

## AMMINEITE, $\text{CuCl}_2(\text{NH}_3)_2$ , A NEW SPECIES CONTAINING AN AMMINE COMPLEX: MINERAL DATA AND CRYSTAL STRUCTURE

HANS-PETER BOJAR<sup>§</sup>

*Department of Mineralogy, Universalmuseum Joanneum, Weinzöttlstraße 16, A-8045 Graz, Austria*

FRANZ WALTER

*Institute of Earth Sciences (Mineralogy and Petrology), University of Graz, Universitätsplatz 2, A-8010 Graz, Austria*

JUDITH BAUMGARTNER

*Institute of Inorganic Chemistry, Technical University of Graz, Stremayrgasse 16/IV, A-8010 Graz, Austria*

GUNNAR FÄRBER

*Bornsche Str. 9, D-39326 Samswegen, Germany*

### ABSTRACT

Ammineite,  $\text{CuCl}_2(\text{NH}_3)_2$ , the first mineral containing an ammine complex, was discovered at Calleta Pabellon de Pica, Tarapaca region, Chile. The mineral is named for the first described ammine complex as naturally occurring crystals. Ammineite occurs as hypidiomorphic mm-sized blue crystals and also as powdery masses, associated with halite, atacamite, salammoniac and darapskite. The Mohs hardness is 1, the streak is light blue, the luster is vitreous, and the calculated density is  $2.38 \text{ g/cm}^3$  at 100 K and  $2.31 \text{ g/cm}^3$  at 293 K. The mineral is biaxial positive, with  $\alpha$  1.676(2),  $\beta$  1.715(2),  $\gamma$  1.785(2),  $2V_{\text{calc}} 76^\circ$  (for  $\lambda$  589 nm). The pleochroism for  $\beta$  and  $\gamma$  is dark blue, and for  $\alpha$ , light blue; the optical orientation is  $X = \mathbf{c}$ ,  $Y = \mathbf{b}$  and  $Z = \mathbf{a}$ . The crystal structure has been solved by direct methods and refined to an *R*1 value of 2.4% on the basis of 231 unique observed reflections at 100 K. Ammineite is orthorhombic, space group *Cmcm*,  $a$  7.688(1),  $b$  10.645(2),  $c$  5.736(1) Å,  $V$  469.4(2) Å<sup>3</sup> from single-crystal XRD data at 100 K, and  $a$  7.790(1),  $b$  10.643(1),  $c$  5.838(1) Å,  $V$  484.1(1) Å<sup>3</sup>, from powder XRD data at 293 K,  $Z = 4$ . The strongest six X-ray powder-diffraction lines [ $d$  in Å(*D*)(*hkl*)] are: 6.285(69)(110), 4.278(55)(111), 3.898(56)(200), 2.920(100)(002), 2.763(36)(221) and 2.660(90)(040,112). The chemical composition of ammineite, Cu 37.60, Cl 41.67, N 16.54, H 3.32 wt.%, was determined from both the results of electron microprobe (for Cu and Cl) and elemental analyzer (for N and H). The empirical formula gives  $\text{Cu}_{1.00}\text{Cl}_{1.99}\text{N}_{1.99}\text{H}_{5.57}$  or, ideally,  $\text{CuCl}_2(\text{NH}_3)_2$ . The basic structural unit, the trans-diammine-dichlorido-copper(II) complex, is layered parallel to (001) and connected to the parallel layered complexes up and down nearly perpendicular by two long Cu–Cl bonds. The resulting polyhedron is a [4 + 2]-distorted  $\text{Cu}^{2+} \text{N}_2\text{Cl}_4$  octahedron. The distorted octahedra are connected by shared edges to form zigzag chains running along [001]. The chains are linked by hydrogen bonding between the equatorial  $\text{NH}_3$  groups and the equatorial Cl atoms of the adjacent chains. Heating experiments with synthetic  $\text{CuCl}_2(\text{NH}_3)_2$  in air show that trans-diammine-dichlorido-copper(II) is stable up to 120°C. After 75 hours and heating to 200°C, the sample in air consists of copper chloride hydroxide hydrate and the synthetic analogue of eriochalcite,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , whereas the sample of  $\text{CuCl}_2(\text{NH}_3)_2$  sealed in a glass tube was unchanged after 75 hours at 200°C.

*Keywords:* ammineite, new mineral species, crystal structure, trans-diammine-dichlorido-copper(II).

### SOMMAIRE

L'ammineïte,  $\text{CuCl}_2(\text{NH}_3)_2$ , le premier minéral à contenir un complexe aminé, a été découvert à Calleta Pabellon de Pica, région de Tarapaca, au Chili. Le nom souligne justement la présence du complexe aminé. L'ammineïte se présente en cristaux bleus millimétriques subidiomorphes ainsi qu'en masses pulvérulentes; lui sont associés halite, atacamite, salammoniac et darapskite. La dureté de Mohs est 1, la rayure est bleu pâle, l'éclat est vitreux, et la densité calculée est  $2.38 \text{ g/cm}^3$  à 100 K et  $2.31 \text{ g/cm}^3$  à 293 K. Le minéral est biaxe positif, avec  $\alpha$  1.676(2),  $\beta$  1.715(2),  $\gamma$  1.785(2),  $2V_{\text{calc}} 76^\circ$  (pour  $\lambda$  589 nm). Le schéma pléochroïque est:  $\alpha$  bleu pâle,  $\beta$  et  $\gamma$  bleu foncé; l'orientation optique est  $X = \mathbf{c}$ ,  $Y = \mathbf{b}$  et  $Z = \mathbf{a}$ . Nous avons résolu la structure

<sup>§</sup> E-mail address: hans-peter.bojar@museum-joanneum.at

crystalline par méthodes directes, et nous l'avons affiné jusqu'à un résidu  $R1$  de 2.4% sur une base de 231 réflexions uniques observées à 100 K. L'ammineite est orthorhombique, groupe spatial  $Cmcm$ ,  $a$  7.688(1),  $b$  10.645(2),  $c$  5.736(1) Å,  $V$  469.4(2) Å<sup>3</sup> selon les données en diffraction X prélevées sur monocristal à 100 K, et  $a$  7.790(1),  $b$  10.643(1),  $c$  5.838(1) Å,  $V$  484.1(1) Å<sup>3</sup> selon les données acquises avec une poudre à 293 K,  $Z = 4$ . Les six raies les plus intenses du spectre de diffraction X (méthode des poudres) [ $d$  in Å( $hkl$ )] sont: 6.285(69)(110), 4.278(55)(111), 3.898(56)(200), 2.920(100)(002), 2.763(36)(221) et 2.660(90)(040,112). Nous avons déterminé la composition chimique de l'ammineite, Cu 37.60, Cl 41.67, N 16.54, H 3.32% (poids), avec une microsonde électronique (Cu, Cl) et un analyseur élémentaire (N, H). La formule empirique est  $Cu_{1.00}Cl_{1.99}N_{1.99}H_{5.57}$  ou, de façon idéale,  $CuCl_2(NH_3)_2$ . L'unité structurale fondamentale, le complexe trans-diammine-dichlorido-cuivre(II), est stratifiée parallèle à (001) et liée aux complexes parallèles alignés de façon presque perpendiculaire par des liaisons Cu–Cl relativement longues. Le polyèdre qui en résulte est un octaèdre [4 + 2] difforme,  $Cu^{2+}N_2Cl_4$ . Ces octaèdres difformes sont agencés par arêtes partagées pour former des chaînes en zigzag le long de [001]. Ces chaînes sont interliées par liaisons hydrogène entre les groupes  $NH_3$  équatoriaux et les atomes de Cl équatoriaux des chaînes adjacentes. Nos expériences montrent que le  $CuCl_2(NH_3)_2$  synthétique, le trans-diammine-dichlorido-cuivre(II), serait stable jusqu'à 120°C. Après 75 heures et chauffage jusqu'à 200°C, l'échantillon contient un mélange de chlorure de cuivre hydroxylé hydraté et de l'analogue synthétique de l'ériochalcite,  $CuCl_2 \cdot 2H_2O$ , tandis que dans un tube de verre scellé, l'échantillon de  $CuCl_2(NH_3)_2$  demeure inchangé après 75 heures à 200°C.

(Traduit par la Rédaction)

**Mots-clés:** ammineite, nouvelle espèce minérale, structure cristalline, trans-diammine-dichlorido-cuivre(II).

## INTRODUCTION

The new mineral ammineite,  $CuCl_2(NH_3)_2$ , was found by Reynaldo Contrera and Gunnar Färber at Calleta Pabellon de Pica (20°55'S, 70°08'W), Tarapaca region, Chile, in an adit possibly part of a long-abandoned mine (de Rivero 1829). The name *ammineite* is given because it is the first mineral with an ammine complex in its crystal structure. The mineral and its name were approved by IMA–CNMNC (IMA 2008–32). The holotype material is deposited at the Universalmuseum Joanneum, Graz, Austria (mineralogical collection, catalogue number 84.935). We present here a full description of the new species, including details of its structure.

## GEOLOGICAL BACKGROUND

The Andes are the most prominent geomorphological feature of Chile. The northern part of Chile is characterized by the Atacama Desert, considered to be the driest place on Earth. Geotectonically, Calleta Pabellon de Pica is part of the Coastal Cordillera, in which Late Paleozoic to Mesozoic igneous rocks are predominant (Pankhurst & Herve 2007). The coarse-grained host rock of our sample consists of amphibole, plagioclase and minor clinocllore. The host rock is probably classified as a hornblende gabbro, though an unambiguous classification was not possible owing to the small size of the rock sample available. A minor component of the rock sample is intergranular chalcocopyrite. The guano of the Tarapaca region was deposited on these plutonic rocks and was exploited since pre-Inca cultures as fertilizer. These deposits (Pabellon de Pica, Punta de Lobos, Guannlios) probably yielded most of the guano produced in Chile. Between 1906 and 1937, around 635000 t of guano was produced. Afterward,

the production decreased because of a serious decline in the population of guano-producing birds (Appelton & Nothold 2002). The guano is produced along the coast by guano birds like cormorants, pelicans and boobies. Bird guano is rich in  $(NH_3)$ . The major source of  $(NH_3)$  is the breakdown of urea or uric acid excretions (Blackall *et al.* 2008). Thus ammineite is likely to be the product of the interaction between  $NH_3$  from guano and Cu from the plutonic rocks.

## APPEARANCE AND PHYSICAL PROPERTIES

The main component of the mineralization is halite. The halite forms coarse-grained centimeter-thick layers and crack fillings in a hornblende gabbro (Fig. 1). Halite is interspersed with millimetric to centimetric solution-cavities that are filled with masses of intense blue ammineite and atacamite (Fig. 2). Salammoniac forms pale blue layers on halite. Narrow voids in halite are occasionally filled with sulfates and carbonates like darapskite, glauberite and thermonatrite. This paragenesis is accompanied by further unknown mineral phases. Mostly these are powdery crusts or small crystals and are composed mainly of copper, nitrogen, carbon, hydrogen and chlorine. The examination of these phases is still in progress. One minor constituent is darapskite, which forms millimetric sprays of thin needles.

Ammineite is product of reaction of a copper mineral with guano. Ammineite occurs as intense sky-blue hypidiomorphic grains up to 3 millimeters across, elongate along [100], with the dominant form {001} (Fig. 3) and also as powdery masses in solution cavities of halite.

Ammineite is deep to sky blue, transparent to translucent, with a vitreous luster; it is non-fluorescent. The tenacity is weak, and the Mohs hardness is estimated to be approximately 1. Among the cleavages, {001} is

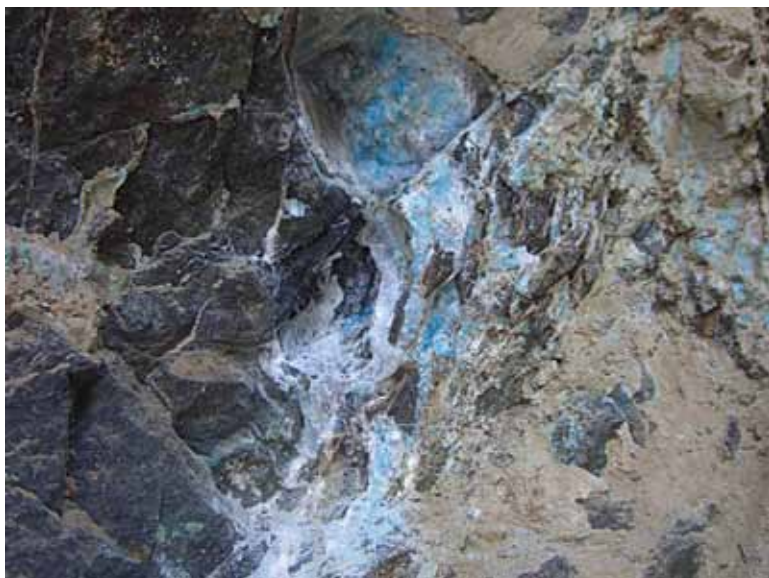


FIG. 1. Crack fillings of ammineite and halite in a hornblende gabbro. Pabellon de Pica, Tarapaca region, Chile. Field of view ~1 m across.

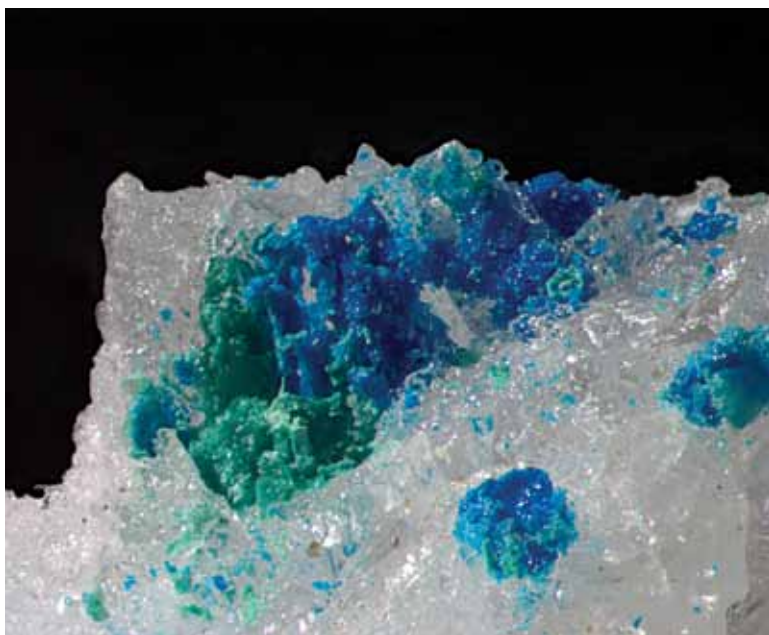


FIG. 2. Ammineite (blue) and atacamite (green) on halite. Pabellon de Pica, Tarapaca region, Chile. Field of view 2 cm across.

perfect, and {110} is good. The calculated density is 2.38 g/cm<sup>3</sup> from structure refinement at 100 K, and 2.31 g/cm<sup>3</sup> with the empirical formula and the cell volume obtained from powder data at 293 K. The density was not measured owing to the instability of ammineite in water.

The mineral is optically biaxial (+); its optical constants measured with 589 nm on a spindle stage are  $\alpha$  1.676(2),  $\beta$  1.715(2),  $\gamma$  1.785(2), with the orientation  $X = \mathbf{c}$ ,  $Y = \mathbf{b}$  and  $Z = \mathbf{a}$ . The 2V and dispersion could not be observed because of the intense blue color of the mineral. The calculated 2V is 76°. Pleochroism for  $\beta$  and  $\gamma$  is dark blue and for  $\alpha$ , light blue.

### SPECTROSCOPY

The FTIR examinations were performed with a diamond Universal ATR sampling accessory on a Perkin Elmer Spectrum 100. The ATR-FTIR spectrum represents a sum of 20 scans with a resolution of 2 cm<sup>-1</sup>. No ATR correction was performed. The sample was dried in a compartment drier, powdered in an agate mortar, and mounted on the ATR accessory. The infrared spectrum of ammineite is compared with that of synthetic trans-diammine-dichlorido-copper(II) in Figure 4.

Most of the infrared frequencies of ammineite can be assigned to the (NH<sub>3</sub>) group. According to Nakamoto

(1997) and Layton *et al.* (1966), antisymmetric and symmetric (NH<sub>3</sub>) stretching, (NH<sub>3</sub>) degenerate deformation, (NH<sub>3</sub>) symmetric deformation, and (NH<sub>3</sub>) rocking vibrations appear in the regions 3400–3000, 1650–1550, 1370–1000 and 950–590 cm<sup>-1</sup>, respectively. Ammineite and trans-diammine-dichlorido-copper(II) give in the (NH<sub>3</sub>) stretching region a band triplet (3316, 3241, 3157 cm<sup>-1</sup>) similar to trans-diammine-dichlorido-palladium (II) (3320, 3240, 3181 cm<sup>-1</sup>) (Layton *et al.* 1966), whereas hexammine complexes have only a band duplet (see compilation list in Nakamoto 1997). The degenerate deformation vibration of ammineite  $\delta_d$ -(NH<sub>3</sub>) has a wavenumber of 1594 cm<sup>-1</sup>, and the symmetric deformation  $\delta_s$ -(NH<sub>3</sub>) has a value of 1245 cm<sup>-1</sup>. The rocking vibrations  $\rho_r$ -(NH<sub>3</sub>) of ammineite have wavenumbers of 661 and 711 cm<sup>-1</sup>. The band doubling corresponds most probably to in-phase and out-of-phase rocking vibration of the (NH<sub>3</sub>) groups. The Cu–N antisymmetric stretching is at 480 cm<sup>-1</sup>. The band at 2487 cm<sup>-1</sup> corresponds to the overtone of the strong band at 1245 cm<sup>-1</sup>. A comparison of the infrared frequencies of ammineite or trans-Cu(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and trans-Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (Layton *et al.* 1966) show a good concordance of most bands. The (NH<sub>3</sub>)-rocking band of ammineite has a noticeably lower wavenumber than in trans-Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>. The weak bands around 1400 cm<sup>-1</sup> are possibly related to traces of an ammonium salt impurity.

### CHEMICAL COMPOSITION

We analyzed the sample for N, H, C, O and S with a Heraeus Vario Elementar Analyzer. In our material, C, O and S are below the detection limit. Concentrations of Cu and Cl were established with a JEOL JSM-6310 electron microscope, equipped with an energy-dispersion spectrometer. The working conditions were 15 kV, with a beam current of 5 nA measured on aluminum. A window of ~5  $\mu\text{m}$  was chosen because of the instability of ammineite under the electron beam. A fragment of a natural ammineite crystal was embedded in resin and polished with oil on a polishing felt. The oil was removed afterward with ethanol. The results of the chemical analyses are given in Table 1. The empirical formula resulting from these analyses is CuCl<sub>1.99</sub>N<sub>1.99</sub>H<sub>5.57</sub> (the number of copper atoms in the formula is assumed to be 1 *apfu*), giving a simplified formula CuCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>.

Ammineite is soluble in HCl and ammonia. In water, ammineite is transformed to an amorphous phase.

### SYNTHESIS AND HEATING EXPERIMENTS

Synthetic trans-diammine-dichlorido-copper(II) was produced by chemical precipitation. For these experiments, synthetic CuCl<sub>2</sub>•2H<sub>2</sub>O was dissolved in 25% liquid ammonia at temperatures around 20°C. The resulting saturated solution is ink-blue. This solution was placed in a small beaker and allowed to evaporate



FIG. 3. Ammineite showing the dominant form {001}, elongate along [100] on halite. Pabellon de Pica, Tarapaca region, Chile. Field of view: 2.5 mm across.

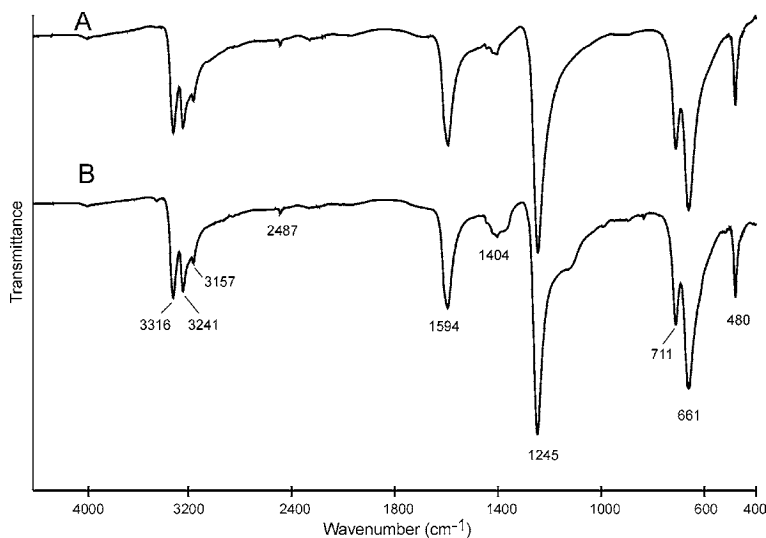


FIG. 4. FTIR-ATR spectra of trans-diammine-dichlorido-copper(II) (a) and ammineite (b). No ATR correction was performed.

TABLE 1. THE CHEMICAL COMPOSITION OF AMMINEITE

	wt. %	range	stand. dev.	apfu
Cu	37.60	37.2 – 37.8	0.5	1.00
Cl	41.67	41.5 – 41.9	0.2	1.99
N	16.54	16.75, 16.33	0.4	1.99
H	3.32	3.21, 3.42	0.4	5.57
Total	99.13			

We analyzed the crystal for Cu and Cl with an electron microprobe with energy dispersion (EDS) using atacamite as a standard. The composition quoted is the average result of three analyses. We analyzed the crystal for N and H with a Heraeus Vario Elemental Analysator (two analyses). The results are expressed in atoms per formula unit (apfu) calculated on the basis of Cu equal to 1 apfu.

until all liquid was lost. No crystallites are visible under a light microscope in the precipitate. Tiny lath-shaped crystals grew in small shrinkage-induced cracks or in cavities between the beaker glass and the precipitation. They are elongate along [100], show the dominant form {001} and have small faces of the forms {100}, {010} and {110}. The size of these crystals is too small (length up to 200  $\mu\text{m}$ , thickness up to 3  $\mu\text{m}$ ) for single-crystal analysis (Fig. 5), but the X-ray powder pattern is in good agreement with that of ammineite. Experiments at lower temperatures (around 10°C) or different pH values did not increase the size of the crystals. Further experiments were performed with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  dissolved in ammonia – hydrochloric acid solutions in the pH range between 7.6 and 13. Only at high values of pH was

the precipitate pure ammineite. At lower pH values, ammineite, salammoniac and atacamite coprecipitated. At pH value lower than 9, ammonium copper chloride hydrate and salammoniac formed.

Heating experiments using a compartment dryer were performed on synthetic  $\text{CuCl}_2(\text{NH}_3)_2$ . One part of the hand-milled sample was sealed in an unevacuated glass tube to prevent reactions with the atmosphere. The second part was heated in an open glass-beaker. All the resulting products were analyzed with XRD and ATR-FTIR. Sixteen hours heating at 120°C did not change the primary sample. Within an hour at 200°C, the color of the sample surface in the beaker turned from bluish to greenish. After that, the complete sample became greenish. After 75 hours, the powder had become brownish. The greenish product consists of copper ammonium chloride hydrate,  $\text{CuCl}_4(\text{NH}_4)_2 \cdot 2\text{H}_2\text{O}$ , as identified by its X-ray powder pattern. An unknown phase formed after 12 hours heating, and copper ammonium chloride hydrate was still present in the sample. After 75 hours at 200°C, the sample consisted of copper chloride hydroxide hydrate  $[\text{Cu}_x\text{Cl}_4(\text{OH})_z \cdot 2\text{H}_2\text{O}]$  and the synthetic analogue of eriochalcite,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , whereas the sealed sample was unchanged after 75 hours at 200°C.

#### X-RAY CRYSTALLOGRAPHY

##### *X-ray powder diffraction*

The X-ray powder-diffraction data for ammineite (A) and the synthetic trans-diammine-dichlorido-

copper(II) (B) were obtained at 293 K using a Bruker AXS D8 diffractometer, with  $\text{CuK}\alpha$  radiation (Table 2). To minimize the background, both samples were placed on low-background silicon wafer; an internal standard was not used. Positions, intensities of reflections and unit-cell parameters were calculated with the program TOPAS (Bruker AXS 2009) using fundamental parameters. Indexing was done with space group and unit-cell parameters given from the single-crystal refinement of the structure of ammineite. The X-ray powder-diffraction patterns ( $\text{CuK}\alpha$  radiation) of ammineite (A), synthetic trans-diammine-dichlorido-copper(II) (B), the calculated pattern of ammineite using parameters from structure refinement (C) and the calculated pattern (D) of the synthetic phase  $\text{Cu}(\text{NH}_3)_2\text{Cl}_2$  determined by Hanic & Cakajdová (1958) are overlain for comparison in Figure 6.

#### *X-ray structure determination*

For X-ray structure analyses, the crystal of ammineite was mounted on the tip of a glass fiber, and data collection was performed with a Bruker AXS SMART APEX CCD diffractometer using graphite-monochromated  $\text{MoK}\alpha$  radiation (0.71073 Å). The data were reduced to  $\text{Fo}^2$  and corrected for absorption effects with SAINT (Bruker AXS 2003) and SADABS (Sheldrick 1998), respectively. The structure was solved by direct methods and refined by full-matrix least-squares method SHELXL-97 (Sheldrick 1997). Systematic absences and

the intensity statistics favor the centrosymmetric space-group  $Cmcm$ . In the structure model, all positions are fully occupied: one Cu and two Cl atoms are located at 4c, one N and one H atom at 8g, and one H atom is at the general 16h position. All non-hydrogen atoms were refined with anisotropic displacement parameters. Information on data collection and selected information on the refinement are given in Table 3. Refined coordinates and displacement parameters are given in Table 4, and selected interatomic distances and angles are listed in Table 5. A table of structure factors and a cif file are available from the Depository of Unpublished Data on the MAC website [document Ammineite CM48\_1359].

#### DESCRIPTION OF THE STRUCTURE

The basic structural unit consists of one central Cu site with a planar four-fold coordination with two  $\text{NH}_3$  molecules and two Cl atoms, to build the inert trans-diammine-dichlorido-copper(II) complex:  $\text{CuCl}_2(\text{NH}_3)_2$ , with two  $\langle\text{Cu}-\text{N}\rangle$  distances of 1.965 Å each and two  $\langle\text{Cu}-\text{Cl}\rangle$  distances of 2.356 and 2.357 Å (Fig. 7a). There are four formula units in the unit cell. The complex is layered parallel to (001) and oriented with  $\text{Cl}(1)-\text{Cu}-\text{Cl}(2)$  parallel to [010] and  $\text{N}-\text{Cu}-\text{N}$  parallel to [100] (Fig. 8). Along [001], Cu is connected to the parallel layered complexes up and down nearly perpendicular by two long bonds  $\langle\text{Cu}-\text{Cl}(2)\rangle$  of 2.868 Å, respectively. The resulting polyhedron is a [4 + 2]-distorted  $\text{Cu}^{2+}\text{N}_2\text{Cl}_4$  octahedron with four equato-

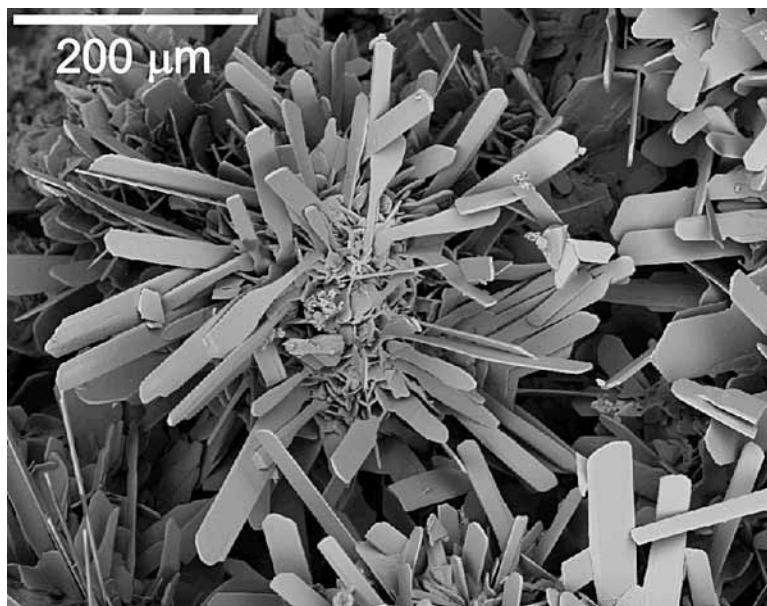


FIG. 5. BSE micrograph of trans-diammine-dichlorido-copper(II) with the dominant crystallographic form {001} and subordinate forms {100}, {010} and {110}.

TABLE 2. X-RAY POWDER-DIFFRACTION DATA AND CALCULATED UNIT-CELL PARAMETERS FOR AMMINEITE AND TRANS-DIAMMINE-DICHLORIDO-COPPER(II) COMPARED WITH POWDER DATA CALCULATED WITH PARAMETERS FROM STRUCTURE REFINEMENT OF AMMINEITE

<i>h k l</i>	A			B			C	
	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>I</i> <sub>obs</sub>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>I</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>I</i> <sub>calc</sub>
1 1 0	6.285	6.286	69	6.279	6.285	52	6.233	100
1 1 1	4.278	4.278	55	4.278	4.279	41	4.221	60
0 2 1		3.933		3.934	3.934	6	3.902	9
2 0 0	3.898	3.895	56	3.894	3.894	43	3.844	52
0 0 2	2.920	2.919	100	2.921	2.922	71	2.868	67
1 3 1	2.824	2.825	5	2.826	2.825	4	2.809	3
2 2 1	2.763	2.767	36	2.768	2.767	19	2.738	12
0 4 0	2.660	2.661	90	2.659	2.660	100	2.661	39
1 1 2		2.648		2.649			2.605	22
3 1 0	2.523	2.523	14	2.522	2.522	12	2.4916	13
0 4 1		2.4212		2.4216	2.4211	2	2.4141	5
2 0 2	2.3355	2.3360	35	2.3370	2.3369	30	2.2987	27
3 1 1	2.3158	2.3157	17	2.3154	2.3155	14	2.2853	14
2 4 0	2.1979	2.1971	23	2.1968	2.1966	23	2.1881	15
1 5 0	2.0540	2.0533	24	2.0533	2.0529	29	2.0519	19
0 4 2	1.9668	1.9665	27	1.9672	1.9670	39	1.9508	25
4 0 0	1.9478	1.9474	24	1.9470	1.9470	22	1.9221	17
1 5 1	1.9371	1.9370	10	1.9371	1.9368	14	1.9320	6
3 1 2	1.9082	1.9087	8	1.9090	1.9091	9	1.8809	9
1 1 3	1.8584	1.8591	6	1.8604	1.8604	6	1.8278	5
2 4 2	1.7552	1.7554	20	1.7559	1.7557	21	1.7396	14
0 6 1		1.6973		1.6974	1.6970	4	1.6950	2
1 5 2	1.6795	1.6795	16	1.6799	1.6797	19	1.6687	18
3 5 0	1.6466	1.6462	10	1.6459	1.6458	11	1.6377	9
4 0 2	1.6200	1.6200	17	1.6202	1.6202	19	1.5967	16
3 5 1	1.5849	1.5844	5	1.5843	1.5842	6	1.5747	3
4 4 0	1.5717	1.5715	14	1.5712	1.5712	16	1.5582	10
5 1 0	1.5413	1.5415	4	1.5413	1.5412	4	1.5219	1
0 0 4	1.4592	1.4596	5	1.4607	1.4608	5	1.4339	5
3 5 2	1.4336	1.4339	9	1.4340	1.4339	8	1.4221	10
4 4 2	1.3836	1.3837	16	1.3837	1.3837	13	1.3692	12

	A, 293 K	B, 293 K	C, 100 K
<i>a</i> (Å)	7.790(1)	7.788(1)	7.688
<i>b</i> (Å)	10.643(1)	10.641(1)	10.645
<i>c</i> (Å)	5.838(1)	5.843(1)	5.736
<i>V</i> (Å <sup>3</sup> )	484.1(1)	484.2(1)	469.4

A: ammineite, observed, B: trans-diammine-dichlorido-copper(II) synthesized by the authors, C: calculated with data from structure refinement of ammineite. The intensities are calculated for CuK $\alpha$ .

rial bonds to N and Cl and two apical bonds to Cl. The distorted octahedra, better described as orthorhombic bipyramids, are connected by shared edges <Cl(2)... Cl(2)> to form zigzag chains running along [001] (Figs. 7b, 9a–c). These shared edges contain the shortest Cl... Cl distances (3.678 Å) of this structure. Some H...Cl distances ranging from 2.69 to 2.79 Å indicate the presence of weak hydrogen bonds, which connect, in addition to the apical <Cu–Cl(2)> bonds, the CuCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> complexes from one layer to the next and also within the (001) layers (Figs. 8, 9b). The presence of weak hydrogen bonds is confirmed also by the IR spectrum. Additional broadening of the N–H stretching vibrations (as compared with other bands) was not observed.

#### CRYSTAL CHEMISTRY OF AMMINEITE AND RELATED COMPOUNDS

In most copper oxysalt minerals, the octahedral coordination for copper is dominant, with an extension of the two axial bonds (a so-called [4 + 2]-coordination) as a result of the well-known Jahn–Teller effect (Jahn & Teller 1937, Dunitz & Orgel 1957). Very regular octahedral coordination of Cu<sup>2+</sup> is caused by high site-symmetry or associated with partially occupied sites (Eby & Hawthorne 1993). In mixed-ligand Cu<sup>2+</sup>–[4 + 2]-distorted octahedra, the Cl ions are located at the apical positions; if more than two Cl ligands are present, the equatorial positions also are occupied by Cl (Burns & Hawthorne 1995).

In ammineite, the equatorial Cu–N distance, 1.96 Å, is in the range of observed equatorial Cu–N distances, from 1.95 Å (Aschwenden *et al.* 1993) to 2.05 Å (Leskelä & Valkonen 1978) for synthetic copper ammine complexes with mixed-ligand  $\text{Cu}^{2+}$ –[4 + 2]-distorted octahedra, and is near the value of the sum of the effective ionic radii of four-coordinated  $\langle\text{Cu}^{2+}\text{--N}^{3-}\rangle$ , 2.03 Å, reported by Shannon (1976). The equatorial Cu–Cl distance of 2.36 Å in ammineite corresponds to the sum of four coordinated  $\langle\text{Cu}^{2+}\text{--Cl}^{-}\rangle$ , 2.38 Å (Shannon 1976), and is in the range of equatorial Cu–Cl distances, from 2.23 to 2.38 Å, of [4 + 2]-distorted  $\text{Cu}^{2+}\text{Cl}_6$  octahedra, given in Burns & Hawthorne (1995). The apical Cu–Cl distance, 2.87 Å in ammineite, lies in the wider range of apical distances in  $\text{Cu}^{2+}\text{Cl}_6$  octahedra, from 2.71 to 3.19 Å, and is smaller than the apical Cu–Cl bond length in eriochalcite (2.94 Å) and chlorothionite (3.05 Å), which have [4 + 2]-distorted  $\text{Cu}^{2+}$  octahedra, with two (O, OH,  $\text{H}_2\text{O}$ ) and four Cl (Burns & Hawthorne 1995).

The distorted  $\text{Cu}^{2+}\text{Cl}_4(\text{H}_2\text{O})_2$  octahedra in eriochalcite,  $\text{CuCl}_2(\text{H}_2\text{O})_2$ , space group *Pbmn*, are also linked in infinite chains by sharing edges with the shortest Cl...Cl

distances (3.671 Å) of the structure (Brownstein *et al.* 1989), like in ammineite, but with a different geometry. In eriochalcite, each octahedron is flanked by two others along [001] in a *trans* arrangement. The resulting chains are linked by hydrogen bonding between the apical  $\text{H}_2\text{O}$  groups and the Cl atoms of the neighboring chains. In ammineite, the distorted octahedra form zigzag chains, which are built by shared edges 3.678 Å in length from the equatorial Cl(2) to the apical Cl(2) (Figs. 7b, 9a).

Most synthetic  $\text{MeCl}_2(\text{NH}_3)_2$  compounds (*Me*: divalent cations) crystallize in space group *Cmmm*, with *Me* in octahedral [4Cl + 2N] coordination and fully occupied positions for *Me*, N and Cl. For *Me* =  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Hg}^{2+}$ , the same structure-type is reported, with *Me* octahedra of two apical N ligands and four equatorial Cl ligands, which are connected into infinite chains by Cl–Cl edges [Mg: Leineweber *et al.* (1999); Fe: Bremm & Meyer (2003); Co: Leineweber *et al.* (2001); Ni: Leineweber & Jacobs (2000); Cd and Hg: MacGillavry & Bijvoet (1936)]. The compound  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  crystallizes in space group *Imam* with Zn in tetrahedral [2Cl + 2N] coordination (Yamaguchi & Lindqvist 1981). Orthorhombic  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  was also described from burned dumps of the Chelyabinsk coal basin, Urals, Russia (Chesnokov *et al.* 1991). They used "amminite" as a name, but this phase is of technogenic origin and therefore not a mineral. The structure of  $\text{Ca}(\text{NH}_3)_2\text{Cl}_2$ , space group *Abm2*, is dominated by Ca octahedra with [4Cl + 2N] coordination, which are shared by the equatorial Cl corners (Westman *et al.* 1981).

The same basic structural unit as in ammineite but with the Pt as central atom instead of Cu is found in trans-dichloro-diammine-platinum(II),  $\text{PtCl}_2(\text{NH}_3)_2$ . In this structure (Milburn & Truter 1966), space group *P12<sub>1</sub>/a1*, all sites are fully occupied. The Pt atom is only in planar coordination with two Cl and two  $\text{NH}_3$  groups, and the neutral complex  $\text{PtCl}_2(\text{NH}_3)_2$  is connected by hydrogen bonds (H...Cl) to the surrounding complexes.

Hanic & Cakajdová (1958) reported the crystal structure of the synthetic  $\text{Cu}(\text{NH}_3)_2\text{Cl}_2$ , space group *Pm*, with fully occupied N and Cl positions and with a partially occupied (1/6) Cu site. In this structure,  $\text{Cu}^{2+}$

TABLE 3. AMMINEITE: CRYSTAL DATA, DATA-COLLECTION INFORMATION, AND DETAILS CONCERNING THE REFINEMENT

<i>a</i> (Å)	7.688(1)	Temperature (K)	100
<i>b</i> (Å)	10.645(2)	Total reflections	1756
<i>c</i> (Å)	5.736(1)	Unique reflections	279
<i>V</i> (Å <sup>3</sup> )	469.4(2)	Unique $ F_o  > 4\sigma F_o$	231
Space group	<i>Cmcm</i>	$R_{\text{merge}}$	0.060
<i>Z</i>	4	Refined parameters, <i>p</i>	24
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	2.38	Goodness of fit, <i>S</i>	1.02
Crystal size (mm)	0.08 × 0.12 × 0.25	$R_1$ ( $ F_o  > 4\sigma F_o$ )	0.024
$F_{000}$	332	$R_1$ (all data)	0.031
$\mu$ (cm <sup>-1</sup> )	56.1	$wR_2$ (all data)	0.065
Radiation	MoK $\alpha$	Largest diff. peak (e.Å <sup>-3</sup> )	0.66
		Largest diff. hole (e.Å <sup>-3</sup> )	-0.35

Note:  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ ;  $w = 1/[\sigma^2(F_o^2) + (0.0388P)^2 + 0.58P]$ , where  $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$ ;  $S = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$ , where *n* is the number of reflections, and *p* is the number of refined parameters.

TABLE 4. FRACTIONAL COORDINATES, EQUIVALENT ISOTROPIC-DISPLACEMENT PARAMETERS AND ANISOTROPIC DISPLACEMENT PARAMETERS OF ATOMS IN AMMINEITE

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Cu	½	0.38685(6)	¼	0.0115(3)	0.0098(4)	0.0115(4)	0.0131(4)	0	0	0
Cl(1)	½	0.16546(12)	¼	0.0122(4)	0.0136(6)	0.0106(8)	0.0125(7)	0	0	0
Cl(2)	½	0.60817(11)	¼	0.0122(4)	0.0153(7)	0.0102(8)	0.0111(7)	0	0	0
N	0.2445(4)	0.3871(3)	¼	0.0124(7)	0.0143(17)	0.0151(15)	0.0079(16)	0	0	0.0001(15)
H(1)	0.210(7)	0.452(4)	¼	0.05*						
H(2)	0.202(4)	0.356(2)	0.131(6)	0.05*						

\* constrained in refinement.



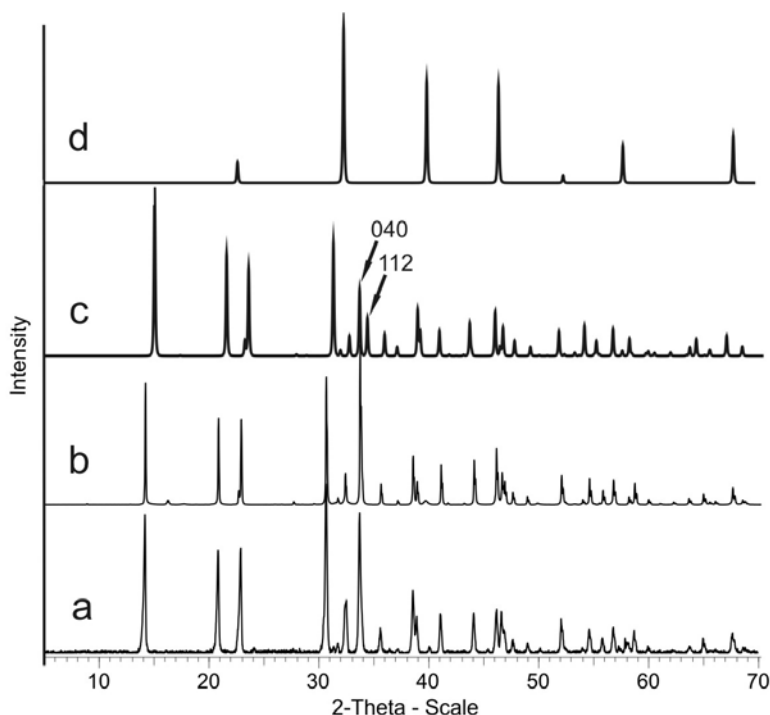


Fig. 6. X-ray powder-diffraction patterns ( $\text{CuK}\alpha$ , 40 kV, 40 mA, 293 K) of ammineite (a) and trans-diammine-dichlorido-copper(II) (b), calculated pattern using parameters from structure refinement of ammineite at 100 K [note the splitting of (040) and (112)] (c) and calculated pattern using parameters for  $\text{Cu}(\text{NH}_3)_2\text{Cl}_2$  determined by Hanic & Cakajdová (1958) (d).

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN AMMINEITE

Cu–N,a	×2	1.965(3)	N–Cu–N,a	179.8(2)
Cu–Cl(1)		2.357(2)	N,a–Cu–Cl(1)	×2 90.1(1)
Cu–Cl(2)		2.356(2)	N,a–Cu–Cl(2)	×2 89.9(1)
Cu–Cl(2) b,c	×2	2.868(1)	N,a–Cu–Cl(2) b,c	×4 90
N–H(1)		0.74(5)	Cl(1)–Cu–Cl(2)	180
N–H(2)	×2	0.83(3)	Cl(1)–Cu–Cl(2) b,c	×2 91.06(3)
H(1)–N–H(2),d	×2	103(3)	Cl(2)–Cu–Cl(2) b,c	×2 88.94(3)
H(2)–N–H(2) d		111(3)	Cl(2)b–Cu–Cl(2) c	177.9(1)
H(1)...Cl(1) e		2.79(4)	Cl(2)...Cl(2) b	3.678(2)
H(1)f...Cl(2)		2.78(4)		
H(2)g...Cl(1)		2.69(3)		

Symmetry positions: a:  $-x + 1, y, -z + \frac{1}{2}$ ; b:  $-x + 1, -y + 1, -z + 1$ ; c:  $-x + 1, -y + 1, -z$ ; d:  $x, y, -z + \frac{1}{2}$ ; e:  $x + \frac{1}{2}, y + \frac{1}{2}, z$ ; f:  $-x + 1, y, z$ ; g:  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ .

is coordinated octahedrally by four equatorial Cl ions, with distances of 2.77 Å, and two apical N sites, with distances of 1.96 Å, resulting in a distorted axially

compressed octahedron with  $\text{Cu}^{2+}$  in [2 + 4] coordination. A calculated X-ray powder pattern with atom parameters from the refinement of Hanic & Cakajdová (1958) does not agree with the observed X-ray powder pattern of synthetic  $\text{CuCl}_2(\text{NH}_3)_2$ , which was produced in the laboratory of the Universalmuseum Joanneum for comparison (Fig. 6). The calculated and observed X-ray powder patterns of ammineite and the observed X-ray powder pattern of our synthetic trans-diammine-dichlorido-copper(II) phase are nearly identical.

The crystal structure of diammonium diammine-copper(II) chloride,  $(\text{NH}_4)_2\text{Cu}(\text{NH}_3)_2\text{Cl}_4$ , was reported by Clayton & Meyers (1976) with the same structure type as  $\text{Cu}(\text{NH}_3)_2\text{Br}_2$ , determined by Hanic & Cakajdová (1958), but with a more reliable  $R$  value, 0.05, than 0.18 refined for the synthetic  $\text{Cu}(\text{NH}_3)_2\text{Cl}_2$  from Hanic & Cakajdová (1958). In the crystal structure of diammonium diamminecopper(II) chloride, the atom sites for Cl and N are fully occupied, whereas the Cu site is only partially occupied (1/12). Also in this structure, the dominant  $\text{Cu}^{2+}$  polyhedron shows a compressed octahedral [2 + 4] coordination, with distances of 1.96

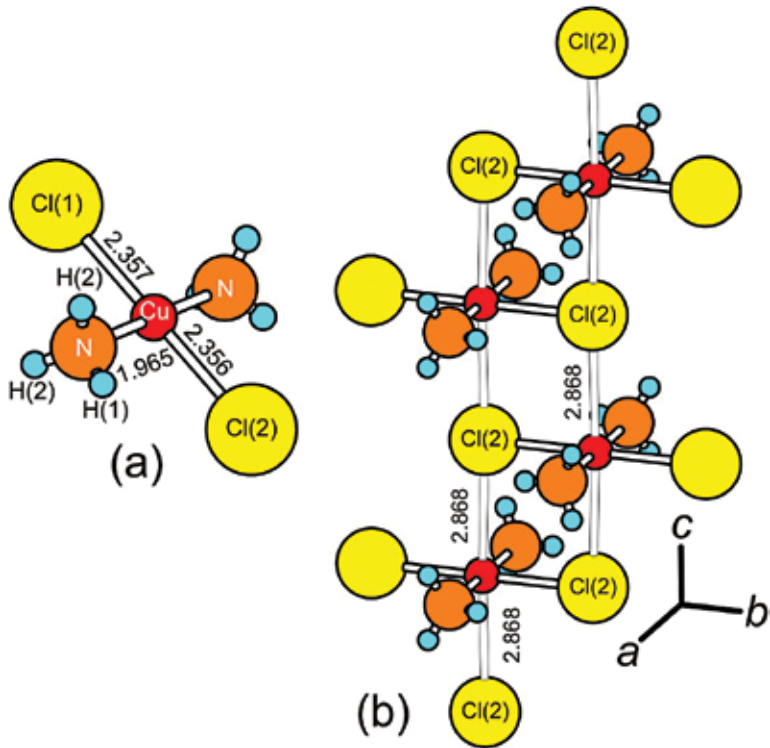


FIG. 7. Crystal-structure details of ammineite: (a) trans-diammine-dichlorido-copper(II) complex, (b) zigzag chain of edge-shared [4+2]-distorted octahedra built by trans-diammine-dichlorido-copper(II) complexes.

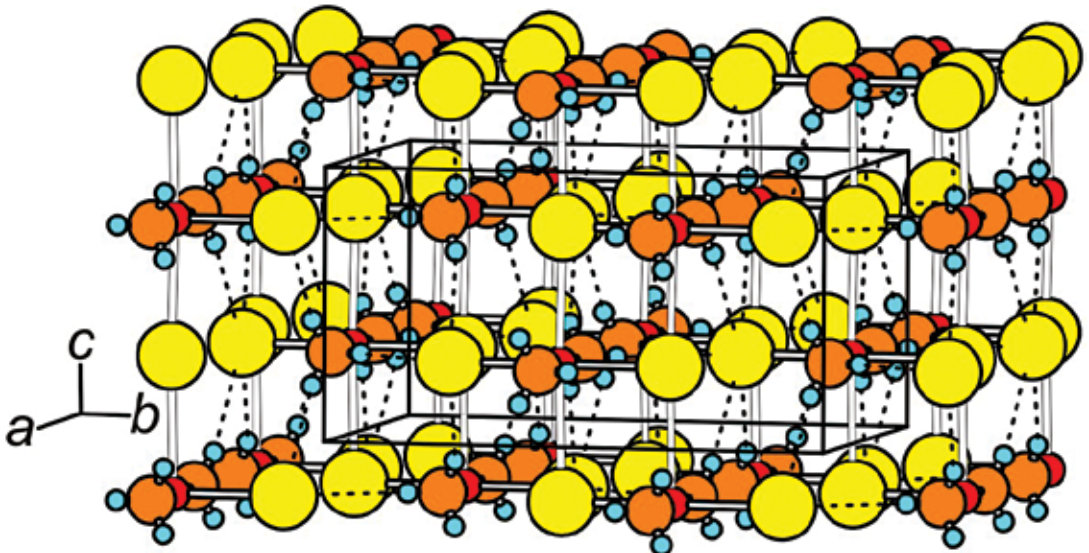


FIG. 8. Crystal structure of ammineite with layered trans-diammine-dichlorido-copper(II) complexes parallel to (001). Dotted lines are hydrogen bonds.

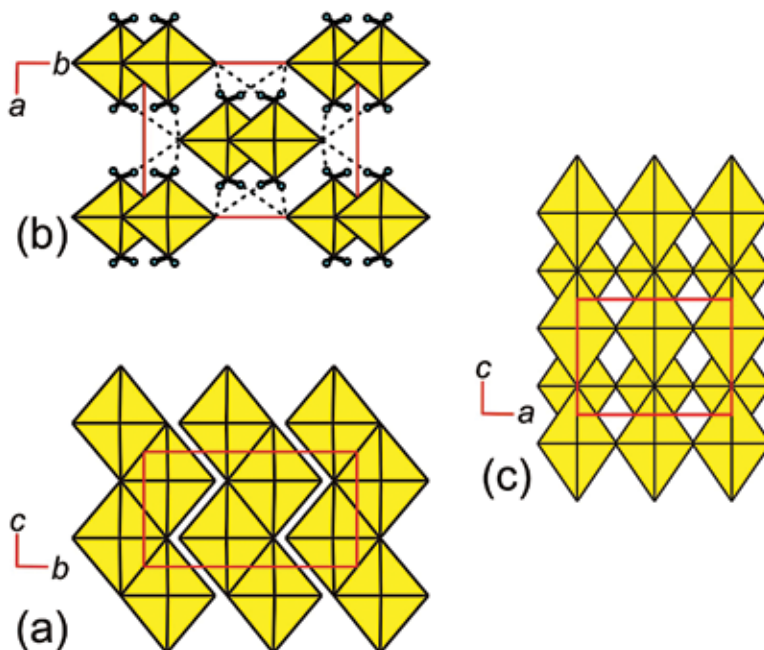


FIG. 9. Crystal structure of ammineite with outlined polyhedra: (a) zigzag chains of [4+2]-distorted octahedra, view along [100], (b) chains connected by hydrogen bonds (dotted lines), view along [001], (c) view along [010].

Å ( $2\times$ ) and 2.77 Å ( $4\times$ ) to N and Cl, respectively. Because of the similarities of the refinement results of Clayton & Meyers (1976) and the structure determination of Hanic & Cakajdová (1958), it is possible to infer that the crystals synthesized by Hanic & Cakajdová (1958) are diammonium diamminecopper(II) chloride,  $(\text{NH}_4)_2\text{Cu}(\text{NH}_3)_2\text{Cl}_4$ , and not  $\text{CuCl}_2(\text{NH}_3)_2$ , the composition of ammineite.

The change of the cell volume of ammineite from  $469 \text{ \AA}^3$  at 100 K to  $484 \text{ \AA}^3$  at 293 K is probably caused by the wider range of possible distances for the apical Cu–Cl bonds along [001] of the distorted [4 + 2] octahedron. From 100 K to 293 K,  $c$  increases by 1.8% and  $a$  increases by 1.3%, whereas the cell parameter  $b$  remains nearly constant. This is also seen in the splitting of the reflections (040) and (112) in the calculated powder-pattern for ammineite; data from the structure refinement at 100 K are compared with the (040) and (112) overlain reflections in the X-ray powder patterns of ammineite and the synthetic trans-diammine-dichlorido-copper(II) measured at 293 K (Fig. 6).

#### ORIGIN AND PROCESS OF FORMATION

Copper chloride phases are a widespread component of the oxide zones of copper deposits in arid zones in northern Chile, whereas in other copper deposits,

they are rare. In oxide zones of copper deposits in humid zones, carbonates, like malachite and azurite, or sulfates, like brochantite and antlerite, are common. Large amounts of atacamite in the oxide zones from deposits require saline solutions for its formation and a hyperarid climate for its preservation (Reich *et al.* 2008). A decrease in pH or an increase in the activity of chlorine (or both) make atacamite or paratacamite more stable than copper oxide or copper carbonates (Woods & Garrels 1986). Saline brines can form in hyperarid climates owing to high rates of evaporation of meteoric waters, or brines may be expelled during dewatering of underlying sediments (Cameron *et al.* 2007). According to Cameron *et al.* (2007), atacamite replaces pre-existing copper oxide phases. In seawater, malachite is more stable than atacamite, but only a slight variation of the seawater composition would favor atacamite over malachite (Woods & Garrels 1986). As Pabelon de Pica is in close proximity to the ocean, seawater is possible a source of the brine. As a possible mode of formation of this mineralization, we contend that brine dissolved ammonia from the guano deposits, and this brine penetrated along zones of weakness in the host rock. Halite crystallized close to surface in small clefts. Pre-existing copper oxides in the host rock were dissolved, and atacamite and ammineite precipitated in small solution-induced cavities in halite.

Synthesis experiments show that ammineite forms at ambient conditions and is only stable at lower temperatures. It decomposes at elevated temperatures and atmospheric conditions to hydrated copper chlorides.

#### ACKNOWLEDGEMENTS

This article benefitted from helpful comments, text corrections and suggestions of Nikita Chukanov, Takuya Echigo and Robert F. Martin. We thank Reynaldo Contreira, who discovered the ammineite-bearing assemblages with one of the authors (G.F.).

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Received June 11, 2010, revised manuscript accepted October 28, 2010.

