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Preparation and Stereochemistry of *trans*-Dianionocobalt(III) Complexes with (*S*)-2-(Methylaminomethyl)pyrrolidine

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trans-Dinitro and dichloro cobalt(III) complexes containing (*S*)-2-(methylaminomethyl)pyrrolidine (*N*-Me-ampr) were prepared. Their stereochemistry differs a great deal from that of other *N*-methylated 1,2-diamines. The *N*-Me-ampr complexes prefer the *trans,cis* instead of the *trans,trans* configuration, the axial *N*-methyl groups being fairly stabilized. In the case of the dinitro complex, only one isomer which has the axial *N*-methyl groups, was isolated, but in the case of the *trans*-dichloro complex two diastereomers (*trans,cis(RR)* and *trans,cis(SS)*) were obtained. These dichloro isomers were slowly converted into an equilibrium mixture in methanol. The CD spectral data of the equilibrium mixture show that the *trans,cis(RR)* is more stable than the *trans,cis(SS)* isomer ($-\Delta G=0.4$ kcal/mol).

Substituents introduced into polyamine ligands have been seen to regulate the configuration of their metal complexes. For example, the dianionobis(diamine)cobalt (III) complexes (diamine=*N*-substituted 1,2-diamine) sterospecifically adopt the *trans* configuration with respect to the unidentate anionic ligands, and the *N*-substituents take *trans* position to each other. Thus the structures of these complexes are not *trans,cis* but *trans, trans* configuration.[1] The *C*- and *N*-substituents in the chelate rings generally prefer the equatorial position[2] and cnsequently the chelate rings are fixed to the δ or λ gauche conformation.

(*S*)-2-(Methylaminomethyl)pyrrolidine (*N*-Me-ampr) has some characteristics differing from other *C*- and *N*-substituted diamines. The absolute configuration of the asymmetric carbon in the five membered chelate ring is *S* and the gauche chelate conformation should be fixed to δ.[3] The asymmetric nitrogen in the pyrrolidine ring is considered to coordinate with the *S* configration.[4] On the other hand, the absolute configuration of the asymmetric nitrogen center with the *N*-methyl groups is capable of having either the *S* or the *R* configuration, corresponding to the axial or the equatorial *N*-methyl groups, respectively.

For the cobalt(III) complexes of the type $[CoX_2(N\text{-Me-ampr})_2]^+$ ($X=Cl^-$ or NO_2^-), we have observed some stereochemical features differing from the complexes of other *N*-methyl diamines. First, the *N*-Me-ampr complexes have the *trans,cis* configuration instead of the *trans,trans*. Second, the axial *N*-methyl groups are fairly stabilized. Third, equilibrium between the isomer having the axial and that having the equatorial *N*-methyl groups is influenced by the kind of apical anionic ligands.

Experimental

trans,cis(SS)-*[Co(NO$_2$)$_2$(*N*-Me-ampr)$_2$]ClO$_4$.* *Air Oxidation Method*: To an aqueous solution of $CoCl_2\cdot 6H_2O$ (1.19 g in 10 cm^3 of water) was added a solution of *N*-Me-ampr (1.14 g in 5 cm^3 of water containing 0.41 cm^3 of concentrated hydrochloric acid), and $NaNO_2$ (0.69 g) then being added quickly. The resulting solution was vigorously aerated in an ice cold bath for 20 min, and then for 2 h at room temperature. The solution was warmed and evaporated to half its volume at 60 °C on a water bath. Yellow crystals appeared on addition of large excess of $NaClO_4$. The crystals were filtered off and washed with a small volume of cold water, and ethanol and then ether, and air dried. The compound was recrystallized from a small volume of hot water. Yield; 0.5 g. Found: C, 30.13; H, 5.59; N, 17.42%. Calcd for $C_{12}H_{28}N_6O_8ClCo$: C, 30.00; H, 6.06; N, 17.13%.

Derivation from Sodium Hexanitrocobaltate (Na$_3$[Co(NO$_2$)$_6$]): A solution of $Na_3[Co(NO_2)_6]$ (4.04 g in 30 cm^3 of water) was mixed with *N*-Me-ampr (2.28 g), warmed on a water bath at 70 °C for 15 min and then filtered. Yellow crystals appeared on addition of an excess of $NaClO_4$ (3 g) to the filtrate, and the mixture was warmed on a water bath at 60 °C for about 5 min. After being stored in a refrigerator overnight, the precipitate was filtered off, washed with a small volume of cold water and ethanol, and dried under reduced pressure. The compound was recrystallized from a small volume of water. Yield; 3.15 g. Found: C, 30.24; H, 5.89; N, 17.56%. Calcd for $C_{12}H_{28}N_6O_8ClCo$: C, 30.00; H, 6.06; N, 17.13%.

The visible absorption, CD and ^{1}H NMR spectral data indicate that the dinitro complexes prepared by two methods are identical.

trans,cis(SS)-*[CoCl(NO$_2$)(*N*-Me-ampr)$_2$]ClO$_4$.* A solution of *trans,cis(SS)*-$[Co(NO_2)_2(N\text{-Me-ampr})_2]ClO_4$ (2.0 g) in concentrated hydrochloric acid (4 cm^3) was warmed at 40 °C on a water bath for 1 h. Excess $LiClO_4$ (0.5 g) was added and the solution was cooled to room temperature. Red crystals were filtered off and washed with a small volume of cold water and ethanol and dried under reduced pressure. The product was recrystallized from methanol. Yield; 1.6 g. Found: C, 30.54; H, 6.14; N, 14.35%. Calcd for $C_{12}H_{28}N_5O_6Cl_2Co$: C, 30.78; H, 6.03; N, 14.96%.

trans,cis(SS)-*[CoCl$_2$(*N*-Me-ampr)$_2$]ClO$_4$.* *trans,cis(SS)*-$[CoCl(NO_2)(N\text{-Me-ampr})_2]ClO_4$ (0.4 g) was dissolved in hydrochloric acid (10 cm^3) and the solution was heated on a water bath at 80 °C until the color of the solution turned from red to deep green. Green crystals formed by the addition of perchloric acid (60% 3 cm^3), were filtered off, washed with a small volume of cold water, ethanol and ether, and air dried. The product was recrystallized from methanol. Yield; 0.3 g. Found: C, 31.41; H, 6.15; N, 12.45%. Calcd for $C_{12}H_{28}N_4O_4Cl_3Co$: C, 31.49, H; 6.17; N, 12.24%.

trans,cis(RR)-*[CoCl$_2$(*N*-Me-ampr)$_2$]ClO$_4$.* To an aqueous solution of $CoCl_2\cdot 6H_2O$ (2.39 g in 15 cm^3 of water) was added *N*-Me-ampr (2.28 g in 10 cm^3 of water) and the resulting solution was aerated for 5 h with carbon dioxide free air. After concentrated hydrochloric acid (15 cm^3) had been added, the solution was heated on a boiling water bath and concentrated to about half of its original volume. Green crystalline powder of the *trans*-dichloro complex was formed by the addition of perchloric acid (60% 10 cm^3), was filtered off, washed with a small amount of ethanol and ether, and air dried.

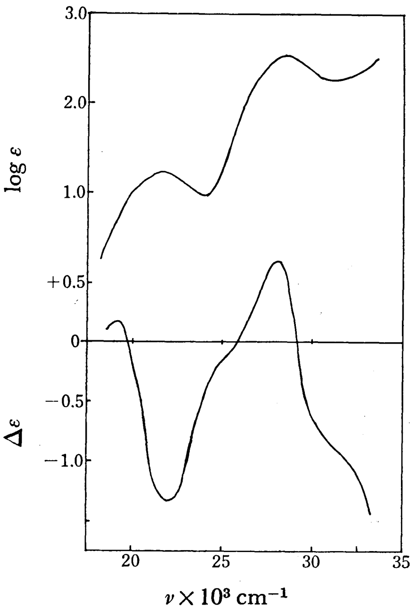

Fig. 1. Absorption (upper) and CD spectra (lower) of *trans*-$[Co(NO_2)_2(N\text{-Me-ampr})_2]ClO_4$.

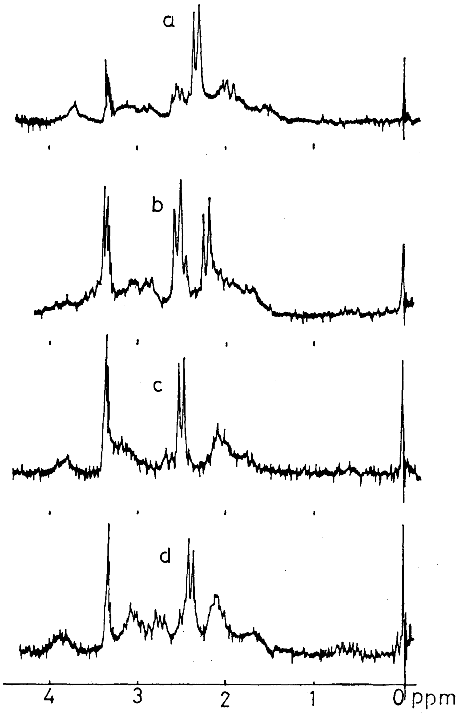

Fig. 2. ^1H NMR spectra of *N*-Me-ampr complexes. a) *trans*-$[Co(NO_2)_2(N\text{-Me-ampr})_2]ClO_4$, b) *trans,cis*-$[CoCl(NO_2)(N\text{-Me-ampr})_2]ClO_4$, c) *trans,cis*(*SS*)-$[CoCl_2(N\text{-Me-ampr})_2]ClO_4$, d) *trans,cis*(*RR*)-$[CoCl_2(N\text{-Me-ampr})_2]ClO_4$.

This product was found to be a mixture of two isomers of *trans,cis(SS)* and *trans,cis(RR)* on the basis of ^1H NMR and CD spectral data. The pure *trans,cis(RR)* isomer was obtained by repeated recrystallization from methanol (less soluble part). Yield; 2.0 g. Found: C, 30.93; H, 6.06; N, 12.49%. Calcd for $C_{12}H_{28}N_4O_4Cl_3Co$: C, 31.49; H, 6.17; N, 12.24%.

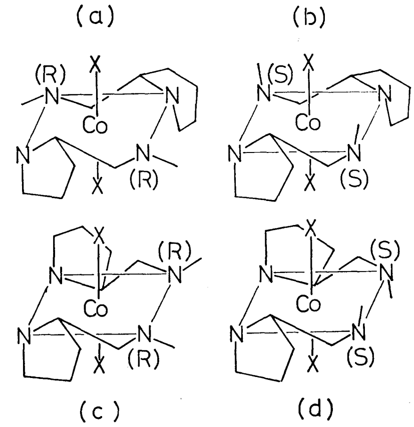

Fig. 3. Four possible structures of *trans*-$[Co(NO_2)_2(N\text{-Me-ampr})_2]^+$ ions.
a) *trans,trans(RR)*, b) *trans,trans(SS)*, c) *trans,cis(RR)*, d) *trans,cis(SS)*.

Results and Discussion

trans-$[Co(NO_2)_2(N\text{-Me-ampr})_2]ClO_4$ was prepared by two methods (usual air oxidation and a reaction of diamine with $[Co(NO_2)_6]^{3-}$ ion). The absorption, circular dichroism (CD) and ^1H NMR spectra of the products obtained by the two methods were identical with each other, indicating the identity of the complexes. The absorption spectrum (Fig. 1) shows two absorption maxima at 465 nm ($\varepsilon = 189.7$) and 354 nm ($\varepsilon = 3720$), indicating that the complex has *trans* configuration with regard to the nitrite ions.[1,5] In the ^1H NMR spectrum of this complex (in CD_3OD), one doublet assignable to the *N*-methyl groups was observed at 2.36 ppm, indicating that the two *N*-Me-ampr are chemically equivalent (Fig. 2). Since the CD spectrum of *N*-Me-ampr complex (Fig. 1) differs a great deal from the other complexes of *N*-substituted diamines with fixed δ conformations, the vicinal contribution from the asymmetric nitrogens would affect the CD pattern.

Four possible structures of the *trans*-$[Co(NO_2)_2(N\text{-Me-ampr})_2]^+$ ion, with equivalent *N*-Me-ampr, are shown in Fig. 3. Two forms (a,b) have the *trans,trans* configuration and the others (c,d) the *trans,cis* configuration. The structures of this type were assigned by converting them into chloronitro complexes in hydrochloric acid.[5] When the dinitro isomer has the *trans,trans* configuration, the chloronitro complex should be composed of two diastereomers, the yields of which would differ. In such diastereomers, however, both chelate rings are situated in identical chemical environment. Consequently, the ^1H NMR spectra of the *trans,trans* isomers would show two kinds of *N*-methyl signals with different intensities. On the other hand, the *trans,cis* isomer should give rise to only one isomer of chloronitro complex. However, the two chelate rings are affected by distinct circumstances of anionic ligands, which will result in two *N*-methyl resonances with equal intensities.

The ^1H NMR spectrum of the $[CoCl(NO_2)(N\text{-Me-ampr})_2]^+$ ion (in CD_3OD) showed two *N*-methyl doublets at 2.24 ppm and 2.58 ppm (Fig. 2). The intensities of these methyl signals could be regraded as practically equal. The spectral pattern did not change after repeated recrystallization from methanol or 1M HCl solution. This indicates that the chloronitro complex adopts the *trans,cis* configuration, though the absolute configuration of the *N*-methyl centers, either the *RR* or the *SS*, can not be determined from the ^{1}H NMR data. The orientation of the *N*-methyl group was clarified by examining the CD curves of dichloro complexes.

The *trans,cis*-[Co(NO$_2$)$_2$(*N*-Me-ampr)$_2$]$^+$ ion was converted into the *trans,cis*-[CoCl$_2$(*N*-Me-ampr)$_2$]$^+$ ion in hydrochloric acid, where no stereochemical change including the inversion of the *N*-methyl centers should occur. The ^{1}H NMR spectrum of the dichloro complex has a single doublet at 2.51 ppm assignable to the *N*-methyl resonances, as expected (Fig. 2). The *trans*-dichloro complex prepared by the usual air oxidation showed a CD curve differing a great deal from that of the *trans,cis*-dichloro complex derived from the *trans,cis*-dinitro complex (Fig. 4). This indicates that the *trans*-(Cl)-[CoCl$_2$(*N*-Me-ampr)$_2$]$^+$ ion exist in at least two isomeric forms. The ^{1}H NMR spectrum of the dichloro complex prepared by air oxidation showed only one doublet at 2.45 ppm assignable to the *N*-methyl groups (Fig. 2), which shows that the *N*-Me-ampr chelates are situated in equivalent circumstances.

Two isomers of the *trans*-dichloro complex show mutarotation in methanol solution, and the CD spectra of both isomers converge to the same curve. This suggests that these complexes isomerize and give rise to the same equilibrium mixture. The configurational rearrangement from *trans,cis* to *trans,trans* and *vice versa* seems to be unlikely. However, it is possible that the inversion of asymmetric nitrogen of *N*-methyl group takes place to contribute to the mutarotation. We thus conclude that the *trans*-dichloro complex prepared from air oxidation also has the *trans,cis* configuration. One of the dichloro isomers should adopt the *RR* configuration and the other the *SS* configuration with respect to the *N*-methyl centers (Fig. 3).

The CD spectrum is considered to arise from the configurational, the conformational and the vicinal effects[6]. In the case of *trans*-dianiono complexes, only the latter two effects should be taken into consideration. It is assumed that the contribution from the δ conformations and asymmetric *S*-nitrogens in pyrrolidine rings are equal for both of the *trans*-dichloro isomers, and that the vicinal contributions from the *S* and the *R* methylated nitrogens are opposite in sign and have approximately equal intensities. Half of the subtract of the CD of *trans,cis(SS)* from that of the *trans,cis(RR)* would be regarded as the vicinal contribution of *R* nitrogens. The half of the CD curve obtained by subtracting the curve of the former dichloro isomer (from dinitro complex) from that of the latter (by air oxidation) are given in Fig. 4 (1/2*(trans,cis(RR)—trans,cis(SS))* or *vice versa*). The vicinal contribution of the *R* nitrogens is known to have a positive and a negative Cotton effect dominating the E_g and the A_{2g} (D_{4h}) components, respectively, in the first d-d transition region[6]. From a positive (E_g) and a negative (A_{2g}) maxima in the subtracted CD curve (Fig. 4), it is considered that the absolute configuration of *N*-methyl centers in the dichloro complex obtained by air oxidation is *R* (equatorially disposed *N*-methyl groups), and that of the dichloro complex prepared from the dinitro complex as well as the parent dinitro complex is *S* (axial *N*-methyl groups).

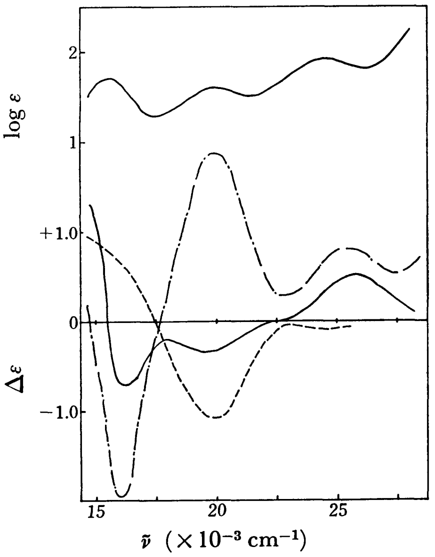

Fig. 4. Absorption (upper) and CD (lower) curves of *traas*-dichloro isomers of *N*-Me-ampr complexes *SS* (——) and *RR*(——), and the differential CD spectrum (1/2×(*RR*−*SS*)) (----).

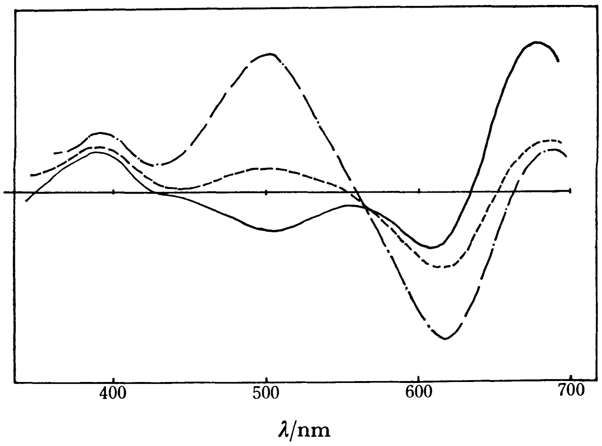

Fig. 5. CD spectra of *trans*-dichloro isomers and the equilibrium mixture (——).

From CD spectral data of an equilibrium mixture, the free energy difference between the axial and the equatorial *N*-methyl groups is calculated to be *ca.* 0.4 kcal/mol (axial(*S*): equatorial (*R*)=1 : 2)(Fig. 5). In *trans*-dianiono complexes *N*-methyl groups in the axial orientation are known to interact with the apical ligands more strongly than those in the equatorial orientation. DeHayes and Busch calculated the free energy difference between the axial and the equatorial *N*-methyl groups to be 0.49 kcal/mol from conformational analysis.[7] However, the experimental data obtained so far show that the equatorial *N*-methyl groups are far more profitable than the axial ones in octahedral Co(III) complexes.

The stereochemistry of *N*-Me-ampr complexes is quite different from that of other *N*-methyl substituted diamines. The *N*-Me-ampr complexes prefer the *trans,cis*

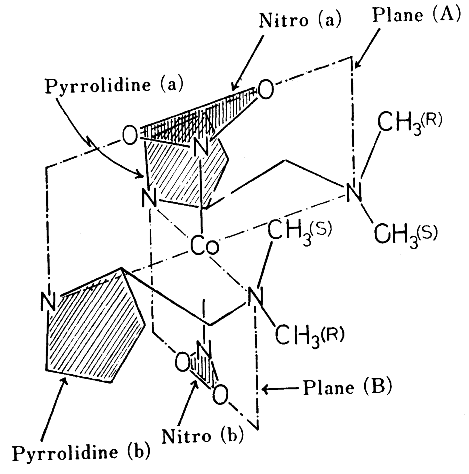

Fig. 6. Illustrative structure of *trans,cis(SS)*-[Co(NO$_2$)$_2$(*N*-Me-ampr)$_2$]$^+$ ion.

rather than the *trans,trans* configuration. The *N*-methyl groups orientate to the axial position more easily than other *N*-methylated diamine complexes. In the *trans*-dinitro complex, the *N*-methyl groups adopt stereospecifically axial positions, and in the *trans*-dichloro complex, two isomers arise due to the difference of the absolute configuration of asymmetric nitrogen centers (axial and equatorial *N*-methyl groups).

The predominance of the axial *N*-methyl groups in the *trans*-dinitro complexes in comparison with the *trans*-dichloro complexes indicates that the orientation of *N*-methyl groups is affected by the kind of apical ligand. The characteristic orientation of the *N*-methyl groups would be attributed to the geometry of apical ligands as well as the steric interaction among the pyrrolidine rings, the apical ligands and the *N*-methyl groups. A possible structure of *trans,cis*-[Co(NO$_2$)$_2$(*N*-Me-ampr)$_2$]$^+$ is illustrated in Fig. 6. The triangular nitro groups[8] result in rotational isomers around the NO$_2^-$–Co–NO$_2^-$ axis. When the nitro group (a) is situated on the plane (A) (Fig. 6), the steric repulsion between nitro group (a) and pyrrolidine ring (a) can be reduced, and another nitro group (b) will locate on the plane (B) for the same reason. The equatorial methyl groups will produce more strict steric repulsions than the axial ones. This may be the reason why the *N*-methyl groups prefer to axial position in the dinitro complex.

Since the chloride ion has spherical symmetry, the *trans*-dichloro complexes has no rotamer around the Cl$^-$–Co–Cl$^-$ axis. The orientation of *N*-methyl groups depends only on stereochemical interactions between the Cl$^-$ and the *N*-methyl groups. The equatorial *N*-methyl groups in the *trans*-dichloro complex are stabilized to a great extent than the axial ones as well as other *N*-methylated diamine complexes. However, the reason why the axial *N*-methyl group is more stabilized than other *N*-methyl derivatives is not clear.

According to the conformational analysis of some *C*- and/or *N*-methyl substituted diamine complexes,[7] the axial *N*- and *C*-methyl groups flatten the chelate ring conformations. It was demonstrated by X-ray crystal structure analysis[9] that a remarkable flattening of the chelate rings takes place in the *cis*-[Co(NO$_2$)$_2$(ampr)$_2$]$^+$, (ampr=(*S*)-2-(aminomethyl)pyrrolidine) relative to ethylenediamine chelate rings. The averaged dihedral angle of N–C–C–N moieties in the ampr complex was 46°, that for ethylenediamine chelate 55°. It is possible that the asymmetric *S*-nitrogen in the pyrrolidine rings of *N*-Me-ampr complexes would also flatten the chelate rings, reducing the energy difference between the axial and the equatorial *N*-methyl groups.

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