The Electronic Single Crystal Spectrum of Binuclear Rhodium(II)acetate Hydrate Rh$_2$(CH$_3$COO)$_4$·2H$_2$O

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Z. Naturforsch. 33b, 1095–1098 (1978); received July 17, 1978

Rhodium(II)acetate Hydrate, UV

The visible and near-ultraviolet spectrum of rhodium(II)acetate hydrate single crystals has been measured in a temperature range from 10 K to 295 K. Two band systems centered at 17,000 cm$^{-1}$ and 22,000 cm$^{-1}$ have been found, both consisting of components polarized parallel to and perpendicular to the rhodium-rhodium z-axis. Polarizations, intensities and temperature dependences are consistent with an assignment of z-polarized $a_g \rightarrow a_u$ and $xy$-polarized $e_g \rightarrow b_{2g}$ transitions for the lower energy band. For the higher energy band it could not be determined definitely whether only the $b_{2g} \rightarrow b_{2u}$ and $e_g \rightarrow b_{2u}$ transitions give rise to the $z$- and $xy$-polarization directions, respectively, or if $b_{1g} \rightarrow b_{2u}$ and $e_g \rightarrow b_{2u}$ also make a contribution.

Introduction

Rhodium(II)acetate hydrate Rh$_2$(CH$_3$COO)$_4$·2H$_2$O is isostructural with copper(II)acetate hydrate [1]. Both are members of a large group of homonuclear acetate complexes, where four acetate bridges coordinate with two transition metal ions. The structure is shown in Fig. 1. The Rh–Rh distance is 2.45 Å, smaller than in the pure metal. The space group is C$_{2h}$ = C2/c, the local symmetry of each Rh$^{2+}$-ion is C$_{4v}$. This results in a D$_{4h}$-symmetry for the whole complex. Since the hydrate of rhodium(II)acetate is isostructural with that of copper(II)acetate, it can be assumed that the Rh–Rh axes in the crystal are oriented as in the copper(II)acetate hydrate crystal, so the direction cosines are (0.716, ± 0.564, −0.410) relative to the crystallographic axes a, b, c', where c' is perpendicular to a and b [2].

The electronic spectrum in solution shows two bands at 17,040 cm$^{-1}$ and 22,370 cm$^{-1}$ [1]. These bands are also found in the spectra of different adducts of rhodium(II)acetate [3, 4]. To assign these bands, investigations on single crystal spectra are necessary. The temperature dependence of the spectra would give some further information.

Experimental

Rh$_2$(CH$_3$COO)$_4$·2H$_2$O was prepared by the method of Johnson et al. [5] with slight changes [6]. Small single crystals were grown by allowing a drop of aqueous solution to evaporate between thin quartz discs (0.5 mm). Single crystals were selected under a polarization microscope and mounted for measurements still attached to the disc. The crystals were oriented between crossed polarizers along the two extinction directions. Absorption measurements were carried out with a double beam absorption spectrometer suited for polarized microoptical investigations of small crystals (min. size 10$^{-3}$ mm$^3$) in the visible and near-ultraviolet spectral range [7]. A He-cryostat was used to cool the sample down to 10 K, with the quartz discs fixed to the cooling body of the cryostat [8]. For determining the crystal faces used for spectroscopic measurements, the crystals were removed from the discs and fastened to thin quartz threads for Weissenberg X-ray investigation.

Polarized electronic spectra

The visible and near-ultraviolet spectra [6] of hydrated rhodium(II)acetate crystals are shown in Fig. 2. The crystal thickness was determined from interference figures.
For the investigated (101) face the relations between the intensities along the crystal extinction directions (Pol 1 and Pol 2) and the molecular xy- and z-orientations can be found by symmetry arguments, since any (h0l) face contains the twofold axis of the monoclinic system. Because of the $D_{4h}$ symmetry of the molecule, $I_x = I_y = I_{xy}$ can be assumed. Thus the supposed direction cosines are:

$$I_1 = I_z$$
$$I_2 = 0.32 I_z + 0.68 I_{xy}$$

(1)

In Fig. 2 the crystal spectra for the (101) face are shown for the directions Pol 1 and Pol 2 at 10 K and 295 K. The experimental data show that the integral intensities of the absorption bands slowly grow as the temperature decreases and that the half-widths drop. One also observes a slight, but distinctive blue-shift of the intensity maxima at low temperatures.

With regard to eq. (1) one of the two components Pol 1 and Pol 2 must be a "pure" spectrum ($I_1 = I_z$). A comparison of their relative maximal intensities and their envelopes shows that the Pol 1-component belongs to the pure spectrum. Thus, at 10 K there are four different bands; a $z$-polarized band at 16,100 cm$^{-1}$, an $xy$-polarized band at 17,300 cm$^{-1}$, a second $z$-polarized band at 21,500 cm$^{-1}$ and another $xy$-polarized band at 23,500 cm$^{-1}$.

**Discussion**

The observed absorptions can be classified in the framework of an one-electron-model applied to the 4$d$-systems of the two rhodium ions. Since the Rh–Rh distance is small, one expects a considerable covalent splitting of molecular bonding and anti-bonding terms*. Classified according to the irreducible representations of the symmetry group $D_{4h}$ these terms are $a_{1g}, e_{1u}, e_{2g}$ and $a_{1g}, e_{1u}, e_{2u}$, respectively. Their relative energetic positions are qualitatively shown in Fig. 3, left side. The additional influence of the surrounding ligands, which are arranged in a quasi octahedral symmetry with a tetragonal distortion on each metal ion, modifies the $D_{4h}$ terms into the intermediate scheme.

On the other hand (right side of Fig. 3) starting with the term-splitting due to the octahedral ligand field, followed by symmetry reduction to $D_{4h}$ and finally by metal-metal interaction one gets the intermediate scheme also.

For the actual case of the rhodium(II)acetate hydrate, one has to take into account both covalent and ligand field effects of comparable magnitude. An essential feature of the intermediate term scheme proposed in Fig. 3 is that the metal-metal bonding effect is not as large for the $e_u$ and $e_g$ terms as for the others, so that these terms are the lowest [6]. In the ground state the 14 4$d$-electrons available fill up the one-electron states to the configuration $(e_u)^4(e_g)^4(a_{1g})^2(b_{2g})^2(b_{1g})^2$ with $b_{1g}$ the highest occupied level.

The integral intensity of the absorption bands does not decrease with decreasing temperature but is slightly increasing. Therefore only parity allowed

* Results of Raman measurements show evidence for metal-metal-resonance [9].
transitions are suitable for assignments. According to Fig. 3 six parity allowed one-electron transitions are possible.

The $z$-polarized absorption band at 16,100 cm$^{-1}$ is assigned to the transition $a_{1u} \rightarrow a_{2u}$, the $xy$-polarized band at 17,300 cm$^{-1}$ arises from the transition $e_g \rightarrow a_{2u}$. This classification explains the polarization of these two bands and also the fact that these bands are depending greatly on the nature of the ligand [4, 5], for $a_{2u}$ originates from the essentially $z$-oriented $d_{z^2}$-state. The $z$-polarized band at 21,500 cm$^{-1}$ has to be assigned to the transition $b_{2g} \rightarrow b_{1u}$, the 23,500 cm$^{-1}$ $xy$-transition to $e_g \rightarrow b_{1u}$.

There exist two more possible transitions in this scheme, $b_{1g} \rightarrow b_{2u}$ and $e_g \rightarrow b_{2u}$, probably hidden under the bands at 21,500 cm$^{-1}$ and 23,500 cm$^{-1}$, respectively. It can be assumed that the splitting of the odd $b_{1u}$ and $b_{2u}$ states and the even $b_{2g}$ and $b_{1g}$ states is of the same order and relatively small in comparison to the splitting caused by metal-metal interaction and tetragonal distortion. Therefore the energy difference between $b_{1u}$ and $b_{2u}$ should result in a broadening of the absorption band at 23,500 cm$^{-1}$. For the 21,500 cm$^{-1}$ band one would expect a doubling of the maximal intensity in comparison to the 23,500 cm$^{-1}$ band and no broadening. This is exactly what is observed.

Decreasing temperature causes a reduction of the intramolecular metal-metal distance which entails a stronger interaction between the metal ions. This leads to an increasing splitting of odd and even terms and to a higher mixing of the orbitals of the two centers. For the absorption spectra one expects a blue shift of the intensity maxima and growing integral band intensities, in accordance with the observed behavior.

Charge transfer transitions would have to lie beyond 30,000 cm$^{-1}$, by comparison with the charge transfer assignments made for the copper(II)-acetate hydrate [10]. A transition of high intensity at 45,000 cm$^{-1}$ observed by Dubicki in the solution spectrum could be connected with charge transfer [4].

Further information could be obtained from X-ray determination of the Rh–Rh distance at varying temperatures and spectroscopic investigation under high pressure. This could be the basis for further discussion and detailed calculations.