The Unusual Coordination Sphere in the Octaammine Calcium(II) Ions of $[Ca(NH_3)_8]Br_2$ and $[Ca(NH_3)_8]I_2$ and the Thermal Decomposition of the Iodide to $[Ca(NH_3)_6]I_2$

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

We report on the synthesis and crystal structure of the octaammine calcium(II) halides $[Ca(NH_3)_8]Br_2$, and $[Ca(NH_3)_8]I_2$, which were synthesized by the reaction of the respective calcium(II) halides with dry liquid ammonia. The compounds form colorless crystals which crystallize isotypically at 123 K with $Z = 4$ in the orthorhombic space group *Pnma* with $a = 12.0478(3)$, $b = 7.4406(2)$, $c = 15.7216(4)$ Å, $V = 1409.33(6)$ Å^3 for the bromide, and $a = 12.1113(4)$, $b = 7.7706(3)$, $c = 16.7145(6)$ Å, $V = 1573.0(1)$ Å^3 for the iodide. Instead of the expected tetragonal antiprism for the eightfold-coordinated Ca^{2+} ions, we observed a coordination polyhedron best described as a twofold capped trigonal prism. After evaporation of the liquid ammonia and warming of $[Ca(NH_3)_8]I_2$ to room temperature, $[Cu(NH_3)_6]I_2$ was obtained as a colorless powder. The hexaammine calcium(II) iodide crystallizes isotypically to $[Mn(NH_3)_6]I_2$ (CaF_2 type) in the cubic space group $Fm\bar{3}m$ with $a = 11.18580(6)$ Å, $V = 1399.59(1)$ Å^3, $Z = 4$ at 293 K.

Key words: Calcium(II), Bromide, Iodide, Liquid Ammonia, Ammine Complexes, Crystal Structures, Calculations

Introduction

The products of the reaction of calcium bromide with dry ammonia were first reported by Rammelsberg [1]. He described a colorless voluminous product of the composition "CaBr · 3 NH$_3$" (sic!). By tensi-eudiometric measurements in the CaBr$_2$/NH$_3$ system Hüttig discussed compounds with the compositions CaBr$_2$ · 8 NH$_3$, CaBr$_2$ · 6 NH$_3$ and CaBr$_2$ · 2 NH$_3$ [2]. He also studied the CaCl$_2$-NH$_3$ system and described the corresponding products. For the CaI$_2$-NH$_3$ system he discovered compounds with the composition CaI$_2$ · x NH$_3$ ($x = 8$, 6, 2, and 1). The first crystallographic evidence of a calcium ammine complex was obtained by Westman and coworkers on the compound "CaCl$_2$(NH$_3$)$_8$", of which they elucidated the structure from powder X-ray patterns and consecutive Rietveld refinements [3]. The cell parameters of this chloride ($a = 12.1143$, $b = 7.3076$, $c = 15.0829$ Å, $V = 1335{,}24$ Å^3, $T = 298$ K) are quite similar to the ones reported here, and the space group is the same (*Pnma*). Therefore we expected the title compounds to be isotypic to this chloride. From the Rietveld refinements the chloride's composition and constitution was established as hexammine calcium(II) chloride ammonia (1/2), $[Ca(NH_3)_6]Cl_2 · 2 NH_3$, with a distorted trigonal prism around the Ca^{2+} ion. However, the authors stated that their refined position parameters for the light atoms are rather imprecise. Therefore we assume that the previously reported $[Ca(NH_3)_6]Cl_2 · 2 NH_3$ is better described as $[Ca(NH_3)_8]Cl_2$ and is isotypic to the bromide and iodide presented here. Ammine complexes such as this chloride have been proposed for energy storage and as ammonia storage materials, and also IR spectroscopic investigations were undertaken [3 – 5].

Results and Discussion

We report on the results of the reactions of $CaBr_2$ and CaI_2 with liquid ammonia at $-40°C$. In both cases colorless crystals were obtained, and our structure elucidations by low-temperature single-crystal X-ray analyses led to octaammine calcium(II) dihalides, $[Ca(NH_3)_8]Br_2$ and $[Ca(NH_3)_8]I_2$. An atypical coordination polyhedron of a twofold-capped trigonal prism was observed instead of the very common tetragonal antiprism reported for aqua complexes of eightfold-coordinated Ca^{2+} ions [6 – 8].

We also studied the behavior of the iodide at room temperature. The powder X-ray diffraction pattern of the colorless substance shows no similarities to the calculated powder pattern obtained from the single-crystal measurement at low temperature. The powder pattern was indexed, and a Rietveld refinement led to a compound with the composition $[Ca(NH_3)_6]I_2$. The hexaammine calcium(II) iodide is isotypic to $[Mn(NH_3)_6]I_2$ [9] and crystallizes in the cubic space group $Fm\overline{3}m$ with the lattice parameter $a = 11.18580(6)$ Å and $V = 1399.59(1)$ Å^3 at 293 K. Thermo-gravimetric analyses and infrared spectra confirm this result.

Preparation and crystal structure analyses of [Ca(NH₃)₈]X₂ (X = Br, I)

Calcium(II) bromide and iodide react with liquid ammonia at $-40°C$ under the formation of colorless crystals of octaammine calcium(II) dihalide $[Ca(NH_3)_8]X_2$ (X = Br, I) (Eq. 1).

$$CaX_2 + 8NH_3 \xrightarrow{-40°C} [Ca(NH_3)_8]X_2 \ (X = Br, I) \quad (1)$$

Fig. 1 (color online). The unit cell of $[Ca(NH_3)_8]Br_2$. Displacement ellipsoids are shown at the 70 % probability level at 123 K, H atoms isotropic with arbitrary radii.

The compounds crystallize in the orthorhombic space group *Pnma* (no. 62) (for further crystallographic data see Table 1). As the crystal structures of the two compounds are isotypical only the crystal structure of the bromide will be discussed in detail. A projection of the unit cell of the bromide is shown in Fig. 1. The calcium atom Ca(1) resides on the special position 4*c* and is coordinated by eight ammine ligands with the nitrogen atoms N(1) to N(5) (Fig. 2). The nitrogen atoms N(1) to N(3) occupy the general position 8*d* and the nitrogen atoms N(4) and N(5) the special position 4*c*. The coordination polyhedron around the Ca^{2+} cation can be best described as a trigonal prism, two faces of which are capped by the nitrogen atoms N(4) and N(5) as shown in
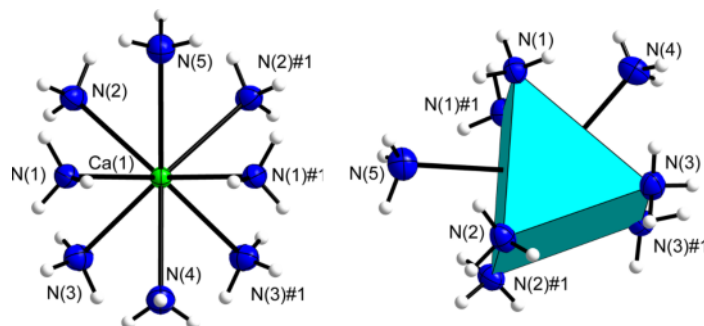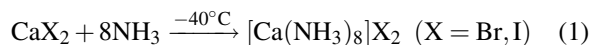

Fig. 2 (color online). The $[Ca(NH_3)_8]^{2+}$ unit of the bromide, best described as twofold-capped triangular prism (right). Displacement ellipsoids are shown at the 70 % probability level at 123 K, H atoms isotropic with arbitrary radii. Symmetry transformation for the generation of equivalent atoms: #1 $x, -y + 1/2, z$.
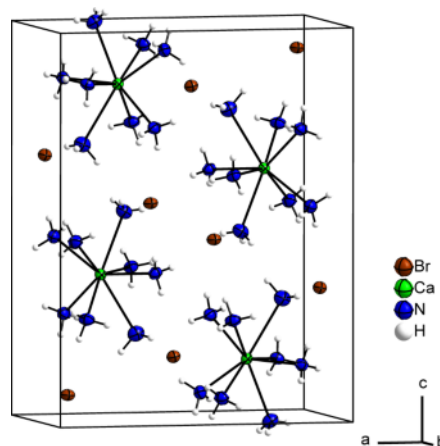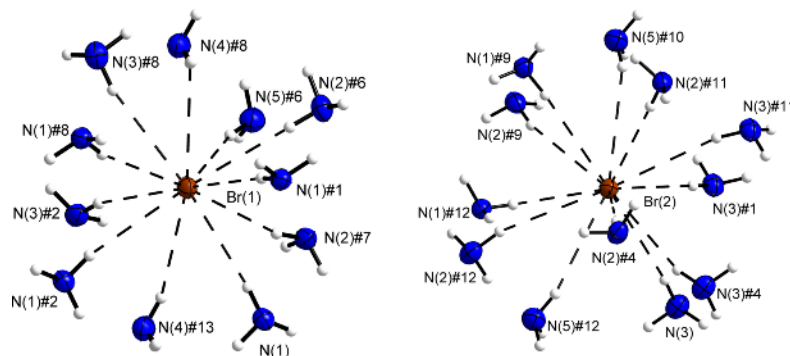
Fig. 3 (color online). A projection of the coordination sphere of the bromine atoms Br(1) and Br(2). N–H···Br hydrogen bonds are dashed in black. Displacement ellipsoids are shown at the 70 % probability level at 123 K, H atoms isotropic with arbitrary radii. Symmetry transformations for the generation of equivalent atoms: #1 x, $-y+1/2$, z; #2 $-x+1$, $-y$, $-z+1$; #4 $-x+2$, $-y$, $-z+1$; #6 $x-1/2$, $-y+1/2$, $-z+1/2$; #7 $x-1/2$, y, $-z+1/2$; #8 $-x+1$, $y+1/2$, $-z+1$; #9 $-x+3/2$, $y+1/2$, $z+1/2$; #10 $-x+3/2$, $-y+1$, $z+1/2$; #11 $-x+2$, $y+1/2$, $-z+1$, #12 $-x+3/2$, $-y$, $z+1/2$; #13 $-x+1$, $y+1/2$, $-z+1$.

Table 1. Selected crystallographic data of the title compounds.

	[Ca(NH$_3$)$_8$]Br$_2$	[Ca(NH$_3$)$_8$]I$_2$	[Ca(NH$_3$)$_6$]I$_2$
Empirical formula	H$_{24}$N$_8$Br$_2$Ca	H$_{24}$N$_8$Ca I$_2$	H$_{18}$N$_6$CaI$_2$
Color and appearance	colorless plates	colorless blocks	colorless powder
Molecular mass, g mol^{-1}	336.17	430.15	396.05
Crystal system	orthorhombic		cubic
Space group	*Pnma* (no. 62)		*Fm$\bar{3}$m* (no. 225)
a, Å	12.0478(3)	12.1113(4)	11.18580(6)
b, Å	7.4406(2)	7.7706(3)	$= a$
c, Å	15.7216(4)	16.7145(6)	$= a$
V, Å^3	1409.33(6)	1573.0(1)	1399.59(1)
Z	4		4
$\rho_{\text{calcd.}}$, g cm^{-3}	1.58	1.82	1.88
λ, Å	0.71073 (MoK$_\alpha$)		1.54051 (CuK$_{\alpha 1}$)
T, K	123		293
μ, mm^{-1}	6.1	4.3	3.9
R_{int}	0.046	0.029	–
$R_{\text{p}}/wR_{\text{p}}$	–	–	0.048/0.063
$R(F)$ ($I > 2\,\sigma(I)$/all data)	0.021/0.040	0.022/0.034	0.024/0.027
$wR(F^2)$ ($I > 2\,\sigma(I)$/all data)	0.043/0.047	0.039/0.041	0.029/0.030
S (all data)	0.75	1.04	0.98
Data/parameter/restraints	4341/108/1	5866/108/1	3816/20/0
$\Delta\rho_{\text{max/min}}$, e Å^{-3}	0.78/$-$0.77	0.83/$-$1.09	–

Fig. 2. The nitrogen atoms N(1) to N(3) and their symmetry equivalents build the trigonal prism. The three rectangular faces of the prism form angles of 54.59(2)°, 60.11(4)° and 65.30(3)° to each other, and the nitrogen atoms N(4) and N(5) reside 1.893(2) and 1.963(2) Å, respectively, above two of the faces of the trigonal prism. The deviation of the atom arrangement from an ideal square antiprism is strong: Least-squares planes through the atoms N(1), N(1)#1, N(4) and N(1), N(1)#1, N(5), show an angle of 25.18(4)° to each other. Angles of 10.39(4)° and 14.79(2)° are observed towards the least-squares plane through the atoms N(2), N(2)#1, N(3), and N(3)#1. For an ideal square antiprism, angles of 0° are expected in all these cases. Thus the coordination polyhedron is best described as a twofold-capped trigonal-prismatic arrangement of the ammine ligands around the Ca^{2+} cation.

Typically, the coordination polyhedron of an eight-fold coordinated calcium ion is a tetragonal antiprism
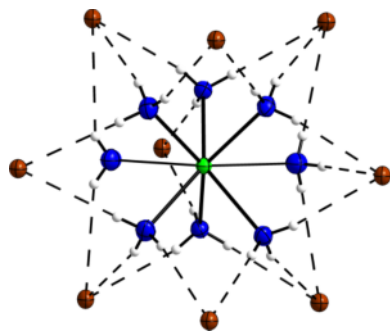
Fig. 4 (color online). Projection of the [Ca(NH$_3$)$_8$]$^{2+}$ cation and its coordination to symmetry-equivalent Br(1)$^-$ and Br(2)$^-$ anions *via* N–H⋯Br hydrogen bonds (dashed in black). Color code: Ca green, N blue, Br brown). Displacement ellipsoids are shown at the 70 % probability level at 123 K, H atoms isotropic with arbitrary radii. Atomic numbering and symmetry transformations are omitted for clarity.

which has been observed in compounds such as CaO$_2$ · 8H$_2$O [6, 7] or [Ca(H$_2$O)$_8$]$_2$[Cd$_3$Cl$_{10}$]·2 H$_2$O [8].

The nitrogen atoms N(1) to N(3) and their symmetry equivalents form the vertices of the polyhedron with Ca-N distances from 2.545(1) to 2.620(1) Å (for the iodide: see Table 2). For the capping nitrogen atoms N(4) and N(5) the Ca-N distances are significantly elongated to 2.675(1) and 2.795(1) Å, respectively (Fig. 2, Table 2) and compare quite well with the results obtained by Rietveld refinement on the compound [Ca(NH$_3$)$_6$]Cl$_2$·2 NH$_3$ (2.52 to 2.72 Å) [3]. As expected, for [Mg(NH$_3$)$_6$]Cl$_2$ a smaller M–N distance of 2.198(3) Å was observed [10], and in [Mn(NH$_3$)$_6$]X$_2$ (X = Cl and I) the M–N distances are 2.27–2.28 Å [11].

The bromine atoms Br(1) and Br(2) reside on the special position 4c and show no direct contact to the calcium atom. The Ca⋯Br distances are 4.8523(3) and 5.3259(3) Å for Ca(1)⋯Br(1) and Ca(1)⋯Br(2),

respectively (iodide: 5.0202(3), 5.5219(3) Å). Both bromine atoms are acceptors of N-H⋯Br hydrogen bonds. The bromine atom Br(1) is an acceptor of in total eleven hydrogen bonds (from four neighboring [Ca(NH$_3$)$_8$]$^{2+}$ units), and the bromine atom Br(2) is an acceptor of in total twelve hydrogen bonds (from five neighboring [Ca(NH$_3$)$_8$]$^{2+}$ units). The coordination spheres of Br(1) and Br(2) are shown in Fig. 3, and the coordination of the [Ca(NH$_3$)$_8$]$^{2+}$ cation by four symmetry-equivalent Br(1) and five symmetry-equivalent Br(2) ions is displayed in Fig. 4. The donor⋯acceptor distance (D⋯A) of N⋯Br is found in a range from 3.558(1) Å for N(1)-H(1B)⋯Br(1)#2 to 3.893(1) Å for N(2)-H(2C)⋯Br(2)#3 (further values, also for the iodide, are given in Table 3). For comparison, the D⋯A distances in "[Ca(NH$_3$)$_6$]Cl$_2$·2 NH$_3$" have been observed in a range from 2.52 to 3.73 Å [3].

The presence of N-H⋯Br hydrogen bonding in [M(NH$_3$)$_6$]Br$_2$ (M = Ca, Mn, Fe, Co, Ni, Cu, and Cd) has been shown by infrared spectroscopy [12]. A decreasing strength of N-H⋯Br hydrogen bonding has been observed going from Cu with the strongest to Ca with the weakest N-H⋯Br contacts. Comparable D⋯A and H⋯A distances are reported for [CrBr$_2$(NH$_3$)$_4$][CrBr$_4$(NH$_3$)$_2$], where N-H⋯Br hydrogen bonds interlink the cations and anions [13].

Decomposition of [Ca(NH$_3$)$_8$]I$_2$ at room temperature

The powder X-ray diffraction pattern (Fig. 5) of the colorless powder obtained after warming of [Ca(NH$_3$)$_8$]I$_2$ to room temperature has no similarity to the powder pattern calculated on the basis of its single-crystal structure. The powder pattern could be indexed in the cubic crystal system with a = 11.18580(6) Å, V = 1399.59(1) Å^3 and turned out to belong to the compound [Ca(NH$_3$)$_6$]I$_2$. It crystallizes formally in the

Table 2. Selected interatomic distances (Å) and angles (deg) of the title compounds. Symmetry transformation for the generation of equivalent atoms: #1 x, $-y + 1/2$, z.

	Distance [Ca(NH$_3$)$_8$]Br$_2$	Distance [Ca(NH$_3$)$_8$]I$_2$		Angle [Ca(NH$_3$)$_8$]Br$_2$	Angle [Ca(NH$_3$)$_8$]I$_2$
Ca(1)–N(1)	2.5451(10)	2.5686(9)	N(1)–Ca(1)–N(1)#1	92.49(5)	96.79(5)
Ca(1)–N(2)	2.6013(10)	2.6180(10)	N(1)–Ca(1)–N(2)	80.45(4)	79.97(3)
Ca(1)–N(3)	2.6198(10)	2.6200(10)	N(2)–Ca(1)–N(2)#1	82.51(5)	81.02(5)
Ca(1)–N(4)	2.6754(15)	2.6575(13)	N(1)–Ca(1)–N(3)	84.93(3)	84.34(3)
Ca(1)–N(5)	2.7953(16)	2.7404(14)	N(3)–Ca(1)–N(3)#1	76.40(5)	74.64(5)
Ca(1)–Br(1)	4.8523(3)	5.0202(3)	N(4)–Ca(1)–N(1)	72.46(3)	72.35(3)
Ca(1)–Br(2)	5.3259(9)	5.5219(3)	N(4)–Ca(1)–N(3)	72.17(4)	73.72(3)
			N(4)–Ca(1)–N(5)	127.36(5)	124.53(5)

Table 3. Selected D–H, H$\cdots$A, D$\cdots$A distances (Å) and $\angle$DHA angles (deg) of the title compounds (D = donor, A = acceptor)[a].

Atoms	D–H	H$\cdots$A	D$\cdots$A	<DHA
N(1)–H(1A)$\cdots$Br(1)	0.894(16)	2.759(16)	3.6412(10)	169.3(13)
N(1)–H(1A)$\cdots$I(1)#2	0.839(18)	2.962(18)	3.7906(10)	169.8(15)
N(1)–H(1B)$\cdots$Br(1)#2	0.833(17)	2.741(17)	3.5576(10)	167.2(14)
N(1)–H(1B)$\cdots$I(1)#3	0.852(18)	3.106(18)	3.9468(9)	169.5(13)
N(1)–H(1C)$\cdots$Br(2)#3	0.871(19)	2.853(19)	3.7185(10)	173.1(15)
N(1)–H(1C)$\cdots$I(1)	0.901(17)	2.984(17)	3.8683(10)	167.4(13)
N(2)–H(2A)$\cdots$Br(2)#4	0.839(18)	2.972(18)	3.8113(11)	177.6(15)
N(2)–H(2A)$\cdots$I(2)#4	0.890(17)	3.091(17)	3.9812(10)	178.7(14)
N(2)–H(2B)$\cdots$Br(1)#5	0.890(18)	2.712(18)	3.5778(10)	164.8(14)
N(2)–H(2B)$\cdots$I(1)#5	0.827(18)	2.982(19)	3.7951(10)	165.5(13)
N(2)–H(2C)$\cdots$Br(2)#3	0.916(18)	2.999(19)	3.8933(11)	165.8(14)
N(2)–H(2C)$\cdots$I(2)#3	0.848(18)	3.201(18)	4.0122(11)	160.8(15)
N(3)–H(3A)$\cdots$Br(1)#2	0.869(16)	2.826(16)	3.6766(11)	166.6(13)
N(3)–H(3A)$\cdots$I(1)#2	0.842(19)	3.089(18)	3.8632(12)	153.9(15)
N(3)–H(3B)$\cdots$Br(2)	0.885(16)	2.954(16)	3.8301(10)	170.8(14)
N(3)–H(3B)$\cdots$I(2)	0.90(2)	3.16(2)	4.0477(10)	169.1(16)
N(3)–H(3C)$\cdots$Br(2)#4	0.869(18)	2.938(18)	3.7854(10)	165.6(14)
N(3)–H(3C)$\cdots$I(2)#4	0.839(19)	3.165(19)	3.9732(11)	162.4(16)
N(4)–H(4A)$\cdots$Br(1)#2	0.81(2)	3.11(2)	3.7668(3)	140.6(18)
N(4)–H(4A)$\cdots$I(1)#2	0.834(18)	3.258(18)	3.9753(3)	145.7(15)
N(4)–H(4B)$\cdots$I(1)	0.88(3)	3.14(3)	3.9946(14)	162(2)
N(5)–H(5A)$\cdots$Br(2)#3	0.83(2)	3.08(2)	3.8180(4)	150.8(18)
N(5)–H(5A)$\cdots$I(2)#3	0.81(3)	3.25(3)	4.0238(4)	163(2)
N(5)–H(5B)$\cdots$Br(1)#5	0.94(2)	2.77(2)	3.6955(16)	168(3)

[a] Symmetry transformations for the generation of equivalent atoms: #2 $-x+1, -y, -z+1$; #3 $-x+3/2, -y, z-1/2$; #4 $-x+2, -y, -z+1$; #5 $x+1/2, y, -z+1/2$.

CaF$_2$ structure type with the [Ca(NH$_3$)$_6$]$^{2+}$ cations on the Ca^{2+} and the I$^-$ anions on the F$^-$ positions. The structure is isotypic to that of the previously reported [Mn(NH$_3$)$_6$]I$_2$ [9]. Details of the Rietveld refinement are given in Table 1, the fit is shown in
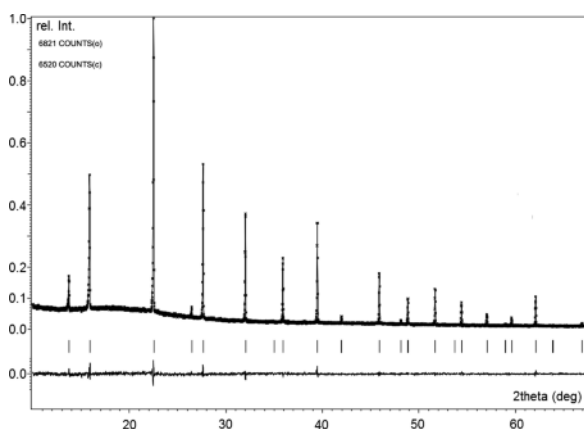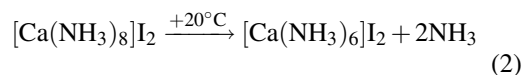

Fig. 5. Powder X-ray diffraction pattern of [Ca(NH$_3$)$_6$]I$_2$ at 20 °C: experimental data (crosses), calculated Rietveld profile, and difference profile. The calculated reflection positions are shown as black ticks.

Fig. 5. The Ca–N distances in the hexammine complex are 2.501(14) Å and as expected slightly shorter compared to the Ca-N distances of the octammine complexes. [Ca(NH$_3$)$_8$]I$_2$ thus decomposes upon warming to room temperature with a loss of two moles of NH$_3$ to [Ca(NH$_3$)$_6$]I$_2$ (Eq. 2).

$$[\text{Ca(NH}_3)_8]\text{I}_2 \xrightarrow{+20°C} [\text{Ca(NH}_3)_6]\text{I}_2 + 2\text{NH}_3 \tag{2}$$

An ATR-IR spectrum of [Ca(NH$_3$)$_6$]I$_2$ shows the asymmetric and symmetric N-H valence bands in the region of 3346 to 3167 cm^{-1} (m). The asymmetric and symmetric deformation modes are observed at 1538 (m) and 1115 cm^{-1} (s), respectively, and the rocking mode is observed at 513 cm^{-1} (vs).

The thermogravimetric decomposition of [Ca(NH$_3$)$_6$]I$_2$ proceeds in two steps (Fig. 6). In the first step, starting at 75°C, 3.6 NH$_3$ are lost, and in the second step, starting at 130°C, another 1.9 NH$_3$ are lost. Thus, 0.5 mole of NH$_3$ are still retained upon heating to 210°C and seem to be gradually lost upon further heating to 500°C. A powder X-ray diffraction
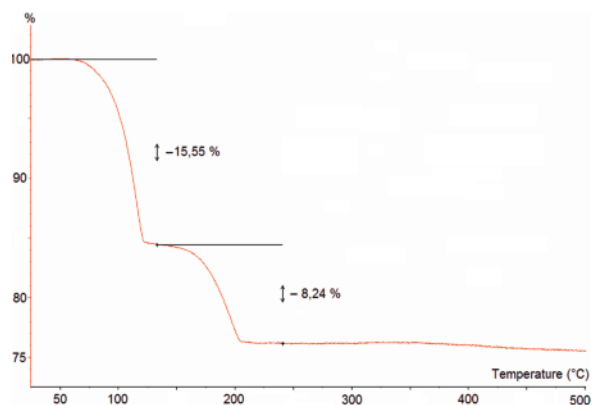
Fig. 6. Thermogramm showing the thermal decomposition of [Ca(NH$_3$)$_6$]I$_2$. Heating rate used: 2 °C min^{-1}. A loss of 1 NH$_3$ corresponds to *ca.* 4.3 % mass loss.

pattern obtained after the thermal decomposition shows the compound to be amorphous. The IR spectrum of the decomposition product confirms that some NH$_3$ is still retained: Asymmetric and symmetric N-H valence bands are observed in the region from 3501 to 3440 cm^{-1} (s), the asymmetric deformation modes at 1592 cm^{-1} (s), and the rocking mode at 473 cm^{-1} (s).

Investigations on the thermal decomposition of [Ca(NH$_3$)$_8$]Br$_2$ are ongoing and are reported elsewhere. It can be expected that the bromide will show a similar behavior compared to that of the iodide and to that of [Mn(NH$_3$)$_6$]Br$_2$ [9, 14].

Quantum-chemical calculations

We carried out quantum-chemical calculations for the [Ca(NH$_3$)$_8$]$^{2+}$ cation in both the tetragonal-antiprismatic (point group S_8) and the twofold-capped trigonal-prismatic (point group C_{2v}) coordination geometries. After a full geometry optimization, the tetragonal antiprism turned out to be 15 kJ mol^{-1} lower in energy than the twofold-capped trigonal prism. Furthermore, a harmonic frequency analysis showed that the C_{2v}-symmetric structure is not a true local minimum as it displays an imaginary frequency of 19i cm^{-1}. Distortion of the structure along the imaginary mode and reoptimization of the resulting C_2-symmetric structure actually transforms the complex to the S_8-symmetric tetragonal-antiprismatic geometry. In summary, the preferred coordination geometry of the [Ca(NH$_3$)$_8$]$^{2+}$ cation in the gas phase is a tetragonal antiprism, suggesting that the experimen-

tally observed twofold-capped trigonal-prismatic geometry arises from hydrogen bonding and other interactions introduced by the crystal packing.

Conclusion

We reported on the synthesis of [Ca(NH$_3$)$_8$]X$_2$ from CaX$_2$ (X = Br, I) and liquid ammonia at −40°C. Their crystal structures were elucidated by low-temperature single-crystal X-ray analysis at 123 K. The compounds crystallize isotypically with $Z = 4$ in the orthorhombic space group *Pnma*. The title compounds represent the first crystallographic evidence for the octaammoniate of CaBr$_2$ mentioned by Hüttig already in the 1920s [2].

The Ca-N distances are in good agreement with distances observed for "[Ca(NH$_3$)$_6$]Cl$_2$ · 2 NH$_3$" [3] which according to our reasoning is [Ca(NH$_3$)$_8$]Cl$_2$.

In contrast to the expected tetragonal-antiprismatic coordination sphere of the eight ammine ligands around the calcium atom, their arrangement in [Ca(NH$_3$)$_8$]$^{2+}$ is much better described as a twofold-capped trigonal prism. Quantum-chemical calculations at the PBE0/def2-TZVPP level of theory showed that the preferred coordination geometry of [Ca(NH$_3$)$_8$]$^{2+}$ is indeed a tetragonal antiprism (favored over a twofold-capped trigonal prism by 15 kJ mol^{-1}). As a consequence, hydrogen bonding seems to have a significant influence on the arrangement of the atoms of the title compounds in the solid state.

After removal of the solvent and warming of [Ca(NH$_3$)$_8$]I$_2$ to room temperature, [Cu(NH$_3$)$_6$]I$_2$ is obtained which gradually releases further ammonia upon heating.

Experimental Section

All work was carried out excluding humidity and air in an atmosphere of dried and purified argon (Westfalen AG) using high-vacuum glass lines or a glove box (MBraun). Liquid ammonia (Westfalen AG) was dried and stored over sodium (VWR) in a special high-vacuum glass line. All vessels for reactions with liquid ammonia were made out of borosilicate glass and were flame-dried before use.

Synthesis of [Ca(NH$_3$)$_8$]X$_2$ (X = Br, I)

CaBr$_2$ and CaI$_2$ were purchased from Sigma-Aldrich (purity 99.98 %) and used without further purification. For the preparation of the title compounds, a reaction vessel was charged with 50 mg (0.25 mmol) CaX$_2$ under argon atmosphere. After evacuation and cooling to −78°C, approximately 10 mL liquid ammonia was condensed on top of the

colorless powder resulting in a clear colorless solution and some colorless residue which dissolved in the course of the reaction. After storage at $-40\,^\circ$C colorless crystals were obtained. The crystals were separated manually at $-40\,^\circ$C under perfluoroether oil (Galden PFPE, Solvay Solexis) and nitrogen atmosphere. The selected crystals were mounted on the diffractometer by using MicroLoops (MiTeGen) and measured at 123 K.

Synthesis of [Ca(NH₃)₆]I₂

[Ca(NH₃)₆]I₂ was obtained by condensation of NH₃ onto CaI₂ and removal of the NH₃ by evaporation at room temperature and by warming [Ca(NH₃)₈]I₂ to room temperature.

Powder X-ray diffractometry

Powder X-ray diffraction patterns were obtained on a Stadi-P-Diffractometer (Stoe, Germany) using CuK$_{\alpha 1}$ radiation, a germanium monochromator and a Mythen1K detector. The data were handled using the WINXPOW software [15]. The compounds were filled onto flat sample holders and measured in transmission geometry. Le Bail profile fitting and Rietveld refinement was done with the JANA2006 software [16, 17]. The powder profile was fitted using the Pseudo-Voigt function, the peak asymmetry was corrected by divergence, and the lattice parameter was refined. For the background ten Chebyshev polynomials and the shift were refined. The structure was solved using the atom positions of the isotypic manganese compound. Due to the room-temperature powder X-ray diffraction data, the Ca, I and N atoms could only be refined isotropically, however without using any restraints.

Single-crystal X-ray analyses

The X-ray structure analyses were carried out using an Oxford XCalibur3 diffractometer with monochromated molybdenum radiation (MoK$_\alpha$, $\lambda = 0.71073$ Å) and a CCD detector. The evaluation of the diffraction data was carried out using the CRYSALISRED [18] software. An empirical absorption correction was applied using spherical harmonics within SCALE3 ABSPACK [18]. The structures were solved using Direct Methods (SHELXS-97) [19, 20] and refined against F^2 (SHELXL-97) [19, 20] by using SHELXLE [21]. Non-hydrogen atoms were located by Difference Fourier synthesis and refined anisotropically. Hydrogen atoms for the

nitrogen atoms N(1) to N(5) were located from the Difference Fourier Synthesis and refined isotropically, some by using restraints. The residual electron density is located close to the halogen atoms.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition number CSD-427511 for [Ca(NH₃)₈]Br₂, CSD-427990 for [Ca(NH₃)₈]I₂ and CSD-427991 for [Ca(NH₃)₆]I₂.

IR spectroscopy

IR spectroscopy was carried out with a Bruker ALPHA FT-IR-spectrometer equipped with a Diamond ATR-cell. The resulting spectra were handled with the OPUS software [22]. Measurements were carried out at room temperature under argon atmosphere.

Thermogravimetric analysis

Thermogravimetric analysis was carried out using a Netzsch STA 409 C instrument equipped with a TASC 414/3 signal amplifier and a mass-selective analyzer Pfeiffer Oninstar GSD 301 O under a steady argon stream (5.0, Westfalen AG) of $50\,\mathrm{cm}^3\,\mathrm{min}^{-1}$. [Ca(NH₃)₆]I₂ was heated from 25 to $500\,^\circ$C at a nominal heating rate of $2\,\mathrm{K\,min}^{-1}$ in a corundum crucible. The data was evaluated by the Netzsch software [23].

Computational details

The quantum chemical calculations were carried out using the PBE0 hybrid density functional method [24, 25] (TURBOMOLE program package, version 6.5 [26]). Triple-zeta-valence + double polarization (def2-TZVPP) level basis sets were applied for all atoms [27]. Harmonic vibrational frequency calculations were performed to check whether the optimized structures were true local minima.

[1] C. Rammelsberg, *Pogg. Ann.* **1842**, *55*, 237 – 253.

[2] G. F. Hüttig, *Z. Anorg. Allg. Chem.* **1922**, *123*, 31 – 42.

[3] S. Westman, P.-E. Werner, T. Schuler, W. Raldow, P. H. Nielsen, *Acta Chem. Scand.* **1981**, *35*, 467 – 472.

[4] J. Schmidt, O. Marcovitch, A. Lubezky, Y. Kozirovski, M. Folman, *J. Colloid Interface Sci.* **1980**, *75*, 85 – 94.

[5] O. Marcovitch, A. Lubezky, Y. Kozirovski, *J. Phys. Chem.* **1976**, *80*, 2530.

[6] R. S. Shineman, A. J. King, *Acta Crystallogr.* **1951**, *4*, 67 – 68.

[7] G. V. Shilov, A. I. Karelin, D. G. Lemesheva, L. S. Leonova, L. O. Atovmyan, *Russ. J. Inorg. Chem.* **2005**, *50*, 921 – 927.

[8] H. Leligny, J. C. Monier, *Acta Crystallogr.* **1982**, *B38*, 355 – 358.

[9] H. Jacobs, J. Bock, C. Stüve, *J. Less.-Common Met.* **1987**, *134*, 207 – 214.

[10] I.-C. Hwang, T. Drews, K. Seppelt, *J. Am. Chem. Soc.* **2000**, *122*, 8486 – 8489.

[11] R. Eßmann, G. Kreiner, A. Niemann, D. Rechenbacher, A. Schmieding, Th. Sichla, U. Zachwieja, H. Jacobs, *Z. Anorg. Allg. Chem.* **1996**, *622*, 1161 – 1166.

[12] R. Eßmann, *J. Mol. Struct.* **1995**, *351*, 91 – 94.

[13] L. Stork, X. Liu, B. P. T. Fokwa, R. Dronskowski, *Acta Crystallogr.* **2009**, *C65*, 54 – 56.

[14] H. Reardon, J. M. Hanlon, M. Grant, I. Fullbrook, D. H. Gregory, *Crystals* **2012**, *2*, 193 – 212.

[15] WINXPOW, Stoe & Cie GmbH, Darmstadt (Germany) **2011**.

[16] V. Petříček, M. Dušek, L. Palatinus, JANA2006, The Crystallographic Computing System, Institute of Physics, Academy of Sciences of the Czech Republic, Prague (Czech Republic) **2006**.

[17] V. Petříček, M. Dušek, L. Palatinus, *Z. Kristallogr. - Cryst. Mater.* **2014**, *229*, 345 – 352.

[18] CRYSALISRED, Oxford Diffraction Ltd., Abingdon, Oxford (U. K.) **2009**.

[19] G. M. Sheldrick, SHELXS/L-97, Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **199**.

[20] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112 – 122.

[21] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281 – 1284.

[22] OPUS, Bruker Optik GmbH, Ettlingen (Germany), **2009**.

[23] TA ANALYSIS, Netzsch Gerätebau GmbH, Selb (Germany) **1996**.

[24] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865 – 3868.

[25] C. Adamo, V. J. Barone, *J. Chem. Phys.* **1999**, *110*, 6158 – 6170.

[26] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *62*, 165 – 169.

[27] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297 – 3305.