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Tolbachite, $CuCl_2$, the first example of Cu^{2+} octahedrally coordinated by Cl^-

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ABSTRACT

The crystal structure of synthetic tolbachite, $CuCl_2$, has been refined by the Rietveld method using an X-ray powder diffractometer modified for atmospheric control. The structure is monoclinic, space group $C2/m$, $a = 6.9038(9)$, $b = 3.2995(4)$, $c = 6.824(1)$ Å, $\beta = 122.197(8)°$, $V = 131.54(5)$ Å^3, $Z = 2$, with Cu^{2+} at (000), and Cl^- at [0.5048(8),0,0.2294(9)]. Final $R_B = 2.4\%$, $R_P = 3.5\%$, $R_{WP} = 4.8\%$, R_{WP} (expected) = 3.2%. The structure contains corrugated sheets of Jahn-Teller (4 + 2) distorted $Cu^{2+}Cl_6$ octahedra, with Van der Waals forces providing the intrasheet bonding. Tolbachite is the only mineral containing $Cu^{2+}Cl_6$ octahedra, and this study provides bond distances for a (4 + 2) distorted $Cu^{2+}Cl_6$ octahedra: $Cu^{2+} - Cl_{equatorial}$ (× 4) = 2.263(6) Å, $Cu^{2+} - Cl_{apical}$ (× 2) = 2.991(6) Å. These bond distances are used to identify the distortion types of mixed ligand $Cu^{2+}\phi_6(\phi = O^{2-}, OH^-, H_2O, Cl^-)$ octahedra observed in minerals.

INTRODUCTION

Tolbachite, $CuCl_2$, occurs in encrustations on basaltic magma flows of the Tolbachin eruption of 1975–1976 and was described as a new mineral by Bergasova and Filatov (1984). It is hygroscopic and hydrates to eriochalcite ($CuCl_2 \cdot 2H_2O$) on continued contact with air. This feature, along with the general lack of good crystals, presents special problems for structure characterization. The crystal structure of synthetic $CuCl_2$ was determined by Wells (1947), but because of the aforementioned problems, was not refined. The unit-cell dimensions and space group given by Wells (1947) and Bergasova and Filatov (1984) indicate that tolbachite is isostructural with synthetic $CuCl_2$.

We are currently interested in bond-distance variations in $Cu^{2+}\phi_6$ (ϕ = unspecified ligand) octahedra in copper oxysalt minerals (i.e., Burns and Hawthorne, unpublished manuscript, 1992; Eby and Hawthorne, unpublished manuscript, 1992). The $Cu^{2+}\phi_6$ octahedra observed in copper oxysalt minerals are almost invariably distorted into a (4 + 2) arrangement because of the Jahn-Teller effect (Jahn and Teller, 1937). In the case of $Cu^{2+}\phi_6$ ($\phi = O^{2-}, OH^-, H_2O$), the octahedral bond-distance distributions observed in minerals are quite well understood and can be quantitatively rationalized by consideration of the Jahn-Teller effect alone (Burns and Hawthorne, unpublished manuscript, 1992). However, a number of Cu minerals contain $Cu^{2+}\phi_6$ octahedra with $\phi = O^{2-}, OH^-, H_2O$, and (1, 2, or 4) Cl^- ligands. Because of the mixture of ligands forming these octahedra, the Cu^{2+} ion cannot achieve a strictly holosymmetric environment, and the Jahn-Teller argument is not directly applicable to such polyhedra. However, a near-degenerate electronic state may occur, and a distortion of the octahedron can then lead to a significant net stabilization of the mixed-ligand octahedra. This effect is usually referred to as the pseudo-Jahn-Teller effect (Hathaway, 1984). In $Cu^{2+}\phi_6$ octahedra with mixed ligands, the bond-distance variations are less straightforward to interpret than in the case of O ligands ($\phi = O^{2-}, OH^-, H_2O$), particularly as we do not have a good value for the ideal equatorial and apical bond distances for a Jahn-Teller-distorted $Cu^{2+}Cl_6$ octahedron. Thus, the role of the pseudo-Jahn-Teller effect in controlling the geometry of mixed-ligand $Cu^{2+}\phi_6$ octahedra is not clear.

We have refined the crystal structure of synthetic tolbachite using powder X-ray diffraction data. Tolbachite is the only mineral that contains $Cu^{2+}Cl_6$ octahedra and gives the bond-distance information needed to evaluate Jahn-Teller relaxation in $Cu^{2+}Cl_6$ and $Cu^{2+}\phi_6$ mixed-ligand octahedra.

EXPERIMENTAL METHODS

Synthetic tolbachite was prepared by heating $CuCl_2 \cdot 2H_2O$ in air at 105 °C for a week. The resulting powder was gently back-pressed into an Al holder, and the upper surface was serrated with a razor blade to reduce preferred orientation effects during data measurement. After sample preparation, the Al holder containing the powder was heated at 105 °C for 1 h to dehydrate any $CuCl_2 \cdot 2H_2O$ that may have formed during sample preparation.

Tolbachite is extremely hygroscopic and quickly hydrates in air. N was used to provide an inert atmosphere during data measurement. The diffractometer sample chamber was modified to provide spaces for inlet and outlet pipes. N was dried by pumping through a Leco rotometer, with the gas passing through concentrated sulphuric acid, ascarite, and magnesium perchlorate before entering the sample chamber. Scans before and after data measurement showed no detectable $CuCl_2 \cdot 2H_2O$.

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TABLE 1. Final structure parameters, *R*-values, bond distances (Å) and bond angles (°) in tolbachite, $CuCl_2$

Cell	Space group *C*2/*m*	*R*-Values*	
a (Å)	6.9038(9)		
b (Å)	3.2995(4)		
c (Å)	6.824(1)	R_B	2.4
β (°)	122.197(8)	R_P	3.5
V (Å³)	131.54(5)	R_{WP}	4.8
Z	2	R_{WP} (exp)	3.2

Positional parameters	*x*	*y*	*z*	*B***
Cu	0	0	0	0.50
Cl	0.5048(8)	0	0.2294(9)	1.00

Bond Distances		Bond Angles	
Cu-Cl × 2	2.991(6)	Cl-Cu-Cla × 4	87.6(2)
Cu-Cla × 4	2.263(6)	Clb-Cu-Clc × 4	92.4(2)
⟨Cu-Cl⟩	2.506	Cla-Cu-Cld × 2	86.4(2)
		Clc-Cu-Cld × 2	93.6(2)
		⟨Cl-Cu-Cl⟩	90.0

Note: a = ½ − *x*, *y* − ½, −*z*; b = −*x*, *y*, −*z*; c = *x* − ½, *y* + ½, *z*; d = ½ − *x*, *y* + ½, −*z*.

* R_B = Rietveld-Bragg agreement index; R_P = Rietveld profile agreement index; R_{WP} = Rietveld weighted profile agreement index.

** Fixed during refinement. The refined overall temperature factor was −0.44(13).

The diffraction data for Rietveld refinement were obtained at 25 °C on a Philips PW1710 X-ray powder diffractometer with Bragg-Brentano geometry using Cu*Kα* X-radiation, fixed ½° slits and a diffracted-beam monochromator. Data were obtained over the range (14° < 2*θ* < 130°) with a step interval of 0.05° 2*θ* and a count time of 5 s per step.

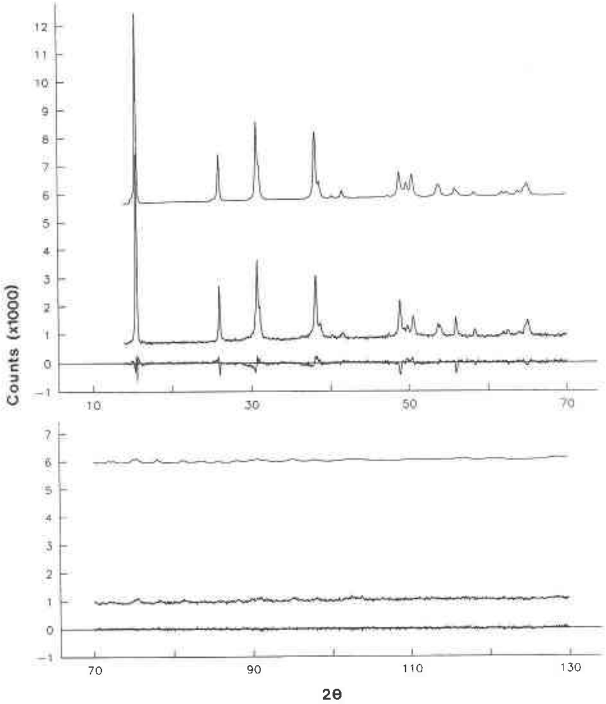

Fig. 1. Powder diffraction patterns for tolbachite. Top: pattern calculated using the refined structure parameters (+5000); middle: observed powder pattern; bottom: $I_{calc} - I_{obs}$.

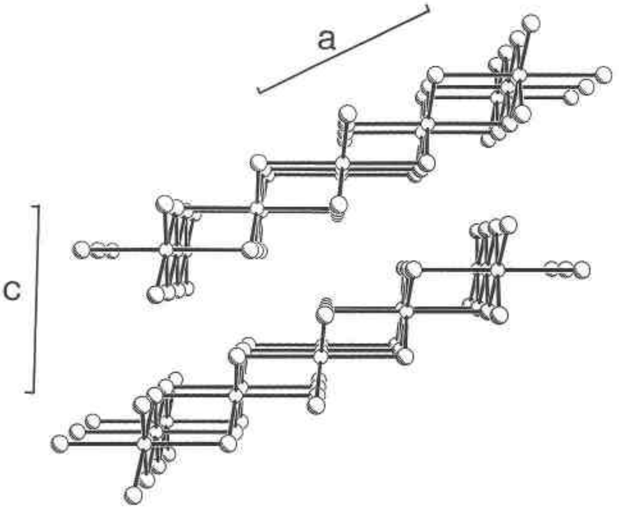

Fig. 2. The crystal structure of tolbachite projected onto (010); smaller circles = Cu^{2+}; larger circles = Cl^-.

STRUCTURE REFINEMENT

The Rietveld structure refinement (Rietveld, 1967, 1969) was done using the program LHMP1 (Howard and Hill, 1986; a modified version of the program by Wiles and Young, 1981). Refinement was initiated in the space group *C*2/*m* with the structure parameters of Wells (1947) as the starting model. The refinement included all data over the range (14° < 2*θ* < 130°). Scattering factors for neutral atoms were taken from the *International Tables for X-Ray Crystallography* (1974). Peaks were modeled using the pseudo-Voigt profile function, which was corrected for peak asymmetry to 30° 2*θ*. The pattern background was modeled using a refinable fourth-order polynomial. Individual isotropic temperature parameters were unstable during the final cycles of refinement and were fixed at accepted single-crystal values with an overall temperature factor refined. The final *R*-values obtained were $R_B = 2.4\%$, $R_P = 3.5\%$, $R_{WP} = 4.8\%$ with R_{WP} (exp.) = 3.2%. The refined structure parameters are given in Table 1, and data for the observed powder pattern are compared to those of the pattern calculated using the refined structure parameters in Figure 1.

DISCUSSION

Tolbachite contains $Cu^{2+}Cl_6$ octahedra distorted such that there are four Cu-Cl equatorial bond distances [2.263(6) Å] and two much longer Cu-Cl apical bond distances [2.991(6) Å], a (4 + 2) distortion. This octahedral environment is a result of the well-known Jahn-Teller effect. Each $CuCl_6$ octahedron shares two $Cl\text{-}Cl_{equatorial}$ edges with adjacent octahedra, and its apical Cl^- ions are equatorial ligands for adjacent octahedra. This linkage

TABLE 2. Examples of $Cu^{2+}\phi_6(\phi = O^{2-}, OH^-, H_2O$, and 1, 2, or 3 Cl^-) octahedra in copper oxysalt minerals (distances in Å)

	$Cu^{2+}\phi_6[\phi = 2(O^{2-}, OH^-, H_2O) + 4Cl^-]$						
	$Cu\text{-}O^{2-}, OH^-, H_2O$		$Cu\text{-}Cl^-$				Ref.
Eriochalcite	1.957(5)	1.957(5)	2.290(4)	2.290(4)	2.940(6)	2.940(6)	1
Chlorothionite	2.019(6)	2.001(6)	2.252(6)	2.237(2)	3.047(2)	3.047(2)	2
	$Cu^{2+}\phi_6[\phi = 4(O^{2-}, OH^-, H_2O) + 2Cl^-]$						
	$Cu\text{-}O^{2-}, OH^-, H_2O$				$Cu\text{-}Cl^-$		Ref.
Chloroxiphite	1.98(3)	1.98(3)	1.99(3)	1.99(3)	2.97(2)	2.97(2)	3
Botallackite, Cu(2)	1.950(5)	1.950(5)	2.001(6)	2.001(6)	2.789(2)	2.789(2)	4
	$Cu^{2+}\phi_6[\phi = 5(O^{2-}, OH^-, H_2O) + 1Cl^-]$						
	$Cu\text{-}O^{2-}, OH^-, H_2O$					$Cu\text{-}Cl^-$	Ref.
Atacamite, Cu(2)	1.993(2)	1.993(2)	2.010(2)	2.010(2)	2.358(4)	2.750(1)	5
Botallackite, Cu(2)	1.995(6)	1.995(6)	1.998(6)	1.998(6)	2.367(9)	2.732(3)	4

Note: 1 = Engberg (1970); 2 = Giacovazzo et al. (1976); 3 = Finney et al. (1977); 4 = Hawthorne (1985); 5 = Parise and Hyde (1986).

results in corrugated octahedral sheets (Fig. 2) of composition $CuCl_2$ parallel to (001). Each sheet is electrostatically neutral, and linkage between adjacent sheets is by Van der Waals forces, explaining why tolbachite quickly hydrates in air.

This study provides bond-distances for a (4 + 2)-distorted $Cu^{2+}Cl_6$ octahedron. Six examples of $Cu^{2+}\phi_6$ octahedral bond distances observed in mixed-ligand copper oxysalt minerals are given in Table 2. All such octahedra are (4 + 2)-distorted, and the pseudo-Jahn-Teller effect is a controlling factor in determining the bond-distance distributions. All $Cu^{2+}\phi_6$ ($\phi = O^{2-}, OH^{1-}, H_2O, Cl^-$) octahedra show the Cl ions to be preferentially located at the apical positions of the (4 + 2)-distorted octahedra. The only examples so far observed of $Cu^{2+}\phi_6$ octahedra with Cl^- in the equatorial positions in mixed-ligand octahedra occur when there are more than two Cl^- ligands involved: where there are four Cl^- ligands, two occur in the apical positions and two occur in equatorial positions (Table 2). The observed $\langle Cu^{2+}\text{-}Cl_{equatorial}\rangle$ distances in eriochalcite and chlorothionite (2.29 and 2.25 Å, respectively) are close to the analogous value in tolbachite (2.26 Å), indicating that these are typical equatorial bonds in the mixed-ligand structures. The $\langle Cu^{2+}\text{-}Cl_{apical}\rangle$ distances in the mixed-ligand minerals lie in the range 2.75–3.05 Å, as compared with the value of 2.99 Å in tolbachite. The wider range of apical vs. equatorial distances is similar to that observed in $Cu^{2+}(O^{2-}, OH^-, H_2O)_6$ octahedra, suggesting that the anharmonicity in the Cu^{2+}-Cl potential is similar to that found for the Cu^{2+}-O potential (Burns and Hawthorne, unpublished manuscript, 1992). Note also that the Cu-Cl apical distances are generally shorter in the mixed-ligand structures than in tolbachite; it will be interesting to see (by means of molecular-orbital calculations) if the presence of O equatorial ligands tends to shorten the apical Cu^{2+}-Cl distances.

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