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The Angular Overlap Model in the Assignment of Molecular Geometries. The Case of Bis(Aspartato)cobalt(III) Complexes

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A routine AOM analysis on the geometric isomers of bis(aspartato)cobalt complexes is performed. Contrary to assignments made on the basis of CD and NMR the AOM treatment gives the correct molecular geometries which agree with crystal structure results.

Introduction

The coordination of trifunctional amino acids to transition metal ions is often accompanied by interesting stereochemical problems. A particularly well characterized example is provided by the bis(L-aspartato)cobalt(III) complexes. The aspartate ligand, $^{-}OOC–CH(NH_2)–CH_2–COO^{-}$, yields three bis-type isomers, which may be represented given in Figure 1. Here aspartate is represented as $O_\alpha–N–O_\beta$, the amino group being α and β to the two carboxylates.

The preparation of the three isomers was reported in 1971 [1] and an assignment made on the basis of circular dichroism and absorption spectra. The *trans*-N isomer was easily identified, while the other two isomers, being quite similar, posed a greater problem. The assignment was made primarily on the basis that the *trans*-O_α structure would be expected to be less symmetric than the *trans*-O_β (this has a two fold axis on the edge indicated in Figure 1), and should therefore be associated with the more intense CD spectrum. An analysis of NMR spectra of the three isomers appeared to confirm this original assignment [2].

This assignment was first questioned in the literature in 1973 by Legg and Neal [3], who compared CD spectra with the spectrum of $[Co(EDDS)]^{-}$, ethylenediaminedisuccinate being a hexadentate ligand comparable to two aspartates. The EDDS ligand coordinates stereospecifically, and the absolute configuration of $[Co(EDDS)]^{-}$ had been confirmed by X-ray crystallography. The CD comparison pointed towards an assignment of *trans*-O_α and *trans*-O_β isomers opposite to that originally offered by Douglas and co-workers.

In 1975 another refutation of the initial assignments appeared, based on an ingenious argument involving successive replacement of aspartate by diaminobutyrate in each of the three isomers of $[Co(asp)_2]^{-}$ [4]. A comparison of CD spectra leads to an unambiguous assignment of all isomers, since a dif-

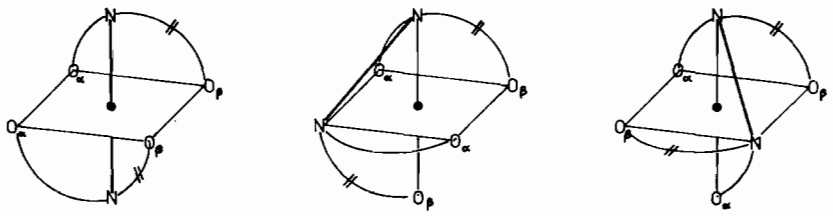

Figure 1. Possible geometric isomers of bis(aspartato) metal complexes.

ferent congeneric isomer is unique (and thus easily identified) for each of the three complexes $[Co(asp)_2]^-$, [Co(asp)(dba)], and $[Co(dba)_2]^+$.

Finally, in 1975 the crystal structure of the *trans*-O_β isomer was determined, with the result that the assignment opposite to that of Douglas and coworkers was confirmed [5].

Ligand field theory is applied routinely to complexes with trigonal, tetragonal, or higher symmetry, but it is often felt that a ligand field analysis of low symmetry complexes is fruitless. Thus in many cases, as with the aspartato complexes discussed here, reliance is placed on CD intensities and, where possible, on NMR fitting procedures [2, 5, 6]. The difficulties rest in the non-additivity of ligand field theory as it is usually applied (non-additive because the parameters refer to a whole molecule with a particular symmetry). In an additive theory (parameters represent interactions between central ion and particular ligands) such as the Angular Overlap Model (AOM) [8, 9], however, the parameters of the model are intended to be transferrable among related complexes [10], and are thus well-suited to problems of molecular structure.

In this paper the original spectroscopic data are interpreted on the basis of the AOM following the lines applied previously to problems of geometric isomer identification [11], with results agreeing with CD and NMR assignments. Since the AOM has now begun filtering into undergraduate textbooks [12, 13], it seems appropriate to take up this point again and demonstrate its usefulness in this respect. The aspartato complexes represent the first case where simple AOM predictions disagree with other routine methods, and it is therefore of some importance to understand the basis behind the AOM arguments.

Angular Overlap Model Analysis

Only the first (lowest energy) band exhibited splittings, and the analysis was carried out on this band. In the AOM, the transition energies in orthoaxial Co(III) complexes are given by (we assume orthoaxiality, even though angles are certainly not 90°; smaller deviations will not affect the results significantly)

$$\Delta E = \langle d_{x^2-y^2} | V | d_{x^2-y^2} \rangle - \langle d_{xy} | V | d_{xy} \rangle - C,$$

obtaining all components by permuting the (x,y,z) coordinates. In terms of the angular overlap parameters, e_σ and e_π, these matrix elements are (neglecting off-diagonal terms to higher excited cubic states):

$$\langle d_{x^2-y^2} | V | d_{x^2-y^2} \rangle = \tfrac{3}{4}(e_{\sigma x} + e_{\sigma y})$$

$$\langle d_{xy} | V | d_{xy} \rangle = (e_{\pi x} + e_{\pi y})$$

Here $e_{\sigma x}$, for example, is the sum of the e_σ parameters for the two ligands on the x axis. The e_σ and e_π parameters represent the extent to which a ligand raises the energy of the metal d orbitals through sigma and pi interactions, respectively, and are related to the usual octahedral ligand field parameter 10 Dq or Δ, by

$$\Delta_L = 3e_{\sigma L} - 4e_{\pi L}$$

For our purpose, Δ_L would apply to a (possibly imaginary) complex ML_6.

Application of the above equations to the aspartate complexes leads to the following results for the three isomers:

trans-NH_2: $\Delta E^-(B_1) = \tfrac{1}{2}\Delta_{O_\alpha} + \tfrac{1}{2}\Delta_{O_\beta} - C$

$\Delta E^+(B_2, B_3) = \tfrac{1}{4}\Delta_{O_\alpha} + \tfrac{1}{4}\Delta_{O_\beta} + \tfrac{1}{2}\Delta_{NH_2} - C$

trans-O: $\Delta E^+(B_2) = \tfrac{1}{2}\Delta_{NH_2} + \tfrac{1}{2}\Delta_{O_\beta} - C$

$\Delta E^-(B_1, B_3) = \tfrac{1}{4}\Delta_{NH_2} + \tfrac{1}{4}\Delta_{O\beta} + \tfrac{1}{2}\Delta_{O_\alpha} - C$

trans-O: $\Delta E^+(B_3) = \tfrac{1}{2}\Delta_{NH_2} + \tfrac{1}{2}\Delta_{O_\alpha} - C$

$\Delta E^-(B_1, B_2) = \tfrac{1}{4}\Delta_{NH_2} + \tfrac{1}{4}\Delta_{O_\alpha} + \tfrac{1}{2}\Delta_{O_\beta} - C$

The + and − notation refers to the higher and lower energy maxima, assuming (*vide infra*) that $\Delta_{NH_2} \gg \Delta_{O\alpha} > \Delta_{O_\beta}$. B_1, B_2, and B_3 are the excited state designations in D_{2h} symmetry (the most general case for orthoaxial complexes in the AOM), and C is the usual Racah parameter.

The band splittings are then:

$$S_{tr\text{-}NH_2} = \tfrac{1}{4}(2\Delta_{NH_2} - \Delta_{O_\alpha} - \Delta_{O_\beta})$$

$$S_{tr\text{-}O_\alpha} = \tfrac{1}{4}(\Delta_{NH_2} + \Delta_{O_\beta} - 2\Delta_{O_\alpha})$$

$$S_{tr\text{-}O_\beta} = \tfrac{1}{4}(\Delta_{NH_2} + \Delta_{O_\alpha} - 2\Delta_{O_\beta})$$

Some spectral data for the aspartate complexes are listed in Table I.

In order to apply the AOM equations we need estimates of the relative values of Δ_{NH_2}, Δ_{O_α}, and Δ_{O_β}. There is no difficulty in placing the amino group at 21 kK + C or above, at a position considerably above the carboxylates. This in itself is enough to identify Isomer 1 as the *trans*-NH_2 complex, from the typical *trans*-CoN_2O_4 characteristics – large splitting, with the high energy component dominant.

TABLE I. First Band Spectral Data (absorption maxima, in kK) for $[Co(asp)_2]^-$ Complexes [1].

Isomer (order of elution)	Dominant Peak	Shoulder	Splitting
1	19.53	15.87	3.66
2	19.23	16.7	2.5
3	17.24	20.0	2.8

TABLE II. Spectral Data for Co(III) Complexes with Amine- and Carboxylate-containing Ligands from Aqueous Solution Absorption spectra, in kK, with Δ Values from Angular Overlap Model Calculations.[a]

Complex	Dominant Peak	Shoulder	Δ_{NH_2}–C	Δ_{O_α}–C	Δ_{O_β}–C	Ref.
fac-$[Co(gly)_3]$	19.3		21.3	17.3		[15]
mer-$[Co(gly)_3]$	18.3	~20.4				
trans-$[Co(\alpha\text{-ala})_2ox]^-$	18.94	16.7	21.2	16.8	15.4	[16]
trans-$[Co(\beta\text{-ala})_2ox]^-$	18.83	16.0				
$[Co(ox)_3]^{3-}$	16.6					
fac-$[Co(\beta\text{-ala})_3]$	19.0		22.0		16.0	[15, 17]
mer-$[Co(\beta\text{-ala})_3]$	20.5	17.6				
$[Co(mal)_3]^{3-}$	16.4			(16.4)		[18]

[a]ala = alanine, ox = oxalate, gly = glycine, mal = malonate.

In Table II are presented some spectral data which allow comparison of Δ values for α- and β-carboxylates in similar complexes. These were also obtained with the aid of the AOM as described above, neglecting off-diagonal elements. It would appear from these, especially from the $[Co(ala)_2ox]^-$ complexes, where both α- and β-alanine were available, that $\Delta_{O_\alpha} > \Delta_{O_\beta}$. The difference is large enough that we can attach some reliability to the result in spite of fluctuations in the ubiquitous C, and in spite of the other approximations inherent in this approach. The data from the tris(amino acid) complexes is less reliable, since the meridional isomers are expected to exhibit three bands, whereas only two were observed. It was assumed that the middle peak (which would correspond to the peak position for the facial isomer) was not observed.

With the inequality

$$\Delta_{NH_2} \gg \Delta_{O_\alpha} > \Delta_{O_\beta}$$

we obtain for the splittings

$$S_{tr\text{-}NH_2} > S_{tr\text{-}O_\beta} > S_{tr\text{-}O_\alpha}$$

From absorption spectra data, this leads to the assignment of Isomer 2 to the *trans*-O_α complex and Isomer 3 to the *trans*-O_β.

Some further inequalities can be derived, concerning the higher and lower energy peaks (assuming no variation in C)

$$\Delta E^-_{tr\text{-}O_\alpha} > \Delta E^+_{tr\text{-}NH_2} > \Delta E^+_{tr\text{-}O_\alpha}$$

and

$$\Delta E^-_{tr\text{-}O_\alpha} > \Delta E^-_{tr\text{-}O_\beta} > \Delta E^-_{tr\text{-}NH_2}$$

The observed order of higher energy peaks supports the above assignment, while the lower energy peaks do not. Still the assignment opposite to that of Douglas, *et al.* [1], is clearly favored (two of the low energy peaks were shoulders, making that comparison less reliable).

As an ancillary point, the relative splittings of Isomers 2 and 3, which served to distinguish *trans*-O_α from *trans*-O_β, may have actually contributed to the earlier misassignment of these two isomers. The CD curve for Isomer 3 exhibited a particularly large $\Delta\epsilon$, at least in the lowest energy component of the low energy band, and this curve was assigned to the *trans*-O_α isomer, for the reason that this isomer deviates more from an arrangement which would produce something like a plane of symmetry (through the O_β-rings) than the *trans*-O_β does.

The large $\Delta\epsilon$ may, however, arise simply from the larger splitting of the first band in the *trans*-O_β isomer. The two components of the band have opposite signs in both cases, and given appropriate true widths, an increase in peak separation by 30% can easily produce an increase in apparent peak heights by a factor of two or more, creating the illusion that Isomer 3 possesses greater asymmetry.

Values for the ligand field parameters can be derived for the aspartato complexes. We use the dominant spectral peak for each isomer to derive:

$\Delta_{NH_2} - C = 23.8$ kK

$\Delta_{O_\alpha} - C = 15.9$ kK

$\Delta_{O_\beta} - C = 14.7$ kK

Conclusions

It should be emphasized that the AOM analysis has been made in the most routine way. No spectral deconvolution has been attempted in order to lend accuracy to the splittings, and in particular the assumption of orthoaxiality was maintained even though the bite angles in chelate complexes are certainly less than 90°. Changes in bite angles do affect energies [14] although relative energies are not likely to be drastically affected if the ligands are not very strongly π-bonding or π-antibonding. Bite angles can be included in the calculations in closed form [9, 14], but with a large loss in simplicity, since e_σ and e_π values for each ligand must be considered separately.

For routine methods of structure determination for low symmetry geometric isomers, one has CD intensities, NMR, and AOM analysis of absorption spectra as the most obvious tools. CD intensities are not all that well understood, and NMR analysis, which is actually not so routine, is dependent on the estimated initial parameters fed into the program. AOM analysis, although certainly not perfect, has proven itself superior and, in most cases, should be the first and most obvious tool to use.

References

1 S. Yamada, J. Hidaka and B. E. Douglas, *Inorg. Chem., 10,* 2187 (1971).
2 L. R. Froebe, S. Yamada, J. Hidaka and B. E. Douglas, *J. Coord. Chem., 1,* 183 (1971).
3 J. I. Legg and J. A. Neal, *Inorg. Chem., 12,* 1805 (1973).
4 M. Watabe and S. Yoshikawa, *Bull. Chem. Soc. Japan, 48,* 2185 (1975).
5 W. A. Freeman and C. F. Liu, *Inorg. Chem., 7,* 764 (1968).
6 Z. Zompa, *Chem. Comm.,* 783 (1969).
7 I. Oonishi, S. Sato and Y. Saito, *Acta Cryst., B31,* 1318 (1975).
8 C. E. Schäffer and C. K. Jørgensen, *Kgl. Danske Videnskab. Selskab., Mat. Fys. Medd., 34,* No. 13 (1965).
9 H.-H. Schmidtke, *Theoret. Chim. Acta, 20,* 92 (1971).
10 J. Glerup. Ø. Monsted and C. E. Schäffer, *Inorg. Chem., 15,* 1399 (1976).
11 H.-H. Schmidtke, *Chem. Phys. Lett., 4,* 451 (1969).
12 R. S. Drago, "Physical Methods in Chemistry", W. B. Saunders, Philadelphia (1977).
13 K. F. Purcell and J. C. Kotz, "Inorganic Chemistry", W. B. Saunders, Philadelphia (1977).
14 E. Larsen, G. N. LaMar, B. E. Wagner, J. E. Parks and R. H. Holm, *Inorg. Chem., 11,* 2652 (1972).
15 N. Matsuoka and Y. Shimura, *Bull. Chem. Soc. Japan, 49,* 2118 (1976).
16 J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Japan, 40,* 2312 (1967).
17 M. B. Celap, S. R. Niketic, J. J. Jancic and V. N. Nikolic, *Inorg. Chem., 6,* 2063 (1967).
18 N. C. Kneten and S. T. Spees, *J. Inorg. Nucl. Chem., 33,* 2437 (1971).