2586 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (9), 2586—2591 (1978) [Vol. 51, No. 9

Absorption and Circular Dichroism Spectra of Cobalt(III) Complexes Containing *N,N*-Dimethylethylenediamine

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(Received March 3, 1978)

Nine new cobalt(III) complexes containing *N,N*-dimethylethylenediamine are prepared. The geometrical configurations of isomers are assigned on the basis of their visible and ultraviolet absorption spectra, proton magnetic resonance spectra, and the optical resolution of the chiral isomers. The absorption and circular dichroism spectra are discussed in comparison with those of the corresponding complexes containing ethylenediamine, *N*-methylethylenediamine, *N,N'*-dimethylethylenediamine, or tris-2-(aminoethyl)amine.

There have been several investigations concerning the Co(III) complexes of *N*-methylethylnediamine (*N*-Me-en)[1–3] and *N,N'*-dimethylethylenediamine (*N,N'*-Me_2-en).[3,4] No Co(III) complexes have ever been reported for *N,N*-dimethylethylenediamine (*N,N*-Me_2-en), though some Cu(II),[5] Ni(II),[6] and Rh(III)[7] complexes have been prepared for this tertiary amine ligand. In this paper the preparation and the properties of the Co(III) complexes containing *N,N*-dimethylethylenediamine are reported.

Experimental

Preparations. *(1)* trans*(NO_2)-[Co(NO_2)$_2$(*N,N*-Me$_2$-en)$_2$]-ClO_4:* This complex was prepared by the same method as that of Buckingham *et al.*[2] for *trans, trans*-[Co(NO_2)$_2$(*N*-Me-en)$_2$]ClO_4. To an ice-cold solution of $CoCl_2 \cdot 6H_2O$(4.76 g, 2.0×10^{-2} mol) in 10 cm^3 of water was added a cold solusion of *N,N*-dimethylethylenediamine(3.52 g, 4.0×10^{-2} mol) in 1.7 cm^3 of 12 M HCl, and then $NaNO_2$(2.8 g, 4.2×10^{-2} mol) was added. A vigorous stream of air was introduced to this red bown solution for 5 h at room temperature. The resulting solution was evaporated to dryness by a rotary evaporator below 40 °C. To the residue was added 50 cm^3 of methanol and the resulting NaCl precipitated was filtered off. Ten grams of $NaClO_4$ was added to precipitate a crystalline powder by scratching the flask. This was filtered and recrystallized from warm water. Found: C, 22.28; H, 5.75; N, 19.66%. Calcd for [Co(NO_2)$_2$(*N,N*-Me$_2$-en)$_2$]ClO_4: C, 22.51; H, 5.68; N, 19.69%.

(2) cis*(Cl)-[$CoCl_2$(*N,N*-Me$_2$-en)$_2$]ClO_4:* Three grams of *trans*(NO_2)-[Co(NO_2)$_2$(*N,N*-Me$_2$-en)$_2$]ClO_4 was suspended in 50 cm^3 of alcoholic hydrogen chloride(saturated at ice-bath temperature) and stirred overnight at room temperature. The blue green powder deposited was filtered, washed with ethanol and ether, and dried in air. Found: C, 23.87; H, 6.15; N, 14.10%. Calcd for [$CoCl_2$(*N,N*-Me$_2$-en)$_2$]ClO_4: C, 23.68; H, 5.97; N, 13.81%.

(3) trans*(N_3)- and* cis*(N_3)-[Co(N_3)$_2$(*N,N*-Me$_2$-en)$_2$]X; X=ClO_4(*trans*) and Cl·H_2O(*cis*):* One gram of *cis*(Cl)-[$CoCl_2$(*N,N*-Me$_2$-en)$_2$]ClO_4 was dissolved in 5 cm^3 of water, and to this blue solution was added 0.6 g of NaN_3 and stirred at 40 °C for 1 h. On cooling to room temperature, dark brown-violet crystals were deposited. The crystals were separated by filtration from the dark green solution and recrystallized from water at 50 °C. From the measurement of absorption spectrum it was found that this brown-violet isomer has a *trans*(N_3) structure. Found: C, 22.69; H, 5.81; N, 33.67%. Calcd for *trans*(N_3)-[Co(N_3)$_2$(*N,N*-Me$_2$-en)$_2$]ClO_4: C, 22.94; H, 5.78; N, 33.45%.

The corresponding *cis* isomer was isolated from the same reaction mixture by column chromatographic method. The reaction mixture was completely dissolved with water and poured into a cation exchanger column(SP-Sephadex C-25, Na^+ form) and eluted with a 0.05 M NaCl aqueous solution. Two bands appeared; dark brown-violet one(*trans* isomer) and dark green one(*cis* isomer), in this order. The dark green band was eluted and evaporated to dryness below 30 °C by a rotary evaporator. From the residue the complex was extracted into methanol and NaCl precipitated was filtered off. The dark green filtrate was evaporated to dryness and the resulting powder was recrystallized from the minimum amount of water and dried in air. This was proved to be a *cis*(N_3) isomer through the optical resolution. Found: C, 25.34; H, 6.94; N, 36.88%. Calcd for *cis*(N_3)-[Co(N_3)$_2$(*N,N*-Me$_2$-en)$_2$]Cl·H_2O: C, 25.77; H, 7.04; N, 37.58%.

(4) Optical Resolution of cis*(N_3)-[Co(N_3)$_2$(*N,N*-Me$_2$-en)$_2$]-Cl·H_2O:* The racemic chloride monohydrate, *cis*(N_3)-[Co(N_3)$_2$(*N,N*-Me$_2$-en)$_2$]Cl·H_2O (0.2 g, 5.6×10^{-4} mol) was dissolved in 2 cm^3 of water and to this dark green solution was added ammonium $(+)_{589}$-(1*R*, 3*S*, 4*S*, 7*R*)-3-bromocamphor-9-sulfonate(0.17 g, 5.0×10^{-4} mol). On stirring, a crystalline powder was deposited, filtered, and washed with a small amount of water. This diastereoisomer was sparingly soluble in water at room temperature but soluble in methanol, ethanol, or acetone. The less soluble diastereoisomer was recrystallized from water at 30 °C, washed with water and dried in air. Found: C, 32.40; H, 6.33; N, 20.83%. Calcd for [Co(N_3)$_2$(*N,N*-Me$_2$-en)$_2$]$C_{10}H_{14}O_4SBr \cdot 2H_2O$: C, 32.48; H, 6.37; N, 21.10%.

The less soluble diastereoisomer was converted into $(+)_{589}$-perchlorate by use of a column chromatographic method. Found: C, 22.61; H, 5.85; N, 33.45%. Calcd for $(+)_{589}$-[Co(N_3)$_2$(*N,N*-Me$_2$-en)$_2$]ClO_4: C, 22.94; H, 5.79; N, 33.45%.

(5) trans*(NCS)- and* cis*(NCS)-[Co(NCS)$_2$(*N,N*-Me$_2$-en)$_2$]-Cl·H_2O:* One and three tenths grams of *cis*(Cl)-[$CoCl_2$(*N,N*-Me$_2$-en)$_2$]ClO_4 and four tenths grams of KSCN were dissolved in 50 cm^3 of water and stirred at 40 °C for thirty min to obtain a red violet solution. The resulting solution was poured into a cation exchanger column(SP-Sephadex C-25, Na^+ form) and the adsorbed complex was eluted with a 0.05 M NaCl aqueous solution. Four bands appeared; dark reddish purple, deep purple, light purple, and dark purple ones in this order. The fractions of each the first and the second band were collected and evaporated to dryness below 30 °C by a rotary evaporator. From the residue the complex was extracted into methanol and the solution was evaporated to dryness. The crystalline powder was recrystallized from water and dried in air. The first dark purple band was proved to be a *trans*(NCS) isomer from the measurement of absorption spectrum. Found: C, 29.14; H, 6.34; N, 21.00%. Calcd for *trans*(NCS)-[Co(NCS)$_2$(*N,N*-Me$_2$-en)$_2$]Cl·H_2O: C, 29.66; H, 6.48; N, 20.76%. The second deep purple band was proved to be a *cis*(NCS) isomer from the successful optical resolution. Found: C, 29.17; H, 6.46; N, 20.62%. Calcd

for *cis*(NCS)-[Co(NCS)$_2$(*N*,*N*-Me$_2$-en)$_2$]Cl·H$_2$O: C, 29.66; H, 6.48; N, 20.76%. The third and fourth bands turned out to be monoisothiocyanato complexes from their elemental analyses.

(6) Optical Resolution of cis*(NCS)-[Co(NCS)$_2$(*N,N-*Me$_2$-en)$_2$]Cl·H$_2$O*: The racemic chloride monohydrate, *cis*(NCS)-[Co(NCS)$_2$(*N*,*N*-Me$_2$-en)$_2$]Cl·H$_2$O (0.23 g, 5.7×10^{-4} mol) and ammonium (+)$_{589}$-(1*R*, 3*S*, 4*S*, 7*R*)-3-bromocamphor-9-sulfonate(0.19 g, 5.8×10^{-4} mol) were dissolved in 30 cm^3 of water at 40 °C. The reddish purple solution was evaporated to half the initial volume and cooled in a refrigerator overnight. Reddish purple crystals deposited were filtered and washed with a small amount of water and dried in air. This diastereoisomer was rather soluble in methanol, ethanol, or acetone than in water. Found: C, 35.55; H, 5.75; N, 12.54%. Calcd for [Co(NCS)$_2$(*N*,*N*-Me$_2$-en)$_2$]C$_{10}$H$_{14}$O$_4$SBr·0.5H$_2$O: C, 35.82; H, 5.87; N, 12.53%.

The less soluble diastereoisomer was converted into (+)$_{589}$-perchlorate by a column chromatographic method: C, 25.78; H, 5.47; N, 18.13%. Calcd for (+)$_{589}$-[Co(NCS)$_2$(*N*,*N*-Me$_2$-en)$_2$]ClO$_4$·0.5H$_2$O: C, 26.11; H, 5.49; N, 18.28%.

*(7) [Co(CO$_3$)(*N,N-*Me$_2$-en)$_2$]ClO$_4$*: The dichloro complex, *cis*(Cl)-[CoCl$_2$(*N*,*N*-Me$_2$-en)$_2$]ClO$_4$(0.4 g, 1.0×10^{-3} mol) was ground with Ag$_2$CO$_3$(0.3 g, 1.1×10^{-3} mol). Five cm^3 of water was added and the grinding was continued for half an hour. The color of the solution changed from blue green to violet. The solid AgCl deposited was filtered off and washed with a small amount of water. The filtrate and washing were evaporated almost to dryness and 10 cm^3 of ethanol was added. The blue-violet crystalline solid precipitated was filtered, washed with ethanol and ether and dried in a desiccator. Found: C, 26.29; H, 6.58; N, 13.99%. Calcd for [Co(CO$_3$)(*N*,*N*-Me$_2$-en)$_2$]ClO$_4$·0.5H$_2$O: C, 26.77: H, 6.25; N, 13.88%.

*(8) [Co(ox)(*N,N-*Me$_2$-en)$_2$]ClO$_4$*: To a solution of *cis*(Cl)-[CoCl$_2$(*N*,*N*-Me$_2$-en)$_2$]ClO$_4$(1.0 g, 2.5×10^{-3} mol) in 10 cm^3 of water was added five tenths grams of oxalic acid dihydrate, and this mixture was heated to 90 °C in a water bath, concentrated to half the initial volume, and cooled to room temperature. The red-purple crystalline powder precipitated was filtered, washed with ethanol and ether, and dried in air. Found: C, 27.11; H, 6.87; N, 12.75%. Calcd for [Co(ox)(*N*,*N*-Me$_2$-en)$_2$]ClO$_4$·H$_2$O: C, 27.27; H, 5.96; N, 12.71%.

*(9) [Co(NH$_3$)$_4$(*N,N-*Me$_2$-en)]Cl$_3$*: Two grams of *cis*(Cl)-[CoCl$_2$(*N*,*N*-Me$_2$-en)$_2$]ClO$_4$ was treated with 30 cm^3 of liquid ammonia in a pressure bottle. The blue green complex dissolved in liquid ammonia to give a pale orange solution. After removal of ammonia by introducing dry air, the pink-orange powder was suspended in methanol, and filtered, washed with ethanol and ether, and recrystallized from the minimum amount of water by adding ethanol. Found: C, 13.38; H, 7.72; N, 24.18%. Calcd for [Co(NH$_3$)$_4$(*N*,*N*-Me$_2$-en)]Cl$_3$·1.5H$_2$O: C, 13.78; H, 7.82; N, 24.11%.

(10) Other Complexes: Other complexes were prepared by the same methods as seen in the literature: en,[8-12] *N*-Me-en,[2] *N*,*N*′-Me$_2$-en,[4] and tris(aminoethyl)amine (tren)[13] complexes. The diazido- and diisothiocyanato-complexes containing *N*-Me-en or tren were prepared by the ligand substitution of *trans*(Cl)-[CoCl$_2$(*N*-Me-en)$_2$]$^+$[2] or [CoCl$_2$(tren)]$^+$[14] with KSCN or NaN$_3$.

Measurements. The visible and ultraviolet absorption measurements were made by a Shimadzu UV-200 spectrophotometer in aqueous solutions, except for the dichloro complex, which was measured in methanol to prevent the aquation. The CD spectra were recorded on a JASCO MOE-1 spectropolarimeter and the PMR spectra were obtained in dimethyl-*d*$_6$ sulfoxide on a Varian XL-100-15 spectrometer using tetramethylsilane(TMS) as an internal standard.

Results and Discussion

Preparation and Isomerization. Three methods were tried for the preparation of the dinitro complex, [Co(NO$_2$)$_2$(*N*,*N*-Me$_2$-en)$_2$]$^+$; by use of atmospheric oxidation of a mixture of Co^{2+}, *N*,*N*-Me$_2$-en, NaNO$_2$, and HCl, and by use of ligand-substitution of either [Co(CO$_3$)$_3$]$^{3-}$ or [Co(NO$_2$)$_6$]$^{3-}$. The air-oxidation method only was successful. The product of this reaction was proved to be a *trans*(NO$_2$) isomer from the parallel relationship between the absorption spectra of this and the corresponding *trans*(NO$_2$)-[Co(NO$_2$)$_2$(en)$_2$]$^+$ complex. The *cis*-dinitro complex was not obtaned, although the *cis* isomers of diazido-, diisothiocyanato-, and dichloro-complexes were prepared. The diammine complex, [Co(NH$_3$)$_2$(*N*,*N*-Me$_2$-en)$_2$]$^{3+}$ was not yielded on the tretment of the dichloro complex, *cis*(Cl)-[CoCl$_2$(*N*,*N*-Me$_2$-en)$_2$]$^+$ with liquid ammonia; the reaction gave only tetraammine complex, [Co(NH$_3$)$_4$(*N*,*N*-Me$_2$-en)]$^{3+}$. When the *trans*-dinitro complex was treated with either alcoholic hydrogen chloride at room temperature of concentrated aqueous hydrogen chloride at 70 °C, only a *cis* isomer of the dichloro complex was obtained, and the reaction of the dichloro complex with NaNO$_2$ yielded only one dinitro complex which was identical with the starting material, *trans*(NO$_2$)-[Co(NO$_2$)$_2$(*N*,*N*-Me$_2$-en)$_2$]$^+$. The dichloro complex was decomposed in the presence of moisture to give a brown insoluble mud. The substitution reaction of *cis*(Cl)-[CoCl$_2$(*N*,*N*-Me$_2$-en)$_2$]$^+$ with NaN$_3$ or KSCN resulted in the production of both *trans* and *cis* isomers of diazido or diisothiocyanato complex. The correseponding substitution reaction of *trans*(Cl)-[CoCl$_2$(*N*-Me-en)$_2$]$^+$ with either NaN$_3$ or KSCN gave only the *trans* isomer, and *trans*(Cl)-[CoCl$_2$(*N*,*N*′-Me$_2$-en)$_2$]$^+$ did not react with these reagents.

Structural Assignments. Figure 1 shows five possible geometrical isomers of a [CoX$_2$(A-B)$_2$] type complex and their symmetries. In this paper X stands for anions (Cl$^-$, NO$_2^-$, N$_3^-$, or NCS$^-$) and A-B for *N*,*N*-dimethylethylenediamine; where A and B signify a

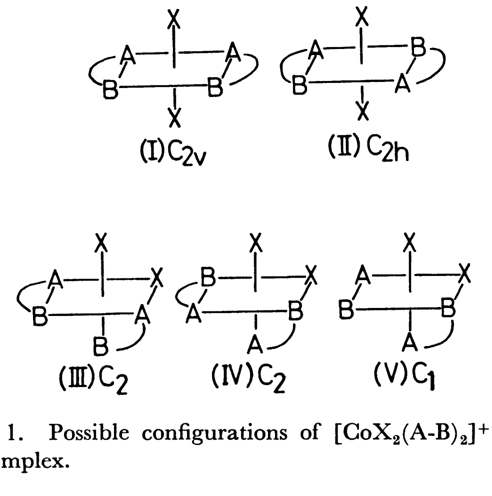

Fig. 1. Possible configurations of [CoX$_2$(A-B)$_2$]$^+$ type complex.

Table 1. Assignment of chemical shifts for PMR of [CoX$_2$(*N*,*N*-Me$_2$-en)$_2$]$^+$ (X=N$_3^-$, NCS$^-$, and NO$_2^-$)
(All frequencies in ppm on low-field side of TMS)

Complex	N-CH$_3$	-CH$_2$-CH$_2$-	N-H	Structure
trans(NO$_2$)-	2.07	≈2.40, 3.11	5.68	II
trans(N$_3$)-	2.09	2.29, 2.82	5.60	II
trans(NCS)-	2.21	≈2.46, 2.91	6.43	II
cis(N$_3$)-	2.10, 2.14	≈2.40, ≈3.2[a]	4.72, 5.56	III
cis(NCS)-	2.25, 2.37	≈2.5,[b] ≈2.95	5.70, 6.00	III

a) Overlapped with -OH signal. b) Overlapped with dimethyl sulfoxide signal.

tertiary and a primary amine, respectively. The upper two complexes I and II in Fig. 1 are *trans*(X) isomers and the lower three III-V *cis*(X) ones. All the three *cis*(X) isomers are chiral and therefore the isomer which can be resolved turns out to be one of the *cis*(X) isomers. PMR spectra can also distinguish among the isomers (I, II), (III, IV), and (V).

Table 1 shows the chemical shifts(in ppm) for PMR spectra of [CoX$_2$(*N*,*N*-Me$_2$-en)$_2$]$^+$(X=NO$_2^-$, NCS$^-$, and N$_3^-$). From the PMR data it is confirmed that the *trans* isomers of dinitro-, diisothiocyanato-, and diazido-complexes have I or II structure and that the *cis* isomers of diazido- and diisothiocyanato-complexes III or IV structure. No well-defined PMR spectrum was obtained for the dichloro complex, because of the unstable nature of this complex. It is impossible to distinguish between isomers I and II or between isomers III and IV solely on the basis of the PMR splitting patterns. However a consideration of molecular models provides the following answers for this problem.

The structure I has bulky *N*,*N*-dimethyl-substituted amines(A) in *cis* positions, which produce rather large repulsion between them and make the structure unstable. A similar consideration is true for the *cis*(X) isomers, that is, the structure IV and V are less stable than the structure III. Accordingly, it is concluded that the *trans*(X) isomers have the structure II and the *cis*(X) isomers the structure III. This conclusion is well supported by the consideration of the absorption spectra mentioned below.

Absorption and Circular Dichroism Spectra. Figure 2 shows the electronic absorption spectra of *trans*-(NO$_2$)-complexes of en, *N*-Me-en, *N*,*N*'-Me$_2$-en, and *N*,*N*-Me$_2$-en. It is found that the increase in the number of the *N*-methyl-groups induces the shift of the spectra to lower side, and that the *N*,*N*-Me$_2$-en complex has its absorption at lower energy than the *N*,*N*'-Me$_2$-en complex. The trough at *ca.* 25000 cm^{-1} disappears in the *N*,*N*-Me$_2$-en complex owing to the overlap of the first charge transfer band at *ca.* 27000 cm^{-1}.

Figures 3 and 4 show the absorption spectra of *trans*-(NCS)- and *trans*(N$_3$)-complexes, respectively. Besides the shift of each band to longer wavelength region with an increase in the degree of *N*-methyl-substitution, two more features are found. The first is the splitting of the first d-d absorption band; there is a broad peak at 19300 cm^{-1} with a shoulder at about 16500 cm^{-1} for the diisothiocyanato *N*,*N*-Me$_2$-en complex, and two distinct peaks at 14300 and 18200 cm^{-1} for the diazido *N*,*N*-Me$_2$-en complex. The second is a new peak (log $\varepsilon \approx 4$) in the ultraviolet region 35000—40000 cm^{-1} for both NCS- and N$_3$-complexes; the band is not found for the corresponding ethylenediamine and *N*-methylethylenediamine complexes. The new ultraviolet absorption band also appears for *cis* isomers of the *N*,*N*-Me$_2$-en complex at about the same position with the same intensity as those for the *trans* isomers (see Figs. 5 and 6, and Table 2).

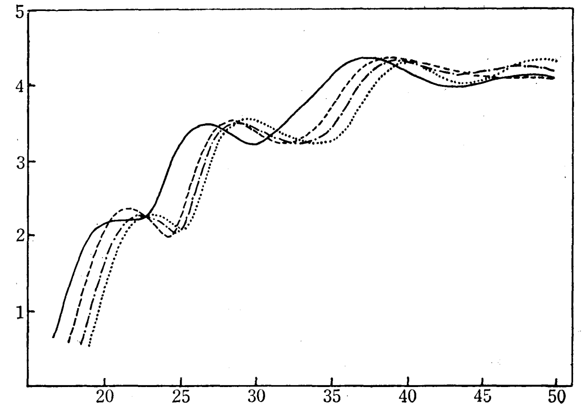

Fig. 2. Absorption spectra of *trans*(NO$_2$)-[Co(NO$_2$)$_2$(diamine)$_2$]$^+$: *N*,*N*-Me$_2$-en (——); *N*,*N*'-Me$_2$-en (----); *N*-Me-en (—·—); and en (······).

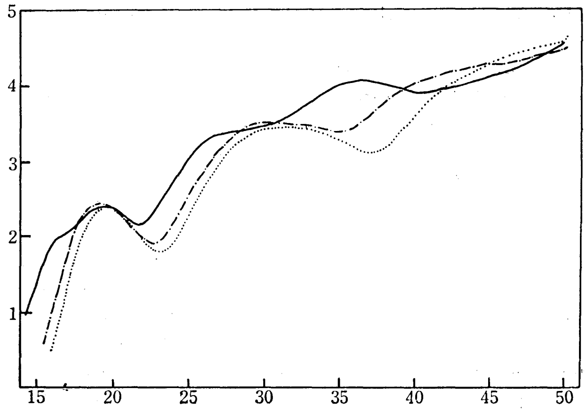

Fig. 3. Absorption spectra of *trans*(NCS)-[Co(NCS)$_2$(diamine)$_2$]$^+$: *N*,*N*-Me$_2$-en (——); *N*-Me-en (—·—); and en (······).

Figures 5 and 6 show the absorption and the CD spectra of *cis*(NCS)- and *cis*(N$_3$)-complexes of en,

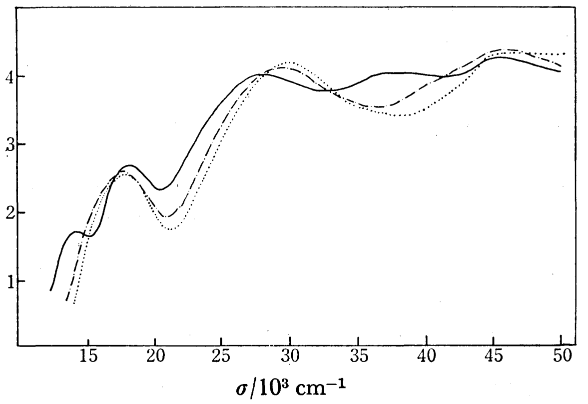

Fig. 4. Absorption spectra of *trans*(N_3)-[Co(N_3)$_2$(diamine)$_2$]$^+$: *N*,*N*-Me$_2$-en (——); *N*-Me-en (—·—); and en (······).

tren, and *N*,*N*-Me$_2$-en. Tren is a tripod tetradentate amine and the *cis*-[CoX_2(tren)]$^+$ complexes (X=NCS$^-$ and N_3^-) have a plane of symmetry and are achiral. Both absorption and CD spectra of *N*,*N*-Me$_2$-en complexes shift to longer wavelength region than those of the en complexes. The CD spectrum of $(+)_{589}$-[Co(N_3)$_2$(*N*,*N*-Me$_2$-en)$_2$]$^+$ correlates to that of $(-)_{589}$-[Co(N_3)$_2$(en)$_2$]$^+$ on the whole, except a small negative band at 38000 cm^{-1} related to the new absorption peak (Fig. 6). On the other hand, the CD spectrum of $(+)_{589}$-[Co(NCS)$_2$(*N*,*N*-Me$_2$-en)$_2$]$^+$ may not correlate at a glance, to that of $(-)_{589}$[Co(NCS)$_2$(en)$_2$]$^+$ in the ultraviolet region (Fig. 5). This is because the intensity ratio of the CD peaks at 25000—35000 cm^{-1} is reversed between *N*,*N*-Me$_2$-en and en complexes; the intensity is weak at 24600 cm^{-1} and strong at 30000 cm^{-1} in the *N*,*N*-Me$_2$-en complex (solid line), but strong at 31000 cm^{-1} and weak at 35000 cm^{-1} in the en complex (broken line). At the new absorption peak of 36600 cm^{-1} one or two negative CD bands appear.

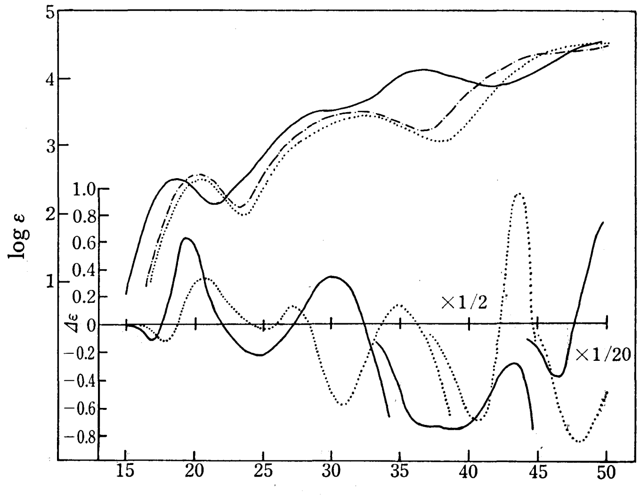

Fig. 5. Absorption and CD spectra of *cis*(NCS)-[Co(NCS)$_2$(amine)]$^+$: $(+)_{589}$-(*N*,*N*-Me$_2$-en)$_2$ (——); tren (—·—); and $(-)_{589}$-(en)$_2$ (······).

Table 2. The absorption data of Co(III) complexes containing *N*,*N*-Me$_2$-en and related amines
(Wave numbers and log ε values (in parentheses) are given in 10^3 cm^{-1} and mol^{-1} dm^3 cm^{-1}, respectively.)

Complex	d-d transition region		Charge transfer region		
trans-[Co(NO$_2$)$_2$(en)$_2$]ClO$_4$·0.5H$_2$O	23.20(2.29)		29.41(3.56)	40.16(4.31)	49.38(4.36)
trans-[Co(NO$_2$)$_2$(*N*-Me-en)$_2$]ClO$_4$	22.57(2.28)		28.90(3.51)	39.53(4.35)	48.08(4.27)
trans-[Co(NO$_2$)$_2$(*N*,*N*′-Me$_2$-en)$_2$]ClO$_4$	21.69(2.37)		28.65(3.53)	39.22(4.37)	48.54(4.13)
trans-[Co(NO$_2$)$_2$(*N*,*N*-Me$_2$-en)$_2$]ClO$_4$	21.32(2.24)		26.81(3.49)	37.45(4.39)	48.08(4.15)
trans-[Co(NCS)$_2$(en)$_2$]Cl·0.5H$_2$O	19.53(2.39)		31.15(3.45)		
trans-[Co(NCS)$_2$(*N*-Me-en)$_2$]Cl·H$_2$O	19.21(2.44)		31.10(3.51)		
trans-[Co(NCS)$_2$(*N*,*N*-Me$_2$-en)$_2$]Cl·H$_2$O	≈16.5 (sh) 19.34(2.39)		≈27.5(≈3.37)	36.50(4.06)	≈44.5(≈4.07)
trans-[Co(N$_3$)$_2$(en)$_2$]Cl·H$_2$O	17.79(2.53)	≈25.7 (sh)	29.85(4.15)	≈35 (sh≈3.4)	46.62(4.29)
trans-[Co(N$_3$)$_2$(*N*-Me-en)$_2$]ClO$_4$	17.66(2.56)		29.41(4.09)		45.87(4.33)
trans-[Co(N$_3$)$_2$(*N*,*N*-Me$_2$-en)$_2$]ClO$_4$	14.29(1.68) 19.34(2.39)		28.01(3.98)	38.02(4.00)	45.46(4.22)
cis-[Co(NCS)$_2$(en)$_2$]Cl	20.37(2.51)		32.15(3.43)		
cis-[Co(NCS)$_2$(*N*,*N*-Me$_2$-en)$_2$]Cl·H$_2$O	18.62(2.52)		≈29.5(≈3.48)	36.63(4.10)	
cis-[Co(NCS)$_2$(tren)]Cl	20.12(2.59)		31.85(3.48)		
cis-[Co(N$_3$)$_2$(en)$_2$]Cl·H$_2$O	19.27(2.52)	≈27.4 (sh)	33.11(4.07)		46.73(4.30)
cis-[Co(N$_3$)$_2$(*N*,*N*-Me$_2$-en)$_2$]Cl·H$_2$O	17.61(2.45)	≈22 (sh)	32.26(3.95)	38.02(4.07)	46.08(4.13)
cis-[Co(N$_3$)$_2$(tren)]ClO$_4$·H$_2$O	19.12(2.57)		33.00(4.14)		46.06(4.29)
cis-[CoCl$_2$(en)$_2$]Cl[23)]	18.87(1.88)	25.64(1.87)		41.67(4.28)	
cis-[CoCl$_2$(*N*,*N*-Me$_2$-en)$_2$]ClO$_4$·0.5H$_2$O	16.31(2.05)	≈24 (≈2.0)		39.06(4.25)	
[Co(CO$_3$)(en)$_2$]ClO$_4$	19.53(2.16)	27.78(2.12)			42.19(4.14)
[Co(CO$_3$)(*N*,*N*-Me$_2$-en)$_2$]ClO$_4$·0.5H$_2$O	17.92(2.09)	25.58(2.10)		39.06(4.22)	45.87(≈4.0)
[Co(CO$_3$)(tren)]ClO$_4$·1.5H$_2$O	19.76(2.13)	≈25.5(≈1.9) 28.05(2.06)			41.24(4.16)
[Co(CO$_3$)(*N*,*N*-Me$_2$-en)$_2$]ClO$_4$·0.5H$_2$O	18.28(2.12)	25.64(2.17)		38.16(4.18)	42.37(4.22)
[Co(NH$_3$)$_4$(*N*,*N*-Me$_2$-en)]Cl$_3$·1.5H$_2$O	20.37(1.88)	28.99(1.84)		≈42.37(≈4.1)	47.85(4.23)

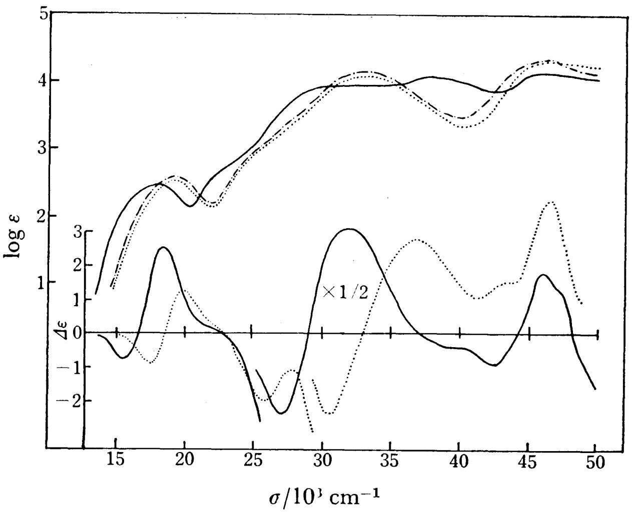

Fig. 6. Absorption and CD spectra of *cis*(N_3)-[Co(N_3)$_2$(amine)]$^+$: $(+)_{589}$-(*N*,*N*-Me$_2$-en)$_2$ (——); tren (—·—); and $(-)_{589}$-(en)$_2$ (……).

The feature of the absorption spectra of the Co(III) complexes containing *N*,*N*-Me$_2$-en is well explained with an assumption that the diamine(A-B) has different ligand-field strengths at each end; the tertiary amine end(A) has very weak ligand-field and the primary amine end(B) the same as ethylenediamine. Yamatera's parameter[15] of the tertiary amine end, δ(A), can be calculated from the absorption data of the *trans*(N_3) isomer which shows a large splitting in the first absorption band region. Such a large splitting can be explained well by the structure II and not by I. Thus the peak situated at lower energy is thought to be shifted by $1/2\delta(N_3)+1/2\delta(A)$ from the peak of the parent complex, [Co(en)$_3$]$^{3+}$(21400 cm^{-1}). That is, $1/2\delta(N_3)+1/2\delta(A)=14300-21400=-7100$ cm^{-1}, and with an assumption that $\delta(N_3)=-7900$ cm^{-1} (from the first absorption band position 17250 cm^{-1} of *mer*-[Co(N_3)$_3$(NH_3)$_3$],[16] we obtain $\delta(A)=-6300$ cm^{-1}, which is weaker than those of the oxalato and carbonato ligands, $\delta(ox)=-4800$ cm^{-1} and $\delta(CO_3)=-5900$ cm^{-1} obtained from the reported absorption spectral data.[17,18] Therefore, on the whole, *N*,*N*-dimethylethylenediamine has somewhat weak strength in the ligand-field as compared with amino acids. From this and the other values, $\delta(NO_2)=+4000$ cm^{-1} and $\delta(NCS)=-4300$ cm^{-1} (from the first absorption band position 23210 cm^{-1} and 19050 cm^{-1} of *mer*-[Co(NO_2)$_3$(NH_3)$_3$][19] and *mer*-[Co(NCS)$_3$(NH_3)$_3$][20], respectively), the first absorption bands of all the *trans* isomers of *N*,*N*-Me$_2$-en complexes can be well explained. Yamatera's rule predicts that the *cis*(N_3) complex of structure III has the split components of the first absorption band at 16300 and 17500 cm^{-1}, while that of the structure IV at 14300 and 17900 cm^{-1}. The observed first absorption band of the *cis*(N_3) complex is located at 17610 cm^{-1}. The absence of the band of 14300 cm^{-1} supports strongly the structure III for this complex. Similarly the *cis*(NCS) complex is assigned to have the strucutre III, which is parallel to the conclusion from pmr and molecular model considerations. The dichloro complex cannot be assigned on the basis of PMR spectra. However, if it is the *trans*(Cl) isomer II, it should have a split component at *ca.* 12900 cm^{-1} (from $\delta(Cl)=-10700$ cm^{-1} [21]). Because the complex shows no component there, it is assigned to the *cis*(Cl) isomer.

In a previous paper we reported that the near ultraviolet charge-transfer band (so-called specific band) of a *trans* isomer of bis(aniono) Co(III) complexes is more bathochromic than that of the corresponding *cis* isomer.[22] This is also the case of the present *N*,*N*-Me$_2$-en complexes; for example, the band of the *trans*-(N_3) complex is at 28010 cm^{-1}, while that of *cis*(N_3) at 32260 cm^{-1}. All the present dianiono complexes of *N*,*N*-Me$_2$-en show a broad absorption band in the region of 35000—39000 cm^{-1} (Table 2). The tetraamine complex, [Co(NH_3)$_4$(*N*,*N*-Me$_2$-en)]$^{3+}$ also shows this kind of band at *ca.* 42000 cm^{-1}. This new band of charge-transfer character is attributed to the coordinated tertiary amine; the observed peak or so-called end absorption at *ca.* 50000 cm^{-1} may be attributed to the coordinated primary amine. In this connection it is worthwhile to point out that none of the tren complexes show the peak attributed to the tertiary amine, which may reflects that the tertiary amine of the tren ligand has a nature different from that of *N*,*N*-Me$_2$-en.

Absolute Configuration. From the parallel relationship between the CD spectra of $(+)_{589}$-[CoX$_2$(*N*,*N*-Me$_2$-en)$_2$]$^+$ and $(-)_{589}$-[CoX$_2$(en)$_2$]$^+$ ($X=N_3^-$ and NCS$^-$), it is concluded that the $(+)_{589}$-isomers of *cis* dianiono complexes of *N*,*N*-Me$_2$-en have the absolute configuration same as that of the $(-)_{589}$-isomers of the corresponding en complexes (see Table 3). Because the latter complexes have been assigned to Λ configuration,[12] the present $(+)_{589}$-*N*,*N*-Me$_2$-en complexes

TABLE 3. THE CD DATA OF *cis*(X)-[CoX$_2$(diamine)$_2$]$^+$ (diamine=en, *N*,*N*-Me$_2$-en) COMPLEXES

(Wave numbers and Δε values (in parentheses) are given in 10^3 cm^{-1} and mol^{-1} dm^3 cm^{-1}, respectively.)

$(-)_{589}$-[Co(NCS)$_2$(en)$_2$]Cl	$(+)_{589}$-[Co(NCS)$_2$-(*N*,*N*-Me$_2$-en)$_2$]ClO$_4$
17.73(−0.130)	16.89(−0.133)
20.60(+0.340)	19.31(+0.642)
25.13(−0.04)	
27.17(+0.13)	
30.77(−0.60)	24.39(−0.233)
34.72(+0.15)	29.85(+0.35)
40.65(−1.42)	36.76(−1.52)
43.48(+1.96)	38.17(−1.55)
47.85(−17.5)	*46.30(−3.73)*
$(-)_{589}$-[Co(N_3)$_2$(en)$_2$]ClO$_4$	$(+)_{589}$-[Co(N_3)$_2$-(*N*,*N*-Me$_2$-en)$_2$]ClO$_4$
17.45(−0.871)	15.24(−0.826)
19.72(+1.286)	18.02(+2.558)
25.77(−1.97)	
30.67(−4.76)	26.81(−4.79)
37.04(+5.47)	31.75(+6.32)
43.48(+2.91)	≈40 (≈−0.8)
	42.37(−1.84)
46.73(+7.93)	45.87(+3.69)

are also assigned to *Λ*.

In a previous paper[12] it was reported that the *Λ* isomers of diazido- and diisothiocyanatobis(ethylenediamine)cobalt(III) complexes show a CD pattern of negative and then positive signs in the order of increasing energy in the longest wavelength charge-transfer band region, so-called specific band region. As is seen in Figs. 5 and 6, and in Table 3, this is also valid for the *N*,*N*-Me_2-en complexes. The CD sign in the region of tertiary amine band is negative for the *Λ* isomers.

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