The Absorption Spectra of Chromium(II) Acetate and Copper(II) Acetate

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Copper(II) acetate and chromium(II) acetate have the same binuclear structure, as Fig. 1 shows.[1,2] The two compounds show a magnetic susceptibilities much lower than those of usual monomeric copper(II) and chromium(II) complexes (1.39 B. M.[3] for copper(II) acetate and nearly zero for chromium(II) acetate[4] at room temperature). Some direct interaction, therefore, has been assumed between two metal ions at a distance of 2.64 Å.

Yamada et al.[5] have reported the electronic spectra of copper(II) acetate and other cupric alkanoates[6] in solution and in the crystalline state; they have pointed out that the band observed at 27.3 kK. is characteristic of the binuclear structure.

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[1] J. N. van Niekerk and F. R. L. Schoening, *Acta. Cryst.*, **6**, 227 (1953).

[2] J. N. van Niekerk, F. R. L. Schoening and J. F. deWet, ibid., **6**, 501 (1953).

[3] B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, **1957**, 3837.

[4] W. R. King and C. S. Garner, *J. Chem. Phys.*, **18**, 689 (1950).

[5] S. Yamada, H. Nakamura and R. Tsuchida, This Bulletin, **30**, 953 (1957).

[6] S. Yamada, H. Nakamura and R. Tsuchida, ibid., **31**, 303 (1958).

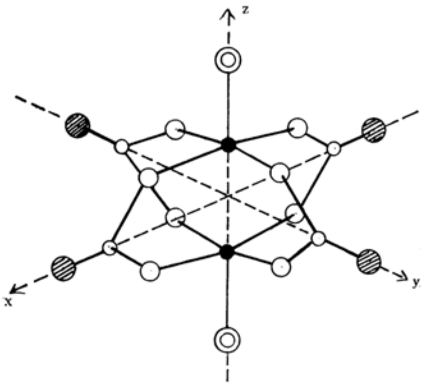

Fig. 1. Molecular structure of chromium- (or copper) (II) acetate.
● Cr or Cu, ○ O, ∘ C, ▨ CH_3
◎ H_2O

The spectrum of chromium(II) acetate in the visible region has been measured by Furlani,⁷⁾ but he has not reported the spectrum of the shorter wavelength region, where one may expect a band corresponding to the band observed at 27.3 kK. in copper(II) acetate.

In this investigation the absorption measurements have been carried out on chromium(II) acetate in solution and in Nujol mull from the visible to the near-ultraviolet region, and the dichroism of the single crystal has been determined.

Experimental

Chromium(II) acetate hydrate, $Cr_2(C_2H_3O_2)_4 \cdot 2H_2O$, was prepared by the method described in "Inorganic Syntheses."⁸⁾ The material was dissolved in 99% ethanol or water which had been distilled in a nitrogen atmosphere, and it was used for absorption measurements. The absorption measurements were carried out with a Shimadzu spectrophotometer model QR-50 using 1 cm. quartz cells. All these procedures were carried out in a nitrogen atmosphere using the apparatus devised for this purpose; the apparatus is shown in Fig. 2. The concentrations of the solutions used for the measurements were determined by the spectrophotometric analysis of chromium⁹⁾ after converting it into chromate ions.

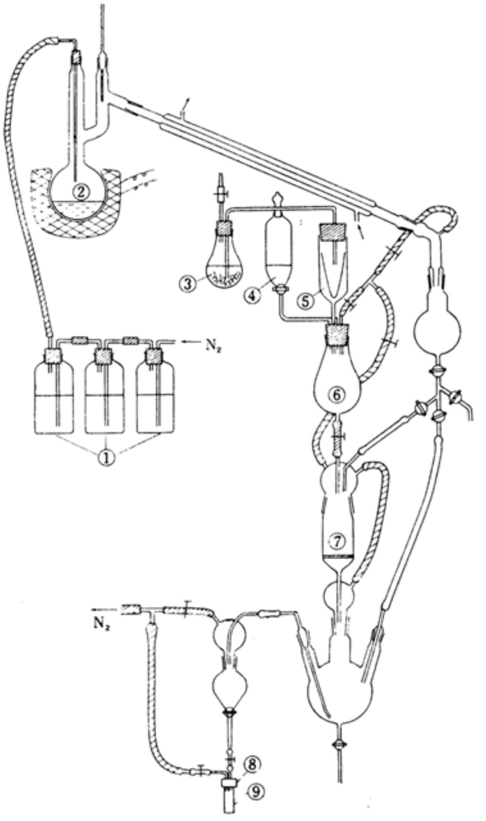

Fig. 2

Chromium(II) acetate anhydrate, $Cr_2(C_2H_3O_2)_4$, was prepared from the hydrate, $Cr_2(C_2H_3O_2)_4 \cdot 2H_2O$, by keeping it at 78°C in vaccuo for 8 hr. in an Abderhalden desiccator. The chromium(II) acetate anhydrate thus obtained showed dark orange color in the powder state. The Nujol mulls of these compounds were prepared in a box filled with nitrogen gas; they were used for the absorption measurements.

Quantitative dichroism measurement was made at room temperature by the microscopic method.¹⁰⁾ The measurement was carried out on the (110) face, using the light polarized along the c-axis and the light polarized perpendicular to it. On the basis of crystal structure analysis, the ratio of K_z to K_{xy} is calculated to be about 1/4.5 for the first band and 4 for the second band, where K represents the molar absorption coefficient, and z refers to the Cr–Cr direction in the molecule.

Results and Discussion

The results of the absorption measurements are shown in Figs. 3 and 4 and in Table I. The alcoholic solution shows the same red color as the crystal and obeys Beer's law. On the other hand, the aqueous solution does not obey Beer's law, and the absorption intensity is much lower than that of the alcoholic solution relative to its chromium concentration. This fact implies that the compound considerably hydrolyzes in an aqueous solution.

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7) C. Furlani, *Gazz. Chim. Ital.*, **87**, 876 (1957).

8) "Inorganic Syntheses," Vol. I, McGraw-Hill, New York (1939), p. 122.

9) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Pub. Inc., New York (1950), pp. 258—260.

10) S. Yamada, *J. Am. Chem. Soc.*, **73**, 1182 (1951); R. Tsuchida and M. Kobayashi, "The Color and the Structure of Metallic Compounds," Zōshindo, Osaka (1944), p. 180 (in Japanese).

However, since the peaks in the two absorption curves are nearly identical, it is obvious that the binuclear molecules still exist in considerable concentration in an aqueous solution. This fact contrasts with the fact that the concentration of the binuclear molecule was observed to be much less in an aqueous solution of copper(II) acetate. The absorption in the visible region agrees with Furlani's result.⁷⁾ In addition to this absorption ($\nu_{max}=20.58$ kK., $\log \varepsilon=1.80$), another absorption ($\nu_{max}=30.77$ kK., $\log \varepsilon=2.22$ with a shoulder at 29 kK.) was newly observed in this experiment. This absorption, which is tentatively named the "second band," seems to correspond with the "second band" observed at 27.3 kK. in copper(II) acetate. The dichroism of chromium(II) acetate is similar to that of copper(II) acetate,⁵⁾ as may be seen in Fig. 4. Thus, the first absorption is more intense in x and y than in z polarization, and vice versa in the case of the second absorption.

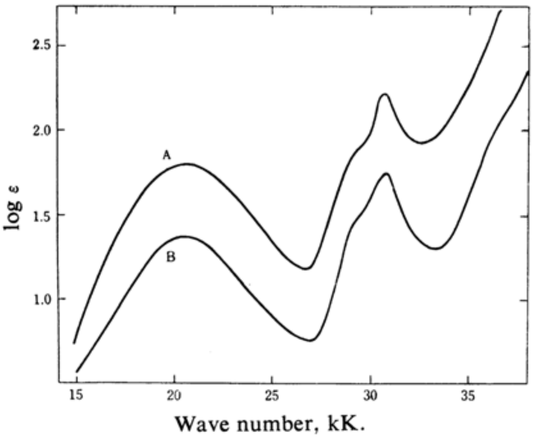

Fig. 3. Absorption spectra of $Cr_2(C_2H_3O_2)_4 \cdot 2H_2O$ in solution: A, in 99% ethanol and B, in water. The extinction coefficient is based on the monomeric formula.

TABLE I. ABSORPTION MAXIMA OF CHROMIUM-(II) ACETATE (in kK.)

	I	II
(1) $Cr_2(C_2H_3O_2)_4 2H_2O$ (Ethanol solution)	20.58	30.77
(2) $Cr_2(C_2H_3O_2)_4 2H_2O$ (Nujol mull)	20.7	30.7
(3) $Cr_2(C_2H_3O_2)_4$ (Nujol mull)	22.0	30.9
(3)—(2)	1.3	0.2

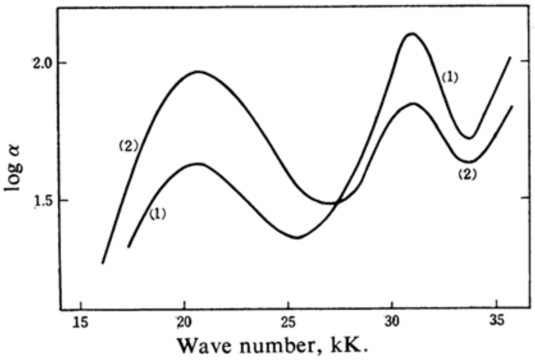

Fig. 4. Absorption spectra of $Cr_2(C_2H_3O_2)_4 \cdot 2H_2O$ in the crystalline state: (1) pale-red polarization and (2) red polarization on the (110) face.

From the frequency and the intensity, the first band of chromium(II) acetate and copper(II) acetate in the visible region can undoubtedly be attributed to the d-d transitions. For the second band of copper(II) acetate, Ross¹¹⁾ has suggested the possibility of a triplet-triplet transition. However, there is no such possibility in the case of chromium(II) acetate, since it is diamagnetic at room temperature. Forster and Ballhausen¹²⁾ attributed both the first and the second band to the d-d transitions on the basis of a molecular orbital scheme. However, the molecular orbital method may not give a good approximation in this case, as will be discussed below, and their conclusions were only tentative. Therefor, the origin of the two bands of both compounds will be the subject of the following discussion.

For this type of compounds, the d-d transitions may be devided into two origins; 1) interatomic transitions such as transitions from a bonding to an anti-bonding orbital, or charge transfers from one ion to another, and 2) transitions in a single ion, which correspond to the origin of a usual ligand field band.

Interatomic d-d Transitions.—Since the interatomic distance between two metal ions is relatively large, the interaction should be weak; Forster and Ballhausen¹²⁾ estimated the overlap integrals of Cu–Cu interaction to be $S(d_{z^2}, d_{z^2})=0.019$, $S(d_{x^2-y^2}, d_{x^2-y^2})=0.002$ and $S(d_{xz}, d_{yz})=0.012$, which are of the magnitude of about $10^{-1}\sim10^{-2}$ of the usual C–C bond. Therefore, the bonding system between two metal ions is best approximated by the valence bond method rather than by the molecular orbital method.*,¹³⁾

According to the valence bond theory, the wave functions of the valence orbitals in a diatomic unit are expressed as;

$$\Psi=(1-\lambda^2)^{-1/2}[2^{-1/2}\{a(1)b(2)+b(1)a(2)\}+2^{-1/2}\lambda\{a(1)a(2)+b(1)b(2)\}] \quad (1)$$

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11) I. G. Ross, *Trans. Faraday Soc.*, **55**, 1057 (1959).

12) L. S. Forster and C. J. Ballhausen, *Acta. Chem. Scand.*, **16**, 1385 (1962).

13) C. A. Coulson, "Valence," Oxford Univ. Press., London (1953), pp. 147—148.

* Discussion was also made of copper(II) acetate on the basis of a similar concept. Cf. M. L. Tonnet, S. Yamada and I. G. Ross, to be published shortly.

for the ground state, where a and b denote atomic wave functions of the different atoms respectively, and λ is a constant which determines the contribution of the ionic term.

In the case of a large interatomic distance, we may neglect the ionic term.

$$\Psi = 2^{-1/2}\{a(1)b(2)+b(1)a(2)\} \qquad (2)$$

Similarly, the next higher singlet state may be expressed as:

$$\Psi' = 2^{-1/2}\{a(1)b(2)-b(1)b(2)\}$$

or

$$2^{-1/2}\{a(1)a(2)+b(1)b(2)\} \qquad (3)$$

The electronic repulsion energies of the two states are calculated from (2) and (3):

$$E(\Psi) = J(ab)+K(ab)$$

$$E(\Psi') = J(aa)-K(ab) \quad \text{or} \quad J(aa)+K(ab)$$

Since we are dealing with the system of large interatomic distance, $J(ab)$ and $K(ab)$ should be much smaller than $J(aa)$.

$$E(\Psi')-E(\Psi) \doteqdot J(aa)$$

This result indicates that the energy of the first spin-allowed transition from the ground state is of the magnitude of $J(aa)$,* which must be larger than 100 kK., as may be roughly estimated from the ionization potentials of the chromium ion.[14]

For the other type of transitions, such as charge transfer from one ion to another, we also have to assign a very high energy to this system, since any charge transfer transition in this system will give rise to a great increase in inter-electronic repulsions, in addition to the energy of the charge separation.

Therefore, the present observed bands are not due to the interatomic d-d transitions.

d-d Transitions in a Single Ion.—To judge from the absorption intensities, the bands under discussion are undoubtedly due to spin-allowed transitions. Therefore, we consider spin-allowed transitions only in this discussion, and, accordingly, the d^4 and the d^9 system can be treated like a d^1 system. In an octahedral field five degenerate d-orbitals are split into triply-degenerate $d\varepsilon$ and doubly-degenerate $d\gamma$ orbitals. In this case only one transition is possible for a d^1-system. As the symmetry goes down from O_h to D_{4h} or C_{4v}, the $d\varepsilon$ and the $d\gamma$ orbital are split, as is shown in Fig. 5: if the tetragonal distortion is considerably large, one can observe two or more separate peaks. However, only one broad band was observed in this region in usual copper(II) and chromium(II) (high spin type) complexes, though these complexes are more or less tetragonally distorted by the Jahn-Teller effect.[15] This fact implies that the tetragonal distortions of these complexes are not large enough to separate the absorption into two distinct peaks. Even if one would assume the larger tetragonal distortion in chromium(II) acetate and copper(II) acetate, the observed value, 8∼10 kK., seems to be too large for the splitting due to the tetragonal distortion.

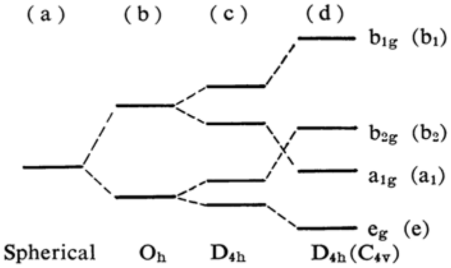

Fig. 5. Energy levels of the d-orbitals.
(c) Weak tetragonal distortion
(d) Strong tetragonal distortion

As Table I shows, the first band of chromium(II) acetate anhydrate shows a remarkable blue shift relative to that of the hydrate. On the other hand, very little blue shift was observed in the second band. This implies that the second band is not as sensitive to the change in the tetragonality of the ligand field as the first band is. Therefore, the second band is not likely to be one of the ligand field bands, since if the band were split and shifted by the effect of the tetragonal distortion, it would show a considerable shift upon the change in the tetragonality.

The result of the dichroism measurements also support the above conclusion. If both the observed bands in the visible and near-ultraviolet region were due to the d-d transitions, the most probable assignment should be b_1-a_1 and b_1-e transitions for the first and the second band respectively, as may be seen in Fig. 5. Since the electric vectors transform like E(x, y) and $A_1(z)$ in the symmetry of C_{4v}, the second band, which has been attributed to the b_1-e transition, would be more intense in x and y than in z polarization. However, the experiments show that the second absorption is z-polarized in both compounds, as is shown in Fig. 4 and Ref. 5. Therefore, it is reasonable to assign the b_1-e transition to

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* In this system the differences in the nuclear attractions and kinetic energies of the two states are negligibly small relative to $J(aa)$. The Coulomb integral, $J(aa)$, corresponds to the difference between the first and the second ionization energy of the ion.

14) "Atomic Energy Levels," Natl. Bur. Standards, Circ. 467, Vol. 2 (1952), p. 14.

15) T. M. Dunn, "The Visible and Ultra-violet Spectra of Complex Compounds," in J. Lewis and R. G. Wilkins, ed., "Modern Coordination Chemistry," Interscience Pub. Inc., New York (1960), pp. 253—261 and references therein.

the first absorption (x, y-polarized) rather than to the second. On this assumption, one can elucidate the fact that the first absorption band of chromium(II) acetate and copper(II) acetate are considerably more intense than the ligand field bands of usual monomeric chromium(II) (high spin type) and copper(II) complexes. Since the b_1-e transition is allowed in the x, y-plane in C_{4v} symmetry, whereas all the d-d transitions in D_{4h} symmetry are forbidden, one can expect a higher absorption in the former case than in the latter. The above discussion may be regarded as essentially correct, even though in these compounds the deviation from D_{4h} is not very large and the vibronic origin is not negligible.

For the origin of the second band, no definite conclusion can be drawn at present. However, since the second band is characteristic of this type of binuclear configuration, some orbitals, which are characteristic of this configuration, must be responsible for the origin of this band. For instance, the ligand and the metal atoms constitute planar 8-membered rings in this molecule, and some electronic transitions among the molecular orbitals of π-orbital systems on these rings may possibly be one of the origin of the second band. In this connection, however, it seems worth mentioning that cupric formate tetrahydrate and cupric benzoate trihydrate, which contain infinite chains, each consisting of alternate cupric ions and formate⁶⁾ or benzoate ions¹⁶⁾, show no absorption band corresponding to band II.

Summary

The electronic absorption spectra of chromium(II) acetate have been determined in ethanol and Nujol mull in the region between 10 and 40 kK. Dichroism in that region has also been determined with a single crystal of the compound. A new absorption band, which has not previously been observed, has been found at about 30.77 kK. (log ε 2.22), in addition to a band at about 20.58 kK.

The origins of these bands have been discussed in relation to the absorption bands of copper(II) acetate.

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16) S. Yamada, H. Nishikawa and S. Miki, to be submitted.