The details of Jahn–Teller distorted \( \text{Cu}^{2+} \) octahedral geometries in \( \text{Cu}^{2+} \) oxysalt minerals are examined. Usually the \( \text{Cu}^{2+} \) octahedron is \((4 + 2)\)-distorted, although both \((2 + 4)\)-distorted and holosymmetric octahedra have been reported in mineral structures. To a first order, the Jahn–Teller theorem indicates that either a \((4 + 2)\) or \((2 + 4)\) distortion of the \( \text{Cu}^{2+} \) octahedron is equally likely to occur, in apparent conflict with the dominance of \((4 + 2)\)-distorted octahedra; this requires an extension of the Jahn–Teller theorem. Examination of reported holosymmetric \( \text{Cu}^{2+} \) octahedra in mineral structures shows that there is no conclusive evidence of a holosymmetric \( \text{Cu}^{2+} \) octahedron. The presence of \((2 + 4)\)-distorted \( \text{Cu}^{2+} \) octahedra in the structures of volborthite and \( \text{KCu}_3\text{(OH)}_2[(\text{AsO}_4)\text{H(AsO}_4)] \), and a \((2 + 2 + 2)\)-distorted \( \text{Cu}^{2+} \) octahedron in the structures of bayldonite and cyanochroite is attributed to a dynamic Jahn–Teller effect, rather than the static distortion that is usual in \( \text{Cu}^{2+} \) oxysalt structures. The most persuasive example of a true \((2 + 4)\)-distorted \( \text{Cu}^{2+} \) octahedron occurs in the structure of demesmaekerite.

**Keywords:** \( \text{Cu}^{2+} \) oxysalt minerals, Jahn–Teller effect, structural distortion, dynamic distortion.

**INTRODUCTION**

The \( \text{Cu}^{2+} \) oxysalt minerals have received considerable attention recently (i.e., Eby & Hawthorne 1993, Burns & Hawthorne 1995a, b), primarily because they show considerable structural diversity and are commonly not isosstructural with non-\( \text{Cu}^{2+} \) analogues. In part, the structural diversity may be attributed to the wide range of coordination geometries displayed by \( \text{Cu}^{2+} \): six-coordinate octahedral, six-coordinate trigonal-prismatic, five-coordinate square-pyramidal, five-coordinate triangular-bipyramidal and four-coordinate square-planar all occur. Of these, the octahedron is by far the most common coordination polyhedron, and it almost invariably involves a very strong distortion away from holosymmetric octahedral coordination.

The strong distortion of \( \text{Cu}^{2+} \) octahedra is due to the Jahn–Teller effect (Jahn & Teller 1937), associated with the degenerate electronic ground state of a \( d^9 \) metal in a holosymmetric octahedral field. However, some details of the Jahn–Teller distortion of \( \text{Cu}^{2+} \) octahedra in mineral
structures are poorly understood. For example, to first order, the Jahn–Teller theorem leads to the prediction that either a (4 + 2) distortion (four short Cu^2+–O equatorial bonds and two long Cu^2+–O apical bonds) or a (2 + 4) distortion is equally likely, although examination of crystal structures shows that (4 + 2)-distorted Cu^2+O_6 octahedra occur almost exclusively (Eby & Hawthorne 1993). In rare instances, apparent (2 + 4)-distorted and holosymmetric Cu^2+O_6 octahedra have been reported in mineral structures. To address these apparent anomalies, the details of Cu^2+O_6 octahedral geometries in Cu^2+ oxysalt structures are considered here.

Jahn–Teller Theory

Screening arguments

Where Cu^2+ is octahedrally coordinated, the metal d_{xy}, d_{xz}, and d_{yz} orbitals are equivalent and involve electron density between the axes containing both the metal ion and the ligands. Both of the d_{xy}, d_{xz}, and d_{yz} orbitals direct electron density toward the ligands. The octahedral arrangement of ligands around the metal ion splits the five d-orbitals into two sets (Fig. 1), one set (t_{2g}) being triply degenerate (corresponding to the copper d_{xy}, d_{xz}, and d_{yz} orbitals), and the other (e_g) being doubly degenerate (corresponding to the copper d_{x^2-y^2} and d_{z^2} orbitals). The t_{2g} orbitals are stabilized, and the e_g orbitals are destabilized relative to their energies in a spherical field, the energy difference between the t_{2g} and e_g orbitals being designated \( \Delta_O \) (Fig. 1). The driving force of the Jahn–Teller distortion of Cu^2+O_6 octahedra results from the unequal occupancies of the two e_g orbitals, which are split by the distortion (Fig. 1). Where the Jahn–Teller distortion occurs, the singly occupied orbital is destabilized by the same energy as the doubly occupied orbital is stabilized, resulting in a net stabilization of energy. Ligand-field arguments (Orgel 1966) show that single occupancy of the d_{x^2-y^2} and d_{z^2} orbitals of Cu^2+ will result in compressed (2 + 4) and elongated (4 + 2) Cu^2+O_6 octahedra, respectively.

Ligand-field arguments for a d^9 metal ion in octahedral coordination indicate that a compressed (2 + 4) geometry is equally as likely as an elongated (4 + 2) geometry. However, examination of [Cu^2+O_6] bond lengths in Cu^2+ oxysalt minerals indicates that (4 + 2)-distorted octahedra are very strongly preferred over either the (2 + 4)-distorted or holosymmetric geometries (Eby & Hawthorne 1993). The same observation holds true for Cu^2+ compounds in general (Hathaway 1984). The details of the Jahn–Teller theory thus are not readily understood using ligand-field theory alone. Various authors have considered additional effects in an attempt to remove these discrepancies; these effects are discussed in the next section.

The dynamic Jahn–Teller effect

Variable-temperature refinements of structures have provided considerable insight into the Jahn–Teller effect associated with a d^9 metal in octahedral coordination. For example, holosymmetric octahedral coordination around Cu^2+O_6 is observed in the structure of K_2Pb[Cu^2+O_6(NO_2)_6] at room temperature (Sidgwick 1950, Cullen & Lingafelter 1971), in apparent violation of the Jahn–Teller theorem. At 195 K, the structure is orthorhombic, and the Cu^2+O_6 octahedron is (2 + 4)-distorted (Sidgwick 1950). A (2 + 4)-distorted Cu^2+O_6 octahedron is observed in the structure of Cs_2Pb[Cu^2+O_6(NO_2)_6] at room temperature (Massey 1973). The structure is cubic at 420 K, with a holosymmetric Cu^2+O_6 octahedron observed (Mullen et al. 1975). When the structure is cooled to 160 K, it becomes monoclinic, with a (4 + 2)-distorted Cu^2+O_6 octahedron (Mullen et al. 1975). The temperature-dependent behavior of the octahedral geometries in these and other Cu^2+ compounds [see Hathaway (1984) for a review] may not be explained using first-order Jahn–Teller effects alone, and the dynamic Jahn–Teller effect must be involved.

Octahedral complexes with an electronic degeneracy in the e_g orbitals, as is the case for Cu^2+O_6, have a single Jahn–Teller active normal mode of vibration of e_g symmetry (Deeth & Hitchman 1986). The even mode of vibration of e_g symmetry is the only mode that can couple with the electronically degenerate ground-state in a cubic system and remove...
the orbital degeneracy (Hathaway 1984). Two energy surfaces arise from this coupling (\(E_o\) and \(E_s\), Fig. 2a), and take a form known as a Mexican-hat potential (Gaţo et al. 1976). The lower-energy surface of the Mexican-hat potential (\(E_o\)) has a potential-energy minimum that is stabilized by \(E_{RT}\) relative to the energy of the \(\text{Cu}^{2+}\phi_6\) octahedron in a holosymmetric configuration (energy \(E_0\)). Coupling of the electronic Hamiltonian (for a doubly degenerate state) with the nuclear vibrations gives rise to both linear and non-linear (higher order) terms (Englman 1972). If only linear coupling terms are important, the Mexican-hat potential has cylindrical symmetry (Gaţo et al. 1976). However, if there is a strong linear coupling and higher-order coupling terms are important, the Mexican hat will be warped, with three energy-minima and three saddlepoints (Bersuker 1984) (Fig. 2b).

The minima in the warped Mexican-hat potential-energy surface (Fig. 2b) may occur at \(\phi = 0, 120\) and \(240^\circ\) or at \(\phi = 60, 180\) and \(300^\circ\) (Hathaway 1984), depending upon the nature of the higher-order coupling terms. In the first case, the energy minima correspond to \((4 + 2)\)-elongated octahedra, whereas the saddlepoints correspond to \((2 + 4)\)-compressed octahedra. In the second case, the energy minima correspond to \((2 + 4)\)-compressed octahedra. Note that in either case, the octahedron can pass from a \((4 + 2)\)-elongated octahedron to a \((2 + 4)\)-compressed octahedron without passing through the energetically unfavorable holosymmetric coordination (Fig. 2b).

Consider the case where the energy minima of the warped Mexican-hat potential occur at \(\phi = 0, 120\) and \(240^\circ\). The energy minima correspond to \((4 + 2)\)-elongated octahedra. This is usually the case, as indicated by the dominance of \((4 + 2)\)-distorted \(\text{Cu}^{2+}\phi_6\) octahedra in \(\text{Cu}^{2+}\) oxysalt minerals and compounds in general. Various authors have proposed factors that are likely to cause dominance of the \((4 + 2)\)-distorted arrangement (e.g., Ōrik & Pryce 1957, Liehr & Ballhausen 1958, Lohr & Lipscomb 1963, Bacci 1979, Yamatera 1979, Burdett 1980, Deeth & Hitchman 1986); these include: (1) addition of an anharmonic term to the vibrational potential, (2) extension to second order of the electronic terms in the total potential-energy expression, and (3) configuration interaction between the \(4s\) and \(3d_{\frac{2}{2}}\) metal orbitals. Deeth & Hitchman (1986) suggested that each of these factors is of similar magnitude, and that (1) and (3) favor a \((4 + 2)\)-distortion, whereas (2) favors a \((2 + 4)\)-distortion.

The circular cross-section through the minimum of the potential-energy surface for energy minima at

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**Fig. 2.** Mexican-hat potentials: (a) the Mexican-hat potential that results from the coupling of the \(e_g\) mode of octahedral vibration with the degenerate electronic state (from Gaţo et al. 1976). \(E_0\) is the energy of a holosymmetric octahedron, \(E_s\) and \(E_o\) are the energy surfaces produced by vibronic coupling, \(E_{RT}\) is the Jahn–Teller stabilization energy; (b) the warped Mexican-hat potential (from Bersuker 1984).
$\phi = 0, 120$ and $240^\circ$ (Fig. 2b) is given in Figure 3. In this case, the energy maxima correspond to $(2 + 4)$-compressed octahedra, each of the three energy wells (Fig. 3a) have the same energy, and the energy barriers between the wells have the value $B$. If $B$ is less than the thermal energy (ca. 200 cm$^{-1}$, Hathaway 1984), there will be equal populations in each of the three wells. The direction of distortion in any given octahedron will vary continuously as the energy barrier $B$ is overcome. As a result, a completely symmetric Cu$^{2+}\phi_6$ octahedron will be observed by (time averaging) crystallographic techniques, as is the case in the structure of K$_2$Pb[Cu$^{2+}$(NO$_2$)$_6$] at room temperature (Sidgwick 1950) and Cs$_2$Pb[Cu$^{2+}$(NO$_2$)$_6$] at 420 K (Mullen et al. 1975).

In crystals, long-range effects are always present and may result in a further warping of the Mexican-hat surface (Bersuker 1984). Two possibilities then arise: (1) there may be two equivalent wells of lower energy than the third well (Fig. 3b); (2) one well may have a lower energy than the other two wells (Fig. 3c). In (1), if the energy $B$ is less than the thermal energy, equal populations will occur in the two lower-energy wells. The two wells involve octahedra that are elongated in different directions, with dynamic interchange between the orientations of the elongated axis. The net result is that an apparent $(2 + 4)$-compressed octahedron will be observed by crystallographic techniques. By the same reasoning, case (2) will result in an apparently elongated rhombic octahedron, with a $(2 + 2 + 2)$-distortion (a $(2 + 2 + 2)$ octahedron has two short trans Cu--Q bonds, two intermediate trans Cu--Q bonds, and two long trans Cu--Q bonds).

The above observations suggest that both $(2 + 4)$-compressed and holosymmetric Cu$^{2+}\phi_6$ octahedra observed in the structures of minerals and other phases may in some cases be a result of the dynamic Jahn–Teller effect. It could also be argued that these octahedra are due to averaged static disorder of the octahedral ligands, but the dynamic Jahn–Teller effect is required to rationalize the temperature dependence of Cu$^{2+}\phi_6$ octahedral coordination-geometries in both K$_2$Pb[Cu$^{2+}$(NO$_2$)$_6$] and Cs$_2$Pb[Cu$^{2+}$(NO$_2$)$_6$], and in various other Cu$^{2+}$ compounds (Hathaway 1984). As expected, X-ray data collected for these phases also show anisotropic-displacement parameters consistent with dynamically distorted Cu$^{2+}\phi_6$ octahedra. Furthermore, electron-spin-resonance (ESR) spectra for these compounds indicate that $(2 + 4)$-distorted and holosymmetric Cu$^{2+}\phi_6$ octahedra are both a result of the dynamic Jahn–Teller effect. According to Hathaway et al. (1981), there are no compounds that have been conclusively shown to contain statically $(2 + 4)$-distorted or holosymmetric Cu$^{2+}\phi_6$ octahedra. It has been noted, however, that dilute concentrations of Cu$^{2+}\phi_6$ octahedra in a parent structure may be $(2 + 4)$-distorted, as indicated by ESR spectroscopy (e.g., Hitchman et al. 1986, Reinen & Krause 1981).

**Cooperative Jahn–Teller effects**

As shown by crystal-structure refinements, the dynamic Jahn–Teller effect apparently does not occur in most Cu$^{2+}$ oxysalt minerals. In most cases, a static Jahn–Teller effect predominates, with Cu$^{2+}\phi_6$ octahedra trapped in one of the energy wells. However, if two or three of the wells are of about the same energy, directional disorder of the distortion could occur, such that long-range averaging (as occurs in diffraction experiments) will show symmetrical octahedra (three equal wells) or $(2 + 4)$-compressed octahedra (two equal wells). Cu$^{2+}$ oxysalt minerals usually have $(4 + 2)$-elongated octahedra, indicating that one energy well is of a lower energy than the other two wells. The directions of elongation of the octahedra are ordered, and this ordering is referred to as the cooperative Jahn–Teller effect (Bersuker 1984).
Ordering of the distortion centers is due to strong electron-phonon coupling that links the effects of adjacent distortion centers.

**Cu\(^{2+}\)\(\phi_6\) geometries in Cu\(^{2+}\) oxysalt minerals**

Eby (1988) and Eby & Hawthorne (1993) compared Cu\(^{2+}\)\(\phi_6\) geometries in Cu\(^{2+}\) oxysalt minerals. However, over the past few years, high-quality structural data for Cu\(^{2+}\) oxysalt minerals have continued to accumulate at the rate of several structures per year. The structures of ninety-one \([6]Cu^{2+}\) oxysalt minerals are considered here, and one hundred and sixty-six symmetrically distinct Cu\(^{2+}\)\(\phi_6\) octahedra occur in these mineral structures. The following sections consider the stereochemical characteristics of these octahedra. Mixed-ligand Cu\(^{2+}\)\(\phi_6\) octahedra (\(\phi\): \(\text{O}^2-\), \(\text{OH}^-\), \(\text{H}_2\text{O}\) and at least one \(\text{Cl}\)) are considered by Burns & Hawthorne (1995a).

**General features of Cu\(^{2+}\)\(\phi_6\) octahedral geometries**

The distribution of Cu–\(\phi\) bond-lengths for all symmetrically distinct Cu\(^{2+}\)\(\phi_6\) octahedra in Cu\(^{2+}\) oxysalt mineral structures is shown in Figure 4. There is a bimodal distribution, with maxima at \(\sim 1.95\) and \(\sim 2.40\) Å, reflecting the dominance of \((4 + 2)\)-distorted octahedra. Although most Cu\(^{2+}\)\(\phi_6\) octahedra in mineral structures are \((4 + 2)\)-distorted, examples of \((2 + 4)\)-distorted and holosymmetric Cu\(^{2+}\)\(\phi_6\) octahedra also occur. Each subclass of Cu\(^{2+}\)\(\phi_6\) geometries, i.e., \((4 + 2)\)-distorted, \((2 + 4)\)-distorted and holosymmetric, is dealt with separately in the following sections.

**\((4 + 2)\)-distorted Cu\(^{2+}\)\(\phi_6\) octahedral geometries**

By far the most common subclass of Cu\(^{2+}\)\(\phi_6\) octahedral geometries observed in minerals is the \((4 + 2)\)-distorted octahedron. There are one hundred and fifty-nine symmetrically unique \((4 + 2)\)-distorted octahedra in the structures of ninety different Cu\(^{2+}\) oxysalt minerals.

For \((4 + 2)\)-distorted Cu\(^{2+}\)\(\phi_6\) octahedra, essentially all of the Cu–\(\phi_{eq}\) (eq: equatorial) distances are in the range 1.875 to 2.125 Å, and the Cu–\(\phi_{ap}\) (ap: apical) distances are in the range 2.225 to 3.125 Å. The \(<\text{Cu–}\phi>\) distance is 2.150 Å, with a standard deviation of 0.28 Å. The \(<\text{Cu–}\phi_{eq}>\) distance is 1.973 Å, and the \(<\text{Cu–}\phi_{ap}>\) distance is 2.505 Å. The equatorial bond-lengths span a much smaller range than the apical bond-lengths, with a standard deviation of 0.048 Å compared to 0.205 Å for the apical bond-lengths.

Bond-valence theory (Brown 1981) predicts that distorted coordination-polyhedra will show longer mean bond-lengths than corresponding regular coordination-polyhedra because of the exponential form of the bond-valence interaction. This was shown to be the case for Cu\(^{2+}\)\(\phi_6\) octahedra by Eby & Hawthorne (1993), who described polyhedral distortion using the parameter \(\Delta\):

\[
\Delta = \frac{1}{6} \sum (l_i - l_0)^2
\]

where \(l_i\) is a Cu–\(\phi\) distance and \(l_0\) is the \(<\text{Cu–}\phi>\) distance. The value of \(\Delta\) for each \((4 + 2)\)-distorted Cu\(^{2+}\)\(\phi_6\) octahedron is plotted versus \(<\text{Cu–}\phi>\) in Figure 5. Extrapolation to \(\Delta = 0\) gives the expected \(<\text{Cu–}\phi>\) distance of 2.083 Å for an undistorted Cu\(^{2+}\)\(\phi_6\).

![Fig. 4](https://example.com/fig4.png)

**Fig. 4.** The distribution of Cu–\(\phi\) bond lengths in all symmetrically distinct Cu\(^{2+}\)\(\phi_6\) octahedra in Cu\(^{2+}\) oxysalt mineral structures.
octahedron, in agreement with the value of 2.084 Å reported by Eby & Hawthorne (1993).

**Holosymmetric Cu$^{2+}\phi_6$ octahedra**

The occurrence of holosymmetric Cu$^{2+}\phi_6$ octahedra in Cu$^{2+}$ oxysalt minerals is unexpected, as it violates the Jahn–Teller theorem. However, Cu$^{2+}\phi_6$ octahedra with little or no distortion do occur, for example in the structures of lyonsite, buttgenbachite and paratacamite.

**Lyonsite**: Lyonsite, Cu$_3^+$(VO$_{10}$)$_2$F$_6$Cl$_6$-Cl$_2$.OH$_{63,3}$·2H$_2$O (Hughes et al. 1987), is a rare high-temperature fumarolic sublimate described by Hughes et al. (1987). The structure of lyonsite is based on a pseudohexagonal close-packed array of oxygen atoms, and contains two symmetrically distinct Cu$^{2+}\phi_6$ polyhedra, one of which [Cu(2)] shows a very unusual Cu$^{2+}\phi_6$ coordination: a distorted trigonal-prism. A similar Cu$^{2+}\phi_6$ coordination polyhedron occurs in claringbullite (Burns et al. 1995), buttgenbachite (Fanfani et al. 1973) and connellite (McLean & Anthony 1972). The Cu(1) site in lyonsite involves a Cu$^{2+}\phi_6$ octahedron that is only very weakly distorted \[ \text{Cu}(1)-\text{O}(1) \times 2 = 2.031(5), \text{Cu}(1)-\text{O}(1) \times 2 = 2.030(5), \text{Cu}(1)-\text{O}(6) \times 2 = 2.070(7) \text{Å}. \] Further examination of the lyonsite structure shows that adjacent Cu$^{2+}(1)\phi_6$ octahedra share faces, with the associated Cu(1) positions only 2.455 Å apart. Such a configuration suggests that adjacent Cu(1) sites are probably not both occupied; site-scattering refinement shows the Cu(1) site to be half-occupied, consistent with this situation (Hughes et al. 1987).

If a site is partly occupied, as is the case for the Cu(1) site in lyonsite, the local atomic configurations are expected to be very different than if the site is fully occupied or vacant. The long-range average configuration measured by X-ray diffraction consists of the sum of these two configurations, and may not resemble either of the local configurations very closely. The fact that regular Cu$^{2+}\phi_6$ configurations are not found where a site is completely filled by Cu$^{2+}$ suggests that the long-range average observed in the structure of lyonsite (and buttgenbachite, see below) consists of distorted Cu$^{2+}\phi_6$ and distorted Cu$^{2+}\phi_6$ configurations that average to regular octahedral geometry. Adding to the uncertainty as to the precise nature of the Cu(1) site is the approximately 50% vacancy and the marked anisotropy of the electron density at the Cu(1) site. The electron-density anisotropy suggests that the room-temperature structure may represent a space average of disordered Cu(1) positions within the octahedron (Hughes et al. 1987). Although it is not possible to directly prove this model, the preponderance of partly filled sites in holosymmetric Cu$^{2+}\phi_6$ configurations suggests that this is the case.

**Buttgenbachite**: The structure of buttgenbachite, Cu$_{33.6}Cl_{16.7}(NO_3)_{2.6}(OH)_{63,3}$·2.1H$_2$O (Fanfani et al. 1973), contains an infinite three-dimensional framework of Cu$^{2+}$ polyhedra with large channels containing (NO$_3$) and Cl. There are five symmetrically distinct Cu$^{2+}$ sites. Three of these sites are octahedrally coordinated and show typical (4 + 2)-distortion (although two contain mixed ligands; see Burns & Hawthorne 1995a), whereas the fourth Cu$^{2+}$ cation is in square-planar coordination. The fifth Cu$^{2+}$ site is in holosymmetric octahedral coordination, with Cu(5)–OH(2) = 2.210(7) Å. According to site-scattering information, this site is only one-third occupied. The argument given for lyonsite also applies to buttgenbachite: the regular arrangement observed around the Cu(5) site is probably a superposition of distorted Cu$^{2+}\phi_6$ and Cu$^{2+}\phi_6$ configurations.

**Paratacamite**: Paratacamite is one of the polymorphic forms of Cu$_3^+$(OH)$_3$Cl. The structure has rhombohedral symmetry, with a distinct substructure (Fleet 1975). The structure contains four symmetrically distinct Cu$^{2+}$ positions. Two of these positions are in (4 + 2)-distorted mixed-ligand octahedral coordination (see Burns & Hawthorne 1995a), and the third Cu$^{2+}$ site has (2 + 4)-distorted octahedral coordination. The Cu(1) site contains one-sixteenth of the copper in the paratacamite structure, and occurs on a 3 axis; the octahedron is holosymmetric, with Cu(1)–O = 2.12 Å. This site is 100% occupied, unlike the holosymmetric octahedron in buttgenbachite or the near-holosymmetric octahedron in lyonsite. The Cu–O value of 2.12 Å is somewhat longer.
than the expected $\langle Cu-\phi \rangle$ distance of 2.083 Å for an undistorted $Cu^{2+}\phi_6$ octahedron. Fleet (1975) reported the structure of a natural specimen of paratacamite, but did not report a chemical composition. If the octahedral site is occupied by $Zn^{2+}$, the average octahedral distance expected would be 2.10 Å (i.e., 1.36 Å + 0.74 Å: Shannon 1976). The increase of zinc-rich paratacamite was reported by Kracher & Pertlik (1983), and electron-microprobe analysis of a crystal of paratacamite from the same sample as studied by Fleet (1975) showed it to contain 2.4 wt% Zn [Jambor et al. 1996, Embrey & Jones (in Kracher & Pertlik 1983)]. Grice et al. (1996) reported the structure of clinoatacamite, $Cu_2(OH)_3Cl$ with no detectable Zn, and showed that the structure has the same topology as paratacamite, but that it has monoclinic symmetry. In the clinoatacamite structure, all $Cu^{2+}$ octahedra show the usual Jahn–Teller distortion (Grice et al. 1996). Jambor et al. (1996) synthesized crystals of $(Cu_{2.4}Zn_0.1)(OH)_3Cl$ composition; $Cu_2(OH)_3Cl$ was found to have the monoclinic structure, whereas crystals with more than 6 mol.% Zn have the rhombohedral structure. Thus, there is considerable evidence that indicates that Zn is required to stabilize the paratacamite structure, but crystals with only 2.4 wt% Zn have the rhombohedral structure, demonstrating that only about one-half of the holosymmetric octahedral site in the paratacamite structure need contain zinc.

**Synthetic compounds:** There are no well-documented examples of holosymmetric $Cu^{2+}\phi_6$ octahedra in mineral structures, as predicted by the Jahn–Teller theorem. Holosymmetric $Cu^{2+}\phi_6$ octahedra have been observed in certain synthetic structures by crystallographic techniques. One such example occurs in $[Cu^{2+}(H_2O)_6](BrO_3)_2$, where the $\langle Cu-\phi \rangle$ distance is 2.079 Å (Blackburn et al. 1991), a value in good agreement with the predicted $\langle Cu-\phi \rangle$ distance of 2.083 Å for an undistorted $Cu^{2+}\phi_6$ octahedron. However, the holosymmetric octahedron observed in $[Cu^{2+}(H_2O)_6](BrO_3)_2$, as well as all other holosymmetric $Cu^{2+}$ octahedra (there are six known), is attributed to a dynamic Jahn–Teller effect that persists at room temperature (Blackburn et al. 1991, Hathaway 1984). Supporting evidence comes from anisotropic-displacement parameters, variable-temperature refinements of the structure, and measurements by ESR spectroscopy (Blackburn et al. 1991, Hathaway 1984).

$\langle 2 + 4 \rangle$-distorted $Cu^{2+}\phi_6$ octahedra

Five $\langle 2 + 4 \rangle$-distorted $Cu^{2+}\phi_6$ octahedra occur in the structures of campigliaite, paratacamite, demesmaekerite and volborthite. Hathaway et al. (1981) suggested that genuine $\langle 2 + 4 \rangle$-distorted $Cu^{2+}\phi_6$ octahedra do not occur in $Cu^{2+}$ compounds. Most (or all) examples of $\langle 2 + 4 \rangle$-distorted $Cu^{2+}\phi_6$ octahedra have been shown to be time-averaged results of the dynamic Jahn–Teller effect. These apparent $\langle 2 + 4 \rangle$-distorted $Cu^{2+}\phi_6$ octahedra result from the time averaging of $\langle 4 + 2 \rangle$-distorted octahedra aligned in two directions. However, some spectroscopists have postulated statically $\langle 2 + 4 \rangle$-distorted $Cu^{2+}\phi_6$ octahedra in some $Cu^{2+}$-doped systems (Hitchman et al. 1986, Reinen & Krause 1981) from ESR measurements. As $\langle 2 + 4 \rangle$-distorted $Cu^{2+}\phi_6$ octahedra are rare (or non-existent) in concentrated $Cu^{2+}$ compounds, it is appropriate to consider each of the mineral examples in some detail.

**Campigliaite:** The structure of campigliaite, $Cu_2^+Mn^{2+}(SO_4)(OH)_4H_2O$, contains sheets of $Cu^{2+}\phi_6$ octahedra interconnected through $SO_4$ tetrahedra and hydrogen bonding. The crystal structure (Sabelli 1982) is of low precision owing to the poor quality of the crystal and the presence of polysynthetic twinning. Both the $Cu(1)$ and $Cu(3)$ sites seem to be in $\langle 2 + 4 \rangle$-distorted octahedral coordination (Table 1). However, it is likely that the observed octahedra are twin-averaged, rather than real $\langle 2 + 4 \rangle$-distorted octahedra.

**Paratacamite:** The structure of paratacamite (Fleet 1975) was discussed in the previous section with reference to the $Cu(1)$ site, which is in a holosymmetric octahedral environment. It was pointed out that the structure of paratacamite may contain significant amounts of Zn, and that the holosymmetric octahedron may contain some Zn. The paratacamite structure also contains one $\langle 2 + 4 \rangle$-distorted $Cu^{2+}\phi_6$ octahedron $Cu(2)$ (Table 1). As this $\langle 2 + 4 \rangle$-distorted octahedral geometry is very similar to that observed in the structure of volborthite and demesmaekerite (Table 1), it seems likely that the $Cu(2)$ site does contain $Cu^{2+}$.

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<tr>
<td></td>
<td></td>
<td>$O(3)$: 2.29(5) $O(3)$: 2.41(5)</td>
</tr>
<tr>
<td>$KCu_2^+(OH)_3$</td>
<td>$[AsO_4]_2[AsO_4]_2$</td>
<td>$Cu(1)$</td>
</tr>
</tbody>
</table>
Demesmaekerite: The structure of demesmaekerite, Pb₂Cu₄⁺(SeO₄)₆(UO₂)₂(OH)₆·2H₂O (Ginderow & Cesbron 1983), consists of layers of [Cu₂⁺ (O,OH₂)₆] octahedra parallel to (010), cross-linked by oblique chains of corner-sharing (U₆O₁₈) and (SeO₂)₆ polyhedra. The structure contains three symmetrically distinct Cu²⁺ sites, two of which are in octahedral coordination with (4 + 2)-distorted geometries. The Cu(1) site lies on a center of symmetry, and shows a (2 + 4)-distorted Cu²⁺φ₈ octahedral geometry (Table 1). Note that this configuration is not a requirement of the site symmetry.

Volborthite: The structure of volborthite, Cu₃⁺(OH)₂V₂O₅·2H₂O (Basso et al. 1988), contains sheets of edge-sharing Cu²⁺φ₈ octahedra. These sheets of octahedra may be derived from a Mg(OH)₂ (brucite) layer in which 25% of the octahedral positions are vacant. VO₄ tetrahedra link to each side of the sheet, and bonding between adjacent sheets is through the apical atoms of oxygen of opposing VO₄ tetrahedra and through hydrogen bonding associated with the interstitial H₂O groups.

The structure of volborthite contains two symmetrically distinct Cu²⁺ sites. The Cu(2) site occurs at a center of symmetry, and is surrounded by a (4 + 2)-distorted octahedron. The Cu(1) site has point symmetry 2/m, and the Cu(1) octahedron is (2 + 4)-distorted (Table 1). The chemical composition of the material used for the structure study (Basso et al. 1988) rules out substitution of another cation at the Cu(1) site. Note that the (2 + 4)-distorted geometries in volborthite, paratacamite and demesmaekerite (Table 1) are very similar.

KCu₂⁺(OH)₂[(AsO₄)H(AsO₄)]: Effenberger (1989) reported a (2 + 4)-distorted Cu²⁺φ₈ octahedron in the structure of KCu₂⁺(OH)₂[(AsO₄)H(AsO₄)], which has not yet been described as a mineral. This material crystallizes in the space group C2/m, and its structure is closely related to that of volborthite. The structure contains the same sheets of octahedra and tetrahedra as volborthite, with AsO₄ tetrahedra replacing the VO₄ tetrahedra. However, unlike volborthite, adjacent sheets are offset, with intersheet bonding provided by 10-coordinated K and hydrogen bonds. The Cu(1) position, which has 2/m symmetry, is at the center of a (2 + 4)-distorted octahedron (Table 1). The Cu(1)-φ bond lengths are similar to those in volborthite, but the <Cu(1)-φ₈> distance is slightly longer, and the <Cu(1)-φ₈> distance, significantly shorter, than the corresponding values in volborthite (Table 1). The Cu(2) site is in (4 + 2)-distorted octahedral coordination, similar to that observed in the volborthite structure.

The occurrence of a (2 + 4)-distorted Cu²⁺φ₈ octahedral geometry in the structures of both volborthite and KCu₂⁺(OH)₂[(AsO₄)H(AsO₄)] suggests that the octahedral geometry results from connectivity constraints associated with the particular sheets of octahedra and tetrahedra that occur in both structures. Possibly a (2 + 4)-distorted octahedron is energetically preferred over a (4 + 2)-distorted octahedron at the Cu(1) site, with this unusual situation somehow tied to the connectivity requirements of the sheets. However, the structural arrangement in bayldonite suggests otherwise.

Bayldonite: Bayldonite, Cu₃⁺Pb(AsO₄)₂(OH)₂ (Ghose & Wan 1979), space group C2/c, has a unit cell that is very similar to those of volborthite and KCu₂⁺(OH)₂[(AsO₄)H(AsO₄)] (Table 2). The bayldonite structure contains sheets of Cu²⁺φ₈ octahedra and AsO₄ tetrahedra that are graphically identical to the sheets of octahedra and tetrahedra in volborthite and KCu₂⁺(OH)₂[(AsO₄)H(AsO₄)]. Adjacent sheets of octahedra and tetrahedra in the structure of bayldonite are connected through irregular Pb²⁺φ₈ polyhedra and hydrogen bonding. The c dimension of bayldonite is double that of volborthite and KCu₂⁺(OH)₂[(AsO₄)H(AsO₄)], and there are three distinct Cu²⁺ sites, each of which is located at a center of symmetry. The Cu²⁺φ₈ bond lengths in bayldonite are compared to those in volborthite and KCu₂⁺(OH)₂[(AsO₄)H(AsO₄)] in Table 2. Note that the Cu(2) site in bayldonite is related to the Cu(1) sites in volborthite and KCu₂⁺(OH)₂[(AsO₄)H(AsO₄)], but the ligand arrangement is not (2 + 4)-distorted. Instead, the Cu(2) octahedron in bayldonite shows an elongated-rhombic distortion, best referred to as a (2 + 2 + 2)-distorted octahedron.

The (2 + 4)-distorted Cu²⁺φ₈ octahedra observed in Cu²⁺ oxysalt minerals are derived from X-ray diffraction data, and as such may be the result of: (i) the presence of a statically (2 + 4)-distorted octahedron, (ii) the dynamic time-averaging of two non-aligned (4 + 2)-distorted octahedra, (iii) the static disorder of (4 + 2)-distorted octahedra. We propose that the (2 + 4)-distorted Cu²⁺φ₈ octahedra in the structures of volborthite and KCu₂⁺(OH)₂[(AsO₄)H(AsO₄)], and the (2 + 2 + 2)-distorted octahedron in the structure of bayldonite, are the result of a dynamic Jahn–Teller effect. Supporting arguments are given below, but first it is necessary to consider (2 + 2 + 2)-distorted Cu²⁺φ₈ geometries in more detail.

(2 + 2 + 2)-DISTORTED Cu²⁺φ₈ OCTAHEDRA IN Cu²⁺ OXYSALT MINERALS

The ligand-field arguments presented above indicate that either a (4 + 2) or (2 + 4) tetragonal distortion of the Cu²⁺φ₈ octahedral environment will remove the energetically degenerate electronic state and stabilize the octahedron. However, examination of Cu²⁺φ₈ octahedra in Cu²⁺ oxysalt minerals shows that tetragonally distorted octahedra are rare: to date, only five such
Cu\textsuperscript{2+}\textit{Q}_{6} octahedra occur in minerals.

Apical and equatorial Cu–\textit{Q} distortion parameters may be defined individually as:

\[
\Delta_{\text{ap}} = \frac{1}{2} \sum [(l_{\text{ap},i} - l_{\text{ap},o})/l_{\text{ap},o}]^2
\]  

(2)

\[
\Delta_{\text{eq}} = \frac{1}{2} \sum [(l_{\text{eq},i} - l_{\text{eq},o})/l_{\text{eq},o}]^2
\]  

(3)

where \(l_{0}\) is the average bond-length. The values of \(\Delta_{\text{ap}}\) and \(\Delta_{\text{eq}}\) for all (4 + 2)-distorted Cu\textsuperscript{2+}\textit{Q}_{6} octahedra in minerals are shown in Figure 6. For ranges of \(\Delta_{\text{eq}}\) from 0 to 0.00075, there is a considerable range of \(\Delta_{\text{ap}}\) observed, i.e., from 0 to 0.023. However, for values of \(\Delta_{\text{eq}}\) ranging from 0.00075 to 0.003, there is generally a very narrow range of \(\Delta_{\text{ap}}\).

Of the one hundred and fifty-nine (4 + 2)-distorted Cu\textsuperscript{2+}\textit{Q}_{6} octahedra in Cu\textsuperscript{2+} oxysalt minerals, forty-two occur on a center of symmetry. Each of these octahedra must have \(\Delta_{\text{ap}} = 0.0\), and plot along the horizontal axis in Figure 6. In many of these cases, the centrosymmetric Cu\textsuperscript{2+}\textit{Q}_{6} octahedra show very large values of \(\Delta_{\text{eq}}\). Note also that there are several occurrences of Cu\textsuperscript{2+}\textit{Q}_{6} octahedra that have large values of \(\Delta_{\text{eq}}\) but low values of \(\Delta_{\text{ap}}\) that are not on centers of symmetry (i.e., \(\Delta_{\text{ap}} \neq 0.0\)).

The Cu\textsuperscript{2+}\textit{Q}_{6} octahedra with high values of \(\Delta_{\text{eq}}\) and low values of \(\Delta_{\text{ap}}\) are rhombically elongated octahedra, and typically have two short \textit{trans} Cu–\textit{Q}_{eq} distances, two long \textit{trans} Cu–\textit{Q}_{ap} distances and two intermediate \textit{trans} Cu–\textit{Q}_{eq} distances. Such a distortion is best referred to as a (2 + 2 + 2) distortion and can be considered as a subclass of the (4 + 2)-distorted Cu\textsuperscript{2+}\textit{Q}_{6} octahedra, as the two intermediate Cu–\textit{Q}_{eq} distances are almost invariably closer to the short Cu–\textit{Q}_{eq} distances than to the long Cu–\textit{Q}_{eq} distances. Examples of (2 + 2 + 2)-distorted Cu\textsuperscript{2+}\textit{Q}_{6} octahedra in minerals are given in Table 3, which contains only (2 + 2 + 2)-distorted octahedra in which the average long Cu–\textit{Q}_{eq} distance is greater than 0.10 \(\text{\AA}\) longer than the average short Cu–\textit{Q}_{eq} distance.

![Fig. 6. Apical and equatorial bond-length distortion parameters for (4 + 2)-distorted Cu\textsuperscript{2+}\textit{Q}_{6} octahedra in Cu\textsuperscript{2+} oxysalt minerals; note the different scales on each axis.](image-url)
TABLE 3. EXAMPLES OF (2+2+2)-DISTORTED Cu2+ OCTAHEDRA OBSERVED IN Cu2+ OXYSALT MINERALS. BOND-LENGTHS IN Å

<table>
<thead>
<tr>
<th>Octahedra on a center of symmetry</th>
<th>Ref.</th>
<th>δr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bayldonite</td>
<td>2.08x2</td>
<td>1.995</td>
</tr>
<tr>
<td>Cyanochroite</td>
<td>2.09x2</td>
<td>2.11</td>
</tr>
<tr>
<td>Turquoise</td>
<td>2.10x2</td>
<td>2.12</td>
</tr>
<tr>
<td>Chalcosiderite</td>
<td>2.07x2</td>
<td>2.08</td>
</tr>
<tr>
<td>Dioctahedrite</td>
<td>2.29x2</td>
<td>2.30</td>
</tr>
<tr>
<td>Voibertite</td>
<td>2.10x2</td>
<td>2.11</td>
</tr>
<tr>
<td>Lutthite</td>
<td>2.57x2</td>
<td>2.58</td>
</tr>
<tr>
<td>Vanadinite</td>
<td>2.06x2</td>
<td>2.07</td>
</tr>
<tr>
<td>Chalcyochroite</td>
<td>2.37x2</td>
<td>2.38</td>
</tr>
<tr>
<td>Cornellite</td>
<td>2.46x2</td>
<td>2.47</td>
</tr>
</tbody>
</table>

For centrosymmetric (2 + 2 + 2)-distorted Cu2+φ6 octahedra, the degree to which a (2 + 2 + 2)-distortion is present is conveniently given by the parameter δr where:

\[ \delta r = \left( \frac{\langle \text{Cu}-\text{O}_{\text{short}} \rangle + \langle \text{Cu}-\text{O}_{\text{interm}} \rangle}{\langle \text{Cu}-\text{O}_{\text{ap}} \rangle} \right) \]

Values of δr (Table 3) range from 0.857 in the structure of lubijbaite to a maximum of 0.923 in cyanochroite; note that cyanochroite and bayldonite are the only Cu2+ oxysalt minerals that contain (2 + 2 + 2)-distorted or a rhombically elongated octahedron with δr > 0.90.

The Mexican-hat potential for the coupling of the eg vibrational modes with the electronic state of Cu2+φ6 is given in Figure 2, and is discussed above. The three possible types of circular cross-sections through the minimum of the potential-energy surface of Figure 2 are given in Figure 3. The energy minima occur at φ = 0, 120 and 240°, and positions I, II and III correspond to a (4 + 2)-distorted Cu2+φ6 octahedron elongated in each of the three possible axial directions.

If the energy barrier B is less than the thermal energy, a dynamic interchange of elongation directions of the (4 + 2)-distorted octahedron will continually occur as the energy barrier is overcome. The Cu2+φ6 geometry observed by crystallographic techniques will be a time-averaged geometry. Depending on the relative energies of the wells, either a holosymmetric, (2 + 4)-distorted or a rhombically elongated octahedron [(2 + 2 + 2)-distorted] will be observed.

The structures of copper Tutton's salts show dynamic Jahn–Teller effects. Considerable variable-temperature structural work has been done for (NH4)2Cu2+(H2O)6(SO4)2, with the structure studied at 295 K (Webb et al. 1965, Montgomery & Lingafelter 1966, Brown & Chibarambaram 1969), 203 and 123 K (Alcock et al. 1984). The room-temperature structure contains a Cu2+φ6 octahedron of rhombically elongated octahedral geometry [a (2 + 2 + 2) distortion] (Table 4). This strong (2 + 2 + 2) distortion suggests that the octahedron may be a result of the dynamic Jahn–Teller effect involving two energy wells of similar but unequal energies, and a third well of considerably higher energy. The octahedron is elongated in the Cu–O(7) direction most of the time, but the energy well corresponding to elongation in the Cu–O(8) direction is also significantly occupied, and a dynamic interchange between these two distortion directions occurs.

The temperature-dependent nature of the Cu–φ bond-lengths in (NH4)2Cu2+(H2O)6(SO4)2 structure (Table 4) indicates that a dynamic Jahn–Teller effect does occur in this structure (Alcock et al. 1984). Continued cooling results in a steady increase of the Cu–O(7) distance, a steady decrease in the Cu–O(8) distance, and no significant change in the Cu–O(9) distance (Table 4).

The structures of some other copper Tutton's salts also have been reported. These include K2Cu2+(H2O)6(SO4)2 (Robinson & Kennard 1972), Rb2Cu2+(H2O)6(SO4)2 (Van der Zee et al. 1972, Smith et al. 1975), Cs2Cu2+(H2O)6(SO4)2 (Shields & Kennard 1972) and Tl2Cu2+(H2O)6(SO4)2 (Shields et al. 1972);


table 4. octahedral bond-lengths (Å) in (NH4)2Cu2+(H2O)6(SO4)2 and (M2+)2Cu2+(H2O)6(SO4)2 m = K, Rb, Cs, Tl

<table>
<thead>
<tr>
<th>Bond-length (Å)</th>
<th>Ref.</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
<th>Tl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-O(7)</td>
<td>2.123(5)</td>
<td>2.15(5)</td>
<td>2.15(5)</td>
<td>2.15(5)</td>
<td>2.15(5)</td>
</tr>
<tr>
<td>Cu-O(8)</td>
<td>2.250(2)</td>
<td>2.250(2)</td>
<td>2.250(2)</td>
<td>2.250(2)</td>
<td>2.250(2)</td>
</tr>
<tr>
<td>Cu-O(9)</td>
<td>1.967(1)</td>
<td>1.967(1)</td>
<td>1.967(1)</td>
<td>1.967(1)</td>
<td>1.967(1)</td>
</tr>
</tbody>
</table>

References: 1: Robinson & Kennard (1972); 2: Brown & Chibarambaram (1969); 3: Smith et al. (1975); 4: Van der Zee et al. (1972); 5: Shields & Kennard (1972); 6: Shields et al. (1972).
of these, $K_2Cu^{2+}(H_2O)_6(SO_4)_2$ is the mineral cyanochroite. The bond lengths for the $Cu^{2+}O_6$ octahedron in each of these structures are included in Table 4. Note that the long Cu$-$O bond is to O(8) in each case rather than to O(7) as in $(NH_4)_2Cu^{2+}(H_2O)_6(SO_4)_2$.

Each of the $(M^{+})_2Cu^{2+}(H_2O)_6(SO_4)_2$ structures contain a rhombically elongated $Cu^{2+}O_6$ octahedron, i.e., a $(2 + 2 + 2)$-distorted octahedron. Alcock et al. (1984) suggested that the Cs salt probably contains a static $(2 + 2 + 2)$-distorted $Cu^{2+}O_6$ octahedron, with only the lowest-energy well of the potential occupied. They indicated that the $Cu^{2+}O_6$ octahedron in the Rb salt has a small but significant dynamic component, as apparently verified by the low-temperature determination of the structure. Alcock et al. (1984) suggested that the K salt (cyanochroite) has a considerable dynamic component, with significant thermal population of the two lower-energy wells. Variable-temperature data for the K salt are not available, but comparison of the $Cu^{2+}O_6$ geometries in $(NH_4)_2Cu^{2+}(H_2O)_6(SO_4)_2$ and $(M^{+})_2Cu^{2+}(H_2O)_6(SO_4)_2$ suggests the presence of a significant dynamic component in $K_2Cu^{2+}(H_2O)_6(SO_4)_2$.

**Possible Dynamic Jahn–Teller Effects in Minerals**

Most $Cu^{2+}$ oxysalt minerals and $Cu^{2+}$ compounds contain $(4 + 2)$-distorted $Cu^{2+}O_6$ octahedra that show little or no evidence of a dynamic Jahn–Teller component. As minerals are typically quite stable, it has generally been assumed that dynamic Jahn–Teller effects will not occur in their structures. However, the arguments developed here suggest otherwise. The presence of $(2 + 4)$-distorted and $(2 + 2 + 2)$-distorted $Cu^{2+}O_6$ octahedra in mineral structures suggests that some may show dynamic Jahn–Teller effects. As a dynamic Jahn–Teller effect may lead to observation of each of these coordination geometries, care must be taken to determine whether a static or dynamic Jahn–Teller effect is observed.

**Recognition of dynamic Jahn–Teller $Cu^{2+}O_6$ octahedra**

$Cu^{2+}$ oxysalt minerals containing $(2 + 4)$- or $(2 + 2 + 2)$-distorted $Cu^{2+}O_6$ octahedra should be investigated further to determine if the configuration is static, dynamic or a result of static disorder. There are three possible means of obtaining this information: (i) variable-temperature crystallographic studies, (ii) crystal-structure refinement followed by the study of anisotropic-displacement parameters, and (iii) electron-spin-resonance (ESR) spectroscopy.

**Possible dynamically distorted $Cu^{2+}O_6$ octahedra**

Several mineral structures contain $Cu^{2+}O_6$ octahedra that may be dynamically distorted. Examples are considered in the following sections, and although a strong case may be made for the presence of dynamically distorted $Cu^{2+}O_6$ octahedra, further verification by variable-temperature structure refinement is desirable. However, in most cases, the limited thermal stability of these hydrous phases is likely to prevent such studies.
Cyanochroite: Cyanochroite, K₂Cu²⁺(H₂O)₆(SO₄)₂, has been described from Mount Vesuvius, Italy, where it occurs as a product of volcanic exhalation. It is a Tutton's salt, all of which have the general formula \( M^+M^{2+}(H₂O)₆(XO₄)₂ \). Cyanochroite is a member of the picromerite group, which includes picromerite, K₂Mg(H₂O)₆(SO₄)₂, möhrite, (NH₄)₂Fe(H₂O)₆(SO₄)₂, boussingaultite, (NH₄)₂Mg(H₂O)₆(SO₄)₂ and nickel-boussingaultite, (NH₄)₂(Ni,Mg)(H₂O)₆(SO₄)₂. The structure of cyanochroite (Robinson & Kennard 1972) (Fig. 7) contains isolated Cu²⁺(H₂O)₆ octahedra that are weakly bonded to the remainder of the structure by K-O bonds and a network of hydrogen bonds. The Tutton's-salt structure allows considerable flexibility of the geometry of the \( M^{2+}(OH₂)₆ \) octahedron (Eby & Hawthorne 1993), so that the structure can accommodate a Jahn–Teller distortion of the octahedral environment; thus Cu²⁺ Tutton's salts are strictly isostructural with non-Cu²⁺ Tutton's salts.

Given the structural compliance of the octahedron in the structure of Tutton's salts, it is surprising that the \( Cu²⁺\phi₆ \) octahedron in cyanochroite shows the strongest rhombic elongation \( [2 + 2 + 2]-\)distortion) of any mineral, as indicated by the \( \Delta₇ \) parameter (Table 3). If such a compliant arrangement were to accommodate a statically distorted \( Cu²⁺\phi₆ \) octahedron, it should show an essentially tetragonal \( (4 + 2)\)-distortion geometry. The observed \( (2 + 2 + 2)\)-distorted \( Cu²⁺\phi₆ \) geometry in cyanochroite is only consistent with a dynamically distorted octahedron, as predicted by Alcock et al. (1984) and as reviewed above.

Bayldonite, volborthite and \( KCu³⁺(OH)_2[(AsO₄)H(AsO₄)] \): Only two mineral structures contain \( (2 + 2 + 2)\)-distorted \( Cu²⁺\phi₆ \) octahedra with \( \Delta₇ > 0.90 \) (Table 3). One of these minerals is cyanochroite, in which we have proposed a dynamic Jahn–Teller effect. The other is the \( Cu(2)\phi₆ \) octahedron in the structure of bayldonite. The Cu–O bond-length distributions in the two minerals with \( \Delta₇ > 0.90 \) are quite similar (Table 3), raising the possibility that the \( Cu(2)\phi₆ \) octahedron in bayldonite also is dynamically distorted.

As noted above, the structures of bayldonite, volborthite and \( KCu³⁺(OH)_2[(AsO₄)H(AsO₄)] \) all contain graphically identical sheets of octahedra and tetrahedra. The \( (2 + 2 + 2)\)-distorted \( Cu(2)\phi₆ \) octahedron in the lower-symmetry sheets in bayldonite is graphically equivalent to the \( (2 + 4)\)-distorted \( Cu(1)\phi₆ \) octahedron in volborthite and \( KCu³⁺(OH)_2[(AsO₄)H(AsO₄)] \). We propose that all three of these octahedra are the result of a dynamic Jahn–Teller effect.

Evidence supporting a dynamic Jahn–Teller \( Cu²⁺\phi₆ \) octahedron in these structures should be obtainable from the anisotropic-displacement parameters for the octahedral ligands. However, anisotropic-displacement parameters were only reported for two of the oxygen atoms in volborthite. The structure refinement of \( KCu³⁺(OH)_2[(AsO₄)H(AsO₄)] \) (Effenerberger 1989) is of good quality, and anisotropic-displacement parameters are available. Therefore, the discussion of the anisotropic-displacement parameters that follows is largely in reference to that structure.

\( KCu³⁺(OH)_2[(AsO₄)H(AsO₄)] \): The structure of \( KCu³⁺(OH)_2[(AsO₄)H(AsO₄)] \) contains two symmetrically distinct \( Cu²⁺\phi₆ \) octahedra; one shows a \( (2 + 4)\)-distortion \( [Cu(1)] \), and the other shows a \( (4 + 2)\)-distortion \( [Cu(2)] \). The \( Cu(1) \) site has \( 2m \) point symmetry such that the four equatorial \( Cu(1)–O(3) \) bonds are equivalent, as are the two apical \( Cu(1)–OH \) bonds (Table 2). The \( Cu(2) \) site has \( 1 \) symmetry, and the octahedron is somewhat \( (2 + 2 + 2)\)-distorted (Table 2).

Fig. 8. Anisotropic-displacement ellipsoids for the \( Cu²⁺\phi₆ \) octahedra in \( KCu³⁺(OH)_2[(AsO₄)H(AsO₄)] \): (a) \( Cu(1)\phi₆ \); (b) \( Cu(1)\phi₆ \); (c) \( Cu(2)\phi₆ \).
Anisotropic-displacement parameters for the \( Cu(1)\phi_6 \) and \( Cu(2)\phi_6 \) octahedra are shown in Figure 8. The parameters for the anions of the \( Cu(1)\phi_6 \) octahedron are consistent with it being dynamically distorted. The maximum principal axis of the \( O(3) \) displacement ellipsoid is subparallel to the \( Cu(1)-O(3) \) direction. The \( OH \) anisotropic-displacement ellipsoid is nearly spherical (Fig. 8), as is normal for a static \( M-\phi \) bond. The \( Cu(2)\phi_6 \) octahedron shows anion anisotropic-displacement parameters consistent with static Jahn-Teller distortion (Fig. 8). In this case, the maximum principal axes of the anions' anisotropic-displacement ellipsoids are not parallel to the \( Cu(2)-\phi \) bond directions.

A dynamic \( Cu(1)\phi_6 \) octahedron must be accommodated by the rest of the structure of \( KCu^{2+}(OH)_2[(AsO_4)H(AsO_4)] \). Unlike most compounds that show dynamic Jahn-Teller \( Cu^{2+}\phi_6 \) octahedron, the \( Cu(1)\phi_6 \) octahedron has strong bonds between the octahedral ligands and other cations in the structure (i.e., \( Cu^{2+} \) and \( As \)). The environment of the \( Cu(1)\phi_6 \) octahedron is shown in Figure 9. The \( Cu(1)-O(3) \) bond is dynamic, whereas the \( Cu(1)-OH \) bond is static. Each \( O(3) \) ligand is also bonded to \( Cu(2) \) and \( As \). The dynamic movement of the \( O(3) \) ligand of the \( Cu(1)\phi_6 \) octahedron must result in a distortion of the \( Cu(2)\phi_6 \) octahedron and a tilting of the \( AsO_4 \) tetrahedron. The \( As \) cation is bonded to two \( O(3) \) atoms, an \( O(1) \) atom and an \( O(2) \) atom (Fig. 9). The \( O(1) \) position is a static ligand shared by two \( Cu(2) \) atoms and acts as an anchor for the \( AsO_4 \) tetrahedron. The \( O(2) \) atom is located at the \( AsO_4 \) apex, and is only very weakly bonded by two long bonds to \( K \) (3.24 Å: Effenberger 1989) and by two hydrogen bonds. Tilting of the \( AsO_4 \) tetrahedron can easily occur owing to the weak bonding to \( O(2) \), and may happen in two ways. The coupled motion of both \( O(3) \) atoms in the same direction will move the \( O(3)-O(3) \) edge of the tetrahedron up and down, such that the \( O(2) \) apical oxygen will move back and forth along the \([100]\) direction. It is also possible that the two \( O(3) \) atoms will move out of phase, such that one moves up while the other moves down. In this case, the \( AsO_4 \) tetrahedron would rotate about the \( As-O(1) \) bond and the \( O(2) \) oxygen atom would move back and forth in the \([010]\) direction. Examination of the anisotropic-displacement parameters for the \( O(2) \) position (Fig. 10) clearly shows significant anisotropic displacement in the \([010]\) direction, indicating that the motion of the two \( O(3) \) ligands belonging to one \( AsO_4 \) tetrahedron are out-of-phase.

Volborthite: The structure of volborthite (Basso et al. 1988) contains a \( Cu(1)\phi_6 \) octahedron analogous to the \( Cu(1)\phi_6 \) octahedron in \( KCu^{2+}(OH)_2[(AsO_4)H(AsO_4)] \). However, Basso et al. (1988) only gave anisotropic-displacement parameters for two of the oxygen atoms, both of which show anomalously high values. One of these oxygen atoms belongs to the interlayer \( H_2O \) group, and the other \([O(1)]\) is the apical (non-sheet) oxygen of the \( VO_4 \) tetrahedron. In volborthite, this atom of oxygen is shared between two \( VO_4 \) tetrahedra that link adjacent sheets, and the \( V-O-V \) bond is linear by symmetry constraints. However, Basso et al. (1988) argued that the large displacement-parameters associated with the \( O(1) \) position indicate positional disorder and a nonlinear \( V-O-V \) bond. The local environment around the \( VO_4 \) tetrahedron is shown in
Figure 11. Note that we predict the Cu(1)–O(2) bonds to be dynamic in this case, as O(2) in volborthite is graphically equivalent to O(3) in KCu$_3^{2+}$[(AsO$_4$)$_2$H(AsO$_3$)]. The O(1) anisotropic-displacement ellipsoid in volborthite is elongated in the same way as the O(2) displacement ellipsoid in KCu$_3^{2+}$[(AsO$_4$)$_2$H(AsO$_3$)] (Fig. 11), consistent with a dynamic Cu(1)O$_6$ octahedron, as well as a nonlinear V–O–V bond.  

**Bayldonite:** Arguments based upon the structural relationships between bayldonite, volborthite and KCu$_3^{2+}$[(AsO$_4$)$_2$H(AsO$_3$)] (see above) lead to the prediction that the (2 + 2 + 2)-distorted Cu(2)O$_6$ octahedron in bayldonite is dynamically distorted, whereas the Cu(1)O$_6$ and Cu(3)O$_6$ octahedra are statically distorted. The dynamically (2 + 2 + 2)-distorted Cu(2)O$_6$ octahedron is elongated in the Cu(2)–O(3) direction two-thirds of the time and in the Cu(2)–O(2) direction one-third of the time. The predicted dynamic interchange of the distortion directions should lead to markedly anisotropic anion-displacement ellipsoids, with their maximum principal axes parallel to the Cu–O bonds. The anisotropic-displacement ellipsoids for each Cu$^{2+}$O$_6$ octahedron in bayldonite (Ghose & Wan 1979) are of low precision, owing to the high X-ray absorption ($\mu_x = 372$ cm$^{-1}$) and poor quality of the crystal, and some of the ellipsoids apparently show anomalous shapes. However, the anisotropic-displacement parameters are generally consistent with the proposed dynamic Cu$^{2+}$O$_6$ octahedron in bayldonite.

Dynamic distortion of the Cu(1)O$_6$ octahedra in the structures of volborthite and KCu$_3^{2+}$[(AsO$_4$)$_2$H(AsO$_3$)] is accommodated by tilting of the tetrahedral group, as shown in Figures 10 and 11. Note that in both cases, the tetrahedrally coordinated cation is located on a mirror plane. The coupled movement of the ligands on either side of the mirror plane causes the apical tetrahedral ligand to sweep out a path perpendicular to the mirror plane, as shown by the anisotropic-displacement ellipsoids (Figs. 10, 11).

The situation is somewhat more complicated in the structure of bayldonite. The local environment of the AsO$_4$ tetrahedron is shown in Figure 12. The As is located on a general position in the space group C2/c, and each of the four tetrahedral ligands are symmetrically distinct. Also, the tetrahedron shares its ligands with two pairs of three symmetrically distinct Cu$^{2+}$ ions. Of these, only the Cu(2)O$_6$ octahedron is dynamically distorted. The effect of the dynamic ligands on the tetrahedron is somewhat different from that observed in the volborthite and KCu$_3^{2+}$[(AsO$_4$)$_2$H(AsO$_3$)] structures. In this case, the Cu(2)–O(3) and Cu(2)–O(2) bonds are dynamic, as indicated by arrows in Figure 12. Also, the Cu(2)–O(3) bond is elongated two-thirds of the time, whereas the Cu(2)–O(2) bond is only elongated one-third of the time. For a given AsO$_4$ tetrahedron, the Cu(2)–O(3) bond is elongated while the Cu(2)–O(2) bond is shortened, and the Cu(2)–O(3) bond is shortened while the Cu(2)–O(2) bond is elongated. This coupled dynamic movement rotates the tetrahedron such that the apical O(4) position rocks back and forth, as clearly shown by the O(4) displacement ellipsoid in Figure 12.

**Discussion**

(1) It is only after careful examination of the geometries of all Cu$^{2+}$O$_6$ octahedra in Cu$^{2+}$ oxysalt minerals that the true importance of the Jahn–Teller effect is apparent. We have shown that probably every Cu$^{2+}$O$_6$ octahedron observed in Cu$^{2+}$ oxysalt minerals is distorted due to the Jahn–Teller effect: *there is no*
conclusive example of a true holosymmetric Cu$^{2+}$ octahedron in these minerals.

(2) The (4 + 2)-distorted Cu$^{2+}$ octahedral geometry is by far the most common in Cu$^{2+}$ oxysalt minerals and in Cu$^{2+}$ compounds in general. However, a considerable range of Cu–$\phi$ bond-lengths is observed in these octahedra, with the apical bond-lengths showing the most dispersion. The (4 + 2)-distorted Cu$^{2+}$ octahedron is flexible and responds to steric effects of the crystal structure.

(3) It remains unclear whether any (2 + 4)-distorted Cu$^{2+}$ octahedra occur in minerals. Possible examples are in the structures of campigliaite, paratacamite, volborthite and demesmaekerite. Of these, those observed in campigliaite are from such an imprecise structure-refinement that the bond lengths cannot be considered reliable. The structure of volborthite contains a (2 + 4)-distorted Cu$^{2+}$ octahedron, but strong arguments have been advanced that the octahedron is dynamically distorted, a time average of two unaligned (4 + 2)-distorted octahedra. The paratacamite structure reportedly contains a (2 + 4)-distorted octahedron (Fleet 1975), but the refinement involved a substructure, and as a consequence, anisotropic-displacement parameters were not refined for the octahedron’s ligands. This octahedron may also be dynamically distorted. Finally, there is a single (2 + 4)-distorted octahedron in the structure of demesmaekerite. This octahedron is the most persuasive example of a true (2 + 4)-distorted Cu$^{2+}$ octahedron, as the anisotropic-displacement ellipsoids reported by Ginderow & Cesbron (1983) do not conclusively indicate that the octahedron is dynamically distorted.

(4) Mineralogists have always assumed that dynamically distorted Cu$^{2+}$ octahedra do not occur in minerals. However, it seems probable that dynamically distorted Cu$^{2+}$ octahedra do occur in the structures of cyanochroite, volborthite and bayldonite; two of these structures have (2 + 2 + 2)-distorted octahedra. Furthermore, a number of other Cu$^{2+}$ oxysalt minerals also show (2 + 2 + 2)-distorted octahedra (Table 3), and it is possible that some of these may also be dynamically distorted.

**ACKNOWLEDGEMENTS**

The Natural Sciences and Engineering Research Council of Canada supported this work with Post-Graduate and Post-Doctoral Fellowships to PCB, and an Operating Grant to FCH. This manuscript was improved following reviews by Dr. M.E. Fleet and an anonymous reviewer, and editorial work by Dr. J.M. Hughes and Dr. R.F. Martin.

**REFERENCES**


CID-DRESDNER, H. (1965): Determination and refinement of the crystal structure of turquoise, CuAl$_6$(PO$_4$)$_4$(OH)$_8$·4H$_2$O. *Z. Kristallogr.* 121, 87-113.


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