

Notes

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Electronic Absorption Spectra of Tetragonal and Pseudotetragonal Cobalt(II). III. $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 2\text{D}_2\text{O}$

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The magnetic structure of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, which is antiferromagnetic,^{1,2} has ferromagnetic linear chains coupled antiferromagnetically. The magnetic susceptibility has orthorhombic symmetry and the principal directions of the susceptibility in the ac plane nearly coincide with the Co-Cl bonds.^{3,4} Oguchi⁵ reanalyzed some of the data and placed the first excited Kramers doublet 260 cm^{-1} above the ground state.

The optical spectrum has been reported by Musa and Hlevca⁶ using unpolarized light, with an analysis based on a cubic field. Lawson⁷ reported polarized measurements, for light incident on the (110) face but made an analysis assuming a cubic crystal field. In the present paper we report the results of a spectroscopic study with polarized light incident on three different crystal faces.

Crystal Structure of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$. The morphology of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ crystals has been described by Neuhaus⁸ and the crystal structure has been determined by Morosin and Graeber.⁹ Figure 1 shows projections of the arrangement on the three crystal faces (bc , $a'b$, $a'c$) chosen for the absorption measurements.

Morosin¹⁰ has reported the temperature dependence of the crystal structure and the contraction of the lattice is quite anisotropic. From 300 to 80 K the contraction is linear and amounts of 1% along a , 0.65% along b , and 0.15% along c .

Experimental Section

Single crystals of cobalt chloride dihydrate were grown by slow evaporation of a saturated aqueous solution of AnalaR $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ at 70° . Growing periods of 1-4 months gave needles with dimensions as large as $5 \times 5 \times 30 \text{ mm}$. Growth is parallel to [001] with well-developed (110) faces.

Crystals of the deuterate were prepared similarly from a solution obtained by dissolving zone-refined CoCl_2 in D_2O , with no attempt to prevent exchange with atmospheric water during evaporation. Contamination by H_2O was less than 1%.

An orthogonal a' , b , c axis system was chosen for the spectroscopic measurements. $a'b$ faces were obtained by sectioning a large crystal, embedded in polyester, followed by hand polishing. The extinction directions define the axes b and a' . With a' and b axes located, other crystals were sectioned along these directions, parallel to c . Extinction directions in the $a'c$ plane were found to lie approximately 30 and 120° to c and labeled c^* and a^* in the figures.

Results and Discussion

Gross Spectral Features. Similarly to the hexahydrate the polarized crystal spectra contain three types of bands: water overtones, normal crystal field bands, and anomalous crystal field bands. In the near-infrared region six sets of polarized spectra were measured for both $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 2\text{D}_2\text{O}$ in order to distinguish electric and magnetic dipole features. The ultraviolet absorption edge lies at approximately $35,000 \text{ cm}^{-1}$.

The Near-Infrared Region. The low-temperature polarized infrared spectra of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 2\text{D}_2\text{O}$ are given

Table I. Oscillator Strengths ($\times 10^{-6}$) of Infrared Bands in $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$

Polarizn ^a	Position ^b		
	6150 cm^{-1}	8200-8500 cm^{-1}	12,000 cm^{-1}
$a'c \parallel a^*$	1.5	2.5	~ 0
$a'c \parallel c^*$	2.5	4.0	~ 0
$bc \parallel b$	~ 0	2.5	2.0
$bc \parallel c$	3.5	2.5	~ 0
$a'b \parallel a'$	4.0	3.5	~ 0
$a'b \parallel b$	~ 0	2.0	2.5

^a Crystal face and direction of the electric vector. ^b Franck-Condon maxima at 10 K.

in Figure 2. The structure due to water overtones in the spectra has been subtracted to simplify the spectra. The complete intensity data for the dihydrate are listed in Table I. Only the low-temperature data are quoted because the bands overlap at room temperature.

We can identify the 6150-cm^{-1} band as a b -polarized magnetic dipole transition superimposed on a weaker ac -polarized electric dipole (vibronic) band. Overlap of the 8200 - and 8500-cm^{-1} bands makes impossible the measurement of their individual intensities and the sums of each are listed in Table I. It appears that these bands possess both electric and magnetic dipole contributions.

The results listed in Table I are reproduced by the spectra of $\text{CoCl}_2 \cdot 2\text{D}_2\text{O}$, with the exception of the $12,000\text{-cm}^{-1}$ band. Deuteration shifts it to lower energy and also weakens it, characteristics of the anomalous crystal field bands discussed in another paper.¹¹ It is therefore assigned to a $d-d$ transition induced by the symmetrical water stretching mode.

The two possible assignment schemes for the infrared region are shown in Figure 3, and the magnetic dipole polarizations are indicated. The z -polarized magnetic dipole character of the 6150-cm^{-1} band poses problems of interpretation within an assumed D_{4h} model. It can only be derived from the transition ${}^4E_g^a \rightarrow {}^4E_g^b$, which requires that this band be assigned to an upper state ${}^4E_g^b$. However the evidence in Figure 2 and Table I strongly suggests that only one excited state is present in this region while there are two states in the region 8200 - 8500 cm^{-1} . Consideration of the orthorhombic field does not help the situation as this requires an unreasonably large splitting of the ${}^4E_g^b$ state to place one level at 6150 cm^{-1} and the other close to the ${}^4B_{2g}$ state. We notice that under assignment I in Figure 3 there is z -polarized intensity associated with the transition ${}^4A_g \rightarrow {}^4A_g$, suggesting this scheme as a possible assignment. However, if we trace the origin of this polarization back to D_{4h} , we see that it comes from the z -polarized transition ${}^4A_{2g} \rightarrow {}^4A_{1g}$ and there are no such transitions available in tetragonal divalent cobalt which could conceivably be considered to provide a source of intensity in the C_{2h} field. We are left with assignment II with the assumption of a very large orthorhombic field which splits the ${}^4E_g^b$ state by about 2000 cm^{-1} .

The Visible Region. The results obtained at 10 K are shown in Figure 4. Apart from the confusion between a^* , c^* polarizations and a' , c polarizations, three different spectra are identified, with one appropriate to each of the crystal directions a' , b , and c .

The tetragonal contribution to the crystal field is shown by the highly anisotropic absorption found for either face containing the b axis. However, unlike the hexahydrate, the absorption in the $a'c$ (xy) plane is also anisotropic, which is an indication of the importance of the orthorhombic field in

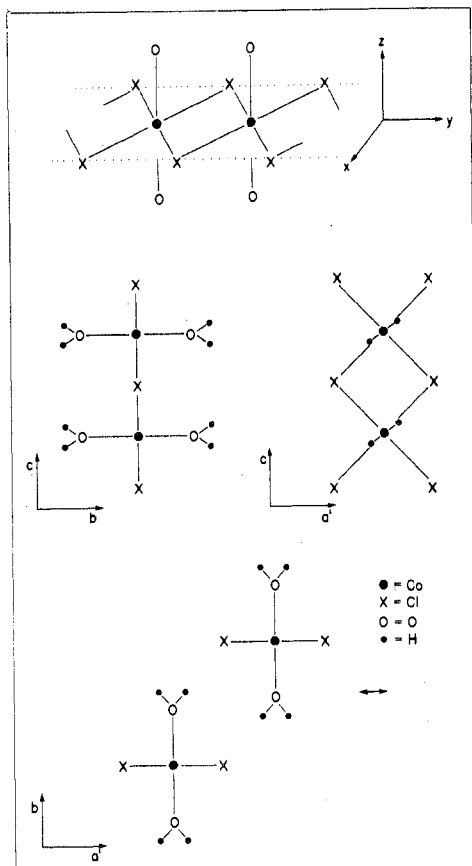


Figure 1. Projections of $(\text{CoCl}_2 \cdot 2\text{H}_2\text{O})$ on bc , $a'c$, and $a'b$ crystal faces.

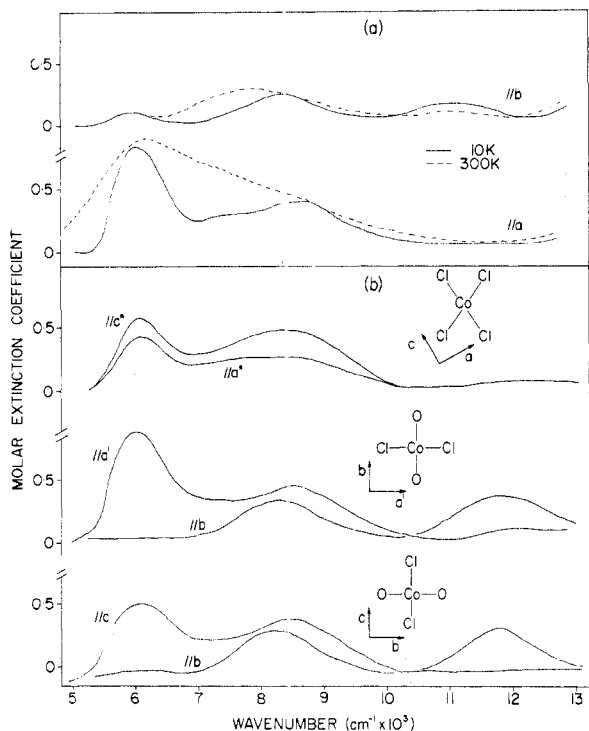


Figure 2. (a) Polarized absorption spectra of $\text{CoCl}_2 \cdot 2\text{D}_2\text{O}$ ($a'b$ face) in the near-infrared region. (b) Polarized absorption spectra of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ in the near-infrared region (10 K).

this crystal. Besides the anomalous bands (considered separately below) there is a strongly polarized band at $25,300 \text{ cm}^{-1}$, which is more intense at low temperature. Its polarization is parallel to a' , *i.e.*, perpendicular to the CoCl_2 -chain

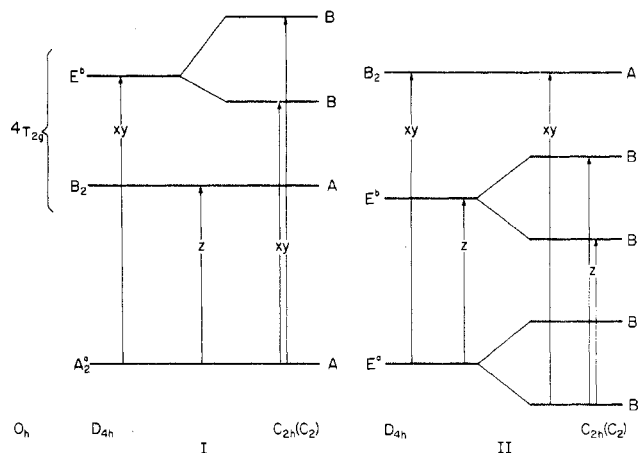


Figure 3. Assignment schemes for the near-infrared region of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$. All states are gerade quartets and the polarizations of the allowed magnetic dipole transitions are indicated (direction of the magnetic vector).

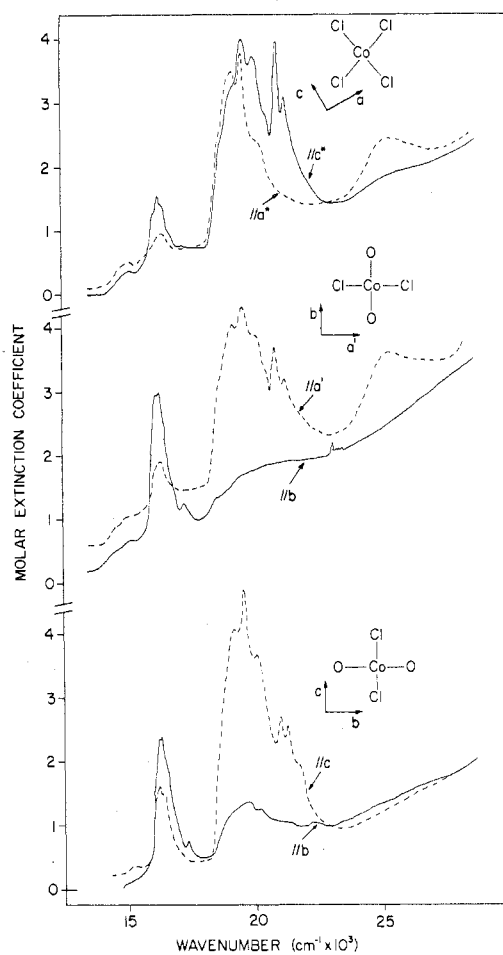


Figure 4. Polarized absorption spectra of $\text{CoCl}_2 \cdot 2\text{D}_2\text{O}$ (10 K).

and it shows no deuterium effect. There is a band with a similar temperature dependence in the same region of the spectrum of CoCl_2 ,¹² which was assigned tentatively to a $\pi\text{Cl} \rightarrow \text{d}$ charge-transfer band.

There are two main absorption regions, a very broad band with maximum near $19,800 \text{ cm}^{-1}$ and a less intense and narrower band near $16,400 \text{ cm}^{-1}$. The intensities are given in Table II. If the assignments for $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ are reversed, placing ${}^4\text{E}_g^c$ higher in energy than ${}^4\text{A}_{2g}^b$, then the large bandwidth of the $19,800\text{-cm}^{-1}$ vibration could be an effect of an orthorhombic splitting. There is additional support for an

Table II. Positions and Intensities of Visible Bands in $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$

Position, ^a cm^{-1}	Oscillator strength ^b		
	$f_{a'}$	f_b	f_c
16,400	2.0	7.5	6.5
19,800	26	3.5	37

^a Centroid at 10 K. ^b Measured at 10 K in units of 10^{-6} ($\pm 10\%$). $f_{a'}$, f_b , and f_c refer to the appropriate polarizations with data taken from $a'b$ and bc faces only.

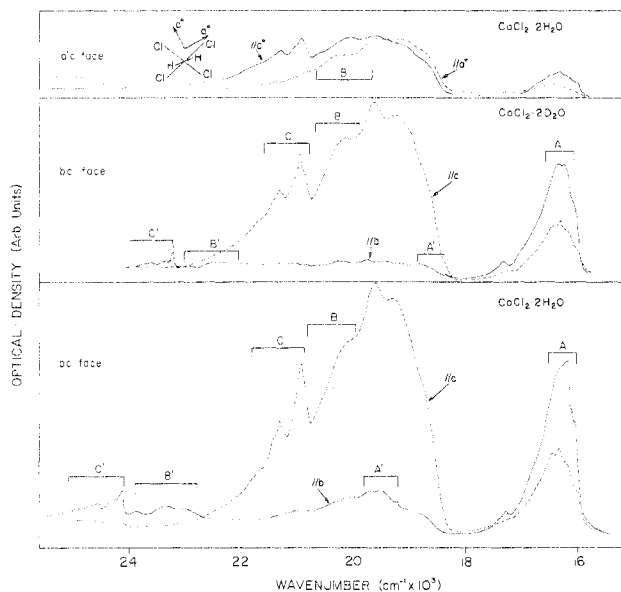


Figure 5. Polarized absorption spectra of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 2\text{D}_2\text{O}$ (10 K) showing details of the anomalous crystal field bands.

appreciable splitting from a consideration of the anomalous crystal field bands, given below.

Crystal Field Parameter. As the ${}^4\text{B}_{2g}$ state cannot be definitely located, we cannot assign a value to Dq . If we assume that it is near $14,500 \text{ cm}^{-1}$ (see Figure 4), then its separation from $8,200 \text{ cm}^{-1}$ (assignment I) gives $Dq = 630 \text{ cm}^{-1}$ while its separation from 6150 cm^{-1} (assignment II) gives $Dq = 835 \text{ cm}^{-1}$. Using both of these values and a range of positive and/or negative D_s and D_t values no reasonable fit of the observed bands in the near-infrared and visible regions could be obtained. We conclude that the effect of the latter is so large that discussion of the assignments in terms of a quantitative tetragonal field theory is not warranted.

The Anomalous Bands. As with the spectrum of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ there are bands in the spectrum of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ which can be assigned to the symmetrical water vibration acting as a perturbing vibration which removes the center of symmetry. From a comparison of the various polarized spectra of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 2\text{D}_2\text{O}$ we can assign four bands in this way. The first is in the near-infrared region, near $12,000 \text{ cm}^{-1}$ in the spectrum of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, mentioned above. The other three occur in the visible region and they are denoted A', B', and C' in Figure 5. The associated normal crystal field bands are shown in A, B, and C. In each case, for the hydrate, the anomalous bands are 3200 cm^{-1} to higher energy. For the deuterate the shift is about 2300 cm^{-1} .

In every case the anomalous bands occur only in b polarization; *i.e.*, they are polarized in the same direction as the symmetrical stretching mode (see Figure 1). The effectiveness of perturbation is greatest for B' and C' (see Figure 5). Now, the state represented by band C must be one or more doublet levels arising, most probably, from the ${}^2\text{P}$ term. Clearly, this requires spin-orbit mixing with the nearby quartet state (B-B'

pair) and, from the similarity of the intensities in bands B' and C', the doublet and quartet states are very strongly mixed.

Although the role of the water vibration in promoting the electronic transition on the cobalt ion appears to be clearly established, the polarizations of the bands A' and B' are not consistent with the expected orbital symmetries of the states A and B. If A is assigned to ${}^4\text{A}_{2g}$ (${}^4\text{A}_g$ in C_{2h}), then B must come from ${}^4\text{E}_g$ (${}^4\text{B}_g$ in C_{2h}) and the a_u symmetrical water stretching mode coupled to each of these states should give rise to opposite polarizations for A' and B', which is contrary to observation.

The presence of more than one excited quartet state under the broad band is shown by the B-B' relationship and the change of polarization in the spectrum of the $a'c$ face (see Figure 5). It is not surprising therefore that efforts to fit the band energies using tetragonal symmetry fail.

Registry No. $\text{CoCl}_2 \cdot 2\text{D}_2\text{O}$, 52918-71-5; $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, 38722-37-1.

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Bimetallic Iron Carbonyl Derivatives of Bidentate Phosphine Ligands

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In preparing a number of bimetallic derivatives, the photochemical reaction of $\text{Fe}(\text{CO})_5$ with a series of bidentate phosphine ligands $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_n\text{P}(\text{C}_6\text{H}_5)_2$, $n = 1, 2, 3$, and 4, was examined. For the $n = 2, 3$, and 4 phosphines, the course of the reaction is similar and a large scale preparation of the principle product $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_n\text{P}(\text{C}_6\text{H}_5)_2[\text{Fe}(\text{CO})_4]_2$, $n = 2, 3$, and 4, was developed. For the $n = 2$ phosphine smaller scale preparations of the principal product had previously been reported.^{1,2}

In the case of the $n = 1$ phosphine, the reaction is more complex and a second major product $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2\text{Fe}_2(\text{CO})_7$ is produced. This product alternatively can be prepared photolytically either from $\text{Fe}_2(\text{CO})_9$ and the $n = 1$ phosphine or from the $n = 1$ bimetallic derivative. The characterization data for this unique product are compatible with a structure formally derived from an isomer of $\text{Fe}_2(\text{CO})_9$ containing only one bridging ligand and four terminal ligands in which the phosphine ligand replaces one terminal carbonyl on each iron atom and serves as a bridging ligand.³ The length of the methylene bridge of the phosphine ligand is apparently important in the formation of this compound since the $n = 2, 3$, and 4 phosphines do not readily form analogous derivatives.