

Linear and Circular Dichroism in Single Crystals of Cobalt(III) Histidinate Complex Isomers

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Crystal linear and circular dichroism spectra in the visible range for two bis(histidinato)cobalt(III) complex isomers, all-*cis*- and *trans*-amine, have been investigated.

It is shown that spectral assignments based on a given model can be verified independently through modulated polarization spectroscopy on crystals of known structure. Thus earlier evaluations of cubic ligand field parameters for the three coordinating groups of histidinate, amine, imidazole and carboxylate, are supported through this study of solid state dichroisms.

Histidinate has three potential metal binding sites: the amino nitrogen atom, one of the imidazole nitrogen atoms and a carboxylate oxygen atom. In case of tridentate chelation in an octahedral complex only *facial* attachment is possible and thus a bis(histidinato)cobalt(III) complex gives rise to five geometrical isomers: (*trans*-imidazole, *cis*-amine, *cis*-carboxylate), (*trans*-amine, *cis*-imidazole, *cis*-carboxylate), (*trans*-carboxylate, *cis*-amine, *cis*-imidazole), (*cis*-imidazole, *cis*-amine, *cis*-carboxylate), and (*trans*-imidazole, *trans*-amine, *trans*-carboxylate) denoted *trans*-i, *trans*-a, *trans*-c, all-*cis*, and all-*trans*, respectively.^{1,2}

Four of these isomers are chiral and circular dichroism spectra of enantiomeric forms of *trans*-a, *trans*-i, *trans*-c and all-*cis* are known.^{1,2} The all-*trans* isomer has so far escaped isolation despite attempts following the procedure used by Freeman and Liu in a successful isolation of the five geometrical isomers of the bis(2,3-diaminopropionato)cobalt(III) complex.³

Recently the optical properties of the four known isomers of the bis(histidinato)cobalt(III) complex

have been discussed in terms of the cubic ligand field parameters for amine (Δ_a), carboxylate (Δ_c) and imidazole (Δ_i), respectively. Applying the concept of holohedrized symmetry the octahedral parent transition ${}^1T_{1g} \leftarrow {}^1A_{1g}$ is decomposed into $B_{1g} \leftarrow A_{1g}$, $B_{2g} \leftarrow A_{1g}$ and $B_{3g} \leftarrow A_{1g}$ of the D_{2h} symmetry group for all of the four isomers; thus visible spectra have been assigned in terms of those three transitions as may be seen from Table 1 of Ref. 2.

Verification of assignments to particular transitions of known polarization direction and transition moment can most reliably be obtained from linear and if possible circular dichroism measurements on crystals with known structure. Of the four isolated isomers of the $[\text{Co}(\text{his})_2]^+$ chromophore, two have been investigated by X-ray crystallographic methods, the *racemic* form of the all-*cis* isomer, *rac*-all-*cis*- $[\text{Co}(\text{p-his})(\text{l-his})]\text{Br}$,⁴ and the *trans*-a isomer, *trans*-amine- $[\text{Co}(\text{l-his})_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$.⁵ For these two compounds we present in this paper an investigation by phase-modulation spectroscopy on single crystals.⁶

EXPERIMENTAL

rac-all-*cis*- $[\text{Co}(\text{p-his})(\text{l-his})]\text{Br}$ and *trans*-amine- $[\text{Co}(\text{l-his})_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ were prepared as described earlier^{1,2} and suitable single crystals for the spectroscopic investigations selected. Dimensions were determined from absorption spectra of the single crystals in question mounted on microscope slides. In order to obtain dichroism spectra the crystals were centered in the light beam of a microscope built into a phase-modulation spectrophotometer, a description of which is given elsewhere.^{6,7}

The obtained signals were analyzed and processed in analogy with earlier papers in this series of solid state phase-modulation spectroscopy studies.⁶⁻¹⁰ Obviously it is in the analysis of spectral data assumed that the measuring light transversing the microscope consists of a bundle of parallel rays. However, the microscope could not fulfil its role as optical magnifier if it were to use collimated light. Its very function is to increase the convergence of light originating from an object. As pointed out by Hárosi and Malerba¹¹ the numerical aperture (NA) of the condenser may in some cases influence the dichroic ratio (D_{\parallel}/D_{\perp}) so that elimination of errors needs to be considered. However, measurements of linear dichroism ($D_{\parallel} - D_{\perp}$) under normal illumination conditions give rise to a linear NA dependence which can be handled during standardization of the absorption scale of the experiments (see appendix).

THEORY

From the crystal structures of all-*cis*-[Co(ι -his)-(ν -his)]Br⁴ and *trans*-amine-[Co(ι -his)₂]ClO₄·2H₂O⁵ we may determine the orientation of a given molecular coordinate system with respect to the crystallographic axes. Such determinations provide the squares of direction cosines given in Tables 1 and 2. The choice of molecular coordinate systems is established through Eqns. 2 and 4 of

Table 1. Squares of direction cosines in all-*cis*-[Co(ν -his)(ι -his)] Br. Monoclinic crystals ($P2_1/c$),⁴ entrance face: (010).

The molecular coordinate system is defined as follows (see Fig. 2 of Ref. 4):
Origin: Co(III) ion.

x-Axis: Towards the imidazole nitrogen atom of the ν -histidinate ion.

y-Axis: Towards the coordinating carboxylate oxygen atom of the ι -histidinate ion.

z-Axis: The vector product of *x* and *y*.

Direction of unit vector	Squares of components of unit electric vector along molecular coordinate axes.		
	<i>x</i>	<i>y</i>	<i>z</i>
along <i>a</i>	0.577	0.316	0.107
along <i>c</i>	0.003	0.642	0.356
along <i>a</i> *	0.606	0.117	0.277
along <i>c</i> *	0.032	0.442	0.526
<i>a</i> - <i>c</i> *	0.545	-0.126	-0.419
<i>c</i> - <i>a</i> *	-0.603	0.525	0.079

Table 2. Squares of direction cosines in *trans*-amine-[Co(ι -his)₂]ClO₄·2H₂O. Orthorhombic crystals $P2_1,2_1,2_1$,⁵ entrance face (001).

The molecular coordinate system is defined as follows (see Fig. 1 of Ref. 5):

Origin: Co(III) ion.

x-Axis: Towards the coordinated carboxylate oxygen atom of one of ι -histidinate ions.

y-Axis: Towards the amine nitrogen atom of the same histidinate ion as is used to define the *x*-axis.

z-Axis: The vector product of *x* and *y*.

Direction of unit vector	Squares of components of unit electric vector along molecular coordinate axes		
	<i>x</i>	<i>y</i>	<i>z</i>
along <i>a</i>	0.813	0.173	0.015
along <i>b</i>	0.040	0.023	0.936
along <i>c</i>	0.147	0.804	0.049
<i>b</i> - <i>a</i>	-0.773	-0.150	0.921

Table 3. Squares of inter-planar cosines in *trans*-amine-[Co(ι -his)] ClO₄·2H₂O.

Crystallographic planes	Molecular planes		
	<i>xy</i>	<i>xz</i>	<i>yz</i>
<i>ab</i>	0.049	0.804	0.147
<i>ac</i>	0.936	0.023	0.040
<i>bc</i>	0.015	0.173	0.813

Ref. 2; the terminology of that paper as far as spectral assignments are concerned is also used here.

Since the three transitions B_1 , B_2 and B_3 are *z*, *y* and *x* polarized, respectively, we may from the tables of squares of direction cosines predict linear dichroism spectra. In Table 1 is given the prediction for the all-*cis* isomer provided the measuring light propagates along the crystallographic *b*-axis, but as the instrument in use measures the difference in absorbance between two mutual perpendicular polarizations we need to determine and use in the prediction the relationship between the molecular coordinate system and the reciprocal lattice (*a** and *c**) of the monoclinic crystals. Thus we see, using the transitional energy relationship $\Delta E(B_1) > \Delta E(B_2) > \Delta E(B_3)$,² that measurement of $Abs_{a^*} - Abs_{c^*}$ should give a spectrum with a positive linear dichroism above 500 nm and a negative below.

In Table 2 is given a prediction of the linear dichroism spectrum of the *trans-a* isomer, light propagated along the crystallographic *c*-axis. Using the transitional energy relationship $\Delta E(B_1) = \Delta E(B_3) > \Delta E(B_2)$, we expect measurement of $Abs_b - Abs_a$ to give a spectrum with a negative linear dichroism above 500 nm and a positive below.

As far as crystal circular dichroism is concerned this is predictable for the *trans-a* isomer only, since the crystal structure known for the all-*cis* isomer is that of the racemate.

The direction of a magnetic dipole transition, *i.e.* the direction of the magnetic transition moment, is perpendicular to the plane in which the transition occurs. Thus we need to evaluate squares of interplanar cosines which, of course, are equal to squares of the cosines to angles between normals. Such values for the *trans-a* isomer are given in Table 3. As magnetic dipole transitions in the *xy*, *xz* and *yz* planes transform as B_1 , B_2 and B_3 respectively, we are able to predict crystal circular dichroism spectra of the *trans-a* isomer using our knowledge of the solution circular dichroism and the above-mentioned transitional energy relation-

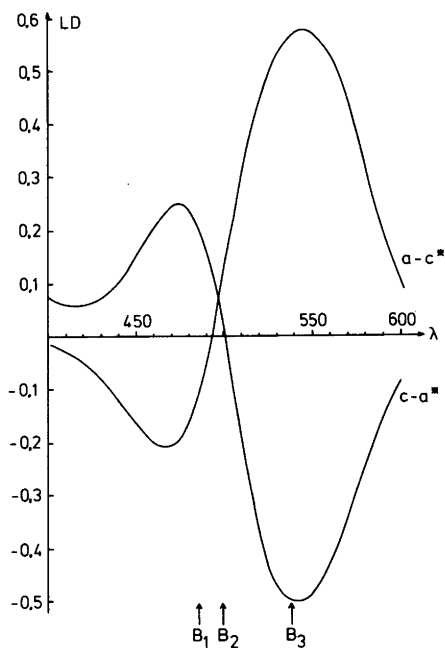


Fig. 1. Crystal linear dichroism of all-*cis*-[Co(his)₂]-Br. Thickness of this crystal: 0.02 mm. Arrows indicate calculated positions of $T_{1g} \leftarrow A_{1g}$ trigonal components (*cf.* Ref. 2).

ship. The crystal circular dichroism, measuring light propagated along the crystallographic *c*-axis, should reflect $\sim 80\%$ of the B_2 transitional rotatory strength (above 500 nm) and $\sim 20\%$ of the B_1 , B_2 transitional rotatory strength, *i.e.* the spectrum should consist of a positive high-wavelength band (> 500 nm) and a somewhat smaller, negative low-wavelength band.

RESULTS AND DISCUSSION

Linear dichroism spectra of the all-*cis* isomer are given in Fig. 1, and it is seen that the envelopes of the spectra are in accordance with the predictions given in Table 1. As far as the *x*-polarized (B_3) transition, occurring at approximately 535 nm,² is concerned we find this in the two spectra ($a-c^*$) and ($c-a^*$) at 546 and 541 nm, respectively.

As far as the *z*-polarized (B_1) and *y*-polarized (B_2) transitions, occurring at approximately 485 and 500 nm respectively,² are concerned we see from Table 1 that the $a-c^*$ spectrum should contain mainly B_1 and the $c-a^*$ spectrum mainly B_2 electronic excitations.

These predictions are certainly reflected in the spectra of Fig. 1, as the $a-c^*$ linear dichroism shows a minimum at 464 nm whereas the $c-a^*$ linear dichroism shows a maximum at 476 nm with a shoulder at 463 nm.

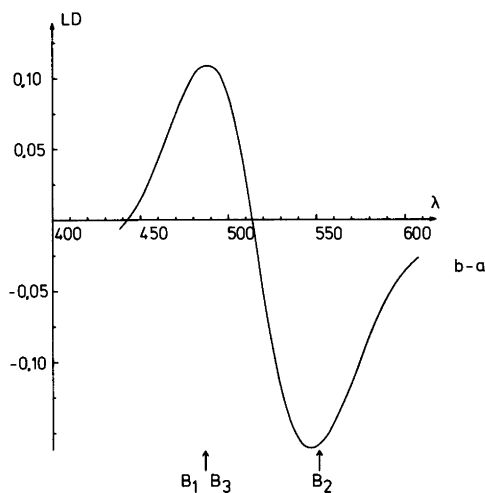


Fig. 2. Crystal linear dichroism of *trans*-amine-[Co(L-his)₂]ClO₄·2H₂O. Thickness of this crystal: 0.03 mm. Arrows indicate calculated positions of $T_{1g} \leftarrow A_{1g}$ trigonal components (*cf.* Ref. 2).

Since linear dichroism spectra are of the "residual wing" type the indicated peak positions are not necessarily situated directly below the absorption maxima, rather they define upper and lower limits for these. Consequently the spectra of Fig. 1 support the earlier assignments to absorption spectra developed through an "angular overlap model" treatment,² the result of which is indicated by arrows in the figure.

The experimental crystal linear dichroism spectrum of the *trans-a* isomer, light propagation along the crystallographic *c*-axis, is shown in Fig. 2. According to earlier assignments² (indicated as arrows in the figure) there is a splitting between the two expected ligand field transitions, (B_2) at 552 nm and (B_1, B_3) at 485 nm, of $2.5 \times 10^3 \text{ cm}^{-1}$. Experimentally we find peaks in the linear dichroism spectrum at 548 and 485 nm (Fig. 2). This means that the splitting obviously is so great that mutual cancellation of the two bands does not occur in the linear dichroism spectrum of the *trans-a* isomer. Thus it is clear that the cubic ligand field parameters given earlier for the three coordinating groups need a minor correction, which cannot be effectuated, however, until we know the crystal structure and the crystal linear dichroism of the *trans-c* isomer also, as this isomer shows an even greater splitting between the two expected bands of $3.2 \times 10^3 \text{ cm}^{-1}$.

The crystal circular dichroism spectrum of the *trans-a* isomer is given in Fig. 3. It is in perfect

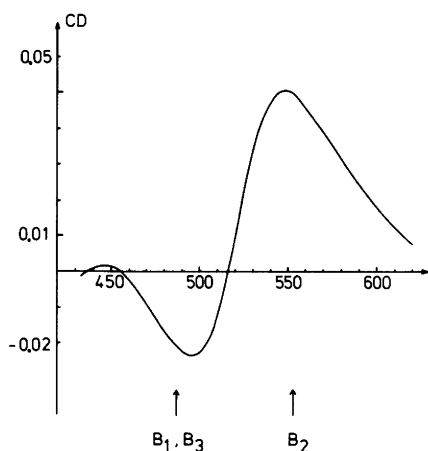


Fig. 3. Crystal circular dichroism of *trans-amine*- $[\text{Co}(\text{L-his})_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$. Thickness of this crystal: 0.03 mm. Arrows indicate calculated positions of $T_{1g} \leftarrow A_{1g}$ trigonal components (cf. Ref. 2).

agreement with the prediction of the theoretical section of this paper, as we find a big positive Cotton effect above 500 nm and a small negative below. The maximum, found at 548 nm, corresponds to the B_2 transition and has a molar absorptivity (in $\text{L}/(\text{mol cm})$) of 4, fixed orientation and procentic contribution taken into consideration. This should be compared with an absorptivity in solution of 3.6,¹ and we may thus conclude that there is very little cancellation between the two components in the solution circular dichroism spectrum, a point which is also demonstrated by the peak positions being 549 and 481 nm there.¹

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APPENDIX

Considering, as did Hárosi and Malerba,¹¹ a uniform illumination of propagation direction x falling perpendicular on the entrance surface of the condenser, we may use their results for distribution of unit polarization vectors in the aperture cone. The result is for light of initially y polarization

$$(1_x, 1_y, 1_z) = (b, a, 0)$$

and for light of initially z polarization

$$(1_x, 1_y, 1_z) = (b, 0, a)$$

where $a = 1 - b$ and $b = \tan^2(\alpha/2)$, α being the half-angle of the object ray cone.

Obviously measurements of linear dichroism ($D_y - D_z$) will vary directly proportional with a , and thus fixation of the numerical aperture before standardization of the absorption scale of the experiment allows the assumption that the ray transversing the medium is collimated.

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