for its ammoniate $[\text{Yb}(\text{NH}_3)_8](\text{N}_3)_2\cdot 2\text{NH}_3$.^[8] Therefore, the energy difference between the two isomers must be quite small in the solid state.

Experimental Section

All work was carried out by excluding moisture and air under dried and purified argon (Praxair, 5.0) using high-vacuum glass lines or a glove box (MBRAUN). Liquid ammonia (Air Liquide, 99.98%) was dried and stored over sodium (VWR) in a special high-vacuum glass line. All glass vessels were flame-dried under vacuum three times before use.

Synthesis of $\text{Eu}(\text{NH}_2)_2$ and $\text{Yb}(\text{NH}_2)_2$: $\text{Eu}(\text{NH}_2)_2$ was obtained, similar to the literature,^[4,36] from the reaction of Eu metal with anhydrous ammonia at $+50^\circ\text{C}$. A pre-dried glass crucible was charged with 0.558 g Eu powder (3.67 mmol , Strem, 99%) in a glove box and transferred into a suitable autoclave vessel. Circa 6 mL of anhydrous ammonia were distilled into the autoclave at -78°C . The autoclave was closed and heated to $+50^\circ\text{C}$ for three days. To prevent boiling delays upon removal of the excess of ammonia, the autoclave was cooled to -26°C using a cryostat. Then, the ammonia was allowed to evaporate via a mercury overpressure valve. Finally, the residual ammonia was

pumped off until a vacuum of 10^{-3} mbar was reached. The autoclave was then opened inside the glove box and 0.675 g of $\text{Eu}(\text{NH}_2)_2$ (3.67 mmol) were obtained as an orange-brown powder. The product was phase-pure as evidenced by powder X-ray diffraction.

$\text{Yb}(\text{NH}_2)_2$ must be synthesized differently as under the same conditions large amount of $\text{Yb}(\text{NH}_2)_3$ are formed. The formation of Yb^{III} can be avoided if the direct contact of liquid ammonia with Yb metal is excluded.^[9,36,37] Therefore, the reaction was carried out, similar to the literature,^[9] in an H-shaped borosilicate glass tube shown in Figure 2.

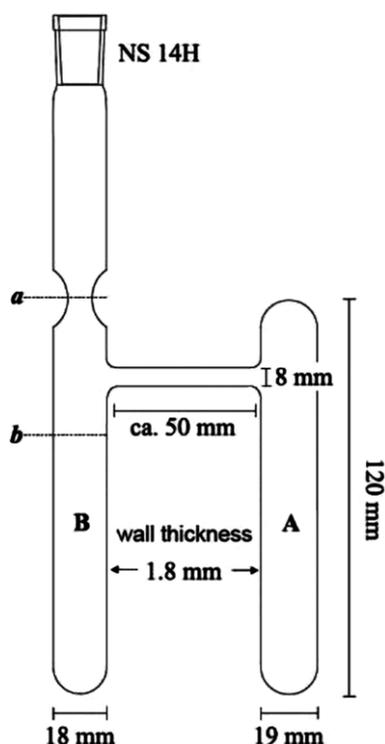


Figure 2. H-tube used for the synthesis of $\text{Yb}(\text{NH}_2)_2$.

Leg **B** was charged with 500 mg of Yb powder (2.89 mmol, Strem, 99%) in a glove-box, and leg **A** was charged with a few milliliters of ammonia by distillation at -78 °C. The ammonia in **A** was then cooled to -196 °C and the H-shaped bomb tube was flame sealed under vacuum at constriction **a**. The maximum batch size is given by the pressure resistance of the bomb tube which must be designed so as to safely withstand the pressure arising from the H_2 formation. The leg with the Yb (**B**) was kept at room temperature, while leg **A** was kept at 0 °C for two days. Then, only gaseous ammonia reacts with the Yb and forms majorly $\text{Yb}(\text{NH}_2)_2$. After two days, the Yb was converted into the diamide, a dark brown powder, which had about 20 times the volume of the used Yb metal. Leg **A** was then cooled to -196 °C, leg **B** was scored at position **b** and inserted into a Schlenk tube under argon as shown in Figure 3. Then, a hot, white-glowing glass rod was used to split off the ampoule at position **b** which falls into the Schlenk tube.

The yield of $\text{Yb}(\text{NH}_2)_2$ was quantitative.

Synthesis of $[\text{Eu}(\text{NH}_3)_8]\text{I}_2$: The compound was obtained as a side product from the reaction of 70 mg of UI_4 (0.09 mmol, 1 equiv.) with 17 mg of $\text{Eu}(\text{NH}_2)_2$ (0.09 mmol, 1 equiv.) which were placed into the

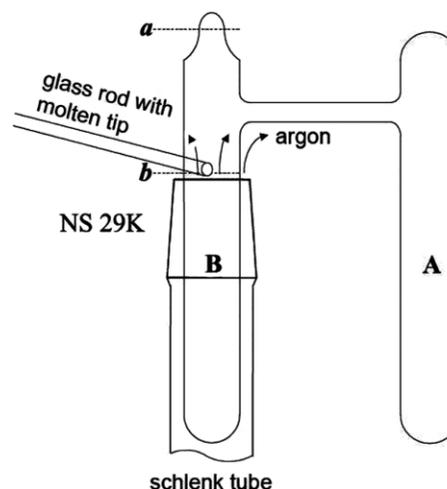


Figure 3. Setup used to open the H-shaped bomb tube containing ammonia in leg **A** under inert conditions to recover the $\text{Yb}(\text{NH}_2)_2$ in leg **B**.

legs of an H-shaped tube separated by a glass frit. Circa 10 mL liquid ammonia were condensed at -78 °C into each leg and a green solution, due to dissolved U^{IV} , was obtained. The green solution was passed over the glass frit onto the $\text{Eu}(\text{NH}_2)_2$. The H-tube was stored at -40 °C for crystal growth for 7 d. The compound crystallized as yellow needles, while the solution was still green from dissolved U^{IV} . Additionally, some brown precipitate formed. A photograph of the crystals in dry perfluoroether oil is shown in Figure 4. We have not investigated its thermal stability.

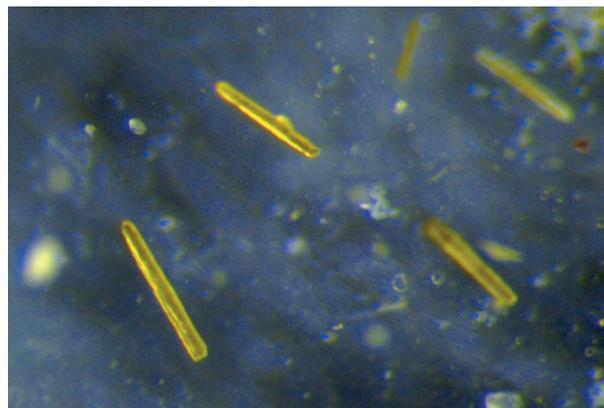


Figure 4. A photograph of the yellow needles of $[\text{Eu}(\text{NH}_3)_8]\text{I}_2$ under perfluoroether oil.

Synthesis of $[\text{Yb}(\text{NH}_3)_8]\text{I}_2$: The reaction of 145 mg NH_4I (1.00 mmol, 1 equiv.) and 205 mg $\text{Yb}(\text{NH}_2)_2$ (1.00 mmol, 1 equiv.) in circa 10 mL liquid ammonia at -78 °C leads to a yellow solution and undissolved starting material. The Schlenk tube was stored at -40 °C for crystal growth for 30 d. The compound crystallizes as orange needles. We have not investigated its thermal stability.

Single Crystal Structure Analyses: Single crystals were selected under nitrogen-cooled, pre-dried perfluorinated oil and mounted using a MiTeGen loop. Intensity data of a suitable crystal were recorded with an IPDS 2T diffractometer (Stoe & Cie). The diffractometer was operated with Mo- K_{α} radiation (0.71073 Å, graphite monochromator) and equipped with an image plate detector. Evaluation, integration and reduction of the diffraction data was carried out using the X-Area software suite.^[38] A numerical absorption correction was applied with the modules X-Shape and X-Red32 of the X-Area software suite. The structure was solved with dual-space methods (SHELXT-2014/5) and refined against F^2 (SHELXL-2018/3).^[39,40] All atoms were refined with anisotropic displacement parameters. The highest residual electron density after the final refinement was 1.20 Å distant from atom Eu for the Eu compound and was 1.11 Å distant from atom I(2) for the Yb compound. Representations of the crystal structures were created with the Diamond software.^[41]

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1994124 and CCDC-1994125 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>)

Computational Details: All calculations were carried out with the TURBOMOLE^[42,43] program suite using the PBE0 hybrid density functional method.^[44,45] Karlsruhe def2-TZVP^[46] basis set was applied for all atoms. Multipole-accelerated resolution-of-the-identity approximation (MA-RIJ) was used to speed up the DFT calculations^[47–49] and “m4” integration grid was used for the numerical integration of the exchange-correlation part. Numerical harmonic frequency calculations were performed to check if the optimized structures are true local minima on the potential energy surface. The optimized structures are available from the Supporting Information.

Supporting Information (see footnote on the first page of this article): Coordinates of the optimized structures in XYZ format.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft for funding. Open access funding enabled and organized by Projekt DEAL.

Keywords: Ytterbium; Europium; Liquid ammonia; Structure elucidation; Quantum-chemical calculations

References

- W. Weyl, *Ann. Phys. Chem.* **1864**, 197, 601–612.
- C. A. Kraus, *J. Am. Chem. Soc.* **1908**, 30, 1323–1344.
- J. C. Warf, W. L. Korst, *J. Phys. Chem.* **1956**, 60, 1590–1591.
- R. Juza, C. Hadenfeldt, *Naturwissenschaften* **1968**, 55, 229–229.
- C. Hadenfeldt, R. Juza, *Naturwissenschaften* **1969**, 56, 282–282.
- M. Krings, M. Wessel, R. Dronskowski, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2009**, 65, i66–i68.
- D. S. Thompson, M. J. Stone, J. S. Waugh, *J. Phys. Chem.* **1966**, 70, 934–935.
- T. G. Müller, J. Mogk, M. Conrad, F. Kraus, *Eur. J. Inorg. Chem.* **2016**, 2016, 4162–4169.
- J. C. Warf, V. Gutmann, *J. Inorg. Nucl. Chem.* **1971**, 33, 1583–1587.
- S. S. Rudel, S. A. Baer, P. Woidy, T. G. Müller, H. L. Deubner, B. Scheibe, F. Kraus, *Z. Kristallogr., Cryst. Mater.* **2018**, 233, 817–844.
- G. Tschirne, D. Naumann, *Z. Anorg. Allg. Chem.* **1967**, 354, 50–55.
- T. G. Müller, F. Karau, W. Schnick, F. Kraus, *Angew. Chem. Int. Ed.* **2014**, 53, 13695–13697.
- P. Woidy, A. J. Karttunen, T. G. Müller, F. Kraus, *Z. Naturforsch. B* **2014**, 69, 1141–1148.
- S. Westman, P.-E. Werner, T. Schuler, V. Raldow, *Acta Chem. Scand. A* **1981**, 35, 467–472.
- S. Lysgaard, A. L. Ammitzbøll, R. E. Johnsen, P. Norby, U. J. Quaade, T. Vegge, *Int. J. Hydrogen Energy* **2012**, 37, 18927–18936.
- A. L. Wayda, J. L. Dye, R. D. Rogers, *Organometallics* **1984**, 3, 1605–1610.
- A. Zalkin, T. J. Henly, R. A. Andersen, *Acta Crystallogr., Sect. C: Struct. Chem.* **1987**, 43, 233–236.
- D. M. Young, G. L. Schimek, J. W. Kolis, *Inorg. Chem.* **1996**, 35, 7620–7625.
- C. C. Quitmann, K. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **2004**, 630, 2422–2430.
- K. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **2007**, 633, 1403–1406.
- M. G. B. Drew, *Coord. Chem. Rev.* **1977**, 24, 179–275.
- D. L. Kepert, *Inorganic Stereochemistry*, Springer-Verlag, Berlin Heidelberg, **1982**.
- D. L. Kepert, *Comprehensive Coordination Chemistry*, Pergamon Press, Oxford, **1987**.
- C. W. Haigh, *Polyhedron* **1995**, 14, 2871–2878.
- J. Garcia, M. J. Allen, *Eur. J. Inorg. Chem.* **2012**, 2012, 4550–4563.
- D. N. Huh, J. W. Ziller, W. J. Evans, *Inorg. Chem.* **2019**, 58, 9613–9617.
- N.-D. H. Gamage, Y. Mei, J. Garcia, M. J. Allen, *Angew. Chem. Int. Ed.* **2010**, 49, 8923–8925.
- C. U. Lenora, F. Carniato, Y. Shen, Z. Latif, E. M. Haacke, P. D. Martin, M. Botta, M. J. Allen, *Chem. Eur. J.* **2017**, 23, 15404–15414.
- T. C. Jenks, M. D. Bailey, B. A. Corbin, A. N. W. Kuda-Wedagedara, P. D. Martin, H. B. Schlegel, F. A. Rabuffetti, M. J. Allen, *Chem. Commun.* **2018**, 54, 4545–4548.
- K. Müller-Buschbaum, C. C. Quitmann, *Z. Anorg. Allg. Chem.* **2003**, 629, 1610–1616.
- M. Panthöfer, U. Wedig, H. Brumm, M. Jansen, *Solid State Sci.* **2004**, 6, 619–624.
- R. E. Johnsen, P. B. Jensen, P. Norby, T. Vegge, *J. Phys. Chem. C* **2014**, 118, 24349–24356.
- H. Oesterreicher, N. Mammano, M. J. Sienko, *J. Solid State Chem.* **1969**, 1, 10–18.
- R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys. Diffr. Theor. Gen. Crystallogr.* **1976**, 32, 751–767.
- C. C. Quitmann, K. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **2005**, 631, 564–568.
- C. Hadenfeldt, H. Jacobs, R. Juza, *Z. Anorg. Allg. Chem.* **1970**, 379, 144–156.
- J. C. Warf, *Angew. Chem.* **1970**, 82, 397–398.
- X-Area, STOE & Cie GmbH, Darmstadt, Germany, **2018**.
- G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, 71, 3–8.
- G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, 71, 3–8.
- K. Brandenburg, H. Putz, *Diamond - Crystal and Molecular Structure Visualization*, Crystal Impact GbR, Bonn, **2019**.
- TURBOMOLE V7.4, a Development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007., **2019**.
- R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, 162, 165–169.

- [44] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- [45] C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158–6170.
- [46] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
- [47] F. Weigend, *Phys. Chem. Chem. Phys.* **2002**, *4*, 4285–4291.
- [48] K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283–290.
- [49] M. Sierka, A. Hogekamp, R. Ahlrichs, *J. Chem. Phys.* **2003**, *118*, 9136–9148.

Received: April 23, 2020

Published Online: June 10, 2020