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Article

First Characterization of the Ammine–Ammonium Complex $[\{NH_4(NH_3)_4\}_2(\mu\text{-}NH_3)_2]^{2+}$ in the Crystal Structure of $[NH_4(NH_3)_4][B(C_6H_5)_4]\cdot NH_3$ and the $[NH_4(NH_3)_4]^+$ Complex in $[NH_4(NH_3)_4][Ca(NH_3)_7]As_3S_6\cdot 2NH_3$ and $[NH_4(NH_3)_4][Ba(NH_3)_8]As_3S_6\cdot NH_3$

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The compound $[NH_4(NH_3)_4][B(C_6H_5)_4]\cdot NH_3$ (**1**) was prepared by the reaction of $NaB(C_6H_5)_4$ with a proton-charged ion-exchange resin in liquid ammonia. $[NH_4(NH_3)_4][Ca(NH_3)_7]As_3S_6\cdot 2NH_3$ (**2**) and $[NH_4(NH_3)_4][Ba(NH_3)_8]As_3S_6\cdot NH_3$ (**3**) were synthesized by reduction of As_4S_4 with Ca and Ba in liquid ammonia. All ammoniates were characterized by low-temperature single-crystal X-ray structure analysis. They were found to contain the ammine–ammonium complex with the maximal possible number of coordinating ammonia molecules, the $[NH_4(NH_3)_4]^+$ ion. **1** contains a special dimer, the $[\{NH_4(NH_3)_4\}_2(\mu\text{-}NH_3)_2]^{2+}$ ion, which is formed by two $[NH_4(NH_3)_4]^+$ ions linked by two ammonia molecules. The $H_3N–H\cdots N$ hydrogen bonds in all three compounds range from 1.82 to 2.20 Å (DHA = Donor-H···Acceptor angles: 156–178°). In **2** and **3**, additional $H_2N–H\cdots S$ bonds to the thioanions are observed, ranging between 2.49 and 3.00 Å (DHA angles: 120–175°). Two parallel phenyl rings of the $[B(C_6H_5)_4]^-$ anion in **1** form a $\pi\cdots\pi$ hydrogen bond (C···C distance, 3.38 Å; DHA angles, 82°), leading to a dimeric $[B(C_6H_5)_4]_2^{2-}$ ion.

Introduction

In contrast to the well-explored $H_3O^+–H_2O$ complexes,[1–7] X-ray studies of the corresponding hydrogen-bonded $NH_4^+–NH_3$ complexes are extremely rare, which is due to the low thermal stability of such ammoniates. However, modern methods of low-temperature X-ray structure analysis now make possible the preparation of ammonia-rich solvate crystals as well as the determination of the proton positions; the latter is indispensable for the characterization of hydrogen bonding. Recently, the cations $[NH_4(NH_3)]^+$, $[NH_4(NH_3)_2]^+$, and $[NH_4(NH_3)_3]^+$ could be identified in the compounds $(NH_4)_3AsS_4\cdot 5NH_3$ and $(NH_4)_3SbS_4\cdot 8NH_3$.[8] Still missing from this group and thus an obvious synthetic target was the ammine–ammonium complex with the maximum number of hydrogen bonds, in which the ammonium ion is surrounded by four ammonia molecules. A rational preparative approach to this larger cationic complex was the choice of larger anions such as the cyclic thioarsenate $As_3S_6^{3-}$ or tetraphenylborate $[BPh_4]^-$. In this work we report the synthesis of the cyclic ammonia–ammine complex $[(NH_4)_2(NH_3)_{10}]^{2+}$ ($[\{NH_4(NH_3)_4\}_2(\mu\text{-}NH_3)_2]^{2+}$) in $[NH_4(NH_3)_4][B(C_6H_5)_4]\cdot NH_3$ and of tetrahedral $[NH_4(NH_3)_4]^+$ in the compounds $[NH_4(NH_3)_4][Ca(NH_3)_7]As_3S_6\cdot 2NH_3$ and $[NH_4(NH_3)_4][Ba(NH_3)_8]As_3S_6\cdot NH_3$.

Results and Discussion

$[NH_4(NH_3)_4][B(C_6H_5)_4]\cdot NH_3$ (**1**) was obtained by batch ion exchange of $Na[B(Ph_4)]$ with a proton-charged ion-exchange resin (Amberlyst 15, Fluka) in liquid ammonia. **1** was characterized by single-crystal X-ray structure analysis at 123 K; it crystallizes in the monoclinic space group $P2_1/c$ (Table 8). The cut-out of the crystal structure of **1** in Figure

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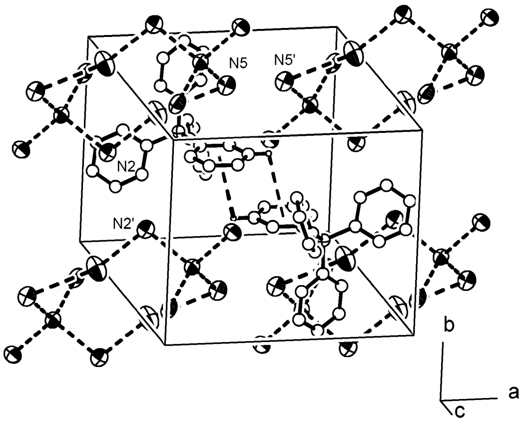

Figure 1. Cut-out of the crystal structure of $[NH_4(NH_3)_4][B(C_6H_5)_4]$ (**1**).

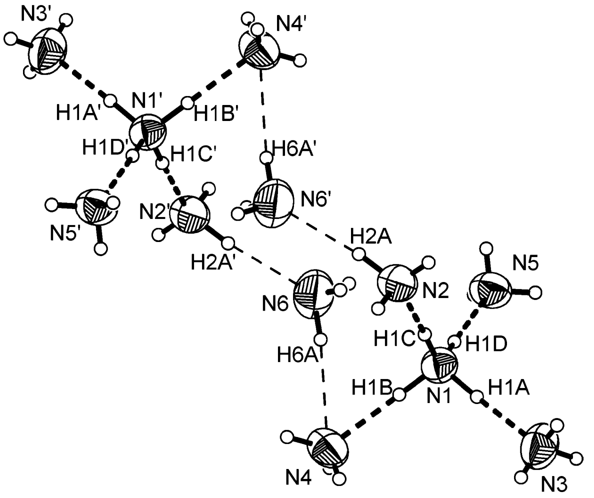

Figure 2. Ammine−ammonia complex $[(NH_4)_2(NH_3)_{10}]^{2+}$ in **1**.

Table 1. Proton Donor···Acceptor Distances/Å and Angles/deg in **1**−**3**

no.	D−H···A	d(D−H)	d(H···A)	d(D···A)	∠(DHA)
1	N(1)−H(1A)···N(3)	1.09(4)	1.82(4)	2.905(4)	177(3)
	N(1)−H(1B)···N(4)	1.05(3)	1.89(3)	2.939(4)	178(2)
	N(1)−H(1C)···N(2)	1.02(3)	1.87(3)	2.882(3)	176(2)
	N(1)−H(1D)···N(5)	1.02(3)	1.94(3)	2.953(4)	172(3)
	N(2)−H(2A)···N(6)	1.02(4)	2.25(4)	3.254(4)	167(3)
	N(6)−H(6A)···N(4)	1.02(7)	2.36(7)	3.384(4)	174(5)
2	N(14)−H(14A)···N(9)	0.84(6)	1.97(6)	2.807(10)	173(6)
	N(14)−H(14B)···N(10)	0.92(7)	2.04(9)	2.900(9)	156(13)
	N(14)−H(14C)···N(8)	0.88(6)	2.06(7)	2.885(9)	156(8)
	N(14)−H(14D)···N(13)	0.79(4)	2.20(5)	2.975(10)	169(6)
3	N(14)−H(14A)···N(9)	0.99(3)	1.85(4)	2.827(8)	168(4)
	N(14)−H(14B)···N(11)	0.99(3)	1.93(4)	2.922(9)	176(11)
	N(14)−H(14C)···N(12)	0.99(3)	1.93(4)	2.896(8)	163(6)
	N(14)−H(14D)···N(13)	0.99(3)	2.01(4)	2.948(11)	156(6)

2 shows the ammonium ion (N1), which has N−H distances from 1.02(3) to 1.09(4) Å and H−N−H angles from 107 to 113°.

It forms a roughly tetrahedral $[NH_4(NH_3)_4]^+$ complex with four surrounding ammonia molecules (N2, N3, N4, N5), to which it is connected by hydrogen bonds (Figure 2). These N1−H···N hydrogen bonds (Table 1) are about 33.8−29.5% shorter than the N−H···N van der Waals distance[9] (2.75 Å), which fulfillls; one of the main criteria for hydrogen bonding.

The N···N distances (2.88−2.95 Å) agree well with Olovsson's results[10] for the structure of $NH_4I\cdot 4NH_3$ (2.95 Å), the single other report on this ammine−ammonium cation so far.

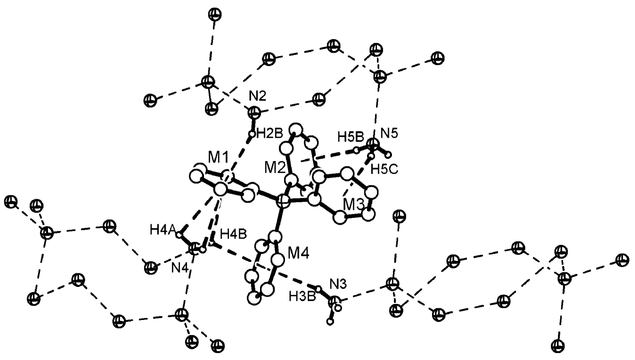

Figure 3. BPh_4^- anion in **1** surrounded by $[(NH_4)_2(NH_3)_{10}]^{2+}$.

Table 2. H-Bridges (Å, deg) in Figure 3 (**1**)

D−H···A	d(D−H)	d(H···A)	d(D···A)	∠(DHA)
N(3)−H(3B)···M(4)	0.94	2.61	3.50	160
N(4)−H(4B)···M(4)	0.86	2.62	3.26	133
N(2)−H(2B)···M(1)	0.93	2.67	3.52	153
N(5)−H(5B)···M(2)	0.87	2.67	3.52	170
N(5)−H(5C)···M(3)	0.93	2.76	3.61	157
N(4)−H(4A)···M(1)	0.92	3.21	3.37	92
N(4)−H(4B)···M(1)	0.86	3.13	3.37	99
N(4)−H(4C)···M(1)	0.84	3.09	3.37	102
C(15)−H(15)···M(3)	1.00	3.43	3.80	104

This structure determination from 1960 did not include the localization of hydrogen atoms, however. The ammine−ammonium substructure is further extended by the single ammonia molecule of crystallization (N6) in the asymmetric unit, which connects two symmetry-equivalent $[NH_4(NH_3)_4]^+$ cations via weaker hydrogen bonds, resulting in a cyclic $[\{NH_4(NH_3)_4\}_2(\mu\text{-}NH_3)_2]^{2+}$ cation. The N6-ammonia molecule serves as a proton acceptor to the N2-ammonia molecule and as a proton donor to the N4-ammonia molecule. The corresponding hydrogen bonds (Table 1) are about 18.2−14.2% shorter than the N−H···N van der Waals distance. Additionally, the crystal structure of **1** shows D−H···π contacts (D = N or C), which point to the center of the benzene ring (Figure 3).

The shorter of these contacts (Table 2) originate from the hydrogen atoms of the ammonia molecules N2, N3, N4, and N5. The corresponding distances using the geometric ring centers M are 2.61−2.76 Å, and the N−H···π angles range between 133 and 170°. The N4-ammonia molecule shows two H···M1 distances of 3.09 and 3.21 Å with N−H···M1 angles of 92 and 102°, which indicates a bifurcated hydrogen bond. Of course, such an interaction cannot be validated through the distance criterion, as the H···π van der Waals distance (1.2 Å for H + 1.7 for sp² carbon atom = 2.9 Å) is shorter than the observed distance. The other observed interactions with the π-system as hydrogen bond acceptors are contacts to aromatic C−H donors. C−H···π interactions are well-known weak interactions,[11] and the phenyl rings can be aligned "vertex-to-face", "edge-to-face", or "face-to-face".

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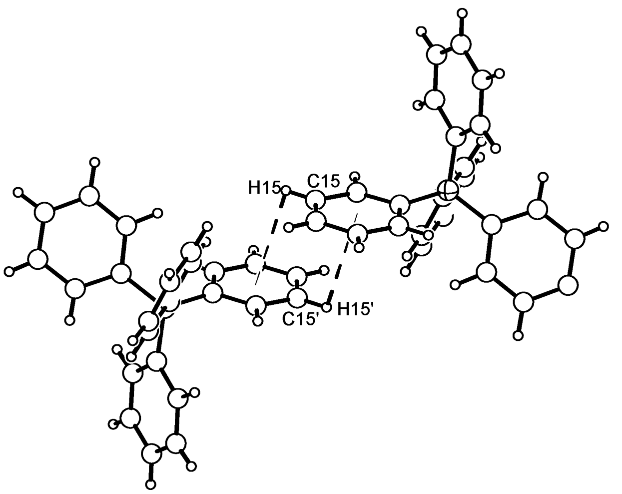

Figure 4. Offset face-to-face C−H···π interaction of two BPh_4^- anions in **1**.

The structure of **1** shows an "offset face-to-face" interaction between two tetraphenylborate anions, which leads to the formation of a anionic dimer ($[B(Ph)_4]_2^{2-}$) (Figure 4).

The C15−C15′ distance of the two parallely oriented phenyl rings is 3.38 Å, which is only just shorter than the C−C VdW distance (3.4 Å). The H15−C15−C15′ angle is 82°, which confirms that the carbon atoms in meta position are almost exactly on top of each other. In comparison, for the phenyl···phenyl interactions in $(Ph_4P)_2[Fe(SPh)_4]$,[12] the authors report phenyl−phenyl distances of 3.2 Å, which are probably shorter and stronger because of the Coulomb interactions between the $[Fe(SPh)_4]^{2-}$ anions and the Ph_4P^+ cations. The anion dimers are surrounded by isolated $[(NH_4)_2(NH_3)_{10}]^{2+}$ cations. The cation−cation distances range between 3.665 (N5−N5′) and 4.083 Å (N2−N2′) (Figure 1).

$[NH_4(NH_3)_4][Ca(NH_3)_7]As_3S_6 \cdot 2NH_3$ (**2**) was obtained by reduction of As_4S_4 with calcium in liquid ammonia and also characterized by single-crystal X-ray structure analysis at 123 K. The compound is built from discrete $[NH_4(NH_3)_4]^+$ cations, heptaamminecalcium(II) complexes, $As_3S_6^{3-}$ anions, and ammonia molecules of crystallization (Figure 5). The $As_3S_6^{3-}$ anion adopts the chair conformation and shows As−S(equatorial) distances of 2.149(1)−2.155(1) Å and As−S(ring) distances of 2.271(1)−2.291(1) Å. The observed S−As−S angles range between 99.83(6) and 100.91(6)°, and the As−S−As angles are between 96.53(5) and 100.47(6)°. These results agree well with the data reported by Kaub and Sheldrick for the same anion.[13] The $Ca(NH_3)_7^{2+}$ cation can be described as a distorted trigonal prism with a capped rectangular face. It displays Ca−N distances of 2.521(6)−2.637(6) Å and N−Ca−N angles of 74.4(2)−154.1(1)°. A similar $Ca(NH_3)_7^{2+}$ cation was described by Kolis et al.[14] The Ca−N distances also agree with the data published by Kerdcharoen et al.,[15] who performed ab initio calculations of $Ca(NH_3)_x^{2+}$ complexes in the gas phase ($x = 1-6$), resulting for the Ca−N distances a linear gradient from 2.44 ($x = 1$) to 2.60 Å ($x = 6$).

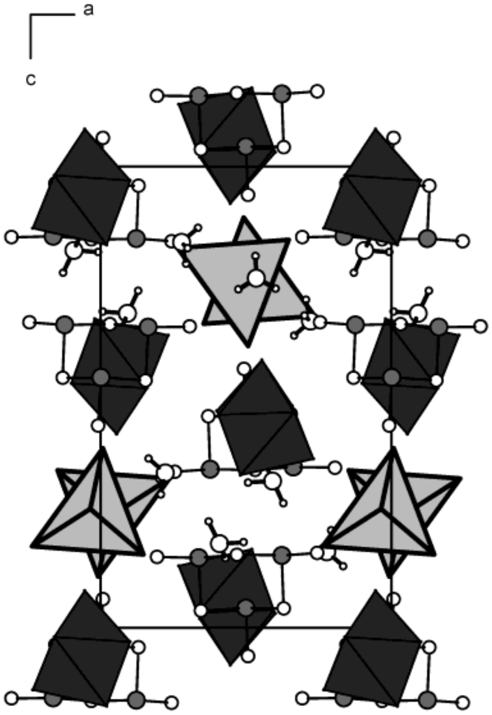

Figure 5. Building units $[NH_4(NH_3)_4]^+$ (light gray tetrahedra), $[Ca(NH_3)_7]^{2+}$ (dark gray polyhedra), $As_3S_6^{3-}$, and free NH_3 in a projection of the structure of $[NH_4(NH_3)_4][Ca(NH_3)_7]As_3S_6 \cdot 2NH_3$ (**2**).

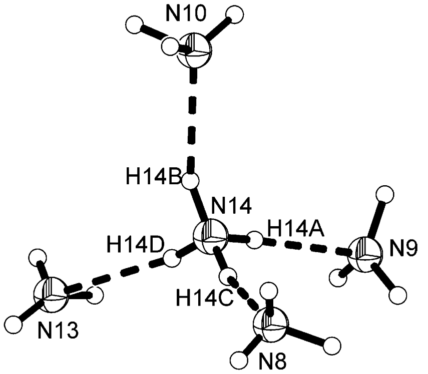

Figure 6. $[NH_4(NH_3)_4]^+$ cation in **2**.

The NH_4^+ cation in **2** has N−H distances of 0.79(4)−0.92(7) Å and H−N−H angles of 96(9)−139(10)°, showing a significant deviation from the ideal tetrahedral angles. This N14-ammonium ion (Figure 6) forms the $[NH_4(NH_3)_4]^+$ complex cation with the ammonia molecules N8, N9, N10, and N13. The N14−H···N hydrogen bonds (Table 1) are between 28.0 and 20.0% shorter than the N−H···N van der Waals distance. The N−H···N angles range between 153 and 172°. This distorted tetrahedral arrangement is surrounded by two ammonia molecules and eight sulfur atoms of the $As_3S_6^{3-}$ anions (Figure 7).

The N10−H10B···N12 bridge and the N13−H13C···N11 bridge (Table 3) cannot be considered as strong interactions, because the H···N distances (2.72(8) and 2.82(13) Å) correspond nearly with the N−H···N van der Waals distance and the N−H···N angles (118(6) and 128(10)°) obviously differ from a linear arrangement. The last mentioned proton

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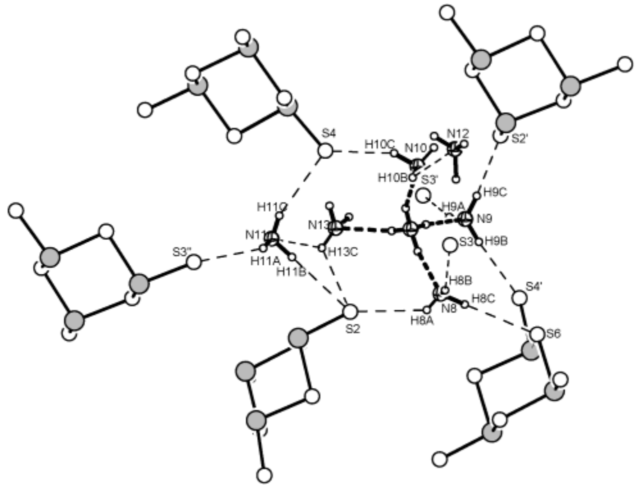

Figure 7. Interactions of the $[NH_4(NH_3)_4]^+$ cation in **2** with neighboring anions and ammonia of crystallization.

Table 3. H-Bridges (Å, deg) in Figure 7 (**1**)

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(8)−H(8A)···S(2)	0.77(6)	2.87(6)	3.404(6)	129(6)
N(8)−H(8B)···S(3)	0.88(5)	2.75(5)	3.543(6)	151(5)
N(8)−H(8C)···S(6)	1.01(7)	2.91(7)	3.856(5)	157(7)
N(9)−H(9A)···S(3)′	0.90(5)	2.62(6)	3.496(5)	163(6)
N(9)−H(9B)···S(4)′	0.97(6)	2.58(6)	3.545(6)	174(7)
N(9)−H(9C)···S(2)′	0.97(6)	2.56(6)	3.522(5)	170(8)
N(10)−H(10B)···N(12)	1.10(8)	2.72(8)	3.384(10)	118(6)
N(10)−H(10C)···S(4)	1.00(7)	2.55(8)	3.437(7)	148(7)
N(11)−H(11A)···S(3)″	1.02(6)	2.96(7)	3.829(8)	143(4)
N(11)−H(11B)···S(2)	0.99(6)	2.99(7)	3.969(7)	167(6)
N(11)−H(11C)···S(4)	0.92(6)	2.92(7)	3.811(7)	162(7)
N(13)−H(13C)···S(2)	0.97(9)	2.98(11)	3.746(10)	137(10)
N(13)−H(13C)···N(11)	0.97(9)	2.82(13)	3.500(12)	128(10)

(H13C) forms a bifurcated hydrogen bond with a second acceptor atom (S2). It is not possible to determine the main component of this hydrogen bond, because the H···S distance (2.98 Å) is nearly identical with the H···S van der Waals distance (3.0 Å) and the N13−H13C···S2 angle with 137(10)° deviates from linearity as much as the N13−H13C···N11 angle (128(10)°). Additionally, the ammonia molecules N8 and N9 of the $[NH_4(NH_3)_4]^+$ complex form H···S bridges to the sulfur atoms S2, S3, S6, S3′, S4′, and S2′. The percentage of the abridgement compared to the H···S van der Waals distance ranges between 4.3 and 14.7%, and the N−H···S angles are between 129(6) and 174(7)°. The shortest H···S distance in the coordination sphere of the $[NH_4(NH_3)_4]^+$ cation is observed for the N10−H10C···S4 hydrogen bond. Its H10C···S4 distance (2.55 Å; DHA angle 148°) is about 15.0% shorter than the H···S van der Waals distance. In comparison with the aforementioned N8−H8A···S2 bridge (N8−S2 distance: 3.404(6) Å), the observed N10−S4 distance (3.437(7) Å) is larger than the N8−S2 distance.

Nevertheless, this is a stronger interaction, because the N10−H10C distance (1.00(7) Å) is significantly longer than the N8−H8A distance (0.77(6) Å), which is indicative of a proton-transfer process. Finally, the interactions between the N11-ammonia molecule and the sulfur atoms S3″, S2, and S4 are without exception weak hydrogen bonds. The H···S distances are only minimally shorter than the H···S van der Waals distance, whereas the DHA angles (143−167°) are relatively close to 180°.

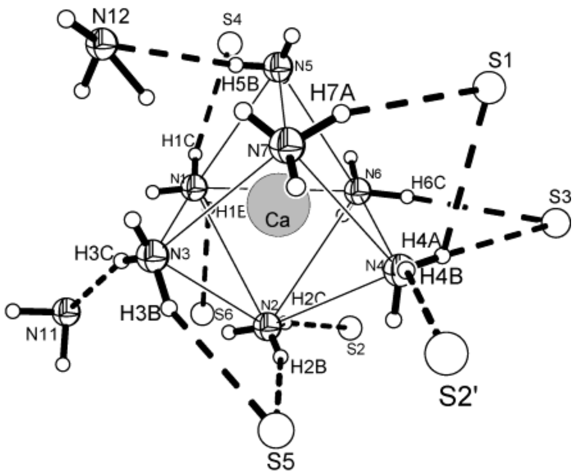

Figure 8. $[Ca(NH_3)_7]^{2+}$ cation in **2** and its interactions.

Table 4. H-Bridges (Å, deg) in Figure 8 (**2**)

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(1)−H(1B)···S(6)	0.87(7)	2.96(8)	3.737(6)	151(9)
N(1)−H(1C)···S(4)	0.82(5)	2.94(5)	3.733(7)	166(4)
N(2)−H(2B)···S(5)	0.79(8)	2.97(13)	3.633(6)	144(14)
N(2)−H(2C)···S(2)	0.79(5)	2.96(5)	3.746(6)	175(6)
N(3)−H(3B)···S(5)	0.93(7)	2.75(8)	3.575(8)	148(7)
N(3)−H(3C)···N(11)	0.97(4)	2.28(4)	3.191(7)	156(5)
N(4)−H(4A)···S(1)	1.01(18)	2.49(16)	3.388(6)	147(26)
N(4)−H(4A)···S(3)	1.01(18)	3.0(3)	3.710(6)	132(21)
N(4)−H(4B)···S(2)′	0.92(6)	2.79(7)	3.656(6)	157(6)
N(5)−H(5B)···N(12)	0.82(7)	2.41(7)	3.219(11)	168(9)
N(5)−H(5C)···S(4)	0.96(7)	2.93(10)	3.760(7)	145(10)
N(6)−H(6C)···S(3)	0.99(8)	2.86(9)	3.835(6)	168(14)
N(7)−H(7A)···S(1)	0.97(5)	2.94(6)	3.812(7)	151(5)

The ammonia molecules of the coordination sphere of the $Ca(NH_3)_7^{2+}$ cation (Figure 8) show three obviously shorter H-bridges in comparison to other H-bridges (Table 4). These are the N3−H3C···N11, the N4−H4A···S1, and the N5−H5B···N12 bridges, which are about 15.7, 17.0, and 11.3% shorter than the comparable van der Waals distance. The DHA angles are 156(5), 147(26), and 168(9)°. It is sufficiently known that short H···A distances should be accompanied by DHA angles near 180°. However, the obvious deviation of the N4−H4A···S1 bridge is clearly due to the formation of a bifurcated H-bridge, the auxiliary component of which is a N4−H4A···S3 interaction with a large H4A···S3 distance (3.0 Å) and an N4−H4B···S3 angle of 132°. The H···S distances to the remaining surrounding S atoms range between 2.97(13) and 2.75(8) Å, and the N−H···S angles lie between 144(14) and 175(6)°.

In Figure 9 all 14 inequivalent nitrogen atoms are displayed, including the ammonia molecules coordinating neither NH_4^+ nor Ca^{2+} (N11 and N12), which connect the $[NH_4(NH_3)_4]^+$ cation and the $Ca(NH_3)_7^+$ cation by very weak hydrogen bonding (Table 5).

The N12-ammonia molecule forms a strong H12A···S3 bridge (H···S3, 2.49 Å; DHA angle, 169°) and a bifurcated H-bridge to the ammonia molecules of the $Ca(NH_3)_7^+$ cations (N3 and N5) and $[Ca(NH_3)_7]^{2+}$ polyhedra via ammonia molecules in **2**.

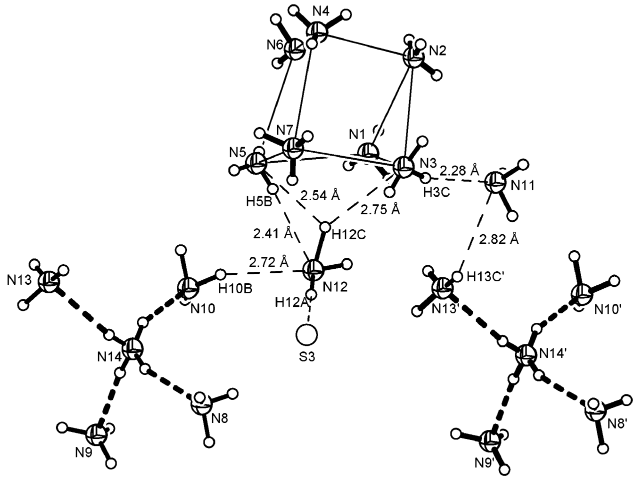

Figure 9. Connection between $[NH_4(NH_3)_4]^+$ cations.

Table 5. H-Bridges (Å, deg) in Figure 9 (**2**)

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(3)−H(3C)···N(11)	0.97(4)	2.28(4)	3.191(7)	156(5)
N(5)−H(5B)···N(12)	0.82(7)	2.41(7)	3.219(11)	168(9)
N(10)−H(10B)···N(12)	1.10(8)	2.72(8)	3.384(10)	118(6)
N(12)−H(12A)···S(3)	1.09(6)	2.49(7)	3.570(8)	169(7)
N(12)−H(12C)···N(5)	1.16(6)	2.54(7)	3.219(11)	116(5)
N(12)−H(12C)···N(3)	1.16(6)	2.75(7)	3.694(12)	138(5)
N(13)′−H(13C)′···N(11)	0.97(9)	2.82(13)	3.500(12)	128(10)

Table 6. H-Bridges (Å, deg) in Figure 11 (**3**)

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(1)−H(1C)···S(4)	0.91	2.79	3.683(5)	166.9
N(2)−H(2A)···S(3)	0.91	2.88	3.434(6)	120.5
N(2)−H(2A)···S(5)	0.91	2.96	3.845(6)	164.0
N(2)−H(2B)···S(4)	0.91	2.78	3.596(6)	149.3
N(3)−H(3B)···N(10)	0.91	2.42	3.269(9)	155.5
N(3)−H(3C)···S(2)	0.91	2.74	3.469(6)	137.6
N(4)−H(4A)···S(4)	0.91	2.96	3.835(6)	160.9
N(5)−H(5A)···S(5)	0.91	3.00	3.817(6)	149.6
N(5)−H(5C)···S(2)	0.91	2.90	3.632(5)	138.8
N(6)−H(6A)···S(6)	0.91	2.87	3.740(7)	161.4
N(6)−H(6C)···S(3)	0.91	2.77	3.591(7)	150.3
N(7)−H(7A)···S(1)	0.91	2.86	3.607(6)	140.8
N(7)−H(7B)···N(10)	0.91	2.60	3.440(10)	153.7
N(10)−H(10C)···S(6)	0.87(4)	2.89(5)	3.752(8)	169(9)

$NH_4(NH_3)_4][Ba(NH_3)_8]As_3S_6 \cdot NH_3$ (**3**) was obtained by reduction of As_4S_4 with barium in liquid ammonia and characterized by single-crystal X-ray structure analysis at 123 K. The compound is built up by discrete $NH_4(NH_3)_4^+$ cations, octaamminebarium(II) cations, $As_3S_6^{3-}$ anions, and ammonia of crystallization (Figure 10). The comparison of Figures 5 and 10 shows the profound similarity of the structures of **2** and **3**, which crystallize in the same space group and have very similar cell parameters (Table 8). The main difference is the single ammonia molecule which in **3** coordinates to Ba^{2+} and which is free in **2**. The $As_3S_6^{3-}$ anion also has chair conformation, the As−S(equatorial) distances are 2.153(2)−2.160(2) Å, and the As−S(Ring) distances are longer with 2.277(1)−2.292(2) Å. The observed S−As−S angles range between 99.58(7) and 101.84(6)°, and the As−S−As angles are between 95.75(5) and 99.36(6)°. The $Ba(NH_3)_8^{2+}$ cation may be described as a distorted dodecahedron with Ba−N distances of 2.869(6)−2.980(5) Å and N−Ba−N angles of 69.6(1)−150.0(1)°, which agrees well with the barium ammine complexes found in $BaCsP_{11} \cdot 11NH_3$.[16] However, as the barium complexes there have the coordination number 9, the complex in **3** is the first example of a dodecahedral octaamminebarium complex.

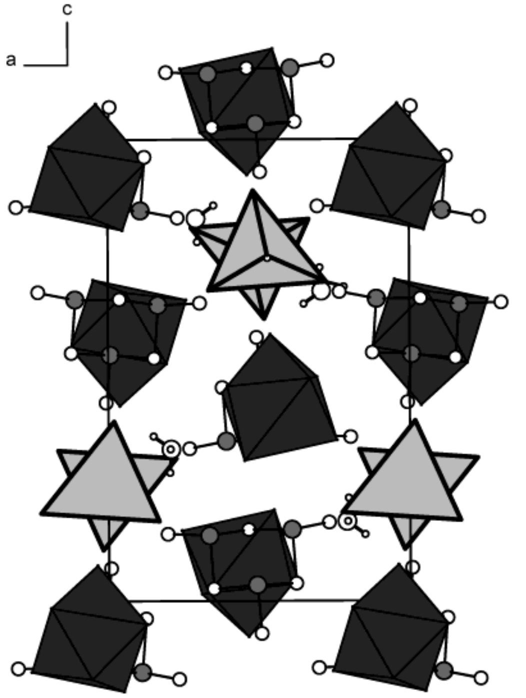

Figure 10. Building units $[NH_4(NH_3)_4]^+$ (light gray tetrahedra), $[Ba(NH_3)_8]^{2+}$ (dark gray polyhedra), $As_3S_6^{3-}$, and free NH_3 in a projection of the structure of $[NH_4(NH_3)_4][Ba(NH_3)_8]As_3S_6 \cdot NH_3$ (**3**).

The NH_4^+ cation (N14) in **3** has N−H distances of 0.99(3) Å and H−N−H angles of 88−123°. It forms the $[NH_4(NH_3)_4]^+$ complex cation with the ammonia molecules N9, N11, N12, and N13. The N14−H···N hydrogen bonds (Table 1) are between 32.7 and 26.9% shorter than the N−H···N van der Waals distance, and the N−H···N angles range between 156 and 176°. The complex cation is surrounded by two bifurcated and four common N−H···S bridges and therefore connected to six $As_3S_6^{3-}$ anions. The H···S distances (Table 6) are between 0.3 and 11.0% shorter than the comparable van der Waals distance. The N−H···S angles amount to 137−169°.

The $Ba(NH_3)_8^{2+}$ cation (Figure 12) is determined by 11 weak hydrogen bonds to sulfur atoms of the anion and two additional hydrogen bonds to the ammonia molecule of crystallization (N10). The H···S distances (Table 7) are shortened about 0−12.0%, and the N−H···S angles are between 120 and 166°. The N10-ammonia molecule is connected to the $Ba(NH_3)_8^{2+}$ cation by the two H-bridges N3−H3B···N10 (H···A, 2.42 Å; DHA, 156°) and N7−H7B···N10 (H···A, 2.60 Å; DHA, 154°). N10 itself forms a H···S bridge to a $As_3S_6^{3-}$ anion.

Comparison of the Ammine−Ammonium Complexes and Conclusion

The compounds reported here contain the cations $[(NH_4)_2(NH_3)_{10}]^{2+}$ and $[NH_4(NH_3)_4]^+$. We have already described

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[16] Korber, N. D.; Daniels, J. D. *ZAACAB* **1996**, *622*, 1833.

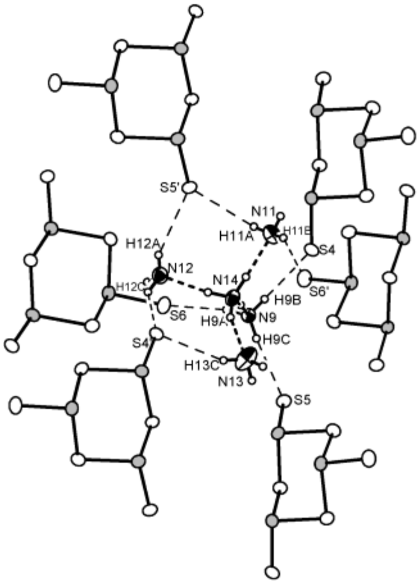

Figure 11. Interactions of the $[NH_4(NH_3)_4]^+$ cation in **3** with neighboring anions.

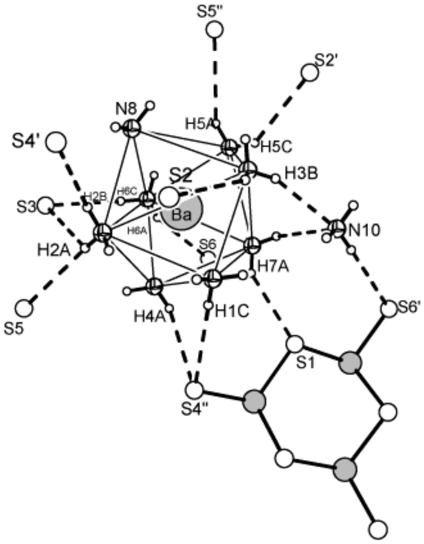

Figure 12. $[Ba(NH_3)_8]^{2+}$ cation in **3** and its interactions.

Table 7. H-Bridges (Å, deg) in Figure 12 (**3**)

D−H···A	d(D−H)	d(H···A)	d(D···A)	∠(DHA)
N(9)−H(9A)···S(6)	0.91(4)	2.69(4)	3.573(5)	163(6)
N(9)−H(9B)···S(4)	0.91(4)	2.67(4)	3.523(5)	157(6)
N(9)−H(9C)···S(5)	0.91(4)	2.66(5)	3.531(6)	161(9)
N(11)−H(11A)···S(5)′	0.79(6)	2.99(18)	3.647(8)	142(25)
N(11)−H(11B)···S(6)′	0.79(6)	2.73(7)	3.453(7)	152(8)
N(12)−H(12A)···S(5)′	0.87(5)	2.96(6)	3.739(7)	151(7)
N(12)−H(12C)···S(4)	0.87(5)	2.79(10)	3.474(6)	137(11)
N(13)−H(13C)···S(4)	0.92(6)	2.75(8)	3.638(8)	161(15)

the cations $[NH_4(NH_3)_3]^+$, $[NH_4(NH_3)_2]^+$, and $[NH_4(NH_3)]^+$ in the compounds $(NH_4)_3AsS_4\cdot 5NH_3$ and $(NH_4)_3SbS_4\cdot 8NH_3$.[8] Additionally, the $[NH_4(NH_3)]^+$ cation was reported by Berthold et al.[17] and Pfisterer and Korber.[18]

Table 8. Crystallographic Data for **1**−**3**

param	1	2	3
chem formula	$C_{24}BN_6H_{39}$	$As_3CaS_6N_{14}H_{43}$	$As_3BaS_6N_{14}H_{43}$
M_r (g·mol^{-1})	422.42	696.68	793.94
temp (K)	123	123	123
cryst system	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
a (Å)	12.4693(9)	12.192(1)	12.393(1)
b (Å)	9.9918(4)	12.428(1)	12.630(1)
c (Å)	21.144(1)	19.396(1)	19382(1)
β (deg)	97.924(8)	90	90
V (Å^3)	2609.2(2)	2938.9(4)	3033.8(6)
Z	4	4	4
ρ_c (g·cm^{-3})	1.075	1.575	1.738
F(000)	920	1424	1568
λ(Mo Kα) (Å)	0.710 73	0.710 73	0.710 73
θ range (deg)	1.94−25.95	2.10−25.93	2.30−25.83
all reflcns	20 126	11 988	13 982
indpndt reflcns (R_{int})	5010 (0.0925)	5137 (0.0601)	5525 (0.0535)
no. of params	436	389	302
no. of restraints	0	45	21
R_1 ($I > 2\sigma(I)$)	0.0432	0.0332	0.0326
wR_2 ($I > 2\sigma(I)$)	0.0774	0.0511	0.0765
R_1 (all data)	0.1151	0.0527	0.0370
wR_2 (all data)	0.0895	0.0544	0.0777
GooF	0.746	0.773	0.980
largest peak and hole	0.187/−0.128	0.329/−0.358	0.750/−0.842
Flack param x (esd)		0.0103 (0.0099)	0.000 (0.012)

Table 9. Average Distances/Å and Angles/deg in Ammine−Ammonium Complexes

cation	existent in compd	$NH_4\cdots NH_3$ dist	N···N dist	DHA angle
$[(NH_4)_2(NH_3)_{10}]^{2+}$	1	1.88	2.92	176
$[NH_4(NH_3)_4]^+$	**2** and **3**	2.00	2.90	165
$[NH_4(NH_3)_3]^+$	ref 6	2.08	2.92	166
$[NH_4(NH_3)_2]^+$	ref 6	2.02	2.88	168
$[NH_4(NH_3)]^+$	ref 6	1.96	2.84	171
$[NH_4(NH_3)]^+$	ref 15	1.86	2.81	162
$[NH_4(NH_3)]^+$	ref 16	2.06	2.88	172

Table 9 summarizes the experimentally determined distances and angles of these known cations. Recent ab initio calculations by Wang et al. predict that a lowering of the number of coordinating ammonia molecules in ammine−ammonium complexes is accompanied by a shortening of the N···N-distances ($[NH_4(NH_3)_4]^+$, 2.97 Å; $[NH_4(NH_3)_3]^+$, 2.91 Å; $[NH_4(NH_3)_2]^+$, 2.83 Å; $[NH_4(NH_3)]^+$, 2.71 Å).[19] As Table 9 shows, there is no real evidence for such a trend in the experimental data. This may be due to the fact that the calculations were made for the gas phase, while the measurements were made on solids, in which a number of other, weaker interactions discussed above might compensate the predicted trend.

In contrast to the situation for the $H_2O-H_3O^+$ complexes, one would predict for the $NH_3-NH_4^+$ system a limit at the composition $[NH_4(NH_3)_4]^+$ due to the fact that ammonia has only one H-bond-accepting lone pair. However, the $[(NH_4)_2(NH_3)_{10}]^{2+}$ cation described here for the first time shows that the formation of polynuclear ammine−ammonium complexes is possible via connecting additional ammonia molecules, which opens up new possiblities for larger molecular ammine−ammonium cations or even extended structures.

Experimental Section

All manipulations were carried out under dry argon in all-glass reaction and handling vessels that were dried in vacuo. Ammonia

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(17) Berthold, H. J.; Vonholdt, E.; Wartchow, R. *Z. Kristallogr.* **1993**, *203*, 199.

(18) Pfisterer K.; Korber, N. *Z. Anorg. Allg. Chem.* **2002**, *628*, 762.

(19) Wang, B. C.; Chang, J. C.; Jiang, J. C.; Lin, S. H. *Chem. Phys.* **2002**, *276*, 93−106.

(Bayer AG) was made anhydrous by distilling it from sodium and was stored as a sodium−ammonia solution at 195 K.

1. Sodium tetraphenylborate was dried for 12 h at 353 K. A 0.300 g (0.877 mmol) amount of Na[B(Ph)$_4$] was added to 0.76 g (4.6 mequiv/g) of Amberlyst 15 (Fluka). This corresponds a molar ratio of 1/4 (Na[B(Ph)$_4$]/Amberlyst 15). A 25 mL volume of ammonia was condensed onto the compounds at 195 K. The resulting colorless solution produced a nearly quantitative yield of **1** as colorless crystals at 233 K.

2 and 3. Calcium (0.137 g, 3.41 mmol) or barium (0.501 g, 3.65 mmol) and realgar As_4S_4 (0.857 g, 0.80 mmol) were filled into a Schlenk-type reaction vessel, and 20 mL of liquid ammonia was added. After several weeks at 233 K, transparent cube-shaped red (**2**) or yellow (**3**) crystals precipitated.

For the crystal preparation, we adapted the technique described by Stahlke et al.[20] to our needs. Small amounts of the reaction products were transferred directly from the liquid ammonia into perfluorether (Galden), which was cooled to 213 K by a stream of cold nitrogen. Single crystals which were suitable for a X-ray structure analysis were selected with the help of a microscope and picked up on the tip of a capillary mounted on a goniometer head. The crystals were then immediately submerged in liquid nitrogen and transferred to the diffractometer. The structures were solved by direct methods (SHELXS-97)[21] and refined against F^2 (SHELXL-97).[22] An absorption correction was applied to the data for **2** and **3** (DELrefABS of the program package PLATON[23]). The H atoms were localized by difference Fourier synthesis and connected to the N atoms with restraints ($s = 0.1$) for **2**. The protons were refined isotropically, and all other atoms anisotropically.

Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic data for **1** have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 218734. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: int. code + (1223) 336−033. E-mail: deposit@ccdc.cam.ac.uk). Details for the structures **2** and **3** may be obtained from Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, by quoting the Registry Nos. 413369 (**3**) and 413368 (**2**).

IC035175Z

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(20) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615.

(21) Sheldrick, G. M. *SHELXS-97, Program for crystal structure solution*, Universität Göttingen: Göttingen, Germany, 1997.

(22) Sheldrick, G. M. *SHELXL-97*, *Program for crystal structure refinement*; Universität Göttingen: Göttingen, Germany, 1997.

(23) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2001.