# Crystal and Molecular Structure of Chromium(II) Sulphate Pentahydrate‡ and Single-crystal Electronic Spectra and Bonding of $CrSO_4{\cdot}5H_2O$, $CuSO_4{\cdot}5H_2O$, and $CuSO_4{\cdot}5D_2O$

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The crystal and molecular structure of $CrSO_4{\cdot}5H_2O$ is reported; this compound is isostructural with the analogous copper(II) salt. The two independent molecules in the unit cell have quite similar, tetragonally elongated ligand co-ordination geometries, the distortion from regular octahedral arrangements being marginally smaller than those in the copper(II) compound. The average Cr–O distance is *ca.* 0.07 Å longer than the average Cu–O bond length, this difference being more marked for the in-plane than the axial bonds. The low-temperature single-crystal electronic spectrum of $CrSO_4{\cdot}5H_2O$ shows bands in the region 10 000—15 000 $cm^{-1}$ assigned as *d–d* transitions coupled to metal–ligand vibrations and a weak peak at 18 450 $cm^{-1}$ thought to be due to coupling with water O–H stretching vibrations. The spectrum of $CuSO_4{\cdot}5H_2O$ is also reported and is similar to that of the chromium(II) compound except that the bands are *ca.* 2 000 $cm^{-1}$ lower in energy. For the copper(II) complex the assignment of the peak due to coupling with O–H stretches of the water molecules was confirmed by measuring the electronic spectrum of the corresponding deuteriated compound. An analysis of the transition energies using the angular overlap model suggests that the ligand interaction with the *d* orbitals is *ca.*20% higher in the chromium(II) compound than in the copper(II) derivative. In both compounds the $d_{z^2}$ orbital is depressed in energy compared with the predictions of the simple bonding model, and better agreement with the observed transition energies is obtained if the π-bonding interaction involving the water molecules is approximately isotropic about the metal–ligand bond axes.

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Copper(II) sulphate pentahydrate is often taken as the archetype of triclinic crystals, and as such has been the subject of numerous structure determinations, both by *X*-ray[1] and neutron diffraction,[2,3] a recent study even involving a crystal grown under the gravity-free conditions of earth orbit.[4] Because of the availability of high quality data, this compound was chosen to form the basis of a recent investigation of the charge density distribution in a typical metal complex.[5] As part of a general investigation of the structure and spectra of complexes of early transition metal ions,[6,7] we therefore felt that a study of the analogous chromium(II) compound would be of interest. A charge density study of this salt will also appear shortly.[8] In addition to measuring the crystal structure and electronic spectrum of $CrSO_4{\cdot}5H_2O$ we also report the low-temperature electronic spectra of $CuSO_4{\cdot}5H_2O$ and its deuteriated analogue, so that the energy levels and metal–ligand bonding parameters in the isostructural pair of compounds may be compared.

## Experimental

Large single crystals of $CrSO_4{\cdot}5H_2O$ were grown by dissolving chromium metal in dilute sulphuric acid under an atmosphere of nitrogen and allowing the resulting solution to evaporate slowly in a vacuum. The crystals were stored under nitrogen gas.

Large crystals of $CuSO_4{\cdot}5H_2O$ were grown by allowing an aqueous solution to evaporate slowly over several days in a refrigerator. The analogous deuteriated compound was obtained by dissolving anhydrous $CuSO_4$ in $D_2O$ and recrystallizing from this solvent twice. A convenient test that the deuteriation was effectively complete was the observation that the intense i.r. overtones due to O–H stretching vibrations in the region 5 500—7 000 $cm^{-1}$ were absent in the electronic spectrum of the crystal of the deuteriated complex.

Electronic spectra were measured using polarised light on a Cary 17 spectrophotometer, the crystals being mounted by a technique described previously,[9] and cooled using a Cryodyne model 22 closed-cycle refrigerator. As $CrSO_4{\cdot}5H_2O$ decomposed slowly in the atmosphere at room temperature the spectrum of this compound was recorded only at low temperature.

*Crystallography.*—*Crystal data.* $H_{10}CrO_9S$, $M = 238.1$, triclinic, space group $P\bar{1}$ ($C_i^1$, no. 2), $a = 6.188(1)$, $b = 10.929(1)$, $c = 6.039(1)$ Å, $\alpha = 82.40(2)$, $\beta = 107.77(1)$, $\gamma = 102.71(2)°$, $U = 378.5(1)$ Å$^3$, $D_c$ ($Z = 2$) = 2.09 g $cm^{-3}$, $F(000) = 244$, monochromatic Mo-$K_\alpha$ radiation, $\lambda = 0.710\,69$ Å, $\mu = 17.5$ $cm^{-1}$; specimen 0.22 × 0.11 × 0.28 mm (capillary), $A^*_{\text{min.,max.}}$ (analytical correction) = 1.33, 1.66, $T = 295$ K.

*Structure determination.* A unique data set was measured to $2\theta_{\text{max.}} = 100°$ using a Syntex $P2_1$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode. 7 906 Independent reflections were obtained, 5 862 with $I > 3\sigma(I)$ being considered 'observed,' and used in the full-matrix least-squares refinement with statistical weights. Thermal parameter refinement was isotropic for the hydrogen atoms and anisotropic for the remainder. Residuals on $|F|$ at convergence ($R$ and $R'$) were 0.031 and 0.044. Neutral complex scattering factors were taken from ref. 10. Computation was with the XTAL program

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* Contact one of these authors for information on spectroscopic aspects of the work.

† Contact this author for information on the crystal structure.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

**Table 1.** Atomic co-ordinates* for $CrSO_4{\cdot}5H_2O$

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Cr(1) | 0.0 | 0.0 | 0.0 |
| Cr(2) | 0.5 | 0.5 | 0.0 |
| S | 0.015 54(3) | 0.287 35(2) | −0.371 14(3) |
| O(1) | −0.092 41(14) | 0.156 07(7) | −0.320 56(15) |
| O(2) | 0.246 22(13) | 0.317 09(8) | −0.202 06(15) |
| O(3) | 0.867 08(15) | 0.373 88(8) | −0.361 40(14) |
| O(4) | 0.043 13(14) | 0.299 18(8) | 0.390 48(13) |
| O(5) | −0.184 49(17) | 0.071 32(9) | 0.166 16(18) |
| O(6) | 0.295 53(16) | 0.121 57(8) | 0.156 57(15) |
| O(7) | 0.465 36(15) | 0.403 24(9) | 0.306 59(14) |
| O(8) | 0.761 47(16) | 0.410 71(11) | 0.020 85(15) |
| O(9) | 0.441 18(15) | 0.128 70(10) | 0.632 38(17) |
| H(54) | −0.131(4) | 0.129(2) | 0.244(4) |
| H(59) | −0.266(4) | 0.033(2) | 0.216(4) |
| H(62) | 0.301(5) | 0.189(3) | 0.079(5) |
| H(69) | 0.351(4) | 0.127(2) | 0.339(4) |
| H(73) | 0.592(4) | 0.389(2) | 0.432(4) |
| H(74) | 0.353(4) | 0.382(2) | 0.318(4) |
| H(83) | 0.799(4) | 0.400(2) | −0.065(4) |
| H(84) | 0.839(4) | 0.401(2) | 0.125(4) |
| H(91) | 0.572(5) | 0.124(3) | 0.685(5) |
| H(92) | 0.422(4) | 0.182(3) | 0.688(4) |

* Atom numbering and cell setting follow that used previously in the studies of copper(II) sulphate pentahydrate.[5]

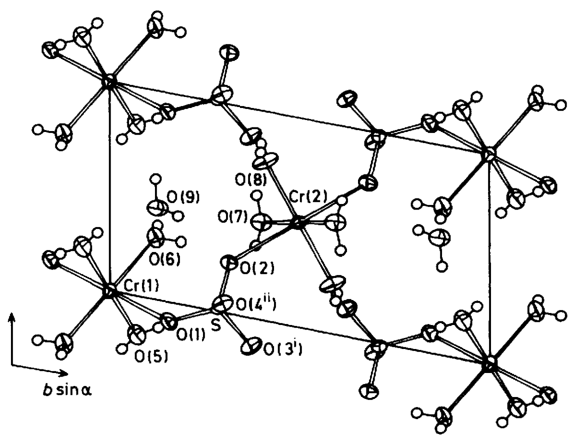


**Figure 1.** Unit-cell contents of $CrSO_4{\cdot}5H_2O$ viewed down $c$ with atomic labelling and 50% thermal ellipsoids shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å

**Table 2.** Non-hydrogen interatomic distances (Å) in $CrSO_4{\cdot}5H_2O$, with values in $CuSO_4{\cdot}5H_2O$ for comparison (ref. 5)

| | $d$(Cr) | $d$(Cu) | $d$(Cr) − $d$(Cu) |
|---|---|---|---|
| Cr(1)–O(1) | 2.421 6(8) | 2.382(1) | 0.040 |
| Cr(1)–O(5) | 2.053 2(13) | 1.964(1) | 0.089 |
| Cr(1)–O(6) | 2.052 1(8) | 1.971(1) | 0.081 |
| Cr(2)–O(2) | 2.458 7(8) | 2.434(1) | 0.025 |
| Cr(2)–O(7) | 2.053 5(9) | 1.960(1) | 0.074 |
| Cr(2)–O(8) | 2.030 8(12) | 1.932(1) | 0.099 |
| S–O(1) | 1.478 2(8) | 1.475(1) | |
| S–O(2) | 1.476 4(7) | 1.476(1) | |
| S–O($3^{i}$) | 1.473 7(11) | 1.474(1) | |
| S–O($4^{ii}$) | 1.486 4(9) | 1.487(1) | |

Transformations of the asymmetric unit: i $x-1, y, z$; ii $x, y, z-1$.

**Table 3.** Non-hydrogen independent interatomic angles (°) in $CrSO_4{\cdot}5H_2O$, with values in $CuSO_4{\cdot}5H_2O$ for comparison (ref. 5)

| | Compound | |
|---|---|---|
| | Cr | Cu |
| O(1)–Cr(1)–O(5) | 88.92(3) | 88.24(3) |
| O(1)–Cr(1)–O(6) | 90.12(3) | 91.41(3) |
| O(5)–Cr(1)–O(6) | 90.55(4) | 91.81(3) |
| O(2)–Cr(2)–O(7) | 87.50(3) | 88.06(3) |
| O(2)–Cr(2)–O(8) | 85.20(4) | 86.89(3) |
| O(7)–Cr(2)–O(8) | 88.82(4) | 89.50(4) |
| O(1)–S–O(2) | 109.13(4) | 109.32(4) |
| O(1)–S–O($3^{i}$) | 110.18(6) | 110.25(4) |
| O(1)–S–O($4^{ii}$) | 108.51(5) | 108.44(4) |
| O(2)–S–O($3^{i}$) | 111.13(5) | 111.07(5) |
| O(2)–S–O($4^{ii}$) | 108.81(5) | 108.88(4) |
| O(3)–S–O($4^{ii}$) | 109.03(5) | 108.82(4) |

Transformations of the asymmetric unit: i $x-1, y, z$; ii $x, y, z-1$.

system[11] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. Final atomic co-ordinates are given in Table 1.

## Results and Discussion

*The Structure of* $CrSO_4{\cdot}5H_2O$ *and Comparison with* $CuSO_4{\cdot}5H_2O$.—The crystal packing and hydrogen-bonding network in the unit cell of $CrSO_4{\cdot}5H_2O$ is identical to that already described in detail for the corresponding copper(II) compound[1–5] and this aspect of the structure will therefore not be considered further. The unit cell, shown viewed down the $c$ axis in Figure 1, contains two independent centrosymmetric formula units, and the atomic co-ordinates of these are listed in Table 1. They have quite similar ligand geometries, with four short bonds to water molecules and two comparatively long bonds to sulphate oxygen atoms (Tables 2 and 3). The average Cr–O bond distance of 2.18 Å is *ca.* 0.07 Å longer than that in the analogous copper(II) compound. This is to be expected because of the contraction caused by the greater effective nuclear charge in $Cu^{2+}$ compared with $Cr^{2+}$.[12] A similar difference (0.06 Å) has been reported for the metal–fluorine distances in $KCrF_3$ and $KCuF_3$.[13] For the $MSO_4{\cdot}5H_2O$ (M = Cr or Cu) pair the difference in bond lengths is more marked for the in-plane bonds than the axial bonds (Table 2), indicating that the chromium(II) compounds undergo slightly smaller tetragonal distortions than the analogous copper(II) compounds. As has also been noted for copper sulphate pentahydrate,[5] the environments of water oxygens O(7) and O(8) do not depart significantly from trigonal (Table 4), and the Cr–O(8) bond is slightly shorter than those to the other water molecules (Table 2).

Although the Jahn-Teller theorem is not strictly applicable to a compound such as $CrSO_4{\cdot}5H_2O$, as the six 'ligands' are not identical, it is still appropriate to discuss the marked tetragonal distortion of the ligand co-ordination polyhedra in terms of the concepts associated with this effect. The magnitude of the distortion away from a regular octahedral geometry may be parametrised by the Jahn-Teller radius ρ defined below,[14,15]

$$\rho = (2\delta x + 2\delta y - 4\delta z)/\sqrt{12}$$

where $\delta x$, $\delta y$, $\delta z$ refer to the deviations of the bonds along the $x,y,z$ axes from the average value. The Jahn-Teller distortions

**Table 4.** Geometries of the water molecules in $CrSO_4{\cdot}5H_2O$

| | Distance (Å) | | Angle (°) |
|---|---|---|---|
| O(5)–H(54) | 0.79(2) | Cr(1)–O(5)–H(54) | 123(2) |
| O(5)–H(59) | 0.70(2) | Cr(1)–O(5)–H(59) | 122(2) |
| Cr(1)–O(5) | 2.053 2(13) | H(54)–O(5)–H(59) | 106(3) |
| | | total | 351 |
| O(6)–H(62) | 0.82(2) | Cr(1)–O(6)–H(62) | 109(2) |
| O(6)–H(69) | 1.05(2) | Cr(1)–O(6)–H(69) | 121(1) |
| Cr(1)–O(6) | 2.052 1(8) | H(62)–O(6)–H(69) | 116(2) |
| | | total | 346 |
| O(7)–H(73) | 0.93(2) | Cr(2)–O(7)–H(73) | 112(2) |
| O(7)–H(74) | 0.70(2) | Cr(2)–O(7)–H(74) | 116(2) |
| Cr(2)–O(7) | 2.053 5(9) | H(73)–O(7)–H(74) | 121(2) |
| | | total | 359 |
| O(8)–H(83) | 0.66(3) | Cr(2)–O(8)–H(83) | 128(2) |
| O(8)–H(84) | 0.67(2) | Cr(2)–O(8)–H(84) | 120(2) |
| Cr(2)–O(8) | 2.030 8(12) | H(83)–O(8)–H(84) | 110(3) |
| | | total | 358 |
| O(9)–H(91) | 0.82(3) | H(91)–O(9)–H(92) | 107(3) |
| O(9)–H(92) | 0.80(3) | | |

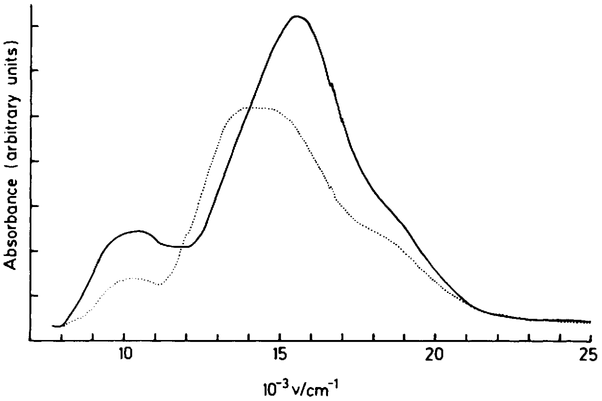


**Figure 2.** Electronic spectra of an arbitrary crystal face of $CrSO_4{\cdot}5H_2O$ measured at *ca.* 18 K with the electric vector parallel to the two extinction directions, —— and ······

in the chromium(II) compound (ρ = 0.45 Å) are marginally smaller than those of copper(II) sulphate pentahydrate (ρ = 0.52 Å). This is perhaps rather unexpected, as the magnitude of the distortion depends upon a balance between an electronic term and the force constant of the Jahn-Teller-active normal mode.[13–16] The electronic term, which is the driving force of the distortion, is expected to be greater for chromium(II) than for copper(II) as the *d–d* transitions are significantly higher in energy (see following section). Although no data are available on the vibrational force constant appropriate to the chromium(II) compound, which is a measure of the resistance to the distortion, the general trends observed for stretching frequencies suggest that this could well be lower than that of the copper(II) compound.[17] The only other accurate information on isostructural chromium and copper compounds of which we are aware is that on $KMF_3$ where ρ = 0.40 for M = Cr and ρ = 0.38 for M = Cu.[13]

The very limited data thus suggest that despite the greater *d*-orbital interaction with the ligands, chromium(II) complexes undergo quite similar distortions to those observed for the analogous copper(II) compounds. It has been suggested[16] that a number of other factors may influence Jahn-Teller distortions in metal complexes: for instance, *ds* orbital mixing, as discussed in the following section, and possibly changes in one of these may counterbalance the increased *d*-orbital interaction mentioned above and so explain why chromium(II) complexes do not undergo significantly greater deviations from regularity than their copper(II) counterparts.

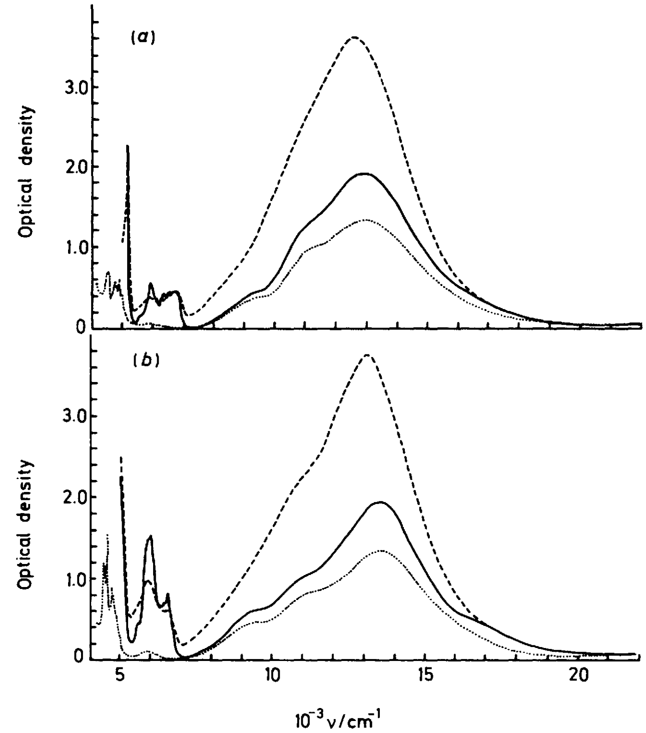
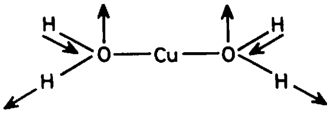


**Figure 3.** Electronic spectra of an arbitrary crystal face of $CuSO_4{\cdot}5H_2O$ measured at *ca.* 18 (——) and 290 K (– – –) with the electric vector parallel to the two extinction directions, (*a*) and (*b*). The low-temperature spectra of the corresponding deuteriated complex are also shown (····)

*Electronic Spectra.*—The electronic spectrum of an arbitrary crystal face of $CrSO_4{\cdot}5H_2O$ measured at *ca.* 18 K, with the electric vector of light parallel to the two extinction directions, is shown in Figure 2. Two major peaks are observed, centred at 13 450 and 15 500 $cm^{-1}$, with weaker bands at 10 000 and 18 500 $cm^{-1}$, the 'best-fit' energies being deduced by Gaussian analysis. In addition, two weak, sharp peaks due to spin-forbidden transitions may be discerned at *ca.* 16 700 $cm^{-1}$. As far as the spin-allowed part is concerned, the spectrum is basically similar to that measured by reflectance at 77 K by Fackler and Holah,[18] and to that reported by Runciman and Syme[19] for a crystal of '$CrSO_4{\cdot}7H_2O$', which we assume was actually the pentahydrate. These workers,[19] however, assigned all four peaks as *d–d* transitions, though it was recognised by the former group[18] that this implied an anomalously large splitting of the π-bonding $d_{xz,yz,xy}$ set of orbitals. We consider it more likely that the weak highest energy peak is in fact due to one or more electronic transitions plus a quantum of an O–H stretching vibration of a water molecule. In the case of the analogous copper(II) compound this assignment was confirmed by deuteriation (see below). The likely assignments of the bands follows that discussed below for the copper(II) compound.

The spectra of an arbitrary crystal face of $CuSO_4{\cdot}5H_2O$, measured at 290 and *ca.* 18 K along the two extinction directions, are shown in Figure 3(*a*) and (*b*), the low-temperature spectrum of the corresponding deuteriated compounds being shown also. Three major peaks can be resolved, centred at 10 750, 12 900, and 13 450 $cm^{-1}$, with weaker bands occurring at 9 100 and 16 850 $cm^{-1}$. These differ somewhat from the peak positions reported for a crystal of this compound studied at room temperature by Holmes and McClure[20] (10 500, 13 000, and 14 500 cm$^{-1}$). As the band at 16 850 cm$^{-1}$ seemed to us too high in energy for a *d–d* transition coupled to a metal–ligand vibration, we considered the possibility that it could be due to coupling with what is formally an O–H stretching vibration of a water molecule. Weak peaks observed in the spectra of other metal hydrates have been assigned in this way.[21–23] To test this idea, the spectrum of the analogous crystal face of $CuSO_4{\cdot}5D_2O$ was measured and the band at 16 850 cm$^{-1}$ was not observed [Figure 3(*a*) and (*b*)]. This is consistent with the proposed mechanism, as deuteriation should cause a transition coupled to a water stretching mode to shift to lower energy by *ca.* 1 000 cm$^{-1}$ so that it will be obscured under the band centred at *ca.* 13 450 cm$^{-1}$.

The intensity of the *d–d* transitions in the present spectra is derived by coupling with *ungerade* vibrations as the complexes are rigorously centrosymmetric. The four lower energy bands all decrease significantly in intensity on cooling from 290 to *ca.* 18 K in agreement with the fact that here the coupling involves metal–ligand vibrations of comparatively low energy (typically *ca.* 300 cm$^{-1}$).[9] One possible cause of the band at 16 850 cm$^{-1}$ is that the intensity derives from combinations of water vibrations which have the effect of producing a non-centrosymmetric environment of oxygen atoms around the metal ion. An example of such a combination, involving the antisymmetric O–H stretch, is illustrated schematically below for just two *trans* water molecules.



The difference in maxima between vibronically-induced bands built upon the same electronic origin should equal the difference in energy of the intensity-inducing modes. The above interpretation thus suggests that if the band at 13 450 cm$^{-1}$ derives its intensity by coupling with vibrations of energy *ca.* 300 cm$^{-1}$, and is based upon the same electronic origin as the band at 16 850 cm$^{-1}$, then the intensity of the latter band is due to one or more vibrations of energy *ca.* 3 700 cm$^{-1}$. The i.r. spectrum of $CuSO_4{\cdot}5H_2O$ shows a broad peak at *ca.* 3 250 cm$^{-1}$ assigned to O–H stretching vibrations[24] and considering the uncertainty in the band maxima, particularly of the band in question, the agreement between the two values is reasonable. Similar arguments imply that the band at 18 450 cm$^{-1}$ in the spectrum of $CrSO_4{\cdot}5H_2O$ is based upon the same electronic origin as that at 15 500 cm$^{-1}$; here this implies an energy of *ca.* 3 250 cm$^{-1}$ in good agreement with the expected energy of the O–H stretching vibrations. Alternatively, the peaks might be derived by coupling with the combination of internal water vibrations of $a_{1g}$ symmetry.

Either of these mechanisms implies that, in marked contrast to the other bands, the peaks at 18 450 and 16 850 cm$^{-1}$ should show virtually no intensity increase on warming to room temperature, because of the very high energy of the coupling mode. In fact, the peak at 16 850 cm$^{-1}$ cannot even be resolved in the room-temperature spectrum of $CuSO_4{\cdot}5H_2O$ (Figure 2) because of the broadening of the band at 13 450 cm$^{-1}$, which is consistent with the proposed mechanisms. The relative complexity of the co-ordination of the water molecules in the present compounds precludes a quantitative investigation of the above high-energy bands. However, we have recently observed a similar band in the electronic spectrum of the complex $[CuCl_2(H_2O)_2]{\cdot}4PPh_3O$ where the vibrational fine-structure, polarisation behaviour, and intensity of the band do allow the investigation of the relative importance of the above mechanisms, and such a study is currently underway.[25] Clearly, the possibility that bands due to the coupling of *d–d* transitions with internal water vibrations may have significant intensity should be considered in the analysis of the optical spectrum of any metal hydrate complex.

*Band Assignments and Metal–Ligand Bonding in the Complexes.*—The fact that the unit cell of the compounds contains two complexes with quite different orientations of the water molecules, combined with the low effective point group of the chromophores if the hydrogen atoms are taken into account, means that it is impractical to use vibronic selection rules to assign the spectra. The band assignments must therefore rest solely upon chemical arguments, and hence are quite tentative. As expected, the spectra of the two compounds resemble one another quite closely, except that the peaks of the chromium(II) complex occur *ca.* 2 000 cm$^{-1}$ higher in energy. As in both compounds the metal–ligand bond distances in the two independent molecules are similar (Table 2) it seems likely that these have quite similar spectra. For a tetragonally distorted complex with reasonably short axial bonds, such as the present ones, the lowest energy band, at 9 100 and 10 000 cm$^{-1}$ in the copper(II) and chromium(II) complexes, respectively, is expected to be due to the transition $d_{z^2} \rightarrow d_{x^2-y^2}$. The remaining bands are then due to transitions involving the split $t_{2g}$ levels of the parent octahedral complex, with the precise assignment depending on the relative effects of bond length differences and the anisotropy of the π-bonding.

In order to investigate the assignments more fully, and to compare the metal–ligand bonding in the complexes, calculations of the energy levels were carried out within the framework of the angular overlap model[26] using the computer program CAMMAG developed by Gerloch and co-workers.[27] This defines each metal–ligand interaction in terms of parameters $e_\sigma$, $e_{\pi s}$, and $e_{\pi c}$. Here, the last two parameters define the π-interaction in and out of the approximate plane formed by the metal and the water oxygen and hydrogen atoms, respectively. (The ligand-based co-ordinate system was actually defined with respect to axes parallel to the metal–oxygen bond, the hydrogen–hydrogen vector, and the cross-product of these two vectors.) For each complex, the total energy of each *d* orbital was then obtained by summing the effects of all the ligands using the angular overlap matrix appropriate to its geometry and the resulting *d*-orbital energy differences were compared with the observed transition energies.

In deciding the bonding parameters which best conform to the visible spectra of the complexes it is clearly impossible to allow a complete freedom of choice for all the ligand molecules. It was therefore assumed that for each water molecule the π-bonding interaction involving the oxygen 'lone-pair' electrons, $e_{\pi c}$, is one quarter the σ-interaction. A relationship of approximately this kind has been observed for the bonding parameters of many oxygen-donor ligands.[28,29]

It is much harder to predict the likely values of the second π-bonding parameter. As far as the covalent contribution to the bonding goes, this should be close to zero, as the appropriate oxygen *p*-orbital is involved in bonding with the hydrogen atoms. However, various studies on complexes with water[30,31] and other similar ligands such as the acetylacetonate anion[32] have shown that this is often not the case, and in practice values of $e_{\pi s}$ close to those of $e_{\pi c}$ have often been reported.[28,29] In the present case, calculations were carried out assuming that $e_{\pi s}$ is both zero and equal to $e_{\pi c}$.

The differences in bond length were taken into account by assuming that the bonding parameters are inversely proportional to the sixth power of the bond length. Such a relationship is predicted by an electrostatic bonding model, in which the

**Table 5.** Metal–ligand bonding parameters[a] and transition energies ($10^3$ cm$^{-1}$) in the complexes

| | | | | | Transition energies | |
|---|---|---|---|---|---|---|
| Compound | | $10^{-3}e_{\sigma}$ | $10^{-3}e_{\pi c}$ | $10^{-3}e_{\pi s}$ | Calculated | Observed |
| $CuSO_4{\cdot}5H_2O$ | Molecule 1 | 5.80 | 1.45 | 1.45 | 8.2, 11.1, 13.0, 13.8 | 9.1, 10.7, 12.9, 13.5 |
| | | 5.32 | 1.33 | 1.33 | | |
| | | 1.45 | 0.36 | 0.36 | | |
| | | 5.05 | 1.26 | 0.00 | 7.1, 11.0, 12.4, 14.5 | |
| | | 4.63 | 1.16 | 0.00 | | |
| | | 1.26 | 0.32 | 0.32 | | |
| | Molecule 2 | 5.26 | 1.31 | 1.31 | 7.0, 10.3, 12.0, 12.7 | |
| | | 5.15 | 1.29 | 1.29 | | |
| | | 1.65 | 0.41 | 0.41 | | |
| | | 4.58 | 1.14 | 0.00 | 6.1, 10.0, 11.9, 13.2 | |
| | | 4.48 | 1.12 | 0.00 | | |
| | | 1.44 | 0.36 | 0.36 | | |
| $CrSO_4{\cdot}5H_2O$ | Molecule 1 | 7.00 | 1.75 | 1.75 | 9.2, 13.6, 15.7, 16.0<br>(16.6, 16.9)[b] | 10.0, 13.4, 15.5<br>(16.61, 16.97)[b] |
| | | 6.55 | 1.64 | 1.64 | | |
| | | 2.22 | 0.56 | 0.56 | | |
| | | 6.00 | 1.50 | 0.00 | 7.9, 12.9, 14.6, 17.1<br>(15.5, 16.5)[b] | |
| | | 5.61 | 1.40 | 0.00 | | |
| | | 1.91 | 0.48 | 0.48 | | |
| | Molecule 2 | 6.58 | 1.64 | 1.64 | 8.3, 13.1, 15.2, 15.2<br>(16.7, 16.7)[b] | |
| | | 6.55 | 1.64 | 1.64 | | |
| | | 2.44 | 0.61 | 0.61 | | |
| | | 5.64 | 1.41 | 0.00 | 7.1, 12.5, 14.4, 16.0<br>(15.6, 16.4)[b] | |
| | | 5.62 | 1.40 | 0.00 | | |
| | | 2.09 | 0.52 | 0.52 | | |

[a] The bonding parameters of the ligands in each independent molecule of the unit cell were assumed to depend inversely on the sixth power of the metal–oxygen bond distance. The correlation of the bonding parameters with particular ligand molecules may be obtained by reference to Table 2. [b] Spin-forbidden transition energies are given in parentheses; the calculated values were obtained using Racah parameters $B$ = 714 and 722 cm$^{-1}$ for molecules 1 and 2, respectively, with $C = 4.61B$.

water molecules behave like dipoles,[33] and it has been pointed out that a very similar relationship is to be expected even if the bonding is essentially covalent.[34] More importantly, experimental evidence suggests that the *d*-orbital splitting in octahedral complexes tends to vary as the fifth or sixth power of the bond length.[35] Only minor bond length differences occur for the in-plane oxygen atoms, so that the above assumption has only a small effect as far as these ligands are concerned. However, the values chosen for the bonding parameters of the axial sulphate oxygen atoms depend strongly upon the relationship, and these can therefore only be considered quite approximate. The π-bonding parameters of these axial ligands were assumed to be symmetrical about the metal–oxygen axis.

Given the above relationships, and the assignment of the bands at 16 850 and 18 450 cm$^{-1}$ as due to coupling with internal water vibrations, optimisation of the observed transition energies with the band maxima observed in the region 10 750—13 450 cm$^{-1}$ for the copper(II) compound, and 13 400—15 500 cm$^{-1}$ for the chromium(II) compound, was achieved using the bonding parameters listed in Table 5. It is apparent that better agreement between the calculated and observed transition energies occurs if the metal–ligand π-bonding is assumed to be isotropic. The effective ligand-field symmetry is then close to $D_{4h}$, the bands at 13 400 and 10 750 cm$^{-1}$ being due to the transition ${}^2B_{1g}(x^2 - y^2) \rightarrow {}^2B_{2g}(xy)$, and those at 15 500 and 12 900, 13 450 cm$^{-1}$ being due to ${}^2B_{1g}(x^2 - y^2) \rightarrow {}^2E_g(xz, yz)$, respectively, with the slight splitting of the higher energy band of the copper(II) complex probably being due to the resolution of the spectra of the individual molecules in the unit cell. The assumption that $e_{\pi s} = 0$, while probably being chemically more reasonable, produces calculated transition energies in much poorer agreement with experiment. The lowering in symmetry which this implies produces a significantly greater spread in the excited-state energies than is observed experimentally.

The fact that the π-bonding with the water molecules is apparently close to axially symmetric in hydrated copper(II) and chromium(II) sulphate tends to confirm conclusions drawn from the analysis of the electronic spectra of a range of complexes containing co-ordinated water, where it has been found that $e_{\pi c} \approx e_{\pi s}$ in two independent studies.[30,31] The values of the metal–ligand bonding parameters of the copper(II) complex are quite similar to those reported for oxygen ligands in analogous complexes; for instance, the values $e_\sigma$ = 4 520 cm$^{-1}$, $e_{\pi c}$ = 1 450 cm$^{-1}$, and $e_{\pi s}$ = 1 530 cm$^{-1}$ have been reported by Bencini *et al.*[31] for $H_2O$ bonded to $Co^{2+}$ at a distance of 2.087 Å. The value of the σ-bonding parameter is somewhat lower than those found in the present work, which is consistent with the longer bond length.

While the band maxima of the higher energy peaks of copper(II) and chromium(II) sulphate can be reproduced quite well by the reported bonding parameters (Table 4), the calculated values of the lowest energy transitions are significantly lower than those observed experimentally. This implies that the $d_{z^2}$ orbital is lower in energy than expected, and this is consistent with observations on other tetragonally distorted complexes. It is now well established that in planar, four-co-ordinate metal complexes the $d_{z^2}$ orbital is substantially depressed in energy from the value predicted by simple bonding models, the depression being *ca.* 5 000—6 000 cm$^{-1}$ for a copper(II) complex.[36–38] This effect has been rationalised by some workers in terms of configuration interaction between the metal 4*s* and 3$d_{z^2}$ orbitals,[36] and by others using the concept of co-ordination 'voids'.[38] While it is clear that the depression will decrease upon axial ligation, becoming zero in a regular octahedral complex, it is a matter of some interest to see what deviations occur in complexes such as those in the present study which have 'semi-co-ordinated' axial ligands. Considering the comparatively short axial bonds in the present complexes (*ca.* 2.4 Å) the observed discrepancy of *ca.* 1 500 $cm^{-1}$ seems reasonable, agreeing well with the pattern established in a recent study by Deeth and Gerloch.[38] In an investigation of a range of *trans* amino acid copper(II) complexes[39] we recently observed similar depressions of the $d_{z^2}$ orbital, these ranging from *ca.* 3 000 $cm^{-1}$ where the axial ligand bond length is 2.6 Å to *ca.* 6 000 $cm^{-1}$ where it is 3.1 Å.

Because of the isostructural nature of the compounds, the present spectra provide a good chance to compare the ligand bonding parameters of an early with a late transition ion. Despite the significantly longer metal–ligand bond lengths, the bonding parameters of the chromium(II) complex are *ca.* 20% higher than those of the copper(II) compound. This difference, which is similar to that observed in other solution studies,[20] is presumably due to the expanded nature of the *d* orbitals of $Cr^{2+}$ compared with $Cu^{2+}$,[12] this allowing better overlap with the ligand orbitals. If the deviation of the $d_{z^2}$ orbital from its expected energy is indeed due to configuration interaction with the metal 4*s* orbital then this might be expected to be less pronounced in the chromium(II) than the copper(II) complex, as the latter orbital should be relatively high in energy in $Cr^{2+}$. The fractional discrepancy between the calculated and observed transition energies of this band is indeed seen to be marginally less for $CrSO_4{\cdot}5H_2O$ than for $CuSO_4{\cdot}5H_2O$, though the difference is probably too small to be significant.

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