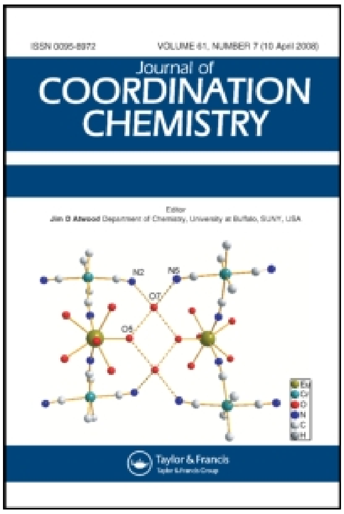

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STEREOCHEMISTRY OF (R)-2-METHYLAZIRIDINE COMPLEXES OF COBALT(III) AND DIMERIZATION OF THE LIGAND

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STEREOCHEMISTRY OF (*R*)-2-METHYLAZIRIDINE COMPLEXES OF COBALT(III) AND DIMERIZATION OF THE LIGAND

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A cobalt(III) complex containing (*R*)-2-methylaziridine (*R*-meaz), $[Co(R\text{-meaz})(NH_3)_5]^{3+}$, was prepared and the two diastereomers arising from the presence of the chiral nitrogen atom (N(*R*) and N(*S*)) were separated by column chromatography. Molecular mechanics calculations estimated the N(*R*)-isomer to be more stable. This result was supported by the x-ray structure determination of the more abundant (*ca.* 94%) isomer, N(*R*)-$[Co(R\text{-meaz})(NH_3)_5]Br_3 \cdot H_2O$. Crystal data: monoclinic, $P2_1$, $a = 7.357(1)$, $b = 9.780(1)$, $c = 10.426(1)$ Å, $\beta = 93.58(1)°$, $V = 748.7(3)$ Å^3, $Z = 2$. Kinetic studies of isomerization (epimerization) between the two isomers revealed that inversion at the nitrogen center was very slow (5×10^{-2} M^{-1} s^{-1} at 25 °C). The small rate constant seems to be related to the strained three-membered structure of the meaz ligand. The reaction of $Na_3[Co(NO_2)_6]$ and *R*-meaz yielded a complex containing two dimerized *R*-meaz chelates, *trans*-$[Co(NO_2)_2(\text{di-}R\text{-meaz})_2]^+$ (di-*R*-meaz =*RR*)-α,2-dimethyl-1-aziridineethanamine). The crystal strucrure of *trans*-$[Co(NO_2)_2(\text{di-}R\text{-meaz})_2]ClO_4 \cdot H_2O$ was established by x-ray crystallography. Crystal data: orthorhombic, $P2_12_12_1$, $a = 11.784(6)$, $b = 21.023(9)$, $c = 8.608(7)$ Å, $V = 2133(2)$ Å^3, $Z = 4$.

Keywords: aziridine-cobalt(III) complex; 2-methylaziridine; dimerization; molecular mechanics calculation; pyramidal inversion; epimerization

INTRODUCTION

Aziridine, a highly strained three-membered heterocycle, is reactive and the ring is readily opened by nucleophiles[1] or acids.[2] Although ring-opening and dimerization reactions of aziridine in several metal complexes have been reported,[3] the coordinated aziridine molecule generally exhibits a much higher ring stability

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than the free molecule towards nucleophiles and acids.[4–5] We are interested in the stereochemistry of optically active aziridine complexes. When optically active (*R*)-2-methylaziridine (*R*-meaz) is coordinated to a metal ion, the nitrogen atom becomes chiral (*R*, *S*), and a pair of diastereomers are possible (Figure 1). Inversion at a chiral N donor center bound to a metal ion is known.[6] In 1966, Halpern and coworkers[7] achieved the resolution of a chiral metal complex, $[Co(CH_3NHCH_2COO)(NH_3)_4]^{2+}$, where a chiral N center is the sole source of chirality. The complex is optically stable in dilute acids, since the N proton is kinetically inert to exchange. However, as the pH increases the complex begins to racemize. The rate law for the racemization is first order in both [complex] and $[OH^-]$. The term in $[OH^-]$ is interpreted as removal of H^+ from the coordinated amine to leave a pyramidal center. The energy barrier for inversion at the chiral nitrogen atom of the present *R*-meaz complex will be larger than that for unstrained amine complexes such as $[Co(CH_3NHCH_2COO)(NH_3)_4]^{2+}$, because the nitrogen atom is incorporated into a three-membered ring and the planar transition state is acquired with difficulty.[8]

In this paper, we report the preparation of a pair of diastereomers of [Co (*R*-meaz)$(NH_3)_5]^{3+}$, kinetic studies of isomerization (epimerization) between them, and the x-ray structure analysis of one of the isomers. The dimerization reaction of *R*-meaz took place when we tried to prepare *trans*-$[Co(NO_2)_2$(*R*-meaz)$_4]^+$; *trans*-$[Co(NO_2)_2$(di-*R*-meaz)$_2]ClO_4 \cdot H_2O$ (di-*R*-meaz denotes (*RR*)- α,2-dimethyl-1-aziridinethanamine) was obtained and the structure was determined by x-ray crystallography.

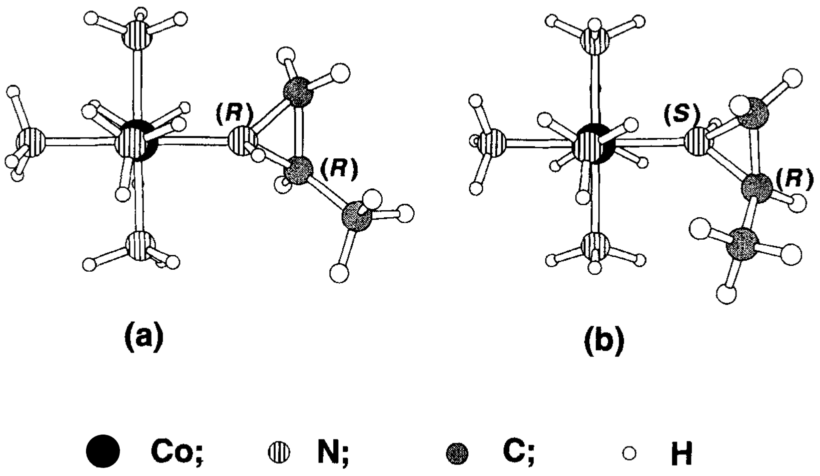


FIGURE 1 Two diastereomers of [Co(*R*-meaz)$(NH_3)_5]^{3+}$: (a) N(*R*-[Co(*R*-meaz)$(NH_3)_5]^{3+}$; (b) N(*S*)-[Co(*R*-meaz)$(NH_3)_5]^{3+}$.

EXPERIMENTAL

(*R*)-2-Methylaziridine was prepared from (*S*)-1-amino-2-propanol by the method of Yahiro.[9] Anhydrous trifluoromethanesulfonic acid was donated from Central Glass Co., Ltd.

^{1}H NMR spectra were measured using a Varian VXR 500 spectrometer. UV-Vis and circular dichroism (CD) spectra were recorded on a JASCO Ubest-30 spectrophotometer and a JASCO J-720 spectropolarimeter, respectively.

All operations involving *R*-meaz were carried out under nitrogen until air-stable cobalt(III) complexes were formed.

Preparation of $[Co(R\text{-meaz})(NH_3)_5]^{3+}$ and Separation of the Isomers

To $[Co(OSO_2CF_3)(NH_3)_5](CF_3SO_3)_2$[10] (0.5 g, 0.85 mmol) in a Schlenk tube was added (*R*)-2-methylaziridine (1 cm^3, 14 mmol). The red starting material dissolved immediately to yield an orange solution. The excess ligand was removed under reduced pressure. The residue was dissolved in methanol (10 cm^3), and by addition of diethyl ether the complex was obtained as an orange powder. Yield: 0.2 g. The complex (*ca.* 0.05 g) was charged on top of an SP-Sephadex C-25 column (ø3.0 cm × 35 cm). Upon elution with 0.4 M NaCl-0.001 M HCl, two orange bands, I and II, appeared in this order. The formation ratio, I:II was about 1:15 assuming the two isomers have the same molar absorption coefficient at 240 nm. The eluate containing band II was evaporated to a small volume, and an aqueous solution of LiBr was added to the concentrate to yield orange crystals. *Anal.* Calcd for $C_3H_{24}Br_3CoN_6O$ =$[Co(R\text{-meaz})(NH_3)_5]Br_3{\cdot}H_2O$(%): C, 7.85; H, 5.27; N, 18.31. Found: C, 7.77; H, 5.27; N, 18.00. Isomer I could not be isolated since the amount was very small, and the eluate was used for the measurements.

Preparation of *trans*-$[Co(NO_2)_2(di\text{-}R\text{-meaz})_2]ClO_4 \cdot H_2O$

To $Na_3[Co(NO_2)_6]$ (0.34 g, 0.85 mmol) was added (*R*)-2-methylaziridine (1 cm^3, 14 mmol). The mixture was stirred for 8 h at room temperature and then kept in a refrigerator for a week. The brown precipitate was collected by filtration and subjected to SP-Sephadex C-25 column chromatography (ø5.0 cm × 35 cm, eluent: 0.1 M $NaClO_4$). The column showed three bands. From the second main (*ca.* 80%) band brown crystals were obtained, and a piece of the crystals was used for x-ray structure determination.

Epimerization Studies

Kinetic studies of isomerization (epimerization) between the two isomers, I and II, were performed in a borate buffer (pH 9.0) by high-performance liquid chromatography.[11] The chromatography was carried out with a TSK-GEL SP-5PW column (ø0.75 cm × 7.5 cm) and 1 M NaCl as the eluent on a JASCO 880-PU system at a flow rate of 0.85 cm^3 min^{-1}. The complexes were detected with a JASCO 875-UV spectrophotometric detector at 240 nm.

X-ray Crystal Structure Determination of N(*R*)-[Co(*R*-meaz)$(NH_3)_5$]$Br_3 \cdot H_2O$ and *trans*-[Co$(NO_2)_2$(di-*R*-meaz)$_2$]$ClO_4 \cdot H_2O$

Experimental details and crystal data are listed in Table I. Diffraction measurements were made using a Rigaku AFC-5R diffractometer with graphite monochromatized Mo *Kα* radiation (λ = 0.71073 Å) at the X-Ray Laboratory of Okayama University. The intensities of three standard reflections were monitored after every 97 reflections; no significant variation was found. The absorption corrections were applied based on φ-scan data. The structures were solved by a direct method and refined by a full-matrix least squares procedure. All non-hydrogen atoms were treated anisotropically. Although four hydrogen atoms (H1C1, H2C1, H1C2, and H1N6) were introduced at idealized positions, the others were not. The absolute configuration of the nitrogen atom was assigned with reference to the known configuration of the carbon atom (*R*). The calculations were performed using TEXSAN[12] for N(*R*)-[Co(*R*-meaz)$(NH_3)_5$]$Br_3 \cdot H_2O$ and Xtal3.2[13] for *trans*-[Co$(NO_2)_2$(di-*R*-meaz)$_2$]$ClO_4 \cdot H_2O$. The atomic parameters of the non-hydrogen atoms are listed in Tables II and III.

TABLE I Crystal data and experimental details

	N(*R*)-[Co(*R*-meaz)$(NH_3)_5$]$Br_3 \cdot H_2O$	*trans*-[Co$(NO_2)_2$(di-*R*-meaz)$_2$]$ClO_4 \cdot H_2O$
Chemical formula	$C_3H_{24}Br_3CoN_6O$	$C_{12}H_{30}ClCoN_6O_9$
Formula weight	458.91	496.79
Crystal color	orange	brown
Crystal habits	prismatic	plate
Crystal size/mm	0.2 × 0.1 × 0.5	0.20 × 0.13 × 0.36
No. of reflections used for unit cell determination (2θ range/°)	25(21–23)	25(20–22)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1$ (No.4)	$P2_12_12_1$ (No.19)
a/Å	7.357(1)	11.784(6)
b/Å	9.780(1)	21.023(9)
c/Å	10.426(1)	8.608(7)
β/°	93.58(1)	
V/$Å^3$	748.7(3)	2133(2)
Z	2	4
D_x/Mg m^{-3}	2.035	1.547
F(000)	448	1040
μ(Mo *K*α)/mm^{-1}	9.062	0.981
T/K	293	298
Scan type	ω–2θ	ω–2θ

TABLE I (*Continued*)

	N(*R*)-[Co(*R*-meaz)$(NH_3)_5$]$Br_3 \cdot H_2O$	*trans*-[Co$(NO_2)_2$(di-*R*-meaz)$_2$]$ClO_4 \cdot H_2O$
Scan width in ω/°	0.94+0.30 tan θ	0.68+0.30 tan θ
Scan speed in ω/°min^{-1}	6	6
$2\theta_{max}$/°	55.0	60
Range of *h*, *k*, *l*	$0 \le h \le 9$	$0 \le h \le 15$
	$0 \le k \le 12$	$0 \le k \le 27$
	$-13 \le l \le 13$	$0 \le l \le 11$
R_{int}	0.039	
No. of reflections used	1429	1590
	$I > 3.0\sigma(I)$	$F > 3.0\sigma(F)$
R^a/R_w^b	0.044/0.045	0.087/0.075
S^c	3.09	1.98
$(\Delta/\delta)_{max}$	0.01	0.57
$\Delta\rho_{max}$/eÅ^{-3}	1.06	0.97
$\Delta\rho_{min}$/eÅ^{-3}	−0.79	−1.11

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; [b] $R_w = [(\Sigma w(|F_o|-|F_c|)^2/\Sigma w F_o^2)]^{1/2}$; [c] $S = [(\Sigma w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$.

TABLE II Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) with their esd's in parentheses for N(*R*)-[Co(*R*-meaz)$(NH_3)_5$]$Br_3 \cdot H_2O$

Atom	*x*	*y*	*z*	U_{eq}
Br1	0.7424(2)	0.9910	0.9981(2)	0.0377(9)
Br2	1.2799(2)	0.3798(2)	0.6257(1)	0.0347(9)
Br3	0.2355(2)	0.9062(2)	0.6549(2)	0.042(1)
Co	0.7358(2)	0.6644(2)	0.7303(2)	0.022(1)
O1W	0.732(2)	0.660(1)	1.117(1)	0.061(8)
N1	0.550(1)	0.652(1)	0.585(1)	0.033(6)
N2	0.544(1)	0.703(1)	0.849(1)	0.028(6)
N3	0.754(2)	0.864(1)	0.696(1)	0.031(6)
N4	0.927(2)	0.626(1)	0.611(1)	0.035(8)
N5	0.924(1)	0.687(1)	0.871(1)	0.031(6)
N6	0.708(1)	0.470(1)	0.765(1)	0.027(6)
C1	0.728(2)	0.397(2)	0.881(1)	0.041(9)
C2	0.839(2)	0.356(1)	0.781(1)	0.029(8)
C3	0.816(3)	0.226(2)	0.707(2)	0.05(1)
H1N6	0.601	0.427	0.713	0.030
H1C1	0.634	0.329	0.909	0.047
H2C1	0.779	0.435	0.958	0.047
H1C2	0.964	0.379	0.795	0.039

$U_{eq} = 1/3\ \{\sum_i \sum_j U_{ij} a^*_i a^*_j a_i \cdot a_j\}$

TABLE III Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) with their esd's in parentheses for *trans*-[Co$(NO_2)_2$(di-*R*-meaz)$_2$]$ClO_4 \cdot H_2O$

Atom	*x*	*y*	*z*	U_{eq}
Co	0.5287(2)	0.47852(9)	0.4132(3)	0.0285(5)
Cl	0.8097(5)	0.2271(2)	1.1994(6)	0.061(2)
O(1)	0.3021(8)	0.4721(6)	0.324(1)	0.059(4)
O(2)	0.3280(9)	0.4484(6)	0.564(2)	0.071(5)
O(3)	0.759(1)	0.483(1)	0.479(2)	0.17(1)
O(4)	0.728(1)	0.524(1)	0.289(3)	0.19(1)

TABLE III (*Continued*)

Atom	*x*	*y*	*z*	U_{eq}
O(5)	0.702(2)	0.215(1)	1.243(3)	0.21(1)
O(6)	0.871(2)	0.2552(8)	1.313(2)	0.147(9)
O(7)	0.787(2)	0.2695(8)	1.090(2)	0.17(1)
O(8)	0.857(1)	0.1713(6)	1.148(2)	0.108(7)
O(9)	0.3995(8)	0.4587(5)	0.917(1)	0.049(4)
N(1)	0.512(1)	0.5663(6)	0.496(1)	0.036(4)
N(2)	0.5025(9)	0.5179(5)	0.208(1)	0.037(4)
N(3)	0.554(1)	0.3919(5)	0.327(1)	0.035(4)
N(4)	0.560(1)	0.4402(5)	0.619(1)	0.031(4)
N(5)	0.3643(9)	0.4638(6)	0.433(2)	0.037(5)
N(6)	0.689(1)	0.4943(6)	0.392(2)	0.053(6)
C(1)	0.521(1)	0.6137(6)	0.365(1)	0.044(5)
C(2)	0.457(2)	0.5831(7)	0.226(2)	0.047(6)
C(3)	0.474(2)	0.6223(7)	0.076(2)	0.064(6)
C(4)	0.568(1)	0.5902(9)	0.649(2)	0.054(7)
C(5)	0.438(1)	0.5813(7)	0.634(2)	0.038(6)
C(6)	0.361(1)	0.6409(7)	0.636(2)	0.049(6)
C(7)	0.615(1)	0.3512(7)	0.445(2)	0.046(6)
C(8)	0.562(1)	0.3663(6)	0.603(2)	0.032(5)
C(9)	0.627(2)	0.3367(8)	0.735(2)	0.059(7)
C(10)	0.580(2)	0.3759(8)	0.165(2)	0.053(7)
C(11)	0.467(2)	0.3589(6)	0.224(2)	0.040(5)
C(12)	0.429(2)	0.2912(7)	0.254(2)	0.065(7)

$U_{eq} = 1/3\ \{\sum_i \sum_j U_{ij} a_i^* a_j^*\ a_i a_j\}$

Molecular Mechanics Calculations

Strain-energy minimization calculations were carried out for the two isomers, I and II, with a modified MM2 computer program[14–15] in order to obtain their relative strain energy and to estimate the stable structure between the isomers. The parameters for the present force fields were mainly adopted from those of MM2 (1985), MM2 and MMP2 (1986), and the literatures.[15–16] The electrostatic interactions were not considered for these calculations.

RESULTS AND DISCUSSION

Upon coordination the nitrogen atom of the *R*-meaz ligand becomes chiral (*R* and *S*), and because there is also an asymmetric carbon atom (*R*), a pair of diastereomers are possible (Figure 1). We could separate the two isomers, I and II, by column chromatography, the formation ratio, I:II, being *ca.* 1:15. Structural assignments were made on the basis of the molecular mechanics calculations. The N(*R*)-$[Co(R\text{-meaz})(NH_3)_5]^{3+}$ isomer is calculated to be more stable than the N(*S*)-one by approximately 2.9 kcal mol^{-1} (Table IV); the calculated energy differences arise primarily from the different bending energies associated with the three-membered aziridine ring. Thus, more abundant isomer II can be assigned to the N(*R*)-isomer. This assignment was confirmed by the x-ray analysis.

Figure 2 shows a perspective view of the bromide monohydrate of isomer II. Bond lengths and angles are listed in Table V. The coordination geometry around the cobalt atom is approximately octahedral. The absolute configuration about the chiral nitrogen atom is N(*R*). The C1—C2 bond (1.42(2) Å) is significantly shorter than that found for free aziridine (1.48 Å).[17] A similar C—C bond length shortening upon complex formation has been reported for several aziridine complexes.[4,18]

Both isomers, I and II, show the first *d-d* absorption band around 480 nm, which is consistent with the CoN_6 chromophore. However, the less abundant isomer I exhibits the band at lower energy (483 nm) than isomer II (476 nm). This result is in accord with the general trend that an isomer involving more strain shows the *d-d* absorption band at lower energy.[19] The corresponding aziridine complex, $[Co(aziridine)(NH_3)_5]^{3+}$, is reported to give the first *d-d* absorption band at 476 nm.[4]

TABLE IV Final energy terms (kcal mol^{-1}) from the minimization for two isomers of $[Co(R\text{-meaz})(NH_3)_5]^{3+}$

Complex	*Total*	*Bond*	*Angle*	*Nonbonded*	*Torsion*
N(*R*)-$[Co(R\text{-meaz})(NH_3)_5]^{3+}$	8.39	0.27	4.38	−2.09	5.83
N(*S*)-$[Co(R\text{-meaz})(NH_3)_5]^{3+}$	11.28	0.97	6.43	−2.26	6.14

TABLE V Bond lengths (*l*/Å) and bond angles (φ/°) of N(*R*)-$[Co(R\text{-meaz})(NH_3)_5]Br_3{\cdot}H_2O$

atom	*atom*	*bond length*	*atom*	*atom*	*bond length*
Co	N1	1.98(1)	Co	N6	1.95(1)
Co	N2	1.97(1)	N6	C1	1.41(2)
Co	N3	1.99(1)	N6	C2	1.47(2)
Co	N4	1.98(1)	C1	C2	1.42(2)
Co	N5	1.97(1)	C2	C3	1.49(2)

atom	*atom*	*atom*	*angle*	*atom*	*atom*	*atom*	*angle*
N1	Co	N2	90.2(5)	N3	Co	N6	177.8(5)
N1	Co	N3	88.6(5)	N4	Co	N5	89.8(5)
N1	Co	N4	89.6(5)	N4	Co	N6	91.1(5)
N1	Co	N5	177.0(5)	N5	Co	N6	92.8(5)
N1	Co	N6	90.2(5)	Co	N6	C1	130(1)
N2	Co	N3	89.1(5)	Co	N6	C2	133.0(9)
N2	Co	N4	179.8(5)	C1	N6	C2	58.8(9)
N2	Co	N5	90.4(5)	N6	C1	C2	62.9(9)
N2	Co	N6	89.0(5)	N6	C2	C1	58.3(9)
N3	Co	N4	90.7(4)	N6	C2	C3	122(1)
N3	Co	N5	88.5(5)	C1	C2	C3	124(1)

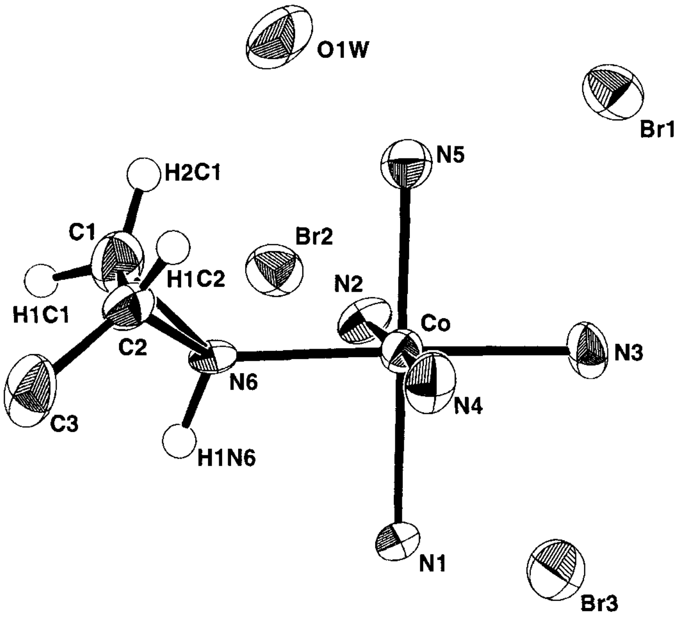


FIGURE 2 ORTEP drawing of N(*R*)-[Co(*R*-meaz)$(NH_3)_5$]$Br_3 \cdot H_2O$ with 50% probability for the thermal ellipsoids.

Figure 3 shows the CD spectra of the two isomers. The optical activity of each isomer originates from two chiral centers, the chiral carbon atom and the chiral nitrogen atom, and usually additivity holds between the two contributions. The halved difference of the CD spectra for isomers I and II, which should show the *S*-contribution of the chiral nitrogen was compared with the CD spectrum for N(*S*)-[Co(sar)$(NH_3)_4$]$^{2+}$ [20–21] (sar = sarcosinate ion, $CH_3NHCH_2COO^-$), which makes only a vicinal contribution of the chiral nitrogen to the spectrum (Figure 3). Unexpectedly, the two CD patterns are quite different. The reason for this result is not understood but may be related to the highly strained structure of the three-membered aziridine ring; *i.e.*, the bond angles involving the chiral nitrogen atom deviate far from the tetrahedral angle.

Kinetic studies of reversible isomerization (epimerization) between the two isomers, I and II, were carried out in an aqueous solution at 25 ° C by observing the change in chromatograms with reaction time. Although the reaction was accompanied slightly by a decomposition reaction, we could estimate the second-order rate constant to be *ca.* 5×10^{-2} $M^{-1}s^{-1}$. This value is much smaller than that for [Co(Me-en)$(NH_3)_4$]$^{3+}$ (Me-en = *N*-methylethylenediamine, 2.5×10^2 $M^{-1}s^{-1}$ at 34.3 °C).[22] The small rate constant seems to be related to the strained three-membered structure of the meaz ligand. The epimerization of the present

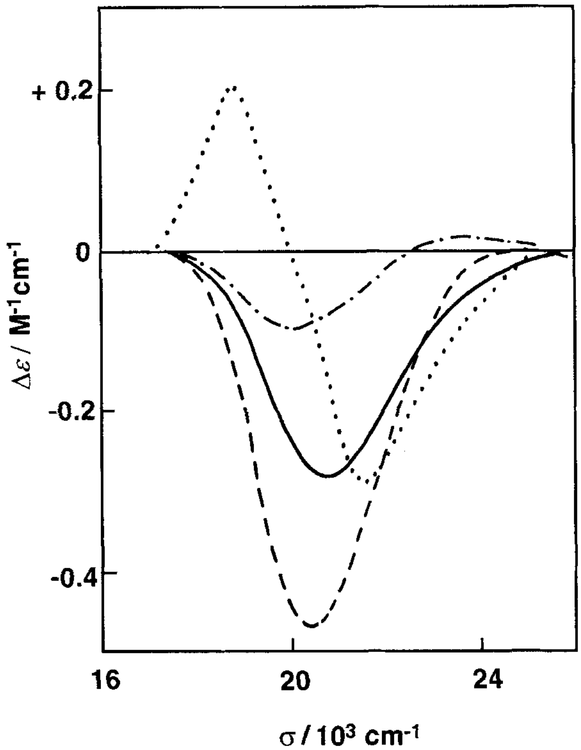
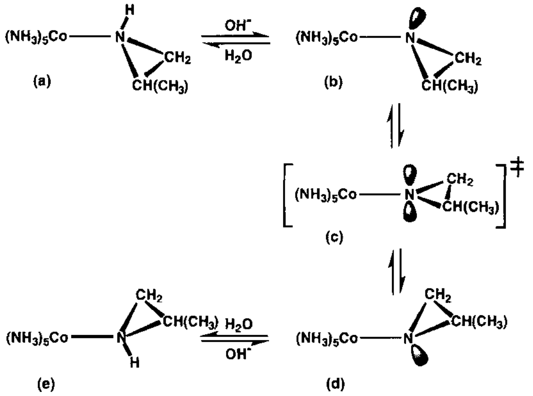


FIGURE 3 CD spectra of N(*R*)-$[Co(R\text{-meaz})(NH_3)_5]^{3+}$ (—), N(*S*)-$[Co(R\text{-meaz})(NH_3)_5]^{3+}$ (- - -), and N(*S*)-$[Co(sar)(NH_3)_4]^{2+}$ (sar = sarcosinate ion, · · · ·), and calculated vicinal CD curve (Δε(N(*S*) from the CD spectra of N(*R*)- and N(*S*)-$[Co(R\text{-meaz})(NH_3)_5]^{3+}$ (1/2{Δε[N(*S*)] - Δε[N(*R*)]}, - · - ·).

complex will proceed according to the mechanism shown in Scheme 1. The process involves passage through a transition state ((c) in Scheme 1), in which the lone pair possesses pure *p* character and the bonds from the nitrogen atom are sp^2. The inverting atom is incorporated into a small three-membered ring; therefore the resultant angle strain will be greater in the transition state than in the ground state. The CNC angle in the ground state deviates about 49° from the unstrained tetrahedral angle but 60° from the sp^2 angle (120°) in the transition state. The added transition-state strain will raise the barrier with respect to the value in unstrained amines such as $[Co(Me\text{-en})(NH_3)_4]^{3+}$. Similar higher barriers for pyramidal inversion have also been found for *N*-methylaziridine (19 kcal mol^{-1}) and for four-membered *N*-methylazetidine (12.5 kcal mol^{-1}); the barrier for nearly unstrained *N*-methylazacycloheptane is only about 7 kcal mol^{-1}.[8] At equilibrium, the relative abundance, isomer I : isomer II, was *ca.* 1 : 12 on the basis of the chromatogram and the ^{1}H NMR spectrum.



Scheme 1

We obtained a brown complex by the reaction of $Na_3[Co(NO_2)_6]$ and *R*-meaz. Jackson and Edwards[3a] prepared *trans*-$[Co(NO_2)_2(\text{aziridine})_4]^+$ under similar reaction conditions and later Ware and coworkers[4] determined the structure by x-ray crystallography. The ^1H NMR spectrum of our brown complex in DMSO-d_6 showed two doublet methyl signals at 1.22 and 1.34 ppm, indicating that the product was not *trans*-$[Co(NO_2)_2(R\text{-meaz})_4]^+$. Figure 4 shows an ORTEP drawing of the brown complex, *trans*-$[Co(NO_2)_2(\text{di-}R\text{-meaz})_2]$ $ClO_4{\cdot}H_2O$. Bond lengths and angles are listed in Table VI. The complex involves two dimerized *R*-meaz chelates and two nitro ligands in *trans* positions. Dimerization reactions of aziridine have been reported to occur in metal complexes.[3] It should be noted that 2-methylaziridine dimerizes more readily than aziridine. More work will be necessary to elucidate the dimerization mechanism.

TABLE VI Bond lengths (l/Å) and bond angles (φ/°) of *trans*-$[Co(NO_2)_2(\text{di-}R\text{-meaz})_2]ClO_4{\cdot}H_2O$

atom	*atom*	*bond length*	*atom*	*atom*	*bond length*
Co	N(1)	1.99(1)	N(3)	C(10)	1.47(2)
Co	N(2)	1.98(1)	N(3)	C(11)	1.53(2)
Co	N(3)	1.99(1)	N(4)	C(8)	1.56(2)
Co	N(4)	1.98(1)	C(1)	C(2)	1.55(2)
Co	N(5)	1.97(1)	C(2)	C(3)	1.54(2)
Co	N(6)	1.92(1)	C(4)	C(5)	1.55(2)
O(1)	N(5)	1.21(2)	C(5)	C(6)	1.54(2)
O(2)	N(5)	1.24(2)	C(7)	C(8)	1.52(2)
O(3)	N(6)	1.14(3)	C(8)	C(9)	1.50(2)
O(4)	N(6)	1.17(3)	C(10)	C(11)	1.47(3)
N(1)	C(1)	1.51(2)	C(11)	C(12)	1.52(2)
N(1)	C(4)	1.55(2)	Cl	O(5)	1.34(2)
N(1)	C(5)	1.51(2)	Cl	O(6)	1.35(2)
N(2)	C(2)	1.48(2)	Cl	O(7)	1.32(2)
N(3)	C(7)	1.51(2)	Cl	O(8)	1.37(1)

TABLE VI (*Continued*)

atom	*atom*	*atom*	*angle*	*atom*	*atom*	*atom*	*angle*
N(1)	Co	N(2)	85.3(5)	Co	N(5)	O(1)	120(1)
N(1)	Co	N(3)	176.9(5)	Co	N(5)	O(2)	117(1)
N(1)	Co	N(4)	94.3(5)	O(1)	N(5)	O(2)	122(1)
N(1)	Co	N(5)	91.0(5)	Co	N(6)	O(3)	128(2)
N(1)	Co	N(6)	88.5(5)	Co	N(6)	O(4)	123(1)
N(2)	Co	N(3)	94.3(5)	O(3)	N(6)	O(4)	109(2)
N(2)	Co	N(4)	178.0(5)	N(1)	C(1)	C(2)	106(1)
N(2)	Co	N(5)	89.4(5)	N(2)	C(2)	C(1)	107(1)
N(2)	Co	N(6)	89.7(6)	N(2)	C(2)	C(3)	111(1)
N(3)	Co	N(4)	86.0(5)	C(1)	C(2)	C(3)	111(1)
N(3)	Co	N(5)	92.1(5)	N(1)	C(4)	C(5)	58.2(9)
N(3)	Co	N(6)	88.5(5)	N(1)	C(5)	C(4)	61(1)
N(4)	Co	N(5)	92.5(5)	N(1)	C(5)	C(6)	121(1)
N(4)	Co	N(6)	88.4(6)	C(4)	C(5)	C(6)	119(1)
N(5)	Co	N(6)	179.0(6)	N(3)	C(7)	C(8)	107(1)
Co	N(1)	C(1)	109.7(8)	N(4)	C(8)	C(7)	107(1)
Co	N(1)	C(4)	124(1)	N(4)	C(8)	C(9)	111(1)
Co	N(1)	C(5)	122.4(9)	C(7)	C(8)	C(9)	112(1)
C(1)	N(1)	C(4)	113(1)	N(3)	C(10)	C(11)	63(1)
C(1)	N(1)	C(5)	119(1)	N(3)	C(11)	C(10)	59(1)
C(4)	N(1)	C(5)	61(1)	N(3)	C(11)	C(12)	122(1)
Co	N(2)	C(2)	110.5(8)	C(10)	C(11)	C(12)	124(1)
Co	N(3)	C(7)	109.9(9)	O(5)	Cl	O(6)	112(1)
Co	N(3)	C(10)	126.4(9)	O(5)	Cl	O(7)	98(1)
Co	N(3)	C(11)	122.0(9)	O(5)	Cl	O(8)	109(1)
C(7)	N(3)	C(10)	115(1)	O(6)	Cl	O(7)	109(1)
C(7)	N(3)	C(11)	117(1)	O(6)	Cl	O(8)	113(1)
C(10)	N(3)	C(11)	58(1)	O(7)	Cl	O(8)	115(1)
Co	N(4)	C(8)	109.3(8)				

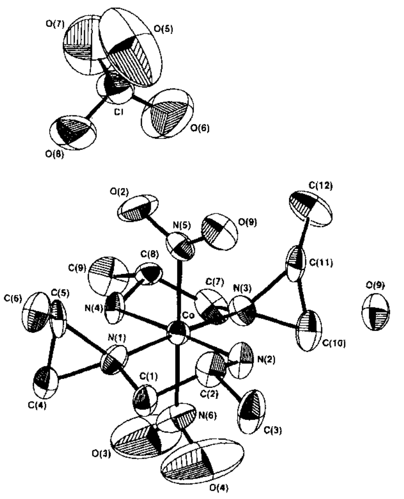


FIGURE 4 ORTEP drawing of *trans*-[Co$(NO_2)_2$(di-*R*-meaz)$_2$]$ClO_4 \cdot H_2O$ (di-*R*-meaz=(*R*,*R*)-α,2-dimethyl-1-aziridineethanamine) with 50% probability for the thermal ellipsoids.

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