Synthesis of *trans*(N)-Carbonatobis(*N*,*N*-dimethylglycinato)cobaltate(III) by Decarboxylation of *N*,*N*-Dimethylglycine

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Trans(N)-$[Co(CO_3)(dmgly)_2]^-$ and *trans*(N)-$[Co(ox)(dmgly)_2]^-$ were prepared and characterized by absorption, circular dichroism, ^1H NMR, and ^{13}C NMR spectra, where Hdmgly and H_2ox denote *N*,*N*-dimethylglycine and oxalic acid, respectively. The carbonato complex was yielded by the reaction of $[CoCl(NH_3)_5]Cl_2$ and Hdmgly without addition of carbonate or hydrogencarbonate ions; decarboxylation of Hdmgly followed by substitution with CO_3^{2-} was suggested. The molecular structure of spontaneously resolved $(+)_{589}$-*trans*(N)-$K[Co(CO_3)(dmgly)_2]\cdot H_2O$ was determined by the single crystal X-ray diffraction method. The crystal data and final *R* value are: orthorhombic, $P2_12_12_1$, $a=15.483(1)$, $b=15.624(2)$, $c=6.092(1)$ Å, $V=1473.7(3)$ Å^3, $Z=4$, $R=0.022$ for 2390 reflections. The crystal used had the *Λ* configuration. The mean Co–N bond length, 1.996 (2) Å is longer than the usual Co–N (primary amine) bond length by 0.03—0.08 Å due to the steric repulsion between the methyl groups and other ligands.

Several complexes of the type, $[CoL(am)_2]^-$ (L= didentate O,O-chelate ligand such as CO_3, Ham=amino acid such as glycine) have been studied.[1—6] However, little attention has been paid to the same type complexes containing *N*,*N*-dialkyl amino acid. This is probably due to the low coordination ability of the tertiary amine nitrogen atom through steric crowding. This paper deals with the preparation and characterization of $[Co(CO_3$ or ox$)(dmgly)_2]^-$ and the molecular structure of *trans*(N)-$K[Co(CO_3)(dmgly)_2]\cdot H_2O$. Special attention is paid to the formation of $[Co(CO_3)(dmgly)_2]^-$ by the decarboxylation of dmgly without addition of carbonate or hydrogencarbonate ions.

Experimental

Preparation of *trans*(N)-$K[Co(CO_3)(dmgly)_2]\cdot H_2O$. Method A. This complex was prepared by nearly the same procedure as that reported by Shibata et al.[1] for $K[Co(CO_3)(gly)_2]$ (Hgly=glycine). To purify it, the product was treated with methanol–ethanol (1 : 1), the insoluble material was filtered off, and the filtrate was gradually evaporated to dryness. The crude complex was extracted with 1-propanol–methanol (5 : 1). The extract was gently evaporated to yield a blue precipitate, which was collected by filtration, with care to avoid collecting colorless salts separated out on the upper side of the beaker. This process was repeated two or three times. The product was dissolved in water, and the solution was chromatographed on Dowex 1×8 with 0.2 M KCl (1 M=1 mol dm^{-3}) as an eluent. No evidence indicative of the presence of the isomers was obtained. The eluate containing the blue band was collected and concentrated to dryness. By treating the residue with 1-propanol–methanol (5 : 1) as described above, the complex was obtained as blue prismatic crystals.

Method B. A solution of Hdmgly·HCl (2.1 g) in water (120 cm^3) was neutralized to pH about 8.5 with 1 M KOH. To this solution $[CoCl(NH_3)_5]Cl_2$ (1.0 g) was added. After stirring at 55—60 °C for 2 h, the pH of the solution was readjusted to about 8.5. Then the mixture was left at 55—60 °C for 24 h. As the reaction proceeded, the color of the solution changed from red to deep blue purple. The resulting solution was diluted 8—10 times with water and poured onto an SP-Sephadex C-25 (K^+ form) column (φ3 cm×20 cm) to remove the red-purple by-products. The effluent was rotary evaporated until dry. Then 50 cm^3 of 1-propanol–diethyl ether (2 : 3) was added to the residue and the mixture was stirred to dissolve as much complex as possible. The mixture was left overnight in a refrigerator. The precipitate was collected by filtration and washed with the above solvent. The solid obtained was mixed with 1-propanol–methanol (5 : 1, 10 cm^3), and the insoluble material was filtered off. The filtrate was evaporated to dryness, the residue was dissolved in a minimum amount of methanol, and the solvent was evaporated on a water bath. When solids appeared on the upper side of the beaker, which were apparently contaminated with impurities, the solution was filtered. The filtrate was further concentrated carefully at 50—60 °C until blue needles began to crystallize at the bottom of the beaker. The crystals were collected by filtration and washed with ethanol. Yield: 0.3 g. Found: C, 28.22; H, 4.79; N, 7.34%. Calcd for $C_9H_{18}N_2CoKO_8$: C, 28.43; H, 4.77; N, 7.37%. A piece of the crystal was used for the X-ray diffraction study.

Optical Resolution of $K[Co(CO_3)(dmgly)_2]\cdot H_2O$. *Λ*-$(+)_{589}$-$[Co(ox)(en)_2]Cl$[7] (590 mg) was added to an aqueous solution (50 cm^3) of $AgCH_3COO$ (320 mg) with stirring. The mixture was ice-cooled and filtered to remove AgCl. The filtrate was concentrated to about 10 cm^3, and to this was added a solution of $K[Co(CO_3)(dmgly)_2]\cdot H_2O$ (760 mg) in water (2 cm^3). The mixture was slowly evaporated to dryness, and to the ice-cooled residue was added four 0.5 cm^3 portions of water–ethanol (1 : 1). The less soluble diastereomer remained undissolved together with a small amount of the more soluble one. After cooling the mixture, the solid was collected by filtration. Attempts to purify this product

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were unsuccessful. The filtrate was concentrated to dryness, and the residue was treated with methanol (10 cm^3). An insoluble solid was filtered off, and the solvent was evaporated to give a blue complex together with a small amount of the resolving agent. This was dissolved in a small amount of water and the solution was applied onto a column of Dowex 1×8 (Cl^- form). After the column was washed with water, the adsorbed complex was eluted with 1 M KCl. The effluent containing the blue band was collected and evaporated to dryness. The residue was dissolved in a minimum amount of methanol and the potassium salt of the complex was purified by the same method as that for the racemate (Method B). Since the optical purity of the complex thus obtained could not be confirmed, the crop showing the maximum specific rotation among several experiments under different conditions was regarded as the pure enantiomer. Found: C, 28.45; H, 4.80; N, 7.13%. Calcd for $C_9H_{18}N_2CoKO_8$: C, 28.43; H, 4.77; N, 7.37%. $[\alpha]_{589}=-2330°$ (*c* 0.05, H_2O).

Preparation of *trans*(N)-K[Co(ox)(dmgly)$_2$]·H$_2$O. To a solution of *trans*(N)-K[Co(CO_3)(dmgly)$_2$]·H_2O (3.8 g) in water (20 cm^3) was added 50% acetic acid (15 cm^3). After this was stirred for 30 min, $K_2C_2O_4$·H_2O (2.2 g) was added, and the mixture was stirred at 40—45 °C for 4 h, and then filtered. The solution was chromatographed with a column of Dowex 1×8 in a similar manner to that for [Co(CO_3)(dmgly)$_2$]$^-$ (Method A), and a mixture of the desired complex and KCl was obtained. The product was extracted with methanol–ethanol (1 : 1, 150 cm^3), and the solvent was evaporated to yield the crude complex. This was recrystallized from the above mixed solvent several times to give the blue crystalline complex. Found: C, 29.72; H, 4.40; N, 6.63%. Calcd for $C_{10}H_{18}N_2CoKO_9$: C, 29.42; H, 4.44; N, 6.86%.

Crystal Structure Determination of (+)$_{589}$-K[Co(CO_3)(dmgly)$_2$]·H$_2$O. A dark blue prismatic crystal of approximate dimensions of 0.2×0.3×0.5mm^3 was used for the measurement. The crystal data of the complex are as follows: $C_9H_{16}N_2CoKO_7$·H_2O, FW 380.3, orthorhombic, $P2_12_12_1$, $a=15.483(1)$, $b=15.624(2)$, $c=6.092(1)$ Å, $V=1473.7(3)$ Å^3, $D_x=1.71$ g cm^{-3}, $Z=4$, μ(Mo $K\alpha$)=14.80 cm^{-1}. Diffraction data were collected to $2\theta=60°$ using graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.71073$ Å) and the θ–2θ scan mode (scan range; 0.80+0.35 tanθ/°) on an Enraf Nonius CAD-4 diffractometer. Lattice constants were calculated from 25 2θ values ($22<2\theta<25°$). Three standard reflections were monitored every 2 h and showed no detectable changes during the data collection. The intensities were corrected for Lorentz and polarization, and empirical absorption correction was applied based on the ψ-scan data. Structure determination and refinement were done using 2390 unique reflections with $|F_o|>3\sigma(|F_o|)$. All the calculations were carried out on a HITAC M-680H computer at the Computer Center of the Institute for Molecular Science with the computation program system UNICS-III.[8] Cobalt was located using MULTAN 78[9] and other non-hydrogen atoms were found by the usual Fourier methods. The space group indicates spontaneous resolution of the complex, and the absolute configuration was determined by the Hamilton's *R* factor test. Block-diagonal least squares refinement minimizing $\Sigma w(|F_o|-|F_c|)^2$ converged to $R=0.022$ and $R_w=0.034$ with the Λ configuration. On the other hand, the refinements in the enantiomeric atomic parameters (the Δ configuration) resulted in the residual values of $R=0.038$ and $R_w=0.059$. From these results, we conclude that the complex has the Λ configuration. The atomic parameters of non-hydrogen atoms are listed in Table 1.[10]

Measurements. Optical rotations were measured using a JASCO DIP-370 polarimeter. Absorption and circular dichroism (CD) spectra were measured with a Shimadzu UV-210A spectrophotometer and a JASCO J-600 spectropolarimeter, respectively. ^{1}H and ^{13}C NMR spectra were obtained with a JEOL JNM-FX-100 spectrometer using DSS and dioxane, respectively as an internal reference.

Results and Discussion

The K[Co(CO_3)(dmgly)$_2$] complex was prepared in two different manners. The complex was conveniently prepared from a reaction mixture of $CoCl_2$·$6H_2O$, H_2O_2, $KHCO_3$, and Hdmgly using the method used for the preparation of [Co(CO_3)(gly)$_2$]$^-$.[1] Purification of K[Co(CO_3)(dmgly)$_2$] was somewhat tedious because of its high solubility in common solvents. Surprisingly, the complex could also be prepared by reaction of [CoCl(NH_3)$_5$]Cl_2 with Hdmgly at pH 8.5 without addition of carbonate or hydrogencarbonate ions. In general, this kind of reaction affords the [Co(am)$_3$]-type complex.[11] The corresponding [Co(dmgly)$_3$] complex was not formed probably due to a steric reason (vide infra). Decarboxylation of dmgly and subsequent substitution by CO_3^{2-} should have occurred to yield [Co(CO_3)(dmgly)$_2$]$^-$. The same result was obtained when the reaction was carried out under a nitrogen atmosphere indicating that the carbonate ion does not originate from the air. Here, we suggest the following reac-

Table 1. Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors

Atom	*x*	*y*	*z*	$B_{eq}^{a)}$(Å^2)
Co	239.8(2)	1550.9(2)	4501.2(4)	1.4
N(1)	−329 (1)	2583 (1)	3230 (3)	1.9
N(2)	989 (1)	634 (1)	5772 (3)	1.8
O(1)	−461 (1)	792 (1)	2799 (3)	2.1
O(2)	−744 (1)	1179 (1)	6128 (3)	2.2
O(3)	736 (1)	2347 (1)	6513 (3)	2.0
O(4)	1161 (1)	1706 (1)	2483 (3)	2.1
O(5)	−1690 (1)	319 (1)	4369 (4)	3.4
O(6)	1066 (1)	3725 (1)	6859 (4)	3.8
O(7)	2546 (1)	1427 (1)	1979 (4)	4.0
C(1)	−1012 (1)	732 (1)	4425 (4)	2.2
C(2)	737 (1)	3127 (1)	5850 (4)	2.3
C(3)	313 (2)	3273 (1)	3643 (4)	2.4
C(4)	−1145 (2)	2806 (2)	4353 (5)	3.0
C(5)	−489 (2)	2507 (2)	835 (4)	2.7
C(6)	1885 (1)	1375 (1)	3055 (5)	2.5
C(7)	1871 (1)	951 (1)	5305 (5)	2.5
C(8)	867 (2)	−200 (1)	4659 (5)	3.2
C(9)	875 (2)	509 (2)	8164 (4)	3.2
K	−1727.9(3)	340.1(3)	9370.9(9)	2.4
O(8)	−2629 (1)	1803 (1)	88 (5)	5.2

a) $B_{eq}=4/3\{\sum_i\sum_j B_{ij}\,\boldsymbol{a}_i\cdot\boldsymbol{a}_j\}$.

tion:

$$(CH_3)_2NCH_2COOH \rightarrow N(CH_3)_3 + CO_2$$

In fact, the characteristic odor of trimethylamine was easily detected during the reaction. Probably CO_2 is liberated from a Co-dmgly intermediate.

Metal complexes containing chelated *N,N*-dialkylamino acidates such as $K[PtCl_2(dmgly)]$,[12] $[Pd\{(2S)\text{-}N^1,N^1\text{-}$ diethyl- 1, 2- propanediamine$\}(dmgly)]ClO_4$,[13] $[Pd(N,N\text{-}$dioctylglycinate$)_2]$,[14] and $[Cu(N\text{-}t\text{-}$butyl-$N\text{-}$methylglycinate$)_2]$[15] have been reported. We attempted to prepare the $[Co(CO_3)(am)_2]^-$-type complexes using *N,N*-diethylglycine, *N,N*-dimethylalanine, and *N,N*-dimethyl-β-alanine by two procedures similar to Method A and Method B. In all cases, the reaction mixture gradually turned dark brown and no corresponding complexes were obtained. The results indicate that *N,N*-dialkylamino acids are a poor ligand toward Co(III) or that the desired complexes are very unstable. We conclude that the preparative method B for $[Co(CO_3)(dmgly)_2]^-$ is very novel and applicable only to the Hdmgly system so far. Attempts to prepare $[Co(ox)(dmgly)_2]^-$ by a direct method similar to that for $[Co(ox)(gly)_2]^-$[3] were unsuccessful. Substitution of the ligating CO_3^{2-} in $[Co(CO_3)(dmgly)_2]^-$ by an oxalate ion gave the desired complex.

The $[CoL(am)_2]^-$ (L = CO_3 or ox) complex can exist in three geometrical forms: *cis*(N)*cis*(O), *cis*(N)*trans*(O), *trans*(N)*cis*(O) (Fig. 1). The $[Co(CO_3)(dmgly)_2]^-$ complex we obtained by two different methods (A and B) contained a single isomer as shown by column chromatography. The ^1H and ^{13}C NMR spectra (Table 2) of $[CoL(dmgly)_2]^-$ show that the two dmgly chelates are equivalent (C_2 symmetry), demonstrating that the complexes have either the *cis*(N)*trans*(O) or the *trans*(N)*cis*(O) configuration. However, the former configuration has two bulky tertiary amino groups in the cis positions, and will be less stable than the latter one. We therefore assign the configuration of $[CoL(dmgly)_2]^-$ to *trans*(N)*cis*(O) (hereafter it is described as *trans*(N)). This assignment was confirmed by the X-ray structure determination of the carbonato complex.

Figure 2 shows a perspective drawing of spontaneously resolved Λ-(+)$_{589}$-*trans*(N)-$[Co(CO_3)(dmgly)_2]^-$. Bond lengths and selected bond angles are listed in Table 3. The cobalt atom forms a distorted

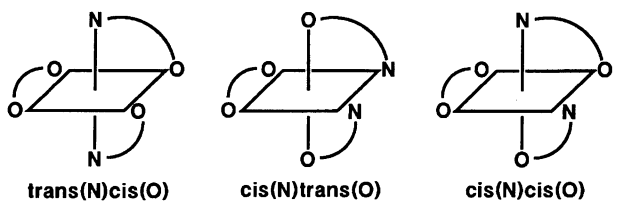

Fig. 1. Three possible isomers of $[CoL(am)_2]^-$ (L= CO_3 or ox, Ham=amino acid).

Table 2. ^1H and ^{13}C NMR Spectral Data for $K[CoL(dmgly)_2]$ (L=CO_3 or ox) in D_2O[a]

	L=CO_3		L=ox	
	^{13}C	^1H	^{13}C	^1H
CH_3	50.00	2.28	50.15	2.11
	50.88	2.57	51.46	2.47
CH_2	68.67	3.23(16)	68.72	3.25(16)
		3.80(16)		3.85(16)
CO_3	168.04			
COO(ox)			168.87	
COO(dmgly)	183.54		183.49	

a) *J* values in Hz are shown in parentheses.

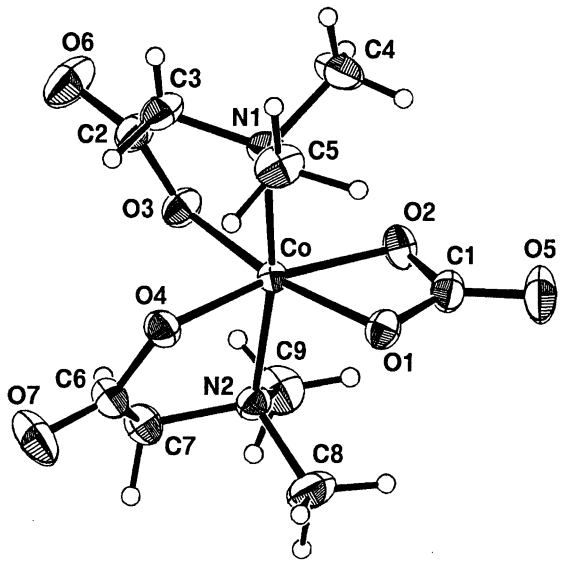

Fig. 2. A perspective view of Λ-(+)$_{589}$-*trans*(N)-$[Co(CO_3)(dmgly)_2]^-$.

octahedron with the *trans*(N) configuration. The structure agrees with the assignment based on the ^1H and ^{13}C NMR spectra. The absolute configuration was determined to be Λ. The mean Co–N bond length, 1.996(2) Å, is longer than the usual Co–N (primary amine) bond length such as that in *cis*(N)*cis*(O)-K$[Co(CO_3)$(L-valinate$)_2]\cdot 2H_2O$ (1.92(2) Å).[16] The longer Co–N bond length of *trans*(N)-K-$[Co(CO_3)(dmgly)_2]\cdot H_2O$ is attributed to the steric repulsion between the methyl groups and other ligands. A long Co–N (tertiary amine) bond length has been observed in [Co(tropolonate)$_2$(*N,N*-dimethylethylenediamine)]ClO_4 where the Co–N (tertiary amine) and Co–N (primary amine) bond lengths are 2.022(4) and 1.930(3) Å, respectively.[17]

The absorption spectra of *trans*(N)-$[Co(CO_3$ or ox)-$(dmgly)_2]^-$ are quite different from those of the corresponding glycinato complexes (Fig. 3). The dmgly complexes exhibit the first and second d–d absorption bands at lower energies than the gly complexes. Moreover, the dmgly complexes show no splitting in the first absorption band, the splitting of which is characteris-

Table 3. Bond Lengths (l/Å) and Selected Bond Angles (ϕ/°)

Co–O(1)	1.913(2)	Co–O(2)	1.908(2)
Co–O(3)	1.908(2)	Co–O(4)	1.899(2)
Co–N(1)	1.994(2)	Co–N(2)	1.999(2)
O(1)–C(1)	1.311(3)	O(2)–C(1)	1.318(3)
O(3)–C(2)	1.284(4)	O(4)–C(6)	1.282(3)
O(5)–C(1)	1.233(4)	O(6)–C(2)	1.229(3)
O(7)–C(6)	1.218(4)	N(1)–C(3)	1.488(3)
N(1)–C(4)	1.477(4)	N(1)–C(5)	1.485(3)
N(2)–C(7)	1.481(3)	N(2)–C(8)	1.481(4)
N(2)–C(9)	1.481(3)	C(2)–C(3)	1.514(4)
C(6)–C(7)	1.523(4)		
O(1)–Co–O(2)	68.89(7)	O(1)–Co–O(3)	168.79(7)
O(1)–Co–O(4)	98.87(7)	O(1)–Co–N(1)	92.32(7)
O(1)–Co–N(2)	95.45(7)	O(2)–Co–O(3)	100.75(7)
O(2)–Co–O(4)	167.17(7)	O(2)–Co–N(1)	95.45(7)
O(2)–Co–N(2)	92.53(7)	O(3)–Co–O(4)	91.73(7)
O(3)–Co–N(1)	84.26(7)	O(3)–Co–N(2)	89.12(7)
O(4)–Co–N(1)	88.70(7)	O(4)–Co–N(2)	84.62(7)
N(1)–Co–N(2)	170.45(8)		

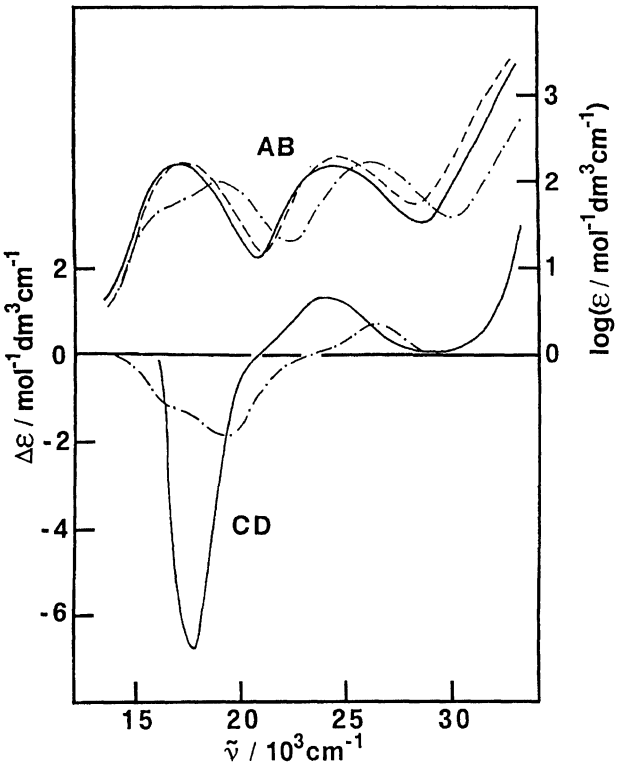

Fig. 3. Absorption and CD spectra of Δ-(−)$_{589}$-*trans*(N)-[Co(CO_3)(dmgly)$_2$]$^-$ (——), *trans*(N)-[Co(ox)(dmgly)$_2$]$^-$ (- - -), and Δ-(+)$_{546}$-*trans*(N)-[Co(ox)(gly)$_2$]$^-$[3] (-·-).

tic of the *trans*(N)-CoN_2O_4 chromophore.[2] The unsplit first band in the dmgly complexes can be explained if we assume that the ligand field strength of the *N,N*-dimethylamino ligand is very weak, comparable to those of the carbonate and oxalate ligands.[17—20]

The CD spectrum of (−)$_{589}$-*trans*(N)-[Co(CO_3)(dmgly)$_2$]$^-$ shows a very strong negative and a medium positive band in the first and second absorption band region, respectively. The spectrum is enantiomeric to that of Λ-(+)$_{589}$-*trans*(N)-[Co(CO_3)(dmgly)$_2$]$^-$, the absolute configuration of which has been determined by the X-ray method. It should be noted that the CD strength in the first absorption band region is almost three times larger than that of Δ-(+)$_{546}$-*trans*(N)-[Co(ox)(gly)$_2$]$^-$.[3] This may be related to the distortion from the regular octahedron caused by steric interactions between the *N*-methyl groups and other ligands.

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