October, 1985] Bull. Chem. Soc. Jpn., 58, 3003—3009 (1985)

Preparation and Characterization of Cobalt(III) Complexes Containing $(CH_3)_2As(CH_2)_nAs(CH_3)_2$ (n=2, 3)

Katsumi Iwata, Masaaki Kojima, and Junnosuke Fujita*
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

(Received June 12, 1985)

Twelve new complexes, *trans*-$[CoX_2(dmae\ or\ dmap)_2]^+$ (X=Cl, Br, I; dmae=1,2-bis(dimethylarsino)ethane, dmap=1,3-bis(dimethylarsino)propane), *cis*-$[CoX_2(dmap)_2]^+$ (X=Cl, Br), $[Co(CO_3)(dmae\ or\ dmap)_2]^+$, and $[Co(acac)_{3-n}(dmap)_n]^{n+}$($n$=0, 1, 2; acac=2,4-pentanedionate ion) were prepared and characterized. From a comparison of the $^1A_{1g}\rightarrow{}^1E_g$ (D_{4h}) d-d absorption bands of analogous *trans*-dichloro complexes of phosphines and amines, the order of spectrochemical series for the group 5B elements was suggested to be P > As > N. Largely reduced interelectronic repulsions between the crystal field levels were observed for the carbonato complexes. Isomerization of *cis*-$[CoCl_2(dmap)_2]^+$ to the trans isomer was studied in methanol in the temperature range of 20.1—49.9 °C. The rate has a first-order dependence on the complex concentration. The rate constant at 54.9 °C, calculated from the $\Delta H^{\neq}$ (115.2 kJ mol^{-1}) and $\Delta S^{\neq}$ (53.8 J mol^{-1} K^{-1}) values, is 10^3 times as large as that reported for *cis*-$[CoCl_2(diars)_2]^+$ (diars=*o*-phenylenebis(dimethylarsine)) at the same temperature.

According to Pearson's HSAB model,[1] a cobalt(III) ion which belongs to a hard acid prefers a hard base such as ammonia or water to a soft base such as arsine ligands in complex formation. However, several arsine ligands such as *o*-phenylenebis(dimethylarsine) (diars)[2–6] and *cis*-bis(dimethylarsino)ethylene[7] have been reported to form stable cobalt(III) complexes. All the cobalt(III)-arsine complexes reported so far involve an unsaturated group which shows strong absorption bands in the ultraviolet region and sometimes makes band assignments of the complexes difficult.

In this paper we report the preparation and absorption spectra of cobalt(III) complexes containing a saturated arsine chelate, 1,2-bis(dimethylarsino)ethane (dmae) and 1,3-bis(dimethylarsino)propane (dmap). The paper also describes isomerization of *cis*-$[CoCl_2(dmap)_2]^+$ to the trans isomer in methanol.

Experimental

The arsine ligands, dmae and dmap were handled under a nitrogen atmosphere until they formed air-stable cobalt(III) complexes. Tetrahydrofuran was dried with sodium and deoxygenated by distillation in a stream of nitrogen.

1,2-Bis(dimethylarsino)ethane, dmae. This compound was prepared by the method of Sommer[8] from $(CH_3)_2AsSAs(CH_3)_2$, metallic sodium, and 1,2-dibromoethane in liquid ammonia. Yield: *ca.* 2%. The compound was not purified by fractional distillation because of the very low yield. Tetramethyldiarsine which was the most abundant by-product was removed by evaporation under reduced pressure, and the residue was used to prepare *trans*-$[CoCl_2(dmae)_2]ClO_4$ (*vide infra*).

1,3-Bis(dimethylarsino)propane, dmap. This compound was prepared by the method of Sommer[8] with a slight modification. A tetrahydrofuran solution (500 cm^3) of sodium dimethylarsenide (0.2 mol) was prepared by the method of Phillips and Vis[9] from sodium (10.3 g, 0.45 mol) and iododimethylarsine[10] (47.9 g, 0.207 mol). To this solution was added 1,3-dibromopropane (21.0 g, 0.104 mol) at 0 °C with stirring. Water (50 cm^3) was added to the resulting white suspension, and then tetrahydrofuran was evaporated under reduced pressure. The residue was shaken with diethyl ether to extract the diarsine. The ethereal layer was separated and dried with anhydrous calcium chloride. The desiccant was filtered off, the ether evaporated, and the residue was distilled at 86—90 °C and 2670 Pa to give a colorless liquid. Yield: 11.3 g (43%). ^{1}H NMR ($CDCl_3$) δ=0.93 (12H, s, $AsCH_3$), 1.26 (2H, m, β-CH_2), and 1.55 (4H, t, $AsCH_2$).

trans-*$[CoCl_2(dmae)_2]ClO_4$.* To an ethanol solution (20 cm^3) of $CoCl_2\cdot 6H_2O$ (0.96 g, 4.0 mmol) was added an ethanol solution (10 cm^3) of dmae prepared from 13.4 g of $(CH_3)_2AsSAs(CH_3)_2$ and 10.5 g of $BrCH_2CH_2Br$ in the manner described above. Air was bubbled through the resulting green solution for 90 min, and then 1 mol dm^{-3} HCl (27 cm^3) was added, a dark green solution being yielded. The ethanol was evaporated under reduced pressure and to the concentrate was added $NaClO_4$ (0.42 g). A green solid which precipitated was collected by filtration, washed successively with 1 mol dm^{-3} $HClO_4$, methanol, ethanol, methanol–diethyl ether (1:10), and diethyl ether, and dried *in vacuo*. Yield: 0.39 g. Found: C, 20.73; H, 4.42%. Calcd for $C_{12}H_{32}As_4Cl_3CoO_4$: C, 20.43; H, 4.57%. ^{1}H NMR (CD_2Cl_2) δ=1.63 (24H, s, $AsCH_3$) and 2.43 (8H, s, $AsCH_2$). The complex is soluble in water and ethanol.

trans-*$[CoBr_2(dmae)_2]ClO_4$.* This complex was prepared from *trans*-$[CoCl_2(dmae)_2]ClO_4$ and KBr by metathesis. To a methanol solution (10 cm^3) of *trans*-$[CoCl_2(dmae)_2]ClO_4$ (0.100 g, 0.14 mmol) was added an aqueous solution (5 cm^3) of KBr (1.0 g, 8 mmol). The mixture was stirred overnight at 40 °C, and then evaporated to dryness under reduced pressure. The residue was extracted with dichloromethane (10 cm^3). The extract was mixed successively with methanol (10 cm^3), water (3 cm^3), and 70% $HClO_4$ (0.5 cm^3), and the solvent was evaporated slowly at room temperature to give a yellow-green precipitate. The product seemed to be impure, since the ^{1}H NMR spectrum in CD_2Cl_2 showed two singlets attributable to the As-methyl protons at 1.73 and 2.09 ppm. The pure complex was obtained by repeated recrystallization from dichloromethane–methanol–70% $HClO_4$ by the method as above until the signal at 2.09 ppm disappeared completely. Yield: 0.06 g (53%). Found: C, 18.63; H, 4.10%. Calcd for $C_{12}H_{32}As_4Br_2ClCoO_4$: C, 18.15; H, 4.06%. ^{1}H NMR (CD_2Cl_2) δ=1.73 (24H, s, $AsCH_3$) and 2.46 (8H, s, $AsCH_2$).

trans-*$[CoI_2(dmae)_2]ClO_4$.* This complex was prepared from *trans*-$[CoCl_2(dmae)_2]ClO_4$ and NaI by metathesis. To an ethanol solution (10 cm^3) of *trans*-$[CoCl_2(dmae)_2]ClO_4$ (0.053 g, 0.075 mmol) was added an excess of NaI (0.35 g, 2.3 mmol), the color of the solution changing from green to brown. The solution was refluxed for 10 min, and to the resulting reddish brown solution was added an aqueous solution (5 cm^3) of $NaClO_4$ (0.50 g). The mixture was evaporated to *ca.* 5 cm^3 to yield reddish brown plates or needles, which were collected by filtration, washed successively with water, ethanol–diethyl ether (1:5), and diethyl ether. Yield: 0.050 g (75%). Found: C, 16.43; H, 3.55%. Calcd for $C_{12}H_{32}As_4ClCoI_2O_4$: C, 16.22; H, 3.63%. ^1H NMR (CD_3CN) δ=1.99 (24H, s, $AsCH_3$) and 2.51 (8H, s, $AsCH_2$).

$[Co(CO_3)(dmae)_2]ClO_4\cdot 2NaClO_4$. To a hot methanol solution (3 cm^3) of *trans*-$[CoCl_2(dmae)_2]ClO_4$ (0.223 g, 0.31 mmol) were added Li_2CO_3 (0.20 g, 2.7 mmol) and water (5 cm^3). The mixture was heated on a water-bath for 15 min, and then allowed to cool to room temperature. The resulting orange reaction mixture was filtered to remove remaining *trans*-$[CoCl_2(dmae)_2]ClO_4$ and Li_2CO_3. The filtrate was mixed with a saturated aqueous solution (2 cm^3) of $NaClO_4$, and the volume of the solution was reduced to *ca.* 5 cm^3 under reduced pressure. The concentrate was stored in a refrigerator to give an orange precipitate. The precipitate was collected by filtration, extracted with methanol, and the extract was mixed with a saturated aqueous solution (2 cm^3) of $NaClO_4$. By evaporating the methanol, the desired complex was obtained as orange plates. They were collected by filtration, washed with methanol–diethyl ether (1:5) and then diethyl ether. Yield: 0.107 g (36%). Found: C, 16.65; H, 3.43%. Calcd for $C_{13}H_{32}As_4Cl_3CoNa_2O_{15}$: C, 16.62; H, 3.43%. ^1H NMR (D_2O) δ=1.46 (6H, s, $AsCH_3$), 1.51 (6H, s, $AsCH_3$), 1.57 (6H, s, $AsCH_3$), 1.89 (6H, s, $AsCH_3$), and 2.3—2.7 (8H, m, $-CH_2-$).

trans-*$[CoCl_2(dmap)_2]Cl\cdot H_2O$.* To an ethanol solution (20 cm^3) of $CoCl_2\cdot 6H_2O$ (1.23 g, 5.2 mmol) was added an ethanol solution (10 cm^3) of dmap (2.6 g, 10.3 mmol). The color of the solution changed from blue to dark green and a precipitate was formed. By adding concd HCl (4 cm^3) the precipitate was dissolved. Air was bubbled through the solution for 1 h, and then water (40 cm^3) was added. The ethanol was evaporated under reduced pressure to give a green precipitate. After cooling the mixture overnight in a refrigerator, the precipitate was collected by filtration and washed successively with 1 mol dm^{-3} HCl, ethanol–diethyl ether (1:10), and diethyl ether. Yield: 3.0 g (84%). Found: C, 24.13; H, 5.51%. Calcd for $C_{14}H_{38}As_4Cl_3CoO$: C, 24.46; H, 5.57%. The presence of water of crystallization was suggested from the IR spectrum. The complex is soluble in water, ethanol, acetonitrile, and dichloromethane.

trans-*$[CoCl_2(dmap)_2]ClO_4$.* This complex was obtained by adding 70% $HClO_4$ (0.1 cm^3) to a methanol solution (5 cm^3) of the chloride (0.30 g, 0.44 mmol). Diethyl ether (15 cm^3) was added to ensure the precipitation of the perchlorate. The green precipitate was collected by filtration and washed successively with 1 mol dm^{-3} $HClO_4$, methanol–diethyl ether (1:3), and diethyl ether. Yield: 0.30 g (94%). Found: C, 22.96; H, 4.95%. Calcd for $C_{14}H_{36}As_4Cl_3CoO_4$: C, 22.93; H, 4.95%. ^1H NMR (CD_2Cl_2) δ=1.52 (24H, s, $AsCH_3$) and 1.9—2.9 (12H, m, $-CH_2-$). The complex is soluble in ethanol, acetonitrile, and dichloromethane, but insoluble in water.

trans-*$[CoBr_2(dmap)_2]ClO_4$.* To an ethanol solution (10 cm^3) of $CoBr_2\cdot 6H_2O$ (0.23 g, 0.70 mmol) were added an ethanol solution (5 cm^3) of dmap (0.35 g, 1.4 mmol), and concd HBr (1 cm^3). Air was bubbled into the solution for 30 min, and then 5 mol dm^{-3} $HClO_4$ (5 cm^3) was added. Yellow-green flocculent crystals formed were collected by filtration and washed succesively with 1 mol dm^{-3} $HClO_4$, cold methanol, and diethyl ether. Yield: 0.51 g (90%). Found: C, 20.49; H, 4.46%. Calcd for $C_{14}H_{36}As_4Br_2ClCoO_4$: C, 20.45; H, 4.41%. ^1H NMR (CD_2Cl_2) δ=1.62 (24H, s, $AsCH_3$) and 2.0—2.6 (12H, m, $-CH_2-$).

$[Co(CO_3)(dmap)_2]ClO_4\cdot 2NaClO_4\cdot CH_3OH$. This complex was prepared by a method similar to that for $[Co(CO_3)(dmae)_2]ClO_4\cdot 2NaClO_4$. To a hot methanol solution (3 cm^3) of *trans*-$[CoCl_2(dmap)_2]Cl\cdot H_2O$ (0.47 g, 0.68 mmol) were added Li_2CO_3 (0.20 g, 2.7 mmol) and water (3 cm^3). The mixture was heated on a water-bath for 15 min, the color of the solution changing from green to dark red. The methanol was removed under reduced pressure at 40 °C, and to the concentrate was added a saturated aqueous solution (1 cm^3) of $NaClO_4$. The mixture was cooled at 0 °C, mixed with 5 mol dm^{-3} $HClO_4$ in order to decompose residual Li_2CO_3, and then filtered to remove remaining *trans*-$[CoCl_2(dmap)_2]ClO_4$. To the concentrate was added dichloromethane (5 cm^3), and the mixture was stirred for a while to form a red precipitate. A saturated solution (5 cm^3) of $NaClO_4$ was added, and the mixture was allowed to stand at 5 °C overnight. The red precipitate was collected by filtration and washed successively with cold water, cold methanol, dichloromethane, and diethyl ether. Yield: 0.21 g (31%). Found: C, 19.22; H, 4.03%. Calcd for $C_{16}H_{40}As_4CoCl_3Na_2O_{16}$: C, 19.18; H, 4.06%. The presence of 1 mol of methanol of crystallization was confirmed by the ^1H NMR spectrum. The complex is soluble in water, methanol, and acetonitrile, but insoluble in dichloromethane.

cis-*$[CoCl_2(dmap)_2]ClO_4$.* To a cold (*ca.* 0 °C), stirred suspension of the carbonato complex (0.50 g, 0.50 mmol) in water (10 cm^3) was added dropwise cold (*ca.* 0 °C) 6 mol dm^{-3} HCl (20 cm^3). The resulting purple solution was filtered, to the filtrate was added $NaClO_4$ (5 g), and the mixture was stored in a refrigerator for 3 h. Purple crystals which precipitated were collected by filtration and washed successively with water, ethanol, dichloromethane–diethyl ether (1:1), and diethyl ether. Yield: 0.32 g (87%). Found: C, 22.95; H, 4.89%. Calcd for $C_{14}H_{36}As_4Cl_3CoO_4$: C, 22.93; H, 4.95%. ^1H NMR (CD_2Cl_2) δ=1.48 (6H, s, $AsCH_3$), 1.56 (6H, s, $AsCH_3$), 1.59 (6H, s, $AsCH_3$), 1.66 (6H, s, $AsCH_3$), and 1.9—2.5 (12H, m, $-CH_2-$). The complex was not recrystallized, since it is liable to isomerization in solution to give the trans isomer (*vide infra*). However, the ^1H NMR spectrum of the complex prepared as above shows no signal attributable to the trans isomer.

cis-*$[CoBr_2(dmap)_2]ClO_4$.* This complex was obtained as dark violet crystals from the carbonato complex by a method similar to that for the corresponding dichloro complex using HBr instead of HCl. Yield: 68%. Found: C, 20.48; H, 4.48%. Calcd for $C_{14}H_{36}As_4Br_2ClCoO_4$: C, 20.46; H, 4.41%. ^1H NMR (CD_2Cl_2) δ=1.54 (6H, s, $AsCH_3$), 1.62 (6H, s, $AsCH_3$), 1.65 (6H, s, $AsCH_3$), 1.88 (6H, s, $AsCH_3$), and 2.0—2.5 (12H, m, $-CH_2-$).

trans-*$[CoI_2(dmap)_2]ClO_4$.* To a solution (12 cm^3) of the carbonato complex (0.10 g, 0.10 mmol) in water–acetonitrile (1:5) were added NaI (0.30 g, 2 mmol) and 5 mol dm^{-3} $HClO_4$ (4 cm^3). The mixture was stirred for 30 min, and then evaporated to a small volume under reduced pressure to form dark red plates. They were collected by filtration, washed successively with water, cold methanol, and diethyl ether, and dried *in vacuo*. Yield: 0.083 g (91%). Found: C, 18.41; H, 3.99%. Calcd for $C_{14}H_{36}As_4ClCoI_2O_4$: C, 18.35; H, 3.96%.

^{1}H NMR (CD_2Cl_2) δ=1.80 (24H, s, $AsCH_3$) and 2.0—2.5 (12H, m, $-CH_2-$). This complex is soluble in dichloromethane and acetonitrile, but insoluble in ethanol and water.

$[Co(acac)(dmap)_2](ClO_4)_2\cdot H_2O$ (acac=2,4-pentanedionate ion). To a warm solution (5 cm^3) of *trans*-$[CoCl_2(dmap)_2]ClO_4$ (0.21 g, 0.29 mmol) in methanol was added an aqueous solution (10 cm^3) of lithium 2,4-pentanedionate (0.05 g, 0.47 mmol). The mixture was heated at 70 °C for 3 h. The resulting red solution was diluted with water (100 cm^3) and applied on a column (ϕ4.5 cm×22 cm) of SP-Sephadex C-25 (Na^+ form). On elution with 0.1 mol dm^{-3} $NaClO_4$, three bands developed; purple ($[Co(acac)_2(dmap)]^+$, small amount), yellow-green (*trans*-$[CoCl_2(dmap)_2]^+$, small amount), and red ($[Co(acac)(dmap)_2]^{2+}$, large amount) in the order of elution. The eluate containing the slowest-moving red band was collected and evaporated to *ca.* 20 cm^3 under reduced pressure. The concentrate was stored in a refrigerator to form a red precipitate. It was collected by filtration and washed successively with cold 1 mol dm^{-3} $HClO_4$, methanol–diethyl ether (1:3), and diethyl ether. Yield: 0.14 g (57%). Found: C, 25.57; H, 4.85%. Calcd for $C_{19}H_{45}As_4Cl_2CoO_{11}$: C, 25.96; H, 5.16%. ^{1}H NMR (CD_3NO_2) δ=1.56 (6H, s, $AsCH_3$), 1.60 (12H, s, $AsCH_3$), 1.69 (6H, s, $AsCH_3$), 1.9—2.5 (12H, m, $-CH_2-$), 2.19 (6H, s, CCH_3), and 5.89 (1H, s, $\underset{\cdot\cdot}{-}CH\underset{\cdot\cdot}{-}$). ^{13}C NMR ($CD_3NO_2$) δ=7.3 (q), 7.5 (q), 10.2 (q), 13.8 (q), 21.2 (t), 27.1 (q), 27.7 (t), 27.8 (t), and 102.3 (d). The complex is soluble in water and methanol, and slightly soluble in ethanol.

$[Co(acac)_2(dmap)]ClO_4$. To a methanol solution (10 cm^3) of $[Co(acac)_3]$ (0.50 g, 1.4 mmol) were added an ethanol solution (10 cm^3) of dmap (0.10 g, 0.4 mmol) and active charcoal (0.10 g). The mixture was stirred for 2 d at room temperature and then filtered. The purple filtrate was diluted with water (20 cm^3), and the unreacted arsine ligand was extracted with petroleum ether. The aqueous phase was diluted with water (100 cm^3) and applied on a column (ϕ4.5 cm×10 cm) of SP-Sephadex C-25 (Na^+ form). The column was washed with water to remove remaining $[Co(acac)_3]$. By elution with 0.05 mol dm^{-3} NaCl, a purple ($[Co(acac)_2(dmap)]^+$) and a red (a mixture of $[Co(acac)(dmap)_2]^{2+}$ and $[Co(H_2O)_6]^{2+}$) band developed in this order. The eluate containing the main purple band was collected and evaporated to a small volume under reduced pressure. To the concentrate was added $NaClO_4$ (0.2 g), and the complex was extracted with dichloromethane. The extract was washed with water, and mixed with a small amount of ethanol. The mixture was evaporated to a small volume, and to the concentrate was added diethyl ether. A purple precipitate was collected by filtration and washed successively with water, methanol–diethyl ether (1:5), and diethyl ether. Yield: 0.22 g (92%). Found: C, 33.57; H, 5.41%. Calcd for $C_{17}H_{32}As_2ClCoO_8$: C, 33.55; H, 5.30%. ^{1}H NMR (CD_2Cl_2) δ=1.23 (6H, s, $AsCH_3$), 1.43 (6H, s, $AsCH_3$), 1.7—2.2 (m, $-CH_2-$), 1.84 (6H, s, CCH_3), 2.19 (6H, s, CCH_3), and 5.48 (2H, s, $\underset{\cdot\cdot}{-}CH\underset{\cdot\cdot}{-}$). ^{13}C NMR ($CD_2Cl_2$) δ=4.9 (q), 5.6 (q), 20.6 (t), 22.9 (t), 26.6 (q), 27.3 (q), and 98.9 (d). The complex is soluble in ethanol and dichloromethane, but insoluble in water.

Measurements. Absorption spectra were obtained using a Hitachi 323 or a JASCO 610B spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL PMX-60 or a JEOL FX 100 spectrometer, and ^{13}C NMR spectra on a JEOL FX 100 spectrometer.

Kinetics. Rates of isomerization of *cis*-$[CoCl_2(dmap)_2]ClO_4$ to the trans isomer in methanol were followed by measuring the change in absorbance at 535 nm in the temperature range of 20.1—49.9 °C. The complex concentrations were *ca.* 1.3×10^{-3} mol dm^{-3}. The temperature of the solutions was kept constant within ±0.1 °C by use of a temperature-controlled circulating bath, Yamato-Komatsu CET-24W. In each kinetic run, the plot of $\ln(A_t-A_\infty)$ *vs.* time gave a straight line at least four half-lives, where A_t and A_∞ denote the absorbance at time t and at infinite time at 535 nm, respectively. The slope gave the first-order rate constant of isomerization, k, and Eyring treatment of $\log(k/T)$ *vs.* T^{-1} yielded the activation parameters.

Results and Discussion

Preparation and Characterization of the Complexes. Because of the very poor yield of the dmae ligand, most of the study has been done on the dmap complexes, although five-membered dmae chelate complexes would be more fundamental.

A *trans*-$[CoCl_2(chelate)_2]^+$ complex is known to be a good starting material for preparing various bis(chelate)cobalt(III) complexes. The two chloride ions in the *trans*-$[CoCl_2(dmae)_2]^+$ and *trans*-$[CoCl_2(dmap)_2]^+$ complexes are also easily replaced by such ligands as a carbonate and a 2,4-pentanedionate ion. Both *trans*-dichloro complexes were prepared in good yield by air-oxidation of a mixture of cobalt(II) chloride hexahydrate and the corresponding arsine ligand in ethanol, and by treating with hydrochloric acid. The trans configuration was suggested by green in color characteristic of a trans (Cl, Cl) configuration and confirmed by the ^{1}H NMR spectra. The *trans*-dichloro complexes give only one resonance attributable to the As-methyl protons. Since the puckering of the chelate rings will be rapid on the NMR time scale, four methyl groups in the trans isomer should be in equivalent environment. On the other hand, the purple $[CoCl_2(dmap)_2]^+$ complex prepared by treating $[Co(CO_3)(dmap)_2]^+$ with hydrochloric acid at *ca.* 0 °C exhibits four resonances in the As-methyl region (1.2—2.0 ppm) and is assigned to the cis isomer. The configurations of the dibromo and diiodo complexes were also assigned on the basis of the NMR and absorption spectra (*vide infra*). The *trans*-$[CoBr_2(dmae)_2]^+$ complex was prepared by reaction between *trans*-$[CoCl_2(dmae)_2]^+$ and potassium bromide in methanol. The complex thus yielded was necessary to recrystallize several times to purify; the most abundant impurity contained in the crude product may be the *trans*-bromochloro complex. In order to avoid contamination by the mixed halogeno complex, *trans*-$[CoBr_2(dmap)_2]^+$ was prepared by a method similar to that for the *trans*-dichloro complex using cobalt(II) bromide hexahydrate and hydrobromic acid instead of cobalt(II) chloride hexahydrate and hydrochloric acid. The *cis*-$[CoBr_2(dmap)_2]^+$ complex was prepared by a method similar to that for the corresponding *cis*-dichloro complex from $[Co(CO_3)(dmap)_2]^+$ and

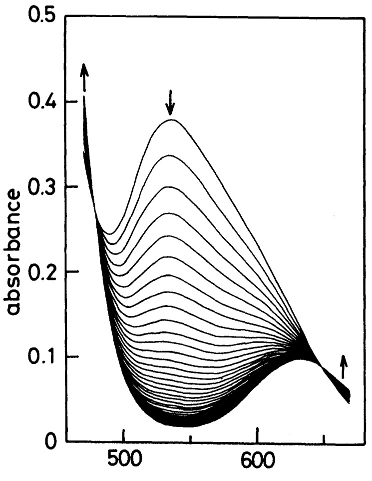

Fig. 1. Change in absorption spectrum of *cis*-[$CoCl_2(dmap)_2$]ClO_4 in methanol at 30.3 °C (recorded intervals: 30 min). Trends of spectral changes with time are shown by arrows.

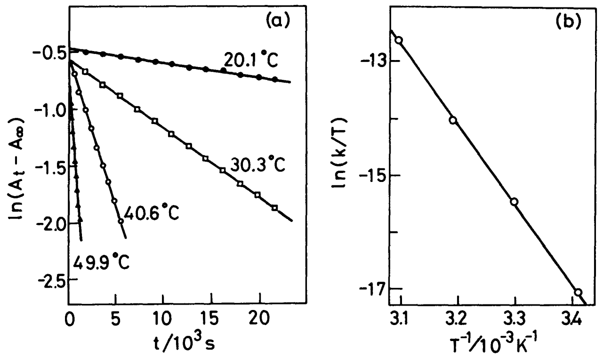

Fig. 2. (a) Plots of $\ln(A_t-A_\infty)$ against time at 20.1, 30.3, 40.6, and 49.9 °C and (b) Eyring treatment of $\ln(k/T)$ against T^{-1}.

Table 1. Rate constants for isomerization of *cis*-[$CoCl_2(dmap)_2$]$^+$ in methanol

t/°C	k/s^{-1}
20.1	$(1.18\pm0.01)\times10^{-5}$
30.3	$(5.92\pm0.02)\times10^{-5}$
40.6	$(2.61\pm0.01)\times10^{-4}$
49.9	$(1.04\pm0.01)\times10^{-3}$
20.2[a]	$(1.03\pm0.01)\times10^{-5}$
30.3[a]	$(4.89\pm0.01)\times10^{-5}$
40.6[a]	$(2.32\pm0.01)\times10^{-4}$
49.8[a]	$(8.61\pm0.02)\times10^{-4}$

a) Lithium chloride added (0.195 mol dm^{-3}).

Table 2. Thermodynamic parameters for isomerization of the complexes

complex	ΔH^*/ kJ mol^{-1}	ΔS^*/ J mol^{-1} K^{-1}	$\Delta G^*_{25°C}$/ kJ mol^{-1}
cis-[$CoCl_2(dmap)_2$]$^+$	115.2±0.7	53.8±2.3	99.2±1.5
cis-[$CoCl_2(dmpp)_2$]$^+$[a]	106.4±0.9	2.1±2.9	105.8±1.7

a) From Ref. 13.

hydrobromic acid.

Both *cis*-dichloro and dibromo complexes isomerize in solution to the trans isomer. Figure 1 shows the change in absorption spectrum at intervals during the isomerization of *cis*-[$CoCl_2(dmap)_2$]ClO_4 in methanol at 30.3 °C. Two isosbestic points were found at 649 and 478 nm in all the experiments (20.1—49.9 °C). The final spectrum was identical with that of a freshly prepared solution of *trans*-[$CoCl_2(dmap)_2$]ClO_4. When the experiment was carried out in deuterated methanol, the final ^{1}H NMR spectrum of the solution showed only signals attributable to the trans isomer. These results indicate that the cis isomer isomerizes to the trans isomer. Rates of the isomerization were followed by measuring the change in absorbance at 535 nm (Experimental, Fig. 2, and Tables 1 and 2). The rate constant 1.97×10^{-3} s^{-1} at 54.9 °C calculated from the ΔH^* and ΔS^* values is larger by a factor of 10^3 than that of *cis*-[$CoCl_2(diars)_2$]$^+$ at the same temperature (1.63×10^{-6} s^{-1}).[11,12] The isomerization of the dmap complex was also studied in the presence of 150 times molar amounts of lithium chloride. The first-order dependence in the complex concentration was maintained, the rates being decreased a little (Table 1).

Table 2 compares the activation parameters of isomerization for *cis*-[$CoCl_2(dmap)_2$]$^+$ with those for the analogous phosphine complex, *cis*-[$CoCl_2(dmpp)_2$]$^+$ (dmpp=1,3-bis(dimethylphosphino)propane). Although the ΔH^* value for the dmap complex is larger than that for the dmpp complex, the former complex isomerizes faster than the latter one at 25 °C because of the large positive activation entropy. If we assume that the two complexes isomerize *via* the same mechanism, the difference in rate may be explained by a steric factor; differences in bond distance, Co–E and E–C (E=As, P), should cause different steric interactions around the E–CH_3 groups. More data are needed to discuss in detail.

The reaction of [$Co(CO_3)(dmap)_2$]$^+$ with sodium iodide and perchloric acid yielded *trans*-[$CoI_2(dmap)_2$]$^+$, and no cis isomer was formed even the reaction was carried out at 0 °C. The *cis*-diiodo complex will be sterically unstable because of the interaction between the two large iodide ions and will isomerize very rapidly to the stable trans isomer. The *trans*-[$CoI_2(dmae)_2$]$^+$ complex was obtained easily from *trans*-[$CoCl_2(dmae)_2$]$^+$ and sodium iodide in ethanol by metathesis. The first diiodo-arsine complex, [$CoI_2(diars)_2$]$^+$ which was prepared by Nyholm[2] was once assigned as the cis isomer from the absorption spectrum,[14] but later assigned as the trans isomer from the ^{1}H NMR spectrum.[5]

The [$Co(acac)_2(dmap)$]$^+$ complex was prepared in high yield from [$Co(acac)_3$] and dmap in methanol–ethanol (1:1) in the presence of active charcoal. Although the reaction was carried out with an excess of

[Co(acac)$_3$], the formation of [Co(acac)(dmap)$_2$]$^{2+}$ was observed in column chromatography. The result suggests that the dmap ligand has a strong affinity toward cobalt(III) in [Co(acac)$_3$] and [Co(acac)$_2$(dmap)]$^+$. However, attempts to prepare [Co(dmap)$_3$]$^{3+}$ by the reaction of [Co(acac)$_3$] or *trans*-[CoCl$_2$(dmap)$_2$]$^+$ with a large excess of dmap were all unsuccessful. Examination of molecular models indicates that [Co(dmap)$_3$]$^{3+}$ involves severe steric interactions among the ligands in any conformation of the six-membered chelate rings. Ohishi *et al.*[15] have suceeded in preparing [Co(dmpe)$_3$]$^{3+}$(dmpe=1,2-bis(dimethylphosphino)ethane) from *trans*-[CoCl$_2$(dmpe)$_2$]$^+$ and dmpe. We have not attempted to prepare the analogous arsine complex, [Co(dmae)$_3$]$^{3+}$, because of the very poor yield of dmae. A complex of the [Co^{III}As$_6$]$^{3+}$-type has been prepared for the diars ligand by Burstall and Nyholm.[3]

Absorption Spectra. Figure 3 shows the absorption spectra of *trans*-[CoCl$_2$(As-As)$_2$]$^+$ where As–As denotes dmae, dmap, and diars,[4] and Table 3 lists the spectral data. The structure of the diars complex has been determined by X-ray analysis.[16] Thus the dmae and dmap complexes which give spectra similar to that of the diars complex can be assigned to the trans isomer. This assignment is in accord with that given from the ^{1}H NMR spectra. All the dichloro complexes exhibit a low energy absorption band with intensities $\log\varepsilon$= 1.8—2.1, and the bands are assigned to the split component (I$_a$, $^1A_{1g}\rightarrow{}^1E_g$ (D_{4h})) of the first absorption band ($^1A_{1g}\rightarrow{}^1T_{1g}(O_h)$) from a comparison with the spectrum of *trans*-[CoCl$_2$(en)$_2$]$^+$ (Fig. 3, en=ethylenediamine).[17,18] The I$_b$ ($^1A_{1g}\rightarrow{}^1A_{2g}$ (D_{4h})) component and the second d-d band are not observed by overlapping of the strong bands (25000—26000 cm^{-1}), which can be assigned as mainly the Co–As and Co–Cl charge-transfer bands.[19] The spectrochemical series for the arsine ligands is determined from examination of maximum positions of the I$_a$ components: diars>dmae>dmap. For a series of *trans*-dichloro cobalt(III) complexes with analogous phosphine ligands a similar order has been reported: *o*-phenylenebis(dimethylphosphine)>dmpe>dmpp.[13] The trend that the d-d absorption bands shift to lower energies as the number of ring members of a chelate ligand increases from five to six has been observed for cobalt(III)-diamine complexes such as *trans*-[CoCl$_2$(en)$_2$]$^+$ (I$_a$: 16100 cm^{-1})[17,18] and *trans*-[CoCl$_2$(tn)$_2$]$^+$ (I$_a$: 15400 cm^{-1}, tn=trimethylenediamine).[20] In a series of *trans*-dichloro cobalt(III) complexes with a five-membered chelate, dmae, dmpe, and en, the energy of the I$_a$ component decreases in the order, dmpe (17300 cm^{-1})[13]>dmae (16100 cm^{-1}) ~en (16100 cm^{-1}). Thus the spectrochemical series for the group 5B elements seems to be $P>As\sim N$. However, dmpe and dmae are a di(tertiary phosphine) and a di(tertiary arsine), respectively, while en is a di(primary amine). It is known that cobalt(III) complexes containing *N,N,N′,N′*-tetramethylethylenediamine (Me$_4$-en), an

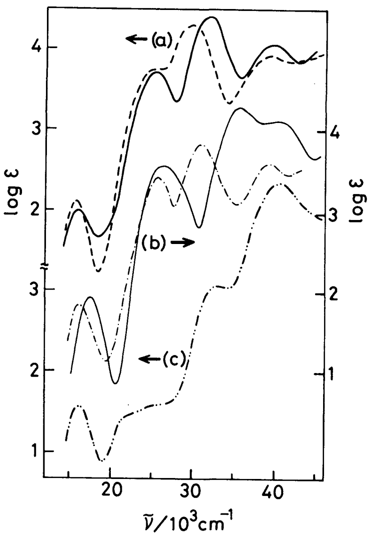

Fig. 3. Absorption spectra of (a) *trans*-[CoCl$_2$(dmae)$_2$]$^+$ (——) and *trans*-[CoCl$_2$(dmap)$_2$]$^+$ (---) in acetonitrile, (b) *trans*-[CoCl$_2$(diars)$_2$]$^+$ (—·—, from Ref. 4) and *trans*-[CoCl$_2$(dmpe)$_2$]$^+$ (——, from Ref. 13) in methanol, and (c) *trans*-[CoCl$_2$(en)$_2$]$^+$ (—··—) in methanol.

TABLE 3. ABSORPTION SPECTRAL DATA

Complex	$\tilde{\nu}_{max}/10^3 cm^{-1}$ ($\log(\varepsilon/cm^{-1} mol^{-1} dm^3)$)
trans-[CoCl$_2$(dmae)$_2$]$^{+a)}$	16.1(2.01) 25.3(3.73) 31.7(4.42) 39.4(4.07)
trans-[CoBr$_2$(dmae)$_2$]$^{+a)}$	15.3(1.94) 23.3(3.52) 30.8(4.29) 34.9(4.18) 42.6(4.13)
trans-[CoI$_2$(dmae)$_2$]$^{+a)}$	14.4(1.97) 18(sh, 2.84) 20.6(3.68) 30.1(4.24) 38.8(4.34) 40.0(4.01)
[Co(CO$_3$)(dmae)$_2$]$^{+b)}$	20.5(2.94) 24.5(2.80) 33.1(4.29)
trans-[CoCl$_2$(dmap)$_2$]$^{+a)}$	15.7(2.11) 25.0(3.77) 29.6(4.31) 39.1(3.94)
trans-[CoBr$_2$(dmap)$_2$]$^{+b)}$	15.0(2.09) 23.3(3.64) 28.7(4.24) 34.9(4.14) 40(sh, 3.95)
trans-[CoI$_2$(dmap)$_2$]$^{+a)}$	14.0(1.99) 17.5(sh, 2.86) 20.5(3.69) 29.9(4.13) 33.8(4.17) 40.1(4.08)
cis-[CoCl$_2$(dmap)$_2$]$^{+a)}$	17(sh, 2.60) 18.7(2.74) 22.5(sh, 3.01) 27.4(4.13) 31.9(4.11) 35(sh, 3.98) 40(sh, 3.97)
cis-[CoBr$_2$(dmap)$_2$]$^{+a)}$	16(sh, 2.57) 17.8(2.68) 25.5(sh, 3.89) 29.2(4.10) 33.8(4.11) 36.6(4.14)
[Co(CO$_3$)(dmap)$_2$]$^{+b)}$	20.1(3.01) 24.4(2.84) 30.9(4.38) 33(sh, 4.16) 35(sh, 4.02) 43(sh, 3.87)
[Co(acac)$_2$(dmap)]$^{+a)}$	17.5(sh, 2.59) 19.9(2.68) 32.3(4.07) 34.2(4.08) 44.4(3.98)
[Co(acac)(dmap)$_2$]$^{2+a)}$	19.5(3.16) 30(sh, 3.99) 34(sh, 4.48) 37.0(4.64)

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

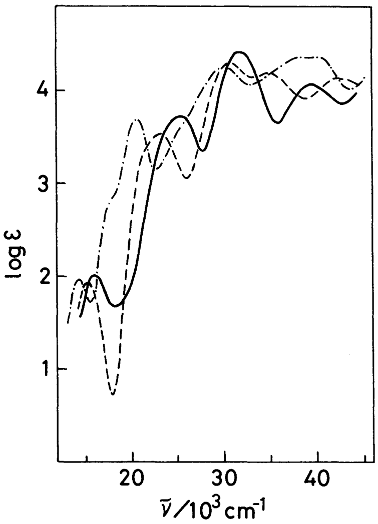

Fig. 4. Absorption spectra of *trans*-$[CoX_2(dmae)_2]^+$ in acetonitrile; X=Cl (——), Br (---), and I (—·—).

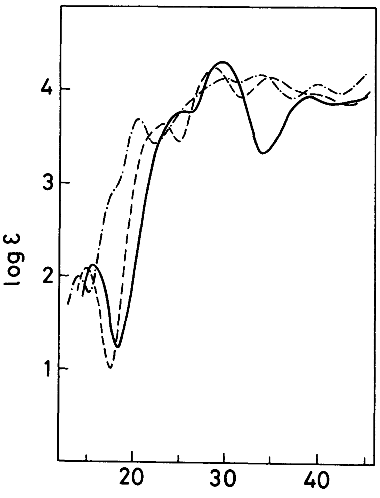

Fig. 5. Absorption spectra of *trans*-$[CoX_2(dmap)_2]^+$ in acetonitrile; X=Cl (——), Br (---), and I (—·—).

analogous ligand to dmpe and dmae, shift the d-d absorption bands to lower energy to a large extent compared with those of the corresponding en complexes (for example, $[Co(acac)_2(en)]^+$: 18450 cm^{-1}, $[Co(acac)_2(Me_4\text{-}en)]^+$: 16600 cm^{-1}).[21–23] Thus the appropriate order for the spectrochemical series would be dmpe (P)>dmae (As)>Me$_4$-en (N). A similar result (P>As) has been reported for $[PdCl_2\{NH_2CH_2CH_2E(n\text{-}C_4H_9)(C_6H_5)\}]$ (E=P, As).[24]

Figures 4 and 5 show the absorption spectra of *trans*-$[CoX_2(dmae)_2]^+$ and *trans*-$[CoX_2(dmap)_2]^+$ (X=Cl, Br, I), respectively. In either series, the energy of the I$_a$ component decreases in the order Cl>Br>I. The diiodo complexes show a shoulder ($\log\varepsilon \approx 2.8$) at *ca.* 18000 cm^{-1}. Such a shoulder is also observed for the analogous phosphine complex, *trans*-$[CoI_2(dmpe)_2]^+$,[13] however, the origin of the transition is unknown.

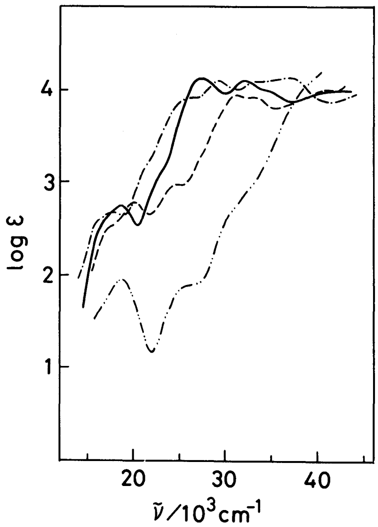

Fig. 6. Absorption spectra of *cis*-$[CoX_2(dmap)_2]^+$ in acetonitrile; X=Cl (——) and Br (—·—), *cis*-$[CoCl_2(diars)_2]^+$ (---, from Ref. 4) in ethanol, and *cis*-$[CoCl_2(en)_2]^+$ (—··—) in water.

The absorption spectra of *cis*-$[CoX_2(dmap)_2]^+$ (X=Cl, Br) are shown in Fig. 6 together with those of the diars and en complexes. The dichloro–dmap complex shows the first absorption band maximum at 18700 cm^{-1} with a shoulder at the low energy side (*ca.* 17000 cm^{-1}). The intensities of these bands are considerably higher than those of *cis*-$[CoCl_2(en)_2]^+$.[25] The large absorption coefficients are also observed for the d-d transitions of other *cis*-$[CoCl_2As_4]^+$-type complexes.[4,19,26,27] If the shoulder at *ca.* 22500 cm^{-1} in the spectrum of *cis*-$[CoCl_2(dmap)_2]^+$ is assigned as mainly the second absorption band, the dmap ligand will reduce largely the interelectronic repulsion of the central cobalt atom; the energy separation between the $^1T_{1g}$ and $^1T_{2g}$ manifolds is much smaller than that of *cis*-$[CoCl_2(en)_2]^+$[25] where the cobalt(III) ion is surrounded by hard donor atoms (Fig. 6). Such largely reduced interelectronic repulsion in a cobalt(III)–arsine complex is more clearly shown for $[Co(CO_3)(dmae)_2]^+$ and $[Co(CO_3)(dmap)_2]^+$; the energy differences (4000 and 4300 cm^{-1}, respectively) between the first and the second absorption bands are about half of that (8260 cm^{-1}) for $[Co(CO_3)(en)_2]^+$[28] (Fig. 7). Small energy differences between the first and the second absorption bands of cobalt(III) complexes have also been reported for phosphine complexes such as $[Co\{(CH_3)_2PCH_2CH_2NH_2\}_3]^{3+}$[29] and $[Co(dmpe)_3]^{3+}$.[15] The spectrum of *cis*-$[CoBr_2(dmap)_2]^+$ is similar to that of the corresponding dichloro complex except that the former is shifted to lower energy side compared to the latter.

Figure 8 shows the absorption spectra of a series of the $[Co(acac)_{3-n}(dmap)_n]^{n+}$ (n=0, 1, 2) complexes. The bands in the region of 16000 to 20000 cm^{-1}, which can be assigned to the first d-d absorption band, shift to higher energy and become more intense as the number

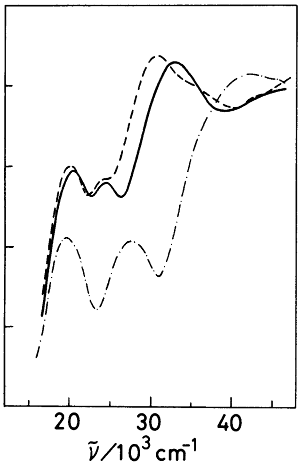

Fig. 7. Absorption spectra of $[Co(CO_3)(dmae)_2]^+$ (——) in methanol, $[Co(CO_3)(dmap)_2]^+$ (---) in methanol, and $[Co(CO_3)(en)_2]^+$ (---) in water.

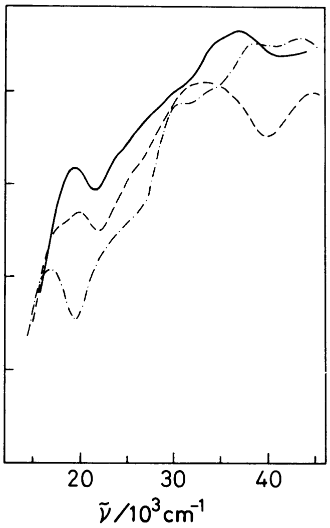

Fig. 8. Absorption spectra of $[Co(acac)_{3-n}(dmap)_n]^{n+}$ n=0 (—·—) in methanol and n=1 (---) and n=2 (——) in acetonitrile.

of dmap increases.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 58470032 from the Ministry of Education, Science and Culture.

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