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Preparation and Characterization of Dithiocarbamatocobalt(III) Complexes Containing Phosphites, and Molecular Structures of *cis*-$[\mathrm{Co}\{(\mathrm{CH_3})_2\mathrm{NCS_2}\}_2\{\mathrm{P(OCH_2)_3CC_2H_5}\}_2]\mathrm{BF_4}$ and $[\mathrm{Co}(\overline{\mathrm{CH_2CH_2CH_2CH_2CH_2N}}\mathrm{CS_2})\{\mathrm{P(OCH_3)_3}\}_4](\mathrm{BF_4})_2$

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Eleven new cobalt(III)–phosphite complexes of the $[\mathrm{Co(S\text{-}S)P_4}]^{2+}$- and $[\mathrm{Co(S\text{-}S)_2P_2}]^{+}$-types were prepared, where S-S denotes bidentate dimethyldithiocarbamate (dtc), diethyldithiocarbamate (etdtc), and piperidyldithiocarbamate (pipdtc) ions, and P is 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (etpb), trimethyl phosphite (pome), and triethyl phosphite (poet). The $[\mathrm{Co(S\text{-}S)_2P_2}]^{+}$-type complexes yielded the cis-isomer in the dark, but isomerized to the trans-isomer in solution by exposure of ultraviolet light. In the photo- and electrochemical reactions, it was inferred that the $[\mathrm{Co(S\text{-}S)P_4}]^{2+}$-type complexes form a linkage-isomer in which a phosphite ligand is bound to Co(III) through the oxygen atom. Molecular structures of *cis*-$[\mathrm{Co(dtc)_2(etpb)_2}]$-$\mathrm{BF_4}$ (**1**) and $[\mathrm{Co(pipdtc)(pome)_4}](\mathrm{BF_4})_2$ (**2**) were determined by the X-ray diffraction method. Crystal data: complex **1**, monoclinic, $C2/c$, $a=23.867(3)$, $b=17.583(2)$, $c=15.243(2)$ Å, $\beta=103.97(2)°$, $V=6208(1)$ Å^3, $Z=8$, and $R=0.054$ for 2533 reflections; complex **2**, monoclinic, $P2_1/c$, $a=11.259(2)$, $b=23.865(4)$, $c=14.293(2)$ Å, $\beta=93.69(1)°$, $V=3832.6(10)$ Å^3, $Z=4$, and $R=0.072$ for 2539 reflections. The average Co–P bond distances of 2.171(1) Å in **1**, and of 2.208(3) (trans to S) and 2.242(2) Å (trans to P) in **2** are a little shorter than those of analogous Co(III)–phosphine complexes.

While a large number of cobalt(III)–phosphine complexes have been prepared recently,[1)] only a few phosphite complexes have been reported for cobalt(III).[2)] Phosphites ($\mathrm{P(OR)_3}$) would be less favorable than phosphines ($\mathrm{PR_3}$) in complex formation with hard Lewis acids such as Co(III), since the electronegative OR group would reduce the electron density of the donor phosphorus atom. In order to compare structural and chemical properties of Co(III)–phosphite complexes with those of analogous Co(III)–phosphine ones, we have prepared and characterized new mixed-ligand cobalt(III) complexes containing phosphites and dithiocarbamates, in addition to X-ray structure analysis of two of these complexes. Dithiocarbamates seem to be a good auxiliary ligand to stabilize Co(III)–phosphorus bonds as evidenced in our previous studies.[3—5)]

The following abbreviations are used in this paper; trimethyl phosphite ($\mathrm{P(OCH_3)_3}$)=pome, triethyl phosphite ($\mathrm{P(OC_2H_5)_3}$) = poet, 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane ($\mathrm{P(OCH_2)_3CC_2H_5}$)=etpb, dimethyldithiocarbamate ion ($(\mathrm{CH_3})_2\mathrm{NCS_2^-}$)=dtc, diethyldithiocarbamate ion ($(\mathrm{C_2H_5})_2\mathrm{NCS_2^-}$)=etdtc, and piperidyldithiocarbamate ion ($\overline{\mathrm{CH_2CH_2CH_2CH_2CH_2N}}\mathrm{CS_2^-}$)=pipdtc.

Experimental

The ligands were handled under a $\mathrm{N_2}$ atmosphere using standard Schlenk tube techniques until air-stable Co(III) complexes were formed. All solvents used for the preparation were deoxygenated by bubbling nitrogen for 20 min before use. Compounds etpb[6)] and *N,N′*-bis(pentamethylene)thiuram disulfide[7)] were prepared by literature methods. Other ligands were purchased from Tokyo Kasei Kogyo Co., Ltd. and used without further purification. Absorption and ^{1}H NMR spectra were recorded on a Hitachi U-3400 spectrophotometer and a Hitachi R-90H spectrometer, respectively. Electrochemical and photochemical measurements were carried out with the same instruments and procedures as those described in our previous papers.[8,9)]

Preparation of Complexes. ***cis*-$[\mathrm{Co(dtc)_2(etpb)_2}]$-$\mathrm{BF_4}$ and $[\mathrm{Co(dtc)(etpb)_4}]$ $(\mathrm{BF_4})_2$.** A dichloromethane solution (200 cm^3) of tetramethylthiuram disulfide (2.40 g, 10.0 mmol) was added dropwise to a methanol solution (250 cm^3) containing $\mathrm{Co(BF_4)_2{\cdot}6H_2O}$ (6.80 g, 20.0 mmol) and etpb (6.48 g, 40.0 mmol) in an ice bath. The resulting red brown solution was stirred for 2 h in an ice bath, for another 1 h at room temperature, and then concentrated under reduced pressure to ca. 50 cm^3. The green precipitate of $[\mathrm{Co(dtc)_3}]$ was filtered off, and the filtrate was applied on a column (ϕ 7 cm×35 cm) of Sephadex LH-20. The adsorbed product was eluted with methanol, affording three major bands of yellow, red, and green in color. Each eluate of the yellow and red bands was evaporated under reduced pressure to dryness. The residue was shaken with a mixture of dichloromethane (50 cm^3) and water (50 cm^3) to extract the complex into the dichloromethane layer. The procedure was repeated several times. The dichloromethane solutions were collected, dried over $\mathrm{Na_2SO_4}$, and then concentrated under reduced pressure to a small volume. On addition of diethyl ether the concentrate yielded yellow or red crystals, which were recrystallized from acetone–diethyl ether. Yields: 0.77 g (4%) for the yellow complex ($[\mathrm{Co(dtc)\ (etpb)_4}](\mathrm{BF_4})_2$) and 1.45 g (10 %) for the red complex (*cis*-$[\mathrm{Co(dtc)_2(etpb)_2}]$-$\mathrm{BF_4}$). The elemental analyses are shown in Table 1, together with those of other complexes. The red complex is soluble in water, methanol, ethanol, acetonitrile, dichloromethane,

Table 1. Absorption, ^{1}H NMR Spectral and Analytical Data

Complex	Absorption$^{\mathrm{a,b)}}$ $\sigma/10^3$ cm^{-1} (log (ε/mol^{-1} dm^3 cm^{-1}))	^{1}H NMR (δ) dtc NCH$_3$$^{\mathrm{c)}}$	C (%) H (%) N (%) Found Calcd
cis-[Co(dtc)$_2$(etpb)$_2$]BF$_4$	19.6 (2.8)$^{\mathrm{sh}}$	3.26$^{\mathrm{d)}}$	30.40 4.89 3.90
($C_{18}H_{34}N_2BO_6F_4P_2S_4Co$)	22.9 (3.17)	3.22	30.43 4.82 3.94
trans-[Co(dtc)$_2$(etpb)$_2$]BF$_4$	18.2 (2.6)$^{\mathrm{sh}}$	3.29$^{\mathrm{e)}}$	30.33 5.05 3.88
($C_{18}H_{34}N_2BO_6F_4P_2S_4Co$)	22.2 (3.0)$^{\mathrm{sh}}$		30.43 4.82 3.94
[Co(dtc)(etpb)$_4$](BF$_4$)$_2$	22.4 (2.7)$^{\mathrm{sh}}$	3.20$^{\mathrm{e)}}$	32.39 5.05 1.36
($C_{27}H_{50}NB_2O_{12}F_8P_4S_2Co$)	25.1 (2.96)		32.39 5.03 1.40
cis-[Co(dtc)$_2$(pome)$_2$]BF$_4$	19.5 (2.9)$^{\mathrm{sh}}$	3.20$^{\mathrm{f)}}$	22.86 4.76 4.32
($C_{12}H_{30}N_2BO_6F_4P_2S_4Co$)	23.5 (3.18)	3.24	22.72 4.77 4.42
[Co(dtc)(pome)$_4$](BF$_4$)$_2$	22.8 (2.8)$^{\mathrm{sh}}$	3.24$^{\mathrm{e)}}$	21.21 4.90 1.63
($C_{15}H_{42}NB_2O_{12}F_8P_4S_2Co$)	25.5 (3.11)		21.22 4.99 1.65
cis-[Co(pipdtc)$_2$(pome)$_2$]BF$_4$	19.1 (2.9)$^{\mathrm{sh}}$		30.20 5.35 3.84
($C_{18}H_{38}N_2BO_6F_4P_2S_4Co$)	23.4 (3.24)		30.26 5.36 3.92
[Co(pipdtc)(pome)$_4$](BF$_4$)$_2$	23.2 (2.8)$^{\mathrm{sh}}$		24.29 5.22 1.58
($C_{18}H_{46}NB_2O_{12}F_8P_4S_2Co$)	25.3 (3.16)		24.32 5.22 1.58
cis-[Co(dtc)$_2$(poet)$_2$]BPh$_4$	19.3 (2.9)$^{\mathrm{sh}}$	3.05$^{\mathrm{d)}}$	53.17 6.79 2.97
($C_{42}H_{62}N_2BO_6P_2S_4Co$)	23.5 (3.18)	3.00	53.05 6.57 2.95
[Co(dtc)(poet)$_4$](BPh$_4$)$_2$	22.4 (2.8)$^{\mathrm{sh}}$	3.19$^{\mathrm{e)}}$	60.92 7.38 0.94
($C_{75}H_{106}NB_2O_{12}P_4S_2Co$)	25.4 (3.12)		60.77 7.21 0.95
cis-[Co(etdtc)$_2$(poet)$_2$]BF$_4$	19.4 (2.9)$^{\mathrm{sh}}$		33.79 6.66 3.52
($C_{22}H_{50}N_2BO_6F_4P_2S_4Co$)	23.5 (3.22)		34.11 6.51 3.62
[Co(etdtc)(poet)$_4$](BPh$_4$)$_2$	22.4 (2.8)$^{\mathrm{sh}}$		61.31 7.42 0.99
($C_{77}H_{110}NB_2O_{12}P_4S_2Co$)	25.6 (3.12)		61.24 7.34 0.93

a) Solvent: CH_3CN. b) sh: shoulder absorption. c) All signals are a singlet. d) in $CDCl_3$. e) in CD_3CN. f) in CD_2Cl_2.

and chloroform, but insoluble in diethyl ether and benzene. The solubility of the yellow complex is similar to that of the red complex, except that it is scarcely soluble in chloroform.

***trans*-[Co(dtc)$_2$(etpb)$_2$]BF$_4$.** A concentrated chloroform solution of *cis*-[Co(dtc)$_2$(etpb)$_2$]BF$_4$ was irradiated by a Xenon lamp with a cooling trap of water to yield a crystalline precipitate of the red trans isomer nearly quantitatively. The precipitate was collected by filtration, washed with chloroform, and dried in air. The solubility of the complex is much less than that of the cis-isomer.

Other Complexes. Other complexes prepared in this study are listed in Table 1 with the results of their elemental analyses. The preparative methods are almost the same as those for the etpb complexes except that tetrahydrofuran was used for the solvent in the preparation of poet complexes. A few complexes were isolated as tetraphenylborate salts. The yields are similar to those of the corresponding etpb complexes.

Crystal Structure Determination. A crystal of *cis*-[Co(dtc)$_2$(etpb)$_2$]BF$_4$ (**1**) with approximate dimensions, 0.50×0.50×0.80 mm^3, which was grown from a chloroform solution of the complex, was used for the data collection. Crystal data: monoclinic, $C2/c$, a=23.867(3), b=17.583(2), c=15.243(2) Å, β=103.97(2)°, V=6208(1) Å^3, D_x=1.51 g cm^{-3}, D_m=1.55(4) g cm^{-3}, Z=8, μ(Mo $K\alpha$)=9.68 cm^{-1}. Diffraction data were collected on a Rigaku AFC-5R diffractometer with graphite monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å). Within the range $2\theta < 55°$, 2533 independent reflections with $|F_o| > 6\sigma(|F_o|)$ were obtained. Absorption corrections were made with the ABEX 80 program of the Computer Center Library of Institute for Molecular Science (Okazaki). The calculations were carried out on a HITAC M-680H computer at the Computer Center of Institute for Molecular Science. The structure was solved by the usual heavy-atom methods; the position of Co was deduced by means of the Patterson synthesis, and all the non-hydrogen atoms were located by the subsequent Fourier synthesis of the program system UNICS III.$^{10)}$ The positions of 15 among 34 hydrogen atoms were identified in subsequent difference-Fourier maps. The structure was refined by the block-diagonal least squares methods with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogen atom. The function minimized was $\Sigma||F_o|-|F_c||^2$. Final R was 0.054 for 2533 observed unique reflections, and the atomic parameters of non-hydrogen atoms are listed in Table 2.

A crystal of [Co(pipdtc) (pome)$_4$](BF$_4$)$_2$ (**2**) with approximate dimensions, 0.80×0.33×0.13 mm^3, which was grown from a dichloromethane solution of the complex, was used for the data collection. Crystal data: monoclinic, $P2_1/c$, a=11.259(2), b=23.865(4), c=14.293(2) Å, β=93.69(1)°, V=3832.6(10) Å^3, D_x=1.54 g cm^{-3}, D_m=1.51(4) g cm^{-3}, Z=4, μ(Mo $K\alpha$)=8.01 cm^{-1}. Diffraction data were collected on a Rigaku AFC-5 diffractometer with graphite monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å). Within the range $2\theta < 60°$, 2539 independent reflections with $|F_o| > 6\sigma(|F_o|)$ were obtained. The structure was solved by the same methods as those for the above etpb complex by use of a HITAC M-680H computer at the Computer Center of Institute for Molecular Science (Okazaki). The positions of 45 among 46 hydrogen atoms were identified. Final R was 0.072 for 2539 observed unique reflections, and the atomic parameters of

Table 2. Positional Parameters ($\times 10^4$) and Equivalent Isotropic Temperature Factors of *cis*-[Co(dtc)$_2$(etpb)$_2$]BF$_4$

Atom	x	y	z	B_{eq}
Co	3102.0(2)	1715.9(3)	2611.5(3)	3.2
S1	2681.7(4)	2057(1)	3740(1)	4.0
S2	2133.5(4)	1624(1)	1969(1)	4.4
S3	3119(1)	459(1)	2979(1)	4.6
S4	3350.4(4)	1133(1)	1437(1)	3.9
P1	3139.6(4)	2839(1)	2042(1)	3.5
P2	3984.8(4)	1790(1)	3419(1)	3.9
O1	3258(2)	3537(2)	2715(3)	5.4
O2	3620(2)	2901(2)	1490(3)	5.4
O3	2577(2)	3134(2)	1323(3)	5.6
O4	4049(2)	1761(6)	4447(3)	9.5
O5	4419(3)	1235(6)	3177(6)	10.0
O6	4328(3)	2526(5)	3288(8)	9.9
N1	1521(2)	1891(3)	3201(4)	4.9
N2	3303(2)	−389(3)	1607(4)	5.0
C1	2030(2)	1864(3)	3002(3)	3.9
C2	1473(3)	2119(4)	4102(5)	6.2
C3	989(3)	1728(6)	2535(7)	7.0
C4	3266(2)	283(2)	1947(3)	3.8
C5	3224(4)	−1076(4)	2078(7)	6.9
C6	3453(3)	−476(4)	734(5)	6.0
C7	3337(3)	4259(4)	2311(5)	6.0
C8	3677(3)	3643(4)	1086(6)	6.1
C9	2643(3)	3874(4)	916(5)	5.7
C10	3243(2)	4187(3)	1279(4)	4.8
C11	3283(4)	4982(4)	868(6)	6.3
C12	3206(4)	5008(5)	−154(6)	7.0
C13	4641(2)	1819(10)	5004(4)	10.0
C14	5002(4)	1249(12)	3802(8)	10.9
C15	4935(4)	2527(8)	3779(10)	9.0
C16	5057(2)	1861(6)	4432(4)	6.3
C17	5682(3)	1925(14)	5012(6)	12.2
C18	5945(5)	1396(19)	5582(12)	14.1
B	98(24)	4269(21)	2432(35)	16.1
F1	38(6)	4366(5)	3210(7)	11.1
F2	444(7)	3491(9)	2816(14)	14.4
F3	268(6)	4222(12)	1937(13)	13.7
F4	−21(16)	3976(13)	2484(40)	16.5

non-hydrogen atoms are listed in Table 3.

Tables of the coordinates of hydrogen atoms, the anisotropic thermal parameters of the non-hydrogen atoms, and the observed and calculated structure factors are kept as Document No. 66012 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Preparation and Structure of the Complexes. All of the complexes were prepared by oxidation of a methanol or tetrahydrofuran solution containing Co(BF$_4$)$_2$·6H$_2$O and the phosphite ligand with tetramethylthiuram disulfide or the related disulfides in chloroform in the molar ratio of 2 : (4—8) : 1, respectively. Addition of excess phosphite ligands results naturally in an increase and a decrease in yields of [Co(S-S) P$_4$]$^{2+}$- and [Co(S-S)$_2$P$_2$]$^+$-type complexes, respectively, but the formation ratio of these complexes depends on the kinds of phosphite ligand. For example, the reaction for the pome complex in the molar ratio of 2 (Co) : 8 (pome) : 1 (disulfide) formed these two type complexes in similar amounts (ca. 14%), but the reaction in the 2 : 4 : 1 ratio yielded a trace amount of [Co(S-S) (pome)$_4$]$^{2+}$. All the [Co(S-S)$_2$P$_2$]-type complexes obtained by this oxidation method were assigned to the cis-isomer on the

Table 3. Positional Parameters ($\times 10^4$) and Equivalent Isotropic Temperature Factors of [Co(pipdtc)(pome)$_4$](BF$_4$)$_2$

Atom	x	y	z	B_{eq}
Co	7952(1)	1105.1(3)	2057(1)	3.0
S1	9775(1)	677(1)	2262(1)	3.9
S2	8458(2)	1191(1)	3623(1)	4.5
P1	8836(1)	1935(1)	1864(1)	3.8
P2	7933(1)	864(1)	571(1)	3.4
P3	6227(2)	1549(1)	2103(1)	4.3
P4	7014(2)	326(1)	2481(1)	4.0
O1	8453(5)	2366(2)	2622(4)	5.4
O2	8529(5)	2206(2)	892(4)	4.8
O3	10227(4)	1957(3)	2043(5)	5.8
O4	8134(5)	213(2)	467(3)	4.5
O5	9041(4)	1134(2)	125(4)	4.7
O6	6820(5)	958(2)	−123(3)	5.0
O7	6181(4)	2106(2)	1526(4)	5.0
O8	5167(5)	1205(4)	1692(11)	13.2
O9	5896(13)	1691(5)	3099(7)	13.6
O10	7771(5)	−158(2)	2973(4)	5.0
O11	6251(5)	42(2)	1640(4)	5.6
O12	6079(6)	446(3)	3220(5)	6.5
N	10616(6)	763(3)	4071(5)	5.5
C1	9757(7)	850(3)	3422(5)	4.3
C2	10527(8)	939(4)	5043(6)	6.1
C3	11462(10)	1419(4)	5214(8)	6.8
C4	12652(11)	1260(5)	4985(8)	7.3
C5	12656(10)	1025(6)	3998(10)	8.7
C6	11809(9)	570(5)	3805(7)	6.9
C7	9217(11)	2760(5)	3131(8)	7.8
C8	8493(13)	2798(4)	681(10)	8.3
C9	11073(10)	1886(6)	1314(11)	8.8
C10	7583(13)	−161(4)	−207(7)	7.8
C11	9547(8)	935(4)	−713(6)	5.7
C12	6475(8)	1493(4)	−552(6)	5.5
C13	5228(11)	2520(6)	1499(13)	9.9
C14	4073(18)	1211(9)	1519(15)	12.6
C15	5829(20)	2026(10)	3696(16)	13.9
C16	8413(10)	−585(4)	2462(7)	6.3
C17	5457(10)	−422(4)	1723(9)	7.2
C18	6053(12)	279(5)	4173(8)	7.9
B1	12782(8)	1984(4)	−1059(10)	7.2
B2	7333(12)	844(6)	−3160(8)	8.2
F1	12239(38)	1590(14)	−813(22)	27.8
F2	11927(40)	2247(21)	−820(28)	26.5
F3	13350(31)	2258(10)	−410(21)	22.3
F4	13373(40)	1893(13)	−1777(28)	25.9
F5	7255(14)	447(6)	−2522(11)	14.9
F6	6489(14)	498(9)	−3606(15)	17.0
F7	6954(14)	1321(5)	−2834(9)	13.9
F8	8339(12)	891(6)	−3534(14)	16.9

basis of ^{1}H NMR and absorption spectra (Table 1), and the structure of *cis*-[Co(dtc)$_2$(etpb)$_2$]BF$_4$ was confirmed by X-ray structure analysis described below.

A perspective view of [Co(dtc)$_2$(etpb)$_2$]$^+$ (**1**) is shown in Fig. 1. The selected bond distances and angles are listed in Table 4. The Co atom forms a distorted octahedron with a cis configuration of two etpb ligands. The Co–P bond distance (av 2.171(1) Å) is similar to that in *trans*-[CoCl(dmgH)$_2$(pome)] (dmgH=dimethylglyoximate ion; 2.165(3) Å).[11] These distances are the shortest one for the Co–P bonds of Co(III)–phosphine[1] and –phosphite complexes. The Co–P bond distances of other Co(III)–phosphite complexes have been reported for *trans*-[Co(NCS)$_2$(poet)$_4$]B(C$_6$H$_5$)$_4$ (av 2.244(6) Å),[12] *trans*-[CoX(dmgH)$_2$(pome)] (X=CN$^-$, CH$_2$CN$^-$, CH$_3^-$, CH$_2$CF$_3^-$) (Co–P=2.222(2)—2.257(2) Å),[13] and *trans*-[Co(*i*-C$_3$H$_7$)(dmgH)$_2${P(OCH$_2$)$_3$CCH$_3$}] (Co–P= 2.270(1) Å).[13] The Co–S distances in the present complex are av 2.284(2) Å for the bonds trans to etpb and av 2.267(1) Å for those trans to dtc. The latter distance is nearly the same as those in [Co(dtc)$_3$] (av 2.264(2) Å)[14] and [Co(dtc)(en)$_2$]$^{2+}$ (av 2.263(3) Å).[15] Elongation of the Co–S bond trans to etpb may indicate trans influence of etpb, but the influence is small (0.017(2) Å) compared with those (0.04—0.06 Å) found for the Co–N and Co–O bonds of mixed-ligand Co(III)–phosphine complexes.[4,16—18]

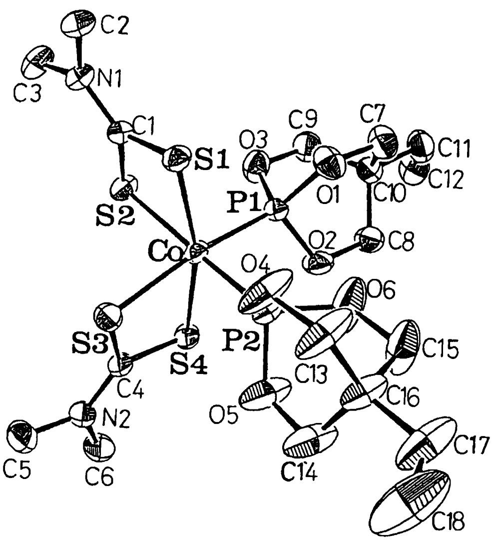


Fig. 1. A perspective view of *cis*-[Co(dtc)$_2$(etpb)$_2$]$^+$.

Table 4. Selected Bond Distances (l/Å) and Angles (ϕ/°) of *cis*-[Co(dtc)$_2$(etpb)$_2$]BF$_4$

Co–S1	2.271(1)	Co–S2	2.288(1)	Co–S3	2.278(2)
Co–S4	2.263(1)	Co–P1	2.169(1)	Co–P2	2.172(1)
P1–O1	1.581(6)	P1–O2	1.582(5)	P1–O3	1.601(5)
P2–O4	1.54(1)	P2–O5	1.53(1)	P2–O6	1.57(1)

S1–Co–S2	76.00(5)	S1–Co–S3	93.13(5)
S1–Co–S4	165.21(5)	S1–Co–P1	97.54(5)
S1–Co–P2	95.76(5)	S2–Co–S3	89.58(6)
S2–Co–S4	93.40(5)	S2–Co–P1	91.61(5)
S2–Co–P2	171.21(6)	S3–Co–S4	76.27(5)
S3–Co–P1	169.23(6)	S3–Co–P2	87.82(5)
S4–Co–P1	92.97(5)	S4–Co–P2	94.13(5)
P1–Co–P2	92.51(5)	Co–P1–O1	117.8(2)
Co–P1–O2	112.4(2)	Co–P1–O3	117.4(2)
O1–P1–O2	104.7(3)	O1–P1–O3	100.5(3)
O2–P1–O3	102.1(3)	Co–P2–O4	114.8(4)
Co–P2–O5	116.4(4)	Co–P2–O6	116.3(4)
O4–P2–O5	108.5(6)	O4–P2–O6	103.3(6)
O5–P2–O6	95.1(6)		

A perspective view of [Co(pipdtc)(pome)$_4$]$^{2+}$ (**2**) is shown in Fig. 2. The selected bond distances and angles are listed in Table 5. The Co–P distances trans to P of av 2.242 (2) Å and trans to S of av 2.208(3) Å are a little longer than that of the above etpb complex. The shorter Co–P distance in the etpb complex may be related to the smaller cone angle[19] of etpb (101°) than pome (107°). The longer distance of the Co–P bonds trans to P than those trans to S is attributalbe to the mutual trans influence of two pome ligands. The Co–S distance of av 2.288(3) Å is the same as that trans to P in the etpb complex. Table 6 compares the average Co–P and Co–S bond distances of the pome complex with those of phosphonite and phosphine complexes of the [Co(S-S)P$_4$] type, [Co(dtc)(dmope)$_2$](BF$_4$)$_2$ (dmope=(CH$_3$O)$_2$PCH$_2$CH$_2$P(OCH$_3$)$_2$)[3] and [Co(dtc)(dmpe)$_2$](BF$_4$)$_2$ (dmpe = (CH$_3$)$_2$PCH$_2$CH$_2$P(CH$_3$)$_2$).[3] No X-ray data of unidentate phosphonite and phosphine complexes of this type have been reported. However, the differences in distance between the Co–P bonds trans to P and trans to S are nearly the same, ca. 0.04 Å for the three complexes. The Co–S bonds which have the phosphorus donor atom in the trans position also have similar distances in these complexes. The data indicate that these phosphite, phosphonite and phosphine ligands exert similar trans influence towards the Co(III) ion. The Co–P distances decrease in the order of the dmpe > pome > dmope complexes. The phosphonite ligand seems to have stronger

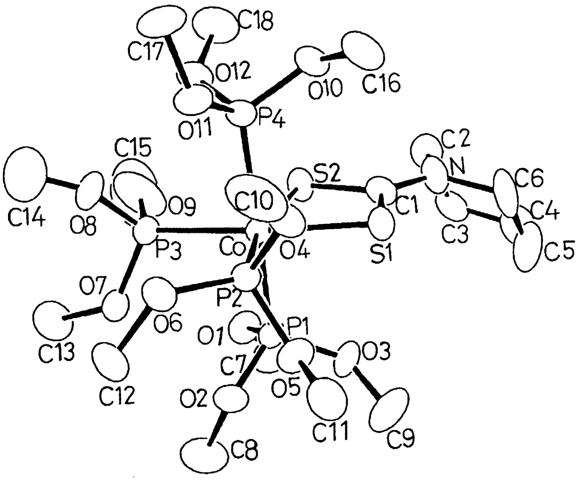


Fig. 2. A perspective view of [Co(pipdtc)(pome)$_4$]$^{2+}$.

Table 5. Selected Bond Distances (l/Å) and Angles (ϕ/°) of [Co(pipdtc)(pome)$_4$] (BF$_4$)$_2$

Co–S1	2.294(2)	Co–S2	2.282(3)	Co–P1	2.242(2)
Co–P2	2.199(2)	Co–P3	2.217(3)	Co–P4	2.241(2)
P1–O1	1.574(6)	P1–O2	1.552(6)	P1–O3	1.571(7)
P2–O4	1.579(6)	P2–O5	1.574(6)	P2–O6	1.564(6)
P3–O7	1.565(6)	P3–O8	1.53(2)	P3–O9	1.53(2)
P4–O10	1.574(6)	P4–O11	1.584(6)	P4–O12	1.566(7)
S1–Co–S2	75.52(7)	S1–Co–P1	90.47(7)		
S1–Co–P2	87.68(7)	S1–Co–P3	170.79(8)		
S1–Co–P4	91.68(7)	S2–Co–P1	87.50(8)		
S2–Co–P2	163.04(8)	S2–Co–P3	95.28(8)		
S2–Co–P4	84.39(8)	P1–Co–P2	95.09(7)		
P1–Co–P3	88.73(8)	P1–Co–P4	170.80(8)		
P2–Co–P3	101.52(8)	P2–Co–P4	93.93(7)		
P3–Co–P4	87.71(8)	Co–P1–O1	110.5(2)		
Co–P1–O2	113.8(2)	Co–P1–O3	117.1(3)		
O1–P1–O2	106.7(3)	O1–P1–O3	100.4(3)		
O2–P1–O3	107.1(3)	Co–P2–O4	110.8(2)		
Co–P2–O5	109.0(2)	Co–P2–O6	122.2(2)		
O4–P2–O5	104.0(3)	O4–P2–O6	101.3(3)		
O5–P2–O6	107.9(3)	Co–P3–O7	113.0(3)		
Co–P3–O8	113.3(6)	Co–P3–O9	113.6(6)		
O7–P3–O8	104.7(7)	O7–P3–O9	107.5(6)		
O8–P3–O9	104.1(8)	Co–P4–O10	118.6(2)		
Co–P4–O11	113.1(2)	Co–P4–O12	112.3(3)		
O10–P4–O11	106.1(3)	O10–P4–O12	101.6(4)		
O11–P4–O12	103.6(4)				

affinity towards Co(III) than phosphite and phosphine ligands, but the reason for this is not clear at present.

For the bond angles around P atoms of etpb and pome in the complexes, the average Co–P–O and O–P–O angles are larger (etpb: 116°, pome: 114°) and smaller (etpb: 102°, pome: 105°), respectively, than the terahedral angle. A similar relation has been found for the bond angles around P donor atoms in the above phosphonite, phosphine, and related complexes.[1)]

Absorption Spectra. Absorption spectra of [Co(dtc)$_{3-n}$(pome)$_{2n}$]$^{n+}$ (n=0—3) are shown in Figs. 3 and 4, together with those of the related dmope and dmpe complexes. Table 1 lists the spectral data in the d–d band region. In each series of the *cis*-[Co(S-S)$_2$P$_2$]$^+$- and [Co(S-S)P$_4$]$^{2+}$-type complexes, the spectral patterns of the pome, dmope and dmpe complexes are similar to one another, and the same band assignment can be given for the pome complexes as those for the dmope[3)] and dmpe[5)] complexes. Thus the shoulders around 19500 and 22800 cm^{-1} of *cis*-[Co(dtc)$_2$(pome)$_2$]$^+$ and [Co(dtc)(pome)$_4$]$^{2+}$, respectively, can be assigned to the first d–d band, and the broad bands at 23500 and 25500 cm^{-1} to the second d–d band. The energy separation between the first and second d–d bands tends to become small for mixed-ligand Co(III) complexes with phosphorus and sulfur donor atoms.[20)] The d–d bands shift to higher energy in the order of the dmpe < pome < dmope complexes. This order is the same as the shortening order of the Co–P bonds given in Table 6 for these complexes. The strong ligand field strength and the short Co–P bond distance in the dmope complex would result from both steric (cone angle: dmope (101°), pome (107°), dmpe (107°)) and electronic factors[19)] of dmope to Co(III), but the details remain unknown.

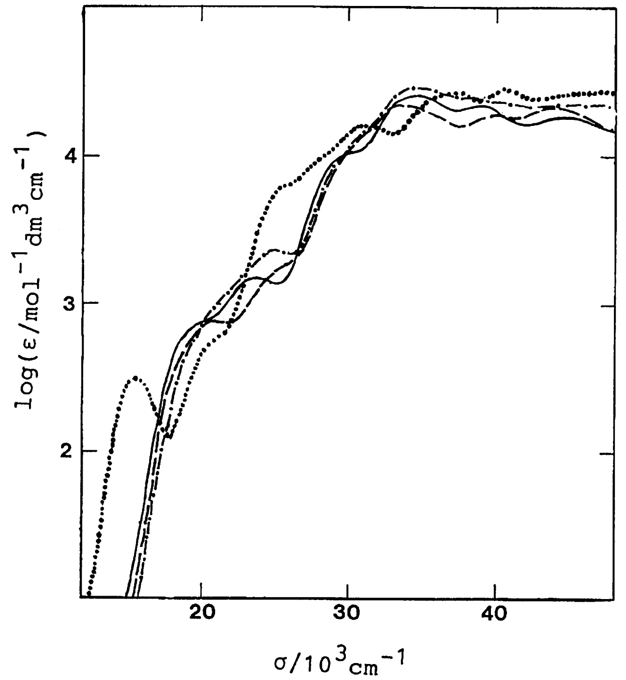


Fig. 3. Absorption spectra of [Co(dtc)$_3$] (····), [Co(dtc)$_2$(dmpe)]$^+$ (---), *cis*-[Co(dtc)$_2$(pome)$_2$]$^+$ (—), and [Co(dtc)$_2$(dmope)]$^+$ (-··-) in CH$_3$CN.

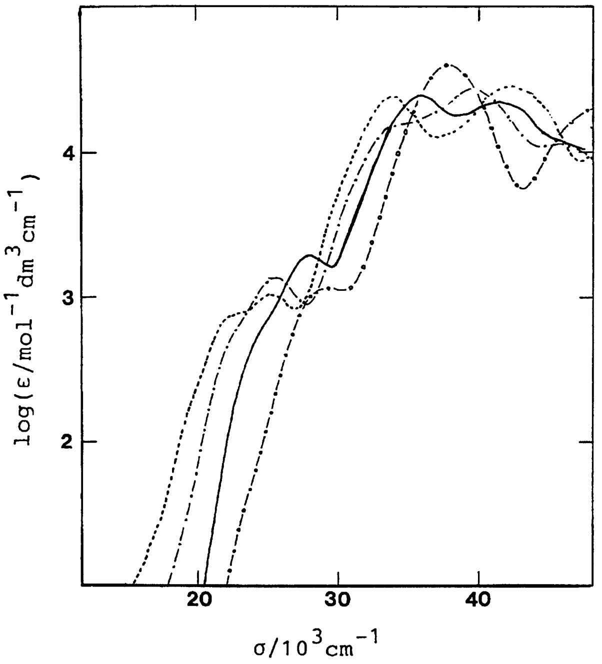


Fig. 4. Absorption spectra of [Co(dtc)(dmpe)$_2$]$^{2+}$ (····), [Co(dtc)(pome)$_4$]$^{2+}$ (-··-), [Co(dtc)(dmope)$_2$]$^{2+}$ (—), and [Co(pome)$_6$]$^{3+}$ (-∘-) in CH$_3$CN.

Table 6. A Comparison of Bond Distances (l/Å) among the Related Complexes

	$[Co(pipdtc)(pome)_4](BF_4)_2$ phosphite: $P(OR)_3$	$[Co(dtc)(dmope)_2](BF_4)_2$[a)] phosphonite: $PR(OR)_2$	$[Co(dtc)(dmpe)_2](BF_4)_2$[a)] phosphine: PR_3
Co–P (*trans* (P,P))	2.242(2)	2.226(3)	2.278(1)
(*trans* (P,S))	2.208(3)	2.186(3)	2.240(1)
Co–S	2.288(3)	2.282(3)	2.288(1)

a) The data were obtained from Ref. 3.

Photochemical Reactions. The complexes prepared in this study are stable in the solid state and in solution, but are fairly sensitive to ultraviolet light in solution. Figure 5 shows absorption spectral changes of *cis*-$[Co(dtc)_2(etpb)_2]^+$ in methanol at 2 min intervals by irradiation of a Xenon short arc lamp (150 W, Ushio Co., Ltd.) at room temperature. Two isosbestic points are observed at 425 and 567 nm. The same spectral change occurred on the complex in acetonitrile, water, and chloroform solutions. The ^{1}H NMR spectrum in $CDCl_3$ also changed with time on the irradiation. Two singlet signals for the methyl groups of dtc at δ=3.22 and 3.26 became a singlet at δ=3.29 after 1 h. Thus the reaction product can be assigned to *trans*-$[Co(dtc)_2(etpb)_2]^+$ from symmetry argument. As stated in Experimental, *trans*-$[Co(dtc)_2(etpb)_2]BF_4$ precipitated from a concentrated chloroform solution of the cis-isomer by irradiation with a Xenon lamp. This product showed the same ^{1}H NMR spectrum as the one given above. Both absorption and ^{1}H NMR spectra changed by the irradiation revert slowly to the original ones in the dark at room temperature. The thermal isomerization of the trans- to cis-isomer at room temperature is much slower than the photochemical one. The quantum yields in an acetonitrile solution obtained by the method reported previously[9)] were ca. 0.17 on the irradiation at 250 and 340 nm and ca. 0.02 at 405 and 500 nm. These values are very large for Co(III) complexes.[21)]

The ^{1}H NMR spectrum of *cis*-$[Co(dtc)_2(pome)_2]BF_4$ in $CDCl_3$ showed a somewhat different change from that of the above etpb complex on irradiation. The spectral changes ceased after 4 h, and the final spectrum around δ=3.2 composed of signals due to the methyl groups of dtc for trans- and cis-isomers as shown in Fig. 6. (The signals around δ=3.8—3.9, which can be assigned to the methyl groups of pome, also changed, but no spectral analysis has been made because of the complexity.) This spectrum reverts to the original one after 10 h in

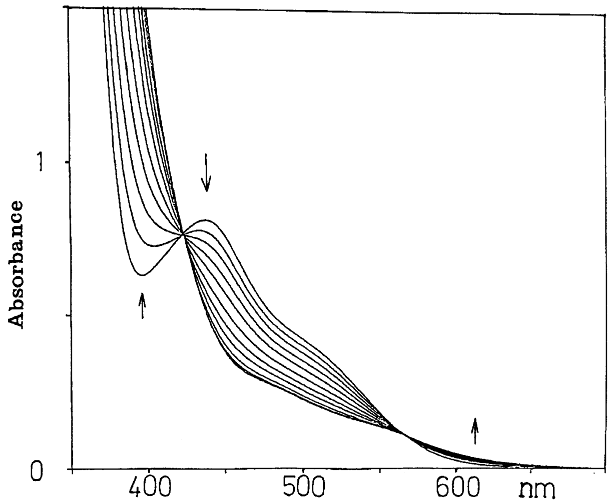


Fig. 5. Absorption spectral changes of *cis*-[Co-$(dtc)_2(pome)_2]^+$ in $CHCl_3$ by irradiation of ultraviolet light.

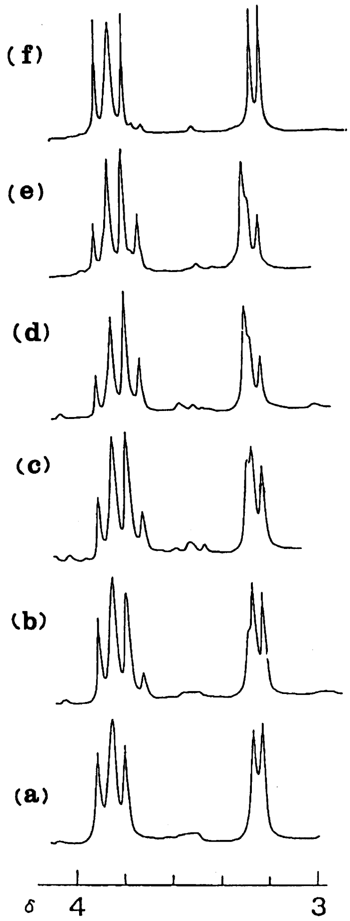


Fig. 6. ^{1}H NMR spectral changes of *cis*-[Co-$(dtc)_2(pome)_2]^+$ in $CDCl_3$ by irradiation of ultraviolet light: (a) before irradiation, (b) 30 min, (c) 1 h, (d) 4 h, (e) 20 h, and (f) 10 h in the dark after 4 h irradiation (d).

the dark at room temperature. Rates of these photo and thermal reactions are fairly slower and faster, respectively, than those of the etpb complex. Thus the pome complex in solution exists in a mixture of the cis- and trans-isomers under the irradiation. The corresponding poet complex has similar reactivity to the pome complex in both photo and thermal reactions. Pure trans-isomers of the pome and poet complexes were not obtained, because of their high solubility and fast isomerization to the cis-isomers.

The [Co(S-S)P_4]$^{2+}$-type complexes in solution are also sensitive to light, showing absorption spectral changes with time. However, the changes largely differ from those of [Co(dtc)$_2$(etpb)$_2$]$^+$ and [Co(dtc)$_2$(pome)$_2$]$^+$. For example, the absorption spectrum of [Co(dtc)$_2$(pome)$_4$]$^{2+}$ changes by irradiation with isosbestic points (375 and 444 nm) at the first step. The band at 392 nm diminishes and a new band appears around 450 nm (Fig. 7). However, the isosbestic points disappear with the lapse of time, indicating another reaction being followed. Further irradiation resulted in decomposition of the complex. The spectrum which showed at the first step reverts fairly rapidly to the original one after keeping the solution in the dark at room temperature. Since the geometrical isomer is not possible for this type of complex, a new changeable species should be formed. Houlding and Miskowski[22] reported that a transient species formed in flash photolysis of [Co(dmope)$_3$]$^{3+}$ may be [Co(dmope)$_2$(dmope-*O*)]$^{3+}$ in which one dmope ligand coordinates to Co(III) through the oxygen atom. The species formed at the first step from [Co(dtc)(pome)$_4$]$^{2+}$ by irradiation may also be its linkage-isomer containing O-bonded pome. The appearance of the new band at the lower wavelength (450 nm) than that of the original complex (392 nm) by irradiation would support the formation of this linkage-isomer, since the ranking of oxygen donor atoms in the spectrochemical series is fairly lower than that of phosphorus donor ones.[23]

Electrochemistry. Table 7 lists the reduction $E_{1/2}$(red) and the oxidation $E_{1/2}$(ox) potentials of several phosphite complexes prepared in this study, together with those of the related dmope and dmpe complexes. The measurements were carried out by rotating disk electrode (RDE) and cyclic voltammetry (CV). Both $E_{1/2}$(red) and $E_{1/2}$(ox) potentials of the phosphite complexes are more positive than those of the dmope and dmpe complexes.[8] The positive shifts of the phosphite complexes would indicate that both of their dσ^* and dπ orbital energies of Co(III) are lower than those of the dmope and dmpe complexes. The filled σ-donor and empty π-acceptor (3d) orbitals of P would be lower in energy for P(OR)$_3$ than for PR_3, since the electron density on P of P(OR)$_3$ should be less than that of PR_3, owing to the more electronegative OR group. The lowering in energy of the σ-donor orbital of P would make the energy of the empty, antibonding dσ^* orbital lower, while the low energy, empty π-acceptor orbital of P will be favorable for back-bonding with the filled dπ orbital of Co(III) to stabilize it.

Figure 8 compares cyclic voltammograms of *trans*- and *cis*-[Co(dtc)$_2$(etpb)$_2$]BF_4 in the 0—−2.0 V region. Both voltammograms are similar, except the wave at −0.82 V (A) of the trans-isomer in the first scan. At ca. −0.97 V, both isomers show a wave (B). Since A and B can be assigned to the reduction waves of the trans- and cis-isomers, respectively, the appearance of wave

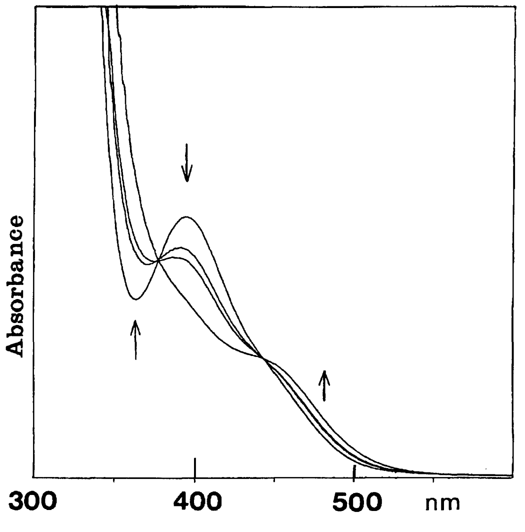


Fig. 7. Absorption spectral changes of [Co(dtc)-(pome)$_4$]$^{2+}$ in CH_3CN by irradiation of ultraviolet light.

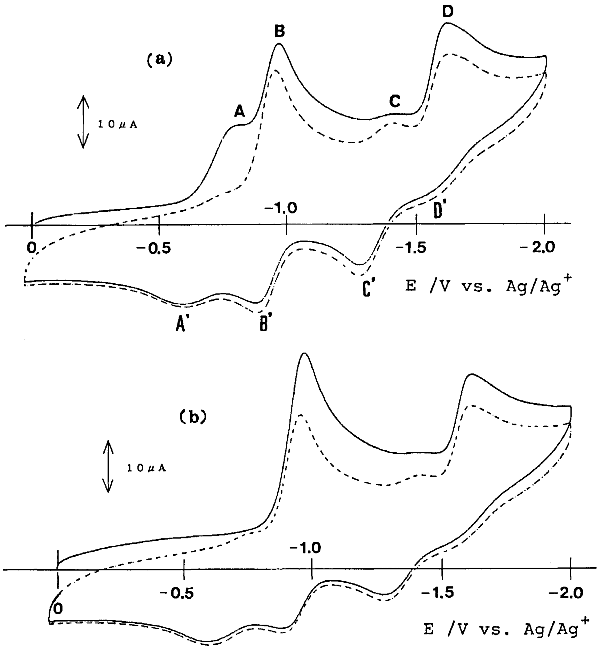


Fig. 8. Cyclic voltammograms of (a) *trans*- and (b) *cis*-[Co(dtc)$_2$(etpb)$_2$]$^+$ in CH_3CN; the first (—) and second (- - -) scans.

Table 7. Electrochemical Data Obtained by Means of RDE Measurements [a)]

Complex	Reduction				Oxidation	
	Co (III)/Co (II)		Co (II)/Co (I)		Co (IV)/Co (III)	
	$E_{1/2}$(red$_1$) V	[1—3][b)] mV	$E_{1/2}$(red$_2$) V	[1—3][b)] mV	$E_{1/2}$(ox) V	[3—1][b)] mV
trans-$[Co(dtc)_2(etpb)_2]BF_4$	−0.98	100	−1.66	70	1.25	85
cis-$[Co(dtc)_2(etpb)_2]BF_4$	−1.04	92	−1.73	80	1.34	68
cis-$[Co(dtc)_2(pome)_2]BF_4$	−1.13	82	−1.68	70	1.22	80
cis-$[Co(pipdtc)_2(pome)_2]BF_4$	−1.05	82	−1.68	65	1.17	78
$[Co(dtc)_2(dmope)]PF_6$[d)]	−1.24	60	c)		1.09	50
$[Co(dtc)_2(dmpe)]BF_4$[d)]	−1.38	55	c)		0.97	60
$[Co(dtc)(pome)_4](BF_4)_2$	−0.75	90	−1.09	68	c)	
$[Co(pipdtc)(pome)_4](BF_4)_2$	−0.78	90	−1.11	65	c)	

a) The measurements were carried out on CH_3CN solutions ([Complex]: 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); i_l means the limiting current.
c) The value was not observed in the potential window of CH_3CN. d) The data were obtained from Ref. 3.

B in the trans-isomer indicates rapid formation of the cis-isomer from reduced $[Co(dtc)_2(etpb)_2]^0$. Both cis- and trans-isomers show similar waves in the −1.4—−1.6 V region (C and D). Together with the RDE data for these isomers in Table 7, waves A–D can be assigned as follows;

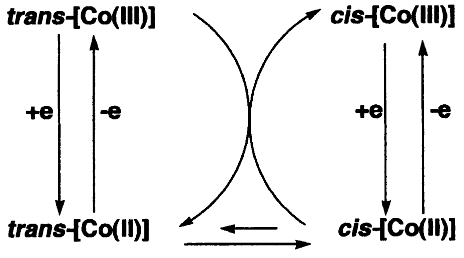
$$\mathrm{A}: \textit{trans}\text{-}[Co(dtc)_2(etpb)_2]^+ + e \rightarrow \textit{trans}\text{-}[Co(dtc)_2(etpb)_2]^0$$

$$\mathrm{B}: \textit{cis}\text{-}[Co(dtc)_2(etpb)_2]^+ + e \rightarrow \textit{cis}\text{-}[Co(dtc)_2(etpb)_2]^0$$

$$\mathrm{C}: \textit{trans}\text{-}[Co(dtc)_2(etpb)_2]^0 + e \rightarrow \textit{trans}\text{-}[Co(dtc)_2(etpb)_2]^-$$

$$\mathrm{D}: \textit{cis}\text{-}[Co(dtc)_2(etpb)_2]^0 + e \rightarrow \textit{cis}\text{-}[Co(dtc)_2(etpb)_2]^-$$

Waves A′—D′ are assigned to those corresponding to the reverse oxidation reactions. The formation of the cis-isomer after the reduction of the trans-isomer indicates rapid isomerization of the reduced *trans*-$[Co(dtc)_2(etpb)_2]^0$ to *cis*-$[Co(dtc)_2(etpb)_2]^0$ isomer and subsequent electron transfer between *trans*-$[Co(dtc)_2(etpb)_2]^+$ and *cis*-$[Co(dtc)_2(etpb)_2]^0$ to yield *cis*-$[Co(dtc)_2(etpb)_2]^+$. The reduced $[Co(dtc)_2(etpb)_2]^0$ species will be in equilibrium between the cis- and trans-isomers, and the equilibrium will be largely shifted to the cis-isomer as indicated by the first and second scan voltammograms of both *trans*- and *cis*-$[Co(dtc)_2(etpb)_2]^+$ in Fig. 8. These redox and isomerization reactions are summarized in the following scheme. (Scheme 1). The *cis*-$[Co(dtc)_2(pome)_2]^+$ and *cis*-$[Co(pipdtc)_2(pome)_2]^+$ complexes exhibit similar CV curves to that of *cis*-$[Co(dtc)_2(etpb)_2]^+$. No RDE data were obtained for trans-isomers of the pome complexes, because they were not isolated.



Scheme 1.

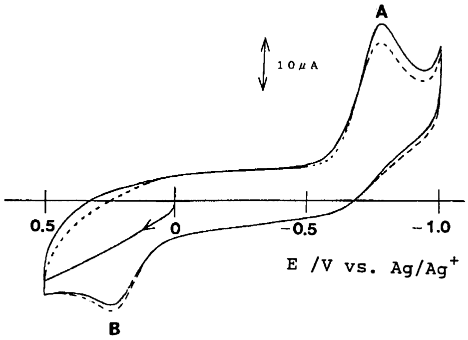


Fig. 9. Cyclic voltammograms in the Co(III)/Co(II) region of $[Co(dtc)(pome)_4]^{2+}$ in CH_3CN; the first (—) and second (---) scans.

Figure 9 shows the CV curve of $[Co(dtc)(pome)_4]^{2+}$. The wave at −0.78 V (A) is assigned to the reduction to $[Co(dtc)(pome)_4]^+$, but no oxidation wave is observed for this reduced species around this region. An oxidation wave (B) appeares at +0.25 V. In the CV curves of the first and second scans only these two waves, A and B are observed. There is no geometrical isomer for this complex. Thus wave B was tentatively assigned to the oxidation of $[Co(dtc)(pome)_3(pome\text{-}O)]^+$ which is a linkage-isomer of the reduced species formed rapidly after the reduction. This isomer isomerizes rapidly to the starting $[Co(dtc)(pome)_4]^{2+}$ complex after the oxidation. These reactions can be expressed as follows;

$$[Co(dtc)(pome)_4]^{2+} + e \rightarrow [Co(dtc)(pome)_4]^+ \quad \text{(wave A)}$$

$$[\mathrm{Co(dtc)(pome)_4}]^+ \rightarrow [\mathrm{Co(dtc)(pome)_3(pome\text{-}}O)]^+ \quad \text{(rapid isomerization)}$$

$$[\mathrm{Co(dtc)(pome)_3(pome\text{-}}O)]^+ - \mathrm{e} \rightarrow [\mathrm{Co(dtc)(pome)_3(pome\text{-}}O)]^{2+} \quad \text{(wave B)}$$

$$[\mathrm{Co(dtc)(pome)_3(pome\text{-}}O)]^{2+} \rightarrow [\mathrm{Co(dtc)(pome)_4}]^{2+} \quad \text{(rapid isomerization)}$$

The O-bonded linkage-isomer of $[\mathrm{Co(dtc)(pome)_4}]^{2+}$ was inferred to yield by irradiation as described in the previous section.

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