

Revision 1

Pabellóndepicaite, $\text{Cu}^{2+}_2(\text{N}_3\text{C}_2\text{H}_2)_2(\text{NH}_3)_2(\text{NO}_3)\text{Cl}\cdot 2\text{H}_2\text{O}$, a new 1,2,4-triazolate mineral from the guano deposit at Pabellón de Pica, Iquique Province, Chile

Anthony R. Kampf^{1*}, Gerhard Möhn², Chi Ma³ and Joy Désor⁴

¹ Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, CA 90007, USA

² Dr.-J.-Wittmannstrasse 5, 65527 Niedernhausen, Germany

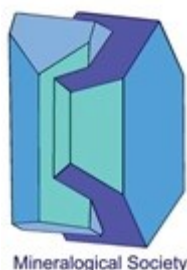
³ Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, USA

⁴ Im Langenfeld 4, 61350 Bad Homburg, Germany

*E-mail: akampf@nhm.org

Abstract

The new mineral pabellóndepicaite (IMA2023-104), $\text{Cu}^{2+}_2(\text{N}_3\text{C}_2\text{H}_2)_2(\text{NH}_3)_2(\text{NO}_3)\text{Cl}\cdot 2\text{H}_2\text{O}$, was found in the guano deposit at Pabellón de Pica, Iquique Province, Chile, where it is a secondary phase formed at the contact between an altered guano deposit and a chalcopyrite-bearing gabbro. Pabellóndepicaite occurs on salammoniac in association with antipinite, bojarite, dittmarite, halite, joanneumite, sampleite,



This is a 'preproof' accepted article for Mineralogical Magazine. This version may be subject to change during the production process.
DOI: 10.1180/mgm.2024.55

struvite, wheatleyite and whewellite. Crystals are rectangular blades or tablets, up to about 0.2 mm long, flattened on {001} and elongated along [100] and exhibiting the forms {010}, {001}, {011} and {102}. Crystals are indigo blue and transparent, with vitreous lustre and light indigo blue streak. The mineral is brittle with curved and stepped fracture. The Mohs hardness is about 2½. Cleavage is perfect on {001} and good on {010}. The density is 1.95(2) g·cm⁻³. Optically, pabellóndepicaite is biaxial (+) with $\alpha = 1.583(3)$, $\beta = 1.596(3)$ and $\gamma = 1.644(3)$ (white light). The $2V$ is 56(2)° with distinct $r > v$ dispersion. The optical orientation is $X = \mathbf{a}$, $Y = \mathbf{b}$, $Z = \mathbf{c}$ and the pleochroism is X light indigo blue, Y indigo blue, Z pale indigo blue; $Y > X > Z$. The empirical formula is Cu₂Cl_{1.25}N₉C₄H_{13.75}O_{4.75} (with H, C and N calculated based on the structure). Pabellóndepicaite is orthorhombic, space group *Pmma*, with cell parameters: $a = 7.2118(12)$, $b = 9.0983(15)$, $c = 11.128(3)$ Å, $V = 730.2(2)$ Å³ and $Z = 2$. The structure ($R_1 = 6.65\%$ for 482 $I > 2\sigma_I$ reflections) contains two types of polyhedral chains (1) a zig-zag chain of CuN₄Cl₂ octahedra linked by sharing Cl atoms and the N-N edges of 1,2,4-triazolate groups and (2) a chain of CuN₄O₂ octahedra alternating with NO₃ triangles. The chains are linked to one another by 1,2,4-triazolate groups to form layers with isolated H₂O groups in their cavities.

Keywords: pabellóndepicaite; new mineral; 1,2,4-triazolate; nitrate; crystal structure; Raman spectroscopy; Pabellón de Pica, Chile

Introduction

Among the numerous guano deposits along the northern coast of Chile, Pabellón de Pica is particular noteworthy because here the guano is in contact with a chalcopyrite-bearing gabbro, and this has resulted in the formation of a remarkable array of unusual mineral species, several containing both Cu²⁺ and organic molecules. New minerals described

previously from this deposit are: ammineite, $\text{Cu}^{2+}\text{Cl}_2(\text{NH}_3)_2$ (Bojar *et al.*, 2010), ammoniotinsleyite, $(\text{NH}_4)\text{Al}_2(\text{PO}_4)_2(\text{OH})\cdot 2\text{H}_2\text{O}$ (Chukanov *et al.*, 2020a), antipinite, $\text{KNa}_3\text{Cu}^{2+}_2(\text{C}_2\text{O}_4)_4$ (Chukanov *et al.*, 2015a), bojarite, $\text{Cu}^{2+}_3(\text{N}_3\text{C}_2\text{H}_2)_3(\text{OH})\text{Cl}_2\cdot 6\text{H}_2\text{O}$ (Chukanov *et al.*, 2020b), chanabayaite, $\text{Cu}^{2+}_2\text{Cl}(\text{N}_3\text{C}_2\text{H}_2)_2(\text{NH}_3, \text{Cl}, \text{H}_2\text{O}, \square)_4$ (Chukanov *et al.*, 2015b), joanneumite, $\text{Cu}^{2+}(\text{C}_3\text{N}_3\text{O}_3\text{H}_2)_2(\text{NH}_3)_2$ (Bojar *et al.*, 2017), möhnite, $(\text{NH}_4)\text{K}_2\text{Na}(\text{SO}_4)_2$ (Chukanov *et al.*, 2015c), shilovite, $\text{Cu}^{2+}(\text{NH}_3)_4(\text{NO}_3)_2$ (Chukanov *et al.*, 2015d) and triazolite, $\text{NaCu}^{2+}_2(\text{N}_3\text{C}_2\text{H}_2)_2(\text{NH}_3)_2\text{Cl}_3\cdot 4\text{H}_2\text{O}$ (Chukanov *et al.*, 2018).

Pabellóndepicaite is the tenth new mineral and the fourth new 1,2,4-triazolate to be described from Pabellón de Pica.

The name pabellóndepicaite is for the name of the locality. The new mineral and the name have been approved by the International Mineralogical Association (IMA2023-104; Warr symbol: Pdp). The description is based upon one holotype specimen deposited in the collections of the Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, CA 90007, USA, catalogue numbers 76305.

Occurrence

Specimens in which pabellóndepicaite were collected by one of the authors (GM) in the guano deposit at Pabellón de Pica, 1.5 km south of Chanabaya village, Iquique Province, Tarapacá Region, Chile ($20^\circ 54' 32''\text{S}$ $70^\circ 08' 17''\text{W}$). Pabellóndepicaite occurs on salammoniac (with embedded fragments of augite, magnesio-hornblende and magnetite) in association with antipinite, bojarite, dittmarite, halite, joanneumite, sampleite, struvite, wheatleyite, whewellite and an unknown phase containing Cu, C, N, S, O and Cl. Pabellóndepicaite is a secondary mineral formed at the contact between the altered guano deposit and the chalcopyrite-bearing gabbro. The organic matter in the guano was the source of N and C, whereas Cu was sourced from the chalcopyrite in the gabbro.

Physical and optical properties

Pabellóndepicaite occurs as rectangular blades or tablets, up to about 0.2 mm long (Fig. 1). Crystals are flattened on {001}, elongated along [100] and exhibit the forms {010}, {001}, {011} and {102} (Fig. 2). The mineral is indigo blue and transparent with light indigo-blue streak. The mineral does not fluoresce in long- or short-wave ultraviolet light. The Mohs hardness is about 2½ based on scratch tests. Crystals are brittle with curved and stepped fracture. Cleavage is perfect on {001} and good on {010}. The density measured by flotation in a mixture of methylene iodide and toluene is 1.95(2) g·cm⁻³. The calculated density is 1.980 g·cm⁻³ for the empirical formula and 1.959 g·cm⁻³ for the ideal formula, in both cases using the single-crystal cell. At room temperature, the mineral is insoluble in H₂O and dissolves slowly in dilute HCl.

Optically, pabellóndepicaite is biaxial (+) with $\alpha = 1.583(3)$, $\beta = 1.596(3)$ and $\gamma = 1.644(3)$ measured in white light. The $2V$ measured directly on a spindle stage is 56(2)°; the calculated $2V$ is 56.3°. Dispersion is $r > v$ distinct and the optical orientation is $X = \mathbf{a}$, $Y = \mathbf{b}$, $Z = \mathbf{c}$. The mineral is pleochroic: X light indigo blue, Y indigo blue, Z pale indigo blue; $Y > X > Z$. The Gladstone-Dale compatibility could not be calculated because coefficients for NH₃ and N₃C₂H₂⁻ groups are unknown.

Raman spectroscopy

Raman spectroscopy was done on a Horiba XploRa PLUS micro-Raman spectrometer using an incident wavelength of 532 nm, 0.2 mW power, a laser slit of 200 μm, 1200 gr/mm diffraction grating and a 100x (0.9 NA) objective. The spectrum from 4000 to 60 cm⁻¹ is shown in Figure 3.

The spectrum exhibits similarities to that of bojarite, $\text{Cu}_3(\text{N}_3\text{C}_2\text{H}_2)_3(\text{OH})\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (Chukanov *et al.*, 2020), except that bands assignable to nitrate are observed in the pabellóndepicaite spectrum. Bands between 3400 and 3200 cm^{-1} are attributed to O–H and N–H stretching. The band at 3157 cm^{-1} is due to C–H stretching with the C atom belonging to the system of conjugated bonds of the triazole ring. The very weak band at 2931 cm^{-1} may correspond to C–H stretching vibrations of an extraneous hydrocarbon impurity. Most of the bands between 1524 and 1016 cm^{-1} are related to the in-plane stretching and mixed vibrations of the 1,2,4-triazolate ring; however, the band at 1040 cm^{-1} is assignable to the symmetric stretching of the nitrate group. The band at 715 cm^{-1} can be assigned to the out-of-plane bending of the nitrate group and that at 668 cm^{-1} to the out-of-plane bending vibrations of the 1,2,4-triazolate ring. The bands at wavenumbers below 500 cm^{-1} are assigned to lattice modes, largely related to Cu–O, Cu–N and Cu–Cl stretching vibrations.

Composition

Analyses (five points) were performed at Caltech on a JEOL JXA-iHP200F field-emission electron microprobe in WDS mode. Analytical conditions were 15 kV accelerating voltage, 5 nA beam current and 10 μm beam diameter. A time-dependent intensity calibration was applied; however significant instability of the mineral led to the loss of much of the volatile content under vacuum and in the beam. This is certainly the cause of much lower than expected N values. Analyses in EDS mode under milder conditions provided significantly higher N values (~22 wt%), but still below the amount predicted by the structure determination. It is worth noting that many of the phases found in the guano deposit at Pabellón de Pica are notorious for their instabilities. The very small amount of material available precluded the determination of N, C and H by CHN analysis or other techniques, so these elements are calculated based on the structure. The volatile loss resulted in higher-than-

expected concentrations for Cu and Cl; therefore, they have been normalized to provide a total of 100% when combined with the calculated constituents. The cause of the excess Cl relative to Cu is unclear; however, a similar excess was reported by Chukanov *et al.* (2020b) in the analyses of bojarite. No other elements with an atomic number larger than 8 were detected. Analytical data are given in Table 1.

The empirical formula based on the formula $\text{Cu}^{2+}_2(\text{N}_3\text{C}_2\text{H}_2)_2(\text{NH}_3)_2(\text{NO}_3)\text{Cl}\cdot 2\text{H}_2\text{O}$ obtained from the structure refinement (see below) is $\text{Cu}^{2+}_2\text{Cl}_{1.25}\text{N}_9\text{C}_4\text{H}_{13.75}\text{O}_{4.75}$. Note that it is not clear where the excess 0.25 Cl *apfu* is accommodated in the structure or even if it may be an artefact resulting from the deterioration of the sample during analysis. Assuming that the excess Cl replaces H_2O , we have chosen to reduce the H_2O by 0.25 and add back 0.25 H for charge balance. The ideal formula is $\text{Cu}^{2+}_2(\text{N}_3\text{C}_2\text{H}_2)_2(\text{NH}_3)_2(\text{NO}_3)\text{Cl}\cdot 2\text{H}_2\text{O}$, which requires Cu 29.50, Cl 8.23, C 11.15, N 29.26, H 3.28, O 18.57, total 100 wt%.

X-ray crystallography and structure refinement

X-ray powder diffraction data for the holotype were recorded using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer with monochromatized $\text{MoK}\alpha$ radiation. A Gandolfi-like motion on the ϕ and ω axes was used to randomize the sample. Observed *d*-values and intensities were derived by profile fitting using JADE Pro software (Materials Data, Inc.). The powder data are presented in Table 2. The unit-cell parameters refined from the powder data using JADE Pro with whole-pattern fitting (space group *Pmma*) are $a = 7.192(6)$, $b = 9.095(9)$, $c = 11.111(10)$ Å and $V = 726.8(14)$ Å³.

Single-crystal X-ray studies were done on the same diffractometer and radiation noted above. Pabellóndepicaite crystals do not diffract strongly and suffer from somewhat high mosaicity (including some satellite reflections along the *c* axis that were included in the

integration). This severely limited the data collection range and consequently provided a relatively low data to parameter ratio.

The Rigaku CrystalClear software package was used for processing the structure data, including the application of an empirical absorption correction using the multi-scan method with ABSCOR (Higashi, 2001). The structure was solved using the intrinsic-phasing algorithm of SHELXT (Sheldrick, 2015a). SHELXL-2016 (Sheldrick, 2015b) was used for the refinement of the structure. The structure solution located all nonhydrogen sites; however, the adjustments had to be made in the assignments of C, N and O sites. The O3 site (H₂O) was modelled as split into two half-occupied sites 1.13(4) Å apart. All nonhydrogen sites were refined successfully with anisotropic displacement parameters. Difference Fourier mapping located all H sites, including those associated with the O3 site. The H sites were refined with the distance restraints C–H 0.95(3), N–H 0.91(3), O–H 0.82(3) and H–H 1.30(3) Å and with $U_{\text{iso}}\text{H} = 1.2U_{\text{eq}}(\text{C/N/O})$. The data collection and refinement details are given in Table 3, atom coordinates and displacement parameters in Table 4, selected bond distances in Table 5 and a bond-valence analysis in Table 6.

Description of the structure

The structure of pabellóndepicaite contains two types of polyhedral chains. CuN₄Cl₂ octahedra are linked by sharing Cl atoms as well as the N–N edges of triazolate groups to form a zig-zag chain along [100]. This chain is the same as the one in the triazolite structure. A second chain, also along [100], is formed by CuN₄O₂ octahedra alternating with NO₃ triangles. The two types of chains are linked to one another by triazolate groups (Fig. 4). The propagation of this linkage forms layers parallel to {001} with isolated H₂O (O3) groups in cavities in the layers (Figs. 5 and 6). Both the CuN₄Cl₂ and CuN₄O₂ octahedra exhibit pronounced 4 + 2 distortion due to the Jahn-Teller effect.

Discussion

Although guano is rich in nitrogen, it does not generally contain azole compounds and specifically compounds containing the 1,2,4-triazole ring. It is likely that the occurrence of 1,2,4-triazolate in minerals, which has only been documented at the Pabellón de Pica guano deposit, is the result of the interaction of N released from the guano with Cu released from the chalcopyrite-bearing gabbro on which the guano has been deposited. Support for this comes from synthetic studies in which Cu^{2+} has been used to promote (mediate or catalyze) the formation of 1,2,4-triazoles from other N-bearing compounds (e.g. Kuang *et al.*, 2014; Romero *et al.*, 2020). The affinity of Cu^{2+} for N is obvious in the structure of pabellóndepicaite, as well as the other 1,2,4-triazolate minerals at Pabellón de Pica, in that all short Cu-ligand bonds in these structures are to N atoms (1,2,4-triazolate and NH_3). Furthermore, Hasnoot (2000) notes that Cu^{2+} shows high affinity for the triazolate ligand.

Based on pseudomorphic relationships, Chukanov *et al.* (2020b) noted that the other three 1,2,4-triazolate minerals form a transformation series: triazolite $\text{NaCu}^{2+}_2(\text{N}_3\text{C}_2\text{H}_2)_2(\text{NH}_3)_2\text{Cl}_3 \cdot 4\text{H}_2\text{O} \rightarrow$ chanabayaite, $\text{Cu}^{2+}_2\text{Cl}(\text{N}_3\text{C}_2\text{H}_2)_2(\text{NH}_3, \text{Cl}, \text{H}_2\text{O}, \square)_4 \rightarrow$ bojarite $\text{Cu}^{2+}_3(\text{N}_3\text{C}_2\text{H}_2)_3(\text{OH})\text{Cl}_2 \cdot 6\text{H}_2\text{O}$, each step involving the loss of one or more components. The presence of bojarite (as an apparent alteration product of chanabayaite and/or triazolite) on the holotype of pabellóndepicaite, which occurs as unaltered crystals, indicates that pabellóndepicaite is not related to this transformation series. Notably, pabellóndepicaite is very rare, having been found on a single specimen, whereas triazolite and chanabayaite are relatively abundant at Pabellón de Pica. Yet triazolite and chanabayaite break down in air with the loss of NH_3 , whereas pabellóndepicaite is stable. The rarity of pabellóndepicaite may be due the required presence of NO_3^- during its formation and the

NO_3^- group in the structural unit of pabellóndepicaite presumably contributes to its greater stability.

Acknowledgements

Nikita Chukanov, structures editor Peter Leverett and an anonymous reviewer are thanked for their constructive comments on the manuscript. A portion of this study was funded by the John Jago Trelawney Endowment to the Mineral Sciences Department of the Natural History Museum of Los Angeles County.

References

- Bojar, H.-P., Walter, F., Baumgartner, J. and Farber, G. (2010) Ammineite, $\text{CuCl}_2(\text{NH}_3)_2$, a New Species Containing an Ammine Complex: Mineral Data and Crystal Structure. *The Canadian Mineralogist*, **48**, 1359–1371.
- Bojar, H.P., Walter, F. and Baumgartner, J. (2017) Joanneumite, $\text{Cu}(\text{C}_3\text{N}_3\text{O}_3\text{H}_2)_2(\text{NH}_3)_2$, a new mineral from Pabellón de Pica, Chile and the crystal structure of its synthetic analogue. *Mineralogical Magazine*, **81**, 155–166.
- Brese, N.E., and O’Keeffe, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, **B47**, 192–197.
- Brown, I.D. (2002) *The Chemical Bond in Inorganic Chemistry. The Bond Valence Model*. Oxford University Press, Oxford.
- Chukanov, N.V., Aksenov, S.M., Rastsvetaeva, R.K., Lyssenko, K.A., Belakovskiy, D.I., Färber, G., Möhn, G. and Van, K.V. (2015a) Antipinite, $\text{KNa}_3\text{Cu}_2(\text{C}_2\text{O}_4)_4$, a new mineral species from a guano deposit at Pabellón de Pica, Chile. *Mineralogical Magazine*, **79**, 1111–1121.

- Chukanov, N.V., Zubkova, N.V., Möhn, G., Pekov, I.V., Pushcharovsky, D.Y. and Zadov, A.E. (2015b) Chanabayaite, $\text{Cu}_2\text{Cl}(\text{N}_3\text{C}_2\text{H}_2)_2(\text{NH}_3, \text{Cl}, \text{H}_2\text{O}, \square)_4$, a new mineral containing triazolate anion. *Geology of Ore Deposits*, **57**, 712–720.
- Chukanov, N.V., Aksenov, S.M., Rastsvetaeva, R.K., Pekov, I.V., Belakovskiy, D.I. and Britvin, S.N. (2015c) Möhnite, $(\text{NH}_4)\text{K}_2\text{Na}(\text{SO}_4)_2$, a new guano mineral from Pabellón de Pica, Chile. *Mineralogy and Petrology*, **109**, 643–648.
- Chukanov, N.V., Britvin, S.N., Möhn, G., Pekov, I.V., Zubkova, N.V., Nestola, F., Kasatkin, A.V. and Dini, M. (2015d) Shilovite, natural copper(II) tetrammine nitrate, a new mineral species. *Mineralogical Magazine*, **79**, 613–623.
- Chukanov, N.V., Zubkova, N.V., Möhn, G., Pekov, I.V., Belakovskiy, D.I., Van, K.V., Britvin, S.N. and Pushcharovsky, D.Y. (2018) Triazolite, $\text{NaCu}_2(\text{N}_3\text{C}_2\text{H}_2)_2(\text{NH}_3)_2\text{Cl}_3 \cdot 4\text{H}_2\text{O}$, a new mineral species containing 1,2,4-triazolate anion, from a guano deposit at Pabellón de Pica, Iquique Province, Chile. *Mineralogical Magazine*, **82**, 1007–1014.
- Chukanov, N.V., Möhn, G., Pekov, I.V., Zubkova, N.V., Ksenofontov, D.A., Belakovskiy, D.I., Vozchikova, S.A., Britvin, S.N. and Desor, J. (2020a) Ammoniotinsleyite, $(\text{NH}_4)\text{Al}_2(\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$, a new mineral species from the guano deposit at Pabellón de Pica, Iquique Province, Chile. *Mineralogical Magazine*, **84**, 705–711.
- Chukanov, N.V., Möhn, G., Zubkova, N.V., Ksenofontov, D.A., Pekov, I.V., Agakhanov, A.A., Britvin, S.N. and Desor, J. (2020b) Bojarite, $\text{Cu}_3(\text{N}_3\text{C}_2\text{H}_2)_3(\text{OH})\text{Cl}_2 \cdot 6\text{H}_2\text{O}$, a new mineral species with a microporous metal–organic framework from the guano deposit at Pabellón de Pica, Iquique Province, Chile. *Mineralogical Magazine*, **84**, 921–927.
- Gagné, O.C. and Hawthorne, F.C. (2015) Comprehensive derivation of bond-valence parameters for ion pairs involving oxygen. *Acta Crystallographica*, **B71**, 562–578.

- Haasnoot, J.G. (2000) Mononuclear, oligonuclear and polynuclear metal coordination compounds with 1,2,4-triazole derivatives as ligands. *Coordination Chemistry Reviews*, **200–202**, 131–185.
- Higashi, T. (2001) *ABSCOR*. Rigaku Corporation, Tokyo.
- Kuang, J., Chen, B. and Ma, S. (2014) Copper-mediated efficient three-component synthesis of 1, 2, 4-triazoles from amines and nitriles. *Organic Chemistry Frontiers*, **1**, 186–189.
- Malcherek, T. and Schlüter, J. (2007) $\text{Cu}_3\text{MgCl}_2(\text{OH})_6$ and the bond-valence parameters of the OH–Cl bond. *Acta Crystallographica*, **B63**, 157–160.
- Romero, A.H., Sojo, F., Arvelo, F., Calderón, C., Morales, A., López, S.E. (2020) Anticancer potential of new 3-nitroaryl-6-(N-methyl) piperazin-1, 2, 4-triazolo [3, 4-a] phthalazines targeting voltage-gated K^+ channel: Copper-catalyzed one-pot synthesis from 4-chloro-1-phthalazinyl-arylhydrazones. *Bioorganic Chemistry*, **101**, 104031.
- Sheldrick, G.M. (2015a) SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallographica*, **A71**, 3–8.
- Sheldrick, G.M. (2015b) Crystal Structure refinement with *SHELX*. *Acta Crystallographica*, **C71**, 3–8.
- Shields, G.P., Raithby, P.R., Allen, F.H. and Motherwell, W.S. (2000) The assignment and validation of metal oxidation states in the Cambridge Structural Database. *Acta Crystallographica*, **B56**, 455–465.

FIGURE CAPTIONS

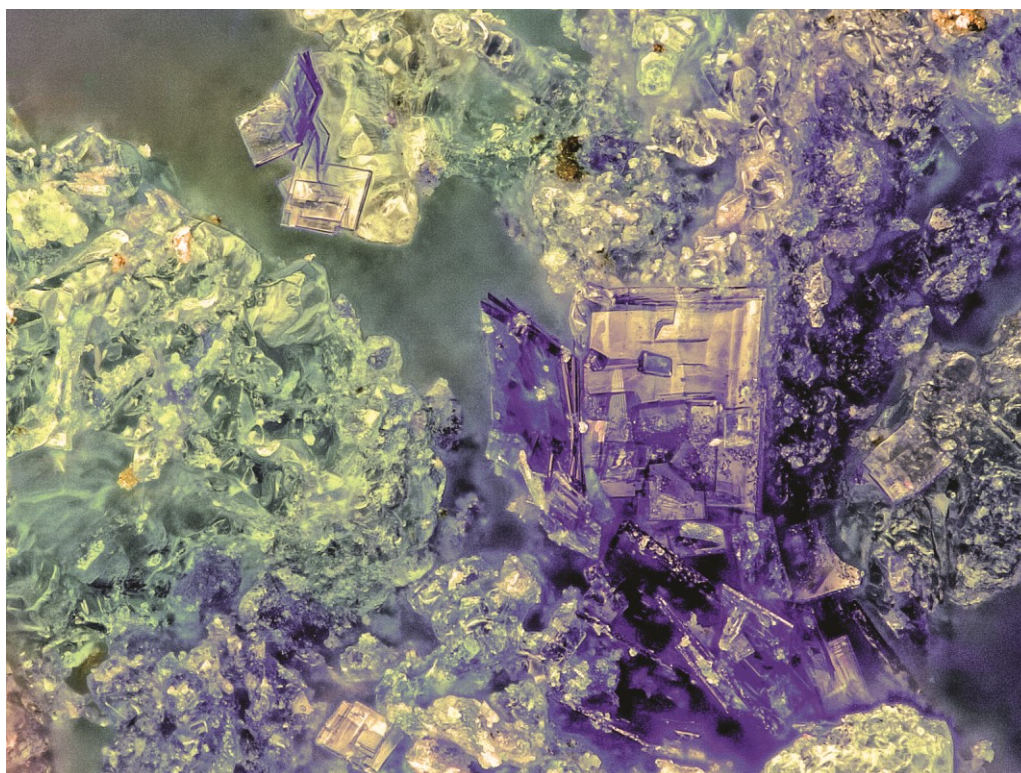


Figure 1. Indigo pabellóndepicaite crystals on green crystals of salammoniac (probably coloured by inclusions of antipinite) on holotype specimen 76305; the field of view is 0.68 mm across.

Prepublished

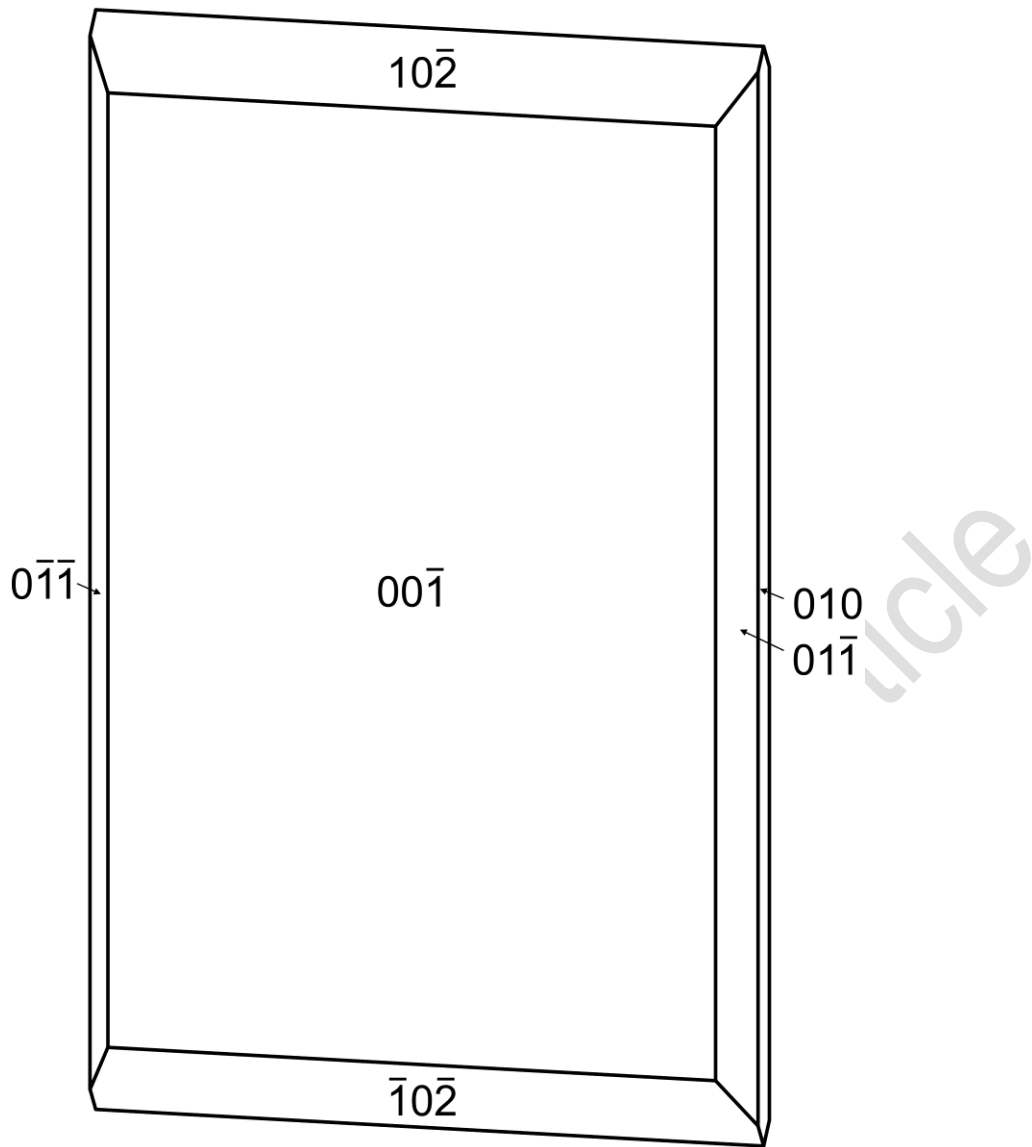


Figure 2. Crystal drawing of pabellóndepicaite; clinographic projection in nonstandard orientation, **a** vertical.

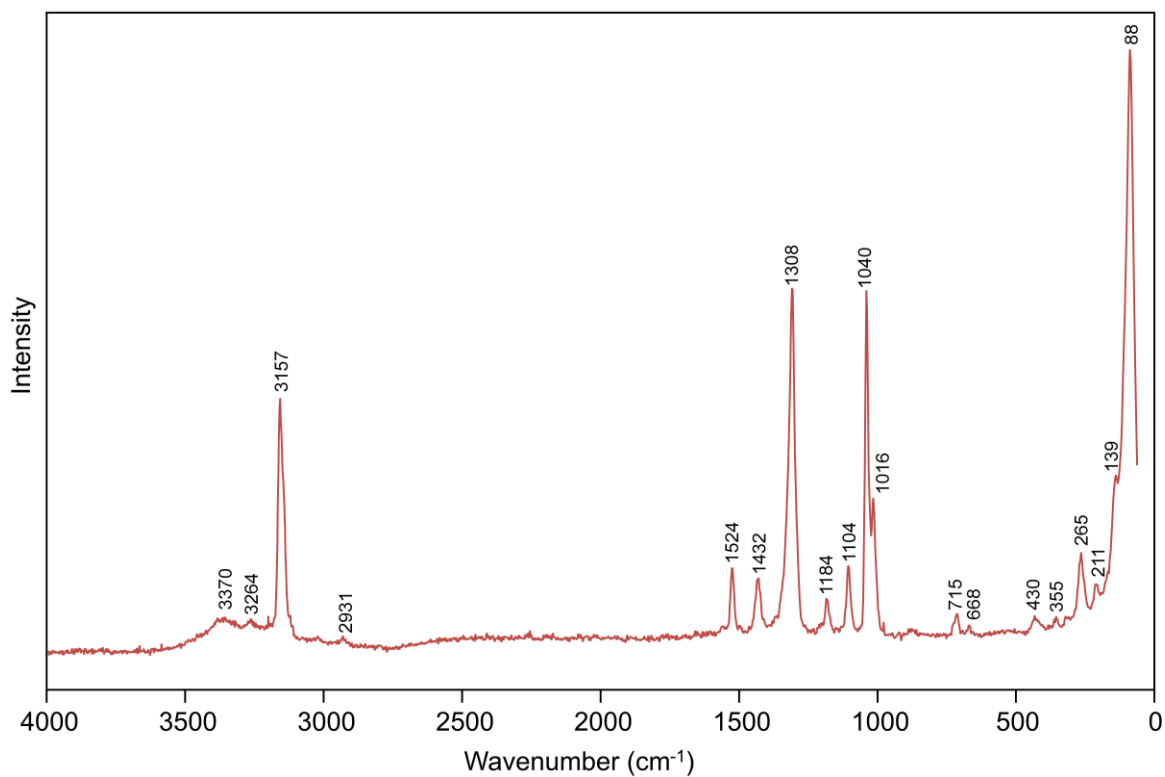


Figure 3. Raman spectrum of pabellóndepicaite recorded with a 532 nm laser.

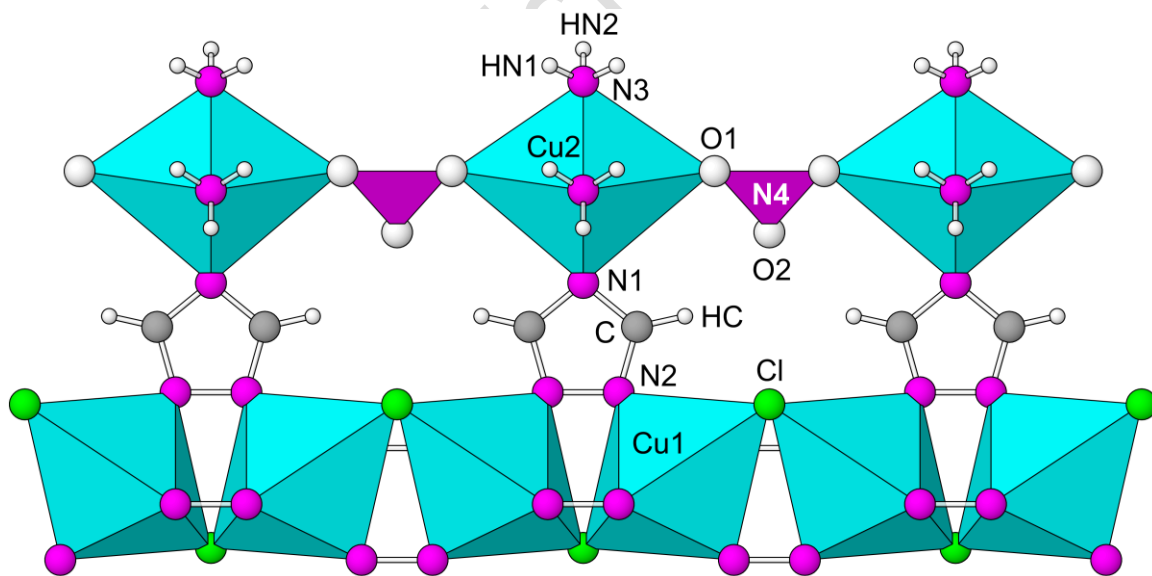


Figure 4. Fragment of the pabellóndepicaite structure showing the two types of polyhedral chains linked together by triazolate rings. The view is down $[01-1]$ with $[100]$ horizontal.

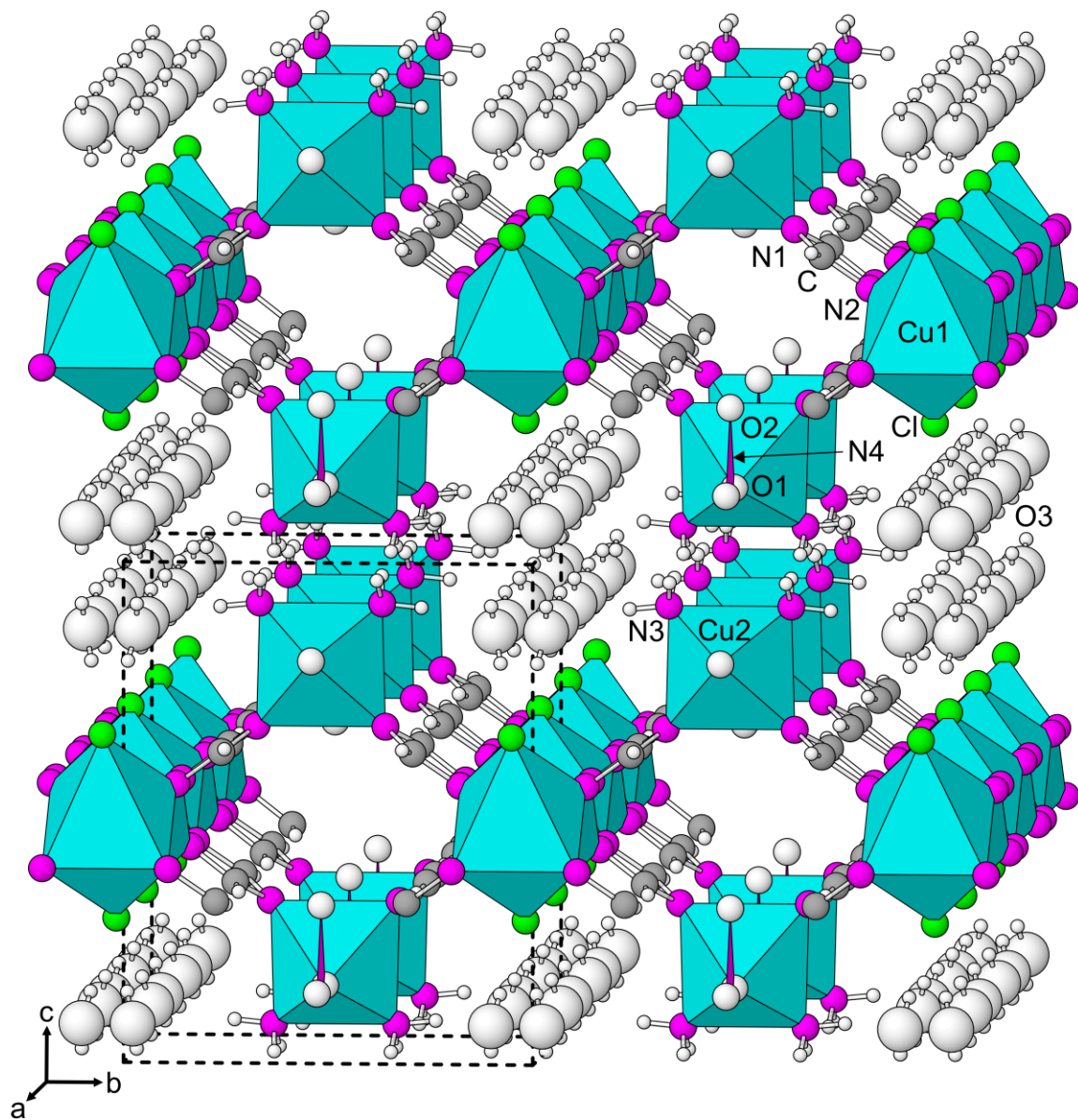


Figure 5. The structure of pabellóndepicaite viewed slightly canted along [100]. The unit-cell outline is shown by dashed lines.

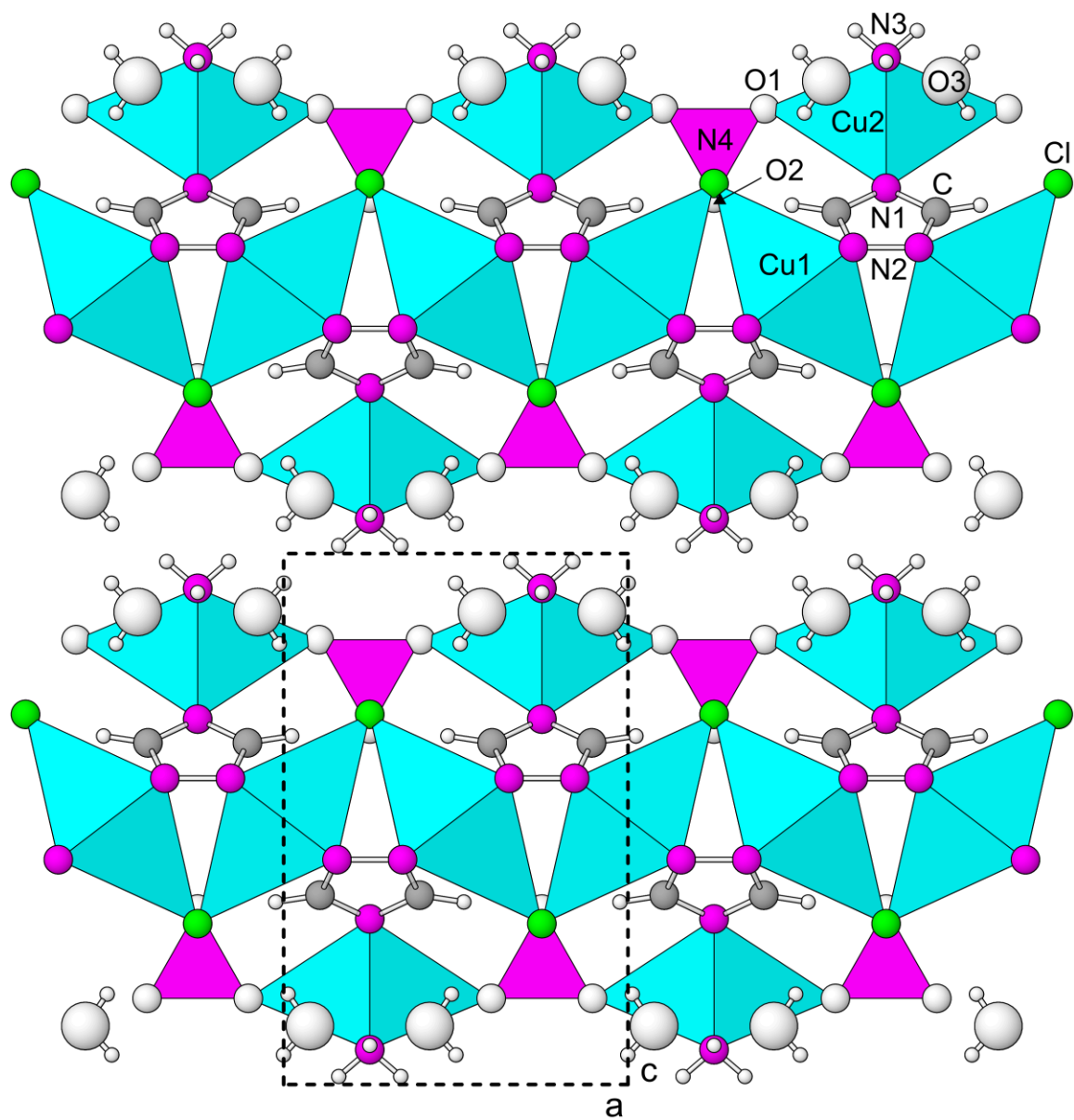


Figure 6. The structure of pabellóndepicaite viewed along [010]. The unit-cell outline is shown by dashed lines.

Table 1. Analytical data (in wt%) for pabellóndepicaite.

Const.	Mean	Range	SD	Standard	Normalized
Cu	31.59	31.32 – 31.88	0.22	Cu metal	29.19
Cl	11.03	10.68 – 11.21	0.22	sodalite	10.19
N	15.55	14.78 – 16.70	0.79	GaN	28.96*
C					11.03*
H					3.18*
O					17.45*
Total					100.00

* Based on the structure (Cu = 2)

Table 2. Powder X-ray diffraction data (d in Å) for pabellóndepicaite. Only calculated lines with intensities > 3.5 are listed.

I_{obs}	d_{obs}	d_{calc}	I_{calc}	hkl
39	11.182	11.128	42	0 0 1
100	7.057	7.044	100	0 1 1
30	6.039	6.052	27	1 0 1
24	5.021	5.039	16	1 1 1
48	4.753	4.747	55	0 1 2
28	4.564	4.549	30	0 2 0
20	3.627	3.636	7	1 2 1
		3.606	6	2 0 0
50	3.350	3.430	5	2 0 1
		3.352	27	2 1 0
		3.299	8	1 0 3
20	3.160	3.165	19	1 2 2
		3.101	7	1 1 3
23	3.029	3.026	17	2 0 2
21	2.879	2.875	25	0 2 3
6	2.665	2.663	7	0 3 2
47	2.511	2.520	26	2 2 2
		2.487	15	2 1 3
38	2.273	2.321	4	2 3 0
		2.275	19	3 1 1
		2.254	7	1 2 4
7	2.214	2.207	4	3 0 2
13	2.149	2.162	7	0 1 5
		2.145	6	3 1 2
20	1.974	1.968	17	2 3 3
7	1.889	1.896	4	2 4 1
10	1.830	1.818	9	2 4 2
20	1.799	1.794	10	0 3 5
16	1.744	1.748	6	2 2 5

Table 3. Data collection and structure refinement details for pabellóndepicaite.

Diffractometer	Rigaku R-Axis Rapid II
X-ray radiation	MoK α ($\lambda = 0.71075 \text{ \AA}$)
Temperature	293(2) K
Structural formula	Cu ₂ (N ₃ C ₂ H ₂) ₂ (NH ₃) ₂ (NO ₃)Cl·2H ₂ O
Space group	<i>Pmma</i> (#51)
Unit cell dimensions	$a = 7.2118(12) \text{ \AA}$ $b = 9.0983(15)$ $c = 11.128(2) \text{ \AA}$
<i>V</i>	730.2(2) \AA^3
<i>Z</i>	2
Density (for above formula)	1.959 g·cm ⁻³
Absorption coefficient	3.131 mm ⁻¹
<i>F</i> (000)	432
Crystal size	130 × 120 × 15 μm
θ range	3.37 to 22.46°
Index ranges	$-6 \leq h \leq 7$, $-8 \leq k \leq 8$, $-10 \leq l \leq 10$
Refls collected / unique	3803 / 555; $R_{\text{int}} = 0.097$
Reflections with $I > 2\sigma_I$	482
Completeness to $\theta = 22.46^\circ$	98.9%
Refinement method	Full-matrix least-squares on F^2
Parameters / constraints	80 / 8
GoF	1.098
Final <i>R</i> indices [$I > 2\sigma_I$]	$R_1 = 0.0665$, $wR_2 = 0.1543$
<i>R</i> indices (all data)	$R_1 = 0.0741$, $wR_2 = 0.1601$
Largest diff. peak / hole	+1.12 / -1.09 e/ \AA^3

$R_{\text{int}} = \Sigma|F_o^2 - F_o^2(\text{mean})| / \Sigma[F_o^2]$. GoF = $S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)\}^{1/2}$. $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.
 $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where a is 0.0633, b is 8.8077 and P is $[2F_c^2 + \text{Max}(F_o^2, 0)] / 3$.

Table 4. Atom coordinates and displacement parameters (\AA^2) for pabellóndepicaite.

	x/a	y/b	z/c	U_{eq}			
Cu1	0.5	0	0.5	0.0284(7)			
Cu2	0.25	0.5	0.80828(18)	0.0317(7)			
Cl	0.75	0	0.6971(4)	0.0499(15)			
O1	0.6028(14)	0.5	0.8377(9)	0.076(4)			
O2	0.75	0.5	0.6696(13)	0.056(4)			
O3*	0.076(2)	0.938(2)	0.8899(13)	0.076(6)			
HW1*	0.000(18)	0.93(2)	0.944(10)	0.091			
HW2*	0.01(2)	0.96(3)	0.830(10)	0.091			
N1	0.25	0.6576(12)	0.6882(8)	0.030(2)			
N2	0.3453(9)	0.8464(8)	0.5766(5)	0.0283(17)			
N3	0.25	0.6496(12)	0.9345(8)	0.038(3)			
HN1	0.160(2)	0.643(8)	0.985(4)	0.046			
HN2	0.25	0.745(4)	0.927(9)	0.046			
N4	0.75	0.5	0.7849(15)	0.044(4)			
C	0.3945(11)	0.7337(10)	0.6435(8)	0.032(2)			
HC	0.523(5)	0.717(10)	0.656(7)	0.039			
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	
Cu1	0.0160(12)	0.0279(13)	0.0414(13)	0	0.0067(9)	0	
Cu2	0.0322(13)	0.0355(14)	0.0274(13)	0	0	0	
Cl	0.027(2)	0.075(4)	0.047(3)	0	0	0	
O1	0.023(5)	0.166(13)	0.040(6)	0	0.006(5)	0	
O2	0.048(9)	0.076(11)	0.044(10)	0	0	0	
O3	0.062(9)	0.112(17)	0.055(9)	-0.012(9)	-0.010(8)	-0.011(10)	
N1	0.019(5)	0.043(7)	0.029(5)	0.000(5)	0	0	
N2	0.015(3)	0.033(4)	0.037(4)	0.007(3)	0.001(3)	0.011(3)	
N3	0.060(7)	0.032(7)	0.023(6)	0.001(5)	0	0	
N4	0.035(11)	0.052(11)	0.044(11)	0	0	0	
C	0.018(4)	0.032(5)	0.047(5)	0.006(4)	0.005(4)	0.008(4)	

* The O3, HW1 and HW2 sites are half-occupied.

Table 5. Selected bond distances (Å) and angles (°) for pabellóndepicaite.

<i>Cu-octahedra</i>		<i>Triazolate group</i>		<i>Nitrate group</i>	
Cu1–N2 (×4)	1.981(7)	C–N1 (×2)	1.347(10)	N4–O1 (×2)	1.213(12)
Cu1–Cl (×2)	2.839(4)	C–N2	1.316(10)	N4–O2	1.28(2)
		N2–N2	1.374(13)	<N4–O>	1.235
Cu2–N3 (×2)	1.956(10)	C–HC (×2)	0.95(3)		
Cu2–N1 (×2)	1.959(10)				
Cu2–O1 (×2)	2.566(10)				
<i>Hydrogen bonds</i>					
D–H···A	D–H	H···A	D···A	<DHA	
C–HC···O2	0.95(3)	2.57(6)	3.343(8)	139(7)	
N3–HN1···O1	0.86(3)	2.40(4)	3.066(13)	135(4)	
N3–HN2···O3	0.88(3)	2.19(3)	2.95(2)	144.4(19)	
O3–HW1···O3	0.82(3)	1.93(8)	2.69(3)	154(17)	
O3–HW2···Cl	0.82(3)	2.44(7)	3.233(15)	163(16)	

Table 6. Bond-valence analysis for pabellóndepicaite. Values are in valence units (*vu*).

	Cu1	Cu2	N4	HC	HN1	HN2	HW1	HW2	sum
N1		0.50 ^{×2↓}							
N2	0.47 ^{×4↓}								
N3		0.59 ^{×2↓}							
O1		0.08 ^{×2↓}	1.78 ^{×2↓}		0.14 ^{×2→}				2.14
O2			1.55	0.12 ^{×4→}					2.03
O3						0.18	0.24, -0.24	-0.06 ^{×4→}	-0.08
Cl	0.10 ^{×2↓→}							0.06 ^{×4→}	0.44
sum	2.08	2.34	5.11						

The sources for bond-valence parameters are as follows: Cu²⁺–N³⁻: Shields et al. (2000); Cu²⁺–Cl: Brese and O’Keeffe (1991); Cu²⁺–O and N⁵⁺–O: Gagné and Hawthorne (2015); H···O: Brown (2002); H···Cl: Malcherek and Schlueter (2007). Bonds within the triazolate group are not included. Negative values indicate donated bond-valences.