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Insight into Compounds with $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ Units: New Ideas for Understanding Cu^{2+} in Tutton Salts

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ABSTRACT: In the last 65 years the properties of Tutton salts containing Cu^{2+} cations have been interpreted on the basis of elongated complexes induced by a static Jahn–Teller effect (JTE). Through the analysis of experimental data and the results of first-principles calculations, we show here that such an idea, though widely followed, is not correct. By contrast, this work proves that the local geometry of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ units in Tutton salts actually arises from a compressed octahedron although hidden by an additional orthorhombic instability fully unrelated to the JTE. For understanding this conclusion, it is crucial to consider the effects of the internal electric field, $E_R(r)$, created by the rest of the lattice ions on the electrons localized in the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ unit. Indeed, the $E_R(r)$ field in Tutton salts opens a gap between $\sim x^2-y^2$ and $\sim 3z^2-r^2$ antibonding molecular orbitals that favors a hole in $\sim 3z^2-r^2$ and triggers an orthorhombic distortion in the XY plane that reasonably explains available experimental data. The conditions responsible for the orthorhombic instability are discussed pointing out the singularity of Cu^{2+} complexes in the realm of 3d divalent cations. For the sake of completeness the properties of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ units in trigonal lattices, where a JTE is clearly observed, are analyzed in detail and compared to results of Cu^{2+} cations in cubic lattices. In the trigonal compounds, the force constant of the Jahn–Teller mode is shown to be smaller than that for hard ligands like O^{2-} or F^- but comparable to the softer ligand Cl^- . This fact helps to promote the orthorhombic instability in the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex when the hole is no longer in the $\sim x^2-y^2$ orbital but in $\sim 3z^2-r^2$.

1. INTRODUCTION

First-row divalent transition metal cations, M, can form 6-fold coordinated $\text{M}(\text{H}_2\text{O})_6^{2+}$ complexes, either in solution or in crystalline compounds, many of which belong to the wide family of Tutton salts well described already at the end of the nineteenth century.^{1,2} The Tutton salts with the formula $\text{M}'_2\text{M}(\text{H}_2\text{O})_6(\text{SO}_4)_2$ or $\text{M}'_2\text{M}(\text{H}_2\text{O})_6(\text{SeO}_4)_2$ contain two different cations M'^+ and M^{2+} and crystallize in the monoclinic space group $P2_1/a$ (Figure 1). The monovalent cation can be K^+ , Rb^+ , Cs^+ , Ti^+ , or NH_4^+ , while M^{2+} can be either a transition metal cation or the closed-shell species Mg^{2+} , Zn^{2+} , and Cd^{2+} , thus implying that the number of compounds belonging to the Tutton salt family is certainly huge.^{1–7} Some of the sulfate Tutton salts appear as minerals, products of fumaroles and geysers, such as the cyanochroite,⁴ $\text{K}_2\text{Cu}(\text{H}_2\text{O})_6(\text{SO}_4)_2$, while other compounds of the family are currently used as UV filters.⁸

Along the series of $\text{M}(\text{H}_2\text{O})_6^{2+}$ complexes (M = transition metal cation) the highest stability is reached⁹ for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. Moreover, that complex, involving the 3d⁹ cation Cu^{2+} , has widely been explored since the advent of the electron paramagnetic resonance (EPR) technique as it is necessarily paramagnetic ($S = 1/2$) according to the Kramers theorem.¹⁰ In particular, since 1950 the properties of Cu^{2+} -doped Tutton

salts $\text{M}'_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2$ ($\text{M}' = \text{K}^+$, Rb^+ , Cs^+ , and NH_4^+) have been deeply investigated by means of the EPR and electron spin–echo envelope modulation (ESEEM) technique in the 4–300 K temperature range.^{3,11–22} For this reason, the Tutton salts doped with Cu^{2+} are currently taken as model systems as their properties are assumed to be well understood.²² Furthermore, at the present time there is a growing interest in copper-doped Tutton salts because of their potential application to the study of a number of copper-containing enzymes whose substrates are proposed to displace water in the active site.^{22,23}

The $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex has also been studied^{24–27} in $\text{Zn}(\text{H}_2\text{O})_6\text{SiF}_6$, a lattice with higher symmetry than a Tutton salt.²⁸ It should be remarked that the trigonal lattice $\text{Zn}(\text{H}_2\text{O})_6\text{SiF}_6$ doped with Cu^{2+} was the first system providing indisputable evidence^{29,12,14,26} on the occurrence of the so-called static Jahn–Teller effect (JTE)^{30–32} at low temperatures, where the geometry of the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex is clearly elongated. For this reason, it has been accepted in the scientific literature of the last 65 years that the local geometry

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Figure 1. Monoclinic structure ($P2_1/a$ space group) of the $K_2Cu(SO_4)_2(H_2O)_6$ Tutton salt where the crystal c axis forms an angle of 75° with the a – b plane. Cu^{2+} ions are placed in layers perpendicular to the a – b plane. $\{X, Y, Z\}$ denote the local axes of a $Cu(H_2O)_6^{2+}$ complex, where the Z direction forms an angle of $\sim 25^\circ$ with the L direction perpendicular to the a – b plane. O_7 , O_8 , and O_9 are the three inequivalent oxygens belonging to H_2O ligands, where O_9 corresponds to a ligand placed along the local Z axis, while the Cu – O_8 bond, along the Y direction, involves the largest metal–ligand distance.

of $Cu(H_2O)_6^{2+}$ in pure and doped Tutton salts essentially corresponds to an elongated octahedron as a result of a static JTE.^{3,11–22,33–38} In this domain, particular attention has been paid to the strong pressure sensitivity of $(ND_4)_2Cu(D_2O)_6(SO_4)_2$ where a pressure of only 0.15 GPa changes the nature of the largest Cu – O axis, a phenomenon that has also been interpreted on the basis of a JTE.^{33,34,36–38} An explanation also founded in the JTE has been proposed for the pressure switching in the currently studied $CuF_2(H_2O)_2(py_z)$ (py_z = pyrazine) compound.^{39,40}

The present work is devoted to gain a better insight into pure and doped compounds involving the $Cu(H_2O)_6^{2+}$ unit. In a first step, we discuss the conditions for observing a static JTE in $Cu(H_2O)_6^{2+}$, a complex whose symmetry can never be octahedral, and provide values for the force and anharmonic constants of the Jahn–Teller mode^{30–32} which determine the nature of the electronic ground state in $Zn(H_2O)_6SiF_6:Cu^{2+}$. In a second step, this work is aimed at demonstrating that the local geometry and ground state of $Cu(H_2O)_6^{2+}$ in the low symmetry Tutton salts are not the result of a JTE as they are determined by mechanisms similar to those recently discussed for *anisotropic* systems^{41,42} like $(CH_3NH_3)_2CdCl_4:Cu^{2+}$, Rb_2CuCl_4 , or K_2CuF_4 .

For achieving these goals we employ the results of first-principles calculations together with an analysis of available experimental data involving $Cu(H_2O)_6^{2+}$ units both in trigonal and Tutton salts.

For clearing up all these issues, the present work is organized as follows. Section 2 provides information on the employed computational tools. For the sake of clarity, the discussion starts with an analysis of the true JTE occurring in the trigonal lattices with Cu^{2+} (section 3) and also in isolated $Cu(H_2O)_6^{2+}$ complexes (section 4). By the contrary, sections 5–9 are devoted to prove, step by step, that, in Tutton salts containing Cu^{2+} , the distortion of the $Cu(H_2O)_6^{2+}$ complexes is not due to a JTE. For achieving this goal the analysis of experimental data and the criticism of the usual JTE interpretation are

reported in sections 5 and 6. The reinterpretation of experimental data together with an analysis of temperature and pressure effects are given in sections 7 and 8, while the origin of the orthorhombic instability is discussed in section 9. Some final remarks are provided in the last section.

2. COMPUTATIONAL METHODS

Periodic geometry optimizations on $K_2M(H_2O)_6(SO_4)_2$ and $M(H_2O)_6SiF_6$ ($M = Cu, Zn$) compounds were performed under the framework of the spin-unrestricted Kohn–Sham formulation of the density functional theory (DFT). First, the calculations were carried out by means of the CRYSTAL17 code,⁴³ where the Bloch wave functions are represented by a linear combination of Gaussian basis functions centered at the atomic positions. All ions were described by means of basis sets taken directly from CRYSTAL’s webpage.⁴³ In particular, we have used the all-electron triple- ζ plus polarization (TZP) basis recently developed for Peitinger et al.⁴⁴ We have also used the B1WC hybrid exchange–correlation functional (including 16% of Hartree–Fock exchange) that has shown to be able to reproduce with great accuracy the geometry and properties of a large number of both pure and doped crystals. Similar results have been found using other basis sets and the PW1PW hybrid functional (including 20% of Hartree–Fock exchange).⁴⁵ All optimized geometries agree with the experimental values within 3% error.

Due to the problems inherent to describe a system with relevant long-range interactions by means of localized basis sets generated for a general purpose, the geometry optimizations under external pressure have been performed with the VASP code^{46–49} that uses a combination of localized orbitals and plane-wave expansions⁵⁰ as basis sets. We used the PBEsol functional which has been shown to yield accurate lattice constants for solids.⁵¹ A 910 eV cutoff energy for plane waves has been used corresponding to hard pseudopotentials for oxygen and hydrogen, and a Monkhorst–Pack of $4 \times 3 \times 6$ was chosen as the k -point mesh and Gaussian smearing of 0.1 eV. Geometries were relaxed until forces were lower than 0.03 Å/eV. At zero pressure, the optimized geometries are slightly better than that obtained through the CRYSTAL code, with a greater improvement when pressure is increased.

Calculations on Cu^{2+} -doped $K_2Zn(H_2O)_6(SO_4)_2$, where Cu^{2+} impurity enters replacing a Zn^{2+} ion of the lattice, were performed with both CRYSTAL17 and VASP codes, using a periodic $1 \times 1 \times 2$ conventional cell containing 124 atoms with the lattice parameters fixed at the experimental values and using a $4 \times 3 \times 3$ k -point mesh. The results were very similar to both codes.

For each crystal structure considered in this work, we have calculated the electrostatic potential $V_R(\mathbf{r}) = \sum_j q_j/|\mathbf{R}_j - \mathbf{r}|$ felt by the electrons localized in the $M(H_2O)_6^{2+}$ ($M = Cu^{2+}, Zn^{2+}$) complex due to all lattice ions lying outside, with charges q_j and positions $\mathbf{R}_j$ taken from our first-principles optimizations. Although often ignored, the $V_R(\mathbf{r})$ potential is actually responsible for the ground state of $K_2ZnF_4:Cu^{2+}$ ⁵² or the different color displayed by ruby, emerald, or alexandrite gemstones.⁵³ Calculation of $V_R(\mathbf{r})$ potentials has been performed following the procedure developed by van Gool and Piken⁵⁴ based on a modified version of the Ewald’s method⁵⁵ in order to accelerate the convergence. It is worth noting however that the shape and anisotropy displayed by $V_R(\mathbf{r})$ are greatly due to few ions lying closer to the complex⁵²

Table 1. M–O Distances (in Å) Measured by X-Ray Diffraction (XRD) for Trigonal $M(H_2O)_6SiF_6$ Pure Compounds ($M = Zn, Cu$) Compared to the Results of Present Calculations^a

compound	method	$R_3 \equiv R_{ax}$	$R_2 \equiv R_{eq}$	$R_1 \equiv R_{eq}$	$\langle R \rangle$	ref
$Zn(H_2O)_6SiF_6$	XRD	2.078	2.078	2.078	2.078	28
$Zn(H_2O)_6SiF_6$	calculations	2.072	2.072	2.072	2.072	this work
$Cu(H_2O)_6SiF_6$	XRD	2.367	1.970	1.970	2.102	58
$Cu(H_2O)_6SiF_6$	calculations	2.442	1.960	1.960	2.12	this work
$Zn(H_2O)_6SiF_6:Cu^{2+}$	calculations	2.370	1.973	1.973	2.10	this work

^aThe calculated distances for Cu^{2+} -doped $Zn(H_2O)_6SiF_6$ are also included.

Table 2. Experimental g -Tensor for $Cu(H_2O)_6^{2+}$ Complexes Embedded in the Trigonal Lattice $Zn(H_2O)_6SiF_6$ ^a

system	T (K)	$g_{ }$	$g_{\perp}$	ref
$Zn(H_2O)_6SiF_6:Cu^{2+}$	4.2	2.460 ± 0.005	2.100 ± 0.005	26
$Mg_3La_2(NO_3)_{12} \cdot 24D_2O:Cu^{2+}$	20	2.465 ± 0.001	2.099 ± 0.001	61
$Mg_3Bi_2(NO_3)_{12} \cdot 24H_2O:Cu^{2+}$	20	2.454 ± 0.003	2.096 ± 0.003	25
$Zn(H_2O)_6TiF_6:Cu^{2+}$	4.2	2.472 ± 0.004	2.097 ± 0.004	62
$Mg(H_2O)_6SiF_6:Cu^{2+}$	4.2	2.47 ± 0.01	2.10 ± 0.01	63

^aAlthough the three Zn–O distances are equal, the experimental g -tensor for $Cu(H_2O)_6^{2+}$ in that host lattice displays a tetragonal symmetry consistent with the formation of an elongated octahedron as a result of a static JTE. Nearly identical $g_{||}$ and $g_{\perp}$ values are measured for $Cu(H_2O)_6^{2+}$ in the trigonal lattices $Mg_3N_2(NO_3)_{12} \cdot 24H_2O$ ($N = Bi, La$) as well as in two other host lattices where there are small departures from trigonal symmetry.

whose contribution to the $V_R(r)$ potential can be calculated by hand.

Additional calculations have been carried out on $Cu(H_2O)_6^{2+}$ complexes in vacuo and also considering the electrostatic potential $V_R(r)$ due to the rest of the ions of a $K_2Zn(H_2O)_6(SO_4)_2$ lattice. These calculations have been carried out with the Amsterdam density functional (ADF) code⁵⁶ that allows performing DFT calculations on each specific electronic configuration. For this goal, we have used the popular B3LYP hybrid functional⁵⁷ in the spin-unrestricted Kohn–Sham formalism of the DFT and high-quality all-electron basis sets of triple- ζ plus polarization (TZP) type formed of localized Slater-type functions as implemented in the 2017.105 version of the ADF code.⁵⁶

3. ANALYSIS OF EXPERIMENTAL DATA AND THEORETICAL RESULTS OF TRIGONAL COMPOUNDS

With regard to the $Cu(H_2O)_6^{2+}$ complex in trigonal lattices, particular attention has been paid to Cu^{2+} -doped $Zn(H_2O)_6SiF_6$ ²⁸ and also to the pure compound $Cu(H_2O)_6SiF_6$.⁵⁸ The $Zn(H_2O)_6SiF_6$ compound belongs to the trigonal $R\bar{3}$ space group and can simply be viewed as a distorted CsCl-type structure, the Cs^+ and Cl^- ions being replaced by $Zn(H_2O)_6^{2+}$ and SiF_6^{2-} octahedra, respectively. Accordingly, two neighbor $Zn(H_2O)_6^{2+}$ units do not share common ligands. If we designate by R_i ($i = 1-3$) the equilibrium M–O distances ($R_3 > R_2 > R_1$) of centrosymmetric $M(H_2O)_6^{2+}$ complexes, in the case of $Zn(H_2O)_6SiF_6$ (Table 1) the three Zn–O distances are equal to 2.078 Å although there is a trigonal perturbation on the $Zn(H_2O)_6^{2+}$ unit due to the next nearest neighbors.^{25,26} As the three main axes of a perfect octahedron remain equivalent under a trigonal perturbation, this also implies that the degeneracy in the e_g level of a complex is not removed when the symmetry becomes trigonal. Accordingly, when Zn^{2+} is replaced by the open-shell cation Cu^{2+} the hole is initially lying in a e_g level, and thus a static JTE can take place. This situation is corroborated by X-ray diffraction data on $Cu(H_2O)_6SiF_6$ ⁵⁸ proving that the

equilibrium geometry of $Cu(H_2O)_6^{2+}$ complexes corresponds to an *elongated* octahedron with $R_3 \equiv R_{ax} = 2.367$ Å and $R_2 = R_1 \equiv R_{eq} = 1.970$ Å (Table 1). Present calculations on $Cu(H_2O)_6SiF_6$ reproduce reasonably the experimental metal–ligand distances but with an overestimation of 3% in the longest axial distance (Table 1). Extended X-ray absorption fine structure (EXAFS) results²⁷ on $Cu(H_2O)_6SiF_6$ give $R_{eq} = 1.954(2)$ Å and $R_{ax} = 2.27(3)$ Å, which are also consistent with the formation of an elongated octahedron, although the reported R_{ax} value is at least 0.07 Å smaller than the figure obtained through X-ray diffraction.⁵⁸

For the sake of completeness we have also calculated the equilibrium geometry of $Cu(H_2O)_6^{2+}$ in $Zn(H_2O)_6SiF_6:Cu^{2+}$, and the obtained values of $R_{ax} = 2.370$ Å and $R_{eq} = 1.973$ Å (Table 1) are practically coincident with those for the pure crystal $Cu(H_2O)_6SiF_6$.

It should be noticed that the EPR results of $Zn(H_2O)_6SiF_6:Cu^{2+}$ at $T = 4.2$ K clearly reveal the simultaneous existence of *three* spectra of axial symmetry, each one corresponding to an octahedron distorted along one of the three 4-fold axes.^{25,26} This key feature is thus a strong experimental support to the existence of a static JTE.^{30–32,59,60} Moreover, the experimental $g_{||}$ and $g_{\perp}$ values for Cu^{2+} -doped $Zn(H_2O)_6SiF_6$ and other trigonal compounds^{25,26,61–63} at low temperature (Table 2) undoubtedly prove that the octahedron is actually elongated as a result of a static JTE, and thus the hole is located in the $b_{1g}(\sim x^2 - y^2)$ antibonding orbital for centers with a Z main axis. Indeed, in this situation and under a weak or moderate covalency the g -tensor can be approximated by^{14,64}

$$g_{||} - g_0 \approx 8u \quad g_{\perp} - g_0 \approx 2u \quad (1)$$

where $u \equiv \xi^*/\Delta$; ξ^* is the spin–orbit coefficient of the central cation reduced by covalency; and Δ is the average of $\sim xy \rightarrow \sim x^2 - y^2$ and $\sim xz, \sim yz \rightarrow \sim x^2 - y^2$ excitations where $\sim xy$ and $\sim x^2 - y^2$ simply denote antibonding molecular orbitals transforming like $d(xy)$ and $d(x^2 - y^2)$, respectively. The experimental $g_{||} = 2.460$ and $g_{\perp} = 2.100$ values for $Zn(H_2O)_6SiF_6:Cu^{2+}$ (Table 2) are reasonably consistent with

eq 1 and $u \cong 0.054$. The reliability of eq 1 for analyzing $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ is underpinned by the present calculations leading to $\sim 70\%$ of $x^2 - y^2$ character in the antibonding $b_{1g}(\sim x^2 - y^2)$ orbital that underlines the existence of a moderate covalency.

When temperature is raised, the static EPR spectrum of $\text{Zn}(\text{H}_2\text{O})_6\text{SiF}_6\text{:Cu}^{2+}$ at $T = 4.2$ K progressively disappears and is replaced by a practically isotropic spectrum^{25,26} whose g factor is given by the average

$$g = (g_{\parallel} + 2g_{\perp})/3 = 2.22 \quad (2)$$

This fact proves the existence of incoherent hopping among the three minima, characteristic of a static JTE, that should be rigorously equivalent in the absence of the unavoidable random strains.^{30–32} At $T = 100$ K only the average spectrum with $g = 2.22$ is observed.^{25,26}

It is worth noting now that the g -tensor of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ units embedded in other trigonal lattices like $\text{Mg}_3\text{La}_2(\text{NO}_3)_{12} \cdot 24\text{D}_2\text{O}$ or $\text{Mg}_3\text{Bi}_2(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ is essentially identical to that for $\text{Zn}(\text{H}_2\text{O})_6\text{SiF}_6\text{:Cu}^{2+}$ when measured at low temperatures (Table 2). Even in host lattices like $\text{Zn}(\text{H}_2\text{O})_6\text{TiF}_6$ where there are small departures from trigonal symmetry,⁶² the experimental $g_{\parallel}$ and $g_{\perp}$ values for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ units are practically identical to those reported for $\text{Zn}(\text{H}_2\text{O})_6\text{SiF}_6\text{:Cu}^{2+}$. This fact thus suggests that the properties of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complexes embedded in trigonal lattices can be understood to a good extent just considering the positively charged complex in vacuo.

4. STUDY OF THE $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ COMPLEX IN VACUO

It is well-known that MX_6 complexes (M = transition metal d^9 ion, $X = \text{F}^-, \text{Cl}^-, \text{O}^{2-}$) in cubic lattices exhibit a JTE.⁵⁹ Indeed when the three metal–ligand distances are equal (O_h symmetry) the electronic e_g level of the complex is perfectly degenerate, a necessary condition for having a JTE.^{30–32} Although an O_h symmetry cannot be reached for an isolated $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex, the symmetry becomes T_h when water molecules are arranged in the shape depicted in Figure 2a.

Figure 2. Isolated $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex with (a) T_h symmetry and (b) D_{2h} symmetry.

That geometry, obtained in the present calculations, is used in the interpretation of infrared spectra of aquo complexes as well.⁶⁵ In that configuration (Figure 2a), if the line joining the two H^+ protons in ligands 1 and 3 is parallel to the Y axis and that of ligands 2 and 4 is parallel to the Z axis, then the H^+ line in ligands 5 and 6 must be parallel to the X axis. In that case, there are three C_3 symmetry axes showing that antibonding $\sim x^2 - y^2$ and $\sim 3z^2 - r^2$ levels are still degenerate when the three $\text{Cu}^{\text{--}}\text{O}$ distances are equal and thus a JTE can

take place. By contrast, for an assumed D_{2h} arrangement of water molecules (Figure 2b), even if the three $\text{Cu}^{\text{--}}\text{O}$ distances are equal to R , the $\sim 3z^2 - r^2$ level is found to lie above $\sim x^2 - y^2$. This fact can simply be understood considering, in that situation, the electrostatic potential, V_p , due to H^+ protons around the central cation as it destroys the cubic symmetry. Indeed, considering the quadrupolar contribution, it can easily be seen that under the D_{2h} configuration depicted in Figure 2b $V_p(0,a,0) > V_p(0,0,a)$ ($a < R$), thus favoring a higher energy for a $\sim 3z^2 - r^2$ electron than for an $\sim x^2 - y^2$ one. By contrast, $V_p(0,a,0) = V_p(0,0,a)$ for the T_h configuration of Figure 2a.

Keeping the T_h configuration of Figure 2a for water molecules, we have explored the equilibrium geometry for placing the hole either in the $\sim x^2 - y^2$ or in the $\sim 3z^2 - r^2$ antibonding level, calculating the energy as a function of the distortion coordinate $Q_\theta = (2/\sqrt{3})(R_{\text{ax}} - R_{\text{eq}})$ transforming like $d(3z^2 - r^2)$. The values of the equilibrium coordinate for both states, together with the associated energy difference, B , computed at the corresponding equilibrium geometry, are collected in Table 3. Such results lead to an elongated

Table 3. Calculated Equilibrium Geometry for the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ Complex in Vacuo for the Ground State (Hole in the $\sim x^2 - y^2$ Orbital and Elongated Geometry) and the Excited State (Hole in the $\sim 3z^2 - r^2$ Orbital and Compressed Geometry), Separated by an Energy Barrier $B = 0.049$ eV^a

electronic state	hole	R_{ax} (Å)	R_{eq} (Å)	$\langle R \rangle$ (Å)	Q_θ (Å)
ground state	$\sim x^2 - y^2$	2.313	2.016	2.115	0.343
excited state	$\sim 3z^2 - r^2$	1.964	2.187	2.113	−0.261

^a R_{ax} and R_{eq} are the axial and equatorial $\text{Cu}^{\text{--}}\text{O}$ distances. $\langle R \rangle$ means the average distance and the equilibrium normal coordinate $Q_\theta = (2/\sqrt{3})(R_{\text{ax}} - R_{\text{eq}})$.

equilibrium geometry and thus a hole lying in the planar $\sim x^2 - y^2$ orbital. Both facts are in agreement with experimental X-ray and EPR data of trigonal lattices (Tables 1 and 2) containing $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ units. Moreover, the calculated R_{ax} and R_{eq} values for the isolated $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex (Table 3) are only 2% smaller than those measured for $\text{CuSiF}_6(\text{H}_2\text{O})_6$ (Table 1).

Interestingly, the calculated value of the energy barrier between two equivalent configurations of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ is equal only to $B = 0.049$ eV (Tables 3 and 4) and explains albeit qualitatively why the EPR spectrum of $\text{Zn}(\text{H}_2\text{O})_6\text{SiF}_6\text{:Cu}^{2+}$ is isotropic at $T = 100$ K.^{24–26} Indeed for the JTE systems NaCl:Ag^{2+} and NaCl:Cu^{2+} , the calculated barrier is $B = 0.065$ eV,⁶⁶ and at $T = 100$ K, the EPR spectrum is already isotropic.^{67,68}

Table 4. Values of the Jahn–Teller Parameters V_{1e} , K , and V_{3a} Derived from the Present Calculations for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ in Vacuo Compared to the First Estimations by Öpik and Pryce^{69a}

Q_θ (Å)	V_{1e} (eV/Å)	K (eV/Å ²)	E_{JT} (eV)	V_{3a} (eV/Å ³)	B (eV)	ref
0.34	1.17	3.9	0.20	0.7	0.049	this work
0.30	2.5	8.2	0.37	3	0.16	69

^aThe values of the Jahn–Teller energy, E_{JT} , the energy barrier, B , and the equilibrium coordinate, Q_θ , are also given.

In the pioneering work by Öpik and Pryce,⁶⁹ it was already pointed out that isolated octahedral JTE complexes should display an elongated equilibrium geometry due to the anharmonicity inevitably present in any molecular vibration. The same situation has proven to happen when the complex is elastically decoupled to a good extent from the rest of the lattice.^{31,32} That circumstance arises, for instance, in NaCl:M²⁺ (M = Cu, Rh, Ag), where the monovalent host cation Na⁺ is replaced by a divalent one, but not for NaCl:Ni²⁺.⁷⁰

Considering the anharmonicity as the dominant cause^{71,32,66} for having an energy barrier $B \neq 0$ in an E⊗E JTE, the energy of the two electronic states as a function of the $Q_\theta \sim x^2 - y^2$ and $Q_\epsilon \sim 3z^2 - r^2$ coordinates can be described by

$$E = \pm V_{1e}Q + (1/2)KQ^2 - V_{3a}(Q_\theta^3 - 3Q_\epsilon^2Q_\theta) + \dots \quad (3)$$

Here, $Q \equiv \sqrt{(Q_\theta^2 + Q_\epsilon^2)}$; V_{1e} is the linear electron-vibration coupling constant; K is the force constant of the Jahn–Teller mode; while the last term depicts the anharmonic energy, where $V_{3a} > 0$ for isolated complexes. The positive (negative) sign in eq 3 corresponds to the hole in $\sim 3z^2 - r^2$ ($\sim x^2 - y^2$).

The values of such parameters together with the Jahn–Teller energy, $E_{JT} = -E(Q_\theta^0)$, for the ground state, derived from the present calculations for Cu(H₂O)₆²⁺, are collected in Table 4. For the sake of clarity, the values of Q_θ , V_{1e} , K , and E_{JT} obtained for some relevant JTE systems are also displayed in Table 5. It can first be noticed that the value $V_{1e} = 1.17$ eV/Å

Table 5. Calculated Values of the Equilibrium Normal Coordinate, Q_θ^0 , the Linear Jahn–Teller Coupling Constant, V_{1e} , the Force Constant, K , and the Jahn–Teller Energy, E_{JT} , for Relevant JTE Systems Involving Either Cu²⁺ or Ag²⁺

system	Q_θ (Å)	V_{1e} (eV/Å)	K (eV/Å ²)	E_{JT} (eV)	ref
MgO:Cu ²⁺	−0.0875	1.26	14.4	0.055	72, 31
CaO:Cu ²⁺	−0.129	1.09	8.45	0.07	72, 31
KZnF ₃ :Cu ²⁺	0.156	1.17	7.5	0.091	60
NaCl:Cu ²⁺	0.346	1.14	3.3	0.197	this work
NaCl:Ag ²⁺	0.326	1.24	3.8	0.201	66
KCl:Ag ²⁺	0.52	1.13	2.2	0.293	66

derived for Cu(H₂O)₆²⁺ (Table 4) is comparable to the figures reported in Table 5 for different JTE systems,^{72,60,66,31} all lying in the 1.1–1.3 eV/Å range.

The present calculated value of the force constant for Cu(H₂O)₆²⁺, $K = 3.9$ eV/Å², is about half that previously estimated by Öpik and Pryce⁶⁹ but consistent with a metal–ligand force constant around 4.5 eV/Å² derived for M(H₂O)₆²⁺ complexes (M = Ni, Mn, Fe, Zn) from infrared and Raman data.⁶⁵ It should be remarked that $\langle R \rangle = 2.12$ Å obtained for Cu(H₂O)₆²⁺ (Table 3) is nearly identical to $\langle R \rangle = 2.14$ Å

derived for the CuO₆^{10−} complex embedded in MgO:Cu²⁺.^{72,31} However, the K value in the former case is about four times smaller than that for the latter but comparable to the K values derived for CuCl₆^{4−} and AgCl₆^{4−} units in NaCl (Table 5). Along this line, it was already pointed out that metal aquo-complexes give rise to weaker force constants than for the corresponding cyanide-, nitro-, or amine-complexes.⁶⁵

With regard to the energy barrier, B , the estimated value by Öpik and Pryce⁶⁹ for Cu(H₂O)₆²⁺ is nearly four times higher than that given in the present calculations. As in KCl:Ag²⁺ the calculated value for the barrier⁶⁶ is $B = 0.13$ eV, and the EPR spectrum becomes isotropic⁶⁸ only at $T = 160$ K these facts support that the first reported value⁶⁹ for Cu(H₂O)₆²⁺, $B = 0.16$ eV, is an overestimation.

Before ending this section, it is worth noting that the equilibrium geometry derived for the Cu(H₂O)₆²⁺ complex in vacuo (Table 3) is also close to that measured by EXAFS^{27,73} for that complex in solution where R_{ax} is found to be ~ 1.96 Å, while R_{eq} lies in the 2.27–2.40 Å range.

5. DISCUSSION OF STRUCTURAL AND EPR RESULTS OF TUTTON SALTS CONTAINING CU²⁺

Among the pure Tutton salts containing Cu²⁺, let us take as a guide the K₂Cu(H₂O)₆(SO₄)₂ compound⁴ whose structure is portrayed in Figure 1. In that compound, Cu²⁺ ions form layers in (*a*, *b*) planes in such a way that the distance between two close layers is $c = 9.09$ Å, and the distance between two neighbor Cu²⁺ ions in a given layer is equal to 6.80 Å. Experimental and calculated lattice parameters and copper–oxygen distances for K₂M(H₂O)₆(SO₄)₂ (M = Cu, Zn) compounds are given in Table 6. The present calculated values reproduce reasonably well such distances, although the largest distance in K₂Cu(H₂O)₆(SO₄)₂ is overestimated by 3%.

As shown in Figure 1 and Table 6 there are three different kind of ligands for Cu(H₂O)₆²⁺ in the Tutton salt K₂Cu(H₂O)₆(SO₄)₂. The three inequivalent oxygens belonging to H₂O ligands are usually denoted in the literature^{3,15,17,19,33–35} as O₇, O₈, and O₉, and their main structural data for K₂M(H₂O)₆(SO₄)₂ (M = Cu, Zn) crystals^{3,4} are reported in Table 7. For both compounds, the shortest metal–ligand distance corresponds to M²⁺–O₉, the Z direction which forms an angle of $\sim 25^\circ$ with the *L* direction perpendicular to the *a*–*b* plane (Figure 1). The largest distance is that of the M²⁺–O₈ bond (*Y* direction) lying in the *XY* plane, perpendicular to the *Z* axis. Interestingly, while the distance between O₇ and O₈ and the nearest K⁺ ion is in the range 2.87–3.10 Å, that between O₉ and the closest K⁺ is clearly higher lying in the 3.8–4.2 Å range for both compounds. It is worth noting that while the intermediate M²⁺–O₇ distance (*X* direction) differs from M²⁺–O₈ only by ~ 0.01 Å for M = Zn and also for M = Ni and Mg,⁴ the difference between them amounts to 0.21 Å for the copper compound.

Table 6. Experimental (First Row) and Calculated (Second Row, In Italics) Lattice Parameters and Cu–O Distances at Equilibrium for K₂M(H₂O)₆(SO₄)₂ (M = Cu, Zn)^a

compound	<i>a</i>	<i>b</i>	<i>c</i>	β	$R_T(\text{Cu}^{2+}\text{--O}_8)$	$R_X(\text{Cu}^{2+}\text{--O}_7)$	$R_Z(\text{Cu}^{2+}\text{--O}_9)$
K ₂ Cu(H ₂ O) ₆ (SO ₄) ₂	6.167	12.130	9.085	75.55	2.279	2.068	1.944
	6.183	12.117	9.145	76.40	2.356	2.021	1.938
K ₂ Zn(H ₂ O) ₆ (SO ₄) ₂	6.147	12.204	9.028	75.20	2.134	2.124	2.031
	6.186	12.108	8.947	76.15	2.149	2.121	2.016

^aThe *Z* local axis forms an angle of $\sim 25^\circ$ with the line *L* perpendicular to the (*a*, *b*) plane of the lattice. All distances are in Å and angles in degrees.

Table 7. Experimental M–O_i and O_i–K (M = Cu, Zn; *i* = 7–9) Interatomic Distances (in Å) of K₂M(H₂O)₆(SO₄)₂ Tutton Salts^a

compound	M ²⁺ –O ₈	O ₈ –K ⁺	M ²⁺ –O ₇	O ₇ –K ⁺	M ²⁺ –O ₉	O ₉ –K ⁺
K ₂ Cu(H ₂ O) ₆ (SO ₄) ₂	2.279	2.872	2.068	3.096	1.944	3.78
K ₂ Zn(H ₂ O) ₆ (SO ₄) ₂	2.134	2.95	2.124	3.09	2.031	4.20

^aThe distances of O₇, O₈, and O₉ oxygens, belonging to H₂O ligands, to both the M²⁺ cation and nearest K⁺ ion describe the three kinds of ligand positions.

The variations of experimental copper–oxygen distances along the series of pure compounds M₂Cu(H₂O)₆(SO₄)₂ (M = K, Rb, Cs)^{3,4,6} are collected in Table 8. It can be noticed that the Cu²⁺–O₉ distance (*R_Z*) is constant within 1% along the series, but *R_Y* – *R_X* increases by 0.10 Å on passing from K₂Cu(H₂O)₆(SO₄)₂ to Cs₂Cu(H₂O)₆(SO₄)₂.

Table 8. Experimental Cu²⁺–O_i Distances (*i* = 7–9) for M₂Cu(H₂O)₆(SO₄)₂ (M = K, Rb, Cs) Tutton Salts^a

compound	<i>R_Y</i> (Cu–O ₈)	<i>R_X</i> (Cu–O ₇)	<i>R_Z</i> (Cu–O ₉)
K ₂ Cu(H ₂ O) ₆ (SO ₄) ₂	2.279	2.068	1.944
Rb ₂ Cu(H ₂ O) ₆ (SO ₄) ₂	2.307	2.031	1.957
Cs ₂ Cu(H ₂ O) ₆ (SO ₄) ₂	2.315	2.004	1.966

^aNote that, while the *R_Z*(Cu²⁺–O₉) distance is constant within 1%, *R_Y*(Cu–O₈) – *R_X*(Cu–O₇) increases by 48% on passing from M = K to M = Cs.

As in the scientific literature there are no data on metal–ligand distances for Cu²⁺-doped Tutton salts, we have calculated them for K₂Zn(H₂O)₆(SO₄)₂:Cu²⁺. The obtained values, *R_Y* = 2.333 Å, *R_X* = 2.025 Å, and *R_Z* = 1.936 Å, are very close to those calculated for the pure compound K₂Cu(H₂O)₆(SO₄)₂ (Table 6).

Concerning Tutton salts doped with Cu²⁺, the experimental *g*-tensors measured in the Q-band³ (*ν* = 37 GHz) for M'₂Zn(H₂O)₆(SO₄)₂:Cu²⁺ (M' = K, Rb, Cs) and also for Rb₂Cu(H₂O)₆(SO₄)₂ are reported in Table 9. In all cases the experimental *g*-tensor^{3,15–17,19–21} displays an orthorhombic symmetry where the largest component is *g_Y*. As taking into account the experimental uncertainties the *g*-tensor of RbZn(H₂O)₆(SO₄)₂:Cu²⁺ is coincident with that reported for the pure compound Rb₂Cu(H₂O)₆(SO₄)₂, this fact supports that the local geometry of Cu(H₂O)₆²⁺ in both systems is essentially the same. Furthermore, the measurement of the *g*-tensor of Cu(H₂O)₆²⁺ in the pure compound Rb₂Cu(H₂O)₆(SO₄)₂ by means of the Q-band stresses that the exchange interaction, *J*, among close Cu²⁺ ions is very weak (*J*/*k_B* < 0.02 K), consistent with a Cu²⁺–Cu²⁺ distance of 7.64 Å. A value of *J*/*k_B* ≅ 0.007 K has been estimated for the (NH₄)₂Cu(H₂O)₆(SO₄)₂ Tutton salt.⁷⁴

The data³ embodied in Table 9 show a slight sensitivity of the *g*-tensor to the host lattice as both *g_Y* – *g_X* and *g_Z* increase on passing from K₂Zn(H₂O)₆(SO₄)₂:Cu²⁺ to Cs₂Zn(H₂O)₆(SO₄)₂:Cu²⁺.

Table 9. Experimental *g*-Tensor Values Measured for M₂Zn(H₂O)₆(SO₄)₂:Cu²⁺ (M = K, Rb, Cs) and the Pure Compound Rb₂Cu(H₂O)₆(SO₄)₂ at *T* = 4.2 K

system	<i>g_Z</i>	<i>g_X</i>	<i>g_Y</i>	<i>g_Y</i> – <i>g_X</i>
K ₂ Zn(H ₂ O) ₆ (SO ₄) ₂ :Cu ²⁺	2.03 ± 0.005	2.15 ± 0.005	2.42 ± 0.005	0.27 ± 0.01
Rb ₂ Zn(H ₂ O) ₆ (SO ₄) ₂ :Cu ²⁺	2.046 ± 0.005	2.132 ± 0.01	2.434 ± 0.005	0.30 ± 0.015
Cs ₂ Zn(H ₂ O) ₆ (SO ₄) ₂ :Cu ²⁺	2.058 ± 0.005	2.121 ± 0.005	2.444 ± 0.005	0.32 ± 0.01
Rb ₂ Cu(H ₂ O) ₆ (SO ₄) ₂	2.056 ± 0.01	2.12 ± 0.02	2.42 ± 0.01	0.30 ± 0.03

Other relevant experimental information concerns the temperature dependence of the *g*-tensor first measured by Silver and Getz¹⁵ for K₂Zn(H₂O)₆(SO₄)₂:Cu²⁺ and subsequently corroborated by Riley et al.,¹⁶ Hitchman et al.,¹⁷ Augustyniak and Usachev,¹⁹ and Hoffman et al.²⁰ The data depicted in Figure 3 prove that, when temperature increases,

Figure 3. Experimental temperature dependence of the *g*-values of Cu²⁺-doped K₂Zn(H₂O)₆(SO₄)₂. Reproduced from ref 15, with the permission of AIP Publishing.

an incoherent dynamic process is activated. Accordingly, while *g_Y* = 2.42 and *g_X* = 2.15 at *T* = 4.2 K, *g_Y* and *g_X* become very close at *T* = 300 K where *g_Y* = 2.31 and *g_X* = 2.26. By contrast, the experimental *g_Z* = 2.03 value is unmodified in the 4.2–300 K temperature range.

It is worth noting now that the temperature dependence^{15,20} of three components of experimental hyperfine tensor, *A*, measured for K₂Zn(H₂O)₆(SO₄)₂:Cu²⁺ looks quite similar to that of the *g*-tensor (Figure 3). In particular, when temperature increases, the *A_Z* component of the hyperfine tensor remains constant, while *A_X* and *A_Y* evolve akin to *g_X* and *g_Y* in Figure 3. All these data suggest that the *Z*-direction displays a singular character.

6. INTERPRETATION OF STRUCTURAL AND EPR DATA OF TUTTON'S SALTS CONTAINING CU²⁺: CRITICISM AND NEW IDEAS

The interpretation of EPR data on Cu²⁺ in Tutton salts started with the pioneering work by Abragam and Pryce.¹¹ Since that early work, it has widely been accepted that the Cu(H₂O)₆²⁺ complexes in Tutton salts display, at low temperature, an elongated geometry with the main axis along the *Y* direction

and the hole in the antibonding $\sim x^2 - z^2$ level (Figure 1). Moreover, the origin of this local distortion has been assumed by a great deal of scientists to be the result of a static JTE,^{15–22,33–38} although there is an additional rhombic perturbation showing that g_X and g_Z are not exactly equal.

This well-followed idea seems to be underpinned by comparing the g -tensor of Cu^{2+} in Tutton salts (Table 9) with that for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ units in $\text{Zn}(\text{H}_2\text{O})_6\text{SiF}_6\cdot\text{Cu}^{2+}$ and other trigonal salts (Table 2) where a true JTE takes place. Indeed, it can be noticed that while the experimental g_Y value for Cu^{2+} in Tutton's salts lies in the range 2.42–2.44 (Table 9) these values are close to $g_{\parallel} = 2.46$ measured for $\text{Zn}(\text{H}_2\text{O})_6\text{SiF}_6\cdot\text{Cu}^{2+}$ (Table 2). Also the value $(g_Z + g_X)/2 = 2.09$ derived for Cu^{2+} in Tutton salts (Table 9) is practically coincident with $g_{\perp} = 2.10$ corresponding to $\text{Zn}(\text{H}_2\text{O})_6\text{SiF}_6\cdot\text{Cu}^{2+}$ (Table 2). Moreover, the equilibrium geometry of d^9 ions in cubic crystals displaying a static JTE usually corresponds to an elongated octahedron,^{30–32,59} the only known exception being CaO:Ni^{2+} where the octahedron is compressed.^{75,76} Finally, for systems with a static JTE an increase of temperature induces incoherent hopping among equivalent distortions,^{30–32,59} and the results of Figure 3 point out that some process of this kind is taking place for $\text{K}_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2\cdot\text{Cu}^{2+}$.

However, looking in more detail to experimental data on Cu^{2+} in Tutton's salts and the conditions for having a JTE, serious doubts are raised by the usual interpretation due to the following reasons:

- (1) The existence of a $\text{E} \otimes \text{e}$ JTE requires an initial situation involving degeneracy in the electronic state and also in the vibrational mode.^{30–32,71} Both conditions are in principle hard to be fulfilled for low-symmetry lattices like the monoclinic Tutton salts.
- (2) Typical systems displaying a static JTE involve a d^9 ion 6-fold coordinated in a cubic lattice. In such systems, the observed equilibrium geometry is tetragonal and not orthorhombic.^{30–32,59,60,67,68,70–72,75,76}
- (3) The JTE in an octahedral complex is easily destroyed by tetragonal perturbations leading to energy changes comparable to the energy barrier, B , usually in the range 0.01–0.1 eV.⁶⁰ Good examples of this situation are $\text{K}_2\text{ZnF}_4\cdot\text{Cu}^{2+}$ and $\text{Ba}_2\text{ZnF}_6\cdot\text{Cu}^{2+}$ where the absence of a JTE has been demonstrated.^{52,60}
- (4) The data of Figure 3 are consistent with some hopping of the long axis of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ but *only* between Y and X directions. The temperature independence of $g_Z = 2.03$ in the 4.2–300 K range underlines that the Z direction is not involved in the hopping process and thus displays a singular character. Moreover, even at $T = 300$ K there is still a difference between $g_Y = 2.31$ and $g_X = 2.26$. This situation is then different from that found in a true JTE system where there are three equivalent distortions, and at room temperature an isotropic spectrum is already observed with an average g factor given by eq 2.^{25,26,30–32,59,60}
- (5) The data gathered in Table 8 on $\text{M}_2\text{Cu}(\text{H}_2\text{O})_6(\text{SO}_4)_2$ ($M = \text{K}, \text{Rb}, \text{Cs}$) compounds also highlight the singular character of the Z direction. Indeed, on passing from $\text{K}_2\text{Cu}(\text{H}_2\text{O})_6(\text{SO}_4)_2$ to $\text{Cs}_2\text{Cu}(\text{H}_2\text{O})_6(\text{SO}_4)_2$, $R_Y - R_X$ increases by 0.10 Å, while R_Z is constant within 1%.

Seeking to clarify this central point, it should first be noticed that the properties of insulating compounds containing a

transition metal cation, M , are usually explained considering only the isolated MX_N complex formed with the N ligands at the right equilibrium geometry.¹⁰ However, this approach, though widely followed, discards the influence of the electric field, $E_R(\mathbf{r})$, due to close ions of the rest of the lattice upon active electrons *confined* in the MX_N complex. The key role played by $E_R(\mathbf{r})$ has been stressed in recent years showing that the internal field not only explains the different color of ruby and emerald^{77,32,53,78} but also has an important influence upon the ground state and the local geometry of layered insulating compounds with Cu^{2+} , Ag^{2+} , or Ni^{2+} .^{79,41,52,60} Owing to this fact we have calculated, in a first step, the shape of the internal electric field felt by localized electrons of the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex in $\text{K}_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2\cdot\text{Cu}^{2+}$.

Calling $V_R(\mathbf{r})$ the potential generating the internal $E_R(\mathbf{r})$ field through $E_R(\mathbf{r}) = -\nabla V_R(\mathbf{r})$, Figure 4 displays the potential

Figure 4. Potential energy $(-e)V_R(\mathbf{r})$ corresponding to the internal electric field created by the rest of the lattice ions of $\text{K}_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2$ on a $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex depicted along the local X , Y , and Z directions of the complex.

energy $(-e)V_R(\mathbf{r})$ of an electron (charge $-e$) under $V_R(\mathbf{r})$ in the case of the $\text{K}_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2$ Tutton salt. That energy is very anisotropic when we compare the results of Figure 4 with $\mathbf{r}$ parallel to the Z -axis of the complex to those derived when $\mathbf{r}$ lies in the XY plane (Figure 1). Indeed, $(-e)\{V_R(0,0,s) - V_R(0,s,0)\} = 1$ eV for $s = 2$ Å (Figure 4). This anisotropy in V_R comes mainly from the different distance from the nearest K^+ ions to each group of oxygen ligands, being greater than 4 Å for O_9 ions and ~ 3 Å for O_7 and O_8 ligands (Table 7).

Thus, for a $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex embedded in a Tutton salt, $(-e)V_R(\mathbf{r})$ raises the energy of an $\sim 3z^2 - r^2$ electron and decreases that of a planar $\sim x^2 - y^2$ electron (Figure 4). This means that even if the three metal–ligand distances of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ are equal $(-e)V_R(\mathbf{r})$ induces a gap between antibonding $\sim x^2 - y^2$ and $\sim 3z^2 - r^2$ levels placing the hole in the $\sim 3z^2 - r^2$ orbital of the complex. This situation is thus quite similar to that found in layered systems like $\text{K}_2\text{ZnF}_4\cdot\text{Cu}^{2+}$,^{79,52,60} $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4\cdot\text{Cu}^{2+}$, K_2CuF_4 , or Cs_2AgF_4 .^{41,42} By contrast, for a MX_N complex in a cubic or trigonal lattice $V_R(\mathbf{r})$ does not destroy the degeneracy in the e_g level as the X , Y , and Z axes remain equivalent.

If $V_R(\mathbf{r})$ in a Tutton salt forces the hole of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ to be in the axial $\sim 3z^2 - r^2$ orbital, it *also* induces changes on the geometry of the complex. Indeed, a hole density along the Z axis tends to reduce the value of the R_Z distance^{41,52,60} and to increase the value of both R_X and R_Y . In other words, according to the shape of $V_R(\mathbf{r})$ (Figure 4), that potential alone would

induce a compressed geometry for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ in Tutton salts whose principal axis would be Z and not Y. These ideas already account for the singular character displayed by the Z direction in the temperature dependence of the g-tensor in Figure 3 and the results of Table 7.

The situation found for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ units in Tutton salts is thus different from that for the JTE system $\text{Zn}(\text{H}_2\text{O})_6\text{SiF}_6\text{:Cu}^{2+}$ where the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex is elongated and the hole resides in the antibonding $\sim x^2 - y^2$ orbital. Moreover, the change of electronic ground state also fosters the existence of a final orthorhombic geometry for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ in Tutton salts. Along this line, we should not forget that force constants do depend on the ground state nature, and in some cases they can become negative.⁸⁰ For instance, in $\text{CdCl}_2\text{:Cu}^{2+}$ or $\text{NaCl}\text{:Cu}^{2+}$ the CuCl_6^{4-} unit has a hole in $\sim x^2 - y^2$ and a tetragonal elongated geometry,^{67,81,64} while for the layered compound $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4\text{:Cu}^{2+}$ with a hole in $\sim 3z^2 - r^2$, the equilibrium geometry is not tetragonal but orthorhombic.⁴¹ The appearance of an orthorhombic instability has also been proved in $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4$ ($n = 1-3$) hybrid compounds, in Rb_2CuCl_4 , in K_2CuF_4 ,^{41,42} and for the $\text{CuCl}_4(\text{H}_2\text{O})_2^{2-}$ unit in NH_4Cl .⁸²

Seeking to clear up this key point for the present case, we have carried out calculations on the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex but forcing the hole to be in the $\sim 3z^2 - r^2$ orbital due to the addition of the internal field. In a first step the calculations are performed under the constraint $R_Y = R_X$, while further on the three distances R_Y , R_X , and R_Z are taken as free variables. Results are embodied in Table 10. As it could be expected,

Table 10. Calculated Equilibrium Geometry for the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ Complex Subject to External Charges Simulating $V_R(r)$ That Forces the Hole to Be Placed in the Antibonding $\sim 3z^2 - r^2$ Orbital^a

conditions	R_Y (Å)	R_X (Å)	R_Z (Å)	ΔE (meV)
forced $R_Y = R_X$	2.225	2.225	1.935	0
free R_Y, R_X, R_Z	2.368	2.054	1.974	-57

^aIn a first step the calculations are carried out under the constraint $R_Y = R_X$, while in a second step the three distances R_Y , R_X , and R_Z are taken as free variables in the geometry optimization. ΔE is the energy difference to both situations. In all cases the water configuration is that depicted in Figure 2a.

under the constraint $R_Y = R_X$ the equilibrium geometry corresponds to a compressed octahedron where the equilibrium value $R_Y = R_X = 2.225$ Å is 0.20 Å larger than that derived when the hole is in the $\sim x^2 - y^2$ orbital (Table 3). As a salient feature when R_Y , R_X , and R_Z are all free parameters it turns out that the obtained equilibrium geometry is no longer tetragonal but orthorhombic, involving an energy gain of 57 meV (Table 10). It should be noted that the equilibrium R_X and R_Z values obtained for the isolated $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex with a hole in $\sim 3z^2 - r^2$ coincide within 1.5% with those measured for $\text{K}_2[\text{Cu}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ (Table 6), while a discrepancy of 3% is derived for the softest bond. This fact already underlines a weak coupling between the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex and the rest of the Tutton salt.

Let us now describe the degree of orthorhombicity through the η parameter given by

$$\eta = 2(R_Y - R_X)/(R_Y + R_X) \quad (4)$$

Using the R_Y and R_X values derived for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ in vacuo with a hole in $\sim 3z^2 - r^2$ (Table 10), we obtain $\eta = 14\%$. This figure, comparable to that derived for $\text{CuCl}_4(\text{H}_2\text{O})_2^{2-}$ units in NH_4Cl ($\eta = 17\%$)⁸² and CuCl_6^{4-} complexes in $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4\text{:Cu}^{2+}$ ($\eta = 10\%$),⁴¹ already suggests that the orthorhombic distortion does not alter significantly the nature of the electronic ground state. In this sense the distortion makes possible that the d-wave function of the hole does not have a pure $d(3z^2 - r^2)$ character but involves a small admixture of $d(x^2 - y^2)$

$$|d\rangle = |d(3z^2 - r^2)\rangle - \mu |d(x^2 - y^2)\rangle \quad (5)$$

The present calculations for $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ yield $\mu^2/(1 + \mu^2) = 18\%$ pointing out that under the final orthorhombic geometry the hole still has a dominant $d(3z^2 - r^2)$ character. Values of $\mu^2/(1 + \mu^2)$ in the range 10%–20% have been estimated for $\text{CuCl}_4(\text{H}_2\text{O})_2^{2-}$ in NH_4Cl ,⁸² CuCl_6^{4-} in $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4\text{:Cu}^{2+}$,⁴¹ and also CuF_6^{4-} in K_2CuF_4 .⁴²

Thus, the results gathered in Table 10 strongly support that the local geometry of Tutton salts with Cu^{2+} can be understood considering the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex under the influence of the internal field, $E_R(r)$, created by the lattice. In a first step, this field forces the hole to be in the $\sim 3z^2 - r^2$ orbital favoring a tetragonal compressed geometry. However, that situation is unstable against a subsequent orthorhombic distortion in the XY plane, producing a perturbation on electronic levels. The actual origin of this symmetry lowering is discussed in section 9.

It should be noted that the orthorhombic instability leads to two equivalent configurations where the long axis in the XY plane can be either the Y or the X axis (Figure 5). The

Figure 5. Two equivalent configurations of the isolated $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex produced by the orthorhombic instability (marked with yellow arrows), where the long axis in the XY plane can be either the Y or the X axis.

existence of two equivalent wells for the isolated $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex with a hole in $\sim 3z^2 - r^2$ already sheds light on the temperature dependence of the g-tensor measured¹⁵ for $\text{K}_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2\text{:Cu}^{2+}$ (Figure 3). In fact, the temperature variation of both g_Y and g_X (Figure 3) is consistent with jumps between those two configurations, while the $g_Z = 2.03$ value, constant in the 4–300 K range, reflects that the Z direction is not involved in that dynamic process. A similar pattern to that displayed in Figure 3 has been observed for the layered $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4\text{:Cu}^{2+}$ system⁴¹ and for $\text{CuCl}_4(\text{H}_2\text{O})_2^{2-}$ in NH_4Cl ,⁸³ both involving an orthorhombic instability.

Nevertheless, when $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ is inserted in the $\text{K}_2\text{Cu}(\text{H}_2\text{O})_6(\text{SO}_4)_2$ lattice the two X and Y directions are not strictly equivalent. Indeed, as shown in Table 7, the distance between O_7 and O_8 ligands to the nearest K^+ ions is not exactly

the same. The influence of this lack of equivalence on the temperature dependence of the g -tensor of $\text{K}_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2:\text{Cu}^{2+}$ is discussed in section 8.

7. REINTERPRETATION OF EXPERIMENTAL LOW-TEMPERATURE EPR DATA OF Cu^{2+} -DOPED TUTTON'S SALTS

As previously indicated, since the early works on Cu^{2+} in Tutton salts, the EPR data have been interpreted on the basis of elongated $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complexes with the main axis along the Y direction.^{11,12,15–22,33–38} Nevertheless, the results of the preceding section show that such an assumption is not correct. For this reason it is now necessary to explore whether the available low-temperature EPR data in Cu^{2+} -doped $\text{M}_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2$ ($M = \text{K}, \text{Rb}, \text{Cs}$) can or not be conciliated with the existence of compressed $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complexes along the Z axis perturbed by an additional orthorhombic distortion in the XY plane.

For Cu^{2+} complexes with small or moderate covalency, the g -tensor is essentially due to $d-d$ excitations.^{14,64} In those cases the expected EPR fingerprint for a compressed tetragonal unit with Z as the main axis involves, in a second-order approximation, $g_{\parallel} \equiv g_Z = g_0$, while $g_{\perp} > g_0$. The results embodied in Table 8 on $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ units in Tutton's salts prove that the experimental g_Z value is indeed close to g_0 , while $(g_Y + g_X)/2$ is in all cases equal to 2.28. In a further step, both the positive $g_Z - g_0$ shift and the $g_Y - g_X$ value measured experimentally can reasonably be accounted for through a small hybridization between antibonding $\sim 3z^2 - r^2$ and $\sim x^2 - y^2$ orbitals (eq 5) accompanying the spontaneous orthorhombic distortion. Accordingly, we can explain $g_Z - g_0$ in a simple way as follows^{14,82}

$$\begin{aligned} g_Z - g_0 &\cong \Delta g_Z(3z^2 - r^2) + \mu^2 \Delta g_Z(x^2 - y^2) \\ \Delta g_Z(3z^2 - r^2) &= -3u'^2 \\ \Delta g_Z(x^2 - y^2) &= 8u' \end{aligned} \quad (6)$$

where $u' = \xi^*/\Delta'$ and Δ' means the average of the energies corresponding to the transition of one electron from $\sim xy$, $\sim xz$, $\sim yz$ levels to the hole level in the ground state. Similarly, under the same approximation, $g_Y - g_0$ and $g_X - g_0$ can be expressed as

$$\begin{aligned} g_Y - g_0 &\cong 6[1 + (\mu/\sqrt{3})]^2 u' \\ g_X - g_0 &\cong 6[1 - (\mu/\sqrt{3})]^2 u' \end{aligned} \quad (7)$$

and thus

$$g_Y - g_X = (4\mu/\sqrt{3})6u' \quad (8)$$

$$(g_Y + g_X)/2 = g_0 + 6u'[1 + (\mu^2/3)] \quad (9)$$

Now, from the experimental value $(g_Y + g_X)/2 = 2.28$ measured for $\text{M}_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2:\text{Cu}^{2+}$ ($M = \text{K}, \text{Rb}, \text{Cs}$) (Table 9) and taking $\mu^2 \cong 0.18$, we obtain $u = 0.044$. With such values, eq 8 leads to $g_Y - g_X \approx 0.26$ which is close to the experimental figures derived for Cu^{2+} -doped $\text{M}_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2$ ($M = \text{K}, \text{Rb}, \text{Cs}$) Tutton salts (Table 9).

It is worth noting now that both $g_Y - g_X$ and g_Z quantities increase on passing from $\text{K}_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2:\text{Cu}^{2+}$ to $\text{Cs}_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2:\text{Cu}^{2+}$ (Table 9). This fact can mainly be

ascribed to an increase of the hybridization quantity, μ^2 , reflecting the higher value of the orthorhombic parameter $\eta = 0.14$ for $\text{Cs}_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2$ when compared to that for $\text{K}_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2$ ($\eta = 0.10$) (Table 8). Calling $\mu^2(\text{K})$ and $\mu^2(\text{Cs})$ the values corresponding to $\text{M}'_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2:\text{Cu}^{2+}$ ($M = \text{K}, \text{Cs}$), we estimate from the experimental $g_Y - g_X$ values gathered in Table 9 a ratio $\mu^2(\text{Cs})/\mu^2(\text{K}) = 1.4 \pm 0.2$. On the other hand, taking $\Delta g_Z(3z^2 - r^2) = -0.01$ in eq 6, we can derive from the experimental g_Z quantities (Table 9) a ratio $\mu^2(\text{Cs})/\mu^2(\text{K}) = 1.7 \pm 0.3$.

The interpretation of the hyperfine tensor, A , is, in principle, more involved than that of the g -tensor. Indeed, aside from u' and μ parameters, it would also depend on the core polarization contribution^{14,64} as well as on the $3d-4s$ admixture,^{84,85} which is already allowed for an $a_{1g}(3z^2 - r^2)$ hole under D_{4h} symmetry. Nevertheless, some useful information can be still extracted by looking only at the sign of the hyperfine components. For instance, under D_{4h} symmetry with Z as the principal axis, and low covalency A_Z should be negative^{14,64} if the hole lies in $b_{1g}(x^2 - y^2)$, whereas it becomes positive^{83–86} with a hole in $a_{1g}(3z^2 - r^2)$. Interestingly, the hyperfine tensor has been derived for $\text{ZnF}_2:\text{Cu}^{2+}$, where the local geometry is slightly orthorhombic, and the hole is placed in an orbital with 97% of $d(3z^2 - r^2)$ character.⁸⁶ The obtained values, $A_Z = 51 \times 10^{-4} \text{ cm}^{-1}$, $A_X = -8.1 \times 10^{-4} \text{ cm}^{-1}$, and $A_Y = -18 \times 10^{-4} \text{ cm}^{-1}$, underline that A_Z is indeed positive, while A_X and A_Y are both negative. Although Silver and Getz¹⁵ do not report the signs of hyperfine components for $\text{K}_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2:\text{Cu}^{2+}$, they have been measured by Hoffmann et al.,²⁰ and the sign of the obtained values ($A_Z = 60 \times 10^{-4} \text{ cm}^{-1}$, $A_X = -19 \times 10^{-4} \text{ cm}^{-1}$, and $A_Y = -98 \times 10^{-4} \text{ cm}^{-1}$) supports the dominant $d(3z^2 - r^2)$ character of the hole.

The interpretation of the superhyperfine tensor of the n oxygen ligand, $A(n)$, is not simple in an orthorhombic complex as we need to know the different admixture of the d -wave function with the $2p(\text{O})$ and $2s(\text{O})$ orbitals of three different kinds of oxygen ligands. Nevertheless, if we only consider the d -wave function of eq 5 it would be exactly equal to $d(x^2 - z^2)$ if $\mu^2/(1 + \mu^2) = 1/4$, and then the electronic density along the X and Z axes would be the same. As the calculated value $\mu^2/(1 + \mu^2) = 0.18$ is smaller than 0.25, the density along Z will be higher than along the X axis, and thus one would expect to have a higher superhyperfine interaction for O_9 than for O_7 ligands. If we now consider the $A_{\parallel}(n)$ superhyperfine constants measured by Getz and Silver⁸⁷ for $\text{K}_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2:\text{Cu}^{2+}$ when the magnetic field is parallel to the $\text{Cu}^{2+}-\text{O}_n$ directions, the obtained values for ligands $n = 7$ and 9 , $A_{\parallel}(7) = 16 \times 10^{-4} \text{ cm}^{-1}$, and $A_{\parallel}(9) = 21 \times 10^{-4} \text{ cm}^{-1}$, are qualitatively consistent with the expectations. In the same vein, the recently measured value $A_{\parallel}(8) = 1.3 \times 10^{-4} \text{ cm}^{-1}$ corresponding to the largest $\text{Cu}^{2+}-\text{O}_8$ bond²² is 1 order of magnitude smaller than $A_{\parallel}(9)$.

8. TEMPERATURE AND PRESSURE EFFECTS

As shown in Figure 3, the experimental g_Y and g_X values measured for $\text{K}_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2:\text{Cu}^{2+}$ are both sensitive to temperature variations. Indeed, while at $T = 4 \text{ K}$, $g_Y = 2.42$ and $g_X = 2.15$, and at $T = 300 \text{ K}$, such values become $g_Y = 2.31$ and $g_X = 2.26$, being thus close but not identical. The pattern depicted in Figure 3, somewhat similar to that found⁴¹ for $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$, thus suggests that the long bond which, at $T = 4 \text{ K}$, is $\text{Cu}^{2+}-\text{O}_8$ can however be $\text{Cu}^{2+}-\text{O}_7$ when temperature increases. However, these two configurations are

Figure 6. Pattern of the ground state energy as a function of the distortion coordinate for $\text{K}_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2:\text{Cu}^{2+}$ derived from the present calculations. In the minima characterized by O_i ($i = 7, 8$) the long axis of the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex is parallel to the $\text{Cu}^{2+}-\text{O}_i$ direction.

not physically equivalent due to the low symmetry of the host lattice (Table 7), and thus it is crucial to evaluate the energy difference between them as well as the involved barrier. Calling $\Delta E(\text{O}_8 \rightarrow \text{O}_7)$ the energy difference between the two nonequivalent structural configurations and $B(\text{O}_i)$, the barrier for the $\text{Cu}^{2+}-\text{O}_i$ direction ($i = 7, 8$), as the long axis, the results obtained through the present calculations for $\text{K}_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2:\text{Cu}^{2+}$ are displayed in Figure 6. It can be noticed that both the calculated values $\Delta E(\text{O}_8 \rightarrow \text{O}_7) = 38$ meV and $B(\text{O}_8) = 41$ meV are of the same order but higher than those estimated¹⁵ from the EPR results, $\Delta E(\text{O}_8 \rightarrow \text{O}_7) = 10$ meV and $B(\text{O}_8) = 15$ meV. A closer agreement is reached when comparing the calculated values $B(\text{O}_7) = 3$ meV with the one derived from EPR data, $B(\text{O}_7) = 5.6$ meV.¹⁵

Thus, the present results support that the long axis can move between O_8 and O_7 positions when temperature is raised, although such positions are not equivalent. This means that the internal motions inside $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complexes are only slightly influenced by the $\text{K}_2\text{Zn}(\text{H}_2\text{O})_6(\text{SO}_4)_2$ host lattice such as it was already pointed out in section 6. It should be noticed that the $\text{O}_8 \rightarrow \text{O}_7$ shift as the long axis is helped by a practically isotropic behavior of $V_{\text{R}}(\mathbf{r})$ (Figure 4) which favors the motion of charges *but only* in the XY plane. By contrast, $V_{\text{R}}(\mathbf{r})$ has stronger effects when we must compare its behavior when $\mathbf{r}$ is either parallel or perpendicular to the Z axis. As we have seen in section 6, the significant anisotropy of $V_{\text{R}}(\mathbf{r})$ plays a key role for placing the hole in a mainly $\sim 3z^2 - r^2$ orbital.

It has been proved for $(\text{ND}_4)_2\text{Cu}(\text{D}_2\text{O})_6(\text{SO}_4)_2$ and $(\text{NH}_4)_2\text{Cu}(\text{H}_2\text{O})_6(\text{SO}_4)_2$ that under low hydrostatic pressures the long axis is already along the $\text{Cu}^{2+}-\text{O}_7$ direction.^{33,34} For instance, while for $(\text{ND}_4)_2\text{Cu}(\text{D}_2\text{O})_6(\text{SO}_4)_2$ at ambient pressure $R_Y = 2.310$ Å, $R_X = 2.022$ Å, and $R_Z = 1.966$ Å, under a moderate pressure of $P = 0.15$ GPa the equilibrium distances become $R_Y = 2.014$ Å, $R_X = 2.272$ Å, and $R_Z = 1.988$ Å.

Owing to this fact, we have explored whether a similar phenomenon takes place for $\text{K}_2\text{Cu}(\text{H}_2\text{O})_6(\text{SO}_4)_2$. From first calculations on this compound we have found that the barrier $\Delta E(\text{O}_8 \rightarrow \text{O}_7)$ is reduced by a factor of *seven* on passing from ambient pressure to $P = 10$ GPa. This result thus points out that the shift of the long axis can also happen for $\text{K}_2\text{Cu}(\text{H}_2\text{O})_6(\text{SO}_4)_2$ but at higher pressures.

9. ORIGIN OF THE ORTHORHOMBIC INSTABILITY

As shown in Table 10, if the hole of the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex is in the $\sim 3z^2 - r^2$ orbital due to the internal electric field, then the tetragonal geometry with four ligands in the equatorial XY plane at a distance $R_{\text{eq}} = 2.225$ Å from Cu^{2+} is not stable. Indeed, there is a spontaneous orthorhombic distortion leading to $R_Y = R_{\text{eq}} + d$ and $R_X = R_{\text{eq}} - d$, with $d = 0.16$ Å. As the internal electric field in Tutton salts with $\text{Cu}(\text{H}_2\text{O})_6^{2+}$

complexes (Figure 4) puts the hole in the $\sim 3z^2 - r^2$ orbital, that instability is behind the local orthorhombic symmetry observed experimentally for such systems (Tables 6–9). However, no orthorhombic instability is found for the elongated $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex, with a $\sim x^2 - y^2$ hole, where the equilibrium geometry is tetragonal with an equatorial distance $R_{\text{eq}} = 2.016$ Å, that is 0.20 Å smaller than the corresponding value in the compressed geometry (Table 3).

As the existence of a mechanical instability requires that the associated force constant, K , becomes negative,^{80,88} it is necessary to underline the mechanisms making possible such a situation. In the framework of quantum mechanics, there are two contributions to the force constant of a given vibrational mode described by the normal coordinate Q .^{80,82} Let us designate by Ψ_0 the ground state electronic wave function corresponding to the frozen Hamiltonian, H_0 . If we start with the four ligands in the XY plane at the same distance, R_p , from copper, a first contribution to K , termed K_0 , only involves the ground state wave function, $\Psi_0(0)$, computed at the initial situation $Q = 0$

$$K_0 = \langle \Psi_0(0) | \partial^2 V / \partial Q^2 | \Psi_0(0) \rangle \quad (10)$$

Here $V(\mathbf{r}, Q)$ is the potential energy reflecting the distortion of nuclei. On the other hand, there is a second contribution to the force constant, termed K_v , due to its vibronic origin, that does reflect how Ψ_0 varies with the Q coordinate

$$K_v = 2 \langle \Psi_0 | \partial V / \partial Q | \partial \Psi_0 / \partial Q \rangle \quad (11)$$

If $V(\mathbf{r}, 0)$ denotes the potential energy with nuclei frozen at $Q = 0$, K_v depends on the linear vibronic coupling, which for the present case can be written as

$$V(\mathbf{r}, Q) = V(\mathbf{r}, 0) + (\partial V / \partial Q)Q + \dots \quad (12)$$

where $\partial V / \partial Q$, depending on the electron coordinate $\mathbf{r}$, transforms like the vibrational coordinate Q . Thus, according to eqs 11 and 12, K_v can finally be written in terms of the excited state wave functions, $\Psi_n(0)$, as

$$K_v = -2 \sum_{n \neq 0} |\langle \Psi_0 | \partial V / \partial Q | \Psi_n \rangle|^2 / (E_n - E_0) \quad (13)$$

Here E_0 and E_n are, respectively, the energies of ground and the n -excited state computed at $Q = 0$. Interestingly, according to eq 13, K_v is always *negative* for the ground state.⁸⁰ However, the development of an instability requires that the total force constant $K = K_0 + K_v$ becomes negative, a fact that is helped by a reduction of K_0 . In this sense, we should not forget that K_0 depends on the copper–ligand distance in the XY plane, R_p , and, in general, on the size of a molecule or a solid. Due to the Grüneisen law, reflecting anharmonic effects, K_0 is expected to decrease when R_p increases.^{89,90} This explains, albeit

qualitatively, why the orthorhombic instability in the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ unit can appear more easily in a compressed situation ($R_p = 2.225 \text{ \AA}$) than in an elongated one where $R_p = 2.016 \text{ \AA}$. Along this line, complexes with low force constants in the elongated situation favor the orthorhombic distortion in a compressed conformation induced by the internal field, $E_R(\mathbf{r})$. Accordingly, aside from Cu^{2+} in Tutton salts, the orthorhombic instability is observed for $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+41}$ but not for $\text{K}_2\text{ZnF}_4:\text{Cu}^{2+}$ with an unpaired electron in the antibonding $\sim 3z^2 - r^2$ orbital.⁵²

These ideas also hold for other instabilities driven by $K < 0$ but associated with different distortion modes.^{32,88,90} As relevant examples, the Cu^{2+} impurity moves off-center in the softer SrCl_2 lattice but not in CaF_2 ,³² while Ni^{2+} and Cu^{2+} impurities are both unable to move off-center in the hard MgO lattice.⁹⁰

The existence of an orthorhombic distortion observed for Cu^{2+} in Tutton salts, in the hybrid organic–inorganic systems $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4$ ($n = 1-3$), $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$, and Rb_2CuCl_4 ,⁴¹ as well as for $\text{CuCl}_4(\text{H}_2\text{O})_2^{2-}$ units in NH_4Cl ⁸² partially reflects the singularity of the Cu^{2+} cation in the realm of divalent 3d cations. Indeed, it has been shown⁸² for $\text{CuCl}_4(\text{H}_2\text{O})_2^{2-}$ in NH_4Cl that charge transfer excitations are the main contribution to K_v (eq 13), in order to reach $K < 0$. Interestingly, the measurements carried out for the series of divalent 3d cations in LiCl and LiBr ^{91,92} demonstrate that the lowest charge transfer excitation is found for Cu^{2+} , a fact intimately related to the highest ionization potential and optical electronegativity⁹³ of Cu^{2+} in that series. Those results thus pinpoint that among 3d cations Cu^{2+} is especially favorable for observing distortions driven by $K < 0$. Therefore, these kinds of distortions are fully unrelated to the JTE, which always involves a positive force constant.³⁰

10. FINAL REMARKS

Although in the last 65 years^{11,12,15–22,33–38} the properties of Cu^{2+} in Tutton salts have widely been interpreted on the basis of elongated $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complexes related to a static JTE, the present analysis demonstrates that such an idea is not correct. By contrast, this work proves that the local geometry of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complexes in Tutton salts actually arises from a compressed octahedron although hidden by an additional orthorhombic distortion induced by a negative force constant.

The present results stress the importance of considering the internal electric field, $E_R(\mathbf{r})$, for a right interpretation of data associated with insulating transition metal compounds. Indeed, for Cu^{2+} in Tutton salts the internal field $E_R(\mathbf{r})$ not only has a strong influence upon the ground state of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complexes but also is partially responsible for the appearance of the orthorhombic instability. This fact thus underlines that, although active electrons are localized inside the transition metal complex, we cannot explain *quantitatively* their properties leaving aside the effects of $E_R(\mathbf{r})$ upon the electronic structure.⁹⁴ So, if we want to understand the lowest d–d transition of $\text{K}_2[\text{Cu}(\text{H}_2\text{O})_6](\text{SO}_4)_2$, measured at 0.92 eV,⁹⁵ through calculations of the *isolated* $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex we obtain a value of 0.69 eV at the equilibrium geometry (Table 6). By contrast, when we include in the calculation the effects of the internal field, $E_R(\mathbf{r})$, the lowest transition increases up to 0.89 eV, a value that better matches the experimental figure. This situation is thus similar to that encountered in $\text{K}_2\text{ZnF}_4:\text{Cu}^{2+94,52}$ or $\text{Ba}_2\text{ZnF}_6:\text{Cu}^{2+60}$ where the energy of the

lowest d–d transition is clearly enhanced by the action of the internal field.

Along this line, the internal field $E_R(\mathbf{r})$, although often ignored, plays a key role for understanding the optical spectra of transition metal cations in insulating compounds. In particular, it is crucial for explaining the color of Cr^{3+} -based gemstones^{32,53,77,78,96} and the Egyptian Blue pigment⁹⁷ or the anomalous behavior of transition metal cations in the BaLiF_3 -inverted perovskite.⁹⁸

The orthorhombic instability is observed for $\text{K}_2[\text{Zn}(\text{H}_2\text{O})_6](\text{SO}_4)_2:\text{Cu}^{2+}$ or $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4:\text{Cu}^{2+}$ but not for Cu^{2+} -doped K_2ZnF_4 ⁵² or Ba_2ZnF_6 ⁶⁰ involving a higher metal–ligand force constant. It should be noted, however, that such instability takes place in the K_2CuF_4 pure compound^{41,42} where neighbor CuF_6^{4-} units share common ligands. The cooperative mechanism fostering the instability in K_2CuF_4 has recently been discussed.⁴¹

According to the present results, the local structure and ground state of compounds involving Cu^{2+} , Ag^{2+} , or Mn^{3+} cations in low-symmetry insulating lattices can hardly be explained through the JTE. By contrast, the ideas developed in this work can be useful for that purpose and, in particular, for explaining the properties of $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$,^{39,40} $\text{K}_2\text{Cu}(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$,⁹⁹ or the model compound CuF_2 .¹⁰⁰ Work along this line is now in progress.

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Notes

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