Crystal structure of tris-tetraamminlithium tetraselenoarsenate(V), $[\text{Li}(\text{NH}_3)_4]_3[\text{AsSe}_4]$

N. Korber* and M. Grothe

Institut für Anorganische Chemie der Universität Regensburg, D-93040 Regensburg, Germany

Received October 16, 2000, CSD-No. 409539

Abstract

$\text{AsH}_3\text{Li}_3\text{N}_{12}\text{Se}_4$, cubic, $\bar{4}3m$ (No. 217), $a = 10.5038(8)$ Å, $V = 1158.9$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.013$, $wR_{\text{ref}}(F^2) = 0.033$, $T = 123$ K.

Source of material

All manipulations were carried out under inert conditions. 11 mg of Li (1.6 mmol) and 128 mg of As (1.7 mmol) were placed into one side, 134 mg of Se (1.7 mmol) into the other side of a u-shaped glass reaction vessel. The compartments were separated by a glass frit with porosity 3. About 20 ml of NH_3 were condensed into the vessel at 77 K. The reaction mixture was allowed to warm to 233 K and was kept at this temperature. After two weeks, yellow needle-shaped crystals of the title compound grew on the frit.

Discussion

In $[\text{Li}(\text{NH}_3)_4]_3[\text{AsSe}_4]$, four NH_3 molecules coordinate the Li^+ ion to form the homoleptic $[\text{Li}(\text{NH}_3)_4]^+$ complex [1]. According to the site symmetry of the Li^+ ion, the NH_3 ligands form a slightly distorted tetrahedron with D_{2d} symmetry ($d(\text{Li}—\text{N}) = 2.090(3)$ Å). On the other hand, the symmetry of the site occupied by the As atom of the AsSe_4^{3-} ion enforces regular tetrahedral ge-

ometry ($d(\text{As}—\text{Se}) = 2.3265(5)$ Å). The anions are surrounded by six plus twelve tetraamminlithium complexes, correspondingly the latter are coordinated by two plus four AsSe_4^{3-} ions.

$[\text{Li}(\text{NH}_3)_4]_3[\text{AsSe}_4]$ is the first tetraselenoarsenate(V) which crystallizes in the $(\text{NH}_4)_3\text{SbS}_4$ structure type [2]. The two other known, solvent-free compounds, Rb_3AsSe_4 and Cs_3AsSe_4 , adopt the orthorhombic $(\text{NH}_4)_3\text{AsS}_4$ type of structure [3]. Therein, the AsSe_4^{3-} ions are surrounded by eight cations, which results in a larger number of close Se–cation contacts (five and seven for the two crystallographically independent cations). In the $(\text{NH}_4)_3\text{SbS}_4$ structure type, only four close contacts are observed. Curiously, the same structure type is adopted by Na_3SbS_4 [4] with the smaller Na^+ ion, which suggests that not only the size of the cation determines which of the two structure types is adopted for analogous A_3EX_4 compounds, but also direct cation–anion interactions according to the HSAB principle. Thus, the softer Rb^+ and Cs^+ cations prefer the greater number of Se contacts, while with the harder Na^+ and $[\text{Li}(\text{NH}_3)_4]^+$ cations electrostatic contributions dominate, which gives rise to the more regular arrangement of the $(\text{NH}_4)_3\text{SbS}_4$ structure type.

Table 1. Data collection and handling.

Crystal:	yellow needle, size $0.02 \times 0.02 \times 0.06$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	77.53 cm ^{−1}
Diffractionmeter, scan mode:	Stoe IPDS, 212 frames, $\Delta\phi = 1.7^\circ$
$2\theta_{\text{max}}$:	51.34°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	7614, 232
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 231
$N(\text{param})_{\text{refined}}$:	20
Programs:	SHELXL-97 [5], DIAMOND [6]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(1A)	48h	0.109(5)	−0.178(4)	−0.387(5)	0.18(3)
H(1B)	24g	0.099(4)	−x	−0.319(4)	0.10(3)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
As(1)	2a	0	0	0	0.0126(2)	U_{11}	U_{11}	0	0	0
Se(1)	8c	0.12788(3)	x	−x	0.0175(2)	U_{11}	U_{11}	−0.0019(1)	− U_{12}	− U_{12}
Li(1)	6b	0	0	−1/2	0.041(3)	U_{11}	0.033(6)	0	0	0
N(1)	24g	0.1128(3)	−x	−0.3809(3)	0.031(1)	U_{11}	0.023(2)	0.008(1)	0.0005(6)	− U_{13}

* Correspondence author

(e-mail: nikolaus.korber@chemie.uni-regensburg.de)

References

1. Korber, N.; Richter, F.: $[\text{Li}(\text{NH}_3)_4]_3\text{P}_{11} \cdot 5\text{NH}_3$: preparation and crystal structure of a Zintl compound with a very high ammonia content. *Chem. Commun.* (1996) 2023-2024.
2. Graf, H.; Schäfer H.; Weiss A.: Die Kristallstruktur des Ammonium-tetrathioantimonats $(\text{NH}_4)_3\text{SbS}_4$. *Z. Naturforsch.* **24b** (1969) 1345-1346.
3. Wachhold, M.; Sheldrick, W. S.: Methanolthermale Synthese und Kristallstruktur von Tetraselenoarsenaten(V) und -antimonaten(V) des Rubidiums und Cäsiums. *Z. Naturforsch.* **51b** (1996) 32-36.
4. Eisenmann, B.; Zagler, R.: Darstellung und Struktur von Na_3SbSe_4 , K_3SbSe_4 und $[\text{Ba}(\text{en})_4]_2[\text{Ba}(\text{en})_3](\text{SbSe}_4)_2$. *Z. Naturforsch.* **44b** (1989) 249-256.
5. Sheldrick G. M.: SHELX97 – A Program System for the Solution and Refinement of Crystal Structures. University of Göttingen, Germany 1997.
6. Brandenburg, K.; Berndt, M.; Bergerhoff, G.: DIAMOND – Visuelles Informationssystem für Kristallstrukturen. University of Bonn, Germany 1999.