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Preparation and Properties of Cobalt(III)-1,2-Bis(dimethylphosphino)ethane (dmpe) Complexes of the $[Co(L)(dmpe)_2]^{n+}$ Type

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Seven new cobalt(III)-phosphine complexes of the type $[Co(L)(dmpe)_2]^{n+}$ were prepared from *trans*-$[Co(Cl\ or\ Br)_2(dmpe)_2]^+$, where dmpe denotes $(CH_3)_2PCH_2CH_2P(CH_3)_2$, and L is $C_2O_4^{2-}$, $NH_2CH_2COO^-$(gly), $NH_2CH(CH_3)COO^-$(ala), $(C_2H_5)_2NCS_2^-$(dtc), $(NCS^-)_2$, $(NCO^-)_2$, or $(CN^-)_2$. Reactions of *cis*-$[CoCl_2(dmpe)_2]^+$ with X^- ($X^-=CN^-$, NCS^-, and NCO^-) yielded only *trans*-$[CoX_2(dmpe)_2]^+$. Qualitative stabilities of the complexes containing a bidentate ligand in aqueous solution were found to decrease in the order L= $CH(CH_3CO)_2^-$(acac), $C_2O_4^{2-}$, dtc>CO_3^{2-}≫gly, ala>$NH_2CH_2CH_2NH_2$(en); the complexes containing O or S donor atoms are thermally more stable than those containing an amino donor group. The d-d absorption bands of the complexes were assigned by comparing the spectra with those of related Co(III)-phosphine and -en complexes. The IR and visible absorption spectra of the NCS^- and NCO^- complexes indicate an N coordination mode of these ambidentate ligands.

In a previous paper,[1] we have prepared all complexes of the series $[Co(acac)_x(en)_y(dmpe)_z]^{(3-x)+}$ and found that $[Co(acac)_{3-n}(dmpe)_n]^{n+}$ (n=1, 2) were more stable than $[Co(en)_{3-n}(dmpe)_n]^{3+}$ (n=1, 2), where acac, en and dmpe denote an acetylacetonate ion, ethylenediamine and 1,2-bis(dimethylphosphino)ethane, respectively. The en complexes in water are reduced to Co(II) on heating over 60 °C, and $[Co(en)(dmpe)_2]^{3+}$ in water containing excess chloride ions affords *trans*-$[CoCl_2(dmpe)_2]^+$ by heating, whereas the acac complexes remain unchanged under the same conditions. The acac ligand seems to stabilize the cobalt(III)-dmpe system.

To examine properties of cobalt(III)-phosphine complexes in more detail, we attempted to prepare cobalt(III)-dmpe complexes containing a variety of ligands. This paper reports the preparation and some properties of the $[Co(L)(dmpe)_2]^{n+}$-type complexes, where L denotes a bidentate ligand such as CO_3^{2-}, $C_2O_4^{2-}$, $NH_2CH_2COO^-$(gly), (S)-$NH_2CH(CH_3)$-COO^-(S-ala) or $(C_2H_5)_2NCS_2^-$(dtc), and two unidentate ions such as NCS^-, NCO^-, CN^-, or H_2O.

Experimental

The dmpe ligand[2] was handled under an atmosphere of nitrogen until it formed cobalt(III) complexes. All solvents used for the preparation of dmpe and the complexes were deoxygenated by bubbling nitrogen for 20 min immediately before use. ^{1}H NMR, absorption, circular dichroism and IR spectra were recorded on a Jeol JNM-PMX 60 spectrometer, a Hitachi 323 spectrophotometer, a Jasco J-40CS spectropolarimeter, and a Jasco A-3 infrared spectrometer, respectively.

Preparation of the Complexes.† $[Co(CO_3)(dmpe)_2]ClO_4\cdot 1.5NaClO_4\cdot H_2O$[3] and *trans*-$[Co(H_2O)_2(dmpe)_2](ClO_4)_3\cdot 2H_2O$[3] were prepared from *trans*-$[CoBr_2(dmpe)_2]ClO_4$[4] and the carbonato complex, respectively by reported methods.

$[Co(C_2O_4)(dmpe)_2]PF_6\cdot 0.5NaPF_6$. An aqueous solution (5 cm^3) of $(NH_4)_2C_2O_4$ (5.36 mg, 0.38 mmol) was added to a solution of *trans*-$[CoCl_2(dmpe)_2]ClO_4$[5] (100 mg, 0.19 mmol) in a mixture of water and methanol (1 : 1, 50 cm^3), and the mixture was stirred for 10 h at room temperature. The resulting yellow solution was diluted with water (1 dm^3) and applied on a column (ϕ 3 cm×120 cm) of SP-Sephadex C-25. The adsorbed products were eluted with 0.1 mol dm^{-3} NaCl, giving a minor green and a major yellow band. The yellow eluate was collected and evaporated to dryness under reduced pressure. A yellow complex was extracted from the residue with methanol, and the extract was mixed with an aqueous solution (5 cm^3) of $NaPF_6$ (300 mg). The mixture was concentrated in a desiccator over P_4O_{10}, yielding yellow crystals, which were filtered, washed with a mixture (30 cm^3) of methanol and diethyl ether (1 : 1), and air-dried. Yield: 80 mg (72%). Found: C, 24.89; H, 5.30%. Calcd for $C_{14}H_{32}O_4F_9P_{5.5}Na_{0.5}Co$: C, 24.86; H, 4.76%. The complex is soluble in water, methanol and ethanol.

$[Co(dtc)(dmpe)_2](ClO_4)_2$. A methanol solution (30 cm^3) containing *trans*-$[CoBr_2(dmpe)_2]ClO_4$[4] (100 mg, 0.16 mmol) and sodium diethyldithiocarbamate (36.4 mg, 0.16 mmol) was stirred for 10 h at room temperature. The yellow crystals which precipitated were filtered, washed with a mixture (20 cm^3) of methanol and diethyl ether (1 : 1) and air-dried. Yield: 52 mg (72%). Found: C, 29.10; H, 6.00; N, 1.97%. Calcd for $C_{17}H_{42}NO_8P_4S_2Cl_2Co$: C, 28.91; H, 5.99; N, 1.98%. The complex is soluble in methanol, ethanol and acetonitrile.

$[Co(gly)(dmpe)_2](ClO_4)_2\cdot 0.5NaClO_4\cdot H_2O$. To *trans*-$[CoCl_2(dmpe)_2]ClO_4$[5] (100 mg, 0.19 mmol) in a mixture (50 cm^3) of water and methanol (1 : 1) were added an aqueous solution (5 cm^3) of sodium glycinate (37 mg, 0.38 mmol) and a small amount of active charcoal. The mixture was stirred for 10 h at room temperature, and then filtered to remove active charcoal. The filtrate was diluted with water (1 dm^3) and applied on a column (ϕ 3 cm×120 cm) of SP-Sephadex C-25. By elution with 0.2 mol dm^{-3} NaCl, a small red (probably$[Co(gly)_2(dmpe)]^+$) and then a yellow band appeared. The eluate of the yellow band was collected and evaporated to dryness under reduced pressure. The residue was treated with methanol (100 cm^3) to extract the complex. To the extract was added an aqueous solution (2 cm^3) of $NaClO_4$ (300 mg), and the mixture was concentrated in a vacuum desiccator over P_4O_{10}, yielding yellow crystals. The crystals were filtered, washed with cold methanol (10 cm^3) and air-dried. Yield: 67 mg (18%). Found: C, 26.10; H, 5.70; N, 2.24%. Calcd for $C_{14}H_{38}NO_{13}P_4Cl_{2.5}Na_{0.5}Co$: C, 26.21; H, 5.97; N, 2.18%. The complex is soluble in water and

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†All of the perchlorate salts of cobalt(III)-phosphine complexes described below are potentially explosive, and should be handled carefully.

methanol.

[Co(*S*-ala)(dmpe)$_2$](ClO$_4$)$_2$·0.5NaClO$_4$. The complex was prepared by a method similar to that for the glycinato complex, using sodium (*S*)-alaninate. The separation of two diastereomers was not achieved by SP-Sephadex column chromatography. Yield: 10%. Found: C, 23.71; H, 4.97; N, 1.95%. Calcd for $C_{15}H_{38}NO_{12}P_4Cl_{2.5}Na_{0.5}Co$: C, 23.45; H, 4.95; N, 1.82%. The solubility of the complex is similar to that of the glycinato complex.

***trans*-[Co(CN)$_2$(dmpe)$_2$]ClO$_4$.** To a solution of *trans*-[CoBr$_2$(dmpe)$_2$]ClO$_4$ (480 mg, 0.776 mmol) in a mixture (15 cm^3) of acetonitrile and water (2 : 1) was added an aqueous solution (3 cm^3) of NaCN (100 mg, 2.04 mmol), and the mixture was stirred at room temperature. After 1 h the solution was concentrated to 5 cm^3 under reduced pressure and cooled at 0 °C. The white crystals which precipitated were filtered, washed with a small amount of cold methanol and air-dried. Yield: 205 mg (52%). Found: C, 32.93; H, 6.32; N, 5.49%. Calcd for $C_{14}H_{32}N_2O_4P_4ClCo$: C, 32.68; H, 6.29; N, 5.44%. The complex is soluble in water and methanol.

***trans*-[Co(NCS)$_2$(dmpe)$_2$]ClO$_4$·2NaClO$_4$.** A solution (50 cm^3) containing *trans*-[CoCl$_2$(dmpe)$_2$]ClO$_4$ (100 mg, 0.19 mmol) and KNCS (36.7 mg, 0.38 mmol) in a mixture of methanol and water (1 : 1) was stirred at 50 °C for 1 h, and then at room temperature for 10 h. The resulting orange solution was evaporated to dryness under reduced pressure, and the residue was dissolved in acetonitrile (10 cm^3). The solution was chromatographed by a column (ϕ 3 cm×40 cm) of Sephadex LH-20. By elution with a mixture of hexane and acetonitrile (1 : 1), a green (the starting dichloro complex) and an orange band appeared. The orange eluate was collected, evaporated to dryness under reduced pressure, and the residue was dissolved again in acetonitrile (5 cm^3). The solution was mixed with an acetonitrile solution (2 cm^3) of NaClO$_4$ (200 mg) and concentrated in a vaccum desiccator over P_4O_{10}. The orange crystals which were formed were filtered, washed with cold methanol (10 cm^3) and air-dried. Yield: 33 mg (21%). Found: C, 20.40; H, 4.06; N, 3.45%. Calcd for $C_{14}H_{32}N_2O_{12}P_4S_2Cl_3Na_2Co$: C, 20.51; H, 3.93; N, 3.41%. The complex is soluble in acetonitrile.

***trans*-[Co(NCO)$_2$(dmpe)$_2$]ClO$_4$·H$_2$O.** A solution containing *trans*-[CoBr$_2$(dmpe)$_2$]ClO$_4$ (300 mg, 0.49 mmol) and KNCO (119 mg, 1.47 mmol) in a mixture (100 cm^3) of methanol and water (2 : 1) was stirred for 3 h at room temperature. The resulting orange solution was diluted with water (1 dm^3) and applied on a column (ϕ 3 cm×120 cm) of SP-Sephadex C-25. By elution with 0.1 mol dm^{-3} NaCl, a green (the starting dibromo complex) and a yellow eluate were obtained. The yellow eluate was concentrated to dryness under reduced pressure, and the residue was dissolved in methanol (30 cm^3). The methanol solution was diluted with water (1 dm^3) and applied on a small column (ϕ 3cm×20 cm) of SP-Sephadex C-25. The adsorbed complex was eluted with 1 mol dm^{-3} NaClO$_4$, and the eluate was concentrated in a desiccator over P_4O_{10} to give yellow-orange crystals. The crystals were filtered, washed with a mixture (20 cm^3) of methanol and diethyl ether (1 : 1), and air-dried. Yield: 200 mg (72%). Found: C, 30.04; H, 5.80; N, 5.35%. Calcd for $C_{14}H_{34}N_2O_7P_4ClCo$: C, 29.99; H, 6.11; N, 5.00%. The complex is soluble in methanol and acetonitrile.

Optical Resolution of [Co(CO$_3$)(dmpe)$_2$]$^+$. One g of [Co(CO$_3$)(dmpe)$_2$]ClO$_4$·1.5NaClO$_4$·H$_2$O in water (1 cm^3) was charged on the top of a column (ϕ 3 cm×30 cm) of SP-Sephadex C-25, and the complex was eluted with an aqueous solution of 0.1 mol dm^{-3} disodium (−)-di-*O*-benzoyltartrate. No resolution of the complex was achieved by this method. The yellow eluate was collected and concentrated to ca. 20 cm^3 under reduced pressure. Excess disodium (−)-di-*O*-benzoyltartrate was removed by chromatography with a column (ϕ 2.5 cm×30 cm) of Toyopearl TSK-GEL and an eluent water. The eluate was evaporated to dryness under reduced pressure, and the residue was dissolved in ethanol (20 cm^3). On addition of diethyl ether (20 cm^3) the solution gave a yellow precipitate. It was recrystallized three times from a mixture of ethanol and diethyl ether (1 : 4). Yield: 36 mg. The product was dissolved in water and the solution was applied on a column (ϕ 1.5 cm×10 cm) of SP-Sephadex C-25. The column was washed with water, and then the complex was eluted with 0.1 mol dm^{-3} NaClO$_4$. The eluate was concentrated to a small volume under reduced pressure, and the concentrate was used for CD measurements. The complex concentration was determined by reference to the ε values of the racemate.

Results and Discussion

The ease of preparation of [Co(L)(dmpe)$_2$]$^{n+}$ from *trans*-[Co(Cl or Br)$_2$(dmpe)$_2$]$^+$ and a bidentate ligand L differs appreciably by the kind of L. Reactions of *trans*-[Co(Cl or Br)$_2$(dmpe)$_2$]$^+$ with acac, CO_3^{2-}, $C_2O_4^{2-}$ or dtc proceeded smoothly at room temperature and the complexes were obtained in 70—90% yields, while those with gly or *S*-ala did not take place even at 50 °C and resulted in decomposition of the *trans*-dihalogeno complex to cobalt(II) species at a higher temperature. The gly and *S*-ala complexes were obtained in a poor yield, 18 and 10%, respectively by the reactions in the presence of active charcoal. The *trans*-[Co(Cl or Br)$_2$(dmpe)$_2$]$^+$ complex did not react with more bulky (*S*)-proline under similar conditions. The [Co(en)(dmpe)$_2$]$^{3+}$ complex is also obtained in a poor yield (18%) by a similar reaction with en.[1] The poor yield of [Co(L)(dmpe)$_2$]$^{n+}$ in which L has an amino donor group may be attributable to instability of the complex shown later.

The *trans*-[Co(Cl or Br)$_2$(dmpe)$_2$]$^+$ complex afforded only *trans*-[CoX$_2$(dmpe)$_2$]$^+$ by reactions with MX (M=Na$^+$ or K$^+$, X=CN$^-$, NCO$^-$ or NCS$^-$) at room temperature. Attempts to prepare the corresponding cis isomers were unsuccessful. The reaction of *cis*-[CoCl$_2$(dmpe)$_2$]$^+$[4] with CN$^-$ took place easily at 0 °C, but only the trans isomer was formed, no fraction indicative of the cis isomer being obtained in column chromatography. The reactions with NCO$^-$ and NCS$^-$ proceeded hardly at 0 °C, and yielded the trans isomer at a higher temperature. Since cis-[CoX$_2$(dmpe)$_2$]$^+$ (X=Cl, Br) can be prepared from [Co(CO$_3$)(dmpe)$_2$]$^+$ by treating with HX at 0 °C,[4] no formation of cis-isomers of these pseudo-halogeno complexes would be due to kinetic reasons. When [Co(CO$_3$)(dmpe)$_2$]$^+$ is treated with HClO$_4$, instead of HX, *trans*-[Co(H$_2$O)$_2$(dmpe)$_2$]$^{3+}$ is formed.[3] For the dinitro complex, neither cis nor trans isomer was formed by the

Table 1. Absorption Spectral Data of $[Co(L)(dmpe)_2]^{n+}$

Complex	$\tilde{\nu}_1/10^3\,cm^{-1}(\log\varepsilon)$	$\tilde{\nu}_2/10^3\,cm^{-1}(\log\varepsilon)$	$\tilde{\nu}_2-\tilde{\nu}_1$	Solvent
$[Co(dtc)(dmpe)_2]^{2+}$	22.5(2.85)	25.1(3.02)	2600	CH_3CN
$[Co(CO_3)(dmpe)_2]^+$	23.5(2.96)	27.1(2.98)	3600	CH_3OH
$[Co(C_2O_4)(dmpe)_2]^+$	23.9(2.90)	27.4(2.93)	3500	CH_3OH
$[Co(S\text{-}ala)(dmpe)_2]^{2+}$	24.1(2.93)	28.4(3.00)	4300	H_2O
$[Co(gly)(dmpe)_2]^{2+}$	24.3(2.92)	28.4(3.01)	4100	H_2O
$[Co(en)(dmpe)_2]^{3+}$	24.8(2.86)	29.4(2.84)	4600	H_2O

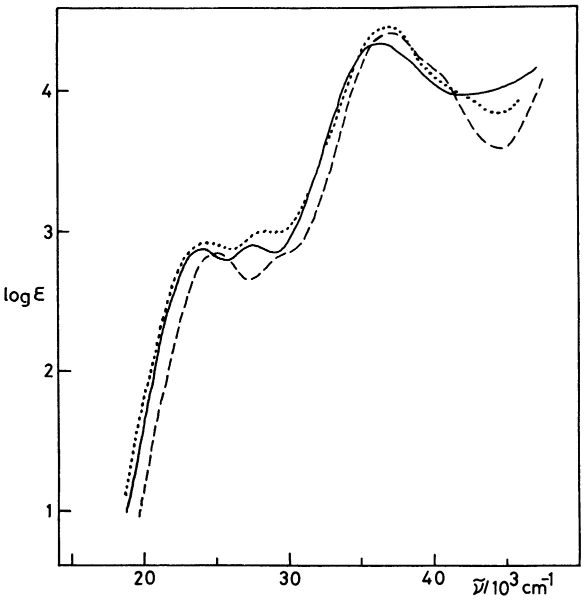

Fig. 1. Absorption spectra of $[Co(C_2O_4)(dmpe)_2]^+$ in methanol (——), $[Co(gly)(dmpe)_2]^{2+}$ in water (······), and $[Co(en)(dmpe)_2]^{3+}$ in water (----).

reaction of *trans*-$[Co(Cl\ or\ Br)_2(dmpe)_2]^+$ with $NaNO_2$. The result will be attributable to steric interactions between the NO_2^- and dmpe ligands as suggested by Miskowski et al.[6] for the corresponding *cis*-1,2-bis(diphenylphosphino)ethylene complex. The $[CoX_2(diars)_2]^{n+}$ (diars=*o*-phenylenebis(dimethylarsine)) complexes have somewhat different properties in chemical reactions. Although *cis*-$[CoCl_2(diars)_2]^+$ yields *trans*- $[Co(NCS)_2(diars)_2]^+$ by the reaction with KNCS,[7] the reaction of $[Co(CO_3)(diars)_2]^+$ with $HClO_4$ affords *cis*-$[Co(H_2O)_2(diars)_2]^{3+}$, from which various *cis*-$[CoX_2(diars)_2]^{n+}$ ($X=Cl^-, NO_2^-, NO_3^-, CH_3CN$) can be derived.[8]

Geometrical structures of $[CoX_2(dmpe)_2]^{n+}$can be easily assigned by comparing the ^1H NMR spectra with those of *cis*- and *trans*-$[CoX_2(dmpe)_2]^+$ ($X=Cl^-, Br^-$).[3]

The $C_2O_4^{2-}$ and dtc complexes appear to have stability similar to that of the acac complexes.[1] The complexes in water in the absence or presence of excess NaCl remain unchanged by heating (60—70 °C). The CO_3^{2-} complex is also stable in hot water, but gives a small amount of *trans*-$[CoCl_2(dmpe)_2]^+$ in the presence of excess NaCl by prolonged heating. On the other hand, the gly and *S*-ala complexes decompose to cobalt(II) species or yield *trans*-$[CoCl_2(dmpe)_2]^+$ under the same conditions. However, these complexes seem to be more stable than $[Co(en)(dmpe)_2]^{3+}$.[1] Thus it can be concluded qualitatively that $[Co(L)(dmpe)_2]^{n+}$ (L=a bidentate ligand) decreases the stability in the order acac, $C_2O_4^{2-}$, dtc$>CO_3^{2-}\gg$ gly, *S*-ala$>$en; the complexes containing an amino group are less stable than those with O or S donor atoms.

The NCS^- and NCO^- ligands are an ambidentate ligand to be able to coordinate to a metal ion through N or S, and N or O, respectively. In the IR spectrum *trans*-$[Co(NCS)_2(dmpe)_2]^+$ shows the C-S stretching band at 839 cm^{-1}, indicating the N-bonding of NCS^-.[9] Related complexes *cis*(NCS,NCS),*trans*(P,P)- and *trans* (NCS,NCS), *cis* (P,P)-$[Co(NCS)_2\{NH_2CH_2CH_2P(C_6H_5)_2\}_2]^+$[10] and *trans*-$[Co(NCS)_2\{cis\text{-}(C_6H_5)_2PCHCHP(C_6H_5)_2\}_2]^+$[6] have also been reported to have the N-bonding of NCS^-. For the coordination mode of NCS^-, Norbury et al.[11,12] pointed out that the NCS^- ligand in a hard metal complex containing π-acceptor ligands tends to coordinate through the S atom. A cobalt(III)-phosphine complex should be the case, but no S-bonding of NCS^- has been reported except for the so-called cobaloxime complexes.[13] The preference of N-bonding may come from a steric factor. The Co-NCS moiety is usually nearly linear (∠CoNC=170—180°), whereas the Co-SCN moiety is bent (∠CoSC=≈105°).[10,11] The atomic (ionic) radius of N should be much smaller than that of S. Thus the S-bonding of NCS^- will require greater space and will be unfavorable in a complex containing bulky ligands such as tertiary phosphines. The coordination mode of NCO^- in *trans*-$[Co(NCO)_2(dmpe)_2]^+$ could not be assigned from the IR spectrum, but will be the N-bonding, since the complex shows the absorption spectrum very similar to that of *trans*-$[Co(NCS)_2(dmpe)_2]^+$ in the first d-d band region (vide post).

Absorption spectra of $[Co(L)(dmpe)_2]^{n+}$ ($L=C_2O_4^{2-}$, gly, en) are shown in Fig. 1 and the data in Table 1. In a previous paper,[1] we assigned the band at 24750 cm^{-1} and the shoulder at 29400 cm^{-1} of the en complex to the first and the second d-d bands, respectively. The $C_2O_4^{2-}$ and gly complexes give two d-d bands similar to those of the en complex. The spectrum of the CO_3^{2-} complex is quite similar to that of the $C_2O_4^{2-}$ complex. These d-d bands shift to the low energy side with an increase in number of the O donor atom according to

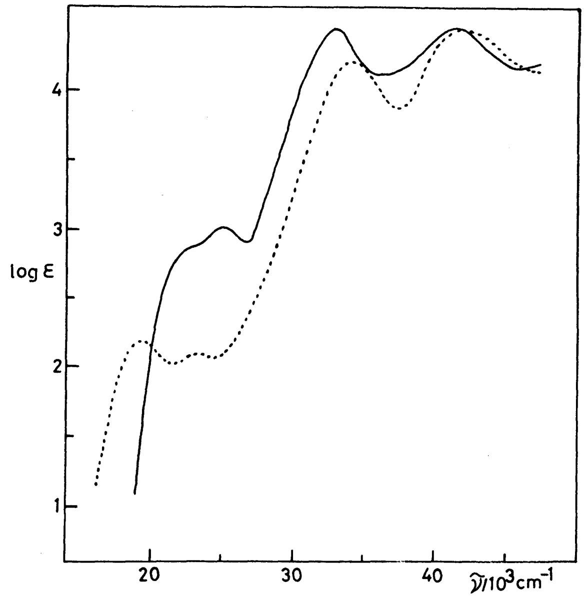

Fig. 2. Absorption spectra of $[Co(dtc)(dmpe)_2]^{2+}$ in acetonitrile (——) and $[Co(dtc)(en)_2]^{2+}$ in water (······).

the spectrochemical series.[14] However, the extent of shift is larger for the second d-d band than that for the first d-d band. As a result, the energy separation between the first and the second d-d bands becomes small with an increase in number of the O donor atom (Table 1). For $[Co(L)(en)_2]^{n+}$, the values of the energy separation are much larger than those of the dmpe complexes and are nearly the same among the L=en (8100 cm^{-1}), gly (8400 cm^{-1}), and $C_2O_4^{2-}$ (8100 cm^{-1}) complexes.[14]

The absorption spectrum of $[Co(dtc)(dmpe)_2]^{2+}$ is compared with that of $[Co(dtc)(en)_2]^{2+}$ [15] in Fig. 2. The bands at 19600 cm^{-1} ($\log\varepsilon=2.21$) and 23300 cm^{-1} ($\log\varepsilon=2.11$) of the en complex have been assigned to the first and the second d-d bands, respectively on the basis of the magnetic circular dichroism study.[15] The energy separation between these two bands (3700 cm^{-1}) is much smaller than that of $[Co(en)_3]^{3+}$ (8100 cm^{-1}), indicating largely reduced interelectronic repulsions between the ligand field levels. It is known that many dtc complexes show large reduction of the interelectronic repulsion.[15] Thus the shoulder at 22500 cm^{-1} and the band at 25100 cm^{-1} of $[Co(dtc)(dmpe)_2]^{2+}$ can be assigned to the first and the second d-d bands, respectively, although the energy separation between them is extremely small (2600 cm^{-1}) as a cobalt(III) complex.

Absorption and circular dichroism (CD) spectra of $(+)_{589}$-$[Co(CO_3)(dmpe)_2]^+$ are compared with those of the corresponding diars[16] and en[17] complexes in Fig. 3. The decreasing order in energy of the first d-d band is dmpe (23500 cm^{-1})>diars (21000 cm^{-1})> en (19600 cm^{-1}), while that of the second d-d band en (27900 cm^{-})>dmpe (27100 cm^{-1})>diars (25000 cm^{-1}). From the data the ligand field splitting parameter (Δ) was estimated by assuming C=4B; 24400 cm^{-1} for dmpe, 22000 cm^{-1} for diars, and 21680 cm^{-1} for en complexes. The Δ values of the en and diars complexes are similar. However, en is a primary diamine and its ligand field strength is known to be much stronger than that of a tertiary diamine *N,N,N′,N′*-tetramethylethylenediamine corresponding to dmpe and diars.[18] Thus it can be concluded that the spectrochemical series for group 5B elements is P>As>N. The same conclusion has been obtained by spectral studies of *trans*-$[CoCl_2(L)_2]^+$ (L=en, dmpe, 1,2-bis(dimethylarsino)ethane).[19]

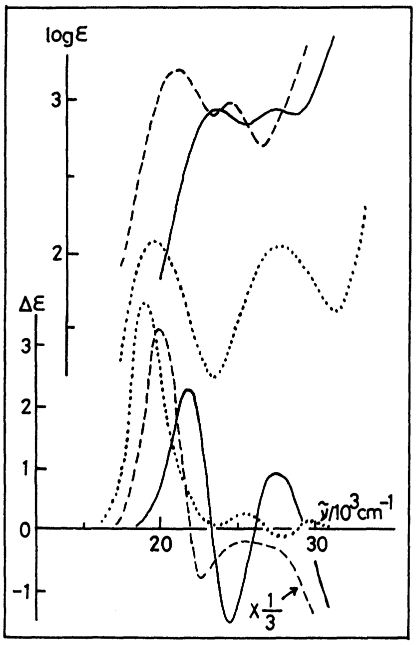

Fig. 3. Absorption and CD spectra of $(+)_{589}$-$[Co(CO_3)(dmpe)_2]^+$ in methanol (——), $(+)_{589}$-$[Co(CO_3)(diars)_2]^+$ in methanol (----),[16] and $(+)_{589}$-$[Co(CO_3)(en)_2]^+$ in water (······).

The CD strength of $(+)_{589}$-$[Co(CO_3)(dmpe)_2]^+$ in Fig. 3 appears to be weak as compared with those of the en and diars complexes. It is not clear whether the weak strength is attributable to incomplete resolution. The $(+)_{589}$-$[Co(CO_3)(dmpe)_2]^+$ isomer exhibits a positive (21800 cm^{-1}, $\Delta\varepsilon=+2.29$) and a negative (24400 cm^{-1}, $\Delta\varepsilon=-1.55$) CD peaks in the first d-d band region. The absolute configurations of $(+)_{589}$-$[Co(CO_3)(en)_2]^+$ [17] and $(+)_{589}$-$[Co(CO_3)(diars)_2]^+$ [16] have been reported to be Λ. From a comparison of three CD spectra in Fig. 3, the $(+)_{589}$-isomer of the dmpe complex can also be assigned to the Λ configuration. The dmpe complex shows a relatively strong negative CD band in the first d-d band region. Similar strong negative bands have been observed for cobalt(III)-phosphine complexes such as Δ-$[Co(en)_n(dmpe)_{3-n}]^{3+}$ (n=1, 2)[1] or Δ-$[Co(en)_n(edmp)_{3-n}]^{3+}$ (n=0, 1; edmp=$NH_2CH_2CH_2P(CH_3)_2$).[20]

Figure 4 shows absorption spectra of *trans*-$[CoX_2(dmpe)_2]^{n+}$($X=H_2O$, CN^-, NCO^-, NCS^-) and Table 2 lists the data. For *trans*-$[Co(H_2O)_2(dmpe)_2]^{3+}$, the

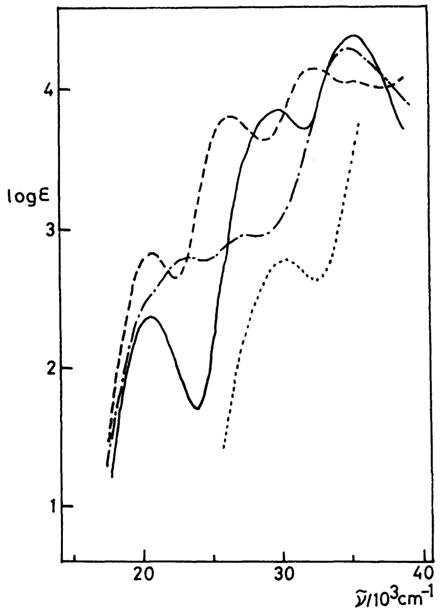

Fig. 4. Absorption spectra of *trans*-[Co(NCS)$_2$(dmpe)$_2$]$^+$ in acetonitrile (----), *trans*-[Co(NCO)$_2$(dmpe)$_2$]$^+$ in acetonitrile (——), *trans*-[Co(OH$_2$)$_2$(dmpe)$_2$]$^{3+}$ in 0.5 mol dm^{-3} HClO$_4$ (-·-·-), and *trans*-[Co(CN)$_2$(dmpe)$_2$]$^+$ in methanol (······).

Table 2. Absorption Spectral Data of *trans*-[CoX$_2$(dmpe)$_2$]$^{n+}$

Complex	$\tilde{\nu}$/10^3 cm^{-1} (logε)	Solvent
trans-[CoCl$_2$(dmpe)$_2$]$^+$	17.3(1.92)	CH$_3$OH
	26.2(3.58)	
	35.1(4.36)	
	40.4(4.16)	
trans-[Co(OH$_2$)(dmpe)$_2$]$^{3+}$	20(2.4)$^{a)}$	b)
	23.3(2.80)	
	27.3(2.96)	
	34.7(4.30)	
trans-[Co(NCS)$_2$(dmpe)$_2$]$^+$	20.6(2.82)	CH$_3$CN
	26.3(3.81)	
	32.1(4.16)	
	35(4.2)$^{a)}$	
	41.5(4.51)	
trans-[Co(NCO)$_2$(dmpe)$_2$]$^+$	20.5(2.37)	CH$_3$CN
	29.6(3.86)	
	34.9(4.39)	
	42(3.8)$^{a)}$	
trans-[Co(CN)$_2$(dmpe)$_2$]$^+$	30.5(2.77)	CH$_3$OH
	40.5(4.63)	

a) Shoulder. b) 0.5 mol dm^{-3} HClO$_4$.

shoulder around 20000 cm^{-1} and the band at 23300 cm^{-1} can be assigned to two components of the splitting first d-d band, and the band at 27300 cm^{-1} to the second d-d band, since *trans*-[Co(H$_2$O)$_2$(en)$_2$]$^{3+}$ shows similar d-d bands with three peaks at 18200, 22500, and 29000 cm^{-1}.[21] The *trans*-[Co(CN)$_2$(dmpe)$_2$]$^+$ complex shows a single d-d band assignable to the first d-d band. The band is rather broad and appears to involve another band. However, it remains unknown whether the band consists of two components of the splitting first d-d band or of the first and second d-d bands with a very small energy difference. The *trans*-[Co(CN)$_2$(en)$_2$]$^+$ complex shows a clear splitting in the first d-d band, giving a shoulder around 21000 cm^{-1} and a band at 24400 cm^{-1}.[22] Neither *trans*-[Co(NCO)$_2$(dmpe)$_2$]$^+$ nor *trans*-[Co(NCS)$_2$(dmpe)$_2$]$^+$ shows splittings on the first d-d band. The *trans*-[Co(NCS)$_2$(en)$_2$]$^+$ complex does not exhibit splitting either, giving a single first d-d band at 19700 cm^{-1}.[23] The NCO$^-$ complex gives the first d-d band at nearly the same position as that of the NCS$^-$ complex, and can be assigned to the N-bonding isomer for NCO$^-$, since the NCS$^-$ ligand in the latter complex has been indicated to coordinate through the N atom by the IR spectrum (vide ante). The energies of the first d-d bands of the NCO$^-$ and NCS$^-$ complexes are rather lower than that of the aqua complex, although the rankings of NCO$^-$, NCS$^-$ and H$_2$O are similar in the spectrochemical series.[14] The phosphine[6] and arsine[24] complexes of cobalt(III) containing NCS$^-$ bonded through the N atom have been reported to give the first d-d band at a lower wavenumber than that expected from the ranking of NCS$^-$ in the spectrochemical series.

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