

## Optical Properties of Bis(histidinato)cobalt(III) Complexes

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

The isomer all-*cis*-[Co(L-his)(D-his)]<sup>+</sup> has been resolved. Improved procedures for the preparation and separation of *trans*-imidazole- and *trans*-amine-[Co(L-his)<sub>2</sub>]<sup>+</sup> are given. The electronic spectra of all the geometrical isomers of bis(histidinato)cobalt(III) are discussed in terms of the angular overlap model.

An octahedral bis(histidinato)cobalt(III) complex gives rise to five geometrical isomers, four of which are chiral. The nine different theoretical structures are shown in Fig. 1.

The absorption spectra of the isomers *trans*-i, *trans*-a, *trans*-c and all-*cis* are reported in the literature.<sup>1,2</sup> The circular dichroism (CD) spectra

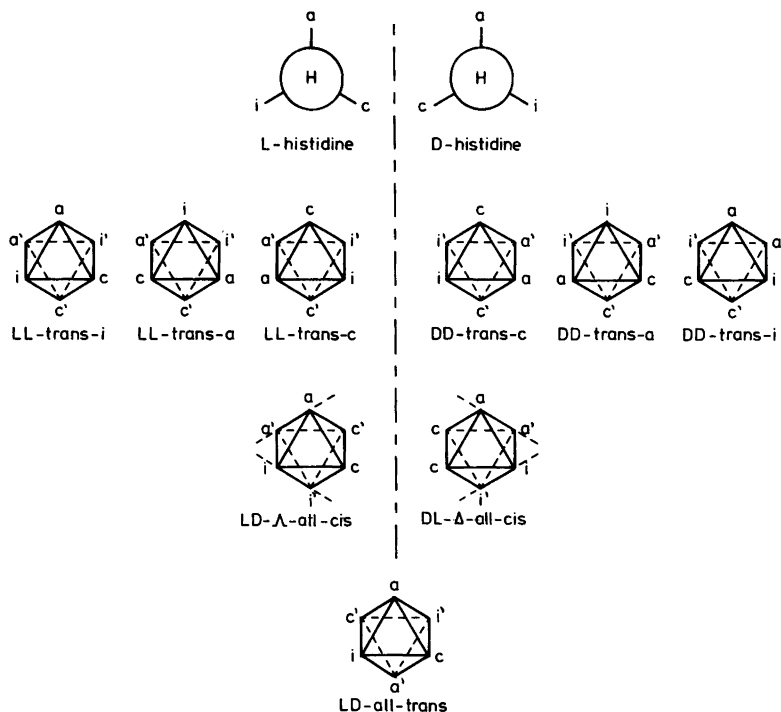


Fig. 1. Newman projections of histidine, and the structures of the bis(histidinato)cobalt(III) isomers.

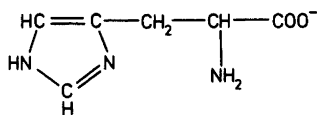


Fig. 2. Histidinate; L-histidine has the (S)-configuration in the Cahn-Ingold-Prelog notation.

of *trans-i*, *trans-a* and *trans-c* are also known.<sup>2</sup> The achiral all-*trans* isomer, however, has not yet been isolated and characterized.

In this work CD spectrum of the all-*cis* isomer is reported.

Schmidtke<sup>3</sup> has successfully used the angular overlap model (AOM), proposed by Schäffer and Jørgensen,<sup>4</sup> to explain the absorption spectra of the three isomers known at that time, namely *trans-i*, *trans-a* and *trans-c*. We have reexamined the application of the model to bis(histidinato)cobalt(III) complexes taking into account all the spectral data now available.

## NOMENCLATURE

In formulas histidinate (Fig. 2) is abbreviated his<sup>-</sup>.

The letters a, i and c are used as symbols for amino, imidazole and carboxylate, respectively.

The IUPAC rules for the designation of absolute configurations of octahedral complexes<sup>5</sup> may be adapted to all-*cis*-[Co(his)<sub>2</sub>]<sup>+</sup> using the pairs of non-orthogonal skew lines indicated in Fig. 1.

## EXPERIMENTAL RESULTS

The racemic isomer all-*cis*-[Co(L-his)(D-his)]Br has been resolved chromatographically using a

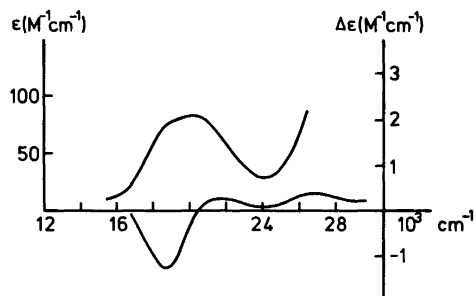


Fig. 3. Spectra of the (-)<sub>589</sub> antipode of the all-*cis*-[Co(L-his)(D-his)]<sup>+</sup> isomer in H<sub>2</sub>O.

Sephadex column. The antipodes separate into two distinct zones, indicating complete resolution.

The absorption and CD spectra are shown in Fig. 3.

An improved procedure for obtaining pure samples of *trans-i*-[Co(L-his)<sub>2</sub>]ClO<sub>4</sub>·1½H<sub>2</sub>O and *trans-a*-[Co(L-his)<sub>2</sub>]ClO<sub>4</sub>·2H<sub>2</sub>O has been worked out. Previously the two isomers were separated by chromatography,<sup>6</sup> whereas the new method makes use of the different crystallization rates of the perchlorates.

*Resolution of rac-all-cis-[Co(D-his)(L-his)]Br.* The complex is prepared as the bromide<sup>2</sup> and is subsequently resolved chromatographically on SP-Sephadex C-25 with 0.1 M aqueous sodium antimonyl-*d*-tartrate as eluent. Our column was 30 cm long and had a diameter of 3 cm; 20 mg complex was eluted with a flow-rate of 0.5 ml/min. After 21 h two separate 1.5 cm broad zones had developed with centers 23 and 27 cm from the top of the column. The (+)<sub>589</sub> antipode is eluted first.

*Preparation of trans-imidazole-[Co(L-his)<sub>2</sub>]ClO<sub>4</sub>·1½H<sub>2</sub>O (red isomer) and trans-amino-[Co(L-his)<sub>2</sub>]ClO<sub>4</sub>·2H<sub>2</sub>O (orange isomer).* 3.57 g CoCl<sub>2</sub>·6H<sub>2</sub>O (15 mmol) and 4.65 g L-histidine (30 mmol) are dissolved in 50 ml H<sub>2</sub>O, and 0.5 g activated charcoal is added. The solution is heated to 75 °C and aerated for 90 min. Then 1 ml 30% H<sub>2</sub>O<sub>2</sub> is added, and the solution is kept at 75 °C for 30 min. The reaction mixture is cooled to ca. 0 °C, and the wall of the flask is scratched with a glass rod to insure that possible small amounts of unwanted products are precipitated. Subsequently the cooled solution is filtered. The volume is adjusted to 50 ml with water, and a solution of 20 g NaClO<sub>4</sub>·H<sub>2</sub>O in 50 ml H<sub>2</sub>O is added. After cooling in an ice bath for 30 min a precipitate of the red isomer is filtered off. Recrystallization from hot (70 °C) water. The mother liquid from the precipitation of the red isomer is left in a refrigerator for a couple of days and crystals of the orange isomer slowly form. Recrystallization from hot (70 °C) water.

*Apparatus.* A Cary 11 spectrophotometer and a Roussel-Jouan Dichrograph II were used for the measurements of optical spectra.

## THEORETICAL RESULTS

The semi-empirical *angular overlap model*<sup>4</sup> is a useful tool for calculating energy levels in transition metal complexes. Application of the concept *hologedricized symmetry*,<sup>4</sup> which for low-symmetry molecules is higher than the actual symmetry, is a simplifying approximation which makes the model easy to deal with. The literature<sup>3,4</sup> should be consulted

for a description of the model and its underlying principles.

The holohedrized symmetry of all the bis(histidinato)cobalt(III) isomers is  $D_{2h}$ . On lowering the symmetry from  $O_h$  to  $D_{2h}$  the  ${}^1T_{1g} \leftarrow {}^1A_{1g}$  parent transition in cobalt(III) is decomposed into  $B_{1g} \leftarrow A_{1g}$ ,  $B_{2g} \leftarrow A_{1g}$ , and  $B_{3g} \leftarrow A_{1g}$ .

In his treatment of the *trans-c*, *trans-a*, and *trans-i* isomers Schmidtke<sup>3</sup> gave the energies of the three component transitions, abbreviated  $\Delta E(B_1)$ ,  $\Delta E(B_2)$ , and  $\Delta E(B_3)$ , in terms of the special AOM parameters. We prefer to express these energies as functions of the usual cubic ligand field parameters for carboxylate ( $\Delta_c$ ), amine ( $\Delta_a$ ), and imidazole ( $\Delta_i$ ). This is possible for low-spin  $d^6$ -systems, as already pointed out by Schäffer and Jørgensen.<sup>4</sup> Otherwise we have used the procedure described by Schmidtke,<sup>3</sup> and we arrive at the following energy expressions:

*trans-c*:

$$\begin{aligned} \Delta E(B_1) &= \frac{1}{2}(\Delta_a + \Delta_i) \\ \Delta E(B_2) = \Delta E(B_3) &= \frac{1}{4}(\Delta_a + \Delta_i + 2\Delta_c) \end{aligned} \quad (1)$$

*trans-a*:

$$\begin{aligned} \Delta E(B_1) = \Delta E(B_3) &= \frac{1}{4}(2\Delta_a + \Delta_i + \Delta_c) \\ \Delta E(B_2) &= \frac{1}{2}(\Delta_i + \Delta_c) \end{aligned} \quad (2)$$

*trans-i*:

$$\begin{aligned} \Delta E(B_1) = \Delta E(B_2) &= \frac{1}{4}(\Delta_a + 2\Delta_i + \Delta_c) \\ \Delta E(B_3) &= \frac{1}{2}(\Delta_a + \Delta_c) \end{aligned} \quad (3)$$

*all-cis*:

$$\begin{aligned} \Delta E(B_1) &= \frac{1}{4}(2\Delta_a + \Delta_i + \Delta_c) \\ \Delta E(B_2) &= \frac{1}{4}(\Delta_a + 2\Delta_i + \Delta_c) \\ \Delta E(B_3) &= \frac{1}{4}(\Delta_a + \Delta_i + 2\Delta_c) \end{aligned} \quad (4)$$

*all-trans*:

$$\begin{aligned} \Delta E(B_1) &= \frac{1}{2}(\Delta_a + \Delta_i) \\ \Delta E(B_2) &= \frac{1}{2}(\Delta_i + \Delta_c) \\ \Delta E(B_3) &= \frac{1}{2}(\Delta_a + \Delta_c) \end{aligned} \quad (5)$$

These equations immediately tell that all-*cis* and all-*trans* have three bands under the  $T_{1g} \leftarrow A_{1g}$  parent transition, whereas each of the isomers *trans-c*, *trans-a*, and *trans-i* because of degeneracy only have two.

Using the assumption of Schmidtke<sup>3</sup>

$$\Delta_a > \Delta_i > \Delta_c$$

which is in accordance with the spectrochemical series,<sup>7,8</sup> it is easily deduced that the relative magnitudes of the transition energies are:

$$\textit{trans-c}: \quad \Delta E(B_1) > \Delta E(B_2) = \Delta E(B_3) \quad (6)$$

$$\textit{trans-a}: \quad \Delta E(B_1) = \Delta E(B_3) > \Delta E(B_2) \quad (7)$$

$$\textit{trans-i}: \quad \Delta E(B_1) = \Delta E(B_2) > \Delta E(B_3) \quad (8)$$

$$\textit{all-cis}: \quad \Delta E(B_1) > \Delta E(B_2) > \Delta E(B_3) \quad (9)$$

$$\textit{all-trans}: \quad \Delta E(B_1) > \Delta E(B_3) > \Delta E(B_2) \quad (10)$$

These five relations may be used for the assignment of the transitions in the experimental spectra.

## DISCUSSION

It appears from eqns. (1)–(5) that if the energies of any three transitions in the five isomers are empirically known, the AOM will predict the energies of all the others.

Three of the transitions may be assigned and quite accurately read from the known experimental absorption spectra, namely the low-energy band of the *trans-c* isomer, and the high-energy bands of the *trans-a* and *trans-i* isomers, respectively. These three bands are marked by arrows in Fig. 4.

Simple calculations yield the values for the three cubic ligand field parameters as well as the transition energies listed in Table 1.

Table 1. Wavenumbers (in units of  $10^3 \cdot \text{cm}^{-1}$ ) of the  $T_{1g} \leftarrow A_{1g}$  components in  $[\text{Co}(\text{his})_2]^+$  isomers.

Isomer	$\Delta E(B_1)$	$\Delta E(B_2)$	$\Delta E(B_3)$
<i>trans-c</i>	21.9	18.7 <sup>a</sup>	18.7 <sup>a</sup>
<i>trans-a</i>	20.6 <sup>a</sup>	18.1	20.6 <sup>a</sup>
<i>trans-i</i>	20.0 <sup>a</sup>	20.0 <sup>a</sup>	19.3
<i>all-cis</i>	20.6	20.0	18.7
<i>all-trans</i>	21.9	18.1	19.3

<sup>a</sup> Experimentally determined values.

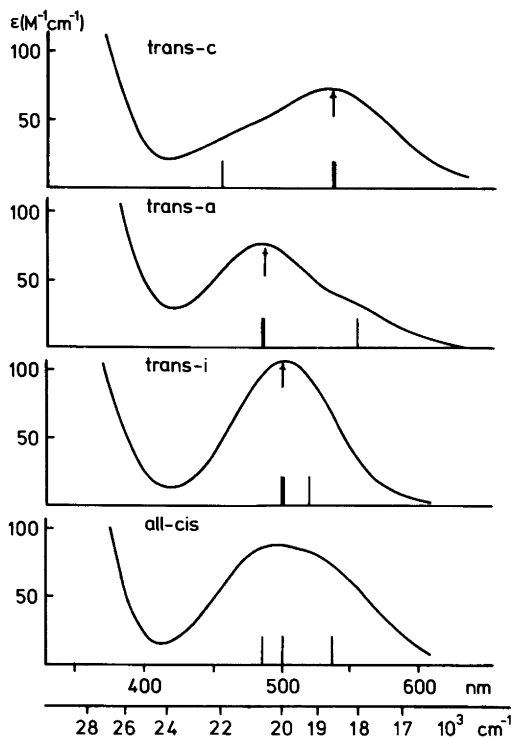


Fig. 4. Experimental absorption spectra of the four known geometrical isomers of the bis(histidinato)cobalt(III) complex. Vertical lines indicate the position of transitions from Table 1.

The energy values from Table 1 are depicted as vertical lines in Fig. 4. The agreement between the experimental spectra and the AOM results is seen to be very satisfactory.

Table 1 includes a prediction of the unknown spectrum of the all-trans isomer, which so far has escaped isolation.<sup>2</sup>

The cubic ligand field parameters obtained,  $\Delta_a = 23.1 \times 10^3 \text{ cm}^{-1}$ ,  $\Delta_i = 20.7 \times 10^3 \text{ cm}^{-1}$  and  $\Delta_c = 15.5 \times 10^3 \text{ cm}^{-1}$ , are in good agreement with expected values from the literature.<sup>7</sup>

The fact that all-cis-[Co(D-his)(L-his)]<sup>+</sup> has been resolved into optical antipodes is a confirmation of its structure<sup>2,9</sup> since the other possibility, all-trans-[Co(D-his)(L-his)]<sup>+</sup>, has a symmetry centrum and would therefore be nonresolvable.

The CD spectra of the four chiral isomers of [Co(his)<sub>2</sub>]<sup>+</sup> turn out to be of little use for the purpose of determining transition energies. Their shapes are typical for so-called "residual wing ab-

sorptions", which arise when positive and negative contributions partially cancel each other.<sup>10</sup>

Since chirality vanishes on holohedrization the simple AOM used above is not appropriate for a detailed discussion of circular dichroism.

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