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Electronic Absorption Spectrum of *trans*-Diaquabis[(±)-hydrogen malato]cobalt(II) Dihydrate Crystals

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Recently, Karipides [1] has measured the crystal structure of *trans*-diaquabis[(±)-hydrogen malato]-cobalt(II) dihydrate, $[Co((\pm)C_4H_5O_5)_2(H_2O)_2]\cdot 2H_2O$, by X-ray diffraction. However, its electronic structure has not been studied extensively so far. We have measured here the electronic absorption spectrum and discuss the experimental results by using the ligand field theory and the radial wave function of non-free cobalt(II).

Suitable crystals of the title compound for spectrum measurements were grown by evaporation of an aqueous solution of the salt which had been prepared from the reaction of cobalt(II) carbonate and (±)-malic acid, and in which some seed crystals were sown. The dimensions of the crystal sample were about 0.5 × 0.5 × 0.8 mm.

The electronic absorption spectrum of the title crystal was measured at room temperature in the region of 6000 ~ 30000 cm^{-1} using the absorption spectrograph for small crystals which was made by the Geochemistry Institute of the Chinese Academy of Sciences [2]. The experimental results are shown in Fig. 1. The low-symmetry crystal field splitting of the spectrum is evident.

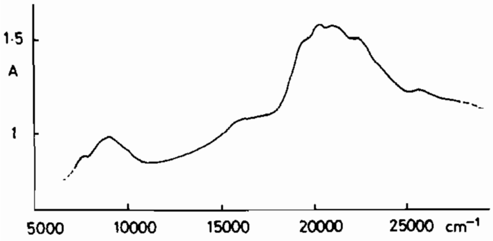

Fig. 1. The electronic absorption spectrum of $[Co((\pm)\text{-}C_4H_5O_5)_2(H_2O)_2]\cdot 2H_2O$.

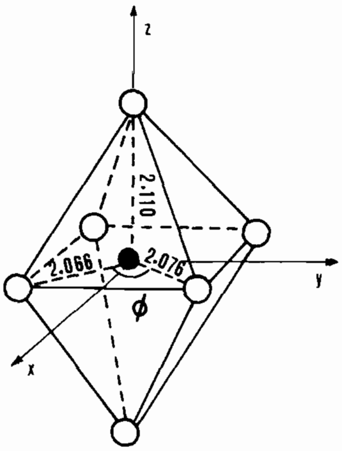

Fig. 2. Coordination of Co^{++} with D_{2h} symmetry in $[Co((\pm)\text{-}C_4H_5O_5)_2(H_2O)_2]\cdot 2H_2O$.

In recent years some investigators were interested in the radial theory of transition metal complexes. Zhao *et al.* [3–5] studied the electronic structure of some complexes of the first transition series by empirical double-ζ radial wave functions. Monro [6] proposed the scaling theory of solids under hydrostatic pressure. Zhang *et al.* suggested the scaling radial theory [7–9] of non-free ions, and proposed the scaling double-ζ radial wave functions of non-free Co(II) [8], Mn(II) and Cu(II) [9]. For cobalt(II) with hexaoxygen coordination, the 3d-radial wave function can be written as [8]:

$$R_{3d}(r) = 0.53517\ \mathrm{STO}(5.6684) + + 0.68259\ \mathrm{STO}(1.8115)$$

According to the calculation formula about double-ζ function [7] and with a DJS-320 computer, we obtained

$$\begin{aligned}
\langle r^2\rangle &= 2.36049\ \text{a.u.}\\
\langle r^4\rangle &= 14.1156\ \text{a.u.}\\
B &= 913.84\ cm^{-1} \qquad (1)\\
C &= 3239.7\ cm^{-1}\\
\zeta_{3d} &= 442.75\ cm^{-1}
\end{aligned}$$

Karipides [1] determined that the Co^{++} in the crystal is hexaoxygen coordinated, *i.e.* two carboxylate, two hydroxyl and two water molecules. Co^{++} occupies a D_{2h} symmetric side approximately, $R_{\parallel} = 2.11$ Å, $R_{\perp} = 2.07$ Å and $\phi = 77.02°$ (see Fig. 2).

According to a complete weak field scheme, all transition bands of quartet states of d^7 configuration in D_{2h} symmetry were calculated with Karipides' crystal structure data and eqn. 1. The spin-forbidden

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TABLE I. The Electronic Absorption Spectrum of $[Co((\pm)\text{-}C_4H_5O_5)_2(H_2O)_2]\cdot 2H_2O$.

Assignment	Calcd.	Obsd.	Assignment	Calcd.	Obsd.
$^4B_{3g}(^4T_{1g}, {}^4F)$	0		$^4B_{3g}(^4T_{1g}, {}^4P)$	18200	19400
$^4B_{2g}(^4T_{2g}, {}^4F)$	7100	7000	$^2T_{1g}(^2P)$	20000	20200
$^2E_g(^2G)$	8300		$^2A_{1g}(^2G)$	21090	21090
$^4A_{1g}(^4T_{2g}, {}^4F)$	8430	8800	$^4B_{1g}(^4T_{1g}, {}^4P)$	22700	22100
$^4B_{3g}(^4T_{2g}, {}^4F)$	8700		$^4B_{2g}(^4T_{1g}, {}^4P)$	22870	
$^2T_{1g}(^2G)$	14200		$^2T_{2g}(^2D)$	24300	25500
$^2T_{2g}(^2G)$	14900		$^2T_{2g}(^2H)$	24340	
$^4B_{1g}(^4A_{2g}, {}^4F)$	15300	16800	$^2T_{1g}(^2H)$	24500	

transition bands of doublet states were calculated in approximate O_h symmetry because the transitions are so weak that an O_h approximate treatment is enough to compare with the experimental results. Here the ligand oxygen atoms were regarded as point charges with $q = 1.06$ and point dipoles with $\mu = 0.961$ D [9]. Thus a polarization factor [9] can be obtained, namely, $P^{(2)} = 1.4431$ and $P^{(4)} = 1.7143$. Covalence factor was considered an adjustable parameter and taken as $N^2 = 0.98$.

The results calculated are shown in Table I. It can be seen that the values calculated are in agreement with the experimental results. This implies that the electronic structure of the compound is in agreement with its crystal structure.

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