400 cm^{-1} which produces a weak interaction with ν_1 and the slightly lower 149-cm^{-1} position. The ν_2 mode for the $K^+Br_2^-$ is expected around 120 cm^{-1} and interaction forces ν_1 to higher frequencies. With increasing alkali metal atom mass, the ν_2 position falls to lower frequencies, the interaction between ν_1 and ν_2 decreases, and, accordingly, the ν_1 position decreases slightly. The dihalide vibrational modes as a function of M^+ are listed in Table I.

The general trend in Raman intensities with exciting wavelength follows the absorption spectrum for $M^+Br_2^-$; stronger Raman signals were observed with red-yellow and blue excitation, near regions of absorption.[4] The strong $\sigma \rightarrow \sigma^*$ transitions of $Cs^+Cl_2^-$, $Cs^+Br_2^-$, and $Cs^+I_2^-$ appeared at 344, 365, and 382 nm, respectively, in absorption; however, the greatest resonance Raman intensity enhancement with blue laser lines was found with $Cs^+Cl_2^-$. In the red region, the $\pi^* \rightarrow \sigma^*$ transitions of $Cs^+Br_2^-$ and $Cs^+I_2^-$ gave absorptions at 660 and 686 nm, respectively, and the latter was clearly more intense than the former.[4] Owing to the greater red absorption coefficient for I_2^- as compared to Br_2^-, the 647.1-nm excited Raman intensity of the I_2^- species was strongly resonance enhanced for $M^+I_2^-$ whereas the present Br_2^- Raman spectrum probably sustained a small amount of resonance intensity enhancement.

Emission Spectra. Turning to the broad bands observed in the emission region for the alkali metal–bromine reactions, the dominant features common to all of the systems studied were the strong emissions centered near 600 and 740 nm. Experiments using alkali bromide and bromine reagents revealed the 600-nm feature, but not the 740-nm emission.[10] Since the absorption spectrum of the CsBr + Br_2 reaction system revealed a strong 268-nm band for $Cs^+Br_3^-$,[4] which is also illustrated in Figure 3, the 600-nm emission is assigned to $Cs^+Br_3^-$, which is a secondary product in the matrix reaction of cesium and bromine. The strong 740-nm emission is unique to the alkali metal–bromine systems, and it is attributed to $M^+Br_2^-$.

The electronic transitions responsible for these emissions can be identified from the absorption spectra. The dibromide anion has a weak red absorption at 660 nm and the 647.1-nm laser line is strongly absorbed which gives the prominent 740-nm emission. The 568.2-nm laser line picks up the blue tail of the red Br_2^- absorption band and produces the 740-nm emission, although with less intensity than the red laser line. Since the diiodide anion exhibits a strong red absorption near 680 nm, the observation of a similar 740-nm emission for $M^+I_2^-$ supports the assignment of the 740-nm emission to $M^+Br_2^-$. The 0–0 band for the $\pi^* \rightarrow \sigma^*$ transition of Br_2^- in the $M^+Br_2^-$ species can be predicted midway between the emission and absorption bands at approximately 700 nm.

The absorption maximum of Br_2 at 415 nm[4] is well above the dissociation limit at 511 nm[14] and the absorption tails out through the visible region; the Br_2 emission peaks in the near-infrared region at 800 nm.[5] The strong 268-nm absorption of $Cs^+Br_3^-$ also tails, with diminishing absorption coefficient, out into the visible region. Hence, absorption of the blue laser lines and the present emissions can be associated with the transition for $Cs^+Br_3^-$ which peaks at 268 nm.

Conclusions

Raman spectra were observed for the matrix reaction product $M^+Br_2^-$ for each alkali metal species. $(Br\leftrightarrow Br)^-$ stretching fundamentals were found in the 149–160 cm^{-1} range except for $Na^+Br_2^-$ where interaction with the $Na^+\leftrightarrow Br_2^-$ mode forced the $(Br\leftrightarrow Br)^-$ mode down to 115 cm^{-1}. The observed Br_2^- Raman intensities using different exciting lines generally correlated with the absorption spectrum. Strong emission bands were observed for $M^+Br_2^-$ and $M^+Br_3^-$ at 740 and 600 nm, respectively.

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Registry No. $Li^+Br_2^-$, 59141-10-5; $Na^+Br_2^-$, 59141-11-6; $K^+Br_2^-$, 59141-09-2; $Rb^+Br_2^-$, 59125-55-2; $Cs^+Br_2^-$, 59141-08-1.

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Electronic Spectrum of the $Cu(H_2O)_6^{2+}$ Ion

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The electronic spectra of the compounds $Cat_2Cu(SO_4)_2{\cdot}6H_2O$ [Cat = K, Rb, Tl, NH_4] and $K_2Cu(ZrF_6)_2{\cdot}6H_2O$ and their deuterated analogues have been recorded, either as single crystals or as mulls, in the range 5000–25 000 cm^{-1}. In each case, the spectrum of the $Cu(H_2O)_6^{2+}$ ion consists of three peaks, centered at ~7500, ~10 000, and ~12 000 cm^{-1}, except for the ammonium salt, for which all four "d–d" transitions were resolved. The spectra have been assigned from the polarization properties of the peaks. The orbital energies are discussed in terms of the geometry of the $Cu(H_2O)_6^{2+}$ ion and the angular overlap simple molecular orbital bonding scheme is used to derive σ- and π-bonding parameters for the water molecule toward copper(II).

Introduction

Probably because of their comparative simplicity, aquo complexes have often formed the basis of theoretical and practical investigations into the electronic structure of transition metal complexes.[1-6] The copper Tutton salts, of general formula $(Cat)_2Cu(SO_4)_2{\cdot}6H_2O$ (Cat = cation), provide a particularly useful series of compounds in this respect, as each of these contains the hexaaquocopper ion, with an octahedral geometry, but with three different Cu–O bond lengths which vary with the cation.[7-11] Moreover, as the hydrogen positions are known in many of these salts, the effects not only of changes in the metal–ligand distance but also of the orientation of the water molecules can be studied. Recently, Marshall and James have reported the molecular magnetic susceptibilities of several of these copper complexes and interpreted their data using the angular overlap molecular orbital bonding scheme.[5,6] In the present study, the single-crystal optical and EPR spectra of the NH_4, K, Rb, and Tl Tutton salts and the analogous compound $K_2Cu(ZrF_6)_2{\cdot}6H_2O$ have been investigated and interpreted in terms of current bonding theories. This paper deals with the electronic spectra of the complexes, while the following one describes the EPR results.

Experimental Section

Preparation of Compounds. The complexes $M_2Cu(SO_4)_2{\cdot}6H_2O$, where M = NH_4, Rb, K, and Tl, were prepared by mixing equivalent aqueous solutions of the two simple sulfates. The compounds are isomorphous, belonging to the space group $P2_1/a$, with two molecules in the unit cell. The unit cell parameters of the ammonium salt are a = 921.05 pm, b = 1237.95 pm, c = 630.16 pm, and β = 106.112°,[11] while those of the other salts are very similar.[7-10] The morphology of the resulting crystals was identified using a stereoscopic polarizing microscope and was found to be the same as that reported by Tutton,[12] with the (001) and (110) etc. faces being well developed. The compound $K_2Cu(ZrF_6)_2{\cdot}6H_2O$ was prepared by the evaporation of a solution containing stoichiometric quantities of copper fluoride, potassium fluoride, and zirconium fluoride in aqueous hydrogen fluoride and was found to crystallize with the (100), (001), and (011) etc. faces well developed. This complex belongs to the space group $P2_1/c$; unit cell parameters are a = 663.1 pm, b = 998.1 pm, c = 1292.1 pm, and β = 114.30°, with two molecules in the unit cell.[13] The compounds all had satisfactory analyses. The corresponding deuterated complexes were prepared by heating ~0.5 g to constant weight at 110 °C, dissolving the resulting solid in ~20 ml of 99.75% D_2O, and evaporating the resulting solution in a desiccator over silica gel.

Electronic Spectra. The electronic spectra of the (001) and (010) faces of crystals of the K, NH_4, and Rb Tutton salts were recorded over the range 2000–400 nm, using a Cary 17 spectrophotometer. The (010) face was obtained by cleaving large crystals, except for the NH_4 salt, where the crystals were set in glue and this face was obtained by grinding. The spectra were recorded with the electric vector of light parallel to the extinction directions of each crystal face, an air-spaced Glan-Thomson prism being used to polarize the light. The spectra were measured at room temperature and 95 K for the K and Rb complexes and at room temperature and 160 K for the ammonium salt (as EPR data have been reported at this temperature). Spectra of the (001) and (011) faces of $K_2Cu(ZrF_6)_2{\cdot}6H_2O$ were similarly measured at room temperature and 95 K. As no crystals of $Tl_2Cu(SO_4)_2{\cdot}6H_2O$ of good optical quality could be grown, the electronic spectrum of this compound was measured at room temperature and 95 K as a Nujol mull held between thin glass plates. The low-temperature spectra were obtained using a simple flow cryostat consisting of an evacuated, double-walled glass tube. One end of this was dipped into liquid nitrogen and cold gas was passed up the tube by means of a heating coil. The sample was mounted over a hole cut in a piece of cadmium sheeting and suspended from the other end of the tube using a glass rod. The temperature was read using two carbon resistors, one mounted above and the other below the crystal, using an Oxford Instruments carbon thermometer. A heating coil wound around the outside of the flow tube prevented condensation of water vapor.

In order to minimize the obscuring effects of the overtones of the infrared transitions of the water molecules, the spectra of the (001) and (010) faces of the K, Rb, and ND_4 deuterated complexes were also measured, as well as mull spectra of the deuterated forms of the other complexes. The spectra of the (001) faces and Nujol mulls of $K_2Zn(SO_4)_2{\cdot}6H_2O$ and its deuterated analogue were also recorded, for comparative purposes. The spectra of the (010) face of $ND_4Cu(SO_4)_2{\cdot}6D_2O$ at 295 and 160 K and the (010) and (001) faces of $Rb_2Cu(SO_4)_2{\cdot}6H_2O$ at 95 K and mull spectra of the potassium, copper, and zinc Tutton salts and their deuterated analogues are shown in Figures 1–3.

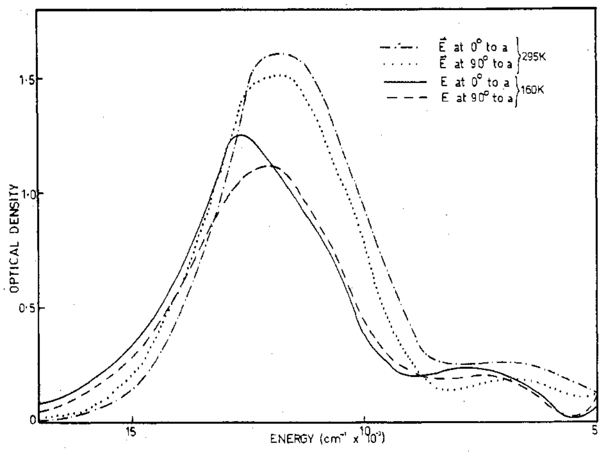


Figure 1. Spectrum of the (010) face of $(ND_4)_2Cu(SO_4)_2{\cdot}6D_2O$ measured at 295 and 160 K.

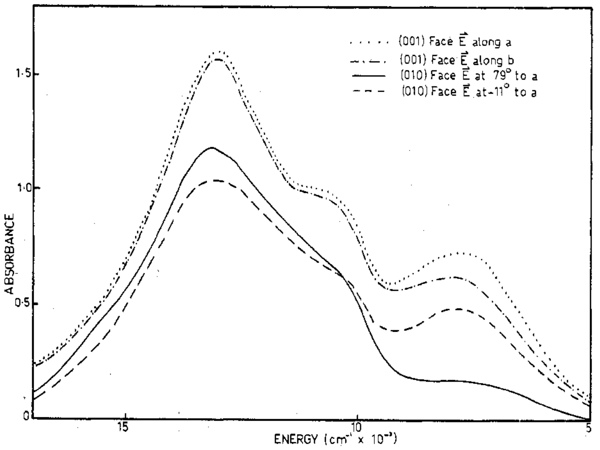


Figure 2. Spectra of the (001) and (010) crystal faces of $Rb_2Cu(SO_4)_2{\cdot}6D_2O$ measured at 95 K.

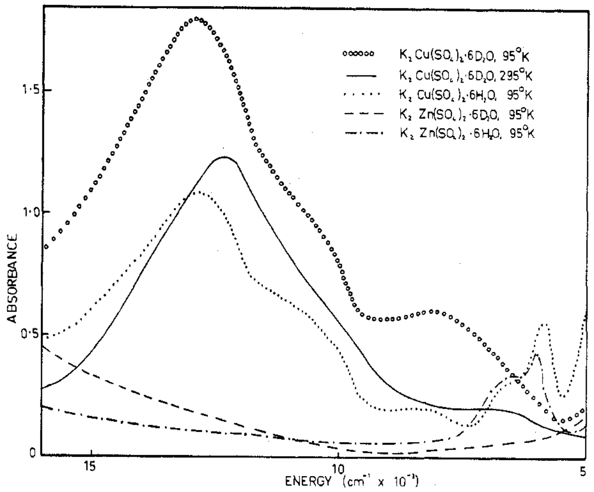


Figure 3. Hexachlorobutadiene mull spectra of the potassium–copper–zinc Tutton salts.

Discussion

Assignment of the Spectra. The molecular geometry of $Cu(H_2O)_6^{2+}$ in each Tutton salt is shown in Figure 4. The

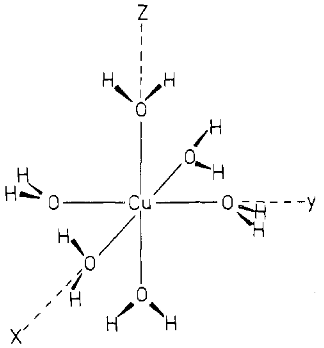


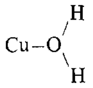
Figure 4. Molecular structure of the $Cu(H_2O)_6^{2+}$ ion in the K, Rb, and Tl Tutton salts; *x*, *y*, and *z* are along the shortest, intermediate, and longest Cu–O bonds. The structure in the NH_4 salt is similar, except that the *y* and *z* axes are interchanged.

Table I. Squares of the Projections Made by the Electric Vector on the Molecular Axes

Compd	Crystal face	Angle,[a] deg	Squared projection		
			x^2	y^2	z^2
$(NH_4)_2Cu(SO_4)_2\cdot6H_2O$	(010)	0	0.0761	0.5617	0.3623
	(010)	90	0.7546	0.0054	0.2399
	(001)	0	0.0761	0.5617	0.3623
	(001)	90	0.1693	0.4329	0.3978
$Rb_2Cu(SO_4)_2\cdot6H_2O$[b]	(010)	−11	0.1682	0.2227	0.6092
	(010)	79	0.6681	0.3247	0.0072
	(001)	0	0.0608	0.3272	0.6121
	(001)	90	0.1638	0.4526	0.3836
$K_2Cu(ZrF_6)_2\cdot6H_2O$	(011)	−4.5	0.4609	0.0177	0.5214
	(011)	85.5	0.2772	0.5200	0.2028
	(001)	0	0.4985	0.0064	0.4950
	(001)	90	0.3184	0.2879	0.3937

[a] Angle made by the electric vector with the *a* crystal axis. A negative sign indicates rotation into the crystal quadrant containing an acute angle. [b] Very similar molecular projections are made by the electric vector in the (010) and (001) planes of the K salt.

strict microsymmetry of the ion is C_i, but if the fact that the atoms in each



$$\text{Cu–O}\begin{smallmatrix}\text{H}\\ \\ \text{H}\end{smallmatrix}$$

grouping are not planar is neglected, as has been done in previous studies,[2,5,6] the point group becomes D_{2h}. In the C_i point group each electronic transition is vibronically allowed in every polarization, but in D_{2h} symmetry three transitions are forbidden: $A_g(x^2-y^2) \rightarrow B_{1g}(xy)$ in *z*, $A_{1g}(x^2-y^2) \rightarrow B_{3g}(yz)$ in *x*, and $A_g(x^2-y^2) \rightarrow B_{2g}(xz)$ in *y* polarization. In order to deduce the molecular projections of the electric vector a molecular coordinate system was defined as follows: *x* is along the shortest Cu–O bond direction, *z* is orthogonal to *x* and the intermediate Cu–O bond direction (almost exactly along the longest Cu–O bond direction), and *y* is orthogonal to *x* and *z* (almost precisely along the intermediate bond direction). The molecular projections made by the electric vector when it is along the extinction directions of the (001) and (010) faces of the NH_4 and Rb Tutton salts and the (001) and (011) faces of $K_2Cu(ZrF_6)_2\cdot6H_2O$ are given in Table I, averaged where necessary over the two molecules in the unit cell. The projections in the NH_4 salt differ from those in the other Tutton salts because of the interchange of the *x* and *z* molecular axes.[7-11] It is clear from the projections that the crystal spectra do not correspond directly to the molecular spectra, and in fact the packing is such that it is impossible to resolve the crystal spectra completely into molecular spectra with any accuracy. This is because of the near coincidence in every case of the directions of two different molecular axes of the independently oriented molecules in the unit cell, these being *y* and *z* in the NH_4 salt and *x* and *y* in the other salts.[14] This means that the only significant changes in the molecular projections occur in the (010) faces, between *x* and *y* in the NH_4 salt and between *x* and *z* for the other cations. Similarly, in $K_2Cu(ZrF_6)_2\cdot6H_2O$ only the (011) face shows any marked changes in molecular projections, these being between *y* and *z*.

The spectrum of the $Cu(H_2O)_6^{2+}$ ion in each complex consists of a broad peak centered at ~12 500 cm^{-1}, with a shoulder at ~10 500 cm^{-1} (this being only poorly resolved in the NH_4 salt) and with peaks assignable to infrared overtones of the water molecules occurring below ~7000 cm^{-1}. The spectra of the deuterated complexes are similar to those of the aquo complexes, except that the ir overtones occur at much lower energy, so that in each case an additional peak assignable to a "d–d" transition is now resolved at 6000–7000 cm^{-1}. On cooling, the peaks show a considerable decrease in intensity, in agreement with the vibronic origin of the intensity, as well as shifts of some of the peak maxima to higher energy.

The peak at ~6500 cm^{-1} can in each case be assigned to the transition $d_{z^2} \rightarrow d_{x^2-y^2}$ (each molecular orbital being denoted by its major d component). As will be discussed later, the unusually low energy of this transition is caused by the comparative shortness of the bond along the *z* axis. As expected from the molecular projections, only the spectra of the (010) faces of the Tutton salts and the (011) face of $K_2Cu(ZrF_6)_2\cdot6H_2O$ show any significant polarization properties. In the spectrum of the NH_4 salt, the peak at ~13 000 cm^{-1} is resolved into two components (Figure 1) and an inspection of the variation in the molecular projections accompanying the intensity changes (Table I) shows that the peak centered at 11 760 cm^{-1} occurs more strongly in *x* than in *y* polarization, while the reverse is true for the peak centered at 12 350 cm^{-1} (at 295 K). This is consistent with effective D_{2h} symmetry, as far as the vibronic intensity mechanism is concerned, with the peak due to $d_{xz} \rightarrow d_{x^2-y^2}$ being centered at 11 760 cm^{-1} and that due to $d_{yz} \rightarrow d_{x^2-y^2}$ having a maximum at 12 350 cm^{-1}. The poorly resolved shoulder at ~10 650 cm^{-1} in the ammonium salt is then assigned as $d_{xy} \rightarrow d_{x^2-y^2}$. In the spectra of the (010) faces of the K and Rb salts (Figure 2) and the (011) face of $K_2Cu(ZrF_6)_2\cdot6H_2O$, the peak at ~12 300 cm^{-1} shows no significant polarization properties, but that at ~7500 cm^{-1} increases in intensity as the projection on the *z* axis increases while that at ~10 000 cm^{-1} decreases (when the contributing effects due to the other peaks are taken into account). This is consistent with the assignment of the peak at ~10 000 cm^{-1} to the transition $d_{xy} \rightarrow d_{x^2-y^2}$, as this is forbidden in *z* polarization, and also with the assignment of the peak at ~7500 cm^{-1} to the transition $d_{z^2} \rightarrow d_{x^2-y^2}$, as this has often been observed to increase in intensity in *z* polarization in similar complexes.[15] It seems probable that the transition $d_{xz} \rightarrow d_{x^2-y^2}$ contributes to the peak centered at ~12 300 cm^{-1}, as no significant polarization properties are expected for this transition. The energy of the transition $d_{yz} \rightarrow d_{x^2-y^2}$ in these salts remains uncertain. The observed transition energies, together with their proposed assignments, are listed in Table II.

Interpretation of the Transition Energies. In most copper compounds having a distorted octahedral structure the transition $d_{z^2} \rightarrow d_{x^2-y^2}$ lies close in energy to the other "d–d" transitions, i.e., at ~10 000–14 000 cm^{-1}, and it has been assigned within this range in a number of copper complexes containing $Cu(H_2O)_6^{2+}$ or similar ions.[4,16,17] Indeed, the spectra of some of the Tutton salts have previously been assigned on this basis.[5,6,18] The spectra of the deuterated complexes presented here, however, strongly suggest that in the Tutton salts the transition $d_{z^2} \rightarrow d_{x^2-y^2}$ occurs at much

Table II. Energies of Band Maxima and Assignments of "d–d" Electronic Spectra of Compounds Containing $Cu(H_2O)_6^{2+}$

	Transition energy ($cm^{-1} \times 10^{-3}$) and assignment of excited state									Calcd energy of $d_{z^2} \rightarrow d_{x^2-y^2}$ at 295 K[b]
	d_{yz}		d_{xz}		d_{xy}		d_{z^2}[c]			
Compd	295 K	95 K	295 K	95 K	295 K	95 K	295 K	95 K	Tetragonality[a]	
$(NH_4)_2Cu(SO_4)_2\cdot 6H_2O$	12.35	12.72	11.76	12.20	~10.65	~10.90	~6.40	~7.35	0.905	5.1
$K_2Cu(SO_4)_2\cdot 6H_2O$	?	?	12.27	12.90	10.00	10.20	7.14	7.58	0.8806	6.2
$Rb_2Cu(SO_4)_2\cdot 6H_2O$	?	?	12.35	12.74	10.00	10.20	7.63	7.75	0.8643	6.6
$Tl_2Cu(SO_4)_2\cdot 6H_2O$	?	?	12.50	13.16	10.20	10.40	8.00	8.26	0.8576	6.9
$K_2Cu(ZrF_6)_2\cdot 6H_2O$	?	?	12.74	13.30	9.76	10.00	~7.80	8.00	0.8575	6.9
Copper hydrogen maleate[d]		13.70		13.60		16.00		11.50	0.7256	12.1

[a] Tetragonality is defined as average bond length along x and y divided by bond length along z. [b] Obtained by taking the ratio of the d_{z^2} orbital to the mean energy of d_{xz}, d_{yz}, and d_{xy} as calculated for $Cu(H_2O)_6^{2+}$ as a function of tetragonality in ref 3. [c] Obtained from the spectra of the deuterated complexes (except in the case of copper hydrogen maleate). [d] Data from ref 15.

Table III. Spectral Fit of Transition Energies at 295 K Calculated Using the Angular Overlap Model

	Transition energies, $cm^{-1} \times 10^{-3}$							
	E_{yz}		E_{xz}		E_{xy}		E_{z^2}	
Compd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
$(NH_4)_2Cu(SO_4)_2\cdot 6H_2O$	12.35	13.29	11.76	11.54	10.65	9.99	~6.40	5.79
$K_2Cu(SO_4)_2\cdot 6H_2O$		14.32	12.27	11.88	10.00	10.32	7.14	7.21
$Rb_2Cu(SO_4)_2\cdot 6H_2O$		14.04	12.35	12.47	10.00	10.10	7.63	7.48
$Tl_2Cu(SO_4)_2\cdot 6H_2O$		14.09	12.50	12.76	10.20	10.09	8.00	7.74
$K_2Cu(ZrF_6)_2\cdot 6H_2O$			12.74		9.76		7.70	7.61

lower energy (6000–8000 cm^{-1}). While this will not greatly affect the interpretation of the magnetic susceptibility data of these compounds, it will significantly alter the discussion of the d-orbital energies in terms of angular overlap bonding parameters.[5,6] The abnormally low energy of the transition $d_{z^2} \rightarrow d_{x^2-y^2}$ in the Tutton salts is probably due to the unusually short Cu–O bonds along the z axes in these complexes.[19] As expected, the observed transition energies decrease as the tetragonality T increases (Table II). Here, T is defined as $0.5(R_x + R_y)/R_z$, where R is the bond length along the axis denoted by the subscript; thus $T = 1$ for a regular octahedral complex, while $T \approx 0.67$ represents an effectively planar complex, with $R_z = 300$ pm. Data reported[16] for the $Cu(H_2O)_6^{2+}$ ion present in copper hydrogen maleate are included in the table; as indicated by its tetragonality, the cation in this compound is close to square planar in structure. On a more quantitative basis, the variation of the d-orbital energies in $Cu(H_2O)_6^{2+}$ as a function of tetragonality has been calculated using a molecular orbital model by Roos.[3] If the slightly different bond lengths used in Roos' calculations are taken into account,[20] the energies of the transitions $d_{z^2} \rightarrow d_{x^2-y^2}$ which his model predicts for the Tutton salts, $K_2Cu(ZrF_6)_2\cdot 6H_2O$, and the $Cu(H_2O)_6^{2+}$ ion in copper hydrogen maleate are in reasonably good agreement with the observed values.

The angular overlap model (AOM) developed by Schäffer[2] and Jorgensen[20] has provided a useful means of interpreting the transition energies of metal complexes in terms of ligand-bonding parameters. The AOM relates the energy e, by which a d orbital is raised upon interaction with one ligand orbital, to the diatomic overlap integral S via the relationship $e = S^2K$. Here, K is a constant which can be taken to represent the ligand field "strength" of the ligand orbital in question. The total energy of each d orbital is obtained by summing over all the ligands using the angular overlap matrix appropriate to the complex. The effects of both σ and π interactions are included. The ligand field "strength" of the water molecule can be parametrized by means of three constants, K_σ representing the σ interaction along the Cu–O bond vector, $K_{\pi c}$ representing the π interaction orthogonal to the H–H vector, and $K_{\pi s}$ representing the π interaction in the plane parallel to that containing the water hydrogen atoms. The matrix elements of the d orbitals of the Tutton salts due to the ligand interaction V are given by

$$\langle x^2 - y^2 | V | x^2 - y^2 \rangle = 2[0.75K_\sigma(S_{\sigma x}^2 + S_{\sigma y}^2)] \quad (1a)$$

$$\langle z^2 | V | z^2 \rangle = 2[K_\sigma S_{\sigma z}^2 + 0.25K_\sigma(S_{\sigma x}^2 + S_{\sigma y}^2)] \quad (1b)$$

$$\langle z^2 | V | x^2 - y^2 \rangle = 0.5[-3^{1/2}K_\sigma(S_{\sigma x}^2 - S_{\sigma y}^2)] \quad (1c)$$

$$\langle yz | V | yz \rangle = 2(K_{\pi c}S_{\pi y}^2 + K_{\pi s}S_{\pi z}^2) \quad (1d)$$

$$\langle xz | V | xz \rangle = 2(K_{\pi c}S_{\pi z}^2 + K_{\pi s}S_{\pi x}^2) \quad (1e)$$

$$\langle xy | V | xy \rangle = 2(K_{\pi c}S_{\pi x}^2 + K_{\pi s}S_{\pi y}^2) \quad (1f)$$

for the K, Rb, and Tl salts; for the NH_4 salt eq 1d–1f become

$$\langle yz | V | yz \rangle = 2(K_{\pi c}S_{\pi z}^2 + K_{\pi s}S_{\pi y}^2) \quad (1g)$$

$$\langle xz | V | xz \rangle = 2(K_{\pi c}S_{\pi x}^2 + K_{\pi s}S_{\pi z}^2) \quad (1h)$$

$$\langle xy | V | xy \rangle = 2(K_{\pi c}S_{\pi y}^2 + K_{\pi s}S_{\pi x}^2) \quad (1i)$$

The above matrix elements were used to calculate the ligand-bonding parameters of the water molecules in the Tutton salts from the observed transition energies using a least-squares technique. The Cu(3d)–O(2p) overlaps reported by Smith[23] were used in this procedure. The calculated ligand-bonding parameters (derived, it should be remembered, from bond lengths measured at room temperature) are

$$K_\sigma = (8.6 \pm 0.4) \times 10^5\ cm^{-1}$$

$$K_{\pi c} = (10.6 \pm 2) \times 10^5\ cm^{-1}$$

$$K_{\pi s} = (11.2 \pm 2) \times 10^5\ cm^{-1}$$

using the room-temperature band maxima. Here the error limits were estimated by allowing for the uncertainties in the bond lengths and band maxima. The "best fit" calculated transition energies are listed in Table III and these agree fairly well with the observed values. The value of K_σ may be compared with that of $K_\sigma = (8.04 \pm 0.25) \times 10^5\ cm^{-1}$ estimated from the energy of the transition $d_{z^2} \rightarrow d_{x^2-y^2}$ in the near-planar hexaaquo ion present in copper hydrogen maleate (the K_π parameters cannot be calculated in this case, as the hydrogen positions are unknown). The agreement is quite good, suggesting that at least as far as σ bonding is concerned the AOM provides a self-consistent means of parametrizing the bonding of the water molecule over a rather wide range of coordination geometry. As far as the π-bonding parameters are concerned, it might be expected that $K_{\pi c}$ would be of the same order of magnitude as K_σ, and this is indeed found to be the case. However, $K_{\pi s}$ is expected to be considerably smaller than $K_{\pi c}$, as it depends upon an interaction with oxygen orbitals which are already involved in bonding to the water hydrogen atoms. In fact, the two π-bonding parameters are about equal, which seems chemically unreasonable. While it is possible that the π bonding about the Cu–O bond is effectively isotropic or that the AOM is inadequate to describe the comparatively weak π interactions, there is also considerable evidence that the Tutton salts undergo a structural change as the temperature is lowered. The magnetic susceptibility data[18] and EPR measurements[24] suggest that, at least in the case of the K and NH_4 salts, the rhombic component to the ligand field is considerably smaller at low temperatures than it is at room temperature. It has been suggested[18] that there may be a dynamic equilibrium between two forms of the $Cu(H_2O)_6{}^{2+}$ ion in these compounds, with the lower energy form having the bonds along x and y more nearly equal than they are in the higher energy form. If this is the case, the electronic spectra are expected to be superimpositions of the spectra of the two molecular forms, weighted according to their Boltzmann distribution. The fact that the electronic spectra show no large shifts in peak positions on cooling argues that no great change in the tetragonality occurs when the temperature is lowered. However, it is noteworthy in this respect that the transitions due to $d_{z^2} \rightarrow d_{x^2-y^2}$, which depend only on σ perturbations, occur at consistently higher energies than those estimated from Roos' calculations (Table II) using structural information derived from room-temperature data; moreover, these transitions show relatively large shifts to higher energies as the temperature is lowered (Table II). This is consistent with a slight decrease in the tetragonality on cooling. Furthermore, if any changes in the hydrogen atom positions occur with variation in temperature, this could significantly affect the interpretation of the band positions in terms of the AOM π-bonding parameters. Clearly a determination of the structure of one of the Tutton salts by neutron diffraction at low temperature would be highly desirable.[25]

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Registry No. $(NH_4)_2Cu(SO_4)_2{\cdot}6H_2O$(salt form), 13587-26-3; $(NH_4)_2Cu(SO_4)_2{\cdot}6H_2O$(coordinated form), 41584-35-4; $K_2Cu(SO_4)_2{\cdot}6H_2O$(salt form), 13587-29-6; $K_2Cu(SO_4)_2{\cdot}6H_2O$(coordinated form), 38797-50-1; $Rb_2Cu(SO_4)_2{\cdot}6H_2O$(salt form), 21349-43-9; $Rb_2Cu(SO_4)_2{\cdot}6H_2O$(coordinated form), 40275-15-8; $Tl_2Cu(SO_4)_2{\cdot}6H_2O$(salt form), 20908-85-4; $Tl_2Cu(SO_4)_2{\cdot}6H_2O$(coordinated form), 39698-58-3; $K_2Cu(ZrF_6)_2{\cdot}6H_2O$, 59492-79-4.

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(25) After the submission of this paper, a neutron diffraction study of $Rb_2Cu(SO_4)_2{\cdot}6H_2O$ at 95 K had been reported: G. Smith, F. H. Moore, and K. H. L. Kennard, *Cryst. Struct. Commun.*, **4**, 407 (1975). In agreement with the above predictions, this compound shows a slight decrease in tetragonality upon cooling (room-temperature bond lengths are 195.7, 203.1 and 203.7 pm; bond lengths at 95 K are 197.8, 200.0, and 231.7 pm). However no significant change in the orientation of the hydrogen atoms occurs when the temperature is lowered, and the use of the low-temperature structural parameters produces AOM bonding parameters quite similar to those calculated using the room-temperature structural data. It would therefore seem either that the π bonding effect of the water molecule is effectively isotropic about the metal–ligand bond axis or, more likely, that the AOM, in the simple form in which it has been used here, cannot adequately deal with the comparatively weak π interactions.