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Cu^2, a Chameleon in Coordination Chemistry

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Electronic effects play a predominant role in the stereochemistry of Cu^{2+}-compounds and are conveniently described in terms of first order or pseudo Jahn-Teller coupling. Examples for the coordination numbers 4, 5 and 6 are given and discussed in detail. Some general conclusions with respect to those geometries, which are stabilized most by the Jahn-Teller effect, are given.

INTRODUCTION

In a purely electrostatic model Cu^{2+} ions are expected to adapt an octahedral coordination with ligands as O, N and F, if the ratios of the cation and ligand ionic radii are considered. For Cl^- and in particular the large Br^- ion a tetrahedral environment should result. The inclusion of electronic effects connected with the electron occupation of the *d* orbitals has significant additional influence on the site preference, however. The first important contributions are the ligand field stabilization energies in the various coordination geometries, which originate from the different overlap of the various *d* orbitals. Based on a d^{10} configuration as the energetic zero point, they can be easily calculated in the hole formalism[1] if one uses the angular overlap model, for example.[2] If one includes the coordination number 5, one finds a relative preference for the octahedral and square pyramidal coordination $-3\ e_\sigma$, followed by the trigonal bipyramid ($-2\frac{3}{4}\ e_\sigma$, assuming equally long equatorial and axial bonds) and the tetrahedron ($-\ {}^4/_3\ e_\sigma\ -\ {}^8/_9\ e_\Pi$) (Figures 1

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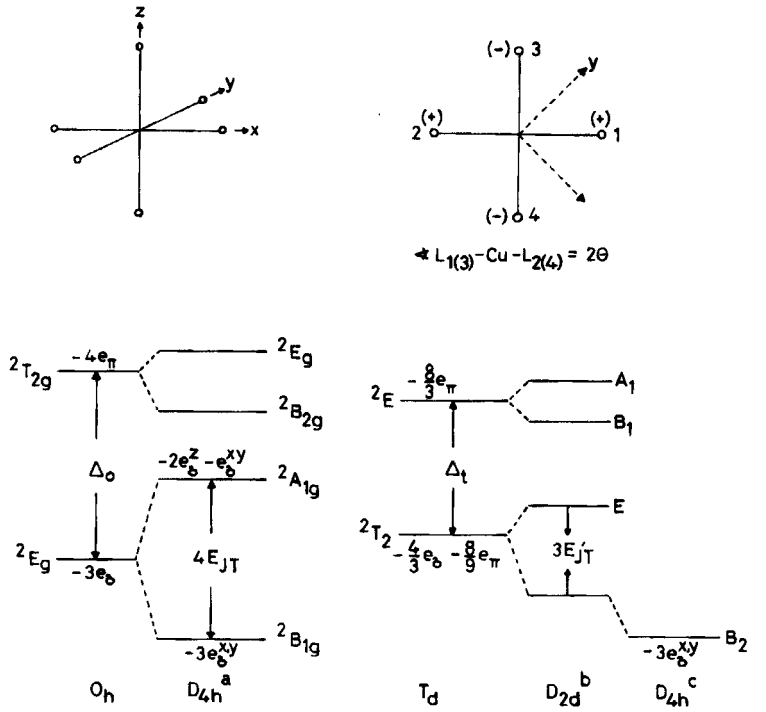

FIGURE 1 Energy diagrams for a d^9 cation in octahedral (left) and tetrahedral coordination (right) and also in lower-symmetry geometries resulting from first order Jahn–Teller effects. a and c: elongated octahedral and square planar, respectively; b: compressed along S_4. Relative AOM energies[9] (hole formalism) are given.

and 2). An even more significant electronic effect is connected with the lowering of the energy of the system induced by the Jahn–Teller theorem. This symmetry principle, formulated by Jahn and Teller in 1937,[3] states that orbitally degenerate ground states are unstable with respect to distortions of otherwise highly symmetric coordination polyhedra (with the exception of linear coordinations). The splitting of the ground state by the lower symmetry distortion generates a new ground state of lower energy and hence stabilizes the system (Figure 1). The coordination chemistry of Cu^{2+} with C.N. = 4 and 6 is indeed strongly influenced and determined by distortions induced by first order Jahn–Teller effects of the described nature, as will be demonstrated in this paper. Some examples of octahedral coordination are given below.

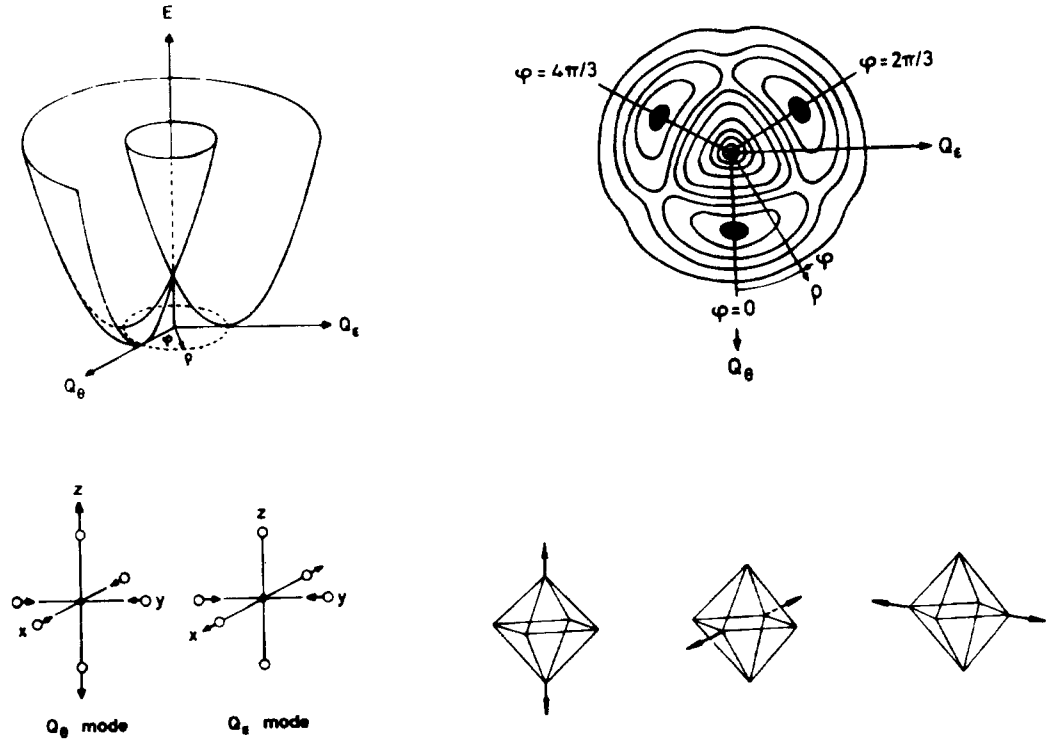

FIGURE 2 Mexican hat potential surface (linear vibronic $E \otimes E$ coupling) (left) and cross section perpendicular to energy coordinate (nonlinear coupling included) (right) The Q_ε [A_{1g}] and Q_θ [B_{1g}] components of the E_g vibrational mode and the three conformations of elongated octahedra are also depicted.

The oxides of the divalent transition metals of the first series (TiO, VO, MnO–ZnO) crystallize in the NaCl structure (octahedral $T^{II}O_6$ coordination) with the exception of ZnO (Wurtzite structure with ZnO_4 tetrahedra) and CuO. The lattice of the latter compound (the mineral tenorite) is a distorted version of the PtO type with a square planar CuO_4 coordination (196 pm bond lengths), which is supplemented to a strongly elongated octahedron by two additional O^{2-} ligands (278 pm distance).[4] Pyridine-*N*-oxide complexes $[T^{II}(ONC_6H_5)_6]X_2$ (X^-: ClO_4^-, BF_4^-, etc.) have structures with regular $T^{II}O_6$ octahedra (T^{II}: Cu^{2+}, Ni^{2+}, Co^{2+}). In case of the Cu^{2+} compounds phase transitions occur below 298 K which lead to low-temperature phases with strongly tetragonally elongated octahedra.[5,6] The apparent regular octahedral coordination at 298 K is the dynamic average over three elongated octahedra with the fourfold axes directed along the *x*, *y* and *z* direction of a cartesian coordinate system (see Figure 2). The structures of the difluorides from VF_2 to ZnF_2 exhibit similar geometric features as the oxides. While most of them crystallize in the tetragonal rutile structure with slightly tetragonally *compressed* $T^{II}F_6$ polyhedra induced by stereochemical packing effects [for example, ZnF_2 with 204 pm (4×), 201 pm (2×) bond lengths],[7,8] CrF_2 and CuF_2 possess monoclinically distorted rutile unit cells with strongly *elongated* Cu(Cr)F_6 octahedra [CuF_2: 200 pm (4×), 243 pm (2×)].[4] Analogous observations are made for the binary chlorides and bromides, in which only the six-coordination of Cr^{2+} and Cu^{2+} deviates appreciably from a regular octahedral geometry. If one considers stronger ligand fields, for example the ligator atom N in the cubic transition metal nitrocomplexes $A_2^I M^{II} T^{II}(NO_2)_6$ (A^I, alkaline ions Tl^+, NH_4^+; M^{II}, alkaline earth ions Pb^{2+}), a regular octahedral geometry of the $T^{II}N_6$ polyhedra is found for T^{II}: Fe^{2+}, Ni^{2+} and for Cu^{2+}, Co^{2+} in the high temperature phases. Cu^{2+} and Co^{2+}, which are low-spin in these compounds, induce phase transitions at lower temperatures to lower symmetry unit cells.[10] As before, appreciably elongated Cu(Co)N_6 octahedra are observed in these phases [$K_2SrCu(NO_2)_6$, 203.5 pm (4×), 231 pm (2×)].

We may deduce from the quoted model examples that the stable static coordination geometry of Cu^{2+} in a chemical environment of six equal ligands is a strongly elonated octahedron (sometimes with a small *o*-rhombic distortion component superimposed). This statement is strictly correct only if the sites offered to Cu^{2+} are regular octahedra. But even for host lattices, in which the octahedra deviate slightly from O_h sym-

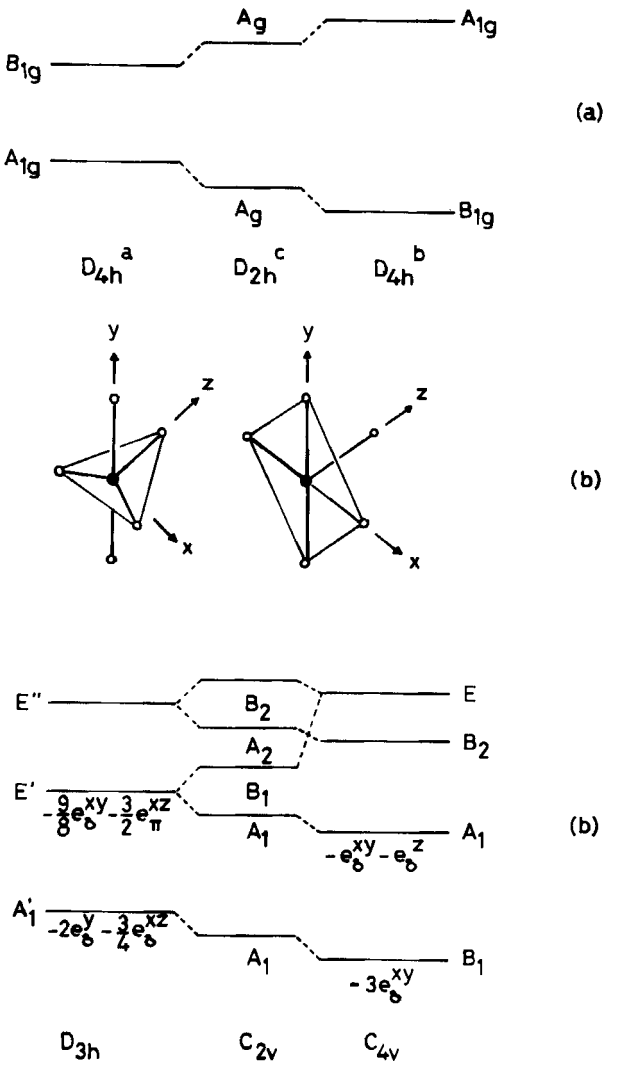

FIGURE 3 Energy diagrams of a d^9 cation in coordination geometries connected via pseudo Jahn–Teller effects. (a) Tetragonal bipyramids (lowest states only). a: compressed along z (d_{z^2} ground state); b: elongated along x [$(\sqrt{3/2})d_{x^2-y^2} + \frac{1}{2}d_{z^2}$ ground state]; c: intermediate o-rhombic geometry. (b) Trigonal bipyramid (D_{3h}) and tetragonal pyramid (C_{4v}). C_{2v}: intermediate geometry. Relative AOM energies[9] (hole formalism) are given. Ground states: $(\sqrt{3/2})d_{x^2-y^2} + \frac{1}{2}d_{z^2}$ and $d_{x^2-y^2}$ in D_{3h} and C_{4v}, respectively.

metry by geometrical packing effects, an essentially elongated configuration is nearly always observed. This behavior is directly connected with the twofold orbital degeneracy of the ^2E_g ground state of Cu^{2+} in octahedral coordination, as will be shown below. It is not restricted to Cu^{2+}, but these geometric features are specific for all transition metal ions in octahedral coordination with one or three electrons in the σ-antibonding e_g subshell:

$$d^4 : {}^5E_g\ (t_{2g}^3 e_g^1)\ (Cr^{2+},\ Mn^{3+},\ Mo^{2+},\ \text{etc.}),$$

$$d^7\ (\text{low spin}) : {}^2E_g\ (t_{2g}^6 e_g^1)\ (Co^{2+},\ Ni^{3+},\ \text{etc.}),$$

$$d^9 : {}^2E_g\ (t_{2g}^6 e_g^3)\ (Cu^{2+},\ Ag^{2+},\ \text{etc.}).$$

Orbitally nondegenerate ground states may also be stabilized by electronic effects of the Jahn–Teller type. In this case a lowering of the ground state may eventually be achieved by configuration interaction with a nearby excited state of the same species, if the system distorts in a symmetry allowed way by proper normal vibrations (higher order or pseudo Jahn–Teller effects).[11] Examples are the interplay between the trigonal bipyramid and the square pyramid, which are connected by the Berry rotation (interaction between the A_1 levels in the intermediate point group C_{2v}, Figure 3b; T action between the A_g states in D_{2h}, Figure 3a)[12] or the transition from a tetragonally to an *o*-rhombically distorted octahedron (inter Π). The various possibilities of stabilization by electronic effects lead to the remarkable flexibility in the coordination chemistry of Cu^{2+}, which can adapt to the various geometries with the coordination numbers 4, 5 and 6 equally well.

Cu^{2+} IONS IN OCTAHEDRAL COORDINATION

In order to realize an energetic stabilization of a polyhedron by symmetry reduction, a vibrational mode of the point group of the respective polyhedron must be present which is able to lift the orbital degeneracy of the E_g ground state and provide a pathway for the distortion. Following the group theoretical argument, the active vibrational modes Γ_v are easily derived from the direct product $E_g \otimes \Gamma_v \otimes E_g$, which must contain the totally symmetric representation of the respective point group.[13] One obtains $\Gamma_v = A_{1g}, E_g$, from which only the latter normal mode can split the E_g ground state by tetragonal and *o*-rhombic deformations.

The "mexican hat" potential surface, which results from the linear coupling between the electronic and nuclear motion—both of E_g symmetry—is illustrated in Figure 2a. The ringlike minimum of the lower potential well represents the energy gain with respect to the position of the undistorted octahedron and can be expressed in terms of the linear coupling constant V_E and the radial distortion parameter ρ, which is defined (for small δi)

$$\rho = \{\Sigma\ 2\ \delta i^2\}^{1/2} \qquad i = x, y, z; \text{ bond lengths: } a_0 + \delta i. \quad (1)$$

Explicitly, the energy[2] is lowered as the consequence of the Jahn–Teller distortion:

$$2\,E_{JT} = e_\sigma^{xy} - e_\sigma^z = \rho \cdot V_E, \quad (2)$$

with a total ground state splitting of 4 E_{JT} (Figures 1 and 2). If one takes nonlinear vibronic coupling terms into account an additional warping is introduced (Figure 2b). The three minima correspond to octahedra which are elongated along one of the fourfold octahedral axes. In many cases the small energy barriers between the minima can be surpassed by thermal excitation, which is equivalent to a pseudorotation around a threefold axis (the dynamic Jahn–Teller effect). Depending on the effective time of measurement of the chosen observation method with respect to the lifetime of the system, in one of the three minima the thermal average over the three orientations of the long axis (regular octahedra) or still a distorted octahedron is observed. More explicit descriptions of the vibronic model are given elsewhere.[10,13] We will now discuss the experimentally observed stereochemistry of Cu^{2+} with CN = 6 in greater detail.

As was stated already, Cu^{2+} nearly always induces a strong tetragonal elongation if it is offered a regular (or nearly regular) octahedral site with six equal ligands. If one actually has to decide whether an observed distortion of octahedral Cu^{2+} is due to the Jahn–Teller effect, the comparison with the Ni^{2+} or Zn^{2+} compounds of the same constitution is most helpful. Ni^{2+} and Zn^{2+} with ionic radii comparable to Cu^{2+} possess orbitally nondegenerate ground states in octahedral coordination and hence are not subject to Jahn–Teller distortion effects.

We have discussed the basic ideas of the *local* Jahn–Teller effect in a strongly σ-antibonding E ground state so far. The elastic coupling

between the distorted octahedra in the unit cell is of additional importance. These interactions usually enhance the extent of the local Jahn–Teller distortion [measured by ρ, Eq. (1)] significantly if the Cu^{2+} concentration in the compound increases (in mixed crystals $Ba_2Zn_{1-x}Cu_xWO_6$ for example).[10] A second aspect is that the distorted octahedra orientate to each other in specific order patterns which reduce the symmetry of the unit cell characteristically. Both features are consequences of cooperative Jahn–Teller effects and are extensively discussed elsewhere.[10]

I now want to consider what occurs if an already irregular octahedron undergoes an additional Jahn–Teller distortion. Particularly interesting are cases in which Cu^{2+} is offered a compressed octahedral site. In terpyridine complexes T^{II} $terpy_2X_2 \cdot nH_2O$, for example, the rigid tridentate ligands impose a compressed N coordination on the T^{II} $terpy_2^{2+}$ cations [T^{II}: Ni^{2+}, X^-: NO_3^-, $n = 3$: $a_z = 200$ pm (2×), $a_{x,y} = 213$ pm (4×)], which is changed for Cu^{2+} towards an elongated TN_6 octahedron [$T^{II} = Cu^{2+}$, $X^- = NO_3^-$, $n = 0$: $a_z = 198.5$ pm (2×), $a_{y(x)} = 2.085$ pm (2×), $a_{x(y)} = 229$ pm (2×)]. The direction of elongation is perpendicular to the short T^{II}–N distances.[14] In $CuCl_2 \cdot 2\,H_2O$ the situation is similar because Cu^{2+} is coordinated by four weak Cl^- ($a_{x,y}$) and two strong OH_2 ligands (a_z). A $CuCl_4O_2$ geometry again results in which an elongation perpendicular to the axial z direction occurs. The Cu–O bond lengths [$a_z = 196$ pm] and two Cu–Cl spacings [$a_{y(x)} = 229$ pm] are rather short, while the remaining Cu–Cl bonds are very weak. [$a_{x(y)} = 294$ pm].[15,16] The distortion of the $Cu(OH_2)_6^{2+}$ polyhedra in the Tutton salts is of the same type. The Zn–O bond lengths in $(NH_4)_2Zn(SO_4)_2 \cdot 6\,H_2O$ are 212.5 ± 5 pm (4×) and 207.5 pm (2×), but 222.5 pm (2×), 196 pm (2×) and 208.5 pm (2×) in the isomorphous Cu^{2+} salt.[17] The change from the given compressed D_{4h} geometry to a polyhedron with D_{2h} symmetry is easily understood in the notion of a pseudo Jahn–Teller effect (Figure 3a).[11] A lowering of a nondegenerate ground state (Γ_g) may eventually occur if the direct product $\Gamma_g \otimes \Gamma_v \otimes \Gamma_e$ contains the totally symmetric representation in the considered point group. With $\Gamma_g \equiv A_{1g}$ and $\Gamma_e \equiv B_{1g}$ as the nearest-lying excited state (Figure 3a), the B_{1g} mode (Figure 2) turns out to be the active vibrational mode. A symmetry reduction will only occur if the force constant for this mode is negative.[11] The given examples demonstrate that this is usually the case for host lattice induced compressed octahedra. One of the very few exceptions is mixed crystals

$Ba_2Zn_{1-x}Cu_xF_6$ ($0 < x \lesssim 0.3$).[10] The ZnF_6 octahedra in the Ba_2ZnF_6 host lattice are slightly tetragonally compressed, which is caused by the specific connection pattern of the polyhedra. The substitution of Zn^{2+} by Cu^{2+} does not change the symmetry but enhances the compression beyond that of the host lattice sites. This observation is also in accord with the vibronic coupling model, which demands that all totally symmetric motions (A_{1g} in D_{4h}; Figure 2) have occurred, until the bond lengths have changed to their best values.[11] For $x > 0.6$ a drastic change in the geometry of the CuF_6 polyhedra is found. Analogous to the examples discussed above, an elongation perpendicular to the direction of compression has taken place. Obviously the force constant for the B_{1g} mode is negative now—caused by cooperative Jahn–Teller forces—and induces a transition from the local D_{4h} into a D_{2h} symmetry.

If Cu^{2+} is offered a site that is already slightly or even strongly elongated, generally an additional elongation occurs. In La_2NiO_4, for example, (K_2NiF_4 structure) the NiO_6 polyhedra are considerably elongated (ρ = 36 pm) by geometric packing effects, while in the corresponding Cu^{2+} compounds the elongation of the CuO_6 octahedra greatly exceeds this value (ρ = 64 pm).[18] Obviously an energetic stabilization by the action of the totally symmetric A_{1g} vibration has occurred, in analogy to the above mentioned $Ba_2Zn_{1-x}Cu_xF_6$ mixed crystals ($x < 0.3$). The argument that the increase of ρ by the vibrational A_{1g} mode in D_{4h} symmetry is not in accord with the symmetry restrictions imposed by the pseudo Jahn–Teller effect[19] is not correct.

One may state after the discussion of the examples above that the coordination chemistry of Cu^{2+} with C.N. = 6 is determined by strongly distorted octahedra, the predominant component of which is nearly always a considerable elongation along two trans Cu^{2+}–ligand bonds. This is also true when ligand or host lattice effects impose an additional distortion on the octahedra. In cases in which different ligands constitute the polyhedron, very often the Cu^{2+} but not the Ni^{2+} or Zn^{2+} complexes exist, because only Cu^{2+} can profit from the anisotropy of the ligand field via the Jahn–Teller effect. To give just one example, While $NiZrF_6$ forms a *hexa*hydrate when exposed to moist air, with regular $Ni(OH_2)_6^{2+}$ octahedra (c.f. above), $CuZrF_6$ (elongated CuF_6 octahedra, $\rho \simeq 28$ pm)[20] transforms into a *tetra*hydrate, in which Cu^{2+} is coordinated by four equatorial H_2O and two rather weakly bonded axial F^- ligands.[21] Obviously H_2O is the ligand with more pronounced σ-donor

properties compared to F^-. By this anisotropic ligand field effect, imposed on the octahedron in addition to the Jahn–Teller distortion, ρ has increased to 41 pm.

Frequently Cu^{2+} polyhedra with C.N. = 6 appear to be regular. This is always indicative of a dynamic Jahn–Teller effect and does not represent the static equilibrium geometry, which appears at low temperatures only. One example is the Cu en_3^{2+} cation in Cu en_3 SO_4 with a nearly regular octahedral CuN_6 geometry at 298 K, which transforms into an elongated octahedron below 180 K.[22] On the other hand the Cu bipy $(hfacac)_2$ complex, also with three two-dentate ligands, is subject to a static Jahn–Teller distortion at room temperature (Figure 4).[23] In spite of the rigidity of the hexafluoroacetylacetonato ligands, each of which bridge a long axial and a short equatorial position, the radial distortion parameter is remarkably large (36 pm). Of particular interest is the fact that the Jahn–Teller induced large anisotropy in the Cu–O bond lengths obviously stabilizes one of the two mesomeric structures of the hfacac anion.

Sometimes the Jahn–Teller distortion is extremely large and leads to the complete removal of the axial ligands. Though in most cases Cu^{2+} tends to weakly bond two additional ligands, a series of compounds is known in which the coordination is square planar. While in La_2CuO_4 the Cu^{2+} sites are six-coordinated with strongly elongated octahedra (see above), a different layer packing in Ln_2CuO_4 (Ln = Nd, Sm, Eu, Gd) induces a square-planar environment of oxygen.[18] A second ex-

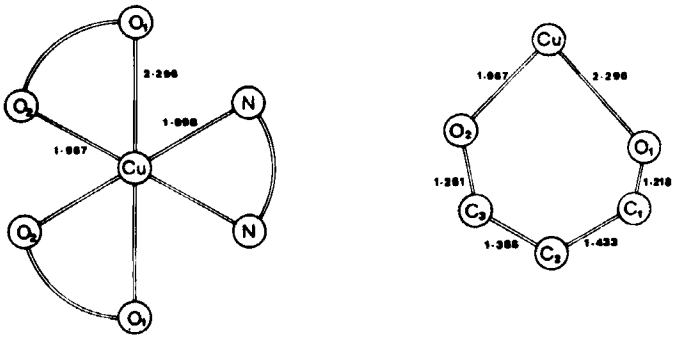

FIGURE 4 Geometry of bis(hexafluoroacetylacetonato) bipyridine Copper (II) and bond lengths in the Cu-diketone ring.[23] C–O and C–C spacings in hexafluoroacetylacetone 125.9 and 140.7 pm, respectively.

ample is Li_2CuO_2, the lattice of which is characterized by chains of edge connected CuO_4 squares.[24]

Cu^{2+} IN TETRAHEDRAL COORDINATION

The examples of Cu^{2+} in a chemical environment with C.N. = 4 are by far not as numerous as those with C.N. = 6. Nevertheless, quite a number of tetrahedral complexes is known. Though Cu^{2+} polyhedra with C.N. = 6, 4 and 5 can be prepared with Cl^- as ligand, a distorted tetrahedral coordination is frequently found in compounds $A_n(CuCl_4)$ where isolated $CuCl^{2-}$ polyhedra constitute the structure.[25] In practically all cases these tetrahedra are compressed along an S_4 axis. The Cu–Cl bond length is 224 ± 3 pm and the bond angle 2θ (Figure 1) varies, depending on the nature of the cationic counterions A, between 129° and 139° but increases to values as high as 160° in some cases.[25] The compound $(PhCH_2CH_2NMeH_2)_2CuCl_4$ is particularly interesting because it contains flattened tetrahedra in the high-temperature phase (2θ = 131°) and square planar $CuCl_4$ entities in the low-temperature phase, corresponding to 2θ = 180° and a transition to D_{4h} symmetry (Figure 1). The described distortions can again be understood in terms of first order Jahn–Teller effects (see below). Usually the flattened tetrahedra deviate from a D_{2d} geometry, however. Because geometric packing effects are mostly present in the respective lattices, the Jahn–Teller compression along the S_4 axis is superimposed by a host lattice distortion component. In order to discriminate between Jahn–Teller and host-lattice induced distortions a comparison with Co^{2+} and Zn^{2+} compounds of analogous constitution is useful because both ions have non-degenerate ground states in T_d symmetry. Taking Br^- complexes as examples, slightly distorted $ZnBr_4^{2-}$ tetrahedra constitute the lattice of Cs_2ZnBr_4 [2θ = 115°, 110° (3×), 106.5° (2×); d(Zn–Br): 239 ± 2 pm].[26] In the isomorphous Cu^{2+} compound a clearly flattened tetrahedron is observed [2θ = 128.5 ± 2° (2×), 101 ± 1° (4×); *d*(Cu–Br): 237 ± 2 pm].[26]

Cu^{2+} is also found in an oxygen coordination with C.N. = 4. In $CuKPO_4$ half of the Cu^{2+} ions occupy sites with a considerably flattened tetrahedral environment [*d*(Cu–O): 192.5 ± 2 pm; 2θ = 149 ± 1.5°].[27] The CuO_4 polyhedra are interconnected by PO_4^{3-} tetrahedra and hence host lattice effects cause deviations from D_{2d} symmetry. In the tetra-

gonally distorted spinel $CuCr_2O_4$ ($c/a < 1$), however, with a normal cation distribution (C.N. = 4 and 6 for Cu^{2+} and Cr^{3+}, respectively) the CuO_4 tetrahedra have a perfect compressed D_{2d} geometry ($2\theta \simeq 120°$),[28] while the corresponding Zn^{2+} and Co^{2+} spinels are cubic with tetrahedra of T_d symmetry.

The given representative examples indicate the presence of specific distortion effects, which are connected with the d^9 configuration of Cu^{2+}. The triply orbitally degenerate (σ + II) antibonding T_2 ground state in T_d symmetry (Figure 1) can be split by either a tetragonal or a trigonal ligand field component. In both cases an orbital singlet as the new ground state results by a compression along an S_4 or C_3 axis. The active vibrational modes Γ_ν are E and T_2, respectively, as follows from the direct product $T_2 \otimes \Gamma_\nu \otimes T_2$.[13] Obviously, only the vibronic interaction with the E mode is strong enough to finally induce a static distortion. Figure 5a illustrates that a linear $T_2 \otimes E$ coupling produces a potential surface with three minima, which are correlated with the three possible conformations of compressed tetrahedra (Figure 5b). The ground state splitting is 3 E'_{JT} and the lowering of the ground state by the tetragonal distortion:

$$\begin{aligned} 2E'_{JT} &= \frac{1}{3} e_\sigma (5 - 18\cos^2\theta + 9\cos^4\theta) \\ &\quad - \frac{4}{9} e_\Pi (2 - 9\cos^2\theta + 9\cos^4\theta) \\ &= \rho' \cdot V'_E, \end{aligned} \tag{3}$$

where V'_E is the linear vibronic coupling constant. The tetrahedral distortion parameter ρ' (for small deviations from the regular geometry) is

$$\rho' = a_t (1 - \sqrt{3}\cos\theta) \qquad a_t \equiv \text{Cu–L bond length.} \tag{4}$$

Because the ground state wavefunctions d_{xy}, d_{xz} and d_{yz} in the three equivalent minima are linearly independent, a system cannot pass from one paraboloid into another. Consequently, a dynamic effect as for the $E \otimes E$ case is not possible.[13] Though the degeneracy of a tetrahedral T_2 ground state can also be lifted by spin-orbit coupling, the energetic stabilization of the system would only be 800 cm^{-1} at most. The lowering

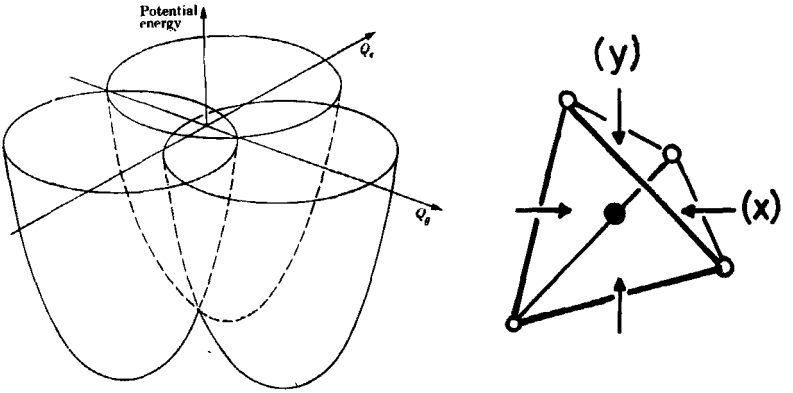

FIGURE 5 The adiabatic potential for an orbital triplet state (linear vibronic $T \otimes E$ coupling) (left); Cu^{2+} in a flattened tetrahedron (compression along one of the three S_4 axes along x, y, z) (right).

of the ground state by vibronic coupling [Eq. (3)] is significantly larger than this value in all known cases of $Cu^{II}L_4$ tetrahedra, however, and hence the Jahn–Teller distortion becomes effective. The same symmetry arguments as for Cu^{2+} are valid for all cations in tetrahedral coordination with an electron occupation of the t_2 subshell which deviates from 6 and 3 (T ground states). Ni^{2+} ($e^4t_2^4 \equiv {}^3T_1$) represents a case for which the LS stabilization (900 cm^{-1} at most) and possible Jahn–Teller energies [Eq. (3)] are apparently comparable. Depending on the magnitude of the vibronic coupling constant V_E in the respective system sometimes a Jahn–Teller distortion is observed (the spinel $NiCr_2O_4$[29]), while usually the Jahn–Teller effect is quenched by LS coupling, for example, $[(C_6H_5)_3AsCH_3]_2NiCl_4$ with regular $NiCl_4^{2-}$ tetrahedra].[30]

The limit of a tetragonal Jahn–Teller distortion in T_d symmetry is a square planar geometry. As discussed above, the same limit results if the axial ligands of a tetragonally elongated octahedron are completely removed. Two of many examples may illustrate this coordination behavior. $CaZnF_4$ crystallizes in the Scheelit lattice with ZnF_4^{2-} tetrahedra, while $CaCuF_4$ possesses the $KBrF_4$ structure with CuO_4 square planes.[31] Similarly the compounds Co[Zn]Hg(SCN)$_4$ contain slightly flattened Co[Zn]N_4 tetrahedra; CuHg(SCN)$_4$ (and possibly also the Ni^{2+} complex) is characterized by a square planar transition metal coordination, however.[32] The Jahn–Teller stabilization energy $2\,E'_{JT}$ is $^5/_3\,e_\sigma - {}^4/_9\,e_\Pi$

in these examples (equal Cu–L bond lengths in T_d and D_{4h}, Eq. (3), Figure 1).

In a few cases an apparently predominant $T_2 \otimes T_2$ coupling is observed. This occurs if the host lattice favors a trigonal rather than a tetragonal deformation of the tetrahedral sites. Cu^{2+} doped into ZnO is one example,[28] the compound $(HNMe_3)_3Cu_2Cl_7$ a second.[33] The latter complex has a pseudohexagonal unit cell containing chains of face-connected $CuCl_6^{3-}$ octahedra parallel to c and isolated $CuCl_4^{2-}$ tetrahedra side by side. The observed local distortion is clearly a trigonal elongation [d(Cu–Cl): 220 (1×), 223 (2×), 230 pm (1×)] without a significant angular deformation [$2\theta = 109.5 \pm 1.5°$] and is most certainly caused by host lattice induced strains. The resulting splitting of the tetrahedral T_2 level would lead to an orbital doublet as the new ground state. The combined action of the trigonal elongation and LS coupling, however, removes this degeneracy, in agreement with the Jahn–Teller theorem.

A final example may demonstrate the interplay of cooperative Jahn–Teller distortions in a model compound. Spinels $Cu^{II}Cr^{III}_{2-x}Fe^{III}_xO_4$ have a normal cation distribution at low x values because the strong octahedral site preference of Cr^{3+} forces Cu^{2+} into the tetrahedral positions. They are tetragonal with $c/a < 1$ induced by the cooperative ordering of flattened CuO_4 tetrahedra. At high x values the cation distribution is inverse, caused by the strong tetrahedral site preference of Fe^{3+}. The resulting lattice distortion is tetragonal with $c/a > 1$ in this case (elongated CuO_6 octahedra). In the intermediate region the flattened CuO_4 tetrahedra and the elongated CuO_6 octahedra compensate their distortion effects and the spinel mixed crystals are cubic.

In nearly all known cases with Cu^{2+} in an environment of C.N. = 4 either flattened tetrahedra (compression along an S_4 axis the dominant distortion component) or (sometimes) square planar coordinations are observed. Both results give evidence for strong first order vibronic coupling effects of the Jahn–Teller type.

Cu^{2+} COORDINATED BY FIVE LIGANDS

Electrostatic calculations[12] for ML_5 compounds give evidence that a trigonal bipyramid (TBP) with larger axial than equatorial M–L bond lengths is energetically slightly preferred with respect to a square pyramid (SP), in which the equatorial M–L bonds are longer than the apical

bond distance. This result is in agreement with most experimental results, if restricted to examples where additional electronic effects are absent. Energetic *d*-electron contributions may change the relative stabilities of the alternative coordination geometries with respect to each other. Though the number of Cu^{2+} complexes in an environment of C.N. = 5 is very large, only a few compounds are known in which isolated Cu^{2+} polyhedra with five identical ligands constitute the lattice. We will discuss first the few cases of this kind, because interconnections or the presence of different and/or polydentate ligands will impose strains on the polyhedra and confuse the issue.

A structure determination of $K[Cu(NH_3)_5](PF_6)_3$[34] and EPR data for this and various compounds $Cu(NH_3)_5X_2$[35] indicate a square pyramidal arrangement of ligands. X-ray evidence places Cu^{2+} above the equatorial plane towards the apical ligand. An important structural feature is the much larger apical [219(2) pm (1×)] compared to the equatorial [203(2) pm (4×)] bond lengths, which is an analogous phenomenon to the tetragonal elongation of octahedral Cu^{2+} complexes as the consequence of a first order Jahn–Teller effect. Similarly, the $CuCl_5^{3-}$ polyhedra in [N(2amet)pipzH_3] $CuCl_5 \cdot 2\ H_2O$ are SP's with short equatorial bonds and a long apical Cu–Cl spacing [231.5 ± 2.5 pm (4×), 257 pm (1×)]. A different situation is met in complexes $[M(NH_3)_6]CUCl_5$ with M = Cr^{III},[36] Co^{III},[37] where axially compressed TBP's are observed at 298 K [230 pm (2×), 239 pm (3×)]. A single crystal EPR experiment with the Co compound reveals a transition into a low-temperature phase in which—as in the complex mentioned before—apically elongated SP's seem to be present.[38] The TBP's observed in the high-temperature modification can be interpreted as the dynamic average of three square pyramidal conformations (Figure 6). This concept is supported by the strongly anomalous temperature ellipsoids of the equatorial ligands in the TPB's,[36,37] which indicate an appreciable angular motion in the high-temperature phase. The vibrational modes, which carry the polyhedron from the SP to the TBP and vice versa, are of the symmetry B_1 (C_{4v}) and E' (D_{3h}), respectively[11]; this process is closely related to the Berry rotation. The A_1' *T* and B_1 ground states in the alternative geometries may be stabilized with respect to each other by second order Jahn–Teller effects because the intermediate C_{2v} symmetry induces configuration interaction between the lowest and the first excited A_1 levels (Figure 3b). The cited experimental results are in accord with a potential surface, in which the SP's represent the geo-

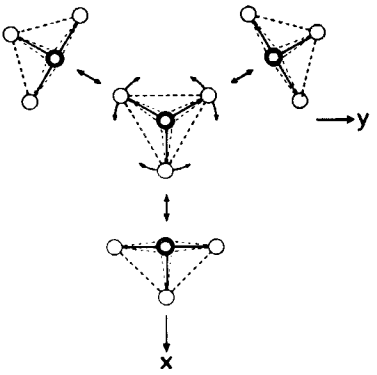

FIGURE 6 The dynamic averaging process between three square-pyramidal conformations proposed for the $CuCl_5^{3-}$ trigonal bipyramids in $Co(NH_3)_6CuCl_5$ at 298 K.

metries of lowest energy. It is of further interest to note that the observed apical elongation and equatorial compression is apparently an important energetic factor in lowering the A_1' and, in particular the B_1 ground state (compare the respective AOM energy in Figure 3b).

Structures with CuO_5 polyhedra are also known. In $KCuPO_4$ half of the Cu^{2+} ions are surrounded by five O^{2-} ligands in a square pyramidal arrangement considerably distorted by host lattice effects, while the other half is tetrahedrally coordinated.[27] In the compounds $CuM^{III}InO_4$ with M^{III} = Al, Ga the pentacoordinated Cu^{2+} ions are forced into sites with a distorted trigonal bipyramidal geometry.[39] The pseudohexagonal compounds contain double layers of TBP's that are interconnected via common edges, and hence constitute a rigid framework which restricts the geometric possibilities for dynamic processes related to the one depicted in Figure 6. Similarly, one can stabilize a TBP by ligand forces. If one substitutes four NH_3 dipoles in $Cu(NH_3)_5^{2+}$ by the tetradentate "tren" ligand with four N-ligator atoms which can adapt more easily to a TBP than to an SP, the C_{4v} symmetry is transformed into an approximate D_{3h} geometry. On the other hand, the [Cu tren NCS]$^+$ polyhedra in Cu tren $(NCS)_2$ possess an intermediate geometry.[40] These examples clearly demonstrate that the alternative A_1' and B_1 ground states of CuL_5 polyhedra (L = N, O, Cl, etc.) do not differ appreciably in

energy (Figure 3b), because host lattice or ligand effects may eventually transform the SP into a TBP. It is interesting to add that the TBP's are always trigonally compressed [CuN_5 polyhedra in (Cu tren NH_3) $(ClO_4)_2$[34]: 203 pm (2×), 208 pm (3×)]. This is again in accord with the AOM energies, which induce a lowering of the A_1' ground state by short equatorial bonds (Figure 3b). There is also agreement with the pseudorotation in Figure 5, in which elongated SP's can only be correlated with compressed TBP's.

We may tentatively state that for CuL_5 polyhedra an elongated square pyramidal geometry is energetically preferred with respect to a compressed TBP, though the energy difference is not great.[38] This is clearly in contrast to the electrostatic predictions, which slightly favor an elongated TBP to a compressed SP. In analogy to coming from elongated octahedral and compressed tetrahedral coordinations the square planar coordination can also be thought of as the extreme of an elongated SP. The complex [Dien H_3]$CuCl_5$ represents an example where $CuCl_4^{2-}$ square planes as well as isolated Cl^- ions are found in the unit cell.[41]

Numerous examples of five-coordinated Cu^{2+} ions are known in which polydentate and/or different ligands constitute the coordination polyhedron. Though all geometries ranging from the compressed TBP to the elongated SP are actually observed, the latter clearly dominate. While the bipyridyl ligand often stabilizes geometries near to the TBP in compounds with $Cu(bipy)_2X$ entities,[42] Cu terpy X_2 complexes with the tridentate terpyridine ligand have symmetries close to the SP.[43] One bond length is distinctly longer than the other in by far the most cases of pentacoordinate Cu^{2+}—even in intermediate geometries and symmetries near the TBP. This again indicates the importance of apical elongation for the stabilization of the ground state. A more detailed discussion of Cu^{2+} in 5-coordination is found elsewhere.[38]

CONCLUSION

It has been demonstrated that the coordination chemistry of Cu^{2+} is strongly influenced by effects which are induced by first or higher order Jahn–Teller couplings between electronic and nuclear motions. Cu^{2+} is never observed in an undistorted octahedron if one excludes dynamically averaged geometries; there are always significant distortions to-

wards tetragonally elongated octahedra. These distortion components are even distinctly evident if ligand or host lattice effects impose a distorted geometry on the Cu^{2+} polyhedra. Frequently complete removal of the two axial ligands leads to a square-planar Cu^{2+} coordination. This behavior is not restricted to Cu^{2+} but is characteristic for all cations with d^9, d^4 and low-spin d^7 configurations.

Cu^{2+} equally distorts a tetrahedral coordination. The degeneracy of the ground state is lifted in most cases by a tetragonal flattening, but also distortions along a threefold axis may eventually be found. Though the extent of distortion is less pronounced in T_d symmetry compared to the octahedron, it is always clearly seen. The square planar geometry may be considered in this context as the extreme of a compression along an S_4 axis.

Cu^{2+} ions in 5-coordination tend to adopt an apically strongly *elongated square pyramidal* coordination, though electrostatic calculations slightly favor an *elongated trigonal bipyramid* with respect to a *compressed square pyramid*. However, rigid ligands and host lattice effects may frequently stabilize *compressed trigonal bipyramids* or intermediate geometries on the pathway between the two alternative geometries. In any case, the influence of electronic effects is evident.

We have restricted the discussion to the coordination numbers 4, 5 and 6 so far, which nearly exclusively occur. To mention just one interesting example outside this range which again emphasizes the importance of electronic stabilization effects in Cu^{2+} stereochemistry, the structure of $Ca_{1/4}Cu_{3/4}TiO_3$ and related compounds can be understood on the basis of the perovskite lattice. Cu^{2+} occupies the 12-coordinated cuboctahedral site, which undergoes a strong Jahn–Teller distortion accompanied by a correspondingly large splitting of the σ- and Π-antibonding $^2T_{2g}$ ground state.[10] The resulting geometry is a square planar coordination with eight additional oxygen ligands very distantly spaced.[44]

The observed deviations of the Cu^{2+} coordinations with C.N. = 6, 5 and 4 from those geometries, which are predicted by electrostatic arguments, are predominantly caused by electronic effects. The remarkable general feature of the resulting polyhedra is either a square planar arrangement supplemented by one or two axial ligands in much larger distance (C.N. = 5, 6) or a coordination which deviates more or less strongly from a square plane towards a flattened tetrahedron

(C.N. = 4). The described features are particularly obvious if ligand and host lattice rigidities are of minor importance.

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