

# Leverettite from the Torrecillas mine, Iquique Province, Chile: the Co-analogue of herbertsmithite

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## ABSTRACT

The new mineral leverettite (IMA 2013-011), ideally  $\text{Cu}_3\text{CoCl}_2(\text{OH})_6$ , was found at the Torrecillas mine, Salar Grande, Iquique Province, Chile, where it occurs as a supergene alteration phase in association with akaganéite, anhydrite, chalcophanite, goethite, halite, manganite, pyrite, quartz and todorokite. Crystals of leverettite are steep rhombohedra to 1 mm with  $\{101\}$  prominent and modified by  $\{001\}$ , sometimes forming V-shaped twins by reflection on  $\{10\bar{2}\}$ . The crystals can also form finger-like, parallel stacked growths along the  $c$  axis. The new mineral is medium to deep green in colour and has a light green streak. Crystals are transparent with a vitreous lustre. Mohs hardness is  $\sim 3$  and the crystals have a brittle tenacity, a perfect cleavage on  $\{101\}$  and a conchoidal fracture. The measured density is  $3.64(2) \text{ g cm}^{-3}$  and calculated density based on the empirical formula is  $3.709 \text{ g cm}^{-3}$ . Optically, leverettite is uniaxial (–) with  $\omega$  and  $\epsilon > 1.8$  and exhibits pleochroism with  $O$  (bluish green)  $> E$  (slightly yellowish green). The empirical formula, determined from electron-microprobe analyses is  $\text{Cu}_3(\text{Co}_{0.43}\text{Cu}_{0.40}\text{Mn}_{0.17}\text{Ni}_{0.07}\text{Mg}_{0.01})_{\Sigma 1.08}\text{Cl}_{1.87}\text{O}_{6.13}\text{H}_6$ . Leverettite is trigonal (hexagonal), space group  $R\bar{3}m$ , unit-cell parameters  $a = 6.8436(6)$  and  $c = 14.064(1) \text{ Å}$ ,  $V = 570.42(8) \text{ Å}^3$ ,  $Z = 3$ . The eight strongest X-ray powder diffraction lines are [ $d_{\text{obs}} \text{ Å}(I)(hkl)$ ]:  $5.469(90)(101)$ ,  $4.701(18)(003)$ ,  $2.905(22)(021)$ ,  $2.766(100)(113)$ ,  $2.269(66)(024)$ ,  $1.822(26)(033)$ ,  $1.711(33)(220)$ ,  $1.383(23)(128)$ . The structure, refined to  $R_1 = 0.023$  for  $183 F_o > 4\sigma F$  reflections, shows leverettite to be isostructural with herbertsmithite and gillardite.

**KEYWORDS:** leverettite, Iquique Province, Chile, new mineral.

## Introduction

SPECIMENS containing the new mineral were discovered by one of the authors (AAMD) in early 2012 at the Torrecillas mine, Iquique Province, Chile. Rhombohedral green crystals on these specimens were determined to contain significant amounts of Cu, Co and Mn, giving the average empirical formula  $\text{Cu}_3(\text{Co}_{0.42}\text{Cu}_{0.33}\text{Mn}_{0.17}\text{Ni}_{0.07}\text{Mg}_{0.01})\text{Cl}_2(\text{OH})_6$ . This formula corresponds to the substituted members of the atacamite

group, corresponding to  $\text{Cu}_3\text{M}^{2+}\text{Cl}_2(\text{OH})_6$ , where M can be a cation with ionic radius comparable to  $\text{Cu}^{2+}$ , such as Zn, Ni and Mg. In recent years, the atacamite group of minerals has expanded considerably to include a series of closely related phases characterized by substitution phenomena. These include herbertsmithite,  $\text{Cu}_3\text{ZnCl}_2(\text{OH})_6$ , (trigonal,  $R\bar{3}m$ ) (Braithwaite *et al.*, 2004) and gillardite,  $\text{Cu}_3\text{NiCl}_2(\text{OH})_6$ , (isostructural with herbertsmithite) (Clissold *et al.*, 2007), paratacamite,  $\text{Cu}_3(\text{Cu,Zn})\text{Cl}_2(\text{OH})_6$ , (trigonal,  $R\bar{3}$ ) (Fleet, 1975; Welch *et al.*, 2013), and the newly described paratacamite-(Mg),  $\text{Cu}_3(\text{Mg,Cu})\text{Cl}_2(\text{OH})_6$ , and paratacamite-(Ni),  $\text{Cu}_3(\text{Ni,Cu})\text{Cl}_2(\text{OH})_6$ , (both

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isostructural with paratacamite) (Kampf *et al.*, 2013; Sciberras *et al.*, 2013, respectively). Single-crystal X-ray structure analysis of the new Co-rich material established that it has trigonal symmetry, unit cell  $a = 6.8436(6)$  and  $c = 14.064(1)$  Å (hexagonal setting), in space group  $R\bar{3}m$ , and is isostructural with herbertsmithite and gillardite.

The mineral is named leverettite in honour of Professor Peter Leverett (*b.* 1944), Professor of Chemistry at the University of Western Sydney, in recognition of his contributions to research and teaching in chemistry and chemical geology. Professor Leverett trained as both a chemist and geologist, before engaging in a research career focused on structural aspects of inorganic compounds and complexes. He has published widely in these areas and has been responsible for structural characterization of several new minerals and many other known species. He has served as an Editorial Board Member of *The Canadian Mineralogist* and is currently Structure Editor for *Mineralogical Magazine*. Professor Leverett has agreed to the naming. The new mineral and the name have been approved by the International Mineralogical Association (IMA 2013-011). Four type specimens are retained in the Natural History Museum of Los Angeles, Los Angeles, California, USA, catalogue numbers 64031 (holotype), and 64032, 64033 and 64034 (cotypes).

## Occurrence

Leverettite occurs at the Torrecillas mine, Salar Grande, Iquique Province, Tarapacá Region, Chile (approximately 20°58'13"S 70°8'17"W). The new mineral is a supergene alteration phase that is found to occur in association with akaganéite, anhydrite, chalcophanite, goethite, halite, manganite, pyrite, quartz and todorokite.

In the area of the Torrecillas mine, four different rock units are exposed. The Coastal Range Batholith (mainly gabbros) extends from the seashore to the Pan-American Road along the base of Torrecillas Hill. At the foot of Torrecillas Hill is a small area of contact metamorphic rocks in which garnet crystals occur in metamorphosed shales. Higher on the hill, the rocks are predominantly andesites and porphyritic lavas of the Jurassic La Negra Formation. The Torrecillas deposit, in which the new mineral is found, consists of two main veins rich in secondary arsenic and copper minerals that intersect metamorphosed marine shales and lavas. These mineralized veins are genetically related to the

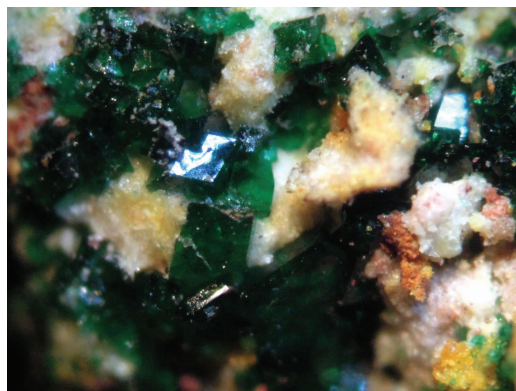


FIG. 1. Rhombohedra of leverettite. Field of view 1 mm.

aforementioned andesites and porphyritic lavas of the Jurassic La Negra Formation. More information on the geology and mineralogy of the area is provided by Gutiérrez (1975).

## Physical and optical properties

Crystals occur as steep rhombohedra, no larger than 1 mm in size (Fig. 1). These rhombohedra are sometimes stacked along the  $c$  axis in finger-like, parallel growths (Fig. 2) or form V-shaped twins (Fig. 3). The  $\{101\}$  rhombohedral form is prominent and is sometimes modified by the basal pinacoid  $\{001\}$  (Fig. 4). The V-shaped twins are by reflection on  $\{10\bar{2}\}$  (Fig. 5). An analysis of the twinning using the program *Geminography* (Nespolo and Ferraris, 2006) indicates that the observed twinning is by reticular pseudo-mero-

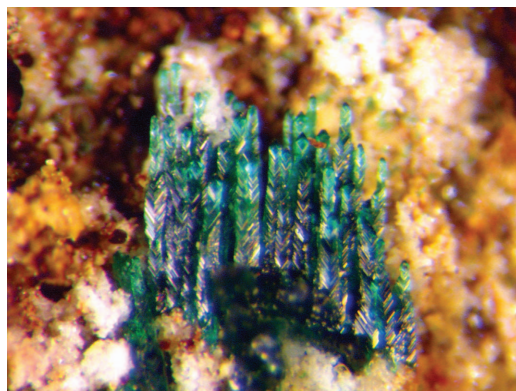


FIG. 2. Rhombohedra of leverettite stacked along the  $c$  axis. Field of view 2 mm.



FIG. 3. V-shaped twins of leverettite rhombs. Field of view 1 mm.

hedry and is based on a pseudo-orthorhombic sublattice with parameters  $a = 6.131$ ,  $b = 36.254$ ,  $c = 6.844$  Å,  $\alpha = 90.00$ ,  $\beta = 90.00$ ,  $\gamma = 90.15^\circ$ ; twin index is 4 and obliquity is  $0.15^\circ$  (Giovanni Ferraris, pers. comm.).

Leverettite crystals are transparent with a medium to deep green colour. They have a light green streak and a vitreous lustre. Leverettite does not fluoresce in long- or short-wave ultraviolet light. Mohs hardness was determined to be  $\sim 3$ . The crystals are brittle with conchoidal fracture and a perfect cleavage on  $\{101\}$ . The calculated density based on the empirical formula is  $3.709 \text{ g cm}^{-3}$ , and the measured density by flotation in Clerici solution is  $3.64(2) \text{ g cm}^{-3}$ . The crystals are optically uniaxial (–) and exhibit distinct pleochroism:  $O$  (bluish green)  $> E$

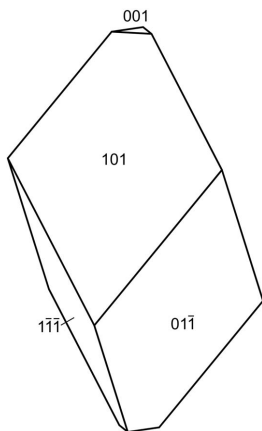


FIG. 4. Crystal drawing of leverettite rhombohedron, clinographic projection.

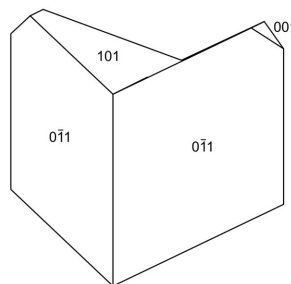


FIG. 5. Crystal drawing of leverettite V-shaped twin, clinographic projection.

(slightly yellowish green). The indices of refraction,  $\omega$  and  $\epsilon$ , are  $>1.8$  and, because crystals react rapidly in refraction index fluids over 1.8, the indices of refraction could not be measured. The mineral is readily soluble in cold, dilute HCl.

### Chemical composition

The composition of leverettite was determined by chemical analyses (9) using a JEOL 8600 electron microprobe operated in WDS mode. A 15 kV accelerating voltage, 20 nA beam current, and  $3 \mu\text{m}$  beam diameter were used. Because insufficient material was available for a direct determination of  $\text{H}_2\text{O}$ , the amount of water was calculated on the basis of eight anions ( $O + Cl$ ) p.f.u., as determined by the crystal structure analysis (see below). Data are presented in Table 1 and no other elements were detected.

As is the case with related minerals herbertsmithite, gillardite, paratacamite-(Mg) and paratacamite-(Ni), the structure is composed of sheets of composition  $\text{Cu}_3\text{Cl}_2(\text{OH})_6^{2-}$  linked by  $\text{M}^{2+}$  ions lying between them. Therefore, the formula may be written as  $\text{Cu}_3\text{MCl}_2(\text{OH})_6$ . The data show the compositions of crystals to be rather variable. Individual analyses gave cation normalized compositions ranging from  $\text{Cu}_3(\text{Co}_{0.31}\text{Cu}_{0.48}\text{Mn}_{0.17}\text{Ni}_{0.03}\text{Mg}_{0.01})(\text{OH})_6\text{Cl}_2$  to  $\text{Cu}_3(\text{Co}_{0.55}\text{Cu}_{0.36}\text{Mn}_{0.05}\text{Ni}_{0.04})(\text{OH})_6\text{Cl}_2$ , with respect to the Co–Cu substitution. From the average data, the empirical composition based on eight anions ( $O + Cl$ ) p.f.u. is  $\text{Cu}_3(\text{Co}_{0.43}\text{Cu}_{0.40}\text{Mn}_{0.17}\text{Ni}_{0.07}\text{Mg}_{0.01})_{\Sigma 1.08}\text{Cl}_{1.87}\text{O}_{6.13}\text{H}_6$  and shows that the interlayer site is dominated by  $\text{Co}^{2+}$ . The sample was unstable in the beam, accounting for the low Cl content. It is assumed that the sample of leverettite examined in this study is an intermediate phase in a solid solution leading to the ideal endmember formula  $\text{Cu}_3\text{CoCl}_2(\text{OH})_6$ , which requires CoO 17.73, CuO

TABLE 1. Electron microprobe analyses of leverettite.

| Constituent      | Wt.%   | Range       | SD   | Standard |
|------------------|--------|-------------|------|----------|
| CuO              | 62.80  | 56.44–67.65 | 3.43 | Cu       |
| CoO              | 7.49   | 5.64–9.85   | 1.33 | Co       |
| NiO              | 1.23   | 0.51–2.77   | 0.71 | Ni       |
| MnO              | 2.72   | 0.78–3.68   | 0.97 | Mn       |
| MgO              | 0.06   | 0.00–0.12   | 0.04 | Olivine  |
| Cl               | 15.40  | 14.58–15.80 | 0.37 | TlCl     |
| H <sub>2</sub> O | 12.57* |             |      |          |
| O $\equiv$ Cl    | –3.47  |             |      |          |
| Total            | 98.80  |             |      |          |

\* Calculated on the basis of eight anions (O + Cl) p.f.u.

56.48, Cl 16.78, H<sub>2</sub>O 12.79, O = Cl -3.79, total 100.00 wt.%,

## X-ray crystallography

### Powder diffraction

Powder diffraction data from a sample of leverettite were collected using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer with monochromated MoK $\alpha$  radiation. Unit-cell parameters refined from the powder data, using the *JADE 2010* software package (Materials Data, Inc., 2011) with whole-pattern

fitting, are  $a = 6.8383(9)$ ,  $c = 14.081(2)$  Å,  $V = 570.2(1)$  Å<sup>3</sup>. Powder-diffraction data are listed in Table 2. There is a high correspondence of peak positions between the X-ray powder data of leverettite and those reported for herbertsmithite, gillardite, paratacamite and its analogues (Braithwaite *et al.*, 2004; Colchester *et al.*, 2007; Jambor *et al.*, 1996; Kampf *et al.*, 2013; Sciberras *et al.*, 2013). The significant mixed occupancy of Co, Mn, Cu and Ni would have significant influence on ideal peak position when compared with material corresponding to Cu<sub>3</sub>CoCl<sub>2</sub>(OH)<sub>6</sub>.

TABLE 2. X-ray powder diffraction data for leverettite.

| $I_{\text{obs}}$ | $d_{\text{obs}}$ | $d_{\text{calc}}$ | $I_{\text{calc}}$ | $h\ k\ l$ | $I_{\text{obs}}$ | $d_{\text{obs}}$ | $d_{\text{calc}}$ | $I_{\text{calc}}$ | $h\ k\ l$ |
|------------------|------------------|-------------------|-------------------|-----------|------------------|------------------|-------------------|-------------------|-----------|
| 90               | 5.469            | 5.4616            | 100               | 1 0 1     | 7                | 1.666            | 1.6629            | 5                 | 0 2 7     |
| 18               | 4.701            | 4.6879            | 18                | 0 0 3     | 5                | 1.632            | 1.6327            | 7                 | 1 3 1     |
| 10               | 4.557            | 4.5318            | 3                 | 0 1 2     | 7                | 1.606            | 1.6072            | 4                 | 2 2 3     |
| 8                | 3.420            | 3.4218            | 5                 | 1 1 0     |                  |                  | 1.6006            | 2                 | 3 1 2     |
| 5                | 3.032            | 3.0239            | 2                 | 1 0 4     | 11               | 1.513            | 1.5119            | 9                 | 2 0 8     |
| 22               | 2.905            | 2.8997            | 25                | 0 2 1     |                  |                  | 1.5106            | 2                 | 3 0 6     |
| 100              | 2.766            | 2.7638            | 84                | 1 1 3     | 15               | 1.497            | 1.4957            | 13                | 2 1 7     |
|                  |                  | 2.7308            | 19                | 2 0 2     | 4                | 1.472            | 1.4735            | 4                 | 4 0 1     |
| 12               | 2.348            | 2.3440            | 12                | 0 0 6     | 4                | 1.450            | 1.4498            | 6                 | 0 4 2     |
| 66               | 2.269            | 2.2659            | 70                | 0 2 4     | 6                | 1.422            | 1.4214            | 4                 | 1 1 9     |
| 7                | 2.215            | 2.2122            | 5                 | 2 1 1     |                  |                  | 1.4192            | 1                 | 3 1 5     |
| 11               | 2.041            | 2.0401            | 11                | 2 0 5     | 23               | 1.383            | 1.3830            | 2                 | 1 2 8     |
|                  |                  | 1.9338            | 1                 | 1 1 6     |                  |                  | 1.3819            | 17                | 2 2 6     |
| 13               | 1.906            | 1.9027            | 12                | 1 0 7     | 8                | 1.364            | 1.3684            | 1                 | 1 0 10    |
| 26               | 1.822            | 1.8205            | 27                | 0 3 3     |                  |                  | 1.3654            | 9                 | 4 0 4     |
| 3                | 1.754            | 1.7523            | 4                 | 1 2 5     | 4                | 1.352            | 1.3534            | 5                 | 3 2 1     |
| 33               | 1.711            | 1.7109            | 32                | 2 2 0     | 3                | 1.311            | 1.3109            | 3                 | 0 4 5     |
|                  |                  | 1.6854            | 1                 | 0 1 8     |                  |                  |                   |                   |           |

*Single-crystal diffraction*

A total of 82 frames at 15-minute exposures were recorded using the same instrumentation and radiation described above for the powder diffraction measurements. The Rigaku *CrystalClear* software package was used for processing the structure data, including the application of an empirical multi-scan absorption correction using *ABSCOR* (Higashi, 2001). A unit cell of  $a = 6.8436(6)$  and  $c = 14.064(1)$  Å was determined from the full data set. No super-structure reflections were observed. The structure was solved by direct methods in space group  $R\bar{3}m$  using *SIR2004* (Burla *et al.*, 2005). *SHELXL-97* (Sheldrick, 2008) was used for the refinement of the structure. The heavy atom positions were located in analogous positions to those found in herbertsmithite. Of the two metal positions identified, the *M2* position at  $9e$  (0.5, 0, 0), which is bonded to four equatorial OH<sup>−</sup> and two axial Cl<sup>−</sup> ligands in a typical (4+2) Jahn-Teller

distorted geometry, has been well established to ideally be fully occupied by Cu (Braithwaite *et al.*, 2004; Clissold *et al.*, 2007; Fleet, 1975). The *M1* site at  $3b$  (0, 0, 0.5), which is bonded to six symmetry equivalent O atoms in a slightly angularly distorted octahedron, exhibits the full extent of Cu substitution. The same approach as in previous studies was followed here with Cu occupying the *M2* site and excess being placed in *M1* along with the average analyses for Co, Mn, Mg and Ni (normalized to 1). The *M1* site metal composition of (Co<sub>0.42</sub>Cu<sub>0.33</sub>Mn<sub>0.17</sub>Ni<sub>0.07</sub>Mg<sub>0.01</sub>) shows that Co is the dominant cation, but occupies <50% of the position due to the minor, but significant, co-occupancy of Mn, Ni and Mg. A difference map revealed the position of the single crystallographic O and corresponding H atom. The O—H distance was constrained to  $0.90 \pm 0.03$  Å. Refinement converged with anisotropic displacement parameters for all non-H atoms. Structure refinement details are given in Table 3. Final atom coordinates and anisotropic

TABLE 3. Crystal data and structure refinement details for leverettite.

|   |  |
|---|--|
| Structural formula  | Cu <sub>3</sub> (Co <sub>0.42</sub> Cu <sub>0.33</sub> Mn <sub>0.17</sub> Ni <sub>0.07</sub> Mg <sub>0.01</sub> )Cl <sub>2</sub> (OH) <sub>6</sub> |
| Formula weight  | 422.98   |
| Temperature (K)   | 293(2)   |
| Wavelength (Å)  | 0.71075  |
| Crystal system  | Trigonal   |
| Space group   | $R\bar{3}m$  |
| Unit-cell dimensions (Å)  | $a = 6.8436(6)$<br>$c = 14.0637(10)$   |
| Volume (Å <sup>3</sup> )  | 570.42(8)  |
| Z   | 3  |
| Density for above formula (g cm <sup>−3</sup> )                             | 3.694  |
| Absorption coefficient (mm <sup>−1</sup> )                                  | 11.214   |
| <i>F</i> (000)  | 606.7  |
| Crystal size (mm)   | 0.15 × 0.10 × 0.09   |
| Theta range for data collection (°)   | 3.73 to 27.32  |
| Index ranges  | $-8 \leq h \leq 8$ , $-8 \leq k \leq 6$ , $-18 \leq l \leq 18$   |
| Reflections collected   | 3409   |
| Independent reflections   | 183 [ $R_{\text{int}} = 0.0203$ ]  |
| Completeness to theta = 27.32°  | 99.5%  |
| Max. and min. transmission  | 0.432 and 0.284  |
| Refinement method   | Full-matrix least-squares on <i>F</i> <sup>2</sup>   |
| Data/restraints/parameters  | 183/1/20   |
| Goodness-of-fit on <i>F</i> <sup>2</sup>                                    | 1.099  |
| Final <i>R</i> [ $I_{\text{obs}} > 2\sigma(I_{\text{obs}})$ ]               | $R_1 = 0.0226$ , $wR_2 = 0.0552$   |
| <i>R</i> indices (all data)   | $R_1 = 0.0226$ , $wR_2 = 0.0552$   |
| $\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e. Å <sup>−3</sup> ) | 1.263 and −0.508   |
| Weighting scheme  | $w = 1/[\sigma^2(F_o)^2 + (0.0386P)^2 + 2.82P]$<br>$P = [\max(0, F_o)^2 + (2F_c)^2]/3$   |



TABLE 4. Final atom coordinates ( $\times 104$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ).  $U_{\text{eq}} = \frac{1}{5}(U^{11} + U^{22} + U^{33})$  for leverettite.

|     | $x/a$         | $y/b$      | $z/c$         | $U_{\text{eq}}$ | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$  | $U^{13}$ | $U^{12}$    |
|-----|---------------|------------|---------------|-----------------|----------|----------|----------|-----------|----------|-------------|
| M1* | 0             | 0          | $\frac{1}{2}$ | 0.0108(3)       | 0.012(1) | $U^{11}$ | 0.009(1) | 0         | 0        | $0.5U^{11}$ |
| M2  | $\frac{1}{2}$ | 0          | 0             | 0.0131(3)       | 0.013(1) | 0.012(1) | 0.015(1) | 0.002(1)  | 0.001(1) | 0.006(1)    |
| Cl  | 0             | 0          | 0.19407(8)    | 0.0170(3)       | 0.018(1) | $U^{11}$ | 0.015(1) | 0         | 0        | $0.5U^{11}$ |
| O   | 0.2064(2)     | -0.2064(2) | 0.0612(2)     | 0.0163(5)       | 0.015(1) | $U^{11}$ | 0.019(1) | -0.002(1) | $U^{23}$ | 0.007(1)    |
| H   | 0.135(3)      | -0.135(3)  | 0.074(4)      | 0.063(20)       |          |          |          |           |          |             |

\* The assigned occupancy for the M1 site is  $(\text{Co}_{0.42}\text{Cu}_{0.33}\text{Mn}_{0.17}\text{Ni}_{0.07}\text{Mg}_{0.01})$ .

displacement parameters are in listed Table 4 and selected bond lengths and angles in Table 5.

## Discussion

The structure determined here (Fig. 6), with dominant Co in the interlayer position, is analogous to those described by Braithwaite *et al.* (2004) for herbertsmithite, Clissold *et al.* (2007) for gillardite and Fleet (1975) for the paratacamite sub-structure, and extends upon the known substitution series for naturally occurring members of the paratacamite group. The composition, however, is far from the ideal  $\text{Cu}_3\text{Co}(\text{OH})_6\text{Cl}_2$  formula, which is expected to possess a unit cell somewhat larger than the determined dimensions of  $a = 6.8436(6)$  and  $c = 14.064(1)$  Å. This would be indicative of the increased influence of high spin  $\text{Co}^{2+}$  with an effective ionic radius of 0.74 Å for a six coordinate environment, being slightly larger than that of  $\text{Cu}^{2+}$  with 0.73 Å and in line with previous analyses of herbertsmithite and gillardite unit cells (Braithwaite *et al.*, 2004; Clissold *et al.*, 2007). Oswald and Feitknecht (1964) reported the unit-cell dimensions of synthetic  $\text{Co}_2(\text{OH})_3\text{Cl}$ , with  $R\bar{3}m$  symmetry as  $a = 6.84$  and  $c = 14.50$  Å. The  $\text{H}\cdots\text{Cl}$  distance in leverettite was determined to be 2.32(3) Å, which is longer than that reported for gillardite (2.26 Å) by Clissold *et al.* (2007). While the true H position is not represented accurately by data collected using X-rays, the  $\text{O}\cdots\text{Cl}$  distance is a more reliable estimate of the strength of H bonding. In the structure reported here, an  $\text{O}\cdots\text{Cl}$  distance of 3.079(3) Å was found and is significantly longer than that reported for gillardite with 3.049(8) Å (Clissold *et al.*, 2007) and herbertsmithite with 3.071 Å (Braithwaite *et al.*, 2004). The H bond network provides additional support between the sheets of

TABLE 5. Selected bond lengths (Å) and angles ( $^\circ$ ) for leverettite.

| Interlayer |          | Intralayer |           |
|------------|----------|------------|-----------|
| M1–O       | 2.114(3) | M2–O       | 1.983(1)  |
| O–M1–O     | 76.1(1)  | M2–Cl      | 2.7821(9) |
| O–M1–O     | 103.9(1) | O–M2–O     | 97.9(2)   |
| O–M1–O     | 180      | O–M2–O     | 82.2(2)   |
|            |          | O–M2–Cl    | 82.36(6)  |
|            |          | Cl–M2–Cl   | 180       |

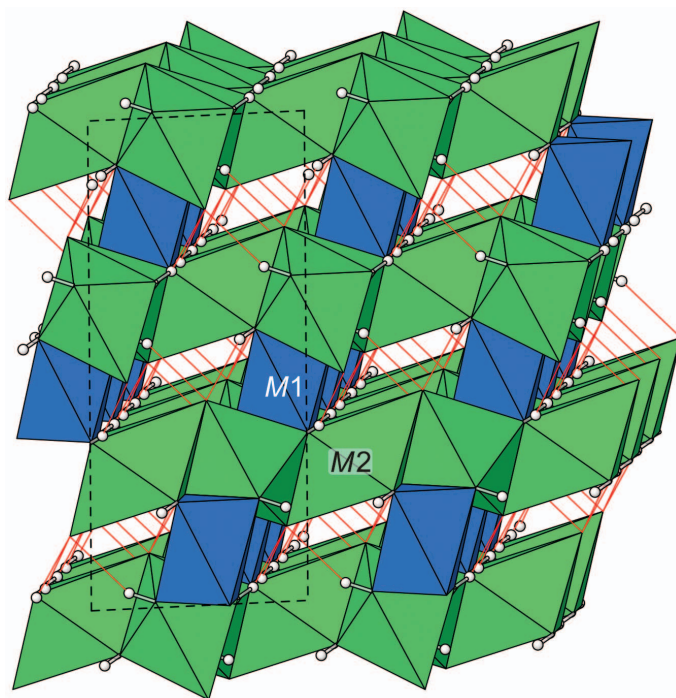


FIG. 6. The crystal structure of leverettite slightly canted down the  $a$  axis with the  $c$  axis vertical. H atoms are shown as white balls. Hydrogen bonds are shown as red lines. The unit cell is shown as a dashed line.

Jahn-Teller distorted  $[\text{Cu}(\text{OH})_4\text{Cl}_2]$ , and is weaker when Co is the dominant substituting cation. By this inference, the strongest H bonding would be expected to occur in the structure of gillardite.

Comparative data for leverettite, herbertsmithite and gillardite are reported in Table 6. Optically and crystallographically it would be difficult to distinguish a crystal of leverettite from the other analogues without recourse to chemical analyses.

This new analogue represents an intermediate composition along the solid solution series described by Jambor *et al.* (1996) and Braithwaite *et al.* (2004). These authors suggested that the monoclinic structure of clinoatacamite is stable with less than 1/3 interlayer occupancy of a substituting cation. They determined from synthetic material that the clinoatacamite structure destabilizes at ~5 wt.% Co substitution. However, in their work two-phase mixtures of

TABLE 6. Comparative data for leverettite, herbertsmithite and gillardite.

|                   | Leverettite*                            | Herbertsmithite**                       | Gillardite**                            |
|-------------------|---|---|---|
| Ideal formula     | $\text{CoCu}_3\text{Cl}_2(\text{OH})_6$ | $\text{ZnCu}_3\text{Cl}_2(\text{OH})_6$ | $\text{NiCu}_3\text{Cl}_2(\text{OH})_6$ |
| Space group       | $R\bar{3}m$                             | $R\bar{3}m$                             | $R\bar{3}m$                             |
| $a$ (Å)           | 6.8383(9)                               | 6.834(1)                                | 6.8364(1)                               |
| $c$ (Å)           | 14.081(2)                               | 14.075(2)                               | 13.8459(4)                              |
| $Z$               | 3                                       | 3                                       | 3                                       |
| Optical character | uniaxial (–)                            | uniaxial (–)                            | uniaxial (+)                            |

\*  $(\text{Cu}_{3.33}\text{Co}_{0.42}\text{Mn}_{0.17}\text{Ni}_{0.07}\text{Mg}_{0.01})_{\Sigma 4.00}\text{Cl}_2(\text{OH})_6$ .

\*\* Close to stoichiometrically pure.

rhombohedral  $\text{Co}_2(\text{OH})_3\text{Cl}$  and monoclinic  $\text{Cu}_2(\text{OH})_3\text{Cl}$  were reported for synthetic material. An endmember of  $\text{Cu}_3\text{Co}(\text{OH})_6\text{Cl}_2$  is proposed for leverettite, based on knowledge of related members of the group. The lower endmember composition for this phase and its relationship with a Co-rich analogue of paratacamite or clinoatacamite are unknown.

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