

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

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[Received 15 December 2014; Accepted 27 January 2015; Associate Editor: P. Leverett]

ABSTRACT

The new oxalate mineral antipinite is found in a guano deposit located on the Pabellón de Pica Mountain, Iquique Province, Tarapacá Region, Chile. Associated minerals are halite, salammoniac, chanabayaite, joanneumite and clays. Antipinite occurs as blue, imperfect, short prismatic crystals up to 0.1 mm × 0.1 mm × 0.15 mm in size, as well as their clusters and random aggregates. The mineral is brittle. Mohs hardness is 2; $D_{\text{meas}} = 2.53(3)$, $D_{\text{calc}} = 2.549 \text{ g cm}^{-3}$. The infrared spectrum shows the presence of oxalate anions and the absence of absorptions associated with H_2O molecules, C–H bonds, CO_3^{2-} , NO_3^- and OH^- ions. Antipinite is optically biaxial (+), $\alpha = 1.432(3)$, $\beta = 1.530(1)$, $\gamma = 1.698(5)$, $2V_{\text{meas}} = 75(10)^\circ$, $2V_{\text{calc}} = 82^\circ$. The chemical composition (electron-microprobe data, C measured by gas chromatography of products of ignition at 1200°C, wt.%) is Na_2O 15.95, K_2O 5.65, CuO 27.34, C_2O_3 48.64, total 99.58. The empirical formula is $\text{K}_{0.96}\text{Na}_{3.04}\text{Cu}_{2.03}(\text{C}_{2.00}\text{O}_4)_4$ and the idealized formula is $\text{KNa}_3\text{Cu}_2(\text{C}_2\text{O}_4)_4$. The crystal structure was solved and refined to $R = 0.033$ based upon 4085 unique reflections with $I > 2\sigma(I)$. Antipinite is triclinic, space group $P\bar{1}$, $a = 7.1574(5)$, $b = 10.7099(8)$, $c = 11.1320(8) \text{ \AA}$, $\alpha = 113.093(1)$, $\beta = 101.294(1)$, $\gamma = 90.335(1)^\circ$, $V = 766.51(3) \text{ \AA}^3$, $Z = 2$. The strongest reflections of the powder X-ray diffraction pattern [d , Å (I ,%) (hkl)] are 5.22 (40) ($1\bar{1}1$), 3.47 (100) ($0\bar{3}2$), 3.39 (80) ($\bar{2}10$), 3.01 (30) ($0\bar{3}3$, 220), 2.543 (40) (122 , $0\bar{3}4$, 104), 2.481 (30) ($\bar{2}13$), 2.315 (30) ($1\bar{4}3$, $\bar{3}10$), 1.629 (30) ($1\bar{4}6$, $\bar{4}14$, $\bar{2}43$, $\bar{1}60$).

KEYWORDS: antipinite, new mineral, oxalate, crystal structure, guano, Pabellón de Pica, Chile.

Introduction

THE mountain of Pabellón de Pica belongs to a belt of Late Paleozoic and Mesozoic igneous rocks stretching along the northern coast of Chile

and bearing numerous bird guano deposits. Some details of the geological setting and the history of guano deposit development in the Tarapacá region are published elsewhere (Ericksen, 1981; Pankhurst and Hervé, 2007; Appelton and Notholt, 2002; Bojar *et al.*, 2010). The guano deposit located on Pabellón de Pica is the type locality of several other N-bearing and organic minerals, ammineite, $\text{CuCl}_2(\text{NH}_3)_2$ (Bojar *et al.*, 2010), joanneumite,

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DOI: 10.1180/minmag.2015.079.5.07



FIG. 1. Aggregate of antipinite crystals on halite. Field of view: 0.7 mm. Photograph: M. Burkhardt.

approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA 2014-027; Chukanov *et al.*, 2014a). The type specimen is deposited in the collections of the Technische Universität, Bergakademie Freiberg, Germany, inventory number 83870. The new mineral is named in memory of Mikhail Yuvenal'evich Antipin (1951–2013), a specialist in the crystallography and crystal chemistry of organometallic and coordination compounds. He was awarded the Prize of the Russian Academy of Sciences for these investigations. He also investigated minerals especially studying electron density distribution. M.Y. Antipin was the head of the laboratory where the crystal structure of antipinite was first solved.

$\text{Cu}(\text{C}_3\text{N}_3\text{O}_3\text{H}_2)_2(\text{NH}_3)_2$ (Bojar and Walter, 2012), chanabayaite, $\text{Cu}_4(\text{N}_3\text{C}_2\text{H}_2)_4(\text{NH}_3)_4\text{Cl}_2(\text{Cl},\text{OH})_2 \cdot \text{H}_2\text{O}$ (Chukanov *et al.*, 2013) and shilovite, $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$ (Chukanov *et al.*, 2014b). The new oxalate mineral antipinite, $\text{KNa}_3\text{Cu}_2(\text{C}_2\text{O}_4)_4$, was found by two of us (GF and GM) in the same guano deposit. The mineral and its name were

Occurrence, general appearance and physical properties

Antipinite occurs in the guano deposit situated in the lower part of the steep northern slope of Pabellón de Pica Mountain, 1.5 km south of Chanabaya village, Iquique Province, Tarapacá

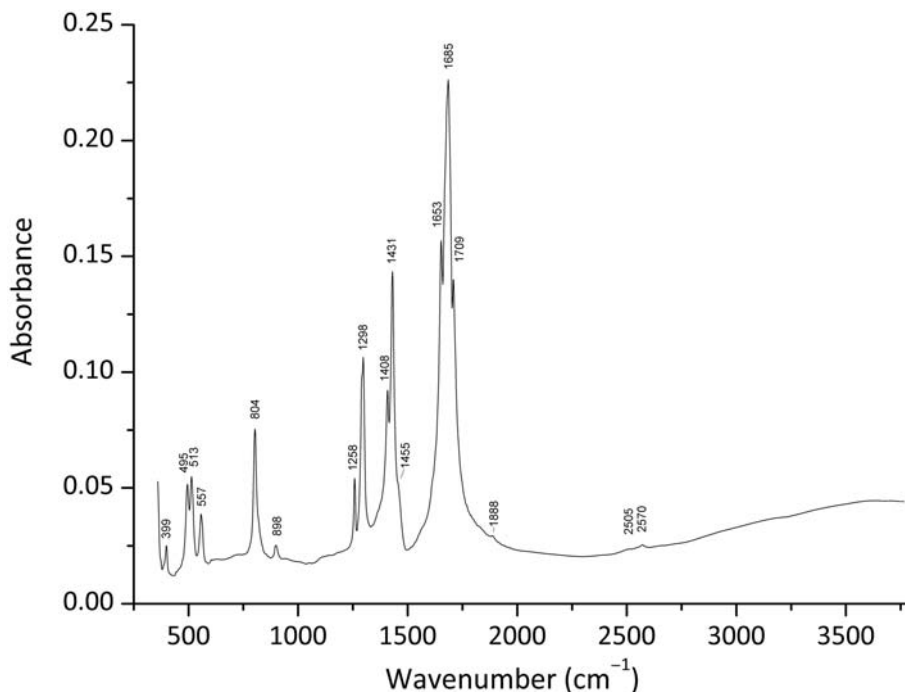


FIG. 2. The powder IR absorption spectrum of antipinite.

ANTIPINITE, A NEW MINERAL

TABLE 1. Analytical results for antipinite (mean of 5 spot analyses).

Constituent (element)	Content, wt. %	Range	Standard deviation	Constituent (oxide)	Content, wt. %	Probe standard
Na	11.83	11.42–12.24	0.34	Na ₂ O	15.95	Albite
K	6.35	5.97–6.95	0.35	K ₂ O	7.65	Sanidine
Cu	21.84	21.34–22.18	0.46	CuO	27.34	CuFeS ₂
C	16.22			C ₂ O ₃	48.64	
Total	56.24				99.58	

TABLE 2. Powder X-ray diffraction data for antipinite.*

<i>I</i> _{meas}	<i>d</i> _{meas}	<i>I</i> _{calc} **	<i>d</i> _{calc} **	<i>hkl</i>	<i>I</i> _{meas}	<i>d</i> _{meas}	<i>I</i> _{calc} **	<i>d</i> _{calc} **	<i>hkl</i>
40	5.22	30	5.26	1 $\bar{1}$ 1	20	2.090	7	2.104	$\bar{2}$ 42
							5	2.100	$\bar{2}$ 40
							8	2.084	$\bar{2}$ 14
100	3.47	80	3.44	0 $\bar{3}$ 2	10	2.067	4	2.078	222
80	3.39	60	3.39	$\bar{2}$ 10	20	1.989	6	2.003	213
							2	1.989	045
							2	1.984	322
30	3.01	5	3.02	0 $\bar{3}$ 3	10	1.831	6	1.838	312
		7	2.98	$\bar{2}$ 20			4	1.832	$\bar{1}$ 36
20	2.96	7	2.98	$\bar{2}$ 20	20	1.794	3	1.803	$\bar{2}$ 42
		4	2.94	$\bar{2}$ 21			3	1.791	$\bar{1}$ 51
							2	1.788	401
30	2.86	14	2.90	$\bar{2}$ 12	20	1.774	3	1.779	062
		14	2.90	$\bar{2}$ 21			2	1.776	053
		2	2.87	130			2	1.775	124
							2	1.767	$\bar{3}$ 42
20	2.77	7	2.80	031	10	1.728	3	1.728	061
		5	2.80	211					
		17	2.74	$\bar{2}$ 20					
20	2.691	6	2.691	$\bar{2}$ 23	10	1.707	5	1.708	$\bar{2}$ 25
							2	1.706	$\bar{1}$ 06
40	2.543	9	2.561	122	20b	1.698	5	1.708	$\bar{2}$ 25
		8	2.537	0 $\bar{3}$ 4			2	1.706	$\bar{1}$ 06
		7	2.533	$\bar{1}$ 04			4	1.696	420
							3	1.694	410
30	2.481	4	2.466	$\bar{2}$ 13	30b	1.629	3	1.629	146
							6	1.628	414
							2	1.627	$\bar{2}$ 43
							2	1.625	$\bar{1}$ 60
10	2.398	2	2.391	$\bar{2}$ 32	10	1.608	4	1.617	340
30	2.315	2	2.316	143	10	1.573	3	1.564	$\bar{2}$ 56
		2	2.315	$\bar{3}$ 10					
10	2.238	7	2.262	044	10	1.459	2	1.463	$\bar{4}$ 44
		7	2.221	310					

*The 100% reflection in the calculated powder X-ray diffraction pattern at 10.0 Å could not be observed experimentally because the data capture range is below 9 Å.

**Calculated from structural data (Brandenburg and Putz, 2005).

Region, Chile (20°55'S 70°08'W). Associated minerals are halite, salammoniac, chanabayaite and joanneumite. The gabbro host rock consists of amphibole, plagioclase and minor clinocllore, and contains accessory chalcopryrite.

Antipinite forms imperfect, isometric and short prismatic crystals up to 0.1 mm × 0.1 mm × 0.15 mm in size, as well as their random aggregates up to 0.6 mm across (Fig. 1). The colour of the mineral is blue. The streak is pale blue, almost white. Crystals of antipinite are translucent, with a vitreous lustre. The mineral is brittle, with Mohs hardness of 2. Cleavage is medium in three directions; directions of cleavage could not be determined because of the absence of perfect crystals. Antipinite is non-fluorescent under UV. Density measured by flotation in heavy liquids is 2.53(3) g cm⁻³. Density calculated from the empirical formula is 2.549 g cm⁻³. Antipinite is optically biaxial (+), $\alpha = 1.432(3)$, $\beta = 1.530(1)$, $\gamma = 1.698(5)$, $2V_{\text{meas}} = 75(10)^\circ$, $2V_{\text{calc.}} = 82^\circ$. Dispersion is strong, $r < v$. Pleochroism is strong, blue on Z, light blue on Y, colourless on X; the absorption scheme is $Z > Y > X$.

In order to obtain an infrared (IR) absorption spectrum, a powdered sample of antipinite was mixed with dried KBr, pelletized and analysed using an ALPHA FTIR spectrometer (Bruker Optics) with a resolution of 4 cm⁻¹ and 16 scans (Fig. 2). The IR spectrum of an analogous pellet of pure KBr was used as a reference. The assignment of absorption bands was made in accordance with Nyquist *et al.* (1996), Frost *et al.* (2003) and Frost (2004). Weak bands above 1800 cm⁻¹ correspond to combination modes. Bands in the range 1500–1750 cm⁻¹ correspond to asymmetric stretching vibrations of carboxylate groups and bands at 1280–1490 cm⁻¹ correspond to their symmetric stretching vibrations. Bands at 780–900 cm⁻¹ are assigned to in-plane bending vibrations of the carboxylate groups, possibly combined with C–C stretching vibrations. Bands from 495 to 557 cm⁻¹ are assigned to out-of-plane bending vibrations of the carboxylate groups. No absorptions associated with H₂O molecules, C–H bonds, CO₃²⁻, NO₃⁻ and OH⁻ ions are present in the IR spectrum. The IR spectrum of antipinite is unique and is considered as a good diagnostic tool for the mineral.

Chemical composition and chemical properties

Three electron microprobe analyses were carried out for Na, K and Cu using a VEGA TS 5130MM

TABLE 3. Crystal parameters, data collection and structure refinement details for antipinite.*

Crystal data	
Formula	KNa ₃ Cu ₂ (C ₂ O ₄) ₄
Formula weight	587.2
Absorption, μ (mm ⁻¹)	3.228
Density, D_x (g cm ⁻³)	2.546
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	7.1574(5)
b (Å)	10.7099(8)
c (Å)	11.1320(8)
α (deg)	113.093(1)
β (deg)	101.294(1)
γ (deg)	90.335(1)
V (Å ³)	766.5(1)
Z	2
Crystal size (mm)	0.10 × 0.15 × 0.15
Data collection	
Diffractometer	SMART APEX2 CCD
Radiation; wavelength (Å)	MoK α ; 0.71073
Data collection method	ω
Temperature (K)	293
$F(000)$	572
Theta range for data collection (°)	2.04 to 33.67
Index ranges	-11 < h < 11 -16 < k < 15 -16 < l < 17
Reflections collected	11,361
Unique reflections / R_{int}	5553 / 2.63
Observed reflections, $I_{\text{obs}} > 2\sigma(I)$	4085
Refinement	
Refinement method	Full matrix least square on F
Weighting scheme:	$w = 1/(\sigma^2 F + 0.000529 F^2)$
Goof on F	1.03
Final R indices	$R_1 = 3.27$; $wR_2 = 4.12$
$\Delta\rho_{\text{min}} / \Delta\rho_{\text{max}}$ (e Å ⁻³)	-0.49 / 0.33

* $R_1 = \sum ||F_{\text{obs}}| - |F_{\text{calc}}|| / \sum |F_{\text{obs}}|$; $wR_2 = \{ \sum [w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2] / \sum [w(F_{\text{obs}}^2)^2] \}^{1/2}$; Goof = $\{ \sum [w(F_{\text{obs}}^2 - F_{\text{calc}}^2)] / (n-p) \}^{1/2}$ where n is the number of reflections and p is the number of refined parameters.

scanning electron microscope equipped with an EDX analyser (INCA Si(Li) detector), at an operating voltage of 20 kV and a beam current of 0.6 nA, beam rastered on an area 16 μm × 16 μm in order to minimize unstable sample damage. The program INCA Energy 200 was used for analytical data calculations. Attempts to use the wavelength dispersive spectroscopy mode with a higher beam current were unsuccessful because of the instability

ANTIPINITE, A NEW MINERAL

 TABLE 4. Fractional atom coordinates and equivalent isotropic displacement parameters (\AA^2) for antipinite.

Site	x/a	y/b	z/c	U_{eq}
K1	-0.11025(6)	0.81681(5)	0.47781(5)	0.0205(2)
Cu1	0.38642(4)	0.83639(3)	0.47877(2)	0.0173(1)
Cu2	-0.21446(4)	0.53028(3)	0.56107(3)	0.0188(1)
Na1	-0.2311(1)	0.5411(1)	0.0532(1)	0.0188(3)
Na2	0.0193(1)	0.0982(1)	0.9013(1)	0.0247(3)
Na3	0.5392(1)	0.2206(1)	0.0123(1)	0.0256(3)
C1	0.3500(3)	0.0149(2)	0.7214(2)	0.0156(6)
C2	0.5679(3)	0.0080(2)	0.7266(2)	0.0151(6)
C3	0.4220(3)	0.6845(2)	0.2264(2)	0.0146(6)
C4	-0.0978(3)	0.7558(2)	0.7875(2)	0.0177(7)
C5	-0.2479(3)	0.4296(2)	0.2942(2)	0.0167(7)
C6	0.2047(3)	0.6904(2)	0.2229(2)	0.0165(7)
C7	-0.2117(3)	0.6558(2)	-0.1776(2)	0.0165(7)
C8	0.6467(3)	0.3217(2)	0.3239(2)	0.0188(7)
O1	0.5299(2)	0.7470(2)	0.3420(1)	0.0186(5)
O2	0.2418(2)	0.9507(2)	0.6052(2)	0.0197(5)
O3	-0.3478(3)	0.3520(2)	0.4486(2)	0.0253(6)
O4	0.1631(2)	0.7609(2)	0.3357(2)	0.0213(5)
O5	0.6816(2)	0.0751(2)	0.8316(2)	0.0204(5)
O6	-0.0899(2)	0.7120(2)	0.6636(2)	0.0215(5)
O7	0.0899(2)	0.6330(2)	0.1164(2)	0.0250(6)
O8	0.4768(2)	0.6271(2)	0.1214(2)	0.0196(5)
O9	0.2955(2)	0.0840(2)	0.8229(2)	0.0253(6)
O10	-0.1604(2)	0.5324(2)	0.3985(2)	0.0211(5)
O11	-0.2784(2)	0.5427(2)	0.7244(2)	0.0230(6)
O12	0.6111(2)	0.9347(2)	0.6151(2)	0.0195(5)
O13	-0.0240(3)	0.8656(2)	0.8756(2)	0.0273(6)
O14	-0.2483(2)	0.4105(2)	0.1784(2)	0.0229(6)
O15	0.5664(2)	0.2183(2)	1.2307(2)	0.0253(6)
O16	-0.2334(2)	0.6901(2)	-0.0624(2)	0.0217(6)

of the mineral. The contents of other elements with atomic numbers >8 are below detection limits. Carbon was measured using gas chromatography (CHN analysis) of the products by annealing at 1200°C with a Vario Micro cube analyser (Elementar GmbH, Germany). Hydrogen was not measured because of the absence of absorption bands for C–H bonds, H_2O molecules and OH⁻ groups in the IR spectrum. Analytical data are given in Table 1. The empirical formula (based on 16 O a.p.f.u.) is $\text{K}_{0.96}\text{Na}_{3.04}\text{Cu}_{2.03}(\text{C}_{2.00}\text{O}_4)_4$. The simplified formula is $\text{KNa}_3\text{Cu}_2(\text{C}_2\text{O}_4)_4$, which requires K 6.66, Na 11.74, Cu 21.64, C 16.36, O 43.59, total 99.99 wt.%. The Gladstone–Dale compatibility index is: $1 - (K_p/K_c) = 0.015$ ('superior'). Antipinite dissolves in water. A concentrated aqueous solution of antipinite has a pH of 9. An aqueous solution of the halite matrix without antipinite has a pH of

7. Tests with HCl and BaCl_2 show the absence of CO_3^{2-} and SO_4^{2-} groups. A test with sodium hexanitrocobaltate(III) solution confirms the presence of K.

X-ray diffraction data and crystal structure

Powder X-ray data were measured with Debye–Scherrer method (camera diameter 57.3 mm) using $\text{CuK}\alpha$ radiation. The data are listed in Table 2. Unit-cell parameters refined from the powder data are $a = 7.17(2)$, $b = 10.73(2)$, $c = 11.17(2)$ \AA , $\alpha = 113.07(6)$, $\beta = 101.29(5)$, $\gamma = 90.39(5)^\circ$, $V = 771(2)$ \AA^3 . Single-crystal X-ray data were collected at room temperature with a Bruker SMART APEX2 CCD diffractometer (Bruker, 2009) with graphite monochromatized

TABLE 5. Anisotropic displacement parameters (\AA^2) for antipinite.

Site	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K1	0.0160(2)	0.0235(2)	0.0217(2)	-0.0009(2)	0.0060(2)	0.0079(2)
Cu1	0.0137(1)	0.0202(1)	0.0119(1)	-0.00115(9)	0.00452(9)	-0.0008(1)
Cu2	0.0280(2)	0.0144(1)	0.0120(1)	-0.0040(1)	0.0067(1)	0.00207(9)
Na1	0.0182(4)	0.0206(4)	0.0170(4)	-0.0014(3)	0.0054(3)	0.0061(3)
Na2	0.0188(4)	0.0307(5)	0.0200(4)	-0.0026(4)	0.0061(4)	0.0045(4)
Na3	0.0272(5)	0.0278(5)	0.0150(4)	-0.0029(4)	0.0051(4)	0.0013(4)
C1	0.0148(9)	0.0137(9)	0.0160(9)	-0.0013(7)	0.0055(7)	0.0026(7)
C2	0.0163(9)	0.0139(9)	0.0146(9)	0.0001(7)	0.0052(7)	0.0042(7)
C3	0.0139(9)	0.0140(9)	0.0148(9)	-0.0003(7)	0.0050(7)	0.0038(7)
C4	0.021(1)	0.0157(9)	0.0153(9)	0.0008(8)	0.0046(8)	0.0049(7)
C5	0.019(1)	0.0145(9)	0.0161(9)	0.0015(7)	0.0039(8)	0.0058(7)
C6	0.0154(9)	0.0172(9)	0.0147(9)	-0.0006(7)	0.0041(7)	0.0036(7)
C7	0.019(1)	0.0159(9)	0.0137(9)	0.0012(7)	0.0055(8)	0.0046(7)
C8	0.023(1)	0.0161(9)	0.0159(9)	-0.0013(8)	0.0036(8)	0.0058(8)
O1	0.0123(7)	0.0245(8)	0.0125(7)	-0.0003(6)	0.0023(5)	0.0008(6)
O2	0.0122(7)	0.0234(8)	0.0149(7)	-0.0014(6)	0.0024(5)	-0.0009(6)
O3	0.040(1)	0.0180(7)	0.0141(7)	-0.0109(7)	0.0065(7)	0.0027(6)
O4	0.0145(7)	0.0273(8)	0.0132(7)	-0.0009(6)	0.0043(6)	-0.0018(6)
O5	0.0174(7)	0.0217(8)	0.0157(7)	-0.0009(6)	0.0015(6)	0.0017(6)
O6	0.0316(9)	0.0163(7)	0.0140(7)	-0.0043(6)	0.0072(6)	0.0024(6)
O7	0.0162(7)	0.0348(9)	0.0153(7)	-0.0027(7)	0.0013(6)	0.0018(7)
O8	0.0185(7)	0.0213(7)	0.0149(7)	-0.0003(6)	0.0069(6)	0.0015(6)
O9	0.0206(8)	0.0275(8)	0.0173(8)	-0.0029(6)	0.0093(6)	-0.0042(6)
O10	0.0311(9)	0.0165(7)	0.0133(7)	-0.0055(6)	0.0068(6)	0.0026(6)
O11	0.0340(9)	0.0174(7)	0.0153(7)	-0.0061(6)	0.0101(7)	0.0020(6)
O12	0.0161(7)	0.0227(8)	0.0135(7)	-0.0006(6)	0.0058(6)	-0.0005(6)
O13	0.041(1)	0.0174(7)	0.0173(8)	-0.0073(7)	0.0081(7)	-0.0001(6)
O14	0.0322(9)	0.0230(8)	0.0125(7)	-0.0046(7)	0.0044(6)	0.0063(6)
O15	0.0346(9)	0.0195(8)	0.0167(7)	-0.0075(7)	0.0019(7)	0.0037(6)
O16	0.0273(8)	0.0236(8)	0.0142(7)	0.0018(6)	0.0088(6)	0.0055(6)

MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) and a CCD detector using the ω scanning mode. The following triclinic unit-cell parameters were obtained by least-squares refinement: $a = 7.1574(5)$, $b = 10.7099(8)$, $c = 11.1320(8) \text{ \AA}$, $\alpha = 113.093(1)$, $\beta = 101.294(1)$, $\gamma = 90.335(1)^\circ$, $V = 766.5(1) \text{ \AA}^3$, space group $P\bar{1}$. A total of 11,361 reflections within the sphere limited by $\theta = 33.67^\circ$ were measured. Raw data were integrated using the program *SAINTE* and then scaled, merged and corrected for Lorentz-polarization effects using the *SADABS* package. The experimental details of the data collection and refinement results are listed in Table 3. The initial structure model was determined by the ‘charge-flipping’ method (Palatinus and Chapuis, 2007) and refined to $R = 3.27\%$ [$4085 I > 2\sigma(I)$] in the anisotropic approximation using the

crystallographic program *Jana2006* (Petricek *et al.*, 2006). Final atom parameters are shown in Tables 4 and 5. Interatomic distances are presented in Table 6.

The structure of antipinite consists of planar C_2O_4 units, a layer of sodium atoms and a layer of Cu atoms with pairs of K atoms (Fig. 3). Both layers are coplanar with the (001) plane and are joined by an O atom shared with oxalate groups. There are eight independent oxalate groups with bond lengths C–O and C–C in the ranges 1.219–1.288 and 1.551–1.560 \AA , respectively. The Cu atoms Cu1 and Cu2 are coordinated to two oxalate groups with orthogonal disposition of CuO_4 planes (Fig. 4a). The Cu-centred polyhedra are square bipyramids with two O atoms forming long Cu–O bonds (Table 6, Fig. 4b). Thus the coordination

ANTIPINITE, A NEW MINERAL

TABLE 6. Interatomic distances (Å) in the crystal structure of antipinite.

K1	O1	2.654(1)	Na3	O9	2.395(2)
	O4	2.678(2)		O14	2.404(2)
	O6	2.696(2)		O15	2.411(2)
	O2	2.717(1)		O5	2.424(2)
	O12	2.760(2)		O16	2.470(2)
	O10	2.818(2)		O8	2.593(2)
	O2	3.071(2)		Mean	2.450
Mean		2.771			
Cu1	O4	1.929(1)	C1–O9	Oxalate group 1	
	O12	1.941(1)			1.223(3)
	O1	1.942(2)		C1–O2	1.285(2)
	O2	1.945(2)		C1–C2	1.553(3)
	O3	2.482(2)		C2–O5	1.227(2)
	O12	3.019(2)		C2–O12	1.282(3)
Mean		2.210			
Cu2	O11	1.916(2)	C3–O8	Oxalate group 2	
	O6	1.930(1)			1.232(3)
	O10	1.932(2)		C3–O1	1.277(2)
	O3	1.939(2)		C3–C6	1.550(3)
	O10	2.764(2)		C6–O7	1.225(2)
	O3	3.382(2)		C6–O4	1.281(3)
Mean		2.311			
Na1	O14	2.347(2)	C4–O13	Oxalate group 3	
	O7	2.354(2)			1.228(2)
	O16	2.410(2)		C4–O6	1.284(3)
	O8	2.427(2)		C4–C7	1.550(4)
	O8	2.448(1)		C7–O16	1.230(3)
	O7	2.464(2)		C7–O11	1.280(2)
Mean		2.408			
Na2	O9	2.295(2)	C5–O14	Oxalate group 4	
	O13	2.352(2)			1.223(3)
	O5	2.369(2)		C5–O10	1.287(2)
	O13	2.404(2)		C5–C8	1.550(4)
	O16	2.530(2)		C8–O15	1.221(2)
Mean		2.390	C8–O3	1.288(3)	

(4+2) of Cu1 and Cu2 ions corresponds to the most common type (Burns and Hawthorne, 1995, 1996; Krivovichev *et al.*, 2013) where apical ligands are further from the central atom due to the Jahn-Teller effect. The Cu2 bipyramid is connected via common edges to form columns running along the *a* axis which are combined into a layer by pairs of the Cu1 bipyramid (Fig. 4). Potassium atoms occupy large loops in the Cu layer. Each Na atom is coordinated with O atoms of the oxalate groups. The Na1O₆ and Na3O₆ polyhedra are distorted octahedra and are combined in bands. The Na2 atom is five-coordinate and these polyhedra connect bands via common edges to form a layer (Fig. 5).

Discussion

Antipinite is the 19th mineral containing the oxalate anion, C₂O₄²⁻. Other copper oxalates known in Nature are moolooite, Cu(C₂O₄)_{*n*}·*n*H₂O (*n* < 1) and wheatleyite, Na₂Cu(C₂O₄)₂·2H₂O. No minerals or synthetic compounds related to antipinite in terms of crystal structure are known. Crystallographic data for Cu oxalates compounds are summarized in Table 7. The crystal structure of the synthetic analogue of wheatleyite, Na₂Cu(C₂O₄)₂·2H₂O (Gleizes *et al.*, 1980; Fig. 6), consists of columns of Cu-centred octahedra running along the *a* axis (*a* = 3.6 Å) and corrugated layers of seven-coordinate Na-centred polyhedra

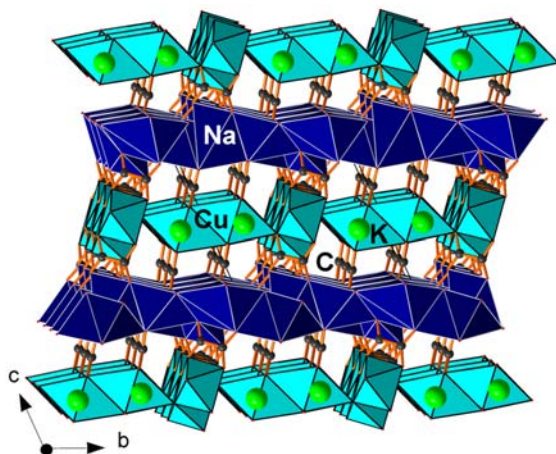


FIG. 3. General view of the antipinite structure projected on (100). The orange lines indicate C–O bonds.

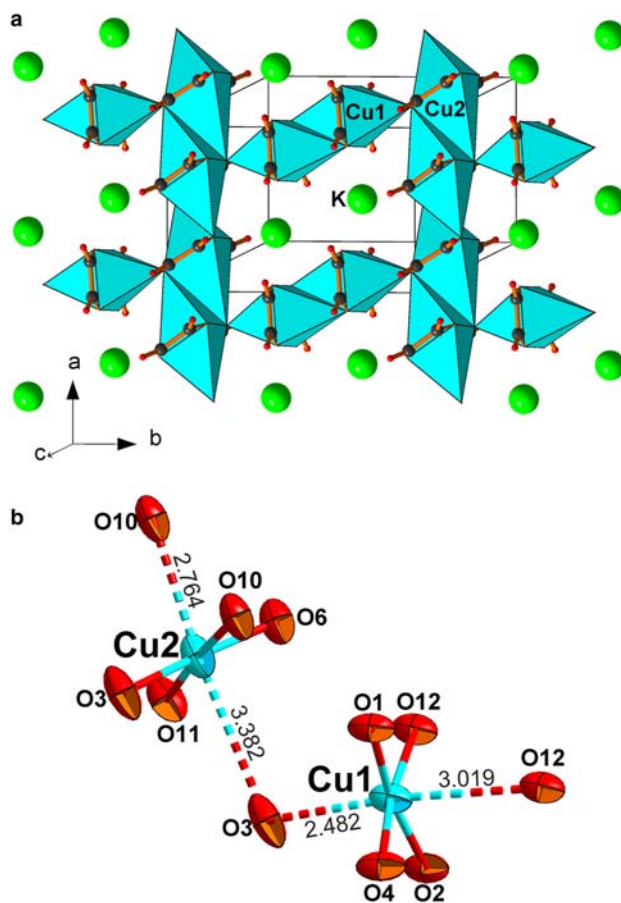


FIG. 4. Layer of Cu-centred bipyramids in the structure of antipinite (*a*) and a representation of high Jahn-Teller distortion of Cu-polyhedra (*b*).

ANTIPINITE, A NEW MINERAL

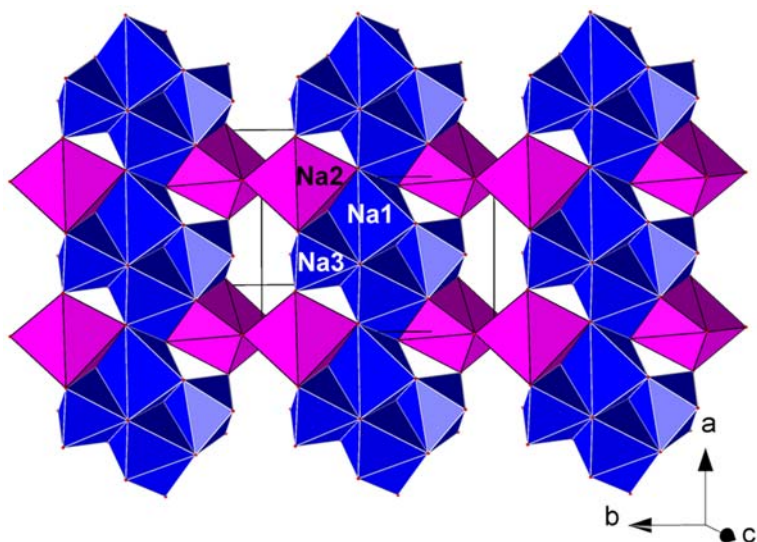


FIG. 5. Layer of Na-centred polyhedra in the structure of antipinite.

TABLE 7. Crystallographic data for natural and synthetic copper oxalates.

Mineral / Compound	Space group, <i>Z</i>	Unit-cell parameters			References*
		<i>a</i> , Å α , °	<i>b</i> , Å β , °	<i>c</i> , Å γ , °	
Moolooite, $\text{Cu}(\text{C}_2\text{O}_4) \cdot n\text{H}_2\text{O}$ ($n = 0.4-0.7$)	<i>Pnmm</i> , 1	5.381–5.348	5.625–5.639	2.548–2.559	1, 2, 3
$\text{Cu}(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$	<i>Pcca</i> , 4	9.760	6.603	10.500	4
$\text{Cu}(\text{C}_2\text{O}_3\text{OH})_4 \cdot 8\text{H}_2\text{O}$	<i>P</i> $\bar{1}$, 1	6.947	8.900	9.045	5
		107.371	98.029	96.476	
Wheatleyite, $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$	<i>P</i> $\bar{1}$, 1	7.536	9.473	3.576	6
		81.9	103.77	108.09	
$\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	<i>P</i> $\bar{1}$, 1	3.583	9.649	7.549	8
		109.07	76.38	103.32	
Antipinite, $\text{KNa}_3\text{Cu}_2(\text{C}_2\text{O}_4)_4$	<i>P</i> $\bar{1}$, 2	7.157	10.710	11.132	This work
		113.093	101.294	90.335	
$\text{K}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$	<i>P2</i> $_1/n$, 2	3.777	14.819	10.756	9
			93.18		
$\text{Rb}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	<i>P</i> $\bar{1}$, 2	7.000	8.949	8.982	10
		108.05	97.69	97.99	
$\text{Sr}_2\text{Cu}(\text{C}_2\text{O}_4)_3 \cdot 7\text{H}_2\text{O}$	<i>P</i> $\bar{1}$, 2	6.349	10.258	15.737	11
		73.21	93.66	76.44	
$\text{Cs}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	<i>P</i> $\bar{1}$, 2	9.298	9.117	7.132	12
		97.524	97.410	107.522	
$\text{BaCu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$	<i>P</i> $\bar{1}$, 2	9.209	10.938	6.547	13, 14, 15
		100.83	99.65	85.45	

*References: 1, Clarke and Williams (1986); 2, Chisholm *et al.* (1987); 3, Schmittler (1968); 4, Wu and Zhai (2007); 5, Yesilel *et al.* (2010); 6, Rouse *et al.* (1986); 7, Gleizes *et al.* (1980); 8, Chananont *et al.* (1980); 9, Jian *et al.* (2001); 10, Kolitsch (2004); 11, Insausti *et al.* (1994); 12, Pannhorst and Löhn (1974); 13, Hallock, *et al.* (1990); 14, Bouayad *et al.* (1995); 15, Kasthuri *et al.* (1996).

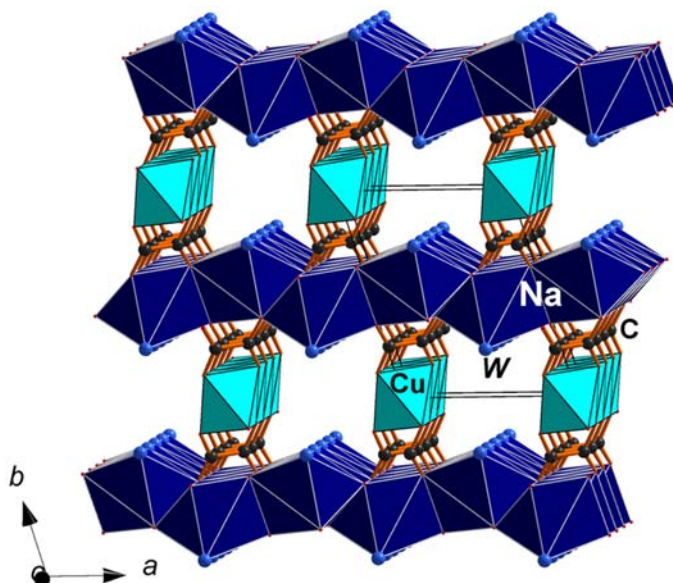


FIG. 6. The crystal structure of wheatleyite.

perpendicular to the b axis ($b = 9.5 \text{ \AA}$). The columns and the layers in wheatleyite are combined by oxalate anions and H bonds of water molecules in the vertices of Na-centred polyhedra.

Antipinite is a supergene mineral formed in the contact zone between a deeply altered guano deposit and chalcopyrite-bearing gabbro. Guano was the source of oxalate groups, and oxidized chalcopyrite was the source of Cu for antipinite and associated chanabayaite and joanneumite (Bojar and Walter, 2012; Chukanov *et al.*, 2013).

Antipinite is the only known anhydrous Cu oxalate compound and the only one that simultaneously contains Na and K.

Acknowledgements

This study was supported by the Russian Scientific Foundation grants 14-17-00048 (characterization excluding XRD and crystal structure) and 14-17-00071 (X-ray diffraction studies and crystal structure). The authors are grateful to P. Leverett, I. Grey and M.J. Sciberras for reviewing the paper and for their helpful comments and corrections.

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