Coordination Chemistry

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Unraveling the Coordination Geometry of Copper(II) Ions in Aqueous Solution through Absorption Intensity**

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Solvation of transition-metal (M) salts in aqueous solution is a seminal issue in coordination chemistry and has implications for life, the environment, and industry.[1–3] A fundamental aspect like the formation of hexaaqua transition-metal complexes $M(H_2O)_6^{2+}$ is unclear for Cu^{2+} ions and still needs clarification. Since the pioneering studies of Cu^{2+} aqueous solutions by optical spectroscopy,[4,5] and later by neutron diffraction,[6] X-ray absorption,[7–9] nuclear magnetic resonance, quantum mechanical calculations, and molecular dynamics simulations,[10–16] the real Cu^{2+} coordination is controversial and lacks of appropriate structural models. In particular, efforts to detect formation of $Cu(H_2O)_5^{2+}$ dynamically exchanging single water molecules among equivalent pyramidal configurations were ineffective through local probes like X-ray absorption[8] or optical absorption.[17] The similitude of the d-d electronic spectra of Cu^{2+} ions in aqueous solution and Tutton salts like $Cs_2Cu(SO_4)_2{\cdot}6\,H_2O$, where copper forms an axially elongated $Cu(H_2O)_6^{2+}$ octahedron of D_{4h} symmetry,[17] suggested that the same complex is present in solution.[4] In fact, chemistry lab courses often use optical absorption spectroscopy to underline the suitability of the $Cu(H_2O)_6^{2+}$ complex as a basic unit for explaining the band structure at 1.5 eV and its associated blue color in both the hydrate salt and aqueous solution in terms of a Jahn–Teller (JT) distorted complex. However, in light of recent dynamical studies, instead of a stable hexaaqua complex in water solution, $Cu(H_2O)_6^{2+}$ ought to be regarded as a time-averaged system rather than the instantaneous coordination of the actual complex, which is assumed to be mainly $Cu(H_2O)_5^{2+}$.[7,10,15] Nevertheless, X-ray and optical spectroscopy with the support of first-principle calculations do not clarify whether the actual coordination corresponds to $Cu(H_2O)_5^{2+}$, $Cu(H_2O)_6^{2+}$, or an intermediate geometry.[14] Instead several $Cu(H_2O)_n^{2+}$ species with n ranging from 4 to 6 were proposed on the basis of X-ray absorption analysis.[8] The closely related free-energy calculated for these species[10,15,16] indicates the delicate balance of the complex stability in aqueous solution. Furthermore, the calculated electronic density of states related to d orbitals provides similar spectral shapes for those coordination geometries, making them barely distinguishable through optical spectroscopy.[14] This peculiarity, together with dilution in water, makes the Cu^{2+} structure in aqueous solution subtle and difficult to unmask, but it still constitutes a fundamental issue in coordination chemistry.

Experimentally, transition energy and oscillator strength of crystal-field d-d transitions can be explained on the basis of the transition-metal complex irrespective of the host (solid or liquid). This is due to the local character of d orbitals involved in the crystal-field transitions. The main role of the host is to exert an effective (chemical) pressure on the complex that can eventually modify both, bond distances and symmetry. Such structural changes can be detected by spectroscopic techniques. In this way the correlations between optical absorption spectroscopy and crystal structure are commonly used to elucidate the actual symmetry of transition-metal ions in proteins. In particular, the oscillator strength is a sensitive parameter to distinguish between centrosymmetric and non-centrosymmetric systems. Bearing all this in mind, we have undertaken a comparative spectroscopic study between hexaaqua D_{4h} $Cu(H_2O)_6^{2+}$ in $Cs_2Cu(SO_4)_2{\cdot}6\,H_2O$ salt, average CuO_5 in glass and Cu^{2+} ions in aqueous solution.[18] Searching for simple ideas to intricate problems, we demonstrate that, unlike the d band structure, the absorption intensity provides key information to unveil the local symmetry of Cu^{2+} ions in aqueous solution. For instance, the oscillator strength of d-d transitions ($f_{d\text{-}d}$) is known to decrease by an order of magnitude upon transformation of CuO_5 (C_{4v}) into CuO_6 (D_{4h}) in $CuMoO_4$.[19] This result makes it an efficient parameter to explore the coordination of the Cu^{2+} ion.

Figure 1 compares similar bluish Cu^{2+} systems containing well-defined coordination geometries: the Tutton salt $Cs_2Cu(SO_4)_2{\cdot}6\,H_2O$ with elongated $Cu(H_2O)_6^{2+}$ of D_{4h} symmetry,[20] $CuSO_4{\cdot}5\,H_2O$ with elongated $Cu[(H_2O)_4O_2]^{2-}$ with two oxygen ligands from SO_4^{2-} anions,[21] and Cu^{2+}-doped glass with average CuO_5 coordination.[22] Although all these systems exhibit quite a similar color (absorption spectrum), the strength of blue portion is markedly different in each system as a consequence of the different coordination polyhedron and the Cu^{2+} concentration. The pale-blue of the Tutton salt contrasts with the stronger blue of $CuSO_4{\cdot}5\,H_2O$ in spite of the fact that the d-d transition oscillator strength of the band at 1.5 eV at room temperature (RT) is similar in both systems ($f_{d\text{-}d} = 5.8 \times 10^{-5}$ and 6.8×10^{-5},

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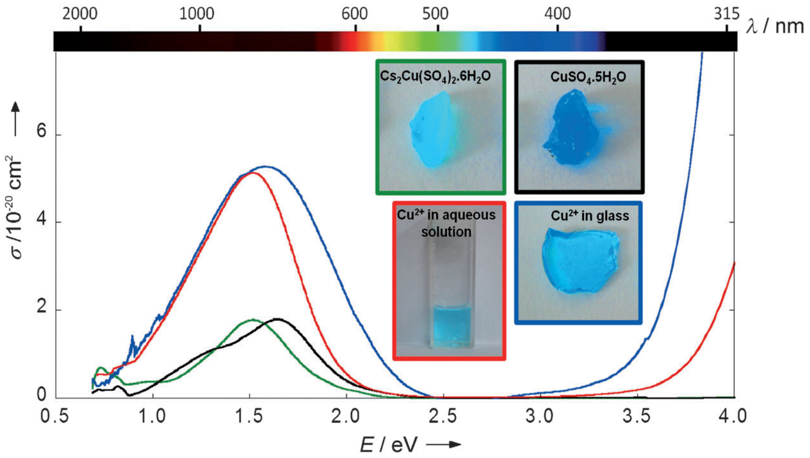

Figure 1. Room-temperature optical absorption spectra of single crystals of $Cs_2Cu(SO_4)_2{\cdot}6\,H_2O$ (green line) and $CuSO_4{\cdot}5\,H_2O$ (black line) with D_{4h} elongated $Cu(H_2O)_6^{2+}$ and $Cu[(H_2O)_4O_2]^{2+}$, respectively; Cu^{2+}-doped glass with average CuO_5 coordination (blue line), and Cu^{2+} in aqueous solution (red line). The Cu^{2+} concentrations are: $[Cu^{2+}] = 2.7{\cdot}10^{21}$ atoms per cubic centimeter ($Cs_2Cu(SO_4)_2{\cdot}6\,H_2O$), $5.5{\cdot}10^{21}$ atoms per cubic centimeter ($CuSO_4{\cdot}5H_2O$), $1.1{\cdot}10^{20}$ atoms per cubic centimeter (glass), and $7.9{\cdot}10^{19}$ atoms per cubic centimeter (aqueous solution). For comparison purposes the absorption coefficient (α) has been normalized to the concentration using the absorption cross-section scale (σ) through the expression $\sigma = \alpha/[Cu^{2+}]$.

respectively). Besides the electronic structure and Cu^{2+} concentration, these results indicate that the absorption intensity strongly depends on Cu^{2+} coordination symmetry. The Cu^{2+} absorption cross-section, defined as $\sigma(E) = \alpha(E)/N$ with $\alpha(E)$ being the absorption coefficient (cm^{-1}) at photon energy E, and N the Cu^{2+} concentration (cm^{-3}), reveals how the absorption intensity increases by an order of magnitude on passing from centrosymmetric $Cu(H_2O)_6^{2+}$ in sulphates ($f_{d\text{-}d} \approx 6\times10^{-5}$) to non-centrosymmetric CuO_5 in glass ($f_{d\text{-}d} = 3\times10^{-4}$), the aqueous solution showing a glassy intermediate behavior ($f_{d\text{-}d} = 2.2\times10^{-4}$) as indicated in Figure 2. Thus, absorption intensity constitutes the most sensitive parameter for probing Cu^{2+} coordination in aqueous solution. Furthermore, its temperature dependence provides additional support and complementary structure information. In centrosymmetric systems, the parity-forbidden d-d transitions are activated by odd vibrations and thus, show strong temperature dependence: the higher the temperature, the stronger the blue color. By contrast, d-d transitions in CuO_5 are symmetry-allowed with weak temperature-dependent (or temperature-independent) oscillator strength. Figure 2 clearly illustrates this behavior. In D_{4h} $Cu(H_2O)_6^{2+}$ and $Cu[(H_2O)_4O_2]^{2-}$, $f_{d\text{-}d}(T)$ is enabled by odd parity vibrations of energy $\hbar\omega = 37$ meV (mainly $Cu(H_2O)_6^{2+}$ a_{2u} mode), following a characteristic thermal dependence as given in Equation (1).

$$f_{d-d}(T) = f_{d-d}(0)\coth\left(\frac{\hbar\omega}{2kT}\right) \qquad (1)$$

The $f_{d\text{-}d}(T)$ values in glasses are consistent with diluted non-centrosymmetric Cu^{2+} systems, irrespective of the local geometry distribution. The enhancement of oscillator strength by temperature because of odd parity vibrationally activated transitions in centrosymmetric Cu^{2+} complexes is not observed in glasses (Figure 2), supporting their non-centrosymmetric nature. In addition, its oscillator strength is an order of magnitude higher than that found in centrosymmetric diluted CuO_6, as estimated from optical reflectance in MgO: Cu^{2+} ($f_{d\text{-}d} \approx 10^{-5}$).[23,24] The significant linear temperature dependence of the Cu^{2+} oscillator strength in aqueous solution is noteworthy. The strong $f_{d\text{-}d}(T)$ variation is unusual for $Cu(H_2O)_5^{2+}$ but the RT oscillator-strength value seems excessive for centrosymmetric $Cu(H_2O)_6^{2+}$. Actually, extrapolation of $f_{d\text{-}d}(T)$ at high temperature foresees a $Cu(H_2O)_5^{2+}$ glassy-like behavior, whereas a crystalline sulphate-like $Cu(H_2O)_6^{2+}$ behavior is found at low temperature. On the assumption that Cu^{2+} could only adopt either the fivefold or sixfold conformations, 35 % would correspond to $Cu(H_2O)_6$ and 65 % to $Cu(H_2O)_5$ according to the RT $f_{d\text{-}d}$ value. Nevertheless, it is not evident whether the observed oscillator strength at a given temperature is the result of a mixture of five- and six-coordinated environments or simply an unique $Cu(H_2O)_5 + H_2O$ complex, the coordination of which is temperature dependent.

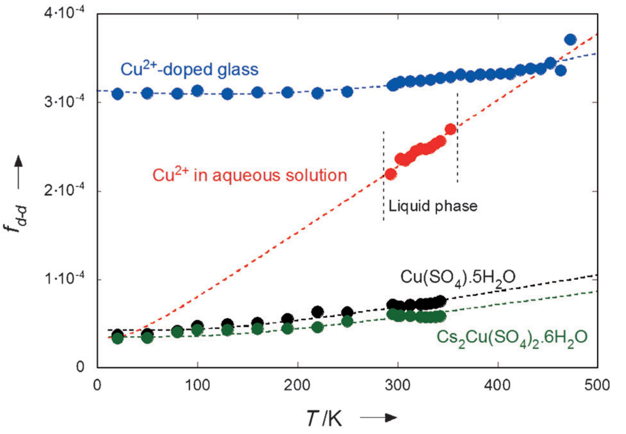

Figure 2. Variation of the oscillator strength of the d-d band at 1.5 eV with a temperature range of 20–500 K. The temperature range is imposed by melting (sulphates) and freezing/evaporation (aqueous solution). Dashed lines correspond to the fitting of experimental data to Equation (1) for $Cs_2Cu(SO_4)_2{\cdot}6\,H_2O$, $CuSO_4{\cdot}5\,H_2O$, and an aqueous solution. Fitting parameters are: $f_{d\text{-}d}(0) = 3.5\times10^{-5}$ and 4.2×10^{-5} for $Cs_2Cu(SO_4)_2{\cdot}6\,H_2O$ and $CuSO_4{\cdot}5\,H_2O$, respectively, with $\hbar\omega = 37$ meV (297 cm^{-1}), and $f_{d\text{-}d}(0) = 3.5\times10^{-5}$ and $\hbar\omega = 8$ meV (65 cm^{-1}) for Cu^{2+} in aqueous solution. A slight linear behavior is observed for a Cu^{2+}-doped glass ($f_{d\text{-}d} = 3\times10^{-4}$). Departures of $f_{d\text{-}d}$ from the regular behavior at high temperature indicate incipient local structure changes around Cu^{2+} ions in glass. Errors are smaller than the symbol size.

We propose a dynamical JT model on the basis of an initial $Cu(H_2O)_6^{2+}$ octahedron framework to explain the major presence of $Cu(H_2O)_5^{2+}$ in aqueous solution. The model considers the strong tendency of the Cu^{2+} ion to distort a regular sixfold coordination geometry (O_h) because of its orbitally degenerated ground-state configuration $3d^9$ (^2E_g: $t_{2g}^6e_g^3$); that is, the JT effect. As a result, Cu^{2+} complexes adopt low-symmetry distortions like those attained in Tutton salts for $Cu(H_2O)_6^{2+}$ or in oxides like $CuMoO_4$[19] and $CuWO_4$[25] for CuO_6. Thus, the Cu^{2+} ion forms D_{4h} distorted complexes even if Cu^{2+} is forced to occupy an O_h site in cubic lattices like CaO or MgO.[26] In such a case, Cu^{2+} exhibits a local D_{4h} symmetry with the distortion axes pointing along either x, y, or z directions with the same probability, preserving the overall O_h symmetry (triply topological or dynamical degeneracy). Besides the JT effect, additional second-order couplings to odd parity vibrations of a_{2u} symmetry may yield vibrational mode hardening (positive coupling) or off-center Cu^{2+} stabilization (negative coupling). Aqueous solution is an ideal polar medium providing negative second-order electron–vibration coupling in this mode (local displacive mode softening) thus leading to destabilization of the initially formed D_{4h} elongated $Cu(H_2O)_6^{2+}$ into pyramidal C_{4v}-elongated off-center $Cu(H_2O)_5 + H_2O$, that is, the pseudo Jahn-Teller effect.

The observed puzzling behavior can be qualitatively described in the framework of the $Cu(H_2O)_6^{2+}$ configurational energy curve as depicted in Figure 3. In this phenomenological model the shape and temperature dependence of the potential-energy surfaces are theoretically justified by total energy calculations and experimentally through the temperature dependence of the oscillator strength. Total energy calculations for different $Cu(H_2O)_n^{2+}$ ($n = 4$–6) complexes indicate that the JT-elongated $Cu(H_2O)_6^{2+}$ complex is unstable to distortions yielding a reduction of one of the two long H_2O-Cu bonds and separation of the opposite H_2O-Cu axial bond. This confirms the relevance of a_{2u} mode coupling in aqueous solution,[15,16] thereby underpinning the model. Indeed the energy of $Cu(H_2O)_5^{2+}$ perturbed by one water molecule in the second coordination sphere is smaller than the energy of $Cu(H_2O)_6^{2+}$, thus providing a better stability for the fivefold coordination geometry. Within a $Cu(H_2O)_6^{2+}$ complex framework, this means that, although the first-order a_{2u} mode coupling is zero by symmetry constraints, the second-order coupling must fulfill Equation (2),

$$\left(\frac{\partial^2 E}{\partial Q_u^2}\right)_{D_{4h}} < 0 \tag{2}$$

with Q_u being the a_{2u} normal coordinate and E the total energy. This inequality implies $Cu(H_2O)_6^{2+}$ destabilization into two equivalent C_{4v} $Cu(H_2O)_5^{2+}$ complexes along the elongation of the D_{4h} $Cu(H_2O)_6^{2+}$ complex. This is represented by two minima in the double-well configurational curve at symmetric positions with respect to $Q(a_{2u}) = 0$ (Figure 3).

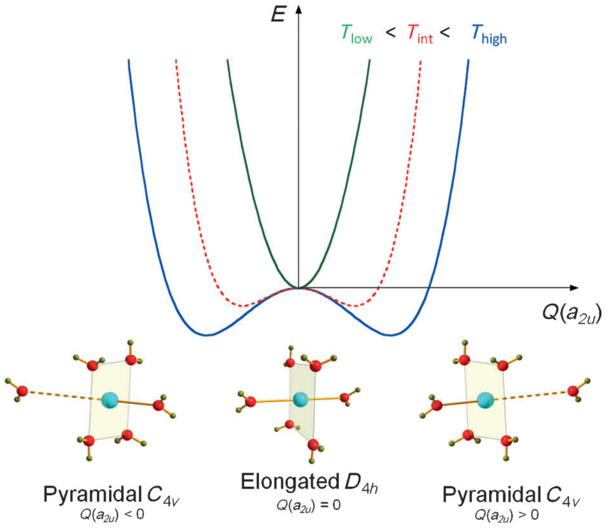

Figure 3. Qualitative configuration energy curve for $Cu(H_2O)_6^{2+}$ as a function of the normal coordinate $Q(a_{2u})$. Solid curves correspond to $Cu(H_2O)_6^{2+}$ and $Cu(H_2O)_5^{2+} + H_2O$ in crystal and aqueous solution, respectively. The dashed curve represents an intermediate configuration. The increase of temperature in aqueous solution modifies the configurational energy curve into a warped parabola with two wells representing off-center complexes, the geometry of which is indicated below. Note that at high temperature the minimum $Q(a_{2u})$ increases yielding delocalization of the dangling water molecule: $Cu(H_2O)_6^{2+}$ $[Q(a_{2u}) = 0] \rightarrow Cu(H_2O)_5^{2+} + H_2O$ $[|Q(a_{2u})| \neq 0]$.

The model envisages six equivalent $Cu(H_2O)_5^{2+}$ complexes depending on the sign (+ or −) of displacement, and the three possible elongations (along x, y, or z) for $Cu(H_2O)_6^{2+}$. Within this model the main difference between Tutton salts and aqueous solution concerns the coupling strength to a_{2u}. In the crystal, Equation (3) is valid

$$\left(\frac{\partial^2 E}{\partial Q_u^2}\right)_{D_{4h}} = \mu\omega^2 > 0 \tag{3}$$

and therefore the configurational energy curve as a function of $Q(a_{2u})$ is described by a parabola with the energy minimum at $Q(a_{2u}) = 0$; that is, a D_{4h}-elongated $Cu(H_2O)_6^{2+}$ ground-state geometry.[20]

On this model, the stabilization of a fivefold (C_{4v}) Cu^{2+} coordination, $Cu(H_2O)_6^{2+} \rightarrow Cu(H_2O)_5^{2+} + H_2O$, is a consequence of a weakening of the $Cu(H_2O)_6^{2+}$ a_{2u} mode provided by the interaction between the complex and the water molecules in aqueous solution. This Cu^{2+} coordination agrees with total energy calculations using DFT and COSMO solvation models to simulate the outer solvation region in liquid water.[15] We estimate from Ref. [15] that the energy barrier between the two minima should be around 8 meV, and therefore must play an important role in the dynamics of the system at RT. The geometrical description in terms of coupling to the a_{2u} mode has been implicitly observed through QM/MM molecular dynamics calculations, where the average equilibrium geometry (4×2.03 Å $+ 1 \times 2.15$ Å $+ 1 \times 2.30$ Å CuO distances), indeed reflects non-centrosymmetric a_{2u} distortions.[13,27] The fast dynamics associated with water ligands would be related to jumps among different configurational minima. Based on the absorption intensity of crystals and solution, we foresee that the initial $Cu(H_2O)_6^{2+}$ complex, which would be stable at low temperature (unattainable experimentally in liquid aqueous solution) continuously transforms to $Cu(H_2O)_5^{2+}$ at high temperature, passing through different intermediate H_2O-perturbed $Cu(H_2O)_5^{2+}$ configurations. Given that the oscillator strength depends on the proximity of the sixth dangling H_2O, it reaches a maximum value at high temperatures when delocalization of the water molecule is complete: $Cu(H_2O)_5^{2+}$. The observed linear dependence of $f_{d\text{-}d}$ with temperature supports this view (Figure 2).

In summary, the proposed model describes the solvation of Cu^{2+} ions in aqueous solution consistently with previous studies but employing an unified model on the basis of a sixfold coordination $M(H_2O)_6$ framework. The Cu^{2+} singularity with respect to other M ions lies on its ability to distort O_h surroundings through electron–vibration couplings because of orbital degeneracy. The fivefold pyramidal coordination rises as a result of the joint coupling to the JT e_g modes (D_{4h}-elongated coordination), and to odd parity a_{2u} displacive modes, the coupling of which is highly enhanced in aqueous solution.

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