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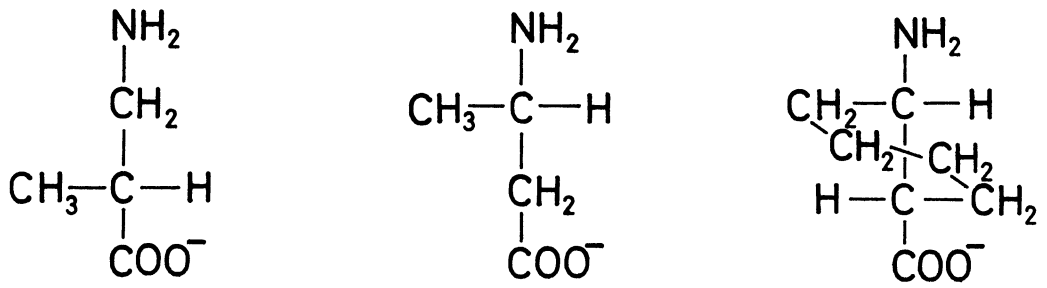
CIRCULAR DICHROISM OF *TRANS(N)*-(AMMONIATRIACETATO)(β-AMINOCARBOXYLATO)-COBALTATE(III) COMPLEXES CONTAINING ONE OR TWO ASYMMETRIC CARBON ATOMS IN A SIX-MEMBERED CHELATE RING

Norio KOINE, Naokazu SAKOTA, Jinsai HIDAKA* and Yoichi SHIMURA*
Department of Industrial Chemistry, Faculty of Engineering,
Ehime University, Bunkyo-cho, Matsuyama
* Department of Chemistry, Faculty of Science, Osaka University,
Toyonaka, Osaka

Three complexes of *trans(N)*-(ammoniatriacetato)(β-aminocarboxylato)cobaltate(III) containing one or two asymmetric carbon atoms in the β-aminocarboxylato chelate ring were prepared and their circular dichroism spectra were measured. Optical activity of these complexes in the spin-allowed *d-d* absorption band region mostly arises from the vicinal contributions of the asymmetric carbon atoms.

In a previous paper on circular dichroism (CD) of *trans(N)*- or *cis(N)*-(alaninate-*N*,*N*-diacetato)(α-aminocarboxylato)cobaltate(III) complexes,[1] the present authors have shown that each of two asymmetric carbon atoms contained in different ligands in a complex independently contributes to the CD spectra; in other word, two vicinal CD contributions from different ligands are approximately additive and separable. In the present letter we are reporting the additivity of vicinal CD contributions from two adjacent asymmetric carbon atoms in a six-membered chelate ring of *trans(N)*-(ammoniatriacetato)(β-aminocarboxylato)cobaltate(III) type complexes, *trans(N)*-[Co(ata)(β-am)]$^-$.

Three kinds of β-aminocarboxylic acid were used as the optically active chelate ligand (Fig. 1). *(R)*-(-)-α-methyl-β-alanine[2] (abbreviated to *(R)*-α-Me-β-alaH): the racemic modification was prepared by Pollack's method[3] and resolved by the method



(R)-(-)-α-Me-β-ala *(S)*-(+)-β-Me-β-ala *(S,S)*-(+)-achc

Fig. 1. The optically active β-aminocarboxylates.

of Kakimoto and Armstrong[4]; $[\alpha]_D^{19}$ -15.3° (*c* 1, water) (lit.[4] $[\alpha]_D^{29}$ -15.4° (*c* 1, water)). *(S)*-(+)-β-methyl-β-alanine[5] (abbreviated to *(S)*-β-Me-β-alaH): the *(S)* isomer was derived from *(S)*-alanine by the method of Balenović[6]; $[\alpha]_D^{15}$ +36.4° (*c* 2, water) (lit.[6] $[\alpha]_D^{19}$ +37.01°±1° (*c* 6, water)). *(1S,2S)*-(+)-*trans*-2-aminocyclohexanecarboxylic acid[7,8] (abbreviated to *(S,S)*-achcH): the racemic modification was prepared by the method of Einhorn and Meyenberg[9] and the optically active isomer was obtained by resolving its *N*-benzoyl derivative using (-)-α-phenethylamine as resolving agent; $[\alpha]_D^{16}$ +77.3° (*c* 2, water) (lit.[8] $[\alpha]_D^{17}$ +66.5° (*c* 2, water)).

The *trans(N)* isomers of K[Co(ata)(β-am)]·xH_2O type complexes were prepared and separated from the corresponding *cis(N)* isomers by means of column chromatography in a similar way as described for the corresponding α-aminocarboxylato complexes.[10] The isomers obtained were assigned to the *trans(N)* structure (Fig. 2) from the marked splitting of their first spin-allowed *d-d* absorption bands.[10-12]

Anal. Calcd for K[Co(ata){*(R)*-α-Me-β-ala}] = $C_{10}H_{14}N_2O_8KCo$: C, 30.93; H, 3.64; N, 7.22%. Found: C, 30.88; H, 3.57; N, 7.18%. Calcd for K[Co(ata){*(S)*-β-Me-β-ala}]·H_2O = $C_{10}H_{16}N_2O_9KCo$: C, 29.60; H, 3.98; N, 6.90%. Found: C, 29.41; H, 4.15; N, 6.59%. Calcd for K[Co(ata){*(S,S)*-achc}]·$3.5H_2O$ = $C_{13}H_{25}N_2O_{11.5}KCo$: C, 31.77; H, 5.14; N, 5.70%. Found: C, 31.91; H, 4.94; N, 5.76%.

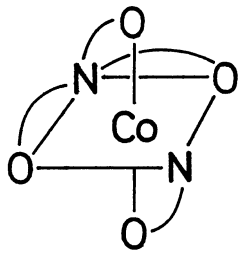


Fig. 2. *trans(N)*-$[Co(ata)(\beta\text{-am})]^-$ structure.

Fig. 3 shows the electronic absorption and CD spectra of the complexes in their first and second spin-allowed *d-d* transition region. The absorption curves of the three complexes are almost identical with one another, and also with that of *trans(N)*-$[Co(ata)(\beta\text{-ala})]^-$ reported previously[10] (β-ala = β-alaninate). The sign of CD components of the isomer containing *(S)* or *(S,S)* ligand are (+), (-) and (+) listing from longer wavelength one in the first absorption band region and (-) in the second absorption band region, though the complex of *(S)*-β-Me-β-ala lacks the second (-) component in the first absorption band region. It is noteworthy that the inverse sequence of signs, (-), (+), (-) and (+) listing from longer wavelength one in the first and second absorption band region has been found for the corresponding *(S)*-α-aminocarboxylato complexes.[10] Most interesting is the fact that CD curve of the *(S,S)*-achc complex is fairly perfectly reproduced by subtracting CD curve of the *(R)*-α-Me-β-ala complex from that of the *(S)*-β-Me-β-ala complex (Fig. 3). This means a simple additivity between the vicinal CD contributions of two adjacent asymmetric carbon atoms in the six-membered chelate ring.

The six-membered chelate ring of β-aminocarboxylato complex must be more stable in non-planar than in planar conformation. In fact, according to X-ray diffraction

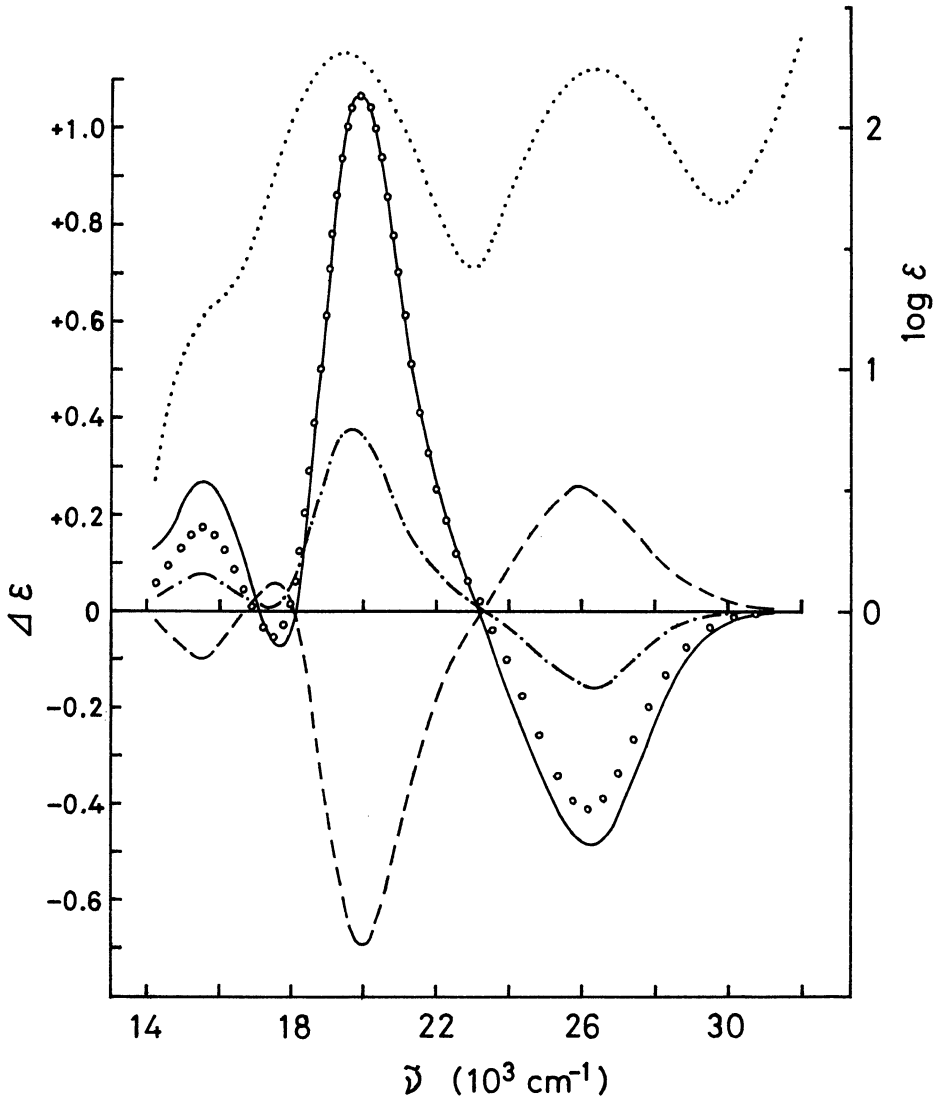


Fig. 3. Absorption and CD curves of *trans(N)*-[Co(ata)(β-am)]$^-$.
Absorption curve: ····· [Co(ata){*(S)*-β-Me-β-ala}]$^-$; CD curves: (1) ----- [Co(ata){*(R)*-α-Me-β-ala}]$^-$, (2) -·-·- [Co(ata){*(S)*-β-Me-β-ala}]$^-$, (3) ——— [Co(ata){*(S,S)*-achc}]$^-$, and (4) ∘∘∘∘∘ calculated curve, (2) - (1).

studies,[13,14] it has been shown that the deviation from flatness is larger in a β-aminocarboxylato chelate ring than in the corresponding α-aminocarboxylato one. Especially in the case of the present *(S,S)*-achc ligand, from consideration by molecular model constructions, the conformation of the six-membered chelate ring must be fixed rather rigidly because the fused-ring system of the coordinated liga is like to that of *trans*-decalin, though the six-membered chelate ring can take either chair or twisted boat conformation. Now, it may be reasonable to assume th the CD curve of *(S,S)*-achc complex is composed from three contributions, each vici one from α and β asymmetric carbon atoms and another one from the chiral conformat of six-membered chelate ring. Therefore, the additivity observed may be explained

showing that the CD of *(S,S)*-achc complex arises mostly from the vicinal contributions of two asymmetric carbon atoms and that the contribution from the chiral conformation of chelate ring is less important. An alternative explanation is to assume that the *(S)*-β-Me-β-ala chelate ring has a conformation same to that of the *(S,S)*-achc chelate ring and that the *(R)*-α-Me-β-ala chelate ring does not have ring conformational CD contribution. This latter postulation may be reasonable if we consider that the β-methyl group strongly demands an equatorial disposition but the α-methyl takes either equatorial or axial disposition.

Here we can remember the case of *(R,R)-trans*-1,2-diaminocyclohexane[15-17] or *(R,R)*-2,3-diaminobutane[18] complexes. In several square planar complexes of these diamine ligands, the rotational strength is approximately proportional to the number of asymmetric carbon atoms.[16] On the contrary, in several praseo type octahedral complexes, the rotational strength is approximately proportional to the number of chelate rings having chiral conformation.[15,17,18] The additivity, which was found in the present six-membered β-aminocarboxylato chelate ring, resembles to the behavior of square planar diamine complexes. Hawkins[14] suggested that the behavior of square planar diamine complexes also may be explained from predominant contribution of conformational effect by considering an equilibrium between equatorial and axial dispositions of methyl group. But the result obtained for the present complexes seems difficult to explain from the predominance of conformational contribution, and seems to support the predominance of true vicinal contributions from the asymmetric carbon atoms.

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