

Paratacamite-(Ni), $\text{Cu}_3(\text{Ni,Cu})\text{Cl}_2(\text{OH})_6$, a new mineral from the Carr Boyd Rocks mine, Western Australia

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ABSTRACT

Paratacamite-(Ni) (IMA 2013-013), $\text{Cu}_3(\text{Ni,Cu})\text{Cl}_2(\text{OH})_6$, is a new Ni-rich mineral with the paratacamite structure. It occurs in the Carr Boyd Rocks nickel mine, Western Australia, as a supergene alteration phase in association with gillardite, spangolite and gypsum. Paratacamite-(Ni) occurs as aggregates of equant rhombohedral crystals up to ca 2 mm in size and exhibits the forms {101}, {021} and {001}. The mineral is dark green with a light-green streak, transparent and has a vitreous lustre. It has good cleavage on {10 $\bar{1}$ 1}. Measured and calculated densities are 3.70 and 3.735 g cm⁻³, respectively. Optically, paratacamite-(Ni) is uniaxial (-) with ω and $\epsilon > 1.8$. The average of eight electron-microprobe analyses gave the empirical formula $\text{Cu}_3(\text{Ni}_{0.71}\text{Cu}_{0.27}\text{Co}_{0.02})\text{Cl}_2(\text{OH})_6$. The new mineral is trigonal, space group $R\bar{3}$, with $a = 13.682(2)$ and $c = 13.916(2)$ Å, $V = 2256.0(7)$ Å³ and $Z = 12$. The strongest reflections in the X-ray powder diffraction pattern are [d_{obs} Å(I)(hkl)]: 5.445(81)(021), 4.637(13)(003), 4.505(8)(202), 2.894(21)(401), 2.751(100)(223), 2.254(65)(404), 1.815(14)(603) and 1.708(9)(440). The structure refined to $R_1 = 0.0225$ and $wR_2 = 0.0660$ for 314 reflections with $F_{\text{obs}} > 4\sigma(F_{\text{obs}})$. The (2+2+2) Jahn-Teller distortion present in the $M(2)\text{O}_6$ octahedron suggests that the new mineral is close to the limit of Cu^{2+} substitution by Ni^{2+} .

INTRODUCTION

During an investigation of the crystal-chemistry of the substituted Cu(II) hydroxychloride minerals, an exhaustive search of specimens from the Carr Boyd Rocks and 132 North nickel deposits (Nickel and Clarke, 1976; Nickel *et al.*, 1994) in Western Australia that are held in the Gartrell Collection of the Western Australian Museum was undertaken by one of the authors (PJD). All of the material from the 132 North deposit had compositions reaching $\text{Cu}_3\text{NiCl}_2(\text{OH})_6$, characteristic of the mineral gillardite, with trigonal symmetry in space group $R\bar{3}m$ (Clissold *et al.*, 2007; Colchester *et al.*, 2007). However, the search brought to light two specimens from the Carr Boyd Rocks mine, including Western Australian Museum specimen number WAM M365.2003 (formerly G3520), that had a somewhat lower Ni content than the 132 North specimens. Chemical analyses revealed significant mixed occupancy of Cu, Ni and minor amounts of Co, giving the composition $\text{Cu}_3(\text{Ni}_{0.71}\text{Cu}_{0.27}\text{Co}_{0.02})\text{Cl}_2(\text{OH})_6$. A single-crystal X-ray structure analysis of material from WAM M365.2003 indicated trigonal symmetry, with a hexagonal unit cell corresponding to $a = 13.665(4)$ and $c = 13.915(4)$ Å in space group $R\bar{3}$ and a strong sub-cell of dimensions $a' = 6.843(1)$, $c' = 13.935(3)$ Å in space group $R\bar{3}m$. This material proved

to be a congener of paratacamite, $\text{Cu}_3(\text{Cu,Zn})\text{Cl}_2(\text{OH})_6$ (Fleet, 1975; Welch *et al.*, 2013), and paratacamite-(Mg), $\text{Cu}_3(\text{Mg,Cu})\text{Cl}_2(\text{OH})_6$ (Kampf *et al.*, 2013a), both with trigonal symmetry, unit cell $a \sim 13.6$ and $c \sim 14.0$ Å in space group $R\bar{3}$, and a pronounced sub-cell equivalent to $a' = \frac{1}{2}a$, $c' = c$ in space group $R\bar{3}m$.

Paratacamite and its congeners are intermediate phases in a solid-solution series extending between $\text{Cu}_4\text{Cl}_2(\text{OH})_6$ and $\text{Cu}_3M^{2+}\text{Cl}_2(\text{OH})_6$, where M^{2+} is a cation with similar ionic radius to Cu^{2+} , such as Zn, Ni, Mg, Co *etc.* Compositions approaching the nominal $\text{Cu}_4\text{Cl}_2(\text{OH})_6$ end-member are characteristic of the monoclinic mineral clinoatacamite, space group $P2_1/n$ (Jambor *et al.*, 1996; Grice *et al.*, 1996). The former authors established that only 2 to 3 wt% Zn or Ni in the clinoatacamite structure is required to stabilise a trigonal phase, believed to be paratacamite.

The new mineral and the name paratacamite-(Ni) have been approved by the International Mineralogical Association (IMA 2013-013). The name is in line with those of other related paratacamite congeners (Kampf *et al.*, 2013a). Type material is retained by the Western Australian Museum, specimen number WAM M365.2003.



Figure 1: Paratacamite-(Ni) associated with gypsum on altered ultramafic rock. The sample is 26.5 cm in length. Photo: P. Downes. Specimen: Western Australian Museum, M365

OCCURRENCE

Paratacamite-(Ni) occurs in the Carr Boyd Rocks nickel mine, Western Australia, situated 80 km north-northeast of the city of Kalgoorlie (30°04'S 121°37'E). A large array of secondary Ni and Cu minerals has been found in the oxidized zone of this deposit. The oxidized zone mineral assemblage includes azurite, malachite, gaspéite, magnesite, carrboydite (TL), chalconatronite, georgeite (TL), glaukosphaerite, hydrohonesite, pecoraite, reevesite, takovite, nickelblöndite (TL), covellite, digenite and morenosite (Bridge *et al.*, 1979; Nickel and Clarke, 1976). The new mineral is associated with gypsum and forms thin crusts coating an altered ultramafic rock (Figure 1). Careful examination of the specimen showed that gillardite and spangolite are also associated with paratacamite-(Ni). Both were confirmed by single-crystal structure determinations. Paratacamite-(Ni) is a secondary mineral formed by the oxidation of pentlandite in a saline environment.

Physical and optical properties

Paratacamite-(Ni) forms aggregates up to 2 mm in size of equant, rhombohedral crystals showing the forms {101}, {021} and {001}. Individual crystals are no larger than 0.25 mm. No twinning was observed. Paratacamite-(Ni) is dark green with a light-green streak. It is transparent and has a vitreous lustre. It is non-fluorescent in long- and short-wave ultraviolet light. The Mohs hardness is 3. It is brittle and has a good cleavage on {10 $\bar{1}$ 1}, but with no observable parting, and an uneven fracture. Calculated density from the empirical formula is 3.735 g cm⁻³ and the measured density determined by flotation in Clerici solution is 3.70 g cm⁻³.

Optically, paratacamite-(Ni) is uniaxial (-), ω and $\epsilon > 1.8$. The mineral reacts rapidly with RI fluids > 1.8 , preventing the indices of refraction from being measured; $n_{av} = 1.81$ using the Gladstone-Dale relationship for the empirical formula. No dispersion or pleochroism is observed.

After dissolution in 6 M HNO₃, reaction with dimethylglyoxime and excess NH₃ gives a heavy precipitate of Ni(DMGH₁)₂. Reaction of the acidic solution with potassium mercuric thiocyanate gives pale, yellow-green rosettes of copper mercuric thiocyanate crystals. Addition of AgNO₃ solution and raising the pH with ammonia gives a white precipitate of AgCl. Related species cannot be distinguished visually and the test for Ni in particular is a guide to the nature of this and related Ni-rich phases.

Chemical composition

Electron microprobe analyses (8) were made using a JEOL 8600 electron microprobe operated in WDS mode with an accelerating voltage of 15 kV, 20 nA and 3 μ m beam diameter. No other elements were detected other than those quoted in Table 1. The empirical formula was calculated as Cu_{3.25}Ni_{0.70}Co_{0.02}Cl_{2.06}O_{5.94}H₆, based on eight anions (O + Cl) *pfu*. H₂O was calculated by stoichiometry from the results of the crystal structure analysis, because of the paucity of the available material. The sample was somewhat unstable in the probe, even with reduced beam current, thus accounting for the high analytical total, even though the derived empirical formula is satisfactory. The structure of paratacamite-(Ni) and the isomorphs paratacamite-(Mg) (Kampf *et al.*, 2013a) and paratacamite (Fleet, 1975; Welch *et al.*, 2013), exhibits continual sheets of composition Cu₃Cl₂(OH)₆²⁻ which are linked together by isolated, edge-sharing interlayer M²⁺(OH)₆ octahedra with all OH⁻ ions located in the above sheets. The empirical formula may be written as (Cu_{3.25}Ni_{0.70}Co_{0.02}) _{Σ 3.97}Cl₂(OH)₆. Normalisation to Σ (cations) = 4 gives the formula Cu₃(Ni_{0.71}Cu_{0.27}Co_{0.02})(OH)₆Cl₂ and shows dominance of the interlayer by Ni²⁺. The simplified formula is Cu₃(Ni,Cu)Cl₂(OH)₆.

Table 1: Electron microprobe analyses of paratacamite-(Ni).

	Average* (wt%)	Range (wt%)	Empirical composition	Normalised composition**	Standard
CuO	62.43(0.98)	61.16-64.37	3.25	3.27	Cu
NiO	12.61(1.11)	11.21-13.95	0.70	0.71	Ni
MgO	0.03(0.05)	0.0-0.13			olivine
CoO	0.31(0.05)	0.24-0.38	0.02	0.02	Co
Cl	17.60(0.20)	17.25-17.78	2.06	2.00	TiCl
H ₂ O	13.04		6.00	6.00	
O = Cl	-3.98				
Total	102.04				

*Standard deviation of the average value is in parentheses. **Normalised to Σ (cations) = 4.

X-ray crystallography

X-ray powder diffraction data were recorded at room temperature using a Bruker D8 Advance diffractometer (Ni-filtered CuK α_1 radiation with pure Si as internal standard; λ = 1.5406 Å). Unit cell parameters refined from the powder data are a = 13.667(2) and c = 13.908(5) Å and V = 2256.0(7) Å³. X-ray powder data are listed in Table 2.

A single-crystal of dimensions 0.14 x 0.18 x 0.20 mm was analysed at 296(2) K, using a Bruker Smart 1000 CCD diffractometer with graphite-monochromatized MoK α radiation. A hexagonal super-cell with parameters a = 13.665(4), c = 13.915(4) Å, with a strong sub-cell of dimensions a = 6.843(1), c = 13.935(3) Å were found. Data reduction to the sub-cell and refinement in space group $R\bar{3}m$ based on the atom coordinates of gillardite (Clissold *et al.*, 2007) resulted in R_1 = 0.014 and wR_2 = 0.035 for 187 reflections with $F_{obs} > 4\sigma(F_{obs})$. However, this approach ignored the presence of a considerable number of observed reflections. The true structure was reached by indexing on the super-cell, taking all observed reflections into account. The structure was refined in space group $R\bar{3}$ based on atom coordinates established for paratacamite

Table 2: X-ray powder diffraction data (Å) for paratacamite-(Ni). The strongest lines are given in bold.

I_{obs}	d_{obs}	d_{calc}	I_{calc}	hkl
81	5.445	5.446	67	0 2 $\bar{1}$
13	4.637	4.636	13	0 0 3
8	4.505	4.507	2	2 0 2
6	3.414	3.417	5	2 2 0
2	3.001	2.998	3	0 2 4
21	2.894	2.894	32	4 0 1
100	2.751	2.750	51	2 2 3
5	2.318	2.318	16	0 0 6
65	2.254	2.253	100	4 0 4
2	2.209	2.208	3	$\bar{1}$ 4 2
1	2.128	2.129	<1	4 2 2
4	2.026	2.027	18	0 4 5
1	1.921	1.918	1	2 2 6
5	1.884	1.884	18	0 2 7
14	1.815	1.815	35	6 0 3
1	1.798	1.803	<1	5 0 5
2	1.744	1.743	3	$\bar{5}$ 2 4
9	1.708	1.708	57	4 4 0
2	1.650	1.650	8	4 0 7
1	1.630	1.630	6	6 2 1
		1.603	3	4 4 3
1	1.602*	1.602	<1	$\bar{4}$ 6 1
		1.597	2	2 6 2
1	1.543	1.545	<1	0 0 9
3	1.500	1.499	16	0 4 8
4	1.486	1.485	12	2 4 7
2	1.471	1.471	9	0 8 1
4	1.376	1.375	17	4 4 6
4	1.362	1.361	19	0 8 4
2	1.351	1.351	5	$\bar{1}$ 6 4

*Not used for unit cell refinement.

(Fleet, 1975; Welch *et al.*, 2013). All heavy atoms and all four O atoms refined satisfactorily. All four H atoms were located in a difference map and were constrained to their respective O atom to a uniform distance of 0.98 ± 0.03 Å. All non-H atoms were allowed to refine with anisotropic displacement parameters. The intralayer M3 and M4 sites were assigned to Cu²⁺ and excess was distributed through the interlayer metal sites, in line with previous studies on other paratacamites (Welch *et al.*, 2013; Kampf *et al.*, 2013a). The X-ray scattering factors of Ni (Z = 28) and Cu (Z = 29) are too similar to allow the occupancies of interlayer M1 at 3*b* and M2 at 9*d* to be determined. Kampf *et al.* (2013a) reported a statistical distribution of Mg between both interlayer sites in paratacamite-(Mg), therefore a similar approach was adopted here. The Ni occupancies were set to 71% of the total 3*b* and 9*d* positions and the small amount of Co was distributed statistically between them. This approach yielded equivalent isotropic displacement parameters between the two interlayer sites, within error. However, it should be noted that this does not reflect the true distribution of Cu and Ni between M1 and M2 sites. The possibility remains that the distribution of Ni is preferentially at M1, with excess occupying M2, as suggested elsewhere in the literature (Grice *et al.*, 1996; Braithwaite *et al.*, 2004). The final structure converged to R_1 = 0.0225 and wR_2 = 0.0660 for 314 reflections with $F_{obs} > 4\sigma(F_{obs})$. The final weighting scheme used was $w=1/[\sigma^2(F_o)^2+(0.0419P)^2+0.68P]$ where $P=[\max(0, F_o)^2+(2F_c)^2]/3$ as defined by SHELX-97 (Sheldrick, 2008).

Structure refinement details of both samples are given in Table 3. Final atom coordinates and anisotropic displacement parameters are listed Table 4 and selected bond lengths and angles in Table 5.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The structure of paratacamite-(Ni) (Figure 2) is analogous to that of paratacamite (Fleet, 1975; Welch *et al.*, 2013) and paratacamite-(Mg) (Kampf *et al.*, 2013a). The Cu sites, M3 and M4, form sheets of edge-sharing CuCl₂(OH)₄ Jahn-Teller distorted octahedra, which are further connected to isolated edge-sharing M1(OH)₆ and M2(OH)₆ octahedra in the interlayer. This layer topology is shared with the other phases of the Cu_{4-x}M_xCl₂(OH)₆ substitution series anatacamite (Malcherek and Schlüter, 2009), clinoatacamite (Grice *et al.*, 1996), herbertsmithite (Braithwaite *et al.*, 2004), gillardite (Clissold *et al.*, 2007) and leverettite (isostructural with herbertsmithite and gillardite) (Kampf *et al.*, 2013b). The most significant difference between these structures is the distortion of the interlayer octahedra. In paratacamite-(Ni) and all other paratacamite congeners, the M1-centred octahedron is bonded to six symmetry equivalent O atoms (O1), while the M2-centred octahedron is bonded to three sets of trans O atoms (O2, O3 and O4) which form a rhombically distorted and tetragonally elongated octahedron. This type of distortion may be described as a (2+2+2) Jahn-Teller configuration (Burns and Hawthorne, 1996), and is a pivotal component in the $R\bar{3}$ structure of

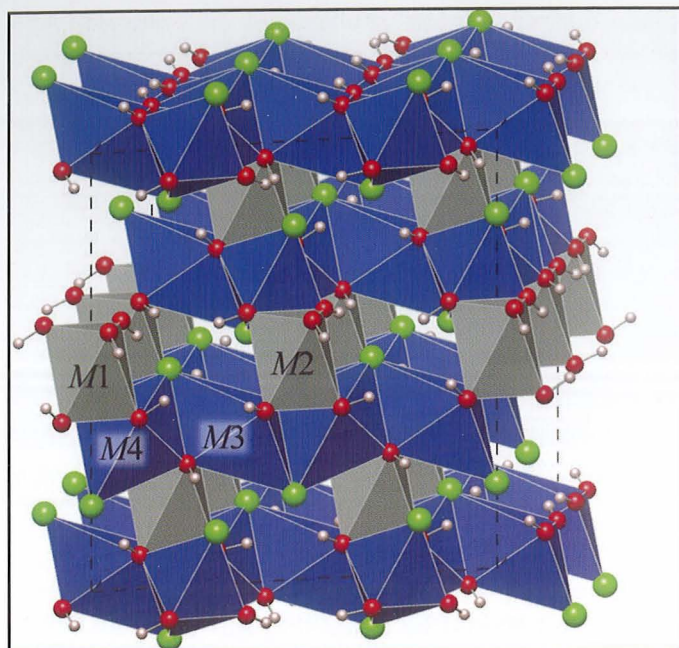


Figure 2: A polyhedral representation of the crystal structure of paratacamite-(Ni), viewed with the *a* axis slightly canted and the *c* axis vertical. Cl atoms are green balls, O atoms are red balls and H atoms are white balls. The unit cell is outlined with a dashed line.

paratacamite-(Ni) and the other paratacamite congeners (Welch *et al.*, 2013; Kampf *et al.*, 2013a). Significantly, the (2+2+2) distortion of the $M(2)O_6$ coordination environment in paratacamite-(Ni) is considerably reduced when compared to that of holotype paratacamite (Welch *et al.*, 2013) and paratacamite-(Mg) (Kampf *et al.*, 2013a) (Table 5). Assuming a statistical distribution of the interlayer cations in the paratacamite structure type, Welch *et al.* (2013) suggested that the (2+2+2) distortion may be derived from a superimposition of Jahn-Teller distorted $Cu(OH)_6$ octahedra with non-tetragonally distorted $M(OH)_6$ octahedra. The average detectable $M-O$ bond lengths would therefore be representative of the relative contribution of the different cations.

Figure 3 displays the $M2O_6$ coordination environment of both paratacamite-(Ni) and paratacamite-(Mg) examined

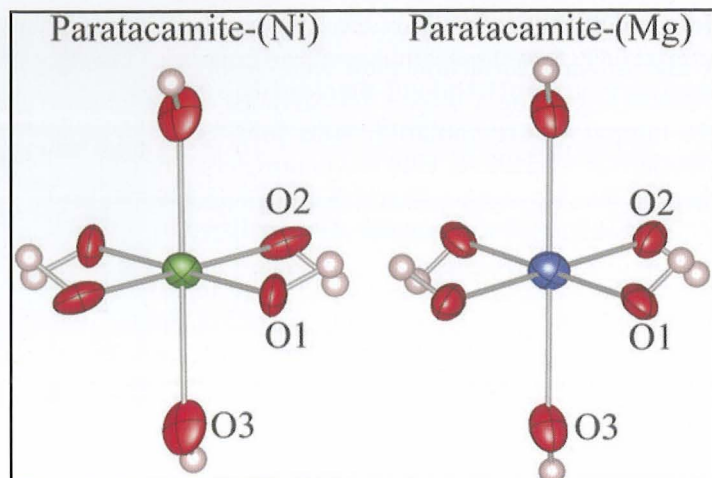


Figure 3: The (2+2+2) Jahn-Teller distortion of the $M(2)O_6$ octahedral coordination environment for paratacamite-(Ni) (this work), and paratacamite-(Mg) (Kampf *et al.*, 2013a). Non-H atoms are represented with anisotropic displacement ellipsoids (probability 85%).

by Kampf *et al.* (2013a). All non-H atoms are pictured with anisotropic displacement ellipsoids (probability 85%). The maximum principal axis of the O2 and O3 displacement ellipsoids are sub-parallel with the direction of the $M2-O$ bond axis. A Ni occupancy of 71% at M2 (Ni-O *ca* 2.08 Å as in gillardite, Clissold *et al.*, 2007) with 29% Cu, split into two orientations of Jahn-Teller distorted octahedra, 2/3 and 1/3 occupancy of each orientation (Jahn-Teller distorted as in clinoatcamite with Cu-O *ca* 2.29, 2.05, and 1.99 Å, Grice *et al.*, 1996) and ignoring the contribution from the small amount of Co, gives an average bond lengths of 2.11, 2.08 and 2.07 Å. These values are similar to the observed data in Table 5. Similarly, in paratacamite-(Mg) (Kampf *et al.*, 2013a) a Mg occupancy of 60% at M2 (Mg-O *ca* 2.09 Å as in synthetic Mg-substituted herbertsmithite, composition $Cu_{3.25}Mg_{0.75}(OH)_6Cl_2$; Chu *et al.*, 2010) with 40% Cu, split into two orientations of Jahn-Teller distorted octahedra, again with 2/3 and 1/3 occupancy of each orientation (Cu-O Jahn-Teller distortion as described above) results in bond lengths of 2.13, 2.09 and 2.07 Å. Again, the averages compare well with the observed $M2-O$ bond lengths of 2.141(5), 2.101(5) and 2.074(4) Å reported in Kampf *et al.* (2013a).

Table 3: Crystal data and structure refinement details for paratacamite-(Ni).

Formula weight	1270.76	Limiting indices	$-17 \leq h \leq 17$
Temperature (K)	296(2)		$-18 \leq k \leq 17$
Wavelength (Å)	0.71073		$-18 \leq l \leq 17$
Crystal system	Trigonal	Reflections /unique	5782/1168
Space group	$R\bar{3}$	R_{int}	0.0236
Unit cell <i>a</i> (Å)	13.665(2)	Completeness to $\theta = 28.23^\circ$	93.8%
<i>c</i> (Å)	13.915(2)	Refinement on F^2	
Volume (Å ³)	2250.2(11)	Data/restraints/parameters	1168/4/87
Z	12	Goodness-of-fit on F^2	0.948
ρ_{calc} (g cm ⁻³)	3.751	Final R [$I_{obs} > 2\sigma(I_{obs})$]	R_1 0.0225
μ (mm ⁻¹)	11.635		wR_2 0.0660
<i>F</i> (000)	2439	<i>R</i> indices (all data)	R_1 0.0599
Crystal size (mm)	0.21 × 0.15 × 0.10		wR_2 0.0897
θ range	2.26 to 28.23°	$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.622 and -0.873

Table 4: Final atom coordinates (x10⁴) and anisotropic displacement parameters* (Å² x10³) for paratacamite-(Ni).

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
<i>M1</i>	0	0	5000	10.5(5)	12.2(8)	<i>U</i> ₂₂	<i>U</i> ₃₃	0	0	0.5 <i>U</i> ₁₁
<i>M2</i>	5000	5000	5000	10.9(2)	12.9(7)	12.2(7)	7.0(5)	0.4(6)	0.9(6)	5.9(6)
<i>M3</i>	4167(1)	3336(1)	3332(1)	13.1(2)	13.8(5)	12.3(4)	13.0(5)	-2.2(3)	-0.8(3)	6.5(4)
<i>M4</i>	4165(1)	5833(1)	3334(1)	12.6(2)	13.4(5)	12.7(4)	11.9(4)	1.0(3)	-0.3(3)	6.8(4)
<i>Cl1</i>	0	0	1937(2)	16.8(7)	19(1)	<i>U</i> ₁₁	12(2)	0	0	0.5 <i>U</i> ₁₁
<i>Cl2</i>	5002(2)	5000(2)	1935(1)	16.1(3)	19(1)	18(1)	11.2(6)	0.8(8)	-0.2(8)	10.1(9)
<i>O1</i>	5631(5)	6262(5)	3953(4)	14(1)	16(3)	10(3)	19(3)	2(2)	-1(2)	9(2)
<i>O2</i>	5639(5)	4380(5)	3956(4)	17(1)	14(3)	23(3)	14(3)	0.4(2.3)	-5(2)	11(3)
<i>O3</i>	3744(5)	4375(5)	3946(4)	19(1)	14(3)	21(3)	25(3)	1(2)	7(2)	12(3)
<i>O4</i>	640(4)	1266(5)	3958(4)	16(1)	9(3)	20(3)	16(3)	-4(2)	-1(2)	5(3)
<i>H1</i>	5942(65)	7049(30)	4118(53)	21						
<i>H2</i>	6037(62)	4046(63)	4275(54)	25						
<i>H3</i>	2994(35)	4063(69)	4186(58)	28						
<i>H4</i>	980(67)	1951(50)	4357(56)	24						

*The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$.
 $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$.

For both paratacamite-(Ni) and paratacamite-(Mg), the difference in observed and calculated bond lengths, by the means set out above, may indicate that three orientations of (4+2) Jahn-Teller distorted octahedra occur with a dynamic interchange between them; the relative occupancy of each orientation are dependent upon temperature (Welch *et al.*, 2013a). The relative occupancy of each orientation would therefore contribute differently towards the observed (2+2+2) distortion. Based on the similarity of the *M1*–*O* and *M2*–*O* bond lengths and the reduced distortion associated with the *M2O*₆ octahedron in paratacamite-(Ni), we suggest that the new mineral is very close to the upper limit of Ni²⁺ occupation in the *R*3̄ structure.

Distinguishing paratacamite-(Ni) from the other isomorphs or from the other closely related Cu(II) hydroxychloride minerals cannot be accurately made using physical or optical methods. Its crystal form and colour makes it virtually indistinguishable from herbertsmithite, gillardite or paratacamite. In addition, the X-ray powder data of paratacamite-(Ni) displays a high degree of correspondence with those of other paratacamite congeners, as well as herbertsmithite, gillardite and anatacamite. Differences in observed and calculated intensities of the X-ray diffraction data suggest that paratacamite-(Ni) is influenced by preferred orientation effects. Single-crystal methods combined with analysis is the best way to distinguish this new mineral from other members of the Cu(II) hydroxychloride group.

Table 5: Selected bond lengths (Å) and angles (°) in paratacamite-(Ni).

<i>Interlayer</i>		<i>Intralayer*</i>			
<i>M1</i> – <i>O4</i> (x6)	2.085(6)	<i>M3</i> – <i>O1</i>	1.980(6)	<i>M4</i> – <i>O1</i>	1.981(6)
<i>O4</i> – <i>M1</i> – <i>O4</i>	180	<i>M3</i> – <i>O2</i>	1.971(6)	<i>M4</i> – <i>O3</i>	1.969(6)
<i>O4</i> – <i>M1</i> – <i>O4</i>	103.0(2)	<i>M3</i> – <i>O2'</i>	1.991(6)	<i>M4</i> – <i>O4</i>	1.975(6)
<i>M2</i> – <i>O1</i> (x2)	2.087(5)	<i>M3</i> – <i>O3</i>	1.976(6)	<i>M4</i> – <i>O4'</i>	1.991(5)
		< <i>M3</i> – <i>O</i> >	1.980	< <i>M3</i> – <i>O</i> >	1.979
<i>M2</i> – <i>O2</i> (x2)	2.081(6)	<i>M3</i> – <i>Cl2</i>	2.768(2)	<i>M4</i> – <i>Cl1</i>	2.766(3)
<i>M2</i> – <i>O3</i> (x2)	2.089(6)	<i>M3</i> – <i>Cl2</i>	2.772(3)	<i>M4</i> – <i>Cl2</i>	2.775(2)
		< <i>M3</i> – <i>Cl</i> >	2.770	< <i>M3</i> – <i>Cl</i> >	2.771
<i>O1</i> – <i>M2</i> – <i>O1</i>	180	<i>O1</i> – <i>M3</i> – <i>O2</i>	179.9(3)	<i>O1</i> – <i>M4</i> – <i>O4</i>	179.8(3)
<i>O2</i> – <i>M2</i> – <i>O2</i>	180	<i>O1</i> – <i>M3</i> – <i>O2</i>	81.5(2)	<i>O3</i> – <i>M4</i> – <i>O4</i>	179.3(3)
<i>O3</i> – <i>M2</i> – <i>O3</i>	180	<i>O2</i> – <i>M3</i> – <i>O2</i>	98.7(4)	<i>O3</i> – <i>M4</i> – <i>O4</i>	98.5(2)
<i>O1</i> – <i>M2</i> – <i>O2</i>	103.6(2)	<i>O2</i> – <i>M3</i> – <i>O3</i>	179.6(3)	<i>O4</i> – <i>M4</i> – <i>O4</i>	81.7(3)
<i>O1</i> – <i>M2</i> – <i>O3</i>	103.7(2)	<i>O2</i> – <i>M3</i> – <i>O3</i>	81.4(2)	<i>O4</i> – <i>M4</i> – <i>O1</i>	97.8(2)
<i>O2</i> – <i>M2</i> – <i>O3</i>	103.3(2)	<i>Cl2</i> – <i>M3</i> – <i>Cl2</i>	179.90(9)	<i>Cl1</i> – <i>M4</i> – <i>Cl2</i>	179.92(9)
		<i>Cl2</i> – <i>M3</i> – <i>O2</i>	98.0(2)	<i>Cl1</i> – <i>M4</i> – <i>O3</i>	98.1(2)
		<i>Cl2</i> – <i>M3</i> – <i>O2</i>	82.4(2)	<i>Cl2</i> – <i>M4</i> – <i>O4</i>	97.3(2)
<i>Other</i>					
<i>O1</i> – <i>Cl2</i>	3.057(5)				
<i>O2</i> – <i>Cl1</i>	3.061(5)				
<i>O3</i> – <i>Cl2</i>	3.071(5)				
<i>O4</i> – <i>Cl2</i>	3.053(7)				

*The *M3* and *M4* sites are Cu exclusively.

Finally, we make the observation that other related phases may exist in Nature. In particular, new mineral species akin to paratacamite-(Ni) or -(Mg), but with ions such as Fe^{2+} , Mn^{2+} or Co^{2+} dominating the interlayer sites of the structure are quite feasible. A further search for these possible species in deposits that are known to contain minerals such as paratacamite and herbertsmithite is under way.

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