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Study of the Reactions of Hexanitrocobaltates(III) with Amino Acids. V. Absolute Configuration and Geometrical Isomerism of Dinitrobis(aminoacidato)cobaltate(III) Ions[1]

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Circular dichroism and proton magnetic resonance data of some cis-*dinitrobis(amino acidato) cobalt(III) ions are reported which establish their absolute configuration and geometrical isomerism. It is shown that rearrangement of the chelate rings must occur during the preparation from tris(aminoacidato) cobalt(III) complexes.*

Introduction

Recent work[1] on the preparation and properties of dinitrobis(aminoacidato) cobalt(III) ions shows that the nitro-groups are in *cis* positions. When a 1,2,3-tris-amino acid complex was treated with nitrite ion only one of the three possible *cis*-dinitro products was obtained. Assuming that both nitro-groups simply replace one aminoacid ligand it follows that the configuration of the product be *cis-cis-cis*.[1] It has been confirmed[1] that neither the 1,2,3 nor the 1,2,6-tris-amino acid complexes rearrange when boiled in aqueous solution for a period, and at a pH, equal to that used in the nitrite substitution. We have, however, been unable to rule out the possibility of rearrangement during the substitution reactions. Moreover, conditions of the preparation are such that the product may be thermodynamically controlled rather than kinetically controlled. We have, therefore, studied some of the physical properties of our compounds in an attempt to independently identify which isomer of the *cis* dinitro compound is formed.

Experimental Section

Preparation and resolution of dinitrobis(aminoacidato)cobaltate(III) complexes with glycine, D-alanine, L-alanine, and β-alanine are described in the previous papers in this series.[1]

Circular dichroism measurements were made on a Roussel-Jouan dichrograph and the absorption spectra were measured on a Cary 14 spectrophotometer. The solvent was water. The NMR spectra were obtained on a Varian A-60 instrument.

Results

We now wish to report the circular dichroism (CD) spectra of these compounds. Table I lists the observed specific rotations and the maximum circular dichroism values. The CD spectra are given in Figure 1, together with a typical absorption spectrum. Only the CD spectra of the (−) isomers are given. Identical CD spectra, but of the reverse sign were obtained for the mirror image compounds. The remainder of the absorption spectra are given in Part IV of this series.[1]

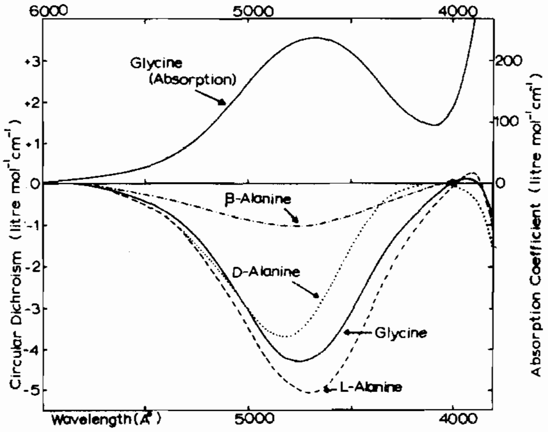

Figure 1. Circular Dichroism spectra of *cis*-dinitrobis(aminoacidato)cobalt(III) ions, and the absorption spectra of the glycine complex ion.

Discussion

The circular dichroism spectra in Figure 1 allows us to assign the absolute configuration of the complexes. The absolute configuration of tris(aminoacidato) complexes of Co^{III} is known[3,4] and the circular dichroism of these complexes has the same sign and characteristics

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[1] Earlier work: T. J. Janjic, M. B. Celap, and P. Spevak, *Glasnik Hem. Društva*, Beograd, *27*, 11 (1962); M. B. Celap, D. J. Radanovic, and T. J. Janjic, *Inorg. Chem.*, *4*, 1494 (1965); M. B. Celap, D. J. Radanovic, T. J. Janjic, and M. J. Malinar, *Glasnik Hem. Društva*, Begrad, in press; M. B. Celap, D. J. Radanovic, T. I. Nikolic, and T. J. Janjic, this journal, preceding paper.

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[3] R. G. Denning and T. S. Piper, *Inorg. Chem.*, *5*, 1056 (1966).

[4] (a) M. G. B. Drew, J. H. Dunlop, R. D. Gillard, and D. Rogers, *Chem. Comm.*, *42* (1966). (b) L. Applequist, R. G. Denning and I. C. Paul, to be published.

Table I. Circular Dichroism (CO) Data and Specific Rotations [a]

Compound	ε_l-ε_r (liter mole^{-1} cm^{-1})	Wavelength (Å)	Specific Rotation α_D^{20}
(−)-Ag[Co(β-alanine)$_2$(NO$_2$)$_2$]	−1.00	4750	−225°
(+)-Ag[Co(β-alanine)$_2$(NO$_2$)$_2$]	+0.99	4750	+222°
(+)-Ag[Co(D-alanine)$_2$(NO$_2$)$_2$]	+5.04	4700	+567°
(−)-Ag[Co(L-alanine)$_2$(NO$_2$)$_2$]	−5.04	4700	576°
(−)-Ag[Co(D-alanine)$_2$(NO$_2$)$_2$]	−3.66	4850	−348°
(−)-Ag[Co(glycine)$_2$(NO$_2$)$_2$]	−4.25	4750	−370°
(+)-Ag[Co(glycine)$_2$(NO$_2$)$_2$]	+4.25	4750	+370°

[a] In aqueous solution (c=0.19/100 ml.)

as that of the tris-diamine complexes of cobalt(III) whose absolute configuration is known by the x-ray method.[5] Furthermore, the absolute configuration of the complex ion (+)-*cis*-dinitrobis(L-propylenediamine)cobalt(III) has recently been determined by x-ray crystallography.[6] Using the relationship between the tris-diamine and tris(aminoacidato) complexes we may reasonably deduce that the dinitro bis(amino acid) complex which has the same sign of circular dichroism as the dinitrobis(L-propylenediamine) complex will have the same absolute configuration. It is important that the electronic structures of the complexes be similar for the argument above to apply. This is supported by the shape of the CD curves. In the region of the first spin allowed "d–d" transition of the cobalt(III) ion there is a dominant CD peak which almost coincides with the position of the absorption maximum, with a small wing of opposite sign to shorter wavelength. The same CD spectrum is observed for the dinitrobis(L-propylenediamine) complex, and implies a small splitting of the electronic state which would be triply degenerate in a regularly octahedral complex.

On this basis we assign the L- or M(C$_2$) absolute configuration to all those complexes which have predominantly negative CD, and D- or P(C$_2$) to those with predominantly positive CD. The symbols L- and M(C$_2$) imply a left-handed sense to the helicity of the two chelate rings when they are observed along the two-fold or pseudo-two-fold axis of the molecule.

Three other points arise from these spectroscopic results. Firstly the low energy absorption band in the β-alanine complex, is at longer wavelength than in the corresponding glycine complex. We believe the lower ligand field to be a direct result of the increase in chelate ring size. It is well known that five membered chelate rings are more stable than six membered rings. Secondly, the rotational strength of the β-alanine complex is much lower than the corresponding glycine complex. We are unable to say whether this arises from the conformational changes in the chelate ring, or because the chelate angular contraction, which is frequently taken to be the source of the optical activity,[7] is reduced. Woldbye[8] has demonstrated a decrease of a similar magnitude when the five-membered ethylenediamine chelate ring is replaced by the six-membered trimethylenediamine chelate ring. Thirdly, the effect of secondary asymmetric centers, often called the "vicinal effect"[9] is seen to follow previous examples.[10] The circular dichroism of the glycine complex lies almost midway between that of the L-alanine and D-alanine complexes in which the "vicinal effects" have opposite signs.

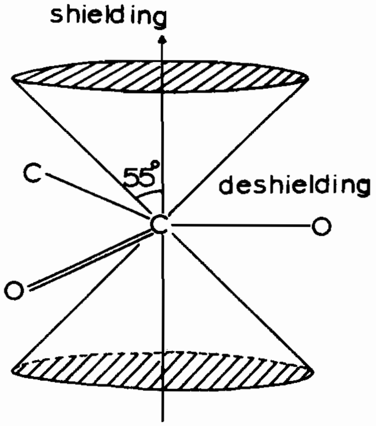

Figure 2. Assumed anisotropic shielding of the carboxylate group.

The three possibilities for geometrical isomerism are shown in Figure 2 of Part IV of this series.[1] We note that (II) and (III) have a two-fold axis of symmetry which bisects the NO$_2$–Co–NO$_2$ angle. It follows that the NMR resonances of any two equivalent protons on different amino-acid rings will necessarily be degenerate. The same is not true for (I) in which the amino-acid protons are no longer equivalent. We have measured the proton resonance of D$_2$O solutions of the potassium salts of the L(−)dinitro complexes with glycine, L-alanine and D-alanine. Table II summarises this data. For the alanine complexes only the methyl protons are reported while the resonances reported for the glycine complex are those of the methylene protons.

The alanine complexes show only two resonances, as expected for a methyl group coupled to a single α-proton with J=7.2 cps. This is very close to the value of 7.0 cps found for the tris-alaninato complexes.[3] The half width of each resonance is less than 1 cps. This is approximately the natural width found in resonances in which no chemical shift splitting is to be expected.[3]

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(5) Y. Saito, K. Nakatsu, M. Shiro, and H. Kuroa, *Acta Cryst.*, *8*, 729 (1955).
(6) G. A. Barclay, E. Goldschmied, N. C. Stephenson, and A. M. Sargeson, *Chem. Comm.*, 540 (1966).
(7) T. S. Piper, and A. G. Karipides, *J. Chem. Phys.*, *40*, 674 (1964).
(8) F. Woldbye, *Proc. Roy. Soc.*, *A*, *297*, 79 (1967).
(9) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, *3*, 1356 (1964).
(10) B. E. Douglas and S. Yamada, *Inorg. Chem.*, *4*, 1561 (1965).

Table II. Proton Magnetic Resonance Spectra in D_2O

Compound	Chemical Shift[a,b]
(—)-K[Co(D-ala)$_2$(NO$_2$)$_2$]	116.6 (1), 123.7 (1)
(—)-K[Co(L-ala)$_2$(NO$_2$)$_2$]	114.0 (1), 121.4 (1)
(—)-K[Co(gly)$_2$(NO$_2$)$_2$]	225.5 (0.03), 243.0 (0.97), 244.2 (0.97), 261.7 (0.03)
trans-[Co(gly)$_3$]	183.0 (1), 202.0 (1), 203.7 (1)
trans(—)-[Co(L-ala)$_3$] [c]	105.0 (1), 112.2 (2), 113.7 (1), 119.3 (1), 120.7 (1)
cis(—)-[Co(L-ala)$_3$] [c]	107.5 (1), 114.5 (1)

[a] In cps, at 60 Mc, downfield from TMS (external). [b] Relative peak areas in parentheses. [c] From reference 3.

These results then strongly suggest, but fail to prove, that the two alanine residues are equivalent in the complex. This restricts the isomeric possibilities to II and III. The glycine complex shows four lines whose intensity ratios are approximately 0.03:0.97:0.97:0.03. This is typical of an AB pair nonequivalent protons, as expected for the coordinated glycine residue. By standard techniques[11] we find $J = 17.5$ cps and $\sigma_A - \sigma_B = 0.11$ ppm or 6.7 cps. Using these values we compute an intensity ratio of 29.8 between the strong and weak resonances. Experimental integration gives the ratio 30.6. These results indicate that the resonances arise from only one type of AB pair. The value $J = 17.5$ cps compares well with $J = 18.0$ cps found for the methylene protons in ethylenediaminediacetic acid complexes of Co^{III}.[12] Thus the results for this complex also are consistent with structures II and III.

To effectively rule out structure I we must analyze the origin of the chemical shift difference which might be expected for this structure. We use as model compounds *trans*(—) tris-L-alaninato cobalt(III), IV, and *cis*(—) tris-L-alaninato cobalt(III),[3] V, whose NMR spectra are included in Table II. We note that the differences in the three types of methyl resonance in IV are 1.4 cps and 7.2 cps, with the methyl group which differs most from the others lying at high field.

We assume that the chemical shift difference in IV arises from neighboring group anisotropic shielding. Since this effect depends on admixture of excited states, the most important contributions will come from groups of atoms with relatively low energy optical transitions — in this case the cobalt atom and the carboxylate group. In a regular octahedral field the cobalt(III) ion would provide an isotropic effect, but departures from octahedral symmetry will provide anisotropy. In a complex with no symmetry elements we cannot determine the principal axis of this anisotropy. However, the absence of appreciable band splitting in the optical spectrum[3] suggests that it is small. Furthermore, if we assume the principal axis of the diamagnetic susceptibility to be the pseudo-three-fold axis of the complex, there is almost no difference in the shielding of the methyl protons on geometrical grounds. We, therefore, assume the carboxylate groups to be the source of the anisotropy. Within any one chelate ring the protons are in a identical enviroment, and the differences must then arise from the influence of neighboring rings. (The effect of chelate ring conformation induced by steric requirements of the methyl group does not seem important, since the tris-glycinato complex shows very similar chemical shift differences, Table II). Following previous workers[13] we assume the principal axis of the carboxylate group diamagnetic susceptibility to be perpendicular to the O—C—O plane. The regions of shielding and deshielding are shown in Figure 2. From molecular models we have calculated the interaction between various rings.

Table III.

Proton Ring	Carboxylate Ring	Angle	Distance	Effect
A	C	59°	5.4 Å	Small
C	A			
B	C	73°	5.1 Å	Deshielding
C	B			
A	B	75°	6.0 Å	Deshielding
B	A	58°	5.0 Å	Small

We identify the three rings by the following method. The coordination sphere of the cobalt contains a plane of three oxygen atoms and, perpendicular to it, a plane of three nitrogen atoms. Within either plane we identify a central or terminal atom. We now label the ring with central N and terminal O atoms, ring A; with central O and terminal N atoms, ring B; with terminal N and terminal O atoms, ring. C. Removal of ring A or B leaves the residue with a two-fold axis of symmetry. Hence, the interaction of ring B with C is equal to that of C with B, and that of A with C is equal to that of C with A. However, the effect of the carboxylate group in ring B on protons in ring A is not equal to the effect of the A ring carboxylate group on the B ring protons. In Table III, we list the approximate position of the protons relative to the shielding axis of the carboxylate groups shielding them.

The shielding is zero at 55° so that only the three interactions at about 75° are important. These are deshielding. Since the magnitude of the effect depends on the inverse cube of the distance of the proton from the carboxylate group, we expect to find the A ring proton at higher fields than those in the B and C rings. The latter two rings have resonances which differ slightly because of the different magnitude of their interaction with the A ring. This mechanism therefore, correctly predicts that one ring will be shielded more than the other two. Some confirmation comes from the chemical shifts of V. In this case all of the rings are related in the same way as the A and B rings in IV. Hence each set of protons will have its shielding largely determined by an effect similar to that of the A ring in IV. In other words we predict that the *cis* isomer will exhibit a resonance at a chemical shift similar to the A ring, rather than the B or C rings. Table II confirms this.

We can now consider the possibility that the *cis*-dinitro compounds may have structure (I) in which accidental degeneracy is occurring. The two rings in (I)

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(11) Pople, Schneider, and Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, p. 119 (1959).

(12) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, *4*, 1576 (1965).

(13) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy", Pergamon Press, Oxford, p. 122 (1959).

have the same initial relationship as the A and B rings in IV. Table III shows that the A ring will be strongly deshielded while the B ring is unaffected by the A ring. We may then predict a large difference in shielding between the two. The anisotropic shielding of the nitro-groups is difficult to assess as it is not known whether the groups are rotating or have fixed planes. However, were accidental cancellation of anisotropic effects possible in, for example, the dinitro-bis-L-alanine cobaltate-(III)ion, the different orientation of methyl groups in dinitro-bis-D-alanine cobaltate(III) ion would make the possibility of a second accidental degeneracy extremely unlikely. We must conclude that these complexes all have structures II or III. A simple choice between them is possible from the absorption spectrum.

The three coordinating species, carboxylate, amine and nitro groups have very different ligand field strengths. A measure is provided by the parameter D_q' defined by Wentworth and Piper[14] who give the values; NO_2, 3120 cm^{-1}; NH_3, 2490 cm^{-1}; and propionate 1904 cm^{-1}.

A strong tetragonal field such as that in *trans*-$[Co(en)_2Cl_2]^+$ ion gives rise to a pronounced splitting in the low energy absorption band of cobalt(III), this splitting being proportional to the difference in the ligand field on the fourfold or pseudo-fourfold axis and that in the plane perpendicular to it.[14] By contrast a complex ion such as *cis*$[Co(en)_2Cl_2]^+$ shows no such splitting. The *cis* and *trans* isomers of the bis-ammine ethylenediaminediacetic acid cobaltate(III) ion[12] are models for the present case. The *trans*-isomer shows a pronounced splitting with components at 460 mμ and 530 mμ. The *cis* complex shows no splitting and has a maximum at about 490 mμ. We see that (III) has a strong tetragonal field with carboxylate groups *trans* to one another and four groups with strong ligand fields in the plane perpendicular to that direction. However, (II) has an almost equal field on each metal-ligand axis. The field of two NH_2 groups will be nearly equal to the combined field of a nitro group and a carboxylate group. We therefore predict little or no splitting and an absorption maximum similar to that in the environment of six amino groups. $Co(en)_3^{3+}$ ion has an absorption maximum at 465 mμ and the present complexes have a single maximum with no sign of splitting at 470 mμ. We, therefore, conclude that the structure is II.

Isomer II is the product of the action of nitrite on *cis-cis-cis*, tris-alaninato-cobalt(III). Hence (a) rearrangement has occurred which involved the amine part of the ligand and (b) II appears to be the only thermodynamically stable product. We will not speculate on the mechanism of the rearrangement here, except to point out that the SN1CB mechanism apparently present in the rearrangement of tris-amino acid complexes[3] provides a path for the shift of an amine group. Further discussion must await a kinetic study.

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[14] R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, *4*, 709 (1965).