Preparation and Characterization of Cobalt(III) Complexes Containing (2-Aminoethyl)dimethylarsine (edma). Resolution and Racemization of *fac*-[Co(edma)$_3$]$^{3+}$

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(2-Aminoethyl)dimethylarsine (edma) and its cobalt(III) complexes, *trans*(*X*,*X*),*cis*(*As*,*As*)-[CoX$_2$(edma)$_2$]$^+$ (X=Cl, Br, and I), *trans*(*As*,*As*)- and *trans*(*As*,*N*)-[Co(acac)(edma)$_2$]$^{2+}$ (acac=acetylacetonate ion), *trans*(*As*,*N*)-[Co(CO$_3$)(edma)$_2$]$^+$, [Co(acac)$_2$(edma)]$^+$, and *fac*-[Co(edma)$_3$]$^{3+}$ were prepared and characterized. From a comparison of the first d–d absorption bands of analogous diamine and (2-aminoethyl)dimethylphosphine (edmp) complexes, the spectrochemical series of Group 5B elements was found to be P>As>N. The *fac*-[Co(edma)$_3$]$^{3+}$ complex was resolved and the absolute configuration of the $(+)_{490}^{CD}$-isomer was assigned to *Λ* on the basis of the CD spectrum. Racemization of *fac*-[Co(edma)$_3$]$^{3+}$ was studied in aqueous solutions in the pH and temperature ranges of 7.88—9.32 and 35.0—50.0 °C, respectively. The racemization obeyed a rate law of the form, $R=k[OH^-][complex]$. The activation enthalpy and entropy values were found to be $\Delta H^*=132\pm4$ kJ mol^{-1} and $\Delta S^*=171\pm11$ J K^{-1} mol^{-1}, respectively.

In previous papers, we reported the preparation of a number of cobalt(III) complexes containing (2-aminoethyl)dimethylphosphine (edmp)[1,2] and its derivatives.[3–5] To our knowledge, however, no cobalt(III) complex with the arsine analog is known. An (aminoalkyl)arsine is an intermediate ligand between a diamine and a diarsine and its complexes will be useful in studying properties of cobalt(III)–arsine complexes, for which several studies have been reported.[6,7] This paper deals with the preparation and characterization of (2-aminoethyl)dimethylarsine (edma) and its several cobalt(III) complexes, including the resolution and absolute configuration of *fac*-[Co(edma)$_3$]$^{3+}$, and its racemization occured in aqueous solution catalyzed by OH$^-$.

Experimental

The arsine ligand was handled under an atmosphere of nitrogen until it formed air-stable cobalt(III) complexes. Tetrahydrofuran was dried with sodium and deoxygenated by distillation in a stream of nitrogen. Other solvents used for the preparation of complexes were deoxygenated by bubbling nitrogen for 20 min immediately before use. Absorption, circular dichroism, and ^{1}H NMR spectra were recorded on JASCO 610B and Hitachi U-3400 spectrophotometers, a JASCO J-40CS spectropolarimeter, and a Hitachi R-90HS spectrometer, respectively.

(2-Aminoethyl)dimethylarsine (edma). A tetrahydrofuran solution of sodium dimethylarsine was prepared by a modified method of Phillips and Vis.[8] To a mixture of tetrahydrofuran (60 cm^3) and metallic sodium (15.4 g, 0.67 mol) in a 300 cm^3 three-necked round bottom flask was added dropwise a tetrahydrofuran solution (80 cm^3) of iododimethylarsine[9] (46.4 g, 0.20 mol) over a period of 90 min with stirring at 0 °C. After a while the mixture was refluxed for 30 min and then cooled to room temperature. The resulting greenish brown solution was filtered to remove precipitated sodium iodide and unreacted sodium. To the filtrate was added aziridine[10] (10.8 g, 0.25 mol), and the solution was stirred at 35 °C for 60 h, the color of the solution becoming pale gradually. Water (40 cm^3) was added dropwise to the solution, and tetrahydrofuran was removed under reduced pressure. The residue was shaken with diethyl ether to extract edma. The extract was evaporated under reduced pressure to give oily, pale yellow edma. Yield: 15.3 g (51% based on AsI(CH$_3$)$_2$). The ligand could not be purifed by distillation because of its decomposition under usual distilling conditions, but done via the nickel(II) complex. The yellow nickel(II) complex (presumably [Ni(edma)$_2$](ClO$_4$)$_2$) was precipitated immediately by the addition of crude edma (15.3 g) to a methanol solution (100 cm^3) of Ni(ClO$_4$)$_2$·6H$_2$O (18.7 g), filtered, washed with methanol and diethyl ether, and air dried. Yield: 14.1 g. The complex is stable in air but tends to be explosive by mechanical or thermal shock. Thus the elemental analysis was not carried out. The free ligand can be obtained from the complex by treating with KCN in water and by extracting with diethyl ether. ^{1}H NMR edma (=(CH$_3$)$_2$AsCH$_2$CH$_2$NH$_2$)(CDCl$_3$, TMS): δ=0.88 (s, 6H, As(CH$_3$)$_2$), 1.53 (t, 2H, AsCH$_2$), 1.83 (s, 2H, NH$_2$), 2.76 (t, 2H, NCH$_2$). The nickel(II) complex (CD$_3$NO$_2$, TMS): δ=1.67 (s, 6H, As(CH$_3$)$_2$), 2.18 (t, 2H, AsCH$_2$), 2.97 (m, 2H, NCH$_2$), 3.56 (br, 2H, NH$_2$).

***trans*(*Cl*,*Cl*)-[CoCl$_2$(edma)$_2$]ClO$_4$.** To an ethanol solution (50 cm^3) of CoCl$_2$·6H$_2$O (5.0 g, 21.0 mmol) was added crude edma (5.0 g, 33.5 mmol) in ethanol (50 cm^3). A pale blue precipitate was observed. Into this mixture air was bubbled for 1 h, then water (1 cm^3) and concd HCl (1 cm^3) were added, and ethanol was removed under reduced pressure. To the resulting green solution was added NaClO$_4$·H$_2$O (10 g) in water (5 cm^3), and the complex was extracted with dichloromethane. The extract was evaporated to dryness, giving green needle crystals, which were filtered and recrystallized from hot methanol. Yield: 2.20 g. Found: C, 17.83; H, 4.62; N, 5.04%. Calcd for C$_8$H$_{24}$N$_2$As$_2$Cl$_3$O$_4$Co: C, 18.21; H, 4.59; N, 5.31%. ^{1}H NMR (CD$_2$Cl$_2$, TMS): δ=1.54 (s, 12H, As(CH$_3$)$_2$), 2.45 (t, 4H, AsCH$_2$), 3.24 (br, 4H, NCH$_2$), 4.80 (br, 4H, NH$_2$).

***trans*(*Br*,*Br*)-[CoBr$_2$(edma)$_2$]ClO$_4$.** A hot methanol solution (10 cm^3) of *trans*(*Cl*, *Cl*)-[CoCl$_2$(edma)$_2$]ClO$_4$ (1.46 g, 2.77 mmol) was mixed with a hot aqueous solution (10 cm^3) of Na$_2$CO$_3$ (0.32 g, 3.0 mmol), and the mixture was warmed at 60 °C for 15 min to give a red solution. Methanol was

removed under reduced pressure, and the solution was passed through a column of QAE-Sephadex (ClO_4^--form) to remove chloride ions. The eluate was concentrated to ca. 2 cm^3 under reduced pressure. On addition of concd HBr (2 cm^3) the concentrate yielded green crystals, which were filtered, washed with methanol and diethyl ether. Recrystallization was carried out from hot methanol. Yield: 1.64 g. Found: C, 15.86; H, 3.40; N, 4.71%. Calcd for $C_8H_{24}N_2As_2Br_2ClO_4Co$: C, 15.59; H, 3.92; N, 4.71%. ^1H NMR (CD_2Cl_2, TMS): δ=1.70 (s, 12H, $As(CH_3)_2$), 2.50 (t, 4H, $AsCH_2$), 3.36 (m, 4H, NCH_2), 5.05 (br, 4H, NH_2).

***trans*(*I*,*I*)-[CoI_2(edma)$_2$]ClO_4.** This complex was obtained as brown crystals by a method similar to that for the above dibromo complex using KI and 60% $HClO_4$ instead of concd HBr. Yield: 76%. Found: C, 14.03; H, 3.40; N, 4.18%. Calcd for $C_8H_{24}N_2As_2ClI_2O_4Co$: C, 13.53; H, 3.41; N, 3.94%. ^1H NMR (CD_2Cl_2, TMS): δ=1.96 (s, 12H, $As(CH_3)_2$), 2.54 (t, 4H, $AsCH_2$), 3.42 (m, 4H, NCH_2), 4.98 (br, 4H, NH_2).

***trans*(*As*,*N*)-[Co(CO_3)(edma)$_2$]B(C_6H_5)$_4$.** A red solution prepared from *trans*(*Cl*,*Cl*)-[$CoCl_2$(edma)$_2$]ClO_4 (1.46 g, 1.77 mmol) and Na_2CO_3 (0.32 g, 3.0 mmol) by the method for *trans*(*Br*, *Br*)-[$CoBr_2$(edma)$_2$]$^+$ was diluted with water (1 dm^3), and the solution was applied on a column (ϕ 3.0×50 cm) of SP-Sephadex C-25. By elution with 0.05 mol dm^{-3} Na_2SO_4 only one red band developed. The eluate was concentrated to a small volume under reduced pressure, and filtered. On addition of $NaB(C_6H_5)_4$ in water the concentrate yielded a red precipitate, which was filtered, washed with water and methanol, and air dried. The complex with other anions such as Cl^- or ClO_4^- was very soluble and could not be isolated. Found: C, 53.80; H, 6.19; N, 3.86%. Calcd for $C_{33}H_{44}N_2As_2BO_3Co$: C, 53.83; H, 6.02; N, 3.80%. ^1H NMR (DMSO-d_6, TMS): δ=1.34, 1.44, 1.55, 1.66 (s, $As(CH_3)_2$).

***trans*(*As*,*As*)- and *trans*(*As*,*N*)-[Co(acac)(edma)$_2$](ClO_4)$_2$ (acac=acetylacetonate ion).** A mixture of *trans*(*Cl*, *Cl*)-[$CoCl_2$(edma)$_2$]ClO_4 (300 mg, 0.57 mmol) and Li(acac) (61 mg, 0.57 mmol) in a mixture of water and methanol (2:1, 20 cm^3) was warmed at 60 °C for 3 h. The resulting red solution was diluted with water (500 cm^3) and applied on a column (ϕ 2.0×150 cm) of SP-sephadex C-25. The adsorbed product was eluted with 0.1 mol dm^{-3} Na_2SO_4, giving a faster-moving violet band ([Co(acac)$_2$(edma)]$^+$) and then two red bands. The separation between the latter two bands was small. The eluate containing each red band was collected, diluted 10 times with water, applied again on a small column of SP-Sephadex C-25, and the adsorbed complex was eluted with 1 mol dm^{-3} $NaClO_4$. The eluate containing the first red band was evaporated to a small volume under reduced pressure, and the complex was extracted with dichloromethane. The extract was concentrated to a small volume under reduced pressure. Dark red crystals of *trans*(*As*, *As*)-[Co(acac)(edma)$_2$](ClO_4)$_2$ were precipitated by slow addition of diethyl ether to the concentrate, filtered, washed with diethyl ether, and air dried. Yield: 29 mg (8%). Found: C, 23.47; H, 4.71; N, 4.12%. Calcd for $C_{13}H_{31}N_2As_2Cl_2O_{10}Co$: C, 23.84; H, 4.77; N, 4.28%. ^1H NMR (CD_3OD, TMS): δ=1.66, 1.91, 2.02 (s, $As(CH_3)_2$ and CCH_3), 5.61 (s, CH), 2.1—2.7 (m, CH_2).

The eluate containing the second red band was concentrated under reduced pressure, yielding red crystals of *trans*-(*As*,*N*)-[Co(acac)(edma)$_2$](ClO_4)$_2$, which were filtered, washed with a small amount of cold water, and recrystallized from methanol and diethyl ether. Yield: 42 mg (11%). Found: C, 23.85; H, 4.70; N, 4.66%. Calcd for $C_{13}H_{31}N_2As_2Cl_2O_{10}Co$: C, 23.84; H, 4.77; N, 4.28%. ^1H NMR (CD_3OD, TMS): δ=1.58, 1.61, 1.70, 1.88, 1.92, 2.28 (s, $As(CH_3)_2$ and CCH_3), 5.70 (s, CH).

[Co(acac)$_2$(edma)]ClO_4. The free ligand was extracted with diethyl ether from a mixture of [Ni(edma)$_2$](ClO_4)$_2$ (780 mg, 1.4 mmol) and KCN (560 mg, 8.4 mmol) in water (3 cm^3), and ether was removed under reduced pressure. To this were added a methanol solution (60 cm^3) of [Co(acac)$_3$] (1.0 g, 2.8 mmol) and active charcoal (ca. 0.3 g). The mixture was stirred at room temperature for 13 h, and active charcoal was filtered off. The filtrate was diluted 10 times with water and applied on a column (ϕ 3.0×20 cm) of SP-Sephadex C-25. The column was washed with water to remove unreacted [Co(acac)$_3$], and then the violet adsorbed product was eluted with 0.05 mol dm^{-3} NaCl, a trace of a pink product remaining on the column. The eluate was evaporated under reduced pressure to ca. 5 cm^3. On addition of a few drops of a saturated aqueous solution of $NaClO_4$ the concentrate yielded violet crystals, which were filtered, washed with a small amount of cold water, and recrystallized from methanol and diethyl ether. Yield: 0.91 g (67%). Found: C, 33.36; H, 2.66; N, 5.15%. Calcd for $C_{14}H_{26}NAsClO_8Co$: C, 33.25; H, 2.77; N, 5.18%. ^1H NMR (D_2O, TSP): δ=1.46, 1.71, 1.99, 2.02, 2.06, 2.33 (s, $As(CH_3)_2$ and CCH_3), 5.69, 5.77 (s, CH).

The complex was also yielded as a by-product in the preparation of [Co(acac)(edma)$_2$]$^{2+}$ from *trans*(*Cl*,*Cl*)-[$CoCl_2$-(edma)$_2$]$^+$ and Li(acac) (1:1) (vide ante).

***fac*-[Co(edma)$_3$]$Br_3\cdot 3H_2O$.** To edma, which was obtained from [Ni(edma)$_2$](ClO_4)$_2$ (560 mg, 1 mmol) and KCN (400 mg, 6 mmol) by the above method, were added $Na_3[Co(CO_3)_3]\cdot 3H_2O$[11] (210 mg, 0.58 mmol) and water (3 cm^3), and the mixture was stirred at 40 °C for 30 min. To the resulting orange solution was added excess $NaClO_4$ (ca. 1 g) dissolved in a minimum amount of water. After 2 h a yellow precipitate ([Co(edma)$_3$](ClO_4)$_3$) was filtered, and dissolved in water. The solution was applied on a column (ϕ 3.0×90 cm) of SP-Sephadex C-25, and the adsorbed product was eluted with 0.5 mol dm^{-3} KBr, giving a single yellow band. Yellow-brown crystals which were precipitated by concentrating the eluate under reduced pressure were filtered, washed with ethanol, and recrystallized from water. Yield: 230 mg (43%). Found: C, 18.10; H, 5.83; N, 5.20%. Calcd for $C_{12}H_{42}N_3As_3Br_3O_3Co$: C, 18.02; H, 5.29; N, 5.25%. ^1H NMR (D_2O, TSP): δ=1.87, 1.97(s, $As(CH_3)_2$).

Resolution of *fac*-[Co(edma)$_3$]$^{3+}$. Complete resolution of *fac*-[Co(edma)$_3$]$^{3+}$ was achieved by a column-chromatographic method similar to that for [Co(en)$_3$]$^{3+}$ (en=$NH_2CH_2CH_2NH_2$).[12] An aqueous solution of *fac*-[Co(edma)$_3$]-$Br_3\cdot 3H_2O$ (ca. 100 mg) was applied on a column (ϕ 3.0×90 cm) of SP-Sephadex C-25, and the adsorbed complex was eluted with 0.1 mol dm^{-3} $Na_2[Sb_2\{(+)\text{-tartrate}\}_2]$. Two yellow bands were eluted in good separation. Each eluate was diluted 10 times with water and applied on a small column of SP-Sephadex C-25. The column was washed thoroughly with water, and the adsorbed complex was eluted with 1 mol dm^{-3} KBr. Yellow-brown crystals of optically active *fac*-[Co(edma)$_3$]$Br_3\cdot 3H_2O$ were obtained from the eluate by the same procedure as that for the racemate. The $(+)^{CD}_{490}$-*A* isomer was obtained from the faster-moving band. Found: C, 17.94; H, 4.88; N, 5.30%. Calcd for $C_{12}H_{42}N_3As_3Br_3O_3Co$=[Co(edma)$_3$]$Br_3\cdot 3H_2O$: C, 18.02; H, 5.29; N, 5.25%.

Kinetic Measurements. Optically active *fac*-$[Co(edma)_3]^{3+}$ (ca. 1.10 mmol dm^{-3}) was racemized in sodium 5,5-diethylbarbiturate ($NaC_8H_{11}N_2O_3$)–HCl buffer solution (pH: 7.88—9.32) with ionic strength of 1.0 (LiCl) in the temperature range of 35.0—50.0 °C. Portions of the solution were withdrawn at intervals, and the decreases in CD strength were recorded in the region of 390—540 nm. In each kinetic run, the plot of ln ($\Delta\varepsilon_t$(492 nm)) vs. time gave a straight line for at least three half-lives, where $\Delta\varepsilon_t$(492 nm) denotes the CD strength at time t and at 492 nm. No change in absorption spectrum was observed during the racemization.

Attempts to examine the racemization of *fac*-$[Co(edmp)_3]^{3+}$ [1] were unsuccessful. The complex was stable to racemization in neutral or acidic solution and decomposed in basic solution to give a blue-white precipitate.

Results and Discussion

Preparation and Characterization of the Complexes. The edma ligand was prepared by a method similar to that for the phosphorus analog, (2-aminoethyl)-dimethylphosphine (edmp)[1] from sodium dimethylarsenide and aziridine in a yield of ca. 50%. 2-Chloroethylamine hydrochloride can be used instead of aziridine but the yield was a little poorer. The ligand could not be purified by vacuum distillation because it decomposed at ca. 40 °C. The purification was carried out via $[Ni(edma)_2](ClO_4)_2$ which easily liberated edma by the addition of excess KCN in water. The yellow $[Ni(edma)_2](ClO_4)_2$ complex in CD_3NO_2 shows sharp signals in the ^1H NMR spectrum and is assumed to be a diamagnetic planar complex. The complex tends to be explosive by mechanical or thermal shock, while the perchlorates of Co(III)–edma complexes prepared in this study are rather stable and burn by heating without exploding.

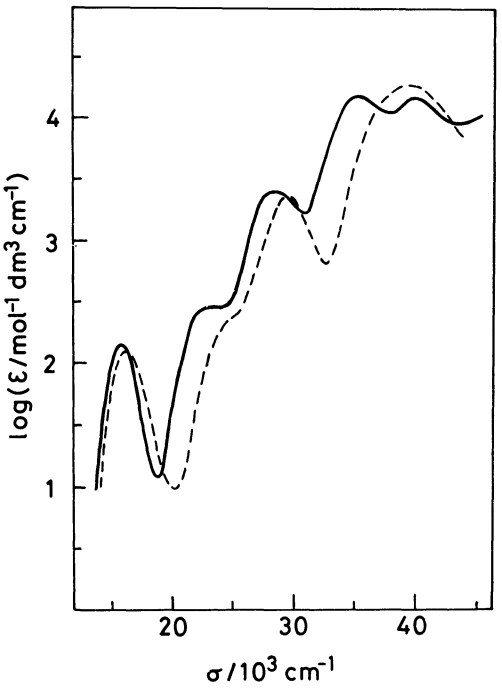

Fig. 1. Absorption spectra of *trans*(*Cl*,*Cl*),*cis*(*As*,*As*)-$[CoCl_2(edma)_2]^+$ (——) and *trans*(*Cl*,*Cl*),*cis*(*P*,*P*)-$[CoCl_2(edmp)_2]^+$ (----) in methanol.

Only one isomer of $[CoCl_2(edma)_2]^+$ was formed by oxidizing a mixture of $CoCl_2 \cdot 6H_2O$ and edma in ethanol with air, although five geometrical isomers are possible for this type of complex. The reaction of $[Co(CO_3)(edma)_2]^+$ with hydrochloric acid yielded the same isomer. The complex is green in color and shows a medium intensity band at 15800 cm^{-1} in the absorption spectrum. The band is characteristic of a *trans*(*Cl*,*Cl*) configuration, and can be assigned to the split component (Ia) of the first d–d band ($^1T_{1g} \leftarrow {}^1A_{1g}$ (O_h)) (Fig. 1). The broad band around 22500 cm^{-1} can be assigned to the other split component (Ib) overlapping with the second d–d band ($^1T_{2g} \leftarrow {}^1A_{1g}(O_h)$). This spectral pattern is very similar to that of *trans*(*Cl*, *Cl*), *cis*(*P*, *P*)-$[CoCl_2(edmp)_2]^+$ [3] shown in Fig. 1. Thus the complex can be assingned to the *trans*(*Cl*, *Cl*), *cis*(*As*, *As*) isomer, although no clear evidence for the *cis*(*As*, *As*) configuration could be obtained from the absorption and ^1H NMR spectra. Table 1 lists the data of absorption spectra.

Figure 2 shows absorption spectra of $[CoX_2(edma)_2]^+$ (X=Br, I), which were prepared from $[Co(CO_3)(edma)_2]^+$ and HX, together with the spectrum of dichloro complex. The lowest energy bands around 15000 cm^{-1} of the dibromo and diiodo complexes are similar in pattern to that of the dichloro complex, and their energies decrease in the order Cl>Br>I in accordance with the spectrochemical series. Thus these dihalogeno complexes can be assigned to the same *trans*(*X*, *X*), *cis*(*As*, *As*) isomer.

No *cis*(*X*, *X*) isomer was obtained by the reaction of

Table 1. Absorption Spectral Data of Mixed Ligand Complexes

Complex	$\sigma_{max}/10^3$ cm^{-1} ($\log(\varepsilon/cm^{-1}\,mol^{-1}\,dm^3)$)
trans(*Cl*,*Cl*)-$[CoCl_2(edma)_2]^{+a)}$	15.8 (2.16), 22.5 (sh, 2.49), 28.4 (3.40), 35.2 (4.17), 39.7 (4.14)
trans(*Br*,*Br*)-$[CoBr_2(edma)_2]^{+a)}$	15.0 (2.23), 27.9 (sh, 3.34), 25.5 (3.27), 34.8 (4.36), 42.7 (4.09)
trans(*I*,*I*)-$[CoI_2(edma)_2]^{+a)}$	14.1 (2.23), 21.5 (3.69), 29.9 (4.12), 37.8 (4.10)
$[Co(acac)_2(edma)]^{+b)}$	19.0 (2.50), 29.9 (sh, 3.80), 35.7 (sh, 4.23), 39.0 (4.37), 45.0 (4.30)
trans(*As*,*As*)-$[Co(acac)(edma)_2]^{2+b)}$	19.2 (3.19), 25.4 (sh 3.80), 28.1 (3.90), 33.0 (4.24), 39.0 (4.10), 45.5 (4.23)
trans(*As*,*N*)-$[Co(acac)(edma)_2]^{2+b)}$	20.4 (2.71), 26.3 (sh, 2.80), 29.9 (sh, 3.56), 35.0 (sh, 4.30), 37.8 (4.49), 42.7 (4.13), 46.6 (4.10)
trans(*As*,*N*)-$[Co(CO_3)(edma)_2]^{+c)}$	19.7 (2.57), 25.6 (sh, 2.43), 36.2 (4.19)

Solvent, a): CH_3OH, b): H_2O, c): CH_3CN.

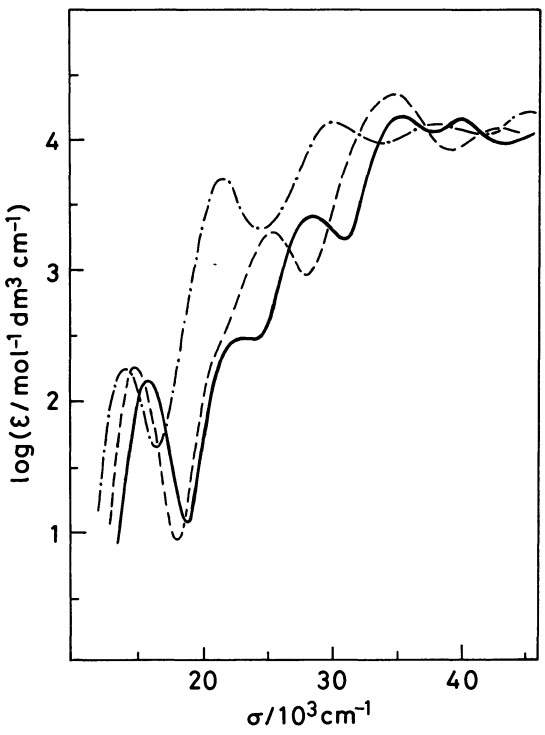

Fig. 2. Absorption spectra of *trans*(*X*,*X*),*cis*(*As*,*As*)-$[CoX_2(edma)_2]^+$ in methanol, X=Cl (——), X=Br (----), and X=I (-·-·-).

$[Co(CO_3)(edma)_2]^+$ with HX under cooling (0 °C). The *cis*(*X*,*X*) isomers of edmp and related (aminoalkyl) phosphine complexes are not known either, while *cis*(*X*,*X*)-$[CoX_2\{(CH_3)_2E(CH_2)_nE(CH_3)_2\}_2]^+$ (n=2, 3. X=Cl, Br. E=P,[13] As[6]) can be prepared from the carbonato complexes by similar procedures. A red aqueous solution of $[Co(CO_3)(edma)_2]^+$ changed to violet and then green fairly rapidly on addition of HX at 0 °C, and gave a green precipitate of the trans dihalogeno complex. The rapid color change from violet to green indicates rapid cis to trans isomerization of the dihalogeno complex.

The $[Co(CO_3)(edma)_2]^+$ complex yielded only one of three possible geometrical isomers, *trans*(*As*, *As*) (C_2 symmetry), *trans*(*As*, *N*) (C_1 symmetry) and *trans*(*N*, *N*) (C_2 symmetry), by the reaction of $[CoCl_2(edma)_2]^+$ with Na_2CO_3. The complex exhibits four kinds of methyl signal in the ^1H NMR spectrum and is clearly assigned to the *trans*(*As*, *N*) isomer from symmetry argument. For the corresponding acac complex, two isomers were obtained by a similar reaction with Li(acac). The isomers are red and dark red in color. The red isomer shows six kinds of methyl signal in the ^1H NMR spectrum and is assigned unequivocally to the *trans*(*As*, *N*) isomer. On the other hand, the dark red isomer gives three kinds of methyl signal, but the structure can not be assigned from the spectrum, since both *trans*(*As*, *As*) and *trans*(*N*, *N*) isomers have a C_2 axis. An analogous phosphine complex, $[Co(acac)\{(C_6H_5)_2PCH_2CH_2NH_2\}_2]^{2+}$ also yields two isomers.[4]

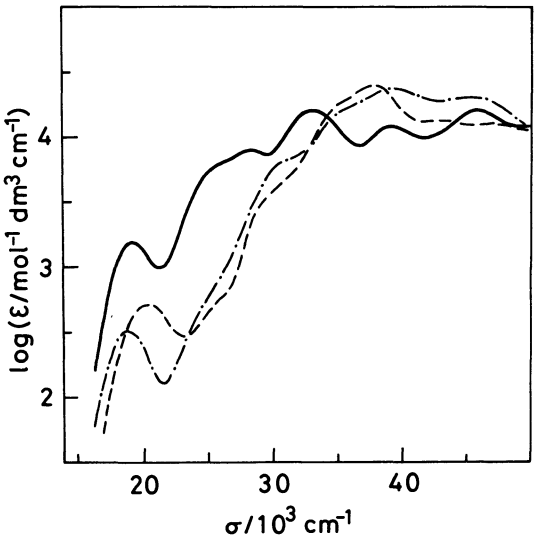

Fig. 3. Absorption spectra of $[Co(acac)_2(edma)]^+$ (-·-·-), *trans*(*As*,*As*)-$[Co(acac)(edma)_2]^{2+}$ (——), and *trans*(*As*,*N*)-$[Co(acac)(edma)_2]^{2+}$ (----) in water.

They were assigned to the *trans*(*P*, *P*) and *trans*(*P*, *N*) isomers on the basis of the coupling constant values between proton or carbon and phosphorus in ^1H and ^{13}C NMR spectra. The isomers of the phosphine complex exhibit absorption spectra quite different from each other; the *trans*(*P*, *P*) isomer shows the first d-d band of strong intensity and a remarkable red shift of charge transfer bands as compared with the corresponding bands of the *trans*(*P*, *N*) isomer. A similar spectral difference is seen between the two isomers of $[Co(acac)(edma)_2]^{2+}$ (Fig. 3). Thus the dark red isomer can be assigned to the *trans*(*As*, *As*) one.

Molecular models indicate that the steric crowding caused by the bulky dimethylarsino group in the three isomers of $[Co(acac)(edma)_2]^{2+}$ increases in the order *trans*(*As*, *As*)<*trans*(*As*, *N*)<*trans*(*N*, *N*). The reason for the *trans*(*N*, *N*) isomer being not formed will be attributable to the most crowded structure. For other two isomers, the more crowded *trans*(*As*,*N*) isomer was formed in a larger amount than the less crowded *trans*(*As*, *As*) isomer. The formation ratio of the dark red *trans*(*As*, *As*) isomer to the red *trans*(*As*, *N*) one was found to be 1:2 by column chromatography of the reaction products. The smaller abundance (less stability) of the less crowded *trans*(*As*, *As*) isomer may be attributable to the trans effect of the arsine donor group. For $[Co(acac)\{(C_6H_5)_2PCH_2CH_2NH_2\}_2]^{2+}$, the formation ratio of the *trans*(*P*, *P*) isomer to the *trans*(*P*, *N*) one is reported to be 1:4.[4] The same reason may be given for the selective formation of more crowded *trans*(*Cl*,*Cl*), *cis*(*As*,*As*)-$[CoCl_2(edma)_2]^+$ than its *trans*-(*Cl*,*Cl*), *trans*(*As*,*As*) isomer.

The violet $[Co(acac)_2(edma)]^+$ complex was obtained by the reaction of $[Co(acac)_3]$ with edma in the presence of active charcoal or as a by-product in the synthesis of $[Co(acac)(edma)_2]^{2+}$. The absorption

spectrum is compared with those of $[Co(acac)(edma)_2]^{2+}$ in Fig. 3.

The reaction of $Na_3[Co(CO_3)_3]$ with edma yielded only one isomer of $[Co(edma)_3]^{3+}$. The isomer showed two kinds of sharp methyl signal in the ^1H NMR spectrum and was assigned to the *fac*-isomer. The phosphorus analog, $[Co(edmp)_3]^{3+}$ also forms only the *fac*-isomer. The selective formation of the *fac*-isomer in these complexes may also be attributable to the trans effect of the arsine or phosphine donor group. The complex was easily resolved on an SP-Sephadex column by elution with an aqueous solution of $Na_2[Sb_2\{(+)\text{-tartrate}\}_2]$. The optically active complex is stable in acidic water but racemizes in basic water (vide infra).

Figure 4 compares the absorption spectrum of *fac*-$[Co(edma)_3]^{3+}$ with those of *fac*-$[Co(edmp)_3]^{3+}$ and

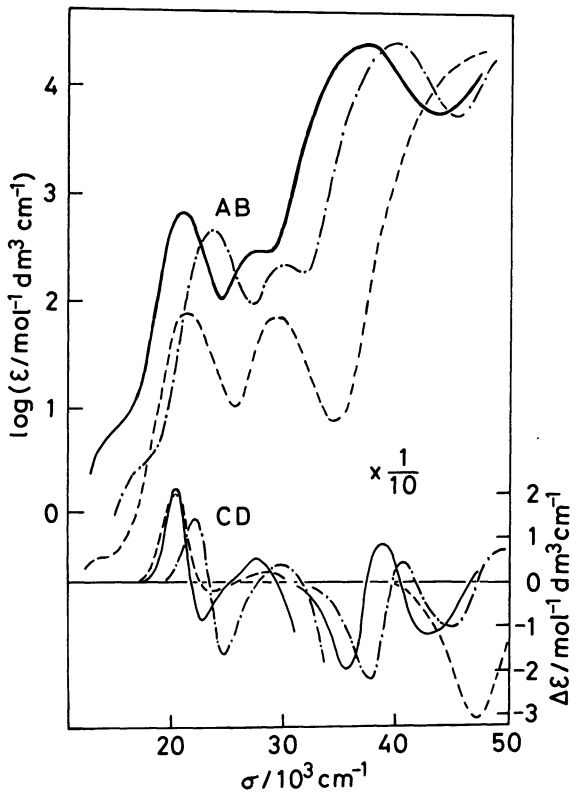

Fig. 4. Absorption and CD spectra of *Λ*-*fac*-$[Co(edma)_3]^{3+}$ (——), *Λ*-*fac*-$[Co(edmp)_3]^{3+}$ (-·-·-), and *Λ*-$[Co(en)_3]^{3+}$ (----) in water.

$[Co(en)_3]^{3+}$, and the data are listed in Table 2. The first absorption band of *fac*-$[Co(edma)_3]^{3+}$ is observed at 21300 cm^{-1}. The energy is almost the same as that of $[Co(en)_3]^{3+}$ (21400 cm^{-1})[14] and much lower than that of *fac*-$[Co(edmp)_3]^{3+}$ (23700 cm^{-1}).[1] The tris-type complex of $(CH_3)_2NCH_2CH_2NH_2$ (Me_2-en) corresponding to edma and edmp is not known. Attempts to prepare $[Co(Me_2\text{-en})_3]^{3+}$ were unsuccessful and bis-diamine complexes such as $[Co(H_2O)_2(Me_2\text{-en})_2]^{3+}$ were yielded even in the presence of a large excess of Me_2-en. However, it is known that cobalt(III) complexes containing Me_2-en exhibit the first d–d band at fairly lower energy than that of the corresponding en complex.[15] For example, the bands of $[Co(acac)_2(Me_2\text{-en})]^+$ and $[Co(acac)_2(en)]^+$ are at 17800 and 18450 cm^{-1}, respectively.[16] Thus it is concluded that the spectrochemical series for the three ligands with donors of the grounp 5B elements is edmp(P)>edma(As)>Me_2-en(N). Besides the first d–d band, *fac*-$[Co(edma)_3]^{3+}$ shows a weak, broad triplet d–d band around 14600 cm^{-1}, the second d–d band at 28000 cm^{-1} and the As to Co(III) charge-transfer band at 37700 cm^{-1}. All these bands are shifted to lower energy by ca. 2000 cm^{-1} than the corresponding bands of *fac*-$[Co(edmp)_3]^{3+}$, but both spectral patterns are very similar. The energy difference between the first and second d–d bands of *fac*-$[Co(edma)_3]^{3+}$ is 6700 cm^{-1}. The value is similar to that of *fac*-$[Co(edmp)_3]^{3+}$ (6500 cm^{-1}) but much smaller than that of $[Co(en)_3]^{3+}$(8100 cm^{-1}). Thus the interelectronic repulsion of the cobalt(III) ion is largely reduced in the edma and edmp complexes. Such large reduction has been reported for other phosphine[1] and arsine complexes[6] of cobalt(III).

Figure 4 shows the CD spectrum of $(+)^{CD}_{490}$-*fac*-$[Co(edma)_3]^{3+}$ togehter with those of *Λ*-*fac*-$[Co(edmp)_3]^{3+}$ [1] and *Λ*-$[Co(en)_3]^{3+}$.[14,17] The $(+)^{CD}_{490}$-$[Co(edma)_3]^{3+}$ isomer gives a similar CD pattern in the first d–d band region to those of other two complexes and can be assigned to the same *Λ* isomer. These isomers are all eluted faster than their antipodes on SP-Sephadex column chromatography by elution with $Na_2[Sb_2\{(+)\text{-tartrate}\}_2]$. In previous papers,[1,18] we reported that the small negative CD component in the first d–d band region of *Λ*-$[Co(en)_3]^{3+}$ is enhanced by replacing en by edmp or $(CH_3)_2PCH_2CH_2P(CH_3)_2$. The strength of the negative CD component of the edma complex is intermedi-

Table 2. Absorption and CD Spectral Data of Tris(chelate)cobalt(III) Complexes in Water

Complex	Absorption $\sigma_{max}/10^3$ cm^{-1} ($\log(\varepsilon/cm^{-1}\ mol^{-1}\ dm^3)$)	CD $\sigma_{ext}/10^3$ cm^{-1} ($\log(\Delta\varepsilon/cm^{-1}\ mol^{-1}\ dm^3)$)
Λ-*fac*-$[Co(edma)_3]^{3+}$	14.6 (sh, 0.67), 21.3 (2.82), 28.0 (2.50), 37.7 (4.43)	20.4 (+2.06), 22.7 (−0.87), 27.6 (+0.55), 35.8 (−19.2), 38.9 (+8.76), 42.7 (−11.7)
Λ-*fac*-$[Co(edmp)_3]^{3+}$ [a]	16.7 (sh, 0.43), 23.7 (2.68), 30.2 (2.36), 39.9 (4.42)	22.3 (+1.54), 24.8 (−1.57), 30.0 (+0.49), 37.9 (−20.6), 41.0 (+4.74), 45.5 (−9.33)
Λ-$[Co(en)_3]^{3+}$ [b]	21.4 (1.97), 29.5 (1.93), 47.1 (4.36)	20.3 (+1.89), 23.4 (−0.16), 28.5 (+0.25), 47.4 (−31)

a) From Ref. 1. b) From Ref. 14.

ate between those of the edmp and en complexes. In the ultraviolet region, both edma and edmp complexes exhibit a negative and a positive CD band from the lower to higher energy side corresponding to each charge-transfer band between the arsine (37700 cm^{-1}), the phosphine (39900 cm^{-1}) or the amine donor group (ca. 50000 cm^{-1}) and the cobalt(III) ion. These CD patterns are also known to be characteristic of *Λ*-[Co(diamine)$_3$]-type complex.[14,19]

Racemization of *fac*-[Co(edma)$_3$]$^{3+}$. Racemization of *fac*-[Co(edma)$_3$]$^{3+}$ was studied in aqueous solutions in the pH and temperature ranges of 7.88—9.32 and 35.0—50.0 °C, respectively. Figure 5 shows a representative CD spectral change of *Λ*-[Co(edma)$_3$]$^{3+}$ in a sodium 5,5-diethylbarbiturate ($NaC_3H_{11}N_2O_3$)–HCl buffer solution (pH: 8.36) at 40 °C in a period of 4225 min. In each kinetic run the plot of $\ln(\Delta\varepsilon_t(492\ nm))$ vs. time at a constant pH gave a straight line for at least three half-lives. Thus the rate of racemization at a constant pH can be expressed as $-d[complex]/dt = k_{obsd}$ [complex], where k_{obsd} is the pseudo-first-order rate constant for racemization at a constant pH. The $k_{obsd}/[OH^-]$ ($=k$) values are constant at a given temperature, indicating that the reaction is first order in $[OH^-]$. The values of k_{obsd} and k are listed in Table 3, where the variation of ionic product of water $k_W=[H^+][OH^-]$ with a change in temperature[20] was taken into consideration. From the temperature dependence of k values, the activation enthalpy and entropy were obtained as 132±4 kJ mol^{-1} and 171± 11 J K^{-1} mol^{-1}, respectively. No detectable change in absorption spectrum was observed during the racemization.

The mechanism for racemization of *fac*-[Co(edma)$_3$]$^{3+}$ is not clear at present. The fact that the racemization is catalyzed by OH^- indicates that the first step of the racemization is deprotonation of the amine hydrogen(s). For the present complex a dissociative mechanism involving the rupture of the Co–As bond will be ruled out, since the absorption spectrum of the complex remained unchanged during the racemization; if the arsine part of edma were released from the cobalt(III) ion the ligand would be oxidized by atmospheric oxygen to cause the decomposition of the complex.

The values of activation parameters for racemization

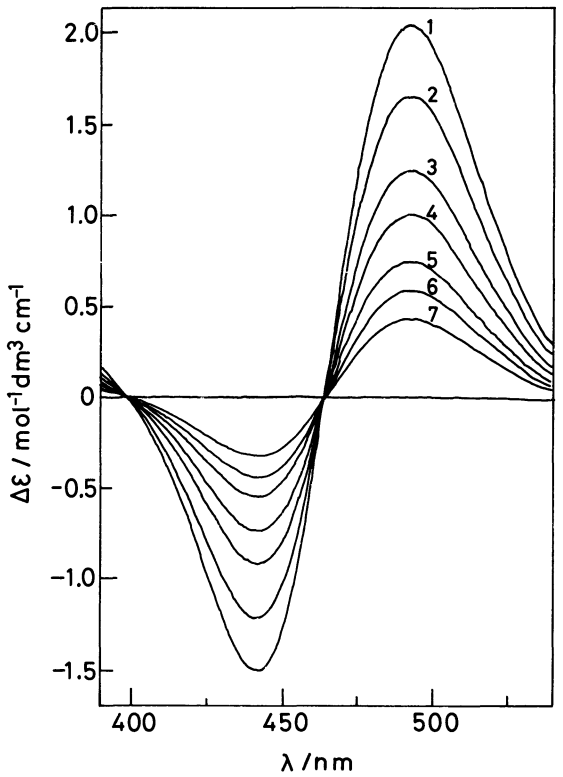

Fig. 5. Change in CD spectrum of *Λ*-*fac*-[Co(edma)$_3$]$^{3+}$ in water at pH 8.36 and 40.0 °C. Spectra 1—7 were measured after 0, 585, 1360, 1960, 2755, 3385, 4225 min, respectively.

Table 3. Racemization Rates of *fac*-[Co(edma)$_3$]$^{3+}$

t / °C	pH	k_{obsd} / 10^{-6} s^{-1}	k / mol^{-1} dm^3 s^{-1}	k (av.) / mol^{-1} dm^3 s^{-1}
50.0	8.39	26.7	1.98	
	8.19	17.3	2.04	2.16 ±0.19
	8.06	13.8	2.20	
	7.88	10.0	2.41	
45.0	8.83	26.3	0.968	
	8.70	19.3	0.958	0.973±0.017
	8.48	12.1	0.997	
	8.32	8.12	0.967	
40.0	8.89	10.6	0.468	
	8.75	7.60	0.463	0.481±0.018
	8.52	4.76	0.493	
	8.39	3.58	0.499	
35.0	9.32	8.10	0.186	
	9.12	3.73	0.171	0.181±0.007
	8.87	2.77	0.179	
	8.68	1.90	0.186	

of *fac*-$[Co(edma)_3]^{3+}$ are similar to those ($\Delta H^{\ddagger}=132\pm6$ kJ mol^{-1}, $\Delta S^{\ddagger}=204\pm18$ J K^{-1} mol^{-1}) reported for racemization of $[Co(stn)]^{3+}$ (stn=$CH_3C(CH_2NHCH_2CH_2CH_2NH_2)_3$), which is also catalyzed by OH^-.[21] For this racemization, a twist intramolecular mechanism via a trigonal twist about the threefold axis of the deprotonated intermediate was proposed. A similar twist mechanism may be assumed for the racemization of *fac*-$[Co(edma)_3]^{3+}$, although it is unknown whether the rupture of the Co–N bond is involved or not.

The *fac*-$[Co(edmp)_3]^{3+}$ complex was stable to racemization in acidic water, but decomposed in basic water to give a blue-white precipitate which was supposed to be cobalt(III) species. The decomposition rate observed by a decrease in intensity of the first d–d band was nearly the same as the diminishing rate of the CD strength. The decomposition of the complex is supposed to take place in preference to the racemization. On the other hand, it is known that $[Co(en)_3]^{3+}$ in water does not racemize and does in the presence of excess en[22] or active charcoal.[23] Such different properties in racemization of three typical complexes, $[Co(en)_3]^{3+}$, *fac*-$[Co(edmp)_3]^{3+}$, and *fac*-$[Co(edma)_3]^{3+}$ will provide useful information in elucidating bonding character between cobalt(III) and 5B group donor atoms.

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