Short Communication

Crystal Structure of Calcium Heptaammine Hexasulfide, $Ca(NH_3)_7S_6$

George L. Schimek, Greg W. Drake[†] and Joseph W. Kolis[*]

Department of Chemistry, Clemson University, Clemson, SC 29634-1905, USA

In our quest to more fully understand the phase equilibria of metal sulfides in supercritical ammonia solutions, the title compound $Ca(NH_3)_7S_6$ was isolated and structurally characterized. It contains isolated six-membered polysulfide chains similar to a number of others previously reported.[1–9] Of greater interest, however, is the countercation. A number of recent reports show that the presence of soft anionic main group clusters serve to stabilize ammine complexes of hard cations. This has led to the isolation and characterization of $[Yb(NH_3)_8]^{3+}$, $[La(NH_3)_9]^{3+}$,[10,11] $[Ba(NH_3)_9]^{2+}$,[12] and $[Sr(NH_3)_8]^{2+}$.[13] In this manuscript we report the first calcium heptaammine complex, $[Ca(NH_3)_7]^{2+}$.

Experimental

Preparation. The title compound was prepared using supercritical fluid methods.[14] Typically, CaS_4 (0.0500 g, 0.297 mmol) was loaded with SnS_2 (0.0542 g, 0.296 mmol) into fused silica tubes (5 mm i.d., 7 mm o.d.) in a drybox. A 40% fill of NH_3 was subsequently distilled into the evacuated tubes before flame-sealing. The tubes were loaded into a Parr autoclave and counter-pressured with argon to 3000 p.s.i. The apparatus was heated in a tube furnace at 160 °C for one week. Yellow polyhedral crystals of $Ca(NH_3)_7S_6$ were the only identifiable phase in the product mixture. To prepare the initial CaS_4, Ca metal (2.381 g, 59.40 mmol) was cut from a large block, divided into smaller portions and loaded into a 500-mL round-bottomed flask with powdered S_8 (7.619 g, 29.70 mmol) in a drybox. The closed flask was purged with argon gas and a condenser was attached before 300 mL of NH_3 were condensed into the flask

using a dry ice–acetone cold bath. The reaction was kept cold and stirred for 3.5 h before allowing the NH_3 to evaporate slowly under an argon purge gas. The dark yellow product, CaS_4, was dried under vacuum and stored in the drybox.

Structure determination. A single crystal of the title phase was isolated from the reaction solution by decanting the liquid ammonia away from the sample, cooling the solvent and then opening the tube and placing the contents immediately in a solution of liquid argon in a cooled pyrex round-bottomed flask. **Caution**: The evaporation of liquid argon creates high pressures if not vented properly. The sample was then poured out of the flask onto a glass frit over a cold nitrogen gas stream at ca. -100 °C.[15] A microscope was mounted over the frit to facilitate crystal selection. A yellow polyhedral crystal was mounted with silicone sealant onto a glass fiber which was attached with epoxy to a copper pin. The copper pin acted to maximize thermal conduction and thereby minimize condensation. The loaded copper pin was quickly moved into the cold nitrogen gas stream over the goniometer. A Rigaku AFC7-R rotating anode diffractometer, equipped with graphite monochromated Mo Kα radiation (0.7107 Å) generated at 11.6 kW, was used. Lattice parameters and an orientation matrix for data collection were derived from 20 centered reflections read from a rotation photograph with a 2θ range of 7.5 to 23.2°. Three standard reflections were measured every 100 reflections and showed less than 2.0% decay during the data collection. Data were collected at -140 °C from 3.0 to 50° in 2θ in the $\pm hkl$ quadrant, using an ω–2θ scan mode at 4° min^{-1} with $\leqslant 5$ rescans. An empirical absorption correction[16] was applied based upon an azimuthal scan of a reflection with an average transmission range of 0.81–0.95. The intensity data were corrected for

*To whom correspondence should be addressed.
†Present address: 10 East Saturn Blvd, Bldg 8451, Air Force Research Laboratory, Edwards Air Force Base, CA 93523, USA.

Table 1. X-Ray crystallographic data.

Formula	$[Ca(NH_3)_7]S_6$
Formula weight	351.7
Crystal system	Monoclinic
Space group (No.), Z	$P2_1/c$ (14), 4
$a/\text{Å}$	12.143(6)
$b/\text{Å}$	11.815(7)
$c/\text{Å}$	11.505(5)
$\beta/°$	93.53(4)
Volume/Å^3	1647(1)
$D_{calc}/\text{g cm}^{-3}$	1.418
Crystal size/mm^3	$0.1 \times 0.12 \times 0.13$
2θ range/°, octants	3.0–50, $\pm h$, $-k$, l
Refl. collected (unique)	3222 (3062)
Observed $[F > 6\sigma(F)]$, R_{int}	1157, 0.0469
Variables	128
μ/mm^{-1}	1.125
Transmission range	0.81–0.95
R,[a] wR[b]	0.0423, 0.0412
R,[a] wR[b] (all data)	0.1509, 0.0563
S[c]	1.35
Residual/$e^- \text{Å}^{-3}$, max shift	0.46/−0.34, 0.001

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/(\sigma^2(F_o) + 0.016F_o{}^2)$. [c] $S = [\Sigma(|F_o|_i - |F_c|_i)/\sigma_i]/(n - m)$; $i = 1$ to n.

Lorentz and polarization effects. Further crystallographic details are given in Table 1.

The space group $P2_1/c$ was uniquely chosen based upon the systematic absences $h0l$: $l = 2n + 1$ and $0k0$: $k = 2n + 1$. The structure was solved by direct methods[17] and refined on $|F|$ by full-matrix, least-squares techniques with a combination of teXsan[18] and SHELXTL-Plus[19] software. Scattering factors for all atoms were taken from the source programs utilized. Refinement proceeded without problems and all non-hydrogen atom thermal parameters were subsequently refined anisotropically. Orienting hydrogen atoms on the nitrogen atoms were located in Fourier difference maps, and subsequently the remaining hydrogen atoms were generated and all were fixed with ideal geometry (109.5°) and bond distances $[d(\text{N-H}) = 0.9 \text{ Å}]$. The amine hydrogen atoms were

refined with a group isotropic thermal parameter $[0.068(7) \text{ Å}^2]$. These results indicated the lack of inclusion of tin into this system. Positional and isotropic thermal parameters are listed in Table 2.

Results and discussion

The title compound is composed of isolated $(S_6)^{2-}$ and $[Ca(NH_3)_7]^{2+}$ ions (Fig. 1). The anionic chain consists of covalently bound sulfur atoms with bond distances that range from 2.027 to 2.075(3) Å and bond angles varying from 109.3(2) to 109.9(1)° (Fig. 2). The observed bond angles and trans conformation minimize repulsions from the pair of lone-pair electrons residing on each sulfur atom. Typical polyhexasulfide dianions have observed distances and angles of 2.007 to 2.101 Å and 106.7 to 112.4°, respectively.[1-8] Torsion angles in the reported anion are 73.7, 82.0 and 83.0°, as compared
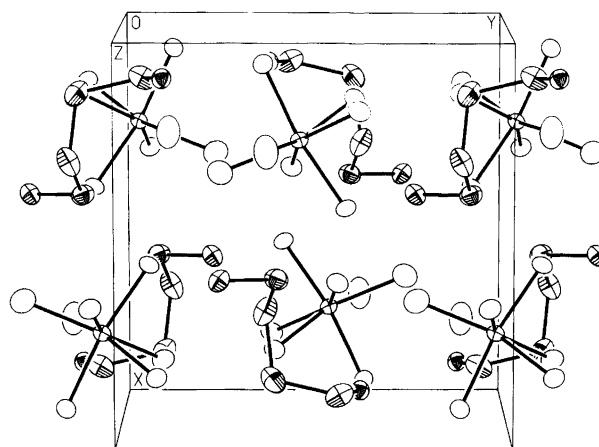

Fig. 1. Packing diagram as viewed nearly parallel to the z-direction in $Ca(NH_3)_7S_6$. Sulfur atoms are shown as full thermal ellipsoids, calcium atoms as principal ellipsoids and nitrogen atoms as boundary ellipsoids, and hydrogen atoms are omitted for clarity. All ellipsoids are at the 60% probability level.

Table 2. Atomic coordinates and equivalent isotropic thermal parameters (in Å^2) for non-hydrogen atoms.

Atom	Wyckoff	X	Y	Z	U_{eq}[a]
S1	4e	0.1007(2)	0.1178(2)	0.8291(2)	0.028(1)
S2	4e	0.1126(2)	0.0636(2)	0.6625(2)	0.042(1)
S3	4e	0.1519(2)	−0.1039(2)	0.6615(2)	0.047(1)
S4	4e	0.3163(2)	−0.1240(2)	0.7181(2)	0.043(1)
S5	4e	0.4140(2)	−0.0947(2)	0.5831(2)	0.038(1)
S6	4e	0.4227(2)	−0.2369(2)	0.4855(2)	0.032(1)
Ca1	4e	0.2640(1)	0.0378(1)	0.1943(1)	0.022(1)
N1	4e	0.0797(5)	0.1295(6)	0.1518(5)	0.031(2)
N2	4e	0.4314(4)	−0.0809(6)	0.2284(5)	0.027(2)
N3	4e	0.1730(5)	−0.1040(6)	0.0494(5)	0.030(2)
N4	4e	0.3516(5)	0.0594(6)	−0.0042(5)	0.030(3)
N5	4e	0.3454(6)	0.2396(6)	0.1960(6)	0.045(3)
N6	4e	0.2729(6)	0.1206(7)	0.4014(5)	0.054(3)
N7	4e	0.1798(5)	−0.1133(6)	0.3235(5)	0.032(2)

[a] The equivalent isotropic temperature factor, U_{eq}, is defined as $1/3\{\Sigma_i\Sigma_j(U_{ij}a_i^* a_j^* \cdot a_i \cdot a_j)\}$, where the summations of i and j range from 1 to 3.
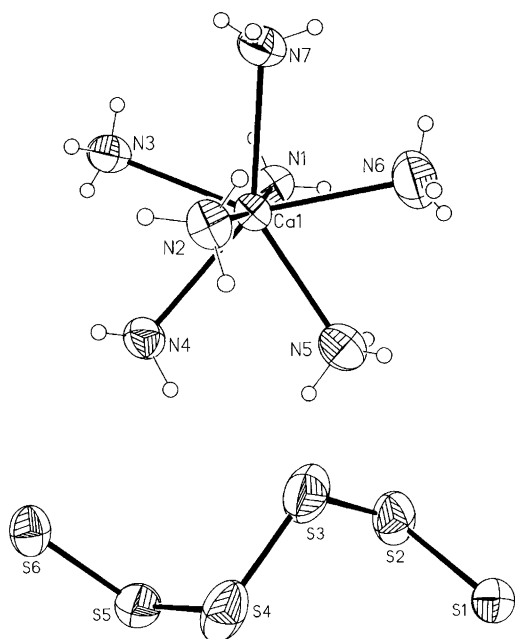
Fig. 2. Detailed view of $Ca(NH_3)_7^{2+}$ (top) and the dianionic hexasulfide chain (bottom). All thermal ellipsoids are at the 60% probability level.

Table 3. Bond distances (in Å) and angles (in °).

S1–S2	2.034(3)	Ca1–N2	2.480(6)
S2–S3	2.036(4)	Ca1–N3	2.566(6)
S3–S4	2.075(3)	Ca1–N4	2.590(6)
S4–S5	2.041(3)	Ca1–N5	2.580(7)
S5–S6	2.027(3)	Ca1–N6	2.571(7)
Ca1–N1	2.508(6)	Ca1–N7	2.576(7)
S1–S2–S3	109.9(1)	N4–Ca1–N5	74.8(2)
S2–S3–S4	109.3(2)	N1–Ca1–N6	90.1(2)
S3–S4–S5	109.6(1)	N2–Ca1–N6	94.7(2)
S4–S5–S6	109.5(1)	N3–Ca1–N6	147.4(2)
N1–Ca1–N2	171.1(2)	N4–Ca1–N6	141.6(2)
N1–Ca1–N3	79.2(2)	N5–Ca1–N6	69.4(2)
N2–Ca1–N3	92.8(2)	N1–Ca1–N7	91.8(2)
N1–Ca1–N4	101.3(2)	N2–Ca1–N7	82.4(2)
N2–Ca1–N4	79.5(2)	N3–Ca1–N7	75.6(2)
N3–Ca1–N4	71.0(2)	N4–Ca1–N7	140.9(2)
N1–Ca1–N5	86.5(2)	N5–Ca1–N7	143.3(2)
N2–Ca1–N5	102.2(2)	N6–Ca1–N7	74.0(2)
N3–Ca1–N5	139.3(2)		

to 85.5, 75.5 and 85.5° in $[HN(CH_3)_3]_2S_6$.[1] Interestingly, all but one[9] of the reported $(S_6)^{2-}$ compounds adopt the trans conformation. The countercation, $[Ca(NH_3)_7]^{2+}$ is the first homoleptic calcium heptaammine to be structurally characterized by single-crystal X-ray diffraction, although Rietveld refinements have been reported for $Ca(ND_3)_6^{20}$ and $Ca(NH_3)_8Cl_2$,[21] both of these complexes contain hexacoordinated calcium. The cation in our compound adopts a slightly distorted pentagonal bipyramidal arrangement of ammine ligands (deviation = 6.1) with N1 and N2 in the axial positions [171.1(2)°, Fig. 2] as derived from an algorithm used to assess the coordination polyhedron.[22] This program indicated deviations of 12.8 and 10.7 for capped octahedral and capped trigonal prismatic geometry, respectively. In contrast, the $[Ca(H_2O)_7]^{2+}$ found in the salt of Orange G takes on a capped octahedral coordination,[23] while two other examples take on capped trigonal prismatic coordination.[24,25] The Ca–N bond distances observed here [2.480 to 2.590(6) Å] are more uniform than those reported for $Ca(NH_3)_8Cl$ (2.52–2.72 Å). A complete listing of distances and angles is given in Table 3. Weak hydrogen bonding interactions between the ammine hydrogen atoms and the polysulfide chain range from 2.61 to 3.40 Å. These distances are in keeping with similar interactions in reported polyhexasulfides (2.16–3.70 Å).[1,2,9]

$Ca(NH_3)_7S_6$ represents another polysulfide member crystallized with a unique countercation. The compound is extremely unstable and rapidly loses NH_3 at room temperature when removed from the mother liquor. The lability of the ammonia precludes any further characterization methods, and perhaps accounts for its absence from the literature. It is interesting to note that the series

$[Ba(NH_3)_9]^{2+}$,[12] $[Sr(NH_3)_8]^{2+}$,[13] and $[Ca(NH_3)_7]^{2+}$ suggests that the size of the divalent cation is a key factor in determining the coordination environment of the alkaline earth dication. The fate of the tin is unknown and is probably soluble in the fluid. Once again supercritical fluid chemistry has provided a valuable route to unreported phases.

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