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Joanneumite, $Cu(C_3N_3O_3H_2)_2(NH_3)_2$, a new mineral from Pabellón de Pica, Chile and the crystal structure of its synthetic analogue

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ABSTRACT

The new mineral joanneumite was found at Pabellón de Pica Mountain, Iquique Province, Tarapacá Region, Chile, where it occurs as violet microcrystalline aggregates up to 2 mm in size in small cracks in a gabbroic rock, which is covered by a guano deposit. Associated minerals are salammoniac, dittmarite, möhnite and gypsum. Joanneumite is non-fluorescent and the Mohs hardness is 1. The calculated density is 2.020 g cm^{-3}. The infrared spectrum of joanneumite shows the frequencies of NH_3 and isocyanurate groups and the absence of absorptions of H_2O molecules and OH^- ions. The chemical composition (electron microprobe data, the hydrogen was calculated from the structural formula, wt.%) is C 20.33, N 31.11, O 28.34, Cu 17.27, Zn 0.24, H 2.82, total 100.11. The empirical formula is $Cu_{0.96}Zn_{0.01}N_{7.84}C_{5.98}O_{6.25}H_{9.96}$ and the idealized formula is $CuN_8C_6O_6H_{10}$ with the structural formula $Cu(C_3N_3O_3H_2)_2(NH_3)_2$. Due to the lack of suitable single crystals the synthetic analogue of joanneumite was prepared for the single-crystal structure refinement. The crystal structure was solved and refined to $R = 0.025$ based upon 1166 unique reflections with $I > 2\sigma(I)$. Joanneumite is triclinic, space group $P\bar{1}$, $a = 4.982(1)$, $b = 6.896(1)$, $c = 9.115(2)$ Å, $\alpha = 90.53(3)$, $\beta = 97.85(3)$, $\gamma = 110.08(3)°$, $V = 290.8(1)$ Å^3, $Z = 1$ obtained from single-crystal data at 100 K, which are in good agreement with cell parameters from powder diffraction data of joanneumite at 293 K: $a = 5.042(1)$, $b = 6.997(1)$, $c = 9.099(2)$ Å, $\alpha = 90.05(3)$, $\beta = 98.11(2)$, $\gamma = 110.95(3)°$ and $V = 296.3(1)$ Å^3. The eight strongest lines of the powder X-ray diffraction pattern are [*d*, Å (*I*,%) (*hkl*)] 6.52 (68) (010), 5.15 (47) (011), 4.66 (21) (100, $\bar{1}10$), 4.35 (9) ($\bar{1}11$), 3.29 (6) ($\bar{1}20$), 3.22 (7) ($\bar{1}\bar{1}1$), 3.140 (100) ($\bar{1}21$), 2.074 (7) ($\bar{1}32$). The crystal structure of joanneumite is identical with the structure of synthetic bis(isocyanurato) diamminecopper(II).

Keywords: joanneumite, new mineral, synthetic analogue, crystal structure, Pabellón de Pica, Chile.

Introduction

Joanneumite occurs in the guano deposit at Pabellón de Pica Mountain (20°54′50″S, 70°08′25″W), Iquique Province, Tarapacá Region, Chile. Tarapacá is an extremely arid region on the pacific coast of Chile; the Atacama Desert is only a few kilometres from the coastal line. The coastal range of Chile is composed of Carboniferous to Permian magmatic rocks (mostly granitoids) and medium-grade metamorphic rocks (Moreno and Gibbons, 2007). In relation to the biogenic processes numerous guano deposits were formed in a supralittoral and continental environment along the coastal range. One of these guano deposits is located at the Pabellón de Pica Mountain, a 250 m high rock. An important feature of this deposit is the convergence of a small disseminated Cu

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mineralization in the hosting gabbro with the guano sites on its top. The nitrogen-rich environment led to the formation of a unique mineralization. Up to now five unique minerals have been described from this locality. Ammineite (Bojar *et al*., 2010) was the first mineral containing NH_3 (ammine) groups. Two further minerals with NH_3 groups are published and both have their type locality at Pabellon de Pica: shilovite (Chukanov *et al.*, 2015*c*) and chanabayaite (Chukanov *et al.* 2015*d*, *e*). The alkali-copper-oxalate antipinite (Chukanov *et al.*, 2015*a*) and möhnite, an alkali-ammonia-copper-sulfate (Chukanov *et al.*, 2015*b*) are two further minerals with the type locality at Pabellón de Pica. Joanneumite is named for the Universalmuseum Joanneum, which had its 200th anniversary in 2011. The mineral and its name were approved by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification, (IMA 2012-001). The holotype specimen has been deposited in the mineral collection of the Universalmuseum Joanneum, Graz, Austria, with registration number 85.011.

Occurrence and physical properties

JOANNEUMITE was discovered in close association with salammoniac, dittmarite, möhnite and gypsum at the Pabellón de Pica Mountain filling cracks in a gabbroic rock. Chukanov *et al.* (2015*a*) also found antipinite and chanabayaite as additional parageneses for joanneumite. Joanneumite forms violet microcrystalline aggregates up to 2 mm in size (Fig. 1). Some specimens of joanneumite show well-shaped cubes which are most probably pseudomorphs after an unidentified mineral. No suitable crystals were available for single-crystal studies. Joanneumite is transparent with a vitreous lustre and a pale violet streak. The mineral is non-fluorescent and the Mohs hardness is ~1. Due to the lack of suitable material the density could not be measured. The calculated density using the ideal formula and single-crystal data is 2.020 g cm^{-3}. The natural material was also not suitable for determination of the optical properties.

FIG. 1. Violet microcrystalline aggregates of joanneumite on salammoniac. Field of view: 4 mm. Photograph: H.-P. Bojar.

Fourier transformed infrared spectroscopy (FTIR) examinations were performed on a Perkin Elmer Spectrum 100 equipped with a diamond Universal ATR Sampling Accessory. The infrared spectra of joanneumite and the synthetic trans-[Cu(cyan-κN)$_2$-(NH$_3$)$_2$] are given in Fig. 2. According to Seifer (2002) the infrared frequencies of joanneumite can be assigned to the NH_3 and isocyanurate groups. N–H stretching vibrations appear in the region of 3331 to 2805 cm^{-1}. An NH_3 deformation band is located at 1249 cm^{-1}. The C–O stretching vibrations of the isocyanurate complex are at 1786 and 1733 cm^{-1}. The bands in the region of 1678 to 1378 cm^{-1} are assigned to the C–N stretching vibration (Table 1). Absorptions of H_2O molecules and OH^- ions are absent.

Chemical composition

Electron microbeam analyses were performed on a Jeol 6610 LV scanning electron microscope equipped with an Oxford 50 mm^2 energy-dispersive spectrometer operated at an accelerating voltage of 20 kV and a beam current of 500 pA. The results of these analyses are presented in Table 2. The beam was rasterized on the area of 90 to 120 µm in order to minimize sample damage. The sample surface was coated with a tiny film of gold, because carbon was also analysed. The standards and the sample were coated simultaneously. The length of sputtering was only 3 s. The measured gold content was excluded from the analytical data. Beside copper, zinc, carbon, nitrogen and oxygen no other elements with an atomic number larger than 8 were detected. Data reduction was performed with the *PAP* routine (Pouchou and Pichoir, 1991) implemented in the *INCA* software of Oxford Instruments. Hydrogen was not determined directly due to lack of material. The given hydrogen value is calculated from the structural formula. The stoichiometric formula of joanneumite was deduced from the average of ten

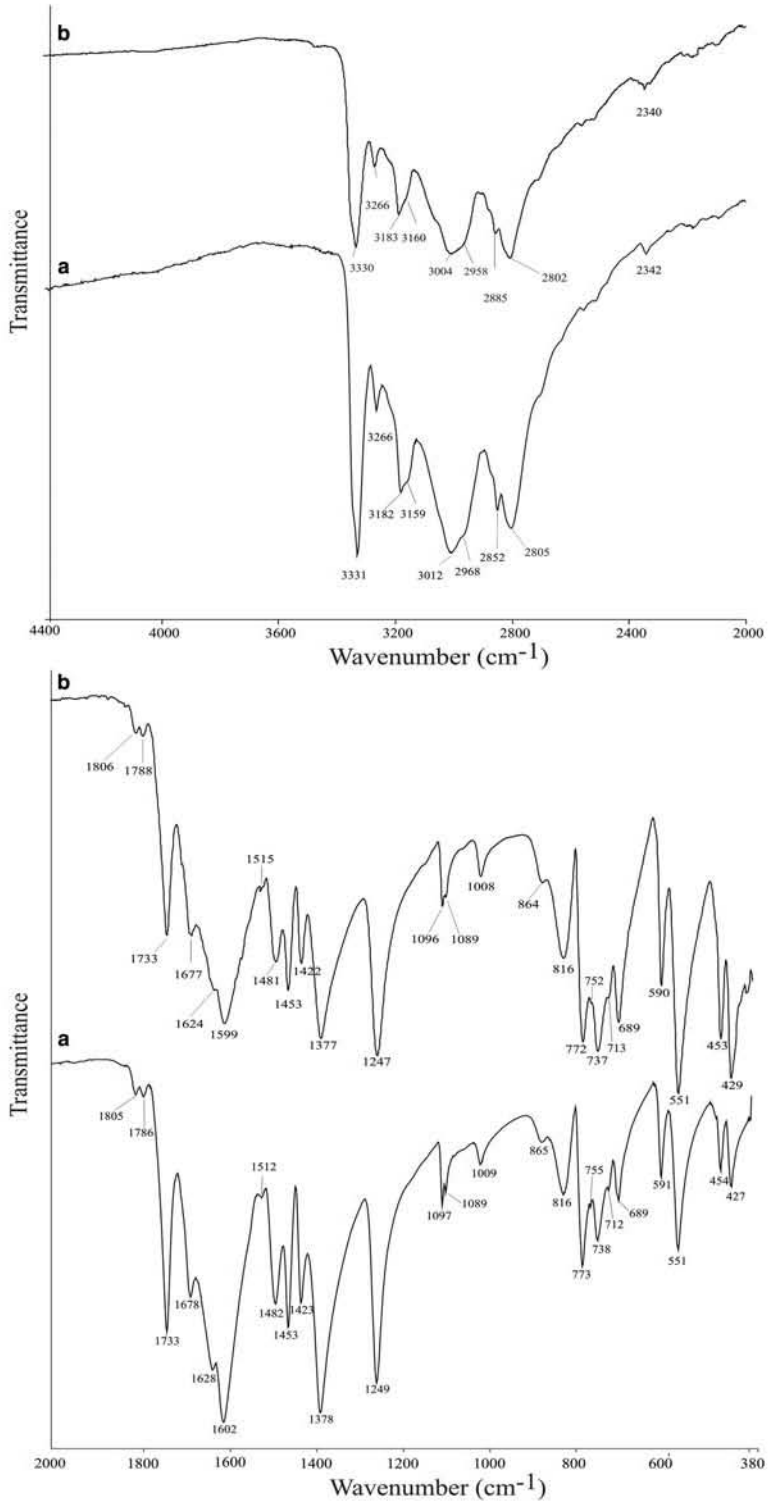

FIG. 2. FTIR ATR spectra of joanneumite (*a*) and of trans-[Cu (cyan-κN)$_2$(NH$_3$)$_2$] = synthetic analogue of joanneumite (*b*).

TABLE 1. FTIR data for joanneumite.

cm^{-1}		Assignment	cm^{-1}		Assignment
3331	s	νNH	1453	m	νCN
3266	w	νNH	1423	m	νCN
3182	m	νNH	1378	s	νCN
3159	m	νNH	1249	s	δNH
3012	s	νNH	1097	m	νCO
2968	w	νNH	1089	w	νCO
2852	m	νNH	1009	w	
2805	m	νNH	865	w	
2342	w		816	m	δCN
1805	w		773	s	πCO
1786	w	νCO	755	w	πCO
1733	s	νCO	738	s	πCO
1678	m	νCN, δNH	712	w	πCO
1628	m	νCN	689	m	δCNC
1602	s	νCN	591	m	
1512	w	νCN	551	s	δCO
1482	m	νCN	454	s	δNCO
			427	s	δNCO

Perkin Elmer Spectrum 100, ATR-diamond-cell, resolution 2 cm^{-1},
Sum of 10 scans (s: strong, m: medium, w: weak, ν: stretch,
δ: deformation, ρ: rock, π: out of plane bend).
Band assignment according to Seifer (2002).

analyses to be $Cu_{0.96}Zn_{0.01}N_{7.84}C_{5.98}O_{6.25}H_{9.96}$. The idealized formula is $CuN_8C_6O_6H_{10}$.

Synthesis

The synthetic analogue of joanneumite was prepared according to Taylor (1972). Powdered malachite was mixed with urea, molten at 190°C in a laboratory stove and cooled down to room temperature. The resulting product is a microcrystalline mass which consisted mainly of trans-$[Cu(cyan\text{-}\kappa N)_2(NH_3)_2]$ with remnants of urea. The sample was powdered, rinsed in distilled water to remove the residual urea and dissolved in hot liquid ammonia. This solution was placed in an evaporating dish, covered with glass and kept overnight in a compartment dryer at 60°C. Violet trans-$[Cu(cyan\text{-}\kappa N)_2(NH_3)_2]$ crystals up to 1 mm precipitated from this solution (Fig. 3).

TABLE 2. Results of analysis for joanneumite.

Constituent	Wt.%	Range	Sd
C	20.33	19.21–21.50	0.76
N	31.11	30.31–32.00	0.64
O	28.34	27.32–29.42	0.61
Cu	17.27	16.72–17.57	0.26
Zn	0.24	bdl.–0.60	0.20
H*	2.82		
Total	100.11		

Average of 10 analyses; bdl.: below the detection limit. Sd: standard deviation. Standards: C and O calcite, N potassium nitrate, Cu atacamite, Zn sphalerite.
*Hydrogen was calculated from the structural formula.

Powder X-ray diffraction

The powder X-ray diffraction (XRD) data (Table 3) for joanneumite and the synthetic analogue of joanneumite, which is identical with the synthetic phase trans-$[Cu(cyan\text{-}\kappa N)_2(NH_3)_2]$, were obtained at 293 K using a Bruker-AXS D8 diffractometer with Cu*K*α radiation. The powder X-ray patterns are overlaid for comparison in Fig. 4. Powder XRD data calculated with parameters of the single-crystal structure refinement for the synthetic analogue of joanneumite at 100 K are also listed in Table 3. In the powder pattern of joanneumite impurities of salammoniac and gypsum are visible (Fig. 4*a*) whereas the synthetic analogue of joanneumite shows no impurities (Fig. 4*d*). To minimize the background, the sample was placed on a low-background silicon wafer. Unit-cell parameters, derived from Rietveld refinements, calculated with *Topas 4.2* software (Bruker-AXS, 2009) for both patterns (Fig. 4*b* and *e*) with fixed atomic

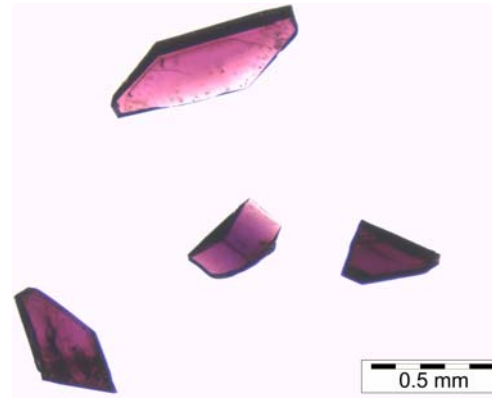

FIG. 3. Transmission-light microscopy image of single crystals of the synthetic analogue of joanneumite. Scale bar: 0.5 mm. Photograph: F. Walter.

TABLE 3. Powder X-ray diffraction data for joanneumite and the synthetic analogue of joanneumite.

Joanneumite		Synthetic analogue of joanneumite		Synthetic analogue of joanneumite from structure refinement				
(293 K)		(293 K)		(100 K)				
I_{obs}	d_{obs}(Å)	I_{obs}	d_{obs}(Å)	I_{calc}	d_{calc}(Å)	h	k	l
				2	9.013	0	0	1
68*	**6.52**	**35**	**6.52**	**45**	**6.465**	**0**	**1**	**0**
47	**5.15**	**52**	**5.15**	**62**	**5.109**	**0**	**1**	**1**
21	**4.65**	**18**	**4.66**	**37**	**4.627**	**1**	**0**	**0**
	4.67		**4.68**	**47**	**4.594**	**$\bar{1}$**	**1**	**0**
2	4.50	1	4.50	8	4.506	0	0	2
				4	4.390	$\bar{1}$	0	1
9	**4.35**	**8**	**4.35**	**23**	**4.279**	**$\bar{1}$**	**1**	**1**
1	3.97	1	3.97	6	3.930	1	$\bar{1}$	1
				3	3.888	1	0	1
1	3.51	1	3.51	7	3.499	$\bar{1}$	0	2
1	3.44	1	3.44	3	3.400	$\bar{1}$	1	2
6	**3.29**	**9**	**3.29**	**10**	**3.229**	**$\bar{1}$**	**2**	**0**
7	**3.22**	**6**	**3.21**	**35**	**3.211**	**$\bar{1}$**	**$\bar{1}$**	**1**
100	**3.140**	**100**	**3.142**	**100**	**3.083**	**$\bar{1}$**	**2**	**1**
2	3.072	1	3.074	14	3.061	1	$\bar{1}$	2
5	3.015	3	3.019	30	3.012	1	0	2
				3	3.004	0	0	3
				3	2.944	1	1	1
3	2.832	1	2.830	10	2.832	$\bar{1}$	$\bar{1}$	2
3	2.783	1	2.782	7	2.789	0	$\bar{1}$	3
1	2.669	1	2.672	3	2.664	0	1	3
				2	2.645	$\bar{1}$	1	3
				3	2.488	1	1	2
				2	2.467	$\bar{2}$	1	0
2	2.403	1	2.405	7	2.402	1	$\bar{1}$	3
1	2.375	<1	2.373	3	2.376	$\bar{1}$	$\bar{1}$	3
3	2.341	1	2.342	12	2.326	$\bar{2}$	0	1
2	2.327	1	2.330	5	2.313	2	0	0
1	2.322	1	2.326	4	2.302	2	$\bar{1}$	1
2	2.308	<1	2.308	6	2.301	1	2	0
2	2.326	1	2.328	5	2.300	$\bar{2}$	1	2
	2.324		2.327	2	2.284	$\bar{2}$	2	1
				7	2.270	0	$\bar{2}$	3
2	2.253	1	2.254	2	2.216	$\bar{1}$	3	1
	2.201	1	2.203	5	2.172	2	$\bar{2}$	1
4	2.163	3	2.163	12	2.169	0	$\bar{1}$	4
	2.175	1	2.178	4	2.165	2	0	1
				3	2.156	$\bar{1}$	0	4
6	2.175	3	2.174	7	2.155	0	3	0
2	2.156	2	2.154	2	2.154	$\bar{1}$	$\bar{2}$	2
2	2.149		2.152	8	2.137	0	2	3
				2	2.089	0	1	4
7	**2.074**	**7**	**2.075**	**9**	**2.043**	**$\bar{1}$**	**3**	**2**
3	1.981	1	1.982	6	1.984	$\bar{1}$	$\bar{1}$	4
1	1.990	1	1.990	2	1.981	$\bar{2}$	0	3

(continued)

TABLE 3. (*contd.*)

Joanneumite		Synthetic analogue of joanneumite		Synthetic analogue of joanneumite from structure refinement				
(293 K)		(293 K)		(100 K)				
I_{obs}	d_{obs}(Å)	I_{obs}	d_{obs}(Å)	I_{calc}	d_{calc}(Å)	h	k	l
2	1.977	1	1.979	3	1.971	2	1	0
1	1.950	1	1.953	4	1.944	2	0	2
				4	1.936	$\bar{2}$	3	1
				2	1.917	1	0	4
2	1.901	1	1.900	7	1.903	0	$\bar{2}$	4
				2	1.900	0	3	2
				2	1.887	$\bar{1}$	2	4
3	1.875	1	1.877	2	1.870	2	1	1
	1.873		1.875	6	1.839	$\bar{2}$	3	2
1	1.819	<1	1.818	3	1.808	1	$\bar{3}$	3
				2	1.803	0	$\bar{3}$	3
2	1.770	1	1.771	4	1.771	$\bar{1}$	0	5
				3	1.741	$\bar{1}$	1	5
				2	1.739	2	$\bar{2}$	3
				2	1.731	1	2	3
				2	1.703	0	3	3
				2	1.672	1	3	1
				3	1.615	1	-4	2
				2	1.599	$\bar{3}$	2	2
				2	1.574	0	4	1
				2	1.562	2	$\bar{1}$	4
				2	1.560	$\bar{2}$	1	5
				2	1.559	$\bar{3}$	0	1
3	1.570	3	1.571	6	1.541	$\bar{2}$	4	2

I_{obs} and d_{obs} from profile fitting using *TOPAS 4.2*.
I_{calc} and d_{calc} calculated with data from structure refinement and $I_{calc} > 1$.
*I_{obs} due to preferred orientation of the cleavage plane (010).

coordinates taken from single-crystal structure refinement are: $a = 5.042(1)$, $b = 6.997(1)$, $c = 9.099(2)$ Å, $\alpha = 90.05(3)$, $\beta = 98.11(2)$, $\gamma = 110.95(3)°$ and $V = 296.3(1)$ Å^3 for joanneumite and $a = 5.049(1)$, $b = 6.995(1)$, $c = 9.105(2)$ Å, $\alpha = 89.92(3)$, $\beta = 98.07(3)$, $\gamma = 111.01(3)°$ and $V = 296.8(1)$ Å^3 for the synthetic analogue of joanneumite. Rwp values of 7.1 for joanneumite and 7.4 for the synthetic analogue of joanneumite also indicate good agreement between the difference patterns (Fig. 4*c* and *f*). Due to the good cleavage of joanneumite parallel to (010) and due to the sample preparation the intensity for (010) of the observed powder pattern is too high in comparison to the (010) intensity of the simulated powder pattern, calculated with data from the single-crystal structure refinement. The intensity of (010) was considered as preferred orientation in the Rietveld calculations.

Crystal structure determination

No crystals suitable for a single-crystal study of joanneumite were available, but data were collected for the synthetic analogue (see description of synthesis).

A violet platy crystal of synthesized trans-$[Cu(cyan\text{-}\kappa N)_2(NH_3)_2]$ was used for X-ray single-crystal data collection on a Bruker AXS Smart Apex CCD diffractometer equipped with graphite-monochromatized Mo$K\alpha$ radiation (0.71073 Å). The data were recorded with the program *SMART*, integrated with the program *SAINT* up to

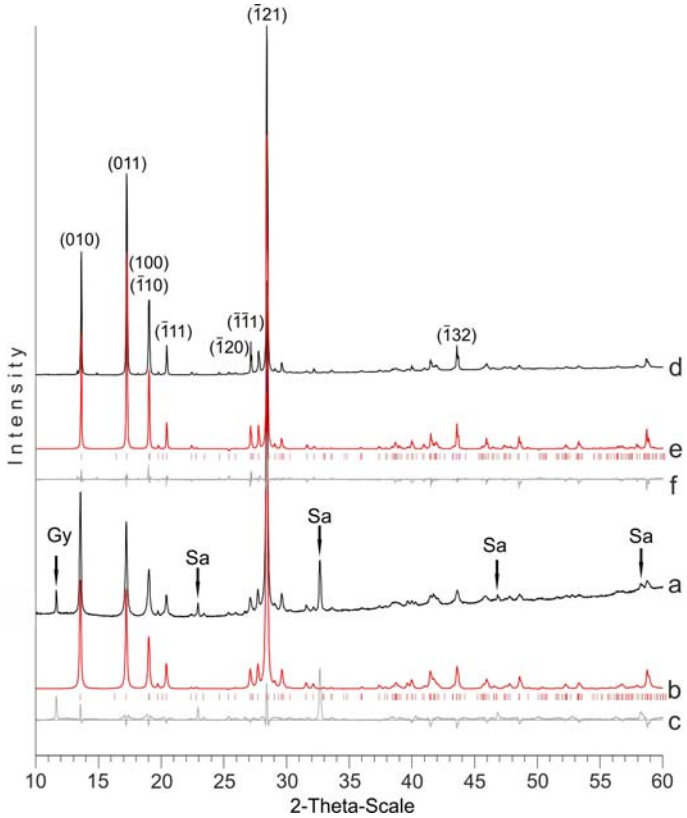

FIG. 4. The powder XRD patterns (Cu*K*α, 40 kV, 40 mA, 293 K) of joanneumite (*a*) with its Rietveld refinement using *TOPAS 4.2* (*b*) and difference pattern (*c*) are in good agreement with those of the synthetic analogue of joanneumite (*d*) and its Rietveld refinement (*e*) with difference pattern (*f*). Impurities of salammoniac (Sa) and gypsum (Gy) in joanneumite (*a*) are visible. The eight strongest lines are indexed.

$\theta_{max} = 26.3°$, and corrected for absorption using the program *SADABS* (Bruker, 2008). With good reflection profiles a diffraction data set with $R_{int} = 0.016$ was obtained. The structure was solved with direct methods (*SHELXS*) and expanded with difference-Fourier syntheses. Systematic absences and the intensity statistics favour the centrosymmetric space group $P\bar{1}$. Least-squares structure refinement using anisotropic displacement parameters for all non-hydrogen atoms was carried out with the program *SHELXL-2013* (Sheldrick, 2015). The five unique hydrogen atoms were located from the difference-Fourier maps and refined constrained to an idealized NH_3 group and N–H with the hydrogen on the external bisector of the C–N–C angle. Details on data collection, crystallographic data and refinement are given in Table 4. Refined atomic coordinates and displacement parameters are given in Table 5, and selected interatomic distances and angles are listed in Table 6.

A crystallographic information file with structural data has been deposited and may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fizkarlsruhe.de/request_for_deposited_data.html) quoting the CSD number 430597.

Description of the crystal structure

The basic structural unit consists of two isocyanurate rings and two ammine ligands each bound through nitrogen atoms to a central Cu atom. This Cu atom, located at the inversion centre, forms a distorted square-planar coordination with two

TABLE 4. Crystal parameters, data collection and structure refinement details for the synthetic analogue of joanneumite.

Idealized formula	$Cu(C_3N_3O_3H_2)_2(NH_3)_2$
Formula weight	353.76
Temperature	100 K
Wavelength	0.71073 Å
Space group	$P\bar{1}$ (No. 2)
Unit-cell dimensions	$a = 4.982(1)$ Å
	$b = 6.896(1)$ Å
	$c = 9.115(2)$ Å
	$\alpha = 90.53(3)°$
	$\beta = 97.85(3)°$
	$\gamma = 110.08(3)°$
Volume	290.8(1) Å^3
Z	1
Density (calc. for above formula)	2.020 g/cm^3
Absorption coefficient	1.928 mm^{-1}
$F(000)$	179
Crystal size (mm)	0.35 × 0.18 × 0.10, violet
Θ range	2.26° to 26.29°
Index ranges	$-6 \le h \le 6$, $-8 \le k \le 8$, $-11 \le l \le 11$
Reflections collected/unique	2305/1166 [$R_{int} = 0.0158$, $R_{sigma} = 0.0238$]
Max. and min. transmission factors	0.831–0.552
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1166 / 0 / 98
Goodness-of-fit on F^2	1.192
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0245$, $wR2 = 0.0632$ (1153 data)
R indices (all data)	$R1 = 0.0249$, $wR2 = 0.0635$ (1166 data)
Largest diff. peak and hole	0.33 and –0.29 eÅ^{-3}

$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.
$w = 1/[\sigma^2(F_o^2) + (0.0242P)^2 + 0.27P]$, $P = (F_o^2 + 2F_c^2)/3$.

<Cu–N> distances of 1.992 and 2.008 Å (Fig. 5*a*). In the planar isocyanurate ring two <C–N> distances of 1.382 and 1.383 Å are significantly longer than the further four <C–N> distances from 1.361 to 1.362 Å. The three short <C–O> distances from 1.231 to 1.237 Å are the result of the double-bond character in this complex. The ammine groups lie ~12.5° away from the normals to the isocyanurate rings. Bond distances and angles are all within the ranges expected of this type of complex. The isocyanurate rings build a topological crenellated ribbon by pairs of hydrogen bonds of 1.93 Å for <O(3)–H(2)> and 1.92 Å for <O(2)–H(1)> respectively. The isocyanurate rings of the $Cu(C_3N_3O_3H_2)_2(NH_3)_2$ molecules in the joanneumite structure are oriented to a layer parallel to ($\bar{1}$ 2 1) (Fig. 6). The three hydrogens of the ammine ligands connect these layers up and down to a three dimensional network by hydrogen bonds of 2.04, 2.22 and 2.31 Å (Fig. 7). In Fig. 8 the projection of the crystal structure along [100] shows the good cleavage parallel to (010). Note, the strongest line in the powder X-ray pattern is ($\bar{1}$21), which is the layer with the highest density of atom-packing in this structure (Table 3).

Discussion

Joanneumite is the first mineral containing the isocyanurate anion, ($C_3N_3O_3H_2$). The basic structural unit in the joanneumite structure is similar to that of ammineite, $CuCl_2(NH_3)_2$, (Bojar *et al.*, 2010). The two Cl atoms in the ammineite structure are replaced by two isocyanurate groups in the joanneumite structure (Fig. 5*a* and *b*). Chemical, powder XRD and FTIR data of joanneumite are nearly identical to data of the synthetic bis(isocyanurato)diammine-copper(II) reported by Slade *et al.* (1973). Falvello *et al.* (1997) described a series

TABLE 5. Atomic coordinates, equivalent isotropic and anisotropic displacement parameters (Å^2) for the synthetic analogue of joanneumite.

Atom	x	y	z	U_{eq}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu	½	½	½	0.0125(1)	0.0148(2)	0.0145(2)	0.0073(2)	0.0026(1)	0.0013(1)	0.0042(1)
N(1)	0.5259(4)	0.6290(3)	0.3035(2)	0.0132(4)	0.0135(8)	0.0154(8)	0.0096(8)	0.0020(7)	0.0017(6)	0.0034(7)
N(2)	0.3515(4)	0.6621(3)	0.0550(2)	0.0134(4)	0.0120(8)	0.0171(9)	0.0087(8)	0.0021(7)	–0.0002(6)	0.0025(7)
N(3)	0.8213(4)	0.8546(3)	0.1511(2)	0.0143(4)	0.0109(8)	0.0176(9)	0.0110(8)	0.0026(7)	0.0018(6)	0.0005(7)
N(4)	0.5365(4)	0.2457(3)	0.4132(2)	0.0169(4)	0.0236(9)	0.0181(9)	0.0097(8)	0.0028(7)	0.0015(7)	0.0084(8)
C(1)	0.7871(4)	0.7711(3)	0.2875(2)	0.0140(4)	0.0153(10)	0.0162(10)	0.0115(10)	0.0016(8)	0.0027(8)	0.0067(8)
C(2)	0.3034(4)	0.5728(3)	0.1887(2)	0.0132(4)	0.0169(10)	0.0136(9)	0.0104(9)	0.0012(7)	0.0024(8)	0.0068(8)
C(3)	0.6084(4)	0.8031(3)	0.0317(2)	0.0134(4)	0.0137(9)	0.0151(10)	0.0123(10)	0.0009(8)	0.0023(8)	0.0060(8)
O(1)	0.9900(3)	0.8258(2)	0.3902(2)	0.0180(3)	0.0158(7)	0.0230(8)	0.0122(7)	0.0020(6)	–0.0014(6)	0.0042(6)
O(2)	0.0631(3)	0.4449(2)	0.1997(2)	0.0164(3)	0.0139(7)	0.0193(8)	0.0127(7)	0.0034(6)	0.0020(6)	0.0013(6)
O(3)	0.6441(3)	0.8763(2)	–0.0900(2)	0.0154(3)	0.0153(7)	0.0198(8)	0.0093(7)	0.0041(6)	0.0032(5)	0.0033(6)
H(1)*	0.208	0.626	–0.019	0.0161						
H(2)*	0.990	0.946	0.141	0.0171						
H(3)*	0.373	0.136	0.419	0.0253						
H(4)*	0.691	0.222	0.464	0.0253						
H(5)*	0.561	0.263	0.316	0.0253						

*Constrained in refinement.
U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.
The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \ldots + 2hka^*b^*U^{12}]$.

TABLE 6. Selected bond distances (Å) and angles (°) in the synthetic analogue of joanneumite.

Cu–N(1)_$6	x2	2.008(2)	N(1)–Cu–N(4)		90.9(1)
Cu–N(4)_$6	x2	1.992(2)	N(1)–Cu–N(4)_$6		89.1(1)
C(1)–O(1)		1.231(3)	O(1)–C(1)–N(1)		121.9(2)
–N(1)		1.361(3)	O(1)–C(1)–N(3)		119.9(2)
–N(3)		1.382(3)	N(1)–C(1)–N(3)		118.2(2)
C(2)–O(2)		1.237(3)	O(2)–C(2)–N(1)		122.5(2)
–N(1)		1.362(3)	O(2)–C(2)–N(2)		119.4(2)
–N(2)		1.383(3)	N(1)–C(2)–N(2)		118.1(2)
C(3)–O(3)		1.233(3)	O(3)–C(3)–N(2)		121.7(2)
–N(2)		1.361(3)	O(3)–C(3)–N(3)		122.9(2)
–N(3)		1.362(3)	N(2)–C(3)–N(3)		115.3(2)
		D–H	H···A	D···A	<(DHA)
N(2)–H(1)···O(2)_$1		0.88	1.92	2.795(2)	171.6
N(3)–H(2)···O(3)_$2		0.88	1.93	2.807(2)	171.2
N(4)–H(5)···O(3)_$3		0.91	2.22	2.984(2)	140.9
N(4)–H(3)···O(1)_$4		0.91	2.31	3.203(3)	167.2
N(4)–H(4)···O(1)_$5		0.91	2.04	2.946(2)	170.6

Symmetry transformations: absent code: *x,y,z*.
$1: $-x$, $-y+1$, $-z$; $2: $-x+2$, $-y+2$, $-z$; $3: $-x+1$, $-y+1$, $-z$;
$4: $x-1$, $y-1$, z; $5: $-x+2$, $-y+1$, $-z+1$; $6: $-x+1$, $-y+1$, $-z+1$.

of nine coordination compounds with ribbons of cyanurates and reported new accurate data for the trans-[Cu(cyan-κN)$_2$(NH$_3$)$_2$] structure type which is identical with joanneumite. They conclude that the cyanurate ribbon connected by hydrogen bonding is an aggregate structure element, also formed by self-assembly, and is a determinative factor in structures with cyanurate and metals of the first transition series.

Joanneumite is a supergene mineral formed in the contact zone between altered guano and chalcopyrite-bearing gabbro. Guano was the source for isocyanurate and ammine groups and the copper originates from chalcopyrite. Pabellón de Pica is the type locality of the rare minerals ammineite, (Bojar *et al.*, 2010), antipinite (Chukanov *et al.*, 2015*a*), chanabayaite (Chukanov *et al.* 2015*d*,*e*), möhnite (Chukanov *et al.*, 2015*b*),

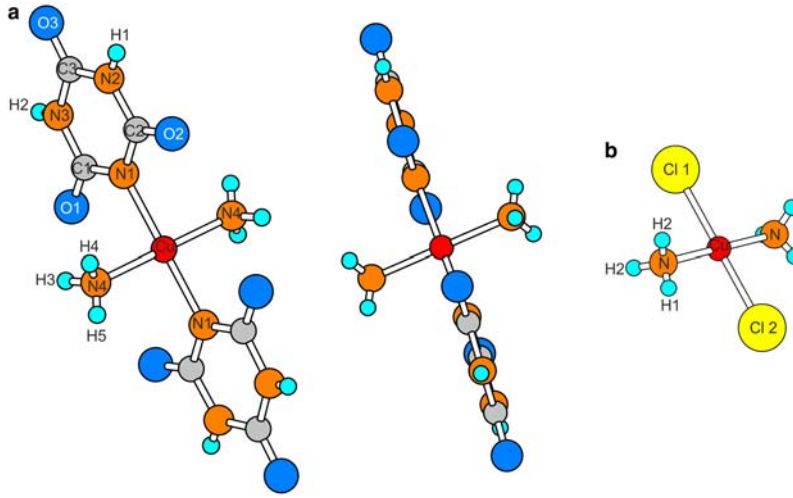

FIG. 5. The basic structural units of joanneumite (*a*) and ammineite (*b*).

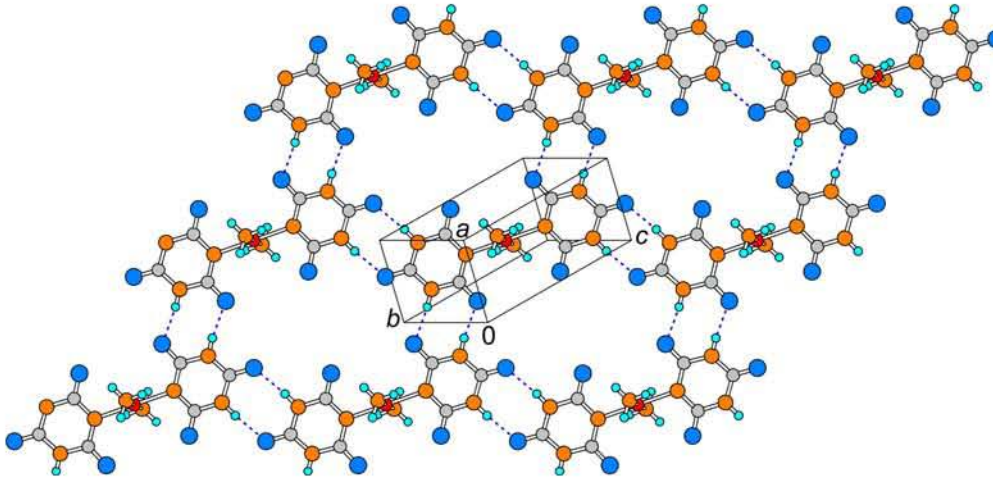

FIG. 6. The isocyanurate rings of the $Cu(C_3N_3O_3H_2)_2(NH_3)_2$ complex in the joanneumite structure are oriented to a layer parallel ($\bar{1}21$). The crenellated isocyanurate ribbon is visible by pairs of hydrogen bonds.

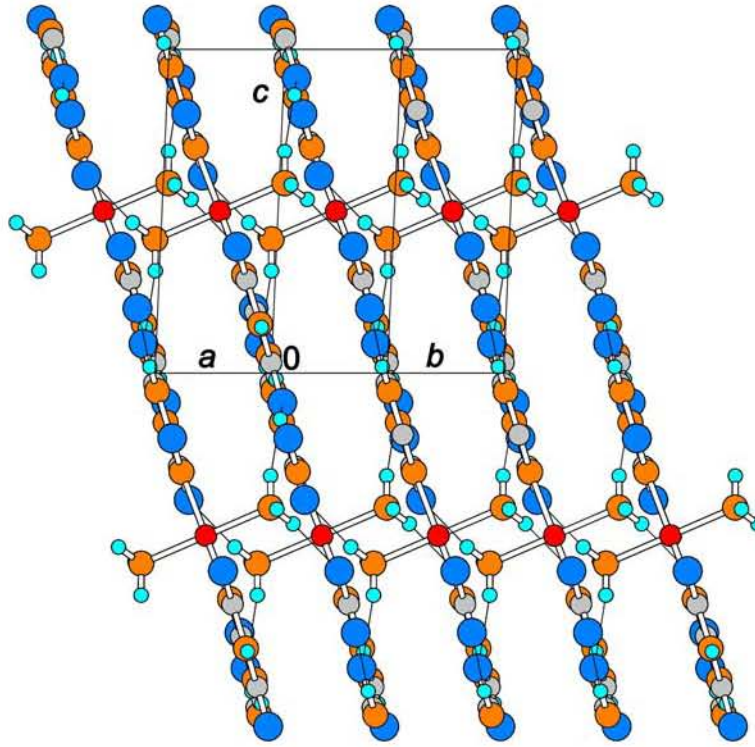

FIG. 7. The crystal structure of joanneumite projected along [210]. The layers parallel ($\bar{1}21$) are connected up and down by hydrogen bonds of the ammine groups to a three dimensional network.

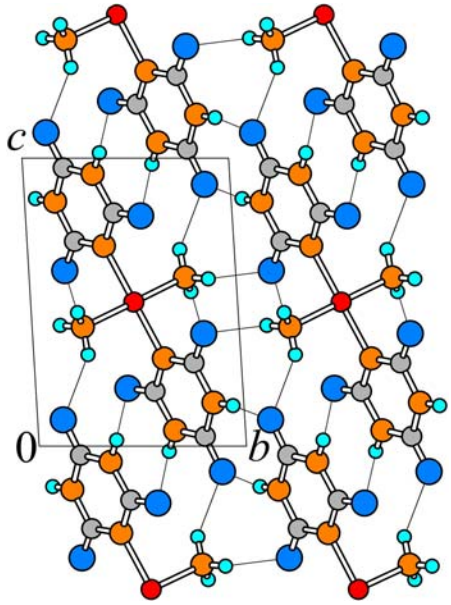

FIG. 8. The projection of the crystal structure of joanneumite along [100] shows the good cleavage parallel to (010).

shilovite (Chukanov *et al.*, 2015*c*) and the natural 1,2,4-triazolate compound $NaCu_2Cl_3[N_3C_2H_2]_2[NH_3]_2 \cdot 4H_2O$ (Zubkova *et al.*, 2015).

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