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PREPARATION AND STRUCTURAL ASSIGNMENT OF ISOMERS OF POTASSIUM *TRANS(N)*-(*C*-METHYL SUBSTITUTED AMMONIATRIACETATO)(β-ALANINATO)COBALTATE(III)

Norio KOINE, Hiroyuki YAMAGUCHI, Teiichi TANIGAKI,
Jinsai HIDAKA*, and Yoichi SHIMURA*
Department of Industrial Chemistry, Faculty of Engineering,
Ehime University, Bunkyo-cho, Matsuyama 790
* Department of Chemistry, Faculty of Science, Osaka University,
Toyonaka, Osaka 560

Potassium *trans(N)*-(*C*-methyl substituted ammoniatriacetato)-(β-alaninato)cobaltate(III) have been prepared, where *C*-methyl substituted ammoniatriacetates are *(S)*-alaninate-*N,N*-diacetate and *(R,S)*- or *(S,S)*-alaninate-*N*-isopropionate-*N*-acetate. Some of the possible isomers concerning the arrangement of three feet of the tripod-like quadridentate ligand have been isolated and assigned structurally on the basis of the nuclear magnetic resonance spectra and isomerization experiments.

When a cobalt(III) ion coordinates with a tripod-like quadridentate ligand having nonidentical feet$^{1)}$ such as *(S)*- or *(R)*-alaninate-*N,N*-diacetate$^{2)}$ or β-alaninate-*N,N*-diacetate,$^{3)}$ several geometrical and/or optical isomers are possible with respect to the arrangement of the three chelate rings. The present paper is concerned with the preparation and structural assignments of such type complexes, *trans(N)*-[Co(*C*-methyl substituted ammoniatriacetato)(β-ala)]$^-$, where the *C*-methyl substituted ammoniatriacetates are *(S)*-alaninate-*N,N*-diacetate(*(S)*-alada^{3-}), *(R,S)*- or *(S,S)*-alaninate-*N*-isopropionate-*N*-acetate(*(R,S)*- or *(S,S)*-alaipa^{3-}), and the bidentate β-ala denotes β-alaninate. The structure of a parent complex, *trans(N)*-[Co(ata)(β-ala)]$^-$ (ata = ammoniatriacetate),$^{4)}$ is shown in Fig. 1. In the present complexes, one or two of the six hydrogen atoms of the ata moiety of the parent complex are substituted with methyl groups. The possible isomers and isolated ones are shown in Table I.

A mixture of *(R,S)*-alaipaH_3(meso) and *(S,S)*-alaipaH_3(optically active) were derived from *(S)*-alanine by the following pathway and they were separated by fractional crystallization from water. *Anal.* Calcd for $C_8H_{13}NO_6$: C, 43.83; H, 5.99; N, 6.39%. Found: C, 43.99; H, 5.91; N, 6.39% for *(R,S)*-alaipaH_3 and C, 43.81; H, 6.05; N, 6.40% for *(S,S)*-alaipaH_3.

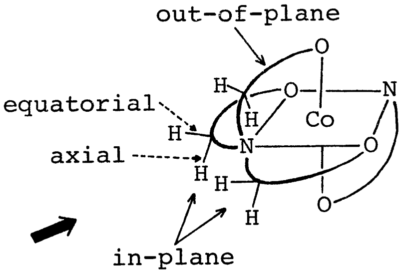
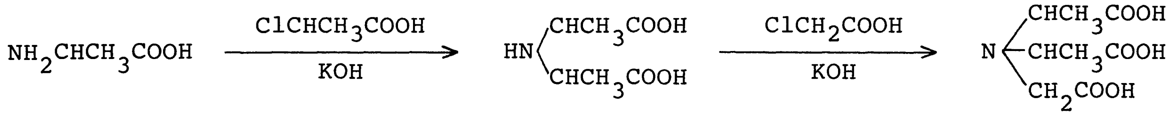


Fig. 1. Parent complex, *trans(N)*-[Co(ata)(β-ala)]$^-$.



$$\mathrm{NH_2CHCH_3COOH} \xrightarrow[\mathrm{KOH}]{\mathrm{ClCHCH_3COOH}} \mathrm{HN}\left\langle\begin{matrix}\mathrm{CHCH_3COOH}\\ \mathrm{CHCH_3COOH}\end{matrix}\right. \xrightarrow[\mathrm{KOH}]{\mathrm{ClCH_2COOH}} \mathrm{N}\left\langle\begin{matrix}\mathrm{CHCH_3COOH}\\ \mathrm{CHCH_3COOH}\\ \mathrm{CH_2COOH}\end{matrix}\right.$$

The cobalt(III) complexes were prepared and chromatographed over ion-exchange resin by the procedure used for the *trans(N)*-(β-alaninate-*N*,*N*-diacetato)(glycinato)-cobaltate(III) complex.3) The desired isomers were obtained by the usual method3) from the eluates of a reddish-purple band which consisted of *trans(N)* isomers.

(S)-alada complexes: One isomer, (*(S)*-alada)-1, was isolated in a dominant yield. *Anal.* Calcd for K[Co(*(S)*-alada)(β-ala)]·$3H_2O$: C, 27.15; H, 4.57; N, 6.33%. Found: C, 27.17; H, 4.69; N, 6.26%. This (*(S)*-alada)-1 isomer was treated with active charcoal in water at 70° for 1 hr. After removing the charcoal, the (*(S)*-alada)-1 complex was recovered from the solution in about 85% yield; then the remainder was chromatographed over ion-exchange resin.3) Two partly overlapped bands, which contain *trans(N)* isomers, were eluted. The earlier eluted isomer was (*(S)*-alada)-1 and the later eluted one was labeled (*(S)*-alada)-2. The (*(S)*-alada)-2 was obtained as a powder contaminated with a small amount of potassium chloride because of difficult crystallization. This isomer isomerized quickly into (*(S)*-alada)-1 by treating as above with active charcoal and the composition of resulting mixture was quite similar to that from the isomerization of (*(S)*-alada)-1. In these treatments, no isomerization occurred from *trans(N)* to *cis(N)* isomer.

(R,S)-alaipa complex: Only one isomer, (*(R,S)*-alaipa)-1, was isolated from the eluate almost quantitatively. *Anal.* Calcd for K[Co(*(R,S)*-alaipa)(β-ala)]·$3.5H_2O$: C, 38.39; H, 4.99; N, 6.02%. Found: C, 38.35; H, 4.96; N, 6.17%. No isomerization was recognized in the treatment with active charcoal.

(S,S)-alaipa complexes: The isomer (*(S,S)*-alaipa)-1 was isolated from the earlier fractions and (*(S,S)*-alaipa)-2 in dominant yield from the later fractions. *Anal.* (*(S,S)*-alaipa)-1: Calcd for K[Co(*(S,S)*-alaipa)(β-ala)]·$4.5H_2O$: C, 27.33; H, 5.22; N, 5.80%. Found: C, 27.20; H, 4.92; N, 5.85%. (*(S,S)*-alaipa)-2: Calcd for K[Co(*(S,S)*-alaipa)(β-ala)]·$3.5H_2O$: C, 28.39; H, 4.99; N, 6.02%. Found: C, 28.51; H, 4.91; N, 6.00%.

The complexes obtained show quite similar *d*→*d* absorption spectra to one another; thus the first band maxima are at 512-516 nm($\varepsilon_{\max}$ = 248-264) with an explicit shoulder near at 625 nm(ε = about 20), and the second band maxima at 379-382 nm ($\varepsilon_{\max}$ = 186-192). The absorption behavior points out that the complexes have *trans(N)* structures.2-5)

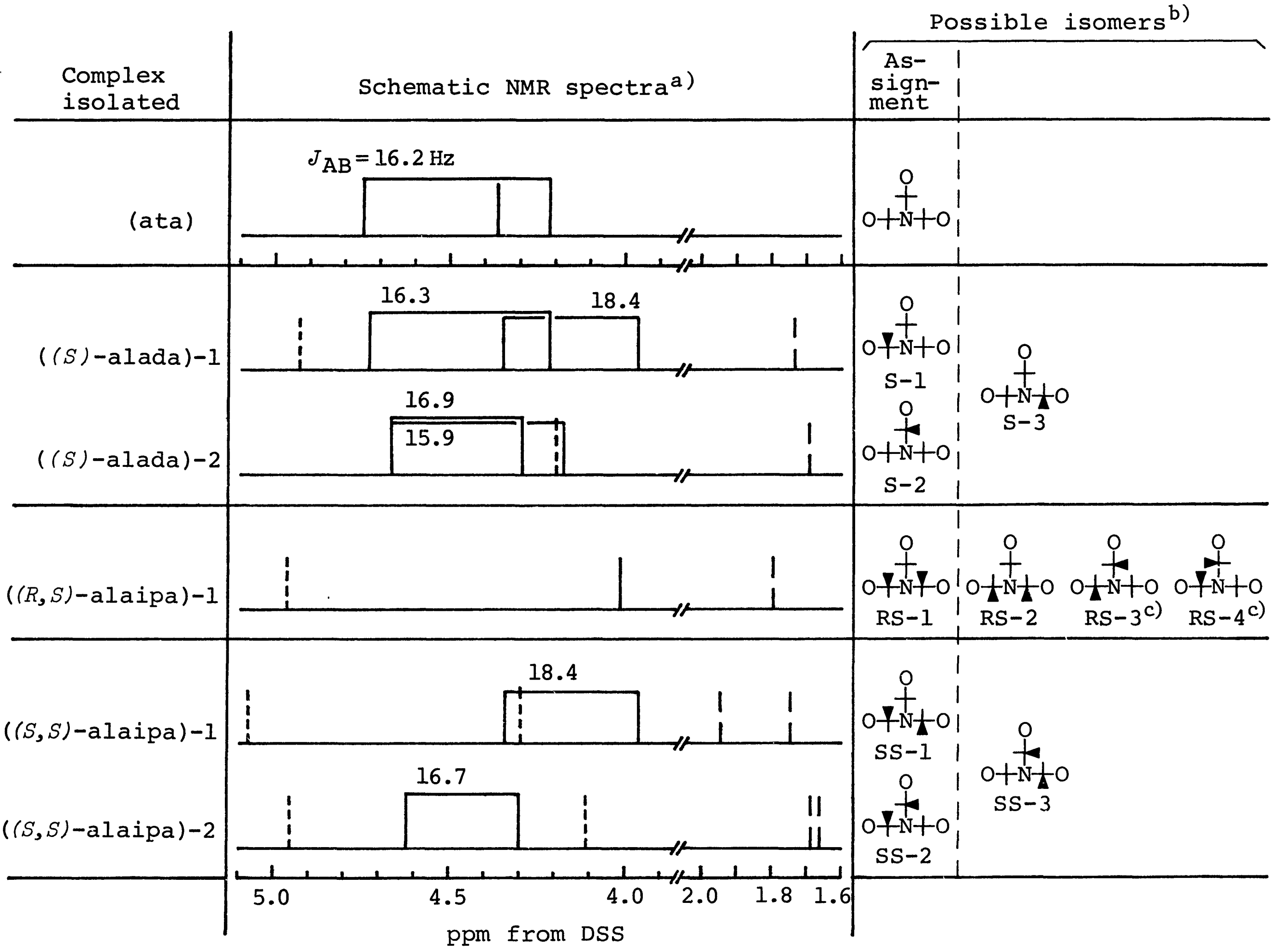
NMR spectrum of each the complex consists of quite sharp and distinct signals except for signals due to the ethylene protons of β-alaninate and the data are shown schematically in Table I with that of the ata complex.4) From the spectra it is reasonably considered that each of the complex consists of only one isomer. Moreover, it is possible to point out that (*(R,S)*-alaipa)-1 is either RS-1 or -2 with C_s symmetry, because of its simple NMR pattern.

The equilibrium experiment for the *(R,S)*-alaipa complex indicate that the (*(R,S)*-alaipa)-1 is much more stable than the other possible isomers. A molecular model examination shows that the two in-plane five-membered chelate rings of the coordinated tripod-like ligand are forced to take a non-planar conformation, and the substituents on the chelate rings are in the equatorial or axial disposition(Fig. 1).

In the RS-2 isomer, severe steric hindrance exists between the two axial methyl groups. In contrast to this, there is no such a hindrance in the RS-1 isomer, and ((*R*,*S*)-alaipa)-1 may be assigned to RS-1.

Sudmeier and co-workers[6)] pointed out that the *N*-acetate geminal proton coupling constants(J_{AB}) are helpful in distinguishing between the in-plane and out-of-plane *N*-acetate chelate rings of multidentate aminocarboxylato cobalt(III) complexes; thus it is approximately 16.0 Hz for the in-plane *N*-acetate and 18.0 Hz for the out-of-plane. In the previous paper,[3)] we confirmed that such a relationship is also held for the cobalt(III) complexes with β-alaninate-*N*,*N*-diacetate, and the J_{AB} values are in the range of 15.7-17.3 Hz for the in-plane acetate rings and 18.1-18.7 Hz for the

Table I. NMR Spectra(100 MHz) in D_2O at 30 °C and Structural Assignments of *trans(N)*-[Co(*C*-methyl substituted ammoniatriacetato)(β-ala)]$^-$ Ions.



(a) *t*-Butanol was used as an internal standard and the chemical shifts are referred to DSS as zero. The signals of ethylene protons of β-alaninate consist of two complicated peaks centered near at 2.5 and 3.1 ppm for all the complexes. The following symbols are used (the position of vertical line shows the chemical shift): ⊓, AB quartet; |, singlet; ¦, AX$_3$ quartet; ╎, AX$_3$ doublet. (b) Only the tripod-like ligand is schematically pictured looking along the arrow in Fig. 1. The symbol, ▼, shows the methyl group. (c) The antipode is also possible.

cut-of-plane. The AB pattern of the ata complex(J_{AB} = 16.2 Hz) is undoubtedly due to the in-plane acetate protons(Table I). Applying such relationship for the present complexes, (*(S)*-alada)-2 and (*(S,S)*-alaipa)-1 are unequevocally assigned to S-2 and SS-1, respectively, and (*(S)*-alada)-1 to either S-1 or -3 and (*(S,S)*-alaipa)-2 to SS-2 or -3.

The methine quartet of (*(S)*-alada)-1 and those of (*(S,S)*-alaipa)-1 and -2 at the lower field are well similar in their chemical shifts to that of (*(R,S)*-alaipa)-1, while those of (*(S)*-alada)-2, and of (*(S,S)*-alaipa)-1 and -2 at the higher field are different clearly from that of (*(R,S)*-alaipa)-1 as seen in Table I. It is considered, therefore, that the (*(S)*-alada)-1, (*(S,S)*-alaipa)-1 and -2 have an axial methine proton on the in-plane acetate ring as in (*(R,S)*-alaipa)-1, and (*(S)*-alada)-1 may be assigned to S-1 and (*(S,S)*-alaipa)-2 to SS-2. The structural assignments of the present complexes are summarized in Table I.

Further support for the assignments is provided by the following observations. On all the complexes in Table I, the chemical shift values are closely related to "position" where the individual proton is situated. Namely, the signals of methylene protons on the in-plane acetate ring appear near at 4.7 and 4.25 ppm and those on the out-of-plane appear near at 4.35 and 3.95 ppm. The signals of methine protons on the out-of-plane appear near at 4.2 ppm. It was confirmed by the spin-decoupling technique that in (*(S,S)*-alaipa)-1 the methyl doublet at the lower field constitute an AX_3 pattern with the methine quartet at the higher field which was assigned to the equatorial methine proton, and hence the doublet is assigned to the axial methyl protons. The doublet of (*(S,S)*-alaipa)-1 at the lower field differs obviously in the chemical shift from those of the other complexes and then the axial methyl group is present only in the (*(S,S)*-alaipa)-1.

In our previous paper,[2] the analogous α-aminocarboxylato complexes, *trans(N)*-[Co(*(R)*- or *(S)*-alada)(α-am)]$^-$ (α-am = glycinate, *(S)*-alaninate or *(S)*-prolinate) were prepared and their NMR and CD spectra were measured. For each of the five α-aminocarboxylato complexes, one isomer was isolated in dominant yield as in the present *(S)*-alada complex. The NMR signals for *(S)*-alada protons of these complexes were quite similar to one another and also well similar on the whole to those of the (*(S)*-alada)-1. It may be reasonable to consider that the geometrical arrangement of coordinated *(S)*-alada in the isomers dominantly isolated is common for all the *(S)*-alada complexes with α- and β-aminocarboxylato ligands. The NMR signals for *(R)*-alada protons of the complexes were also well similar on the whole to those of the (*(S)*-alada)-1. It is clear that the geometrical arrangement of coordinated *(R)*-alada in the isomers dominantly isolated is antipodal to that in the *(S)*-alada complexes.

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