3042 © 1992 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, ***65***, 3042—3048 (1992) [Vol. 65, No. 11

Preparation and Characterization of Co(III)-Dimethyldithiocarbamato Complexes Containing 1,2-Bis(dimethoxyphosphino)ethane. Molecular Structures of $[Co\{(CH_3)_2NC(S)S\}\{R_2P(CH_2)_2PR_2\}_2](BF_4)_2$ ($R=CH_3O$ and CH_3)

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(Received June 11, 1992)

The $[Co(dtc)_{3-n}(dmope)_n]^{n+}$ (n=1, 2) complexes were prepared, where dtc and dmope denote a dimethyldithiocarbamate ion and 1,2-bis(dimethoxyphosphino)ethane, respectively. The absorption and magnetic circular dichroism (MCD) spectra, and reduction and oxidation potentials were compared with those of the corresponding 1,2-bis(dimethylphosphino)ethane (dmpe) and related complexes. The molecular structures of $[Co(dtc)(dmope)_2](BF_4)_2$ (**1**) and $[Co(dtc)(dmpe)_2](BF_4)_2$ (**2**) were determined by the X-ray diffraction method. Crystal data are; for **1**, monoclinic, Cc, a=18.154(5), b=12.533(2), c=14.447(3) Å, β=101.69(2)°, V=3219(1) Å^3, D_x=1.61, D_m=1.60(3) g cm^{-3}, and Z=4, R=0.044 for 3259 reflections; for **2**, monoclinic, $P2_1/a$, a=18.967(3), b=10.333(1), c=14.459(2) Å, β=90.10(2)°, V=2833.8(7) Å^3, D_x=1.53, D_m=1.54(4) g cm^{-3}, Z=4, R=0.052 for 5662 reflections. The average Co–P bond distance trans to S is 2.186(2) Å for **1** and 2.240(1) Å for **2**, and that trans to P is 2.226(2) Å for **1** and 2.278(1) Å for **2**. The Co–P distances in **1** are shorter by ca. 0.05 Å than those in **2**, while the average Co–S bond distances are similar, 2.288(1) Å for **1** and 2.282(3) Å for **2**.

While a large number of cobalt(III)–phosphine complexes have been prepared recently, only $[Co(dmope)_3]^{3+}$ (dmope=$(CH_3O)_2PCH_2CH_2P(OCH_3)_2$[1]) and $[Co(X)(dmgH)_2\{(P(OCH_3)_2(C_6H_5)\}]$ (X=Cl, CH_3; dmgH= dimethylglyoximate ion)[2] have been reported for cobalt(III)–phosphonite complexes to our knowledge. Phosphonites ($PR(OR)_2$) as well as phosphites ($P(OR)_3$) are said to be unfavorable ligands for hard metals such as cobalt(III) because of the stronger π-acidity than phosphines (PR_3).[3,4] On the other hand, $PR(OR)_2$ and $P(OR)_3$ have smaller cone angles[5] than those of the corresponding PR_3, and may be sterically favorable for complex formation. Thus it is interesting to compare structures and properties of phosphite or phosphonite complexes with those of the corresponding phosphine complexes. This paper describes the preparation of new dmope complexes, $[Co(dtc)_{3-n}(dmope)_n]^{n+}$ (dtc= dimethyldithiocarbamate ion; n=1,2) and comparisons of their spectral and electrochemical properties with those of the corresponding $(CH_3)_2PCH_2CH_2P(CH_3)_2$ (dmpe) complexes,[6] in addition to the X-ray crystal analyses of $[Co(dtc)(dmope)_2](BF_4)_2$ and $[Co(dtc)(dmpe)_2](BF_4)_2$. For X-ray crystal structure analysis of the dmope complex, only $[Mo(\eta^5\text{-}C_5H_5)(CO)(C_2H_4)(dmope)]PF_6$ has been reported so far.[7]

Experimental

The dmope ligand was prepared by the method of King and Rhee[8] and handled under an atmosphere of nitrogen until it formed air-stable cobalt(III) complexes. The $[Co(dtc)_{3-n}(dmpe)_n](BF_4)_n$ (n=1, 2) complexes were prepared as described previously.[6]

$[Co(dtc)(dmope)_2](BF_4)_2$. To a methanol solution (15 cm^3) of $Co(BF_4)_2\cdot 6H_2O$ (1.36 g, 4.0 mmol) was added a solution of dmope (1.93 g, 9.0 mmol) in 6 cm^3 of methanol with stirring. A pale yellow precipitate appeared immediately. The suspension was stirred for 1 h, and then mixed with a solution of bis(dimethylthiocarbamoyl) disulfide (0.480 g, 2.0 mmol) in 100 cm^3 of methanol–dichloromethane (20 : 1). The mixture was stirred for 12 h. The resulting pale green precipitate (1.75 g) was collected by filtration and washed with 50 cm^3 of dichloromethane to remove green $[Co(dtc)_3]$. The remained pale yellow precipitate (0.95 g) was dissolved in 1 dm^3 of water and applied on a column (ϕ 3 cm×25 cm) of SP-Sephadex C-25. The adsorbed product was eluted with 0.1 mol dm^{-3} Na_2SO_4. A yellow band appeared and was followed by a colorless band ($[Co(dmope)_3]^{3+}$). The yellow eluate was concentrated to ca. 2 cm^3 under reduced pressure. On addition of a methanol solution (3 cm^3) of $LiBF_4$ (1.0 g) and cooling in a refrigerator for 12 h the concentrate yielded yellow needle-like crystals, which were collected by filtration and washed with cold methanol (5 cm^3) and diethyl ether (5 cm^3). Yield: 0.32 g (9.9%). Found: C, 23.01; H, 5.08; N, 1.79%. Calcd for $[Co(dtc)(dmope)_2](BF_4)_2$=$C_{15}H_{38}NB_2CoF_8O_8P_4S_2$: C, 23.07; H, 4.90; N, 1.79%. ^{1}H NMR (CD_3CN) δ=3.27 (s, $N(CH_3)_2$), 3.88 (m, $P(OCH_3)_2$).

$[Co(dtc)_2(dmope)]PF_6$. To a mixture of $[Co(dtc)_3]$ (0.840 g, 2.0 mmol) and active charcoal (0.1 g) in 160 cm^3 of dichloromethane–methanol (3 : 5) was added a methanol solution (2 cm^3) of dmope (0.64 g, 3.0 mmol). The mixture was stirred at room temperature for 3 d, and then active charcoal was filtered off. The reddish green filtrate was evaporated to dryness under reduced pressure. The residue was washed with diethyl ether (200 cm^3×2), mixed with 1 dm^3 of water, and insoluble $[Co(dtc)_3]$ was filtered off. The orange filtrate was applied on a column (ϕ 3 cm×25 cm) of SP-Sephadex C-25, and the adsorbed products were eluted with 0.03 mol dm^{-3} Na_2SO_4. The eluate of a major orange band was evaporated to dryness under reduced pressure, and the orange complex was extracted with 50 cm^3 of ethanol. The extract was evaporated again to dryness under reduced pressure, and the residue was dissolved in 3 cm^3 of water. On addition of an aqueous solution of NH_4PF_6 (0.8 g) the solution afforded orange crystals immediately, which were collected by filtration and washed with cold water (5 cm^3). Yield: 0.03 g (2.3%). Found: C, 21.91; H, 4.23; N, 4.27%. Calcd for $[Co(dtc)_2(dmope)]PF_6$= $C_{12}H_{28}N_2CoF_6O_4P_3S_4$: C, 21.89; H, 4.29; N, 4.25%. ^{1}H NMR

(CD_3CN) δ=3.16 (s, $N(CH_3)_2$), 3.23 (s, $N(CH_3)_2$), 3.83 (t, $P(OCH_3)_2$).

[Co(dmope)$_3$](PF$_6$)$_3$. This complex was prepared by a modified method of Houlding and Miskowski.[1] To a methanol solution (20 cm^3) of $Co(BF_4)_2 \cdot 6H_2O$ (0.34 g, 1 mmol) was added dmope (0.80 g, 3.3 mmol). A pale-yellow precipitate was yielded immediately. After 1 h, air was bubbled through the mixture for 12 h. The pale yellow precipitate turned white. It was collected by filtration and dissolved in 1 dm^3 of water. The solution was applied on a column (ϕ 3 cm×20 cm) of SP-Sephadex C-25. By elution with 0.15 mol dm^{-3} Na_2SO_4, the eluate of a main colorless band was collected and evaporated to dryness under reduced pressure. The complex was extracted from the residue with methanol (30 cm^3), and the extract was evaporated again to dryness under reduced pressure. The complex was dissolved in 3 cm^3 of water, and an aqueous solution of NH_4PF_6 (1.6 g) was added to the solution. White crystals were obtained on cooling the mixture in a refrigerator overnight, collected by filtration, and washed with cold water. Yield: 0.38 g (33.5%). Found: C, 18.7; H, 4.31%. Calcd for [Co(dmope)$_3$](PF$_6$)$_3$=$C_{18}H_{48}CoF_{18}O_{12}P_9$: C, 19.03; H, 4.26%. ^{1}H NMR (CD_3CN) δ=3.98 (br, $P(OCH_3)_2$).

Crystal Structure Determination. A yellow crystal of [Co(dtc)(dmope)$_2$](BF$_4$)$_2$ (**1**) (0.90×0.43×0.38 mm^3), which was obtained by slowly cooling a saturated CH_3CN–C_6H_6 (2:1) solution at 40 °C, was used for the data collection. Crystal data: monoclinic, Cc, a=18.154(5), b=12.533(2), c=14.447(3) Å, β=101.69(2)°, V=3219(1) Å^3, D_x=1.61, D_m=1.60 (3) g cm^{-3}, Z=4, μ(Mo $K\alpha$)=9.3 cm^{-1}. For [Co(dtc)(dmpe)$_2$](BF$_4$)$_2$ (**2**), a yellow-orange crystal (0.28×0.40×0.40 mm^3), which was grown from a methanol solution, was used for the X-ray work. Crystal data: monoclinic, $P2_1/a$, a=18.967(3), b=10.333(1), c=14.459(2) Å, β=90.10(2)°, V=2833.8(7) Å^3, D_x=1.53, D_m=1.54(4) g cm^{-3}, Z=4, μ(Mo $K\alpha$)=10.2 cm^{-1}. Diffraction data for both **1** and **2** were collected on a Rigaku AFC-5R diffractometer with graphite monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å). Within the range $2\theta < 60°$, 3259 and 5562 independent reflections were obtained for **1** and **2**, respectively, with $|F_o| > 3\sigma(|F_o|)$. All the computations were performed on a HITAC M-680H computer at the Computer Center of the Institute for Molecular Science with the program system UNICS III.[9] Absorption corrections were made by using the DABEX program of the Computer Center. The structures were solved by the usual heavy-atom method. For **1**, the positions of all the non-hydrogen atoms were identified in subsequent Fourier maps, but those of hydrogen atoms could not be determined. Final R was 0.044 for 3259 unique reflections, and the atomic parameters of non-hydrogen atoms are listed in Table 1. For **2**, the positions of all the non-hydrogen atoms were identified in a similar manner in subsequent Fourier maps, and those of 31 among 38 hydrogen atoms were identified on the difference-Fourier synthesis. Final R was 0.052 for the 5662 reflections. The atomic parameters of non-hydrogen atoms are listed in Table 2. The anisotropic thermal parameters for all the non-hydrogen atoms, hydrogen atomic parameters, and the complete lists of $|F_o|$ and $|F_c|$ values of both complexes are deposited as Document No. 9042 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Spectroscopic and Electrochemical Measurements. Absorption and MCD spectra were obtained with a Hitachi U-3400 spectrophotometer and a JASCO MOE-1 spectropolarimeter at the 1.5 T magnetic field at 25 °C, respectively. ^{1}H NMR spectra were recorded on a Hitachi R-90HS spectrometer at 36 °C.

Electrochemical measurements were carried out by rotating disk electrode voltammetry (RDE) on CH_3CN solutions ([Co]: 1.0×10^{-3} mol dm^{-3}, 0.1 mol dm^{-3} Bu_4NBF_4) at 25±1 °C by using a FUSO 321B potential sweep unit and a FUSO HECS 317B potentiostat. A grassy-carbon rotating-disk (1500 rev min^{-1}) attached to a Yanako P10-RE Mark II head, a platinum-wire, and a Ag/Ag$^+$ electrode (Ag/0.01 mol dm^{-3} $AgNO_3$) were used as the working, auxiliary, and reference electrodes, respectively. The oxidation wave of ferrocene was observed at +0.08 V vs. Ag/Ag$^+$.

Table 1. Positional Parameters (×10^4) and Equivalent Isotropic Temperature Factors of [Co(dtc)(dmope)$_2$](BF$_4$)$_2$

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
Co	3539(1)	4038.4(4)	3806(1)	2.6	C(13)	2313(4)	3348(5)	1867(4)	4.0
S(1)	3278(1)	5474(1)	4675(1)	3.4	C(21)	4839(4)	3481(5)	1930(5)	4.6
S(2)	3795(1)	5452(1)	2946(1)	3.4	C(22)	4265(3)	896(4)	2665(6)	4.8
P(1)	2360(1)	4096(1)	2966(1)	3.3	C(23)	2776(4)	2362(6)	2074(5)	4.9
P(2)	3722(1)	2844(1)	2786(1)	3.2	C(31)	2869(8)	816(7)	4909(8)	8.9
P(3)	3345(1)	2838(1)	4840(1)	3.2	C(32)	2175(5)	3401(11)	5645(7)	8.4
P(4)	4709(1)	4084(1)	4627(1)	3.2	C(33)	4216(3)	2437(5)	5492(4)	3.7
O(11)	1986(2)	5174(4)	2637(3)	4.7	C(41)	5499(4)	5853(7)	4425(8)	6.8
O(12)	1784(2)	3494(4)	3488(3)	4.2	C(42)	6007(4)	3114(9)	4564(7)	6.8
O(21)	4074(2)	3220(4)	1901(3)	4.2	C(43)	4715(4)	3485(6)	5767(5)	5.2
O(22)	4186(2)	1839(3)	3251(3)	4.0	B(1)	1831(6)	9783(11)	2153(6)	6.8
O(31)	2902(3)	1844(3)	4399(3)	4.4	B(2)	5269(4)	291(5)	318(6)	4.2
O(32)	2992(3)	3254(4)	5651(3)	4.9	F(11)	2535(3)	9865(7)	2271(10)	13.8
O(41)	5073(2)	5197(3)	5007(3)	4.4	F(12)	1536(4)	8829(5)	1816(7)	11.4
O(42)	5261(2)	3499(4)	4106(4)	5.1	F(13)	1333(5)	10527(7)	2260(8)	12.8
N(1)	3533(8)	7284(3)	3804(11)	4.3	F(14)	1714(10)	10266(15)	1445(8)	19.7
C(1)	3512(7)	6237(3)	3820(10)	3.3	F(21)	4652(5)	171(6)	−257(6)	12.1
C(2)	3718(6)	7889(5)	3023(6)	6.2	F(22)	5658(7)	−187(10)	−112(10)	16.2
C(3)	3279(5)	7900(5)	4563(6)	5.7	F(23)	5404(10)	1186(12)	113(22)	26.2
C(11)	1537(5)	5912(6)	3048(5)	5.5	F(24)	4969(9)	−94(10)	1111(10)	17.2
C(12)	991(4)	3307(8)	3043(8)	7.3					

Table 2. Positional Parameters ($\times 10^4$) and Equivalent Isotropic Temperature Factors of $[Co(dtc)(dmpe)_2](BF_4)_2$

Atom	x	y	z	$B_{eq}/Å^2$	Atom	x	y	z	$B_{eq}/Å^2$
Co	4453.9(3)	4077.0(5)	2482.2(4)	2.3	C(2)	6360(3)	7347(6)	1780(4)	5.6
S(1)	5054(1)	5548(1)	1594(1)	3.1	C(3)	6715(3)	6359(7)	3280(4)	5.7
S(2)	5404(1)	4632(1)	3369(1)	3.3	C(4)	3627(3)	5571(5)	4382(4)	4.6
P(1)	3878(1)	5742(1)	3181(1)	3.0	C(5)	4295(3)	7329(5)	3206(4)	4.7
P(2)	3512(1)	3980(1)	1549(1)	2.9	C(6)	3054(3)	6071(5)	2551(4)	4.3
P(3)	5114(1)	2516(1)	1784(1)	3.2	C(7)	2781(2)	4847(5)	2104(4)	4.1
P(4)	4101(1)	2504(1)	3441(1)	2.9	C(8)	3637(3)	4833(5)	476(3)	3.9
F(1)	4072(2)	−531(4)	5128(3)	8.9	C(9)	3097(3)	2476(5)	1184(4)	4.9
F(2)	3448(2)	−1688(5)	6119(3)	9.4	C(10)	4909(3)	2072(6)	584(4)	4.9
F(3)	2973(3)	−941(6)	4817(4)	10.8	C(11)	6063(3)	2752(6)	1706(4)	5.0
F(4)	3237(3)	394(6)	5933(4)	12.9	C(12)	5042(3)	1023(5)	2459(4)	4.8
F(5)	3116(3)	7808(4)	503(3)	10.9	C(13)	4333(3)	936(5)	2932(4)	4.4
F(6)	3310(3)	9756(4)	−44(3)	8.9	C(14)	4565(3)	2506(5)	4536(3)	4.1
F(7)	2853(3)	9480(4)	1361(4)	10.7	C(15)	3186(3)	2255(6)	3797(4)	5.0
F(8)	3937(3)	9068(7)	1100(3)	12.1	B(1)	3448(3)	−677(7)	5536(5)	4.9
N	6209(2)	6402(4)	2505(3)	4.2	B(2)	3313(4)	9022(6)	724(5)	4.9
C(1)	5646(2)	5647(4)	2490(3)	3.2					

Results and Discussion

In a previous paper,[6] $[Co(dtc)(dmpe)_2](BF_4)_2$ and $[Co(dtc)_2(dmpe)]BF_4$ were isolated in yields of 17 and 14%, respectively, from the product resulted by oxidation of a methanol solution containing $Co(BF_4)_2 \cdot 6H_2O$ and dmpe with bis(dimethylthiocarbamoyl) disulfide ($((CH_3)_2NC(S)S-)_2$). A similar reaction with dmope, in place of dmpe yielded only $[Co(dtc)(dmope)_2](BF_4)_2$ in poor yield (9.9%) other than $[Co(dtc)_3]$ and $[Co(dmope)_3]^{3+}$. Disproportionation might occur in this reaction. The $[Co(dtc)_2(dmope)]^+$ complex was obtained by reaction of $[Co(dtc)_3]$ with dmope in a mixture of CH_2Cl_2 and CH_3OH in the presence of active charcoal, but the yield was very poor (2.3%). Several attempts for more efficient synthesis of these mixed complexes were unsuccessful. The $[Co(dtc)_2(dmope)]BF_4$ and $[Co(dtc)(dmope)_2](BF_4)_2$ complexes are stable both in the solid state and solution.

Figures 1 and 2 show the structures of complex ions of **1** and **2**, respectively. The bond distances and angles are listed in Tables 3 and 4. The Co atoms in both complexes are octahedrally coordinated by four P and two S atoms. Both dmope and dmpe chelate rings take a nearly typical gauche conformation, and the average torsion (P–C–C–P) and chelate (P–Co–P) angles are 53.1 (5)° and 85.3(1)° in **1**, and 43.9(4)° and 85.54(5)° in **2**, respectively. The chelate structure of dmpe in **2** is very similar to those in $[Co(O_2)(dmpe)_2]^+$ [10] and $[Co(en)_2(dmpe)]^{3+}$ (en=$NH_2CH_2CH_2NH_2$).[11] The Co–P distances are fairly different between **1** and **2**. The distances in **1**, 2.226(3) Å (av, trans to P) and 2.186(3) Å (av, trans to S) are shorter by ca. 0.05 Å than the corresponding distances in **2**, 2.278(1) Å (av, trans to P) and 2.240(1) Å (av, trans to S). The differences in Co–P distance between **1** and **2** may be attributed to the difference in bulkiness of donor groups of dmope and dmpe. The bulkiness estimated by the cone angle[5] is

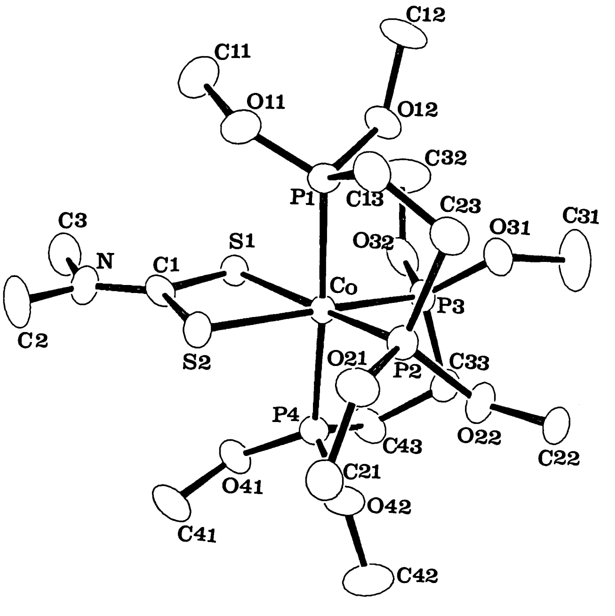

Fig. 1. A perspective view of $[Co(dtc)(dmope)_2]^{2+}$.

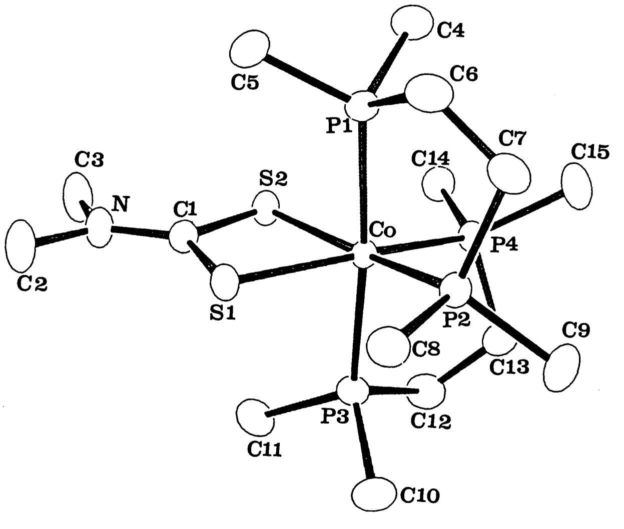

Fig. 2. A perspective view of $[Co(dtc)(dmpe)_2]^{2+}$.

Table 3. Bond Distances (l/Å) and Angles (ϕ/°) of $[Co(dtc)(dmope)_2](BF_4)_2$

Co–S(1)	2.298(2)	Co–S(2)	2.265(2)	P(2)–Co–P(3)	93.26(9)	P(2)–Co–P(4)	96.86(9)
Co–P(1)	2.237(2)	Co–P(2)	2.172(2)	P(3)–Co–P(4)	85.51(9)	Co–S(1)–C(1)	86.2(5)
Co–P(3)	2.199(2)	Co–P(4)	2.214(2)	Co–S(2)–C(1)	85.5(5)	Co–P(1)–O(11)	120.6(2)
S(1)–C(1)	1.683(15)	S(2)–C(1)	1.757(15)	Co–P(1)–O(12)	112.0(2)	Co–P(1)–C(13)	109.0(2)
P(1)–O(11)	1.544(5)	P(1)–O(12)	1.597(5)	O(11)–P(1)–O(12)	105.6(3)	O(11)–P(1)–C(13)	103.9(3)
P(1)–C(13)	1.831(7)	P(2)–O(21)	1.613(5)	O(12)–P(1)–C(13)	104.4(3)	Co–P(2)–O(21)	118.5(2)
P(2)–O(22)	1.587(5)	P(2)–C(23)	1.912(8)	Co–P(2)–O(22)	113.7(2)	Co–P(2)–C(23)	109.8(3)
P(3)–O(31)	1.549(5)	P(3)–O(32)	1.536(5)	O(21)–P(2)–O(22)	107.8(3)	O(21)–P(2)–C(23)	97.1(3)
P(3)–C(33)	1.742(6)	P(4)–O(41)	1.593(5)	O(22)–P(2)–C(23)	108.6(3)	Co–P(3)–O(31)	114.3(2)
P(4)–O(42)	1.554(5)	P(4)–C(43)	1.807(8)	Co–P(3)–O(32)	115.8(2)	Co–P(3)–C(33)	108.2(2)
O(11)–C(11)	1.438(10)	O(12)–C(12)	1.473(13)	O(31)–P(3)–O(32)	109.0(3)	O(31)–P(3)–C(33)	109.2(2)
O(21)–C(21)	1.418(9)	O(22)–C(22)	1.477(9)	O(32)–P(3)–C(33)	99.1(3)	Co–P(4)–O(41)	119.5(2)
O(31)–C(31)	1.491(16)	O(32)–C(32)	1.493(15)	Co–P(4)–O(42)	111.8(2)	Co–P(4)–C(43)	107.8(3)
O(41)–C(41)	1.498(12)	O(42)–C(42)	1.462(12)	O(41)–P(4)–O(42)	108.4(3)	O(41)–P(4)–C(43)	97.2(3)
N(1)–C(1)	1.313(21)	N(1)–C(2)	1.455(19)	O(42)–P(4)–C(43)	111.1(3)	P(1)–O(11)–C(11)	133.4(5)
N(1)–C(3)	1.488(18)	C(13)–C(23)	1.490(10)	P(1)–O(12)–C(12)	123.0(6)	P(2)–O(21)–C(21)	125.9(4)
C(33)–C(43)	1.599(10)			P(2)–O(22)–C(22)	119.8(4)	P(3)–O(31)–C(31)	124.1(7)
				P(3)–O(32)–C(32)	127.2(7)	P(4)–O(41)–C(41)	120.9(5)
S(1)–Co–S(2)	76.99(8)	S(1)–Co–P(1)	89.50(9)	P(4)–O(42)–C(42)	124.4(6)	C(1)–N(1)–C(2)	123.1(14)
S(1)–Co–P(2)	170.7(1)	S(1)–Co–P(3)	94.91(9)	C(1)–N(1)–C(3)	119.5(13)	C(2)–N(1)–C(3)	117.1(12)
S(1)–Co–P(4)	88.18(9)	S(2)–Co–P(1)	87.57(9)	S(1)–C(1)–S(2)	111.3(8)	S(1)–C(1)–N(1)	126.3(12)
S(2)–Co–P(2)	95.20(9)	S(2)–Co–P(3)	170.7(1)	S(2)–C(1)–N(1)	122.3(12)	P(1)–C(13)–C(23)	109.0(5)
S(2)–Co–P(4)	89.57(9)	P(1)–Co–P(2)	85.12(9)	P(2)–C(23)–C(13)	104.7(5)	P(3)–C(33)–C(43)	107.7(5)
P(1)–Co–P(3)	97.08(9)	P(1)–Co–P(4)	176.7(1)	P(4)–C(43)–C(33)	102.5(5)		

Table 4. Bond Distances (l/Å) and Angles (ϕ/°) of $[Co(dtc)(dmpe)_2](BF_4)_2$

Co–S(1)	2.293(1)	Co–S(2)	2.283(1)	P(2)–Co–P(3)	98.03(5)	P(2)–Co–P(4)	94.05(5)
Co–P(1)	2.276(1)	Co–P(2)	2.239(1)	P(3)–Co–P(4)	85.74(5)	Co–S(1)–C(1)	86.6(2)
Co–P(3)	2.279(1)	Co–P(4)	2.240(1)	Co–S(2)–C(1)	87.1(2)	Co–P(1)–C(4)	118.6(2)
S(1)–C(1)	1.717(5)	S(2)–C(1)	1.711(5)	Co–P(1)–C(5)	118.7(2)	Co–P(1)–C(6)	109.1(2)
P(1)–C(4)	1.811(5)	P(1)–C(5)	1.820(5)	C(4)–P(1)–C(5)	100.7(3)	C(4)–P(1)–C(6)	105.6(3)
P(1)–C(6)	1.839(5)	P(2)–C(7)	1.838(5)	C(5)–P(1)–C(6)	102.3(3)	Co–P(2)–C(7)	108.5(2)
P(2)–C(8)	1.800(5)	P(2)–C(9)	1.820(6)	Co–P(2)–C(8)	113.1(2)	Co–P(2)–C(9)	123.9(2)
P(3)–C(10)	1.836(6)	P(3)–C(11)	1.820(6)	C(7)–P(2)–C(8)	103.8(2)	C(7)–P(2)–C(9)	102.5(2)
P(3)–C(12)	1.831(5)	P(4)–C(13)	1.833(5)	C(8)–P(2)–C(9)	103.0(3)	Co–P(3)–C(10)	118.7(2)
P(4)–C(14)	1.809(5)	P(4)–C(15)	1.829(5)	Co–P(3)–C(11)	118.5(2)	Co–P(3)–C(12)	108.6(2)
N(1)–C(1)	1.324(6)	N(1)–C(2)	1.462(8)	C(10)–P(3)–O(11)	100.6(3)	C(10)–P(3)–C(12)	106.1(3)
N(1)–C(3)	1.475(7)	C(6)–C(7)	1.511(8)	C(11)–P(3)–C(12)	102.8(3)	Co–P(4)–C(13)	108.7(2)
C(12)–C(13)	1.513(8)			Co–P(4)–C(14)	113.3(2)	Co–P(4)–C(15)	124.1(2)
				C(13)–P(4)–C(14)	103.7(2)	C(13)–P(4)–C(15)	102.5(3)
S(1)–Co–S(2)	75.91(4)	S(1)–Co–P(1)	89.21(5)	C(14)–P(4)–C(15)	102.3(3)	C(1)–N(1)–C(2)	122.8(4)
S(1)–Co–P(2)	95.04(5)	S(1)–Co–P(3)	86.99(5)	C(1)–N(1)–C(3)	121.2(4)	C(2)–N(1)–C(3)	116.0(4)
S(1)–Co–P(4)	167.64(5)	S(2)–Co–P(1)	86.55(5)	S(1)–C(1)–S(2)	110.4(2)	S(1)–C(1)–N(1)	125.1(4)
S(2)–Co–P(2)	167.92(5)	S(2)–Co–P(3)	89.57(5)	S(2)–C(1)–N(1)	124.6(4)	P(1)–C(6)–C(7)	110.4(4)
S(2)–Co–P(4)	94.05(5)	P(1)–Co–P(2)	85.33(5)	P(2)–C(7)–C(6)	109.6(3)	P(3)–C(12)–C(13)	111.0(4)
P(1)–Co–P(3)	175.13(5)	P(1)–Co–P(4)	94.05(5)	P(4)–C(13)–C(12)	110.1(4)		

100° for dmope and 107° for dmpe. The less bulky ligand could come close to the Co(III) ion to form shorter Co–P bonds than those formed with dmpe. The dmope ligand will be sterically more favorable than dmpe. For the related complexes, Marzilli et al.[2] have reported that the Co–P distances in *trans*-$[Co(X)(dmgH)_2\{(P(C_6H_5)_{3-n}(OCH_3)_n\}]$ (X=Cl, CH_3; n=0, 1, 2, 3) become shorter progressively by replacing the bulky C_6H_5 group with the small OCH_3 one.

The Co–S distances are similar in **1** (av, 2.282(2) Å) and **2** (av, 2.288(1) Å). These distances are similar to that trans to P in $[Co(S_2COC_2H_5)_2(dmpe)]^+$ (2.290 (2) Å),[12] but fairly longer than that trans to S in this dmpe complex (av. 2.255(1) Å) and those in $[Co(dtc)_3]$ (av, 2.264(2) Å)[13] and $[Co(dtc)(en)_2]^{2+}$ (2.263(3) Å).[14] Thus trans influences of dmope and dmpe are larger than those of the sulfur ligands, and these phosphorus donor ligands exert influence to a similar extent on the Co(III) ion. In **1** and **2** the longer distances of the Co–P bonds trans to P than those trans to S are attributable to the mutual effect of two trans labilizing phosphorus donor atoms in the trans positions.

The absorption and MCD spectra of $[Co(dtc)_2(P\text{–}P)]^+$ and $[Co(dtc)(P\text{–}P)_2]^{2+}$ (P–P=dmope and dmpe) are given in Figs. 3 and 4, respectively. Figure 5 shows the absorption and MCD spectra of $[Co(dtc)_3]$ and

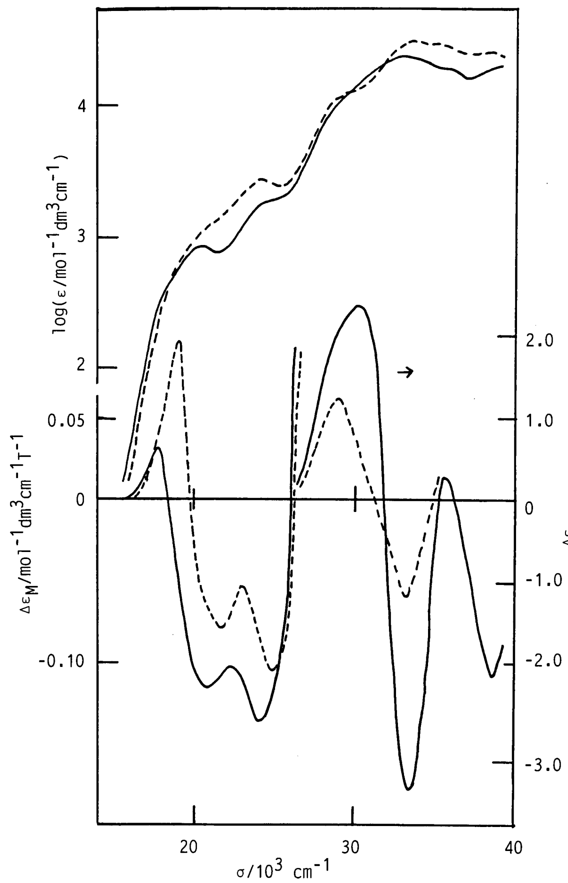

Fig. 3. Absorption and MCD spectra of $[Co(dtc)_2(dmpe)]BF_4$ (——) and $[Co(dtc)_2(dmope)]PF_6$ (---) in CH_3CN solutions.

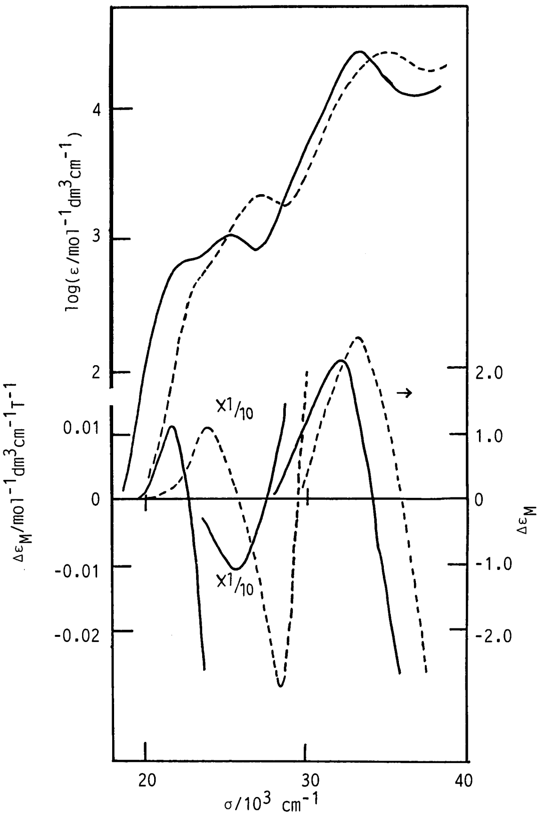

Fig. 4. Absorption and MCD spectra of $[Co(dtc)(dmpe)_2](BF_4)_2$ (——) and $[Co(dtc)(dmope)_2](BF_4)_2$ (---) in CH_3CN solutions.

$[Co(dmope)_3]^{3+}$. Table 5 lists the spectral data of these complexes. The mixed ligand complexes show a few broad ligand field bands in the absorption spectra. The MCD spectra were taken for estimating peak positions of the broad bands and that of the related $[Co(dmope)_3]^{3+}$ complexes. The dmope complexes show absorption and MCD spectra similar to those of the corresponding dmpe complexes, except that the spectra in the ligand field band region of the dmope complexes are shifted to the higher energy than those of the dmpe complexes. It is known that the ligand field strength of $P(OR)_3$ is stronger than that of PR_3.[1] The ligand field strength of dmope is also stronger than that of dmpe, and the result is consistent with the data of X-ray analysis that the Co–P bond is shorter than that in **2**.

The first d-d bands of $[Co(dtc)_2(dmope)]^+$ (*cis*-$[CoS_4P_2]$-type) and $[Co(dtc)(dmope)_2]^{2+}$ (*cis*-$[CoS_2P_4]$-type) are expected to split into two components. The split components can be estimated from the observed band energies of $[Co(dtc)_3]$ and $[Co(dmope)_3]^{3+}$ on the basis of the Yamatera rule.[15] The MCD peaks at 16050 and 30300 cm^{-1} of $[Co(dtc)_3]$ and $[Co(dmope)_3]^{3+}$, were used for the band energies respectively. The calculated values of 19600 and 23200 cm^{-1} for $[Co(dtc)_2$-

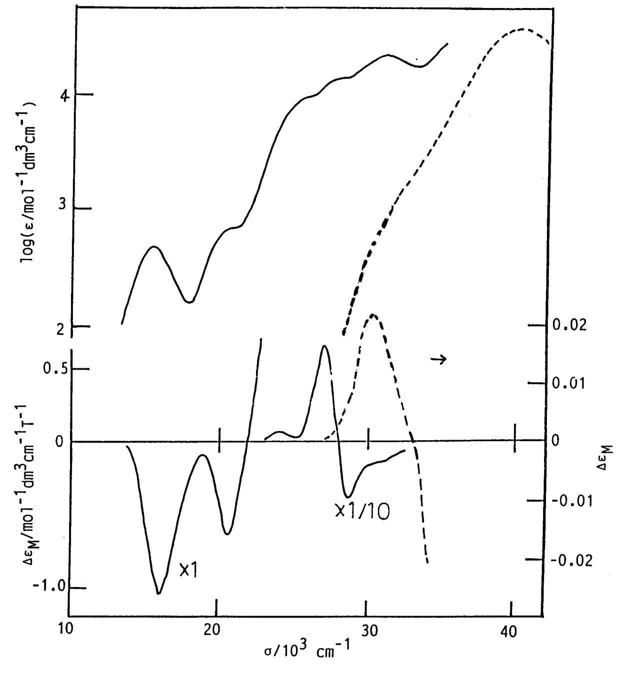

Fig. 5. Absorption and MCD spectra of $[Co(dtc)_3]$ (——) and $[Co(dmope)_3](PF_6)_3$ (---) in CH_3CN solutions.

Table 5. Absorption and MCD Spectral Data of $[Co(dtc)_{3-n}(dmope\ or\ dmpe)_n]^{n+}$ ($n=0$—3) Complexes[a)]

Complex	σ (log ε)[b)] / σ ($\Delta\varepsilon_M$)[b)]
$[Co(dtc)_3]$	15.5 (2.86), 21.1 (2.82), 26.0 (3.96)^{sh}, 28.1 (4.10)^{sh}, 31.3 (4.35)
MCD	16.0 (−0.11), 20.6 (−0.06), 24.1 (+0.32), 27.0 (+3.35), 28.7 (−1.96)
$[Co(dtc)_2(dmope)]PF_6$	22.0 (3.16)^{sh}, 24.4 (3.42), 30.0 (4.11)^{sh}, 34.5 (4.47), 37.8 (4.39)^{sh}
MCD	19.0 (+0.09), 22.0 (−0.08), 24.7 (−0.11), 29.0 (+1.28), 33.0 (−1.31)
$[Co(dtc)(dmope)_2](BF_4)_2$	24.5 (2.86)^{sh}, 27.3 (3.28), 35.0 (4.38), 40.7 (4.33)
MCD	23.5 (+0.09), 28.2 (−0.29), 33.3 (+2.36)
$[Co(dmope)_3](PF_6)_3$	32.5 (3.42)^{sh}, 40.0 (4.55)
MCD	30.3 (+0.02)
$[Co(dtc)_2(dmpe)]BF_4$	20.7 (2.92), 25.2 (3.30)^{sh}, 29.2 (4.06)^{sh}, 33.2 (4.40)
MCD	17.7 (+0.03), 20.6 (−0.10), 24.1 (−0.14), 30.8 (+2.32), 35.7 (+0.31), 38.5 (−2.22)
$[Co(dtc)(dmpe)_2](BF_4)_2$	22.7 (2.84)^{sh}, 25.2 (3.00), 29.5 (3.65)^{sh}, 33.4 (4.43)
MCD	21.5 (+0.01), 25.6 (−0.11), 30.8 (+1.73)

sh: shoulder. a) All data were obtained in CH_3CN solution. b) σ, ε, and $\Delta\varepsilon_M$ are $10^3\ cm^{-1}$, $mol^{-1}\ dm^3\ cm^{-1}$, and $mol^{-1}\ dm^3\ cm^{-1}\ T^{-1}$ units.

Table 6. Electrochemical Data Obtained by Means of RDE Measurements[a)]

Complex	Reduction			Oxidation		
	$E_{2/1}$ (red)	[1−3][b)]	i_l/C[c)]	$E_{2/1}$ (ox)	[3−1][b)]	i_l/C[c)]
	V	mV	A $mmol^{-1}$	V	mV	A $mmol^{-1}$
$[Co(dtc)_3]$	−1.44	95	72	0.56	55	78
$[Co(dtc)_2(dmope)]PF_6$	−1.24	60	80	1.09	50	114
$[Co(dtc)(dmope)_2](BF_4)_2$	−1.11	90	118	1.62	50	68
$[Co(dmope)_3](PF_6)_3$	−1.26	110	118	d)		
$[Co(dtc)_2(dmpe)]BF_4$	−1.38	55	63	0.97	60	112
$[Co(dtc)(dmpe)_2](BF_4)_2$	−1.10	55	65	1.54	50	112

a) The measurements were carried out on CH_3CN solutions ([Co]: 1.0×10^{-3} mol dm^{-3}, 0.1 mol dm^{-3} Bu_4NBF_4). b) [1−3] or [3−1] means a difference between the potential values at $i=1/4(i_l)$ and $3/4(i_l)$. c) The limiting current value per the concentration. d) The value is more positive than the voltage limit of CH_3CN (ca. +1.8 V).

(dmope)]$^+$ are assignable to the MCD peaks at 19000 and 22000 cm^{-1}, respectively. These two components are not apparently observed in the absorption spectra. For $[Co(dtc)(dmope)_2]^{2+}$, the calculated values are 23200 and 26700 cm^{-1}. The former value would correspond to the MCD peak at 23500 cm^{-1}, but the latter one seems to be small to assign the MCD peak at 28200 cm^{-1}. In a previous paper,[6)] the absorption band at 25200 cm^{-1} (MCD: 25500 cm^{-1}) of $[Co(dtc)(dmpe)_2]^{2+}$, which may correspond to the absorption band at 27300 cm^{-1} of $[Co(dtc)(dmope)_2]^{2+}$, was assigned to the second d–d band on the basis of the Angular Overlap Model treatment. No indication of the presence of bands or peaks is observed in the energy region estimated for the other split component in the spectra of both $[Co(dtc)(dmope)_2]^{2+}$ and $[Co(dtc)(dmpe)_2]^{2+}$. Further studies are needed to make clear the ligand field bands of this type of complexes.

Table 6 lists the electrochemical data of $[Co(dtc)_{3-n}(dmope)_n]^{n+}$ (n=0, 1, 2, 3,) and $[Co(dtc)_{3-n}(dmpe)_n]^{n+}$ (n=1, 2). Representative RDE and cyclic voltammograms are shown in Fig. 6. The reduction potentials ($E_{1/2}$(red)) of these complexes change a little, while the oxidation potentials ($E_{1/2}$(ox)) increase fairly largely by replacing dtc with dmope or dmpe in the complexes. A large part of the increase in $E_{1/2}$(ox) may be attributed to the increase in positive charge of the complex resulted by replacement of a negative ligand with a neutral one.[16)] The $E_{1/2}$(ox) values of the dmope complexes are larger than those of the corresponding dmpe complexes, although the differences are small. The HOMO levels of the present Co(III) complexes will be filled $(d\pi)^6$ orbitals, and their energies will be closely related to the $E_{1/2}$(ox) (Co(III)/Co(IV)) values.[16)] The larger $E_{1/2}$(ox) values of the dmope complexes may indicate that the energy levels of their dπ orbitals are lower than those of the dmpe complexes. The lower energy of the dπ orbitals would suggest more stabilization of these orbitals by interactions with vacant π-type orbitals of P donors or less destabilization by interactions with filled π-type orbitals of P donors.[6)] However, no detailed discussion can be given for the small differences in

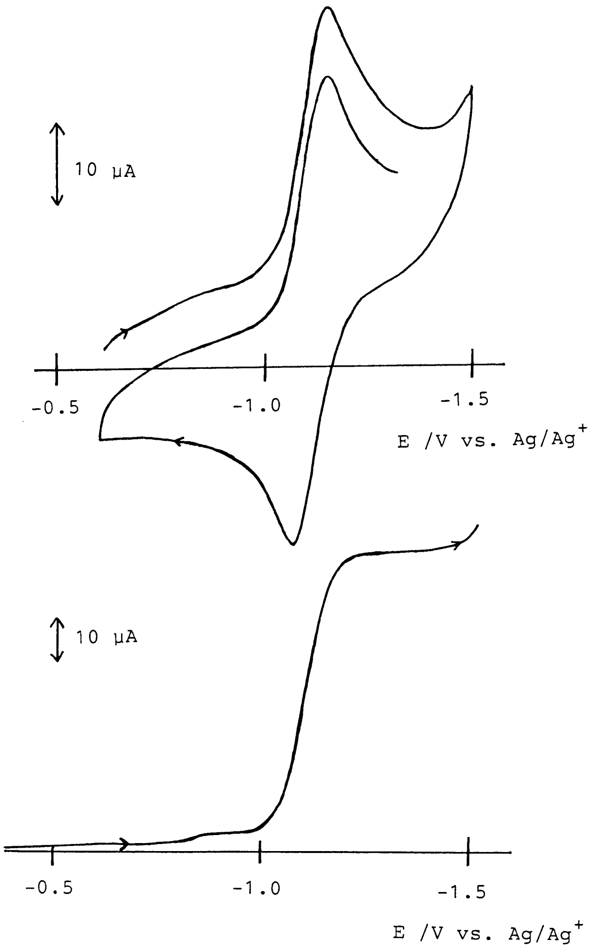

Fig. 6. RDE (bottom) and cyclic (upper) voltammograms of $[Co(dtc)(dmpe)_2](BF_4)_2$. The CV measurement was carried out at a scan rate, 200 mV s^{-1} and other conditions are the same as those for RDE measurements.

$E_{1/2}$(ox) at present.

This work was supported by a Grant-in-Aid for Scientific Research No. 03453047 from the Ministry of Education, Science and Culture. We wish to thank the Institute for Molecular Science (Okazaki) for the use of X-ray measurement and computation facilities.

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