

# Shilovite, natural copper(II) tetrammine nitrate, a new mineral species

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## ABSTRACT

The new mineral shilovite, the first natural tetrammine copper complex, was found in a guano deposit located on the Pabellón de Pica Mountain, near Chanabaya, Iquique Province, Tarapacá Region, Chile. It is associated with halite, ammineite, atacamite (a product of ammineite alteration) and thénardite. The gabbro host rock consists of amphibole, plagioclase and minor clinocllore, and contains accessory chalcocopyrite. The latter is considered the source of Cu for shilovite. The new mineral occurs as deep violet blue, imperfect, thick tabular to equant crystals up to 0.15 mm in size included in massive halite. The mineral is sectile. Its Mohs hardness is 2.  $D_{\text{calc}}$  is  $1.92 \text{ g cm}^{-3}$ . The infrared spectrum shows the presence of  $\text{NH}_3$  molecules and  $\text{NO}_3^-$  anions. Shilovite is optically biaxial (+),  $\alpha = 1.527(2)$ ,  $\beta = 1.545(5)$ ,  $\gamma = 1.610(2)$ . The chemical composition (electron-microprobe data, H calculated from ideal formula, wt.%) is Cu 26.04, Fe 0.31, N 30.8, O 35.95, H 4.74, total 100.69. The empirical formula is  $\text{H}_{12.56}(\text{Cu}_{1.09}\text{Fe}_{0.01})\text{N}_{5.87}\text{O}_{6.00}$ . The idealized formula is  $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$ . The crystal structure was solved and refined to  $R = 0.029$  based upon 2705 unique reflections having  $F > 4\sigma(F)$ . Shilovite is orthorhombic, space group  $Pnn2$ ,  $a = 23.6585(9)$ ,  $b = 10.8238(4)$ ,  $c = 6.9054(3) \text{ \AA}$ ,  $V = 1768.3(1) \text{ \AA}^3$ ,  $Z = 8$ . The strongest reflections of the powder X-ray diffraction pattern [ $d$ ,  $\text{ \AA}$  ( $I$ ,%) ( $hkl$ )] are: 5.931 (41) (400), 5.841 (100) (011), 5.208 (47) (410), 4.162 (88) (411), 4.005 (62) (420), 3.462 (50) (002), 3.207 (32) (031), 2.811 (40) (412).

**KEYWORDS:** shilovite, new mineral, tetrammine copper complex, crystal structure, guano, Pabellón de Pica, Chile.

## Introduction

THE new mineral shilovite,  $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$ , the first natural copper(II) tetrammine complex, was found by two of us (G.M. and M.D.) and Arturo Molina Donoso in 2013 in a guano deposit on the

Pabellón de Pica Mountain, Tarapacá Region, Chile. Pabellón de Pica Mountain is the type locality of three other nitrogen-bearing minerals, ammineite,  $\text{CuCl}_2(\text{NH}_3)_2$  (Bojar *et al.*, 2010), joanneumite,  $\text{Cu}(\text{C}_3\text{N}_3\text{O}_3\text{H}_2)_2(\text{NH}_3)_2$  (Bojar and Walter, 2012) and chanabayaitite,  $\text{Cu}_4(\text{N}_3\text{C}_2\text{H}_2)_4(\text{NH}_3)_4\text{Cl}_2(\text{Cl},\text{OH})_2 \cdot \text{H}_2\text{O}$  (Chukanov *et al.*, 2013).

The mineral and its name were approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2014-

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016, Chukanov *et al.*, 2014). The holotype specimen is deposited in the collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, registration number 4542/1. Shilovite was named in honour of the outstanding Russian chemist and Academician of the Russian Academy of Sciences, Professor Alexander Evgen'evich Shilov (1930–2014), a specialist in biomimetics and the chemistry of nitrogen. One of his discoveries is the fixation of molecular nitrogen in solutions containing metal complexes, which appears to be important in terms of the origin of  $[\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$  in Nature. Professor Shilov had agreed to the naming of the mineral. Unfortunately, he died suddenly, a week after shilovite was approved by the IMA-CNMNC.

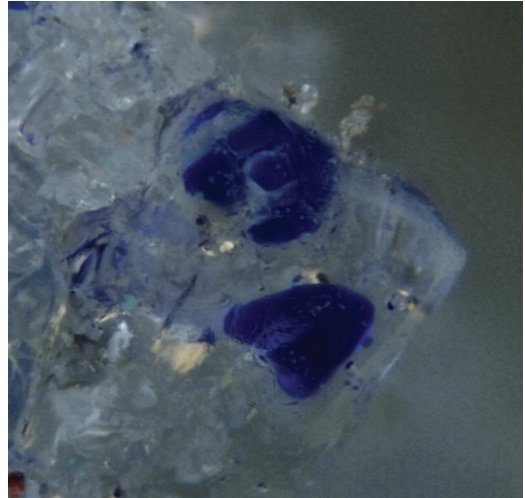


FIG. 1. Single-crystal grains of shilovite (dark violet blue) in halite. Field of view = 0.4 mm. Photograph: M. Burkhardt.

### Occurrence, general appearance and physical properties

Numerous guano deposits occur in the Atacama Desert, in a narrow band (69°30' to 70°10'W, 19°30' to 26°S) attached to the Coastal Range composed of Late Paleozoic and Mesozoic igneous rocks and stretching along the northern coast of Chile. Most of these deposits are situated on low-lying hills that were formerly islands. Some details of the geological setting and the history of guano deposits development in the Tarapacá region are published elsewhere (Erickson, 1981; Pankhurst and Herve, 2007; Appleton and Nothold, 2002; Bojar *et al.*, 2010).

Shilovite occurs in one such deposit situated on the lower part of the steep northern slope of Pabellón de Pica Mountain, 1.5 km south of Chanabaya, Iquique Province, Tarapacá Region, Chile (20°55'S 70°08'W). Associated minerals are halite, ammineite, atacamite (a product of ammineite alteration) and thénardite. The gabbro host rock consists of amphibole, plagioclase and minor clinocllore, and contains accessory chalcopryrite.

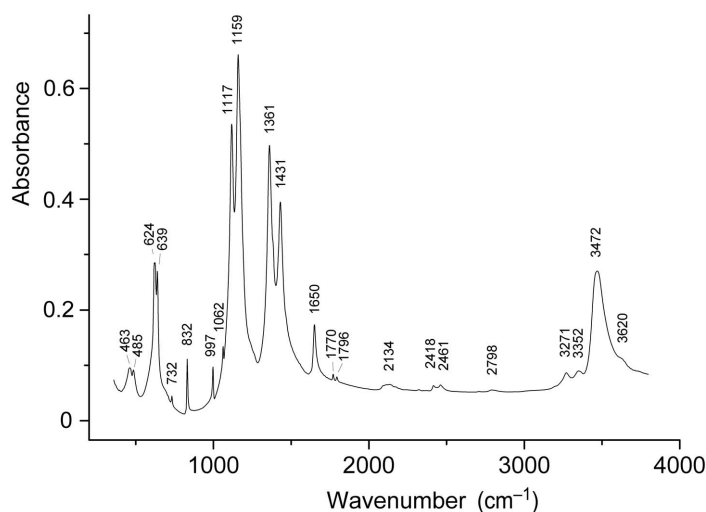


FIG. 2. The powder IR spectrum of shilovite.

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TABLE 1. Chemical composition of shilovite (mean of three analytical spots).

Constituent	Content (wt.%)	Range	Standard deviation	Probe standard
Cu	26.04	24.67–27.09	1.01	CuFeS <sub>2</sub>
Fe	0.31	0.22–0.48	0.12	Fe
N	30.80	29.77–32.39	1.14	TiN
O	35.95	34.28–37.77	1.43	SiO <sub>2</sub>
H	4.74*			
Total	97.84			

\* Calculated from the ideal formula.

Shilovite forms imperfect, thick tabular to equant crystals up to 0.15 mm in size included in massive halite (Fig. 1). The colour of the mineral is deep violet blue. The streak is violet blue and becomes light blue as a result of decomposition and loss of NH<sub>3</sub>. Crystals of shilovite are translucent, with a vitreous lustre. The mineral is sectile, with Mohs hardness  $\leq 2$ ; cleavage is not observed. Shilovite is non-fluorescent.

Density could not be measured because of the small grain size of crystals and the instability of the mineral in available heavy liquids. Density calculated from the empirical formula is 1.92 g cm<sup>-3</sup>.

The new mineral is optically biaxial (+),  $\alpha = 1.527(2)$ ,  $\beta = 1.545(5)$ ,  $\gamma = 1.610(2)$ . 2V was estimated between 40 and 50°, but could not be

determined accurately because the mineral decomposes rapidly in immersion liquids.  $2V_{\text{calc.}} = 57^\circ$ .

### Infrared spectroscopy

In order to obtain an infrared (IR) spectrum, a powdered sample of shilovite was mixed with dried KBr, pelletized, and analysed using an ALPHA FTIR spectrophotometer (Bruker Optics) with a resolution of 4 cm<sup>-1</sup> and 16 scans (Fig. 2). The IR spectrum of a pellet of pure KBr was used as reference.

Assignment of absorption bands was made in accordance with Kótai *et al.* (2002) and Nakamoto (2008, 2009) and is as follows. Bands in the range 3200–3700 cm<sup>-1</sup> correspond to N–H stretching vibrations. Weak bands in the range 1700–3000 cm<sup>-1</sup> correspond to overtones and

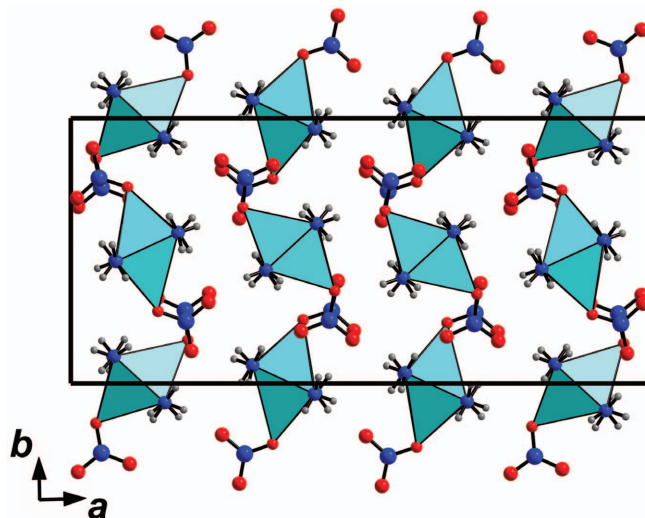


FIG. 3. The crystal structure of shilovite. Cu-centred polyhedra are light blue. O atoms are shown by red circles. Blue and light grey circles correspond to N and H atoms, respectively.

TABLE 2. Powder XRD data for shilovite.

<i>I</i> <sub>meas</sub>	<i>d</i> <sub>meas</sub>	<i>I</i> <sub>calc</sub>	<i>d</i> <sub>calc</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>I</i> <sub>meas</sub>	<i>d</i> <sub>meas</sub>	<i>I</i> <sub>calc</sub>	<i>d</i> <sub>calc</sub>	<i>h</i>	<i>k</i>	<i>l</i>
1	6.606	1	6.645	1	0	1	3	1.956	3	1.956	4	5	1
2	6.407	1	6.394	3	1	0			1	1.947	5	4	2
<b>41</b>	<b>5.931</b>	<b>47</b>	5.935	4	0	0			1	1.946	12	1	0
<b>100</b>	<b>5.841</b>	91	5.836	0	1	1	4	1.947	5	1.945	0	3	3
4	5.432	8	5.427	0	2	0			1	1.926	11	2	1
		2	5.290	1	2	0	2	1.873	4	1.874	12	1	1
<b>47</b>	<b>5.208</b>	41	5.207	4	1	0			1	1.859	12	2	0
1	4.473	1	4.475	3	2	0	3	1.849	5	1.849	4	3	3
<b>88</b>	<b>4.162</b>	100	4.161	4	1	1			1	1.815	9	3	2
<b>62</b>	<b>4.005</b>	66	4.005	4	2	0			1	1.807	7	4	2
3	3.919	2	3.916	5	0	1			1	1.806	11	1	2
		1	3.573	5	2	0			1	1.801	13	1	0
		8	3.467	4	2	1	4	1.796	8	1.796	8	1	3
<b>50</b>	<b>3.462</b>	51	3.461	0	0	2			1	1.745	1	6	1
		1	3.237	7	1	0			1	1.735	11	2	2
32	3.207	32	3.206	0	3	1			2	1.733	8	4	2
4	3.176	2	3.177	1	3	1	4	1.732	9	1.731	0	0	4
		1	3.175	5	2	1	2	1.718	5	1.718	12	0	2
23	3.089	29	3.089	4	3	0			1	1.715	5	5	2
1	3.046	1	3.046	7	0	1	1	1.700	4	1.698	8	5	1
		1	3.044	3	1	2	1	1.685	3	1.684	12	3	1
1	2.987	1	2.990	4	0	2	1	1.661	1	1.661	4	0	4
1	2.975	1	2.972	3	3	1			1	1.660	9	4	2
6	2.917	8	2.918	0	2	2			2	1.642	4	1	4
<b>40</b>	<b>2.881</b>	59	2.882	4	1	2	2	1.638	4	1.638	12	2	2
		5	2.863	8	1	0			1	1.634	11	3	2
25	2.821	30	2.821	4	3	1	1	1.629	4	1.627	8	3	3
2	2.713	4	2.713	0	4	0	2	1.601	3	1.603	0	6	2
2	2.699	2	2.696	1	4	0			1	1.599	12	4	0
		1	2.657	5	3	1			2	1.598	13	1	2
8	2.645	14	2.645	8	1	1	2	1.588	5	1.589	4	2	4
11	2.618	19	2.619	4	2	2	2	1.583	2	1.581	0	5	3
4	2.602	4	2.604	8	2	0	2	1.571	3	1.571	3	6	2
2	2.512	1	2.512	1	4	1	2	1.566	1	1.566	9	3	3
5	2.487	3	2.487	1	3	2			1	1.561	7	4	3
		4	2.486	5	2	2			1	1.550	3	5	3
		2	2.474	7	3	0			2	1.548	4	6	2
9	2.469	14	2.468	4	4	0	3	1.546	3	1.545	8	6	0
		3	2.372	9	2	0	1	1.529	1	1.528	4	5	3
4	2.366	6	2.364	7	1	2	1	1.513	1	1.513	0	7	1
		1	2.305	4	3	2			1	1.510	1	7	1
4	2.295	5	2.294	8	3	0			1	1.510	4	3	4
		1	2.257	0	1	3	1	1.495	1	1.495	8	0	4
8	2.252	14	2.253	8	0	2			1	1.494	11	5	1
		1	2.244	9	2	1	1	1.488	3	1.488	12	1	3
4	2.212	1	2.213	5	3	2			1	1.484	15	2	1
8	2.178	12	2.178	8	3	1			1	1.480	13	4	1
4	2.161	2	2.162	1	5	0	1	1.467	2	1.466	4	7	1
7	2.134	7	2.135	0	4	2	1	1.460	1	1.459	0	4	4
		2	2.131	9	3	0	1	1.452	1	1.451	12	4	2
		2	2.127	1	4	2			1	1.450	15	3	0
6	2.109	9	2.110	4	1	3			1	1.442	5	7	1
10	2.079	16	2.081	8	2	2	1	1.441	1	1.441	8	2	4
		4	2.071	0	5	1			2	1.438	16	1	1
3	2.039	1	2.039	4	5	0	1	1.432	1	1.431	16	2	0
		1	2.037	9	3	1			1	1.431	12	5	1
		1	2.026	7	4	1	1	1.418	2	1.417	4	4	4
10	2.008	15	2.009	4	4	2	1	1.411	2	1.411	8	6	2
		2	2.006	11	2	0	1	1.395	1	1.395	8	5	3
		2	2.004	3	5	1	1	1.388	1	1.387	12	3	3
		3	2.003	8	4	0	1	1.373	1	1.373	0	1	5
2	1.978	1	1.978	12	0	0	1	1.348	1	1.347	16	3	1

The strongest lines are given in bold.

combination modes involving N–O stretching and H–N–H bending. The band at  $1650\text{ cm}^{-1}$  is assigned to degenerate bending vibrations of  $\text{NH}_3$  molecules. Strong bands at  $1361$  and  $1431\text{ cm}^{-1}$  correspond to asymmetric stretching vibrations of  $\text{NO}_3^-$  anions. Strong bands in the range  $900\text{--}1200\text{ cm}^{-1}$  correspond to bending modes of  $\text{NH}_3$  molecules. Bands at  $882$  and  $732\text{ cm}^{-1}$  are assigned to out-of-plane and in-plane bending vibrations of  $\text{NO}_3^-$  anions, respectively. Bands below  $700\text{ cm}^{-1}$  correspond to rocking and translational modes of  $\text{NH}_3$  molecules. The IR spectrum of shilovite is unique, very specific, and is considered as a good diagnostic tool for the mineral.

### Chemical composition and chemical properties

Three electron microprobe analyses were carried out for Cu, Fe, N and O using a VEGA TS 5130MM scanning electron microscope equipped

with an EDS analyzer (INCA Si(Li) detector), at an operating voltage of 20 kV and a beam current of 0.6 nA, with the beam rastered on an area  $8\text{ }\mu\text{m} \times 8\text{ }\mu\text{m}$  in order to minimize damage to the unstable sample. Analysis of the data was carried out using *INCA Energy 200* software (Oxford Instruments Analytical, 2006) supplemented by software developed in the Institute of Experimental Mineralogy of RAS.

Attempts to use the wavelength dispersive spectroscopy mode with a higher beam current were unsuccessful because of the instability of the mineral. The contents of other elements with atomic numbers  $>6$  are below detection limits. The hydrogen content could not be measured because of insufficient amounts of substance available but was calculated by stoichiometry from the ideal formula. Analytical data are given in Table 1.

The empirical formula (based on 6 O atoms per formula unit, a.p.f.u.) is  $\text{H}_{12.56}(\text{Cu}_{1.09}\text{Fe}_{0.01})\text{N}_{5.87}\text{O}_{6.00}$ . The simplified formula is

TABLE 3. Crystal parameters, data collection and structure-refinement details for the crystal of shilovite.

<b>Crystal parameters</b>	
Formula	$[\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$
Crystal size (mm)	$0.04 \times 0.05 \times 0.07$
Crystal system	Orthorhombic
Space group	<i>Pnn2</i>
<i>a</i> (Å)	23.6585(9)
<i>b</i> (Å)	10.8238(4)
<i>c</i> (Å)	6.9054(3)
<i>V</i> (Å <sup>3</sup> )	1768.3(1)
<i>Z</i>	8
<i>D</i> (g cm <sup>-3</sup> )	1.92
<b>Data collection</b>	
Instrument	Bruker APEX DUO (CCD detector)
Radiation	$\text{MoK}\alpha$ ( $\lambda = 0.71073\text{ Å}$ )
Average temperature (K)	293
$2\theta$ range (°)	$3.44\text{--}56.00$
Total collected reflections	12,489
Unique reflections	3267
Unique observed $ F_o  \geq 4\sigma_F$	2705
<i>R</i> <sub>int</sub>	0.019
<i>R</i> <sub>σ</sub>	0.013
<i>hkl</i> range	$-31 \leq h \leq 31; -14 \leq k \leq 14; -9 \leq l \leq 6$
<b>Structure refinement</b>	
Number of refined parameters	243
<i>R</i> <sub>1</sub> ( $ F  \geq 4\sigma(F)$ )	0.029
<i>R</i> <sub>1</sub> (all data)	0.035
<i>wR</i> <sub>2</sub>	0.087
<i>S</i> = Goof	1.040
Flack parameter	0.23(4)

TABLE 4. Fractional atom coordinates and isotropic displacement parameters ( $\text{\AA}^2$ ) in the crystal structure of shilovite\*.

Site	Atom	$x/a$	$y/b$	$z/c$	$U_{\text{eq}}^{**}$
Cu1	Cu	0.118248(11)	0.01356(2)	0.5862(3)	0.03169(10)
N1A	N	0.0733(2)	0.1008(5)	0.3770(8)	0.0408(13)
H1AA	H	0.0672	0.0490	0.2791	0.049
H1AB	H	0.0927	0.1660	0.3348	0.049
H1AC	H	0.0404	0.1257	0.4254	0.049
N1B	N	0.1627(2)	-0.0722(7)	0.3758(9)	0.0459(15)
H1BA	H	0.1697	-0.0191	0.2804	0.055
H1BB	H	0.1427	-0.1355	0.3301	0.055
H1BC	H	0.1952	-0.0997	0.4243	0.055
N1C	N	0.1622(2)	-0.0722(6)	0.7977(9)	0.0396(14)
H1CA	H	0.1864	-0.1254	0.7451	0.048
H1CB	H	0.1384	-0.1126	0.8748	0.048
H1CC	H	0.1811	-0.0163	0.8666	0.048
N1D	N	0.0753(2)	0.1024(6)	0.7943(9)	0.0481(16)
H1DA	H	0.0537	0.1605	0.7410	0.058
H1DB	H	0.0996	0.1373	0.8763	0.058
H1DC	H	0.0537	0.0488	0.8580	0.058
N1E	N	0.05297(8)	-0.26230(18)	0.5819(13)	0.0338(5)
O1A	O	0.04376(8)	-0.15007(17)	0.5907(15)	0.0578(8)
O1B	O	0.10177(8)	-0.30335(19)	0.5889(12)	0.0550(6)
O1C	O	0.01270(10)	-0.3337(2)	0.5943(15)	0.0804(12)
N1F	N	0.19772(8)	0.27510(18)	0.5853(13)	0.0358(5)
O1D	O	0.20230(8)	0.16239(17)	0.5893(14)	0.0584(7)
O1E	O	0.15015(10)	0.3230(2)	0.5877(13)	0.0669(7)
O1F	O	0.23923(12)	0.3398(3)	0.5964(17)	0.0998(15)
Cu2	Cu	0.368677(11)	0.01548(3)	0.5859(3)	0.03392(11)
N2A	N	0.3143(2)	0.0694(6)	0.3754(7)	0.0398(13)
H2AA	H	0.3335	0.1036	0.2786	0.048
H2AB	H	0.2900	0.1243	0.4236	0.048
H2AC	H	0.2954	0.0040	0.3317	0.048
N2B	N	0.4234(2)	-0.0375(6)	0.3788(9)	0.0407(13)
H2BA	H	0.4043	-0.0619	0.2746	0.049
H2BB	H	0.4444	-0.0996	0.4226	0.049
H2BC	H	0.4456	0.0258	0.3476	0.049
N2C	N	0.4213(2)	-0.0401(5)	0.7981(9)	0.0418(14)
H2CA	H	0.4536	-0.0661	0.7463	0.050
H2CB	H	0.4054	-0.1016	0.8639	0.050
H2CC	H	0.4282	0.0228	0.8777	0.050
N2D	N	0.3147(2)	0.0677(6)	0.7923(10)	0.0536(17)
H2DA	H	0.2824	0.0917	0.7382	0.064
H2DB	H	0.3295	0.1301	0.8591	0.064
H2DC	H	0.3081	0.0045	0.8716	0.064
N2E	N	0.04887(8)	-0.22557(17)	0.0848(11)	0.0324(5)
O2A	O	0.09813(8)	-0.26021(19)	0.0944(12)	0.0605(8)
O2B	O	0.03815(9)	-0.11352(17)	0.0833(14)	0.0586(6)
O2C	O	0.01050(9)	-0.3013(2)	0.0939(16)	0.0733(10)
N2F	N	0.19921(8)	0.23451(18)	0.0821(12)	0.0347(5)
O2D	O	0.15083(10)	0.2719(2)	0.0998(12)	0.0740(11)
O2E	O	0.20846(11)	0.1226(2)	0.0804(14)	0.0707(8)
O2F	O	0.23820(12)	0.3067(3)	0.0915(19)	0.1090(14)

\* All sites are fully occupied. Positions of the H atoms were calculated based on a riding model.

\*\*  $U_{\text{iso}}$  for H atoms.

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[Cu(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub>, which requires Cu 24.85, N 32.87, O 37.54, H 4.74, total 100.00 wt.%.

Shilovite dissolves in water. A concentrated aqueous solution of shilovite has a pH of 9. An aqueous solution of the halite matrix without shilovite has a pH of 7. Tests with HCl and BaCl<sub>2</sub> show the absence of CO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> groups. Trace amounts of SO<sub>4</sub><sup>2-</sup> detected in the halite matrix are due to inclusions of thénardite. A test with sodium hexanitrocobaltate(III) solution at pH 4 gave an orange precipitate confirming the presence of NH<sub>3</sub>.

Shilovite is unstable in air at room temperature. After being extracted from the halite matrix, shilovite grains completely decompose over a period of several weeks with the evolution of NH<sub>3</sub>.

### X-ray diffraction data and crystal structure

The powder XRD pattern of shilovite (Table 2) was obtained using a Rigaku R-AXIS Rapid II diffractometer (curved image plate),  $d = 127.4$

mm, Debye-Scherrer geometry, CoK $\alpha$ , 40 kV, 15 mA, exposure 20 mins. Unit-cell parameters and calculated intensities were obtained using *ATOMS* v.6.1 software (Dowty, 2000) based on atom coordinates taken from single-crystal data. The unit-cell dimensions refined from the powder data are  $a = 23.741(9)$ ,  $b = 10.853(1)$ ,  $c = 6.922(2)$  Å,  $V = 1783.6(1)$  Å<sup>3</sup>.

Single-crystal XRD data for shilovite were collected at room temperature in a full sphere of reciprocal space using a Bruker APEX DUO diffractometer equipped with a CCD detector and microfocus tube with MoK $\alpha$  radiation. Primary data processing was carried out with *CrysAlisPro* v.1.171.36.32 software (Agilent Technologies, 2013). Information related to data collection and structure refinement is given in Table 3. Two possible space groups, *Pnmm* (centrosymmetric) and *Pnn2* (non-centrosymmetric) were taken into consideration. The choice of either space group for the synthetic analogue of shilovite, [Cu(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub> was a matter of debate

TABLE 5. Anisotropic displacement parameters (Å<sup>2</sup>) of atoms in the crystal structure of shilovite.

Site	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
Cu1	0.02833(15)	0.03013(15)	0.03660(19)	0.0010(6)	0.0000(6)	0.00161(10)
N1A	0.040(3)	0.040(3)	0.042(3)	0.003(3)	-0.001(3)	0.003(3)
N1B	0.045(3)	0.045(4)	0.047(4)	-0.002(3)	0.008(3)	-0.001(3)
N1C	0.032(3)	0.035(3)	0.051(4)	0.010(3)	-0.003(3)	-0.002(2)
N1D	0.034(3)	0.053(4)	0.057(4)	-0.009(3)	0.005(3)	0.003(3)
N1E	0.0360(10)	0.0322(9)	0.0332(12)	0.003(4)	-0.002(3)	-0.0029(7)
O1A	0.0359(9)	0.0311(9)	0.106(2)	-0.011(4)	0.008(4)	-0.0021(7)
O1B	0.0422(10)	0.0488(11)	0.0739(17)	0.002(4)	-0.002(4)	0.0121(8)
O1C	0.0554(13)	0.0508(13)	0.135(3)	0.028(4)	0.005(5)	-0.0227(11)
N1F	0.0368(10)	0.0329(10)	0.0378(13)	-0.007(4)	0.000(3)	-0.0020(8)
O1D	0.0446(10)	0.0316(9)	0.099(2)	0.009(4)	-0.002(4)	0.0020(8)
O1E	0.0592(13)	0.0624(13)	0.079(2)	-0.004(5)	0.012(4)	0.0269(11)
O1F	0.0723(17)	0.077(2)	0.150(4)	-0.035(5)	-0.003(5)	-0.0414(15)
Cu2	0.02704(16)	0.03351(16)	0.0412(2)	0.0010(6)	-0.0002(6)	0.00322(10)
N2A	0.031(3)	0.059(4)	0.029(2)	-0.002(3)	-0.005(2)	0.009(3)
N2B	0.035(3)	0.042(3)	0.046(3)	-0.002(3)	0.005(3)	-0.001(2)
N2C	0.039(3)	0.032(3)	0.055(4)	-0.002(3)	-0.003(3)	0.006(2)
N2D	0.042(3)	0.040(3)	0.079(4)	0.002(3)	0.005(3)	0.002(3)
N2E	0.0343(10)	0.0303(9)	0.0325(12)	-0.004(3)	-0.010(3)	-0.0022(7)
O2A	0.0368(10)	0.0420(10)	0.103(3)	-0.013(3)	-0.022(3)	0.0053(8)
O2B	0.0638(13)	0.0315(9)	0.0806(18)	0.008(4)	0.008(4)	0.0083(9)
O2C	0.0461(12)	0.0537(12)	0.120(3)	-0.001(5)	0.018(4)	-0.0228(10)
N2F	0.0339(10)	0.0330(10)	0.0372(13)	-0.004(4)	0.006(3)	-0.0035(8)
O2D	0.0520(13)	0.0769(16)	0.093(3)	0.017(4)	0.028(3)	0.0218(12)
O2E	0.0940(18)	0.0435(11)	0.075(2)	-0.008(4)	-0.020(4)	0.0196(12)
O2F	0.0829(19)	0.101(2)	0.143(4)	-0.017(8)	-0.005(6)	-0.0606(18)

TABLE 6. Interatomic distances (Å) in the crystal structure of shilovite (excluding H atoms).

Site1	Site2	Distance	Notes
Cu1	N1A	2.027(6)	
Cu1	N1B	2.019(6)	[Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup>
Cu1	N1C	2.019(6)	
Cu1	N1D	2.005(6)	
Cu1	O1A	2.4987(18)	
Cu1	O1D	2.5593(18)	
N1E	O1A	1.236(3)	
N1E	O1B	1.238(3)	(NO <sub>3</sub> ) <sup>-</sup>
N1E	O1C	1.230(3)	
N1F	O1D	1.225(3)	
N1F	O1E	1.239(3)	(NO <sub>3</sub> ) <sup>-</sup>
N1F	O1F	1.208(3)	
Cu2	N2A	2.028(5)	
Cu2	N2B	2.012(6)	[Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup>
Cu2	N2C	2.014(6)	
Cu2	N2D	1.996(6)	
Cu2	O2A	2.552(3)	
Cu2	O2D	2.679(3)	
N2E	O2A	1.226(3)	
N2E	O2B	1.239(3)	(NO <sub>3</sub> ) <sup>-</sup>
N2E	O2C	1.224(3)	
N2F	O2D	1.220(3)	
N2F	O2E	1.231(3)	(NO <sub>3</sub> ) <sup>-</sup>
N2F	O2F	1.211(3)	

(Karovičová and Mad'ar, 1960; Morosin, 1976) and the question is still not completely resolved. The analysis of *E* statistics in the diffraction pattern of shilovite provides evidence for the non-centrosymmetric space group *Pnn*2 which we have adopted for further solution and refinement. The crystal structure of shilovite (Tables 4–6, Fig. 3) was solved by direct methods and refined with *SHELX-97* (Sheldrick, 2008). Shilovite contains two alternating crystallographically independent units, Cu(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (Fig. 4), in which Cu atoms are coordinated by four NH<sub>3</sub> molecules in a nearly square planar fashion with mean Cu–N distances of 2.018 Å for Cu1 and 2.013 Å for Cu2, and two nitrate anions coordinating *via* oxygen atoms with Cu–O distances exceeding 2.5 Å. Each H atom of NH<sub>3</sub> groups provides one H bond to the oxygen atoms except H2CC and probably H1DA and H2DC which provide bifurcated H bonds. Hydrogen

bonds in the structure of shilovite are listed in Table 7. The crystal structures of shilovite and synthetic [Cu(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub> (Morosin, 1976) are similar. The only difference is in the arrangement of H atoms of NH<sub>3</sub> groups which leads to the non-centrosymmetric space group in the case of shilovite.

A peculiar feature of shilovite, like its synthetic analogue, is a reversible transformation to a monoclinic (*P2*<sub>1</sub>/*m*) polymorph upon cooling to 100 K (Morosin, 1976).

## Discussion

Shilovite is the natural analogue of synthetic [Cu(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub> (Table 8). Different salts of copper(II) tetrammine cation were synthesized long ago (von Meyeren and Brennecke, 1965). Some of them, including copper(II) tetrammine nitrate, are impact-sensitive explosives having the ability to burn in an inert atmosphere (Gorbunov and Shmagin, 1972).

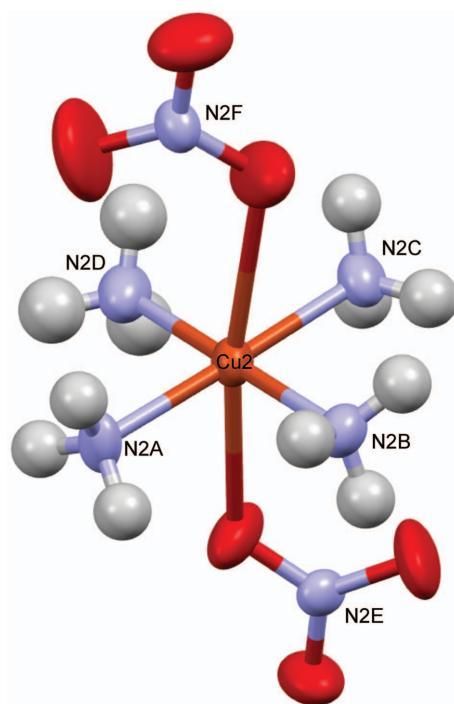


FIG. 4. The structural unit of shilovite with a Cu atom coordinated by four NH<sub>3</sub> molecules in near-square planar fashion (with a mean Cu–N distance of 2.013 Å for Cu2) and two nitrate anions coordinating *via* oxygen atoms.



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TABLE 7. Hydrogen bonds in shilovite (*D* – donor, *A* – acceptor).

<i>D</i> –H	<i>d</i> ( <i>D</i> –H) (Å)	<i>D</i> –H... <i>A</i>	<i>d</i> (H– <i>A</i> ) (Å)	<i>d</i> ( <i>D</i> – <i>A</i> ) (Å)	∠( <i>D</i> –H... <i>A</i> ) (°)
N1A–H1AA	0.89	N1A–H1AA...O2B	2.32	3.192(9)	165.3
N1A–H1AB	0.89	N1A–H1AB...O2D	2.42	3.234(7)	152.7
N1A–H1AC	0.89	N1A–H1AC...O1A	2.31	3.184(8)	167.2
N1B–H1BA	0.89	N1B–H1BA...O2E	2.26	3.127(9)	165.2
N1B–H1BB	0.89	N1B–H1BB...O2A	2.36	3.202(8)	157.1
N1B–H1BC	0.89	N1B–H1BC...O2F	2.20	3.072(10)	165.9
N1C–H1CA	0.89	N1C–H1CA...O2F	2.20	3.050(9)	159.2
N1C–H1CB	0.89	N1C–H1CB...O2A	2.40	3.261(8)	163.1
N1C–H1CC	0.89	N1C–H1CC...O2E	2.20	3.074(9)	165.6
		N1D–H1DA...O1A	2.53	3.191(8)	131.5
N1D–H1DA	0.89	N1D–H1DA...O1C	2.65	3.538(8)	177.9
N1D–H1DB	0.89	N1D–H1DB...O2D	2.44	3.317(8)	167.0
N1D–H1DC	0.89	N1D–H1DC...O2B	2.38	3.196(9)	153.5
N2A–H2AA	0.89	N2A–H2AA...O1B	2.25	3.124(8)	166.2
N2A–H2AB	0.89	N2A–H2AB...O1D	2.41	3.195(7)	148.0
N2A–H2AC	0.89	N2A–H2AC...O1F	2.54	3.390(10)	159.1
N2B–H2BA	0.89	N2B–H2BA...O1E	2.21	3.057(8)	159.5
N2B–H2BB	0.89	N2B–H2BB...O2C	2.24	3.083(8)	159.1
N2B–H2BC	0.89	N2B–H2BC...O1C	2.52	3.318(9)	149.8
N2C–H2CA	0.89	N2C–H2CA...O2C	2.23	3.064(8)	155.6
N2C–H2CB	0.89	N2C–H2CB...O1E	2.19	3.009(9)	153.5
		N2C–H2CC...O1B	2.48	3.301(8)	152.9
N2C–H2CC	0.89	N2C–H2CC...O1C	2.57	3.408(10)	157.0
N2D–H2DA	0.89	N2D–H2DA...O1D	2.29	3.175(8)	176.6
N2D–H2DB	0.89	N2D–H2DB...O1B	2.38	3.170(9)	147.5
		N2D–H2DC...O1F	2.62	3.482(11)	164.5
N2D–H2DC	0.89	N2D–H2DC...O1E	2.66	3.445(9)	148.1

Shilovite is the only known mineral with the  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  cation. The  $\text{NH}_3$  groups coordinating  $\text{Cu}^{2+}$  form an almost planar square with

$\text{Cu}$ – $\text{N}$  distances ranging from 2.005(6) to 2.027(6) Å for Cu1 and from 1.996(6) to 2.028(5) Å for Cu2. Two O atoms with elongated

TABLE 8. Comparative data for shilovite and synthetic  $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2^*$ .

	Shilovite	Synthetic copper(II) tetrammine nitrate
Formula	$\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$	$\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pnn2</i>	<i>Pnn2</i> or <i>Pnmm</i>
<i>a</i> , Å	23.6585	23.62–23.693
<i>b</i> , Å	10.8238	10.79–10.840
<i>c</i> , Å	6.9054	6.88–6.902
<i>Z</i>	8	8
Density, $\text{g cm}^{-3}$	1.92 (calc.)	1.93 (meas.)
References	This work	Karovičová and Mad'ar (1960); Morosin (1976)

\* Unit-cell parameters of synthetic  $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$  are given in the setting accepted for shilovite, transformation matrix 0 –1 0/–1 0 0/0 0 1.

Cu–O distances (2.499(3) and 2.559(3) Å for Cu1; 2.552(3) and 2.678(3) Å for Cu2) complete the coordination environment of Cu (a strongly elongated octahedron). This configuration is typical for synthetic compounds containing  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  cations, as well as interatomic distances Cu–N and Cu–O in their structures which usually range from 1.95 to 2.07 Å (Cu–N) and from 2.45 to 2.87 Å (Cu–O). In particular, the planar copper tetraammine complex is present as a distorted octahedron with two distant  $\text{H}_2\text{O}$  molecules in the structure of  $\text{Cu}^{2+}$ -ammine-exchanged heulandite (Armbruster *et al.*, 2003). Oxygen atoms of  $\text{H}_2\text{O}$  molecules are usually distant ligands for tetraammine complexes, and distorted  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  octahedra were also found in the structures of  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$   $[\text{Nb}_2\text{W}_4\text{O}_{19}]\cdot 8\text{H}_2\text{O}$  (Anderson *et al.*, 2008) and  $\text{Cu}(\text{NH}_3)_4\text{SO}_4\cdot\text{H}_2\text{O}$  (Morosin, 1969). In the structure of  $\text{Cu}(\text{NH}_3)_4\text{SeO}_4$  (Morosin, 1969) the  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  squares are supplemented by O atoms of  $\text{SeO}_4$  tetrahedra (Morosin, 1969); O atoms of tetrahedral permanganate groups provide [4+2] coordination of  $\text{Cu}^{2+}$  in  $\text{Cu}(\text{NH}_3)_4(\text{MnO}_4)_2$  (Seferiadis *et al.*, 1986). The Cu(II) atom is octahedrally coordinated by four ammonia molecules in the equatorial positions and two peroxy oxygen atoms originating from the  $[\text{VO}(\text{O}_2)_2(\text{NH}_3)]^-$  anions in axial positions in the structure of  $\{[\text{VO}(\text{O}_2)_2(\text{NH}_3)]_2\} \{\mu\text{-Cu}(\text{NH}_3)_4\}$  (Chrappová *et al.*, 2008). Oxygen atoms participate in the formation of distorted octahedra in the structures of  $[\text{Cu}(\text{NH}_3)_4] [\text{N}(\text{NO}_2)_2]_2$  (Ang *et al.*, 2002),  $[\text{Cu}(\text{NH}_3)_4] (\text{ReO}_4)_2$  (Khramenko *et al.*, 2009) and  $\text{Cu}(\text{NH}_3)_4\text{S}_2\text{O}_6$  (Leskelä and Valkonen, 1978).

Only three minerals containing  $\text{NH}_3$  molecules as a species-defining component are known, shilovite, ammineite and chanabayaite. In addition, orthorhombic  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  ( $a = 8.12$ ,  $b = 8.46$ ,  $c = 7.77$  Å) from burnt dumps of the Chelyabinsk coal basin, South Urals, Russia was described by B.V. Chesnokov (1991) under the name “amminite”. All these compounds are very rare, both in Nature and in technical wastes, due to their instability.

Shilovite is a supergene mineral formed in the contact zone between a deeply altered guano deposit and chalcopyrite-bearing gabbro. Guano was the source of nitrogen and oxidized chalcopyrite was the source of Cu for shilovite, ammineite and chanabayaite. The high affinity of Cu for  $\text{NH}_3$  as a ligand favoured the formation of these minerals.

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