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Preparation and Characterization of $[CoX_2(edpp)_2]^+$(edpp=$NH_2CH_2CH_2P(C_6H_5)_2$, X=Cl^-, Br^-, I^-, NCO^-, NCS^-, N_3^-, NO_2^-) and $[CoX_2(en)(dppe)]^+$(en=$NH_2CH_2CH_2NH_2$, dppe=$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, X=$Cl^-$, Br^-, NCS^-). Crystal Structures of *trans*(NCS,NCS),*cis*(P,P)-$[Co(NCS)_2(edpp)_2]Br\cdot 3H_2O\cdot (CH_3)_2CO$ and *cis*-(NCS,NCS),*trans*(P,P)-$[Co(NCS)_2(edpp)_2]$-$Br\cdot CH_3OH$

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Dianionocobalt(III) complexes of the $[CoX_2(edpp)_2]^+$-type (X=Cl^-, Br^-, I^-, NCO^-, NCS^-, N_3^-, NO_2^-) have been prepared, where edpp is (2-aminoethyl)diphenylphosphine. The corresponding $[CoX_2(en)(dppe)]^+$ complexes are rather unstable and have been obtained only for X=Cl^-, Br^-, and NCS^-, where en and dppe denote ethylenediamine and 1,2-bis(diphenylphosphino)ethane, respectively. Except for the NCS^- complex of edpp, only one geometrical isomer has been obtained for all the complexes. Two geometrical isomers of $[Co(NCS)_2(edpp)_2]^+$ have been isolated, and crystal structures of *trans*(NCS,NCS),*cis*(P,P)-$[Co(NCS)_2(edpp)_2]Br\cdot 3H_2O\cdot (CH_3)_2CO$ and *cis*(NCS,NCS),*trans*(P,P)-$[Co(NCS)_2(edpp)_2]Br\cdot CH_3OH$ have been determined by X-ray analyses. The NCS^- ions in these complexes coordinate to the cobalt(III) ion through their nitrogen atoms with nearly linear Co–N–C–S fragments. The Co–P distances in the isomers are similar to one another, but the average Co–NH_2 and Co–NCS distances in the *trans*(NCS,NCS) isomer (2.010 and 1.882 Å) are longer and shorter than those of the *cis*(NCS,NCS) isomer (1.970 and 1.960 Å), respectively. Absorption spectra of all the complexes in solution have been recorded and the results compared with those of related dianionocobalt(III) complexes.

In previous papers, we have reported the preparation[1] and molecular structure[2] of *trans*(Cl,Cl),*cis*(P,P)-$[CoCl_2(edpp)_2]^+$ (edpp=$NH_2CH_2CH_2P(C_6H_5)_2$). The complex will be a useful starting material for preparing various bis(edpp) complexes. For example, it easily reacts with chelate ligands such as acetylacetonate or oxalate ions to afford the $[Co(O–O)(edpp)_2]^{n+}$-type complexes.[1] This paper deals with the $[CoX_2(edpp)_2]$-type complexes obtained by reactions of the dichloro complex with various unidentate anions X^-. There are five possible geometrical isomers of $[CoX_2(edpp)_2]^+$. Except for the NCS^- complex, however, only one isomer has been obtained for all of the complexes. For the NCS^- complex, two geometrical isomers have been isolated and the crystals subjected to X-ray structure analysis in order to determine the geometrical configuration as well as the linkage isomerism of the NCS^- ligand. Some structurally related $[CoX_2(en)(dppe)]^+$ complexes (en=$NH_2CH_2CH_2NH_2$, dppe=$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$) have been prepared. Absorption spectra of all the complexes have been recorded and the results compared with those of related diacidato cobalt(III) complexes.

Experimental

The edpp ligand was prepared by the literature method,[3] and handled under a nitrogen atmosphere until it formed cobalt(III) complexes. The dppe ligand was purchased from Strem Chemicals Inc. and used as received. Absorption spectra of the complexes were recorded on a Hitachi 323 spectrophotometer.

The starting complexes, *trans*(Cl,Cl)-$[CoCl_2(edpp)_2]ClO_4$, *trans*-$[CoCl_2(en)(dppe)]ClO_4\cdot H_2O$, *trans*-(P,N)-$[CoCO_3(edpp)_2]Cl\cdot 3.5H_2O$, and $[CoCO_3(en)(dppe)]ClO_4$ were prepared by methods reported previously.[1]

trans(Br,Br)-$[CoBr_2(edpp)_2]Br\cdot 2H_2O$. To a methanol solution (20 cm^3) of *trans*(P,N)-$[CoCO_3(edpp)_2]Cl\cdot 3.5H_2O$ (100 mg) was added 47% HBr (1.0 cm^3) at 5 °C. The resulting brown solution turned green on heating at 60 °C, and then was cooled in an ice bath. On addition of a small amount of water yellow-green crystals were precipitated, collected, washed with water and diethyl ether, and air-dried. Yield: 65 mg(55%). Found: C, 42.12; H, 4.30; N, 3.45%. Calcd for $C_{28}H_{36}N_2Br_3CoO_2P_2$: C, 42.40; H, 4.57; N, 3.53%. The complex is soluble in methanol and CH_2Cl_2, but insoluble in water and diethyl ether.

$[CoI_2(edpp)_2]I$. A methanol solution (20 cm^3) of *trans*(P,N)-$[CoCO_3(edpp)_2]Cl\cdot 3.5H_2O$ (100 mg) was degassed with nitrogen. To the solution was added colorless 57% HI (2.1 g) purified by passing a column of Dowex 1×8 (I^- form) dropwise at room temperature with stirring in an atmosphere of nitrogen. The color of the solution changed from red to brown, and a brown precipitate appeared. After 30 min the precipitate was filtered, washed with water and diethyl ether, and air-dried. Yield: 47 mg(35%). Found: C, 37.45; H, 3.99; N, 2.99%. Calcd for $C_{28}H_{32}N_2I_3CoP_2$: C, 37.44; H, 3.59; N, 3.12%.

cis(NCS,NCS)-$[Co(NCS)_2(edpp)_2]Cl\cdot H_2O$ *and trans(NCS, NCS)-*$[Co(NCS)_2(edpp)_2]Cl\cdot 1/2(NaCl)\cdot H_2O$. A methanol solution (300 cm^3) containing *trans*(Cl,Cl)-$[CoCl_2(edpp)_2]ClO_4$ (500 mg) and KNCS (200 mg) was stirred overnight at room temperature. The color of the solution slowly changed from green to dark red. The resulting solution was diluted with methanol (200 cm^3) and water (1 dm^3), and applied on a column (ϕ3 cm×10 cm) of SP-Sephadex C-25. The adsorbed product was eluted with 0.1 mol dm^{-3} NaCl in water–methanol (1:1), and the eluate was evaporated to half of its original volume at 35 °C under reduced pressure. The complex in the concentrate was extracted with CH_2Cl_2, and the extract was evaporated to dryness under reduced pressure. The residue was dissolved in the minimum amount of benzene-methanol (3:1), and the solution was chromatographed by use of a column (ϕ3 cm×50 cm) of Sephadex LH-20 and an eluent, benzene-methanol (3:1). The column showed two separate bands, the first orange and the second red bands, the complexes in which were determined to have the *cis*(NCS,NCS) and *trans*-(NCS,NCS) structures, respectively, by X-ray structure analysis (*vide infra*). Each eluate of the two bands was evaporated to dryness under reduced pressure, and the complex was dissolved in a small amount of methanol. The solution was mixed with an aqueous NaCl solution and stored in a refrigerator to yield crystals of the chloride of the complex, which were filtered, washed with water, and air-dried. Yield: The *cis*(NCS,NCS) isomer=94 mg(19%), the *trans*(NCS,NCS) isomer=184 mg (35%). Found for the *cis*(NCS,NCS) isomer: C, 52.07; H, 4.67; N, 7.79%. Calcd for $C_{30}H_{34}N_4ClCoOP_2S_2$: C, 52.44; H, 4.98; N, 8.15%. Found for the *trans*(NCS,NCS) isomer: C, 50.21, H, 4.44; N, 7.64%. Calcd for $C_{30}H_{34}N_4Cl_{1.5}CoNa_{0.5}OP_2S_2$: C, 50.30; H, 4.78; N, 7.82%. These complexes are soluble in acetone, alcohols, and CH_2Cl_2, but insoluble in water and diethyl ether.

trans*(NCO,NCO)-[Co(NCO)$_2$(edpp)$_2$]Cl·3.5H$_2$O.* This complex was prepared by the same method as that for the NCS$^-$ complex, using *trans*(Cl,Cl)-[CoCl$_2$(edpp)$_2$]ClO$_4$ (200 mg) and KNCO (80 mg). A very small orange band assignable to the *cis*(NCO,NCO) isomer was observed in column chromatography, but the complex could not be isolated. Yield: 41 mg(20%). Found: C, 51.37; H, 5.21; N, 7.72%. Calcd for $C_{30}H_{39}N_4ClCoO_{5.5}P_2$: C, 51.47; H, 5.61; N, 8.00%. The complex is purplish red in color, and its solubility is similar to that of the NCS$^-$ complex chloride.

trans*(N$_3$,N$_3$)-[Co(N$_3$)$_2$(edpp)$_2$]Cl·NaCl.* A methanol solution (80 cm^3) containing *trans*(Cl,Cl)-[CoCl$_2$(edpp)$_2$]-ClO$_4$ (100 mg) and NaN$_3$ (80 mg) was stirred at 50 °C for 1 h. The resulting greenish-brown solution was evaporated to dryness under reduced pressure, and the residue was mixed with water (100 cm^3) to yield a greenish-brown precipitate, which was collected and dissolved in a small amount of methanol. The solution was mixed with an aqueous NaCl solution and allowed to stand to yield a yellow-green crystalline precipitate, which was collected, washed with water and diethyl ether, and air-dried. In column chromatography of the product, no fraction indicative of other isomers was observed. Yield: 45 mg(45%). Found: C, 48.36; H, 4.78; N, 15.82%. Calcd for $C_{28}H_{32}N_8Cl_2CoNaP_2$: C, 48.36; H, 4.64; N, 16.11%. The complex is soluble in methanol and CH_2Cl_2, but insoluble in water and diethyl ether.

trans*(NO$_2$,NO$_2$)-[Co(NO$_2$)$_2$(edpp)$_2$]Cl·H$_2$O.* The complex in solution is photosensitive, and the following procedures should be carried out in the dark. A mixture of *trans*-(Cl,Cl)-[CoCl$_2$(edpp)$_2$]ClO$_4$ (300 mg) and NaNO$_2$ (160 mg) in methanol (220 cm^3) was stirred at 40 °C for 40 min to give a yellow solution. On further heating at 40 °C for 20 min the solution gave a yellow precipitate, and then Dowex 1X8 in the chloride form (1.0 g) was added to it. The mixture was stirred overnight at room temperature and filtered. The filtrate was diluted with water (1 dm^3), and the solution was applied on a column (ϕ3 cm×40 cm) of SP-Sephadex C-25. By elution with 0.05 mol dm^{-3} NaCl in methanol–water (1:4), a yellow, a very small yellow-orange, and a large brown bands were eluted separately. The eluate of the first yellow band was evaporated to a small volume under reduced pressure. The concentrate was mixed with NaCl and stored in a refrigerator to yield yellow crystals, which were filtered, washed with a small amount of cold water and diethyl ether, and air-dried. Yield: 18 mg (6.2%). Found: C, 50.59; H, 4.96; N, 8.17%. Calcd for $C_{28}H_{34}N_4ClCoO_5P_2$: C, 50.73; H, 5.17; N, 8.45%. The complex is soluble in water, methanol, and ethanol, but insoluble in diethyl ether.

The complex in the second yellow-orange band could not be isolated because of a small amount. The color of the last band became faint during the elution.

trans*-[CoBr$_2$(en)(dppe)]ClO$_4$.* To a methanol solution (15 cm^3) of [CoCO$_3$(en)(dppe)]ClO$_4$ (100 mg) was added dropwise 47% HBr at 20 °C. The resulting brown solution turned green on warming at 40 °C on a water bath. The green solution was further warmed at 45 °C for 2 min, and then NaClO$_4$·H$_2$O (1 g) was added. After cooling to room temperature, the precipitated green crystals were filtered, washed with water, and air-dried. Yield: 44 mg(40%). Found: C, 44.06; H, 4.31; N, 3.56%. Calcd for $C_{28}H_{32}N_2Br_2ClCoO_4P_2$: C, 43.30; H, 4.15; N, 3.56%. The complex is soluble in methanol and CH_2Cl_2, but insoluble in water and diethyl ether.

trans*-[Co(NCS)$_2$(en)(dppe)]Cl·1.5H$_2$O.* This complex was prepared by a method similar to that for the [Co(NCS)$_2$-(edpp)$_2$]$^+$ complex, using *trans*-[CoCl$_2$(en)(dppe)]ClO$_4$·H$_2$O and KNCS. Yield: 23%. Found: C, 51.93; H, 4.86; N, 7.95%. Calcd for $C_{30}H_{35}N_4ClCoO_{1.5}P_2S_2$: C, 51.77; H, 5.07; N, 8.05%. The complex is red in color and its solubility is similar to that of *trans*(NCS,NCS)-[Co(NCS)$_2$(edpp)$_2$]Cl·1/2(NaCl)·H$_2$O. In column chromatography a trace of an orange complex assignable probably to the cis isomer was observed, but it could not be isolated.

Attempts to prepare the [CoX$_2$(en)(dppe)]$^+$-type complexes with other X$^-$ ions such as I$^-$, NCO$^-$, N$_3^-$, or NO$_2^-$ were all unsuccessful.

TABLE 1. CRYSTALLOGRAPHIC DATA

	Complex **1**[a)]	Complex **2**[b)]
Formula	CoBr-$C_{33}H_{44}N_4O_4P_2S_2$	CoBr-$C_{31}H_{36}N_4OP_2S_2$
FW	825.64	745.55
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/a$	$P\bar{1}$
a/Å	23.094(3)	13.158(2)
b/Å	17.513(3)	14.138(2)
c/Å	9.755(2)	9.723(1)
α/deg	90	104.99(1)
β/deg	105.23(1)	97.41(1)
γ/deg	90	103.6(2)
V/Å^3	3806(1)	1663.1(5)
Z	4	2
d_c/g cm^{-3}	1.44	1.49
d_m/g cm^{-3}	1.43[c)]	1.46[d)]
Crystal size/mm	0.40×0.32×0.16	0.16×0.24×0.48
μ/mm^{-1}	1.819	2.058
2θ range	2—55°	2—60°
No. of data	5342	6790
R	0.044	0.056
Rw[e)]	0.060	0.051

a) Diffraction data at 168 K. Unit cell parameters at 292 K are a=23.232(3), b=17.621(3), c=9.827(2) Å, β=105.45(1)°, V=3877(1) Å^3. b) Diffraction data at 173 K. Unit cell parameters at 293 K are a=13.194(2), b=14.239(2), c=9.808(1) Å, α=105.15(1), β=97.27(1), γ=103.66(2)°, V=1693.0(5) Å^3. c) At 298 K. d) At 293 K. e) The weight (ω) was taken as $\omega=[\sigma_c^2+(0.0151|F_o|)^2]^{-1}$, where σ_c denotes a standard deviation of F_o calculated from counting statistics.

X-Ray Analyses. For X-ray studies, the bromides of *trans*(NCS,NCS)- and *cis*(NCS,NCS)-$[\mathrm{Co(NCS)_2(edpp)_2}]^+$ were prepared by methods similar to those for the corresponding chlorides, using KBr instead of NaCl. Single crystals of *trans*(NCS,NCS)-$[\mathrm{Co(NCS)_2(edpp)_2}]\mathrm{Br\cdot 3H_2O\cdot (CH_3)_2CO}$ (**1**) and *cis*(NCS,NCS)-$[\mathrm{Co(NCS)_2(edpp)_2}]\mathrm{Br\cdot CH_3OH}$ (**2**) were obtained by recrystallizing the respective bromides from methanol-acetone (1:1) and methanol-water (2:1) solutions, respectively.

Diffraction data were collected on a Rigaku AFC-5 four-

TABLE 2. POSITIONAL PARAMETERS FOR NON-HYDROGEN ATOMS[a]

trans(NCS,NCS),*cis*(P,P)-$[\mathrm{Co(NCS)_2(edpp)_2}]\mathrm{Br\cdot 3H_2O\cdot (CH_3)_2CO}$

Atom	x	y	z	B_{eq}/Å^2
Br	45195 (3)	11000 (3)	22604 (6)	2.7
Co	58282 (3)	15900 (4)	69470 (7)	1.4
P(1)	58333 (6)	18896 (7)	92163 (14)	1.6
P(2)	64714 (6)	24515 (8)	64230 (14)	1.7
S(1)	43044 (7)	32756 (9)	47579 (18)	3.2
S(2)	72927 (8)	−2625 (10)	84640 (19)	3.8
N(1)	51965 (18)	22639 (23)	61285 (43)	1.8
N(2)	64459 (18)	8866 (23)	76955 (43)	1.8
N(3)	52075 (19)	8041 (23)	70806 (45)	1.9
N(4)	57786 (19)	11535 (25)	50222 (43)	2.0
C(1)	48234 (23)	26622 (29)	55650 (54)	1.9
C(2)	67869 (23)	4222 (31)	79974 (51)	1.9
C(3)	54433 (25)	10433 (29)	96083 (56)	2.2
C(4)	49461 (25)	8869 (30)	83047 (61)	2.5
C(5)	62827 (24)	22852 (33)	45077 (53)	2.4
C(6)	62258 (26)	14290 (34)	43112 (56)	2.6
C(7)	65412 (23)	19535 (29)	105613 (50)	1.8
C(8)	67894 (24)	26663 (30)	109900 (54)	2.2
C(9)	73501 (26)	27238 (36)	119734 (61)	3.0
C(10)	76536 (26)	20588 (39)	125334 (61)	3.3
C(11)	74017 (27)	13546 (34)	121351 (59)	2.9
C(12)	68532 (25)	12973 (30)	111605 (54)	2.2
C(13)	54006 (22)	27026 (28)	95928 (53)	1.8
C(14)	53186 (23)	33623 (29)	87707 (54)	2.0
C(15)	49922 (26)	39630 (31)	90978 (61)	2.7
C(16)	47544 (24)	39206 (31)	102642 (61)	2.6
C(17)	48375 (25)	32745 (31)	110869 (57)	2.4
C(18)	51529 (23)	26677 (30)	107656 (53)	2.1
C(19)	63625 (23)	34633 (29)	66777 (56)	2.0
C(20)	59041 (22)	38716 (31)	57459 (57)	2.2
C(21)	58286 (25)	46350 (32)	59800 (65)	2.8
C(22)	61918 (28)	50013 (33)	71603 (72)	3.3
C(23)	66370 (28)	46054 (34)	80823 (67)	3.3
C(24)	67353 (25)	38397 (31)	78494 (58)	2.5
C(25)	72848 (23)	23277 (28)	70745 (53)	1.8
C(26)	76467 (24)	26215 (30)	62518 (59)	2.3
C(27)	82609 (26)	25920 (32)	67673 (64)	2.7
C(28)	85229 (24)	22926 (33)	80799 (65)	2.9
C(29)	81678 (25)	20151 (34)	88975 (60)	2.8
C(30)	75563 (24)	20290 (31)	83880 (55)	2.2
O(1)	70671 (18)	41646 (23)	44256 (42)	3.2
O(2)	90903 (18)	44892 (23)	50172 (39)	2.9
O(3)	65028 (21)	−7019 (28)	107638 (45)	4.5
O(4)	81923 (20)	45842 (26)	63161 (45)	3.9
C(31)	67839 (25)	46880 (33)	37436 (60)	2.6
C(32)	62678 (31)	45360 (43)	25318 (71)	4.4
C(33)	69433 (31)	55125 (35)	40649 (72)	3.8

cis(NCS,NCS),*trans*(P,P)-$[\mathrm{Co(NCS)_2(edpp)_2}]\mathrm{Br\cdot CH_3OH}$

Atom	x	y	z	B_{eq}/Å^2
Br(A)[b]	49434 (4)	31649 (4)	64473 (5)	2.7
Br(B)[c]	50281 (72)	19414 (77)	63560 (89)	5.4
Co	70130 (4)	26213 (4)	32526 (5)	1.4
S(1)	62816 (15)	2741 (11)	−13893 (14)	6.4
S(2)	103986 (9)	43694 (10)	29152 (13)	4.0
P(1)	60699 (7)	35292 (7)	22965 (9)	1.5
P(2)	78433 (7)	16019 (7)	41495 (9)	1.6
N(1)	67787 (20)	16244 (21)	13030 (28)	1.4
N(2)	83530 (23)	34570 (23)	30718 (29)	1.7
N(3)	71916 (24)	36679 (24)	51384 (31)	2.1
N(4)	56944 (23)	17825 (23)	35911 (31)	2.0
C(1)	65612 (32)	11075 (32)	2982 (48)	2.9
C(2)	91573 (30)	38436 (27)	30269 (35)	1.9
C(3)	60607 (29)	44989 (28)	39481 (37)	2.0
C(4)	70876 (31)	46815 (29)	50029 (38)	2.3
C(5)	66836 (30)	5810 (28)	40724 (41)	2.2
C(6)	58234 (31)	10893 (32)	44853 (42)	2.6
C(7)	47075 (26)	28438 (25)	13952 (35)	1.5
C(8)	44774 (30)	23742 (28)	−1020 (28)	2.1
C(9)	34418 (31)	18094 (30)	−8138 (41)	2.6
C(10)	26400 (32)	16900 (36)	−303 (48)	3.5
C(11)	28637 (32)	21407 (37)	14571 (47)	3.5
C(12)	38853 (30)	27179 (32)	21725 (39)	2.4
C(13)	66382 (26)	41801 (26)	10802 (35)	1.6
C(14)	73381 (30)	38185 (28)	2366 (37)	2.0
C(15)	77604 (30)	43439 (31)	−6692 (39)	2.2
C(16)	75042 (30)	52299 (30)	−7507 (39)	2.2
C(17)	68125 (32)	55742 (31)	511 (42)	2.6
C(18)	63703 (30)	50554 (29)	9697 (39)	2.1
C(19)	85884 (29)	21178 (28)	60113 (35)	1.9
C(20)	82645 (32)	17749 (32)	71461 (39)	2.6
C(21)	88861 (37)	21758 (35)	85165 (40)	3.2
C(22)	98214 (38)	29271 (37)	88062 (41)	3.6
C(23)	101549 (36)	32959 (36)	76952 (45)	3.5
C(24)	96326 (34)	28926 (32)	63133 (40)	2.8
C(25)	87546 (27)	10166 (27)	32088 (35)	1.7
C(26)	89960 (30)	1937 (30)	35603 (38)	2.2
C(27)	97637 (32)	−2085 (31)	29681 (41)	2.6
C(28)	102845 (31)	2024 (32)	20215 (42)	2.7
C(29)	100206 (31)	10075 (32)	16319 (40)	2.6
C(30)	92420 (30)	14021 (29)	22022 (38)	2.1
C(31)	19962 (48)	21886 (47)	53721 (63)	6.1
O(A)[d]	25981 (31)	14784 (32)	49361 (54)	5.3
O(B)[e]	18338 (115)	29634 (106)	47678 (150)	1.6

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a) The values are multiplied by 10^5. The thermal parameters are given by the equivalent temperature factors.
b) Occupancy factor: 0.94. c) Occupancy factor: 0.06. d) Occupancy factor: 0.84. e) Occupancy factor: 0.16.

circle diffractometer with use of graphite-monochromatized Mo-*K*α radiation at 168K for complex **1** and at 173K for complex **2**. The low-temperature measurements were made with an attached Rigaku variable-temperature apparatus based on a cold nitrogen gas stream method. The procedures used for data collections as well as the methods used in the solution and refinement of the structure were standard and have been described previously.[4] The intensity data were corrected for Lorentz-polarization effects and for absorption. Non-hydrogen and hydrogen atoms were refined anisotropically and isotropically, respectively. Pertinent crystallographic data are summarized in Table 1. Tables 2 lists positional parameters for non-hydrogen atoms in complexes **1** and **2**. In complex **2** the bromide ion and the oxygen atom of methanol are disordered and located at two positions with occupancy factors (P) of $P_{Br(A)}=0.94$ and $P_{Br(B)}=0.06$, and $P_{O(A)}=0.84$ and $P_{O(B)}=0.16$, respectively. The F_o-F_c data, final thermal parameters, and hydrogen atomic coordinates are preserved by the Chemical Society of Japan (Document No. 8450).

All the calculations were carried out on a HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with the Universal Computation Program System UNICS III.[5]

Results and Discussion

Structure of trans*(NCS,NCS),*cis*(P,P)-[Co(NCS)*$_2$*(edpp)*$_2$*]Br·3H*$_2$*O·(CH*$_3$*)*$_2$*CO (1) and* cis*(NCS,NCS),*trans*(P,P)-[Co(NCS)*$_2$*(edpp)*$_2$*]Br·CH*$_3$*OH (2).* Figures 1 and 2 show stereoviews of the complex cations in **1** and **2**, respectively. The relevant bond lengths and bond angles based on the atomic numbering scheme in these figures are listed in Tables 3 and 4. All the cations have a distorted octahedral coordination with two P and four N atoms, the NCS$^-$ ions coordinating to the cobalt(III) ion through their N atoms.

In complex 1 the complex cation has a *trans*(NCS, NCS),*cis*(P,P) configuration. The two edpp chelate rings adopt a skew (gauche) conformation of δδ or λλ chirality (racemic).[6] The same structure has been found for the bis(edpp) moiety of *trans*(Cl,Cl),*cis*(P,P)-[CoCl$_2$(edpp)$_2$][CoCl$_4$]$_{1/2}$,[2] (complex **3**). The orientation of phenyl groups on the P atoms in complex **1** is also very similar to that in complex **3**. The average Co-P distance of 2.270 Å in complex **1** is slightly longer than that in complex **3** (2.255 Å), whereas the average Co-NH$_2$ distance (2.010 Å) is slightly shorter than that in complex **3** (2.024 Å), although the differences may be less meaningful on the statistical ground. The average P-Co-P angle in complex **1** (103.3°) is also widened as has been seen in complex **3** (103.1°) to alleviate the overcrowding due to bulky substituents on the P atoms. Other structural parameters on the edpp chelate ligand are almost similar to those in complex **3**. The NCS$^-$ ions are almost linear and coordinate to the cobalt(III) ion through their N atoms with a slightly bent structure, the Co-N-C angles ranging from 171.8—176.2°. The Co-NCS distances (1.881, 1.883 Å) are nearly the same as those reported for *trans*-[Co(NCS)$_2$\{P(OC$_2$H$_5$)$_3$\}$_4$]$^+$ (1.838, 1.874 Å) and *trans*-[Co(NCS)$_2$(trien)]$^+$ (1.901, 1.884 Å; trien=triethylenetetramine).[8]

On the other hand, complex **2** has a *cis*(NCS,NCS), *trans*(P,P) structure. The formation of only *trans*(P,P) isomer in *cis*(NCS,NCS)-[Co(NCS)$_2$(edpp)$_2$]$^+$ is rather unusual, since complexes of the [Co(O-O)(edpp)$_2$]$^{n+}$ type, where O-O is a bidentate ligand such as an oxalate or acetylacetonate ion, form always the *trans*(P,N) isomer in the largest abundance among three possible isomers, *trans*(P,P), *trans*(P,N), and *trans*(N,N).[1] The Co-P distances (2.263, 2.275 Å) in complex **2** are nearly the same as those in complex **1** (2.272, 2.268 Å), despite the two trans-labilizing P donor atoms are in the trans positions to each other. On the other hand, the Co-NH$_2$ distances (1.976, 1.982 Å) are fairly shorter than those in complex **1** (2.003, 2.016 Å) and are nearly the same as those in cobalt(III) diamine complexes such

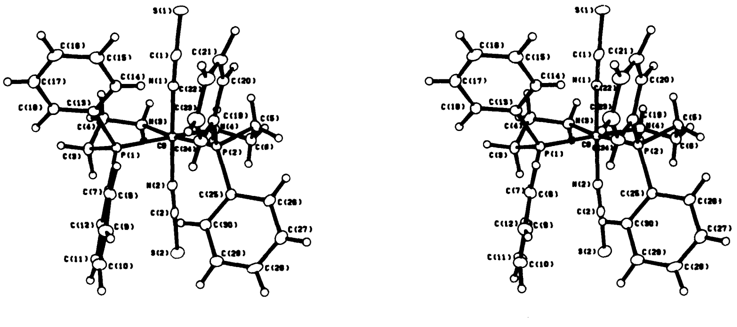

Fig. 1. ORTEP stereoview of *trans*(NCS,NCS),*cis*(P,P)-[Co(NCS)$_2$(edpp)$_2$]$^+$ in complex **1**.

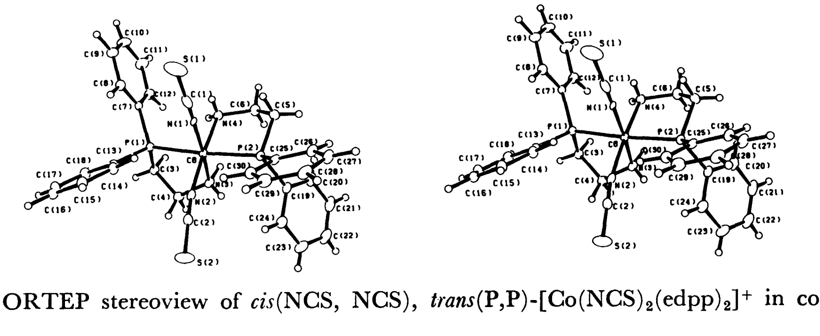

Fig. 2. ORTEP stereoview of *cis*(NCS, NCS), *trans*(P,P)-[Co(NCS)$_2$(edpp)$_2$]$^+$ in complex **2**.

TABLE 3. SELECTED BOND LENGTHS (Å) FOR *trans*-(NCS,NCS),*cis*(P,P)-$[Co(NCS)_2(edpp)_2]Br\cdot 3H_2O\cdot (CH_3)_2CO$ (**1**) AND *cis*(NCS,NCS),*trans*(P,P)-$[Co(NCS)_2(edpp)_2]Br\cdot CH_3OH$ (**2**)

	1	2
Co-P(1)	2.272(2)	2.263(3)
Co-P(2)	2.268(2)	2.275(3)
Co-N(1)	1.883(4)	1.984(3)
Co-N(2)	1.881(4)	1.935(5)
Co-N(3)	2.016(4)	1.982(3)
Co-N(4)	2.003(4)	1.976(5)
P(1)-C(3)	1.826(6)	1.825(4)
P(1)-C(7)	1.811(5)	1.805(4)
P(1)-C(13)	1.831(5)	1.809(4)
P(2)-C(5)	1.827(5)	1.816(6)
P(2)-C(19)	1.816(5)	1.815(3)
P(2)-C(25)	1.831(5)	1.821(4)
N(1)-C(1)	1.132(6)	1.015(5)
N(2)-C(2)	1.116(7)	1.083(5)
N(3)-C(4)	1.480(8)	1.508(6)
N(4)-C(6)	1.469(8)	1.492(6)
C(1)-S(1)	1.648(5)	1.690(4)
C(2)-S(2)	1.652(5)	1.658(5)
C(3)-C(4)	1.498(7)	1.512(5)
C(5)-C(6)	1.513(8)	1.520(7)

TABLE 4. SELECTED BOND ANGLES (ϕ/°) FOR *trans*-(NCS,NCS),*cis*(P,P)-$[Co(NCS)_2(edpp)_2]Br\cdot 3H_2O\cdot (CH_3)_2CO$ (**1**) AND *cis*(NCS,NCS), *trans*(P,P)-$[Co(NCS)_2(edpp)_2]Br\cdot CH_3OH$ (**2**)

	1	2
P(1)-Co-P(2)	103.3(1)	175.5(0)
P(1)-Co-N(1)	94.2(1)	90.4(1)
P(1)-Co-N(2)	87.9(1)	92.2(1)
P(1)-Co-N(3)	85.2(1)	85.7(1)
P(1)-Co-N(4)	170.4(1)	90.6(1)
P(2)-Co-N(1)	88.2(1)	87.3(1)
P(2)-Co-N(2)	92.8(1)	91.8(1)
P(2)-Co-N(3)	171.0(1)	96.5(1)
P(2)-Co-N(4)	85.5(1)	85.5(1)
N(1)-Co-N(2)	177.4(2)	94.0(2)
N(1)-Co-N(3)	88.3(2)	176.2(1)
N(1)-Co-N(4)	89.7(2)	89.3(2)
N(2)-Co-N(3)	90.4(2)	86.2(2)
N(2)-Co-N(4)	88.0(2)	175.7(1)
N(3)-Co-N(4)	86.2(2)	90.8(2)
Co-P(1)-C(3)	98.0(2)	100.3(2)
Co-P(1)-C(7)	119.5(2)	115.5(2)
Co-P(1)-C(13)	120.8(2)	117.8(1)
Co-P(2)-C(5)	97.5(2)	99.5(1)
Co-P(2)-C(19)	119.7(2)	117.2(1)
Co-P(2)-C(25)	121.1(2)	121.5(2)
Co-N(1)-C(1)	176.2(5)	172.9(3)
Co-N(2)-C(2)	171.8(4)	171.2(4)
Co-N(3)-C(4)	115.7(3)	114.1(2)
Co-N(4)-C(6)	116.3(3)	117.0(2)
N(1)-C(1)-S(1)	177.2(5)	176.3(4)
N(2)-C(2)-S(2)	179.3(5)	176.7(4)
N(3)-C(4)-C(3)	108.6(5)	108.6(3)
N(4)-C(6)-C(5)	108.3(5)	110.1(4)
C(3)-P(1)-C(7)	107.4(2)	108.7(2)
C(3)-P(1)-C(13)	105.3(3)	107.7(2)
C(7)-P(1)-C(13)	104.1(2)	106.3(2)
C(5)-P(2)-C(19)	106.9(3)	108.3(2)
C(5)-P(2)-C(19)	106.5(3)	107.3(2)
C(19)-P(2)-C(25)	103.6(2)	102.3(2)
P(1)-C(3)-C(4)	106.3(4)	106.9(3)
P(2)-C(5)-C(6)	106.1(4)	106.1(3)

as $[Co(en)_3]^{3+}$ (1.978 Å).[9] The elongation of Co-NH_2 distance in complex **1** is attributable to trans influence of the P atom.[2,10] The Co-NCS fragment is nearly linear geometry similar to those in complex **1**, but significant differences in bond distance are found between the two isomers. The average Co-N distance in complex **2** (1.960 Å) is longer than that in complex **1** (1.882 Å), whereas the average N-C distance in the former (1.049 Å) is shorter than that in the latter (1.124 Å). No significant difference is found for the C-S distance between complex **1** (1.650 Å) and complex **2** (1.674 Å). The octahedral angles around the cobalt(III) ion in complex **2** are not largely deviated from the right angle (85.3—96.5°). The two edpp chelate rings take δ and λ conformations, and the complex ion can be designated as a *lel·ob* isomer.

Complexes **1** and **2** include acetone and methanol, respectively as organic solvents of crystallization. Such inclusion of organic solvents in crystals has often been found in metal complexes containing bulky organic groups such as $-PPh_2$. Nonbonded distances in the crystals and stereoviews of the crystal structures are given in the supplementary materials (Document No. 8450).

Preparation and Absorption Spectra of the Complexes. The $[CoX_2(edpp)_2]^+$-type complexes ($X=NCO^-$, NCS^-, N_3^-, NO_2^-) were obtained by substitution reactions between *trans*(Cl,Cl)-$[CoCl_2(edpp)_2]^+$ and MX (M=Na or K) in methanol. The Br^- and I^- complexes were prepared by treating *trans*(P,N)-$[CoCO_3(edpp)_2]^+$ with HBr and HI, respectively, in order to avoid the contamination of mixed-halogeno complexes. The reaction for the I^- complex was carried out under an atmosphere of nitrogen to prevent oxidation of I^- to I_3^- which forms a quite insoluble salt with $[CoI_2(edpp)_2]^+$. For each complex only one isomer was obtained except for the NCS^- complex. It formed two isomers, *trans*-(NCS,NCS),*cis*(P,P)- and *cis*(NCS,NCS),*trans*(P,P)-isomers as described in the preceeding section. The formation ratio of the two isomers, trans:cis was *ca.* 2:1 under the given experimental conditions. Both isomers in ethanol are stable and do not isomerize even at a boiling point.

Attempts to prepare the corresponding $[CoX_2(en)(dppe)]^+$ complexes were made by procedures similar to those for $[CoX_2(edpp)_2]^+$, using *trans*-$[CoCl_2(en)(dppe)]^+$ and MX (M=Na or K, $X=NCO^-$, NCS^-, N_3^-, NO_2^-), and $[CoCO_3(en)(dppe)]^+$ and HX (X=Br, I). However, the complexes obtained are only those of Br^-

and NCS^-. No reaction took place between *trans*-$[CoCl_2(en)(dppe)]^+$ and KNCO at room temperature, reactions at higher temperatures or in the presence of large excess of KNCO causing reduction of cobalt(III) to cobalt(II). A dark-geen complex assignable to $[Co(N_3)_2(en)(dppe)]^+$ was yielded by a similar reaction with NaN_3, but the complex decomposed in the course of purification. In the case of the I^- complex, orange-yellow crystals were obtained from the reaction mixture. However, elemental analysis revealed the product to be the composition of $Co(dppe)_2I$. The reaction with $NaNO_2$ resulted in the formation of *trans*-$[Co(NO_2)_2(en)_2]^+$ and $[Co(NO)_2(dppe)]^+$.[11]

Figure 3 shows absorption spectra of $[CoX_2(edpp)_2]^+$ in methanol for $X=Cl^-$ and Br^-, and in CH_2Cl_2 for $X=I^-$. Spectral data are given in Table 5. The near infrared spectra of the Cl^- and Br^- complexes were obtained in CH_2Cl_2 solutions. The structure of the Cl^- complex has been determined by X-ray analysis to have a *trans*-(Cl,Cl),*cis*(P,P) configuration.[2] Thus the Br^- complex which gives a spectrum similar to that of the Cl^- complex can be assigned to the *trans*(Br,Br),*cis*(P,P) isomer. The bands around 16000 cm^{-1} of these Cl^- and Br^- complexes are assigned to the split component (Ia) of the first d-d absorption band from a comparison with the spectrum of *trans*-$[CoCl_2(en)_2]^+$.[12] The I^- complex shows a broad spectrum with no peak except the band at 10200 cm^{-1} which can be assigned to the spin-forbidden d-d band described below, the spin-allowed, first d-d band being hidden by strong I^- to Co^{III} charge-transfer bands.[13] Thus the structure of this complex can not be assigned unequivocally from the spectrum. No good NMR spectrum of the complex was obtained because of its instability. The infrared spectrum somewhat differs from those of *trans*(X,X)-$[CoX_2(edpp)_2]X$ ($X=Cl^-$, Br^-). The structure of the I^- complex remains unknown at present.

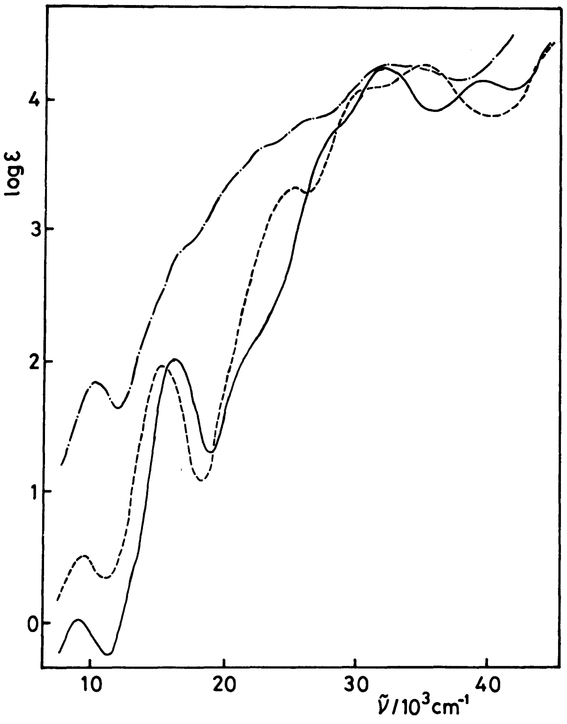

Fig. 3. Absorption spectra of *trans*(X,X)-$[CoX_2(edpp)_2]^+$: $X=Cl^-$ (——), Br^- (----), and I^- (—·—).

All of the halogen complexes of edpp show a distinct band around 10000 cm^{-1}. The peak positions are not much different among the complexes, and the band intensities increase in the order of the $Cl^- < Br^- < I^-$ complexes. These features are similar to those of the spin-forbidden d-d bands in the series of cobalt(III) halogeno complexes such as $[CoX(NH_3)_5]^{2+}$ (*ca.* 11000 cm^{-1})[14] or $[CoX(CN)_5]^{3-}$ (*ca.* 20000 cm^{-1}).[15] Thus the bands around 10000 cm^{-1} in the present halogeno complexes can be assigned to the spin-forbidden d-d band. The yellow-green $[CoBr_2(en)(dppe)]^+$ complex is assigned to the trans isomer, since the spectrum quite resembles that of *trans*-$[CoCl_2(en)(dppe)]^+$[1] as shown in Fig. 4. The corresponding X^- complexes of dppe and edpp show spectra similar to each other.

In Fig. 5 are compared absorption spectra of *trans*-(NCS,NCS),*cis*(P,P)- and *cis*(NCS,NCS),*trans*(P,P)-$[Co(NCS)_2(edpp)_2]^+$ and $[Co(NCS)_2(en)(dppe)]^+$ in methanol solutions. The spectrum of the dppe complex is very similar to that of the *trans*(NCS,NCS),*cis*-(P,P) isomer of the edpp complex, and the complex can be assigned to the trans isomer. The first d-d band of the *cis*(NCS,NCS),*trans*(P,P) isomer is observed as a shoulder absorption at *ca.* 20000 cm^{-1}. The shoulder

TABLE 5. ABSORPTION SPECTRAL DATA OF THE COMPLEXES ($\tilde{\nu}/10^3$ cm^{-1} (log ε))

trans(Cl,Cl),*cis*(P,P)-$[CoCl_2(edpp)_2]^+$	8.8(0.13), 15.9(2.03), 21.5(2.1)*, 27.5(3.8)*, 31.5(4.27), 39.0(4.19)
trans-$[CoCl_2(en)(dppe)]^+$	16.5(2.13), 22.5(2.6)*, 28(3.6)*, 33.0(4.27), 39.0(4.44)
trans(Br,Br),*cis*(P,P)-$[CoBr_2(edpp)_2]^+$	9.3(0.50), 15.1(1.96), 24.9(3.34), 30(4.1)*, 34.5(4.30)
trans-$[CoBr_2(en)(dppe)]^+$	15.9(2.24), 24.5(3.2)*, 31(4.1)*, 35.0(4.35)
$[CoI_2(edpp)_2]^+$	10.2(1.84), 14(2.2)*, 16.5(2.8)*, 20(3.3)*, 22.5(3.6)*, 26.5(3.9)*, 32.5(4.26)
trans(NCS,NCS),*cis*(P,P)-$[Co(NCS)_2(edpp)_2]^+$	18.5(2.65), 27(3.9)*, 33.5(4.21)
trans-$[Co(NCS)_2(en)(dppe)]^+$	18.9(2.68), 27(3.7)*, 33.5(4.25)
cis(NCS,NCS),*trans*(P,P)-$[Co(NCS)_2(edpp)_2]^+$	20(3.0)*, 26.9(4.07), 33.1(4.15)
$[Co(NCO)_2(edpp)_2]^+$	18.4(2.35), 24(2.4)*, 30.8(4.33), 37(4.0)*
$[Co(N_3)_2(edpp)_2]^+$	15(2.0)*, 17.5(2.43), 27.5(4.09), 32.9(4.21)
$[Co(NO_2)_2(edpp)_2]^+$	22.5(2.9)*, 28.8(4.56)

* Shoulder absorption

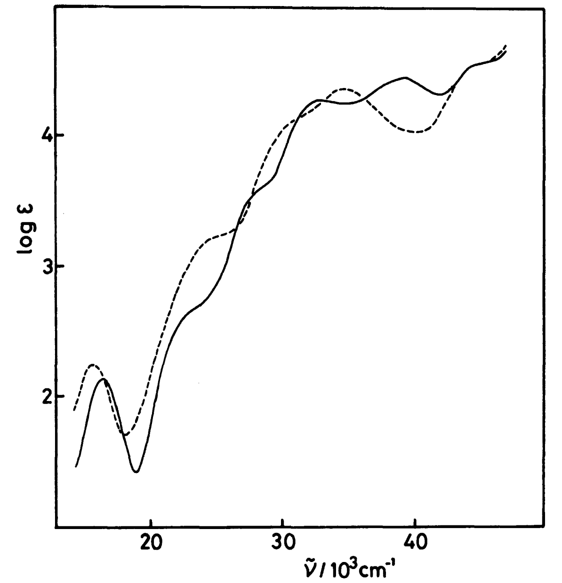

Fig. 4. Absorption spectra of *trans*-$[CoX_2(en)(dppe)]^+$: X=Cl^- (——), and Br^- (----).

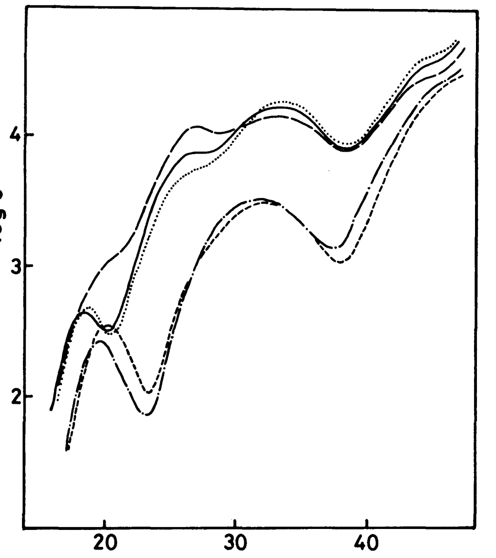

Fig. 5. Absorption spectra of bis(isothiocyanato) complexes: *trans*(NCS, NCS), *cis*(P,P)-$[Co(NCS)_2(edpp)_2]^+$ (——), *cis*(NCS, NCS), *trans*(P,P)-$[Co(NCS)_2(edpp)_2]^+$ (— —), *trans*-$[Co(NCS)_2(en)(dppe)]^+$ (······), *trans*-$[Co(NCS)_2(en)_2]^+$ (—·—), and *cis*-$[Co(NCS)_2(en)_2]^+$ (----).

lies in the high energy side and its intensity is fairly strong as compared with the first d-d band of the *trans*(NCS,NCS),*cis*(P,P) isomer. A similar spectral difference has been reported between the first d-d bands of *cis*- and *trans*-$[Co(NCS)_2(en)_2]^+$ (cis isomer: 20400 cm^{-1}, $\log\varepsilon=2.54$; trans isomer: 19700 cm^{-1}, $\log\varepsilon=2.44$).[16] However, the difference in band intensity between the two isomers of the edpp complex is remarkable. The strong intensity of the cis isomer may be attributable to the *trans*(P,P) configuration involved in this isomer, since *trans*(P,P)-$[Co(C_2O_4)(edpp)_2]^+$ shows the first d-d band (20400 cm^{-1}, $\log\varepsilon=3.08$) much stronger than that of the corresponding *trans*(P,N) isomer (20000 cm^{-1}, $\log\varepsilon=2.54$).[1]

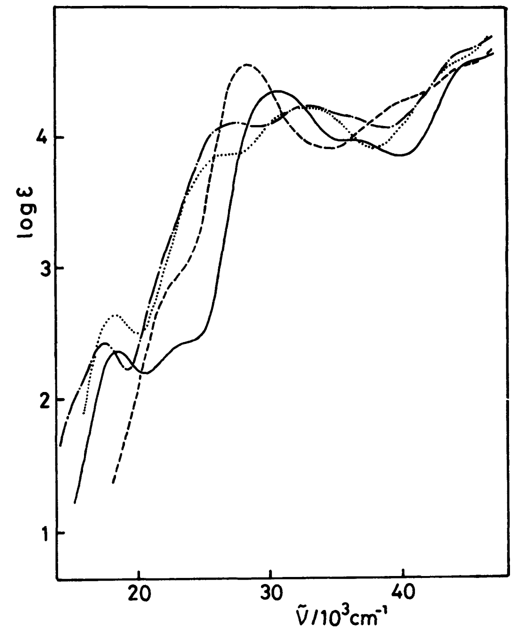

Fig. 6. Absorption spectra of $[CoX_2(edpp)_2]^+$: X= NCO^- (——), N_3^- (—·—), NO_2^- (----), and NCS^- (······).

Figure 6 compares absorption spectra of $[CoX_2(edpp)_2]^+$ (X=NCO^-, N_3^-, and NO_2^-) in methanol solutions with that of *trans*(NCS,NCS),cis(P,P)-$[Co(NCS)_2(edpp)_2]^+$. At present, we can not assign geometrical structures of the complexes unequivocally on the basis of these spectra. In column chromatography using SP-Sephadex C-25 or Sephadex LH-20, however, any fractions of each of these complexes did not show optical activity, while *cis*(NCS,NCS),*trans*(P,P)-$[Co(NCS)_2(edpp)_2]^+$ was partially resolved by similar chromatography. Further, complexes of the $[CoX_2(edpp)_2]^+$ type seem to be more stable in the *trans*(X,X) isomer than the *cis*(X,X) one as exemplified by the formation ratio of the NCS^- complex. On the basis of these facts, all the complexes in Fig. 6 may be assigned to the *trans*(X,X) isomer. That the first d-d band of the N_3^- complex is at lower energy than that of the NCS^- complex is consistent with the ranking of N_3^- in the spectrochemical series.[17] The d-d band positions of the NCO^- and NO_2^- complexes clearly indicate the isocyanato and nitro coordination modes, respectively. The observed shoulder at *ca.* 24000 cm^{-1} in the NCO^- complex may be assigned to the second d-d band, although the energy separation between this shoulder and the first band is rather small. In general, the separation between the first and second d-d bands in cobalt(III) phosphine complexes has been reported to become small.[18] The intensities of d-d bands of the NCO^- and N_3^- complexes are not so strong as that of *cis*(NCS,NCS),*trans*(P,P)-$[Co(NCS)_2(edpp)_2]^+$. Thus the complexes will have the *trans*(X,X),*cis*(P,P) configuration. The NO_2^- complex shows the first absorption band with fairly strong intensity, and the spectral pattern in this band region resembles that of *cis*(NCS, NCS),*trans*(P,P)-[Co(NCS)$_2$(edpp)$_2$]$^+$, indicating the *trans*(NO$_2$,NO$_2$),*trans*(P,P) configuration. Examination of molecular models indicates that the NO$_2^-$ ligands in the *trans*(NO$_2$,NO$_2$),*cis*(P,P) configuration cause a big hindrance with the phenyl groups, while such a hindrance is much reduced in the *trans*(NO$_2$, NO$_2$),*trans*(P,P) configuration. In fact, the [CoX$_2$(en)-(dppe)]$^+$- and [CoX$_2$(dpee)$_2$]$^+$-type complexes (dpee= *cis*-1,2-bis(diphenylphosphino)ethylene)[19], where the PPh$_2$ groups are in the cis positions, do not form stable complexes with NO$_2^-$ ions.

For a given X$^-$ ligand, the first d-d band of *trans*-(X,X)-[CoX$_2$(edpp)$_2$]$^+$ is observed at slightly lower energy than that of *trans*(X,X)-[CoX$_2$(en)(dppe)]$^+$ (X= Cl$^-$, Br$^-$, NCS$^-$), and at similar energy to that of *trans*-(X,X)-[CoX$_2$(dpee)$_2$]$^+$ (X=Cl$^-$, Br$^-$, NCO$^-$, N$_3^-$).[19] The NCS$^-$ complex of dpee is reported to show the band at anomalously low energy (16800 cm^{-1}).[19] The corresponding *trans*(X,X)-[CoX$_2$(en)$_2$]$^+$ complex gives the first d-d band at the highest energy among these edpp, dppe, and dpee complexes.

In the ultraviolet region, the present phosphine complexes exhibit strong absorption bands due to charge-transfer transitions between the X$^-$, PPh$_2$, and NH$_2$ groups and cobalt(III). In order to assign properly these spectra, more spectral data will be needed.

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References

1) M. Atoh, I. Kinoshita, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **55**, 3179 (1982).

2) I. Kinoshita, Y. Yokota, K. Matsumoto, S. Ooi, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **56**, 1067 (1983).

3) K. Issleib and D. Haferburg, *Z. Naturforsch., Teil B*, **20**, 916 (1965).

4) M. Sugimoto, J. Fujita, H. Ito, K. Toriumi, and T. Ito, *Inorg. Chem.*, **22**, 955 (1983).

5) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).

6) In the crystal structure of hexafluorophosphate of *trans*(NCS,NCS),*cis*(P,P)-[Co(NCS)$_2$(edpp)$_2$]$^+$, two edpp chelate rings have been found to assume a $\delta\lambda$(meso) form. The X-ray crystal analysis (R=0.056) and elemental analysis are best fitted to the composition of [Co(NCS)$_2$(edpp)$_2$](PF$_6$)$_{1/3}$·F$_{2/3}$·(PF$_5$)$_{1/3}$·H$_2$O. M. Atoh, K. Kashiwabara, J. Fujita, T. Ito, and H. Ito, 31st Symposium on Coordination Chemistry Japan (Sendai), 1981, Abstr. No. 3C14.

7) G. Albertin, G. Pelizzi, and E. Bordignon, *Inorg. Chem.*, **22**, 515 (1983).

8) Y. Kushi, M. Kuramoto, S. Utsuno, and H. Yoneda, *Bull. Chem. Soc. Jpn.*, **56**, 2742 (1983).

9) M. Iwata, K. Nakatsu, and Y. Saito, *Acta Crystallogr., Sect. B*, **33**, 1378 (1969).

10) a) I. Kinoshita, K. Kashiwabara, J. Fujita, K. Matsumoto, and S. Ooi, *Bull. Chem. Soc. Jpn.*, **54**, 2683 (1981); b) S. Ohba, Y. Saito, T. Ohishi, K. Kashiwabara, and J. Fujita, *Acta Crystallogr., Sect. C*, **39**, 49 (1983); c) T. Ohishi, K. Kashiwabara, H. Ito, T. Ito, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **56**, 1551 (1983).

11) Inorg. Synth., **16**, 16 (1976).

12) M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **271**, 101 (1952).

13) H. Yamatera, *Naturwissenschaften*, **44**, 632 (1957); *J. Inorg. Nucl. Chem.*, **15**, 50 (1960).

14) M. Linhard and M. Weigel, *Z. Phys. Chem., N, F.*, **11**, 308 (1957).

15) J. Fujita and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **36**, 1281 (1963).

16) K. Yamasaki, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **50**, 2624 (1977).

17) Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, **29**, 311 (1956).

18) T. Ohishi, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **56**, 3441 (1983).

19) V. M. Miskowski, J. L. Robbins, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **98**, 2477 (1976).