

$\text{Cu}_3\text{MgCl}_2(\text{OH})_6$ and the bond-valence parameters of the OH—Cl bond

Thomas Malcherek* and Jochen Schlüter

Mineralogisch-Petrographisches Institut, Universität Hamburg, Grindelallee 48, D-20146 Hamburg, Germany

Correspondence e-mail: thomas.malcherek@uni-hamburg.de

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The title compound is a new mineral consisting of sheets made from edge-sharing $\text{Cu}(\text{OH})_4\text{Cl}_2$ and $\text{Mg}(\text{OH})_6$ octahedra. The sheets are only weakly linked by O—H—Cl bridges, giving rise to perfect cleavage along (001) and to strong texture effects in powder diffraction measurements. Owing to low bond-valence sums at the Cl sites of $\text{Cu}_3\text{MgCl}_2(\text{OH})_6$ and of several related compounds, bond-valence parameters for the H/Cl pair have been refined to $R_0 = 1.336$ and $b = 0.53 \text{ \AA}$ based on the crystal structures of selected hydroxychlorides.

1. Introduction

Recently the crystal structure of the new mineral kapellasite, $\text{Cu}_3\text{ZnCl}_2(\text{OH})_6$, has been described by Krause *et al.* (2006). Judging by the similarity of the powder diffraction data, these authors identified kapellasite as a member of a group of synthetic hydroxychlorides that had been synthesized by Feitknecht & Maget (1949). The title compound of the present study was probably also among the synthesized compounds, but its crystal structure has, to the authors' knowledge, never been completely determined before. $\text{Cu}_3\text{MgCl}_2(\text{OH})_6$ is found as a mineral in the Tarapacá province of northern Chile. The mineral data have been submitted to the International Mineralogical Association for approval as a new mineral.

2. Experimental

The stoichiometry of the sample was confirmed to be $\text{Cu}_3\text{MgCl}_2(\text{OH})_6$ by microprobe analysis in wavelength-dispersive mode. Single-crystal X-ray diffraction data were collected on a Nonius KappaCCD diffractometer with Mo $K\alpha$ radiation (Table 1).¹ The data have been integrated using *DENZO SMN* (Otwinowski & Minor, 1997) and processed using *WinGX* (Farrugia, 1999). An empirical absorption correction has been applied using *SORTAV* (Blessing, 1995) as implemented in *WinGX*. Powder diffraction measurements have been made using a Philips Xpert diffractometer with Cu $K\alpha$ radiation and a secondary beam graphite monochromator. Lattice parameters $a = 6.2728(1)$ and $c = 5.7462(1) \text{ \AA}$ have been refined using a model-independent full profile fit, as implemented in the *GSAS* program (Larson & Von Dreele, 1994).

3. Crystal structure of $\text{Cu}_3\text{MgCl}_2(\text{OH})_6$

The crystal structure has been solved by placing Mg on the 1(*a*) and Cu on the 3(*f*) Wyckoff positions of space-group symmetry $P\bar{3}$. The positions of the other atoms, including H, were subsequently located on difference-Fourier maps. The resulting structure proved to be consistent with the higher space-group symmetry $P\bar{3}m1$.

Structure refinement based on squared structure factors has been carried out in the space group $P\bar{3}m1$ using *JANA2000* (Petricek *et al.*, 2000). All atoms except H have been refined with anisotropic

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: SO5007). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

Crystal data	
Chemical formula	$\text{Cl}_2\text{Cu}_3\text{H}_6\text{MgO}_6$
M_r	387.9
Cell setting, space group	Trigonal, $P\bar{3}m1$
Temperature (K)	293
a, c (Å)	6.2733 (4), 5.7472 (5)
V (Å ³)	195.88 (2)
Z	1
D_x (g cm ⁻³)	3.287
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	8.81
Crystal form, color	Irregular, greenish-blue
Crystal size (mm)	0.17 × 0.15 × 0.08
Data collection	
Diffractometer	Nonius KappaCCD
Data collection method	φ scans and ω scans with κ offsets
Absorption correction	Multi-scan (based on symmetry-related measurements)
T_{\min}	0.271
T_{\max}	0.401
No. of measured, independent and observed reflections	8900, 628, 562
Criterion for observed reflections	$I > 3\sigma(I)$
R_{int}	0.039
θ_{\max} (°)	44.6
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.020, 0.085, 1.14
No. of reflections	628
No. of parameters	20
H-atom treatment	Refined independently
Weighting scheme	Based on measured s.u.s., $w = 1/[\sigma^2(I) + 0.0036I^2]$
$(\Delta/\sigma)_{\max}$	< 0.0001
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	0.45, -0.38
Extinction method	B-C type 1 Lorentzian isotropic (Becker & Coppens, 1974)
Extinction coefficient	0.00055 (15)

Computer programs used: COLLECT (Bruker AXS BV, 1997–2004), HKL DENZO and SCALEPACK (Otwinowski & Minor, 1997), JANA2000 (Petricek *et al.*, 2000).

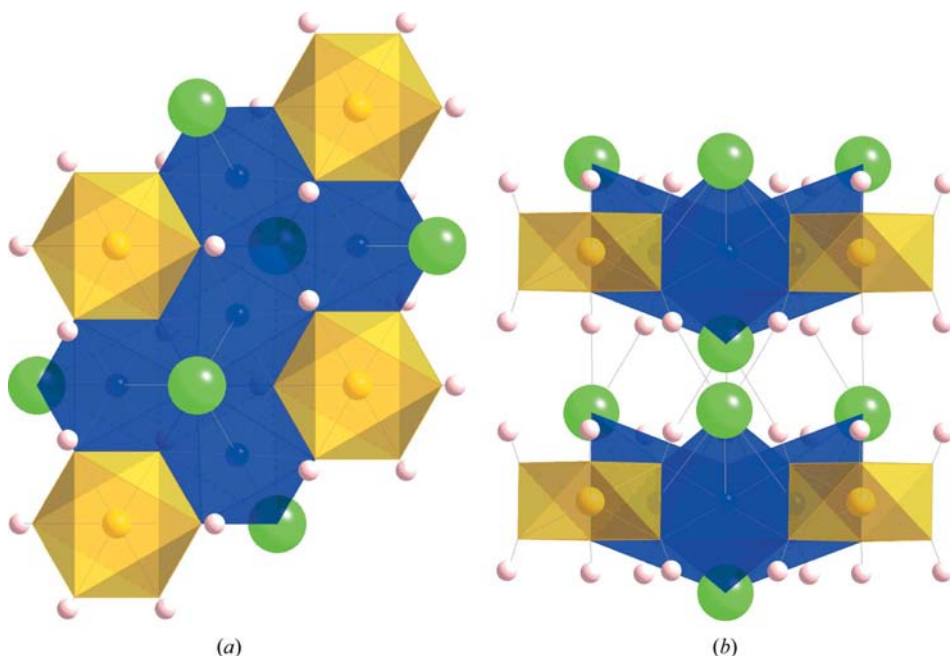


Figure 1
The crystal structure of $\text{Cu}_3\text{MgCl}_2(\text{OH})_6$ projected down $[001]$ (left) and down $[210]$ (right). Blue and yellow octahedra are occupied by Cu and Mg, respectively, with the Cl atoms shown in green. O atoms at the corners of the polyhedra are not shown. H atoms are represented by pink spheres.

displacement parameters. No restraints were used on the H-atom coordinates.

The structure of $\text{Cu}_3\text{MgCl}_2(\text{OH})_6$ is shown in Fig. 1. Cl is coordinated by three H and three Cu nearest-neighbor (NN) cations, forming a trigonal antiprism. The H–Cl bonds that connect individual sheets of octahedrally coordinated Cu and Mg atoms have a length of 2.48 (3) Å. Similar inter-layer bonding occurs in the mineral botallackite, $\text{Cu}_2(\text{OH})_3\text{Cl}$. Other NN distances (in Å) are: 2.111 (1) (Mg–O), 1.977 (1) (Cu–O), 2.7650 (3) (Cu–Cl) and 0.79 (3) (H–O). The bond-valence sums (BVS) calculated with the parameter values given by Brese & O’Keeffe (1991) and with $d_0 = 0.569$ and $b = 0.94$ for the O–H bond (Brown, 2006) yield reasonable charges for Cu, Mg and H (2.04, 1.94 and 1.02, respectively), while oxygen appears overbonded with a valence of 2.19. However, the calculated BVS of Cl is only 0.5. As the only bond-valence parameter available for the H/Cl pair is that given by Brese & O’Keeffe (1991), its redetermination was expected to improve the predicted atomic valence of Cl.

4. Calculation of bond-valence parameters

The bond valence (BV) associated with an anion–cation pair X/A may be approximated as

$$v_{A-X} = \exp\left(\frac{R_0 - R_{A-X}}{b}\right),$$

where R_0 and b are the BV parameters of the particular pair and R_{A-X} is the interatomic distance. By summation of the individual v_{A-X} values for all counterions coordinating a given cation A or anion X , an empirical measure of the valence of that ion is obtained in the form of the BVS. This measure can be compared with the ideal or expected atomic valence. Literature values of the BV parameters (Brown & Altermatt, 1985; Brese & O’Keeffe, 1991; Brown, 2006) commonly imply that $b = 0.37$ Å. However, the universal character of b is in many cases based on the inclusion of only NN ions in the

derivation of the strongly correlated BV parameters R_0 and b (Adams, 2001). Unrealistically small values of the BVS may result in cases where a bond is in fact softer than implicitly assumed in the derivation of its BV parameters.

A search of the ICSD (version 1.2006) for hydroxylchlorides with H–Cl bonds up to 3 Å yielded 87 hits. Only those with a reported R value below 0.04, without potentially strain-inducing steric groups and without disorder, have been considered further. The resulting list includes X-ray and neutron diffraction measurements as well as one structure determination by first-principle computational methods (#51677, botallackite). The use of structure data obtained by X-ray

Table 2

Bond-valence sums of the title compound and of selected (Cu,Pb)-hydroxychlorides using the derived BV parameters and those given by Brese & O'Keeffe (1991).

The structural data of kapellasite have been obtained from Krause *et al.* (2006) and combined with the hydrogen position of this study. The cut-off for interatomic distances was set to 3.5 Å. BV calculations have been performed using JANA2000 (Petricek *et al.*, 2000).

	Mineral name	ICSD	H	Cl	O	Cu	Mg	Zn	
Cu ₃ MgCl ₂ (OH) ₆	–	–	1.24	0.91	2.28	2.04	1.94	–	
Cu ₃ ZnCl ₂ (OH) ₆	Kapellasite	–	1.24	0.90	2.28	2.06	–	1.91	
			H1	H2	Cl	O1	O2	Cu1	Cu2
Cu ₂ (OH) ₃ Cl	Botallackite	51677	1.01	1.01	1.07	1.97	2.07	1.93	2.22
Cu ₂ (OH) ₃ Cl	Atacamite	61252	1.06	1.14	1.03	1.98	2.17	2.04	1.97
			H	Cl	O	Cu1	Cu2		
Cu ₂ (OH) ₃ Cl	Paratacamite	64956	0.96	1.42	1.81	1.89	2.02		
			H	Cl	O	Cu	Pb		
Pb(OH)Cl	Laurionite	404572	0.99	0.96	2.10	–	2.07		
Pb(OH)Cl	Paralaurionite	74291	0.92	1.00	2.01	–	2.08		
			H	Cl1	Cl2	O	Cu	Pb	
Pb ₂ Cu(OH) ₄ Cl	Diaboleite	81589	0.94	1.05	0.93	2.01	2.11	2.09	

structure refinement potentially poses problems in the derivation of BV parameters of interest here, as the observed primary O–H bonds are well known to appear systematically short by up to 0.2 Å with respect to the distance between the atomic nuclei. Therefore, judging by information contained in the ICSD only three samples (#51677, #83509, #404572) remain for BV-parameter refinement, if hydrogen positions based exclusively on X-ray diffraction data are to be avoided. Using all anion (Cl or O) contacts within a range of 3.5 Å around each Cl-bonded hydrogen, a set of 20 H-atom coordination environments including the title compound has been compiled. The nearest-neighbor O–H distances in this set range between 0.72 and 1.14 Å. Only four of these coordination environments have been used for parameter fitting. A set of 15 Cl-atom coordination environments corresponds to the selected H atoms. Apart from H⁺ seven other cation species ($X = \text{Li}^+, \text{Ag}^+, \text{Cu}^{2+}, \text{Pb}^{2+}, \text{Cd}^{2+}, \text{Zn}^{2+}$ and Sm^{3+}) fall into the selected cut-off range of 3.5 Å for the chosen set of Cl environments. Bond-valence parameters of these X –Cl bonds have been taken from Brese & O'Keeffe (1991). Again only three Cl environments have been used for parameter fitting (Fig. 2*a*). Initial calculation of the chlorine BVS values yields an average of 0.7 ± 0.2 . The low average BVS is also seen on the left-hand side of Fig. 2*a*). The average BVS at the hydrogen sites is 1.05 ± 0.13 with the initial parameters.

Non-linear least-squares optimization of the BV parameters for the H/Cl and O/H pairs against the expected BVS for the seven well determined coordination environments yields the parameters $R_0(\text{HCl}) = 1.336$, $b(\text{HCl}) = 0.53$ and $R_0(\text{HO}) = 0.781$, $b(\text{HO}) = 0.56$ Å, respectively. In order to achieve equal weighting of the calculated BVSs with respect to the number of cations and anions involved, the smaller number of Cl environments has been compensated by weighting the corresponding BVS differences with a factor of 4/3. The better agreement achieved with the final parameter values manifests itself in an average BVS of 1.06 ± 0.1 at the Cl sites, while the average BVS at the H sites is the same as before, albeit with a smaller standard deviation. If only those environments involved in fitting (Fig. 2*a*) are taken into consideration, both types of sites average to a BVS of 1.0.

5. Results and discussion

The bond valence as a function of the bond distance is shown in Fig. 2*b*). The H–Cl bond appears to have considerably further range than predicted with the parameters derived by Brese & O'Keeffe (1991). Calculated BVSs of the title compound and of several other hydroxychlorides are shown in Table 2. In several cases O and H appear overbonded, while Cl appears slightly underbonded. Some of these deviations (Fig. 2*a*) can be attributed to the incorrect determination of the H position in X-ray diffraction studies. This is obviously the case for the title compound, where the effects of shifting H away from the electron density maximum towards the (assumed) position of the nucleus can be demonstrated: If the shift is 0.15 Å this accounts for a reduction in bond valence by 0.23 v.u. (Fig. 2*b*). Simultaneously Cl gains approximately 0.04 v.u. by a corresponding shortening of the hydrogen bond. The resulting BVS for O, H and Cl are close to ideal (2.05, 1.01 and 1.03). Some hydrogen positions obtained from X-ray data may have been subject to a soft constraint (*e.g.* #81589; Cooper & Hawthorne, 1995), thus their BVS values appear close to ideal in Fig. 2*a*). Very strong Cl overbonding is obtained for paratacamite (Table 2 and Fig. 2*a*), where the Cl coordination is similar to Cu₃MgCl₂(OH)₆. This is due to an extremely short H–Cl bond of 1.953 Å for the $R\bar{3}m$ substructure (Fleet, 1975) that is given as entry #64956 in the ICSD. Cation mixing on the Cu₁ site of paratacamite probably stabilizes the rhombohedral structure against monoclinic distortion towards clinoatacamite (Braithwaite *et al.*, 2004). Unfortunately, neither the H positions of clinoatacamite (Grice *et al.*, 1996) nor those of the $R\bar{3}$ superstructure of paratacamite (Fleet, 1975) appear to have been determined yet. The strong deviations of the Cl-BVS in this case seem to reflect the incompleteness of the existing structural models rather than inadequacy of the derived BV parameters.

The final BV parameters for the O/H pair are not considered to be generally superior to the initial parameters. Their refinement has been carried out in order to optimize the parameters for the given set of data and the given bond length cut-off. Concerning the parameters obtained for the H/Cl pair, a bond valence of 1 corresponds to a

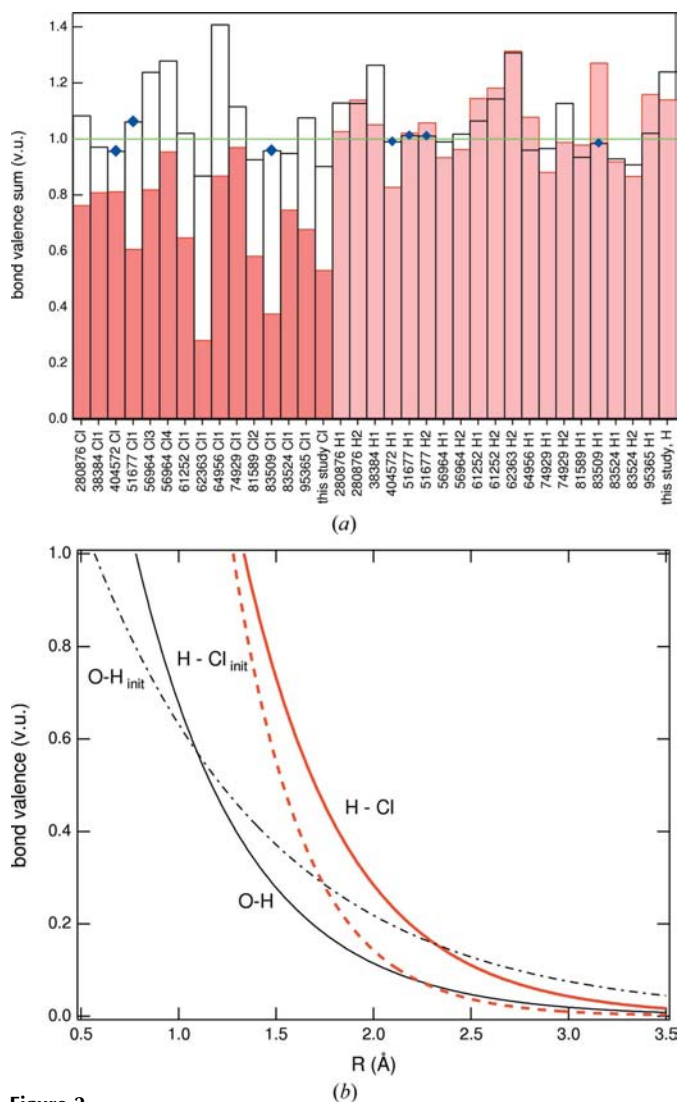


Figure 2
 (a) Bond-valence sum at the Cl and H sites of various hydroxychloride structures specified by their ICSD entry number, before (filled red bars) and after parameter optimization (open black bars). Blue diamonds mark data points used for parameter refinement. (b) Bond valence as a function of bond distance. Red represents H/Cl, black represents O/H. The dashed and the dot-dashed curves show the respective functions with the initial set of parameters. This figure is in color in the electronic version of this paper.

distance of 1.336 Å. This value approaches the actual H–Cl bond distance of 1.274 Å in isolated hydrogen chloride.

The H atoms that surround Cl of the title compound at a distance of 3.20 (1) Å each contribute 0.03 v.u. to the Cl-BVS, compared with a valence of 0.12 (or 0.15 for the corrected bond) and 0.13 for the NN bonds to the H and Cu atoms, respectively. Hence, Cl may be regarded as 12 coordinated by nine H and three Cu atoms.

The structure data of kapellasite as given by Krause *et al.* (2006) may be completed by inserting the H position refined for Cu₃MgCl₂(OH)₆ with a shift of (0,0,1/2). The resulting BVSs for kapellasite are listed in Table 2, demonstrating the strong similarity of the two compounds. The most obvious difference is the smaller *c/a* ratio of kapellasite, which is linked to its slightly smaller O–H–Cl bond angle. This in turn is related to a slightly shorter Cu–O bond.

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