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Preparation and Characterization of Cobalt(III) Complexes Containing 1,1,1-Tris(dimethylphosphinomethyl)ethane (mmtp), and the Crystal Structure of $[Co(mmtp)_2][Co(CN)_6]\cdot 2.25H_2O$

Tadashi Ando, Masakazu Kita, Kazuo Kashiwabara, Junnosuke Fujita,*
Saeko Kurachi,† and Shigeru Ohba†
Department of Chemistry, Faculty of Science, Nagoya University,
Chikusa-ku, Nagoya 464-01
†Department of Chemistry, Faculty of Science and Technology, Keio University,
3-14-1, Hiyoshi, Kohoku-ku, Yokohama 223

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Eight new cobalt(III) complexes of the type, $[CoX_3(mmtp)]^{n+}$ (mmtp=1,1,1-tris(dimethylphosphinomethyl)ethane, X_3=$(Cl)_3$, $(Br)_3$, $(CN)_3$, $(NH_3)_3$, mmtp, 3-azapentane-1,5-diamine (dien), 1,4,7-triazacyclononane (tacn), and 1,4,7-trithiacyclononane (ttcn)), were prepared and characterized. All of the complexes are stable in the solid state, but the halogeno complexes aquate rapidly in water, and the ammonia complex liberates NH_3 slowly in 1 mol dm^{-3} HCl to give $[CoCl_2(NH_3)(mmtp)]^+$, other complexes including $[Co(mmtp)_2]^{3+}$ being stable in solution. The crystal structure of $[Co(mmtp)_2][Co(CN)_6]\cdot 2.25H_2O$ was determined by X-ray analysis. Crystal data: orthorhombic, space group $Pca2_1$, a=31.579(5), b=10.521(1), c=23.458(3) Å, V=7794(2) Å^3, Z=8, R=0.084 for 4196 reflections. The Co–P bond distances are 2.291(9)—2.357(7) Å (av 2.331 Å), which are appreciably longer than those usually found in Co(III)–phosphine complexes. The absorption spectra of the complexes were compared with one another and with those of the related complexes.

While metal complexes with a tripod-like phosphine ligand, 1,1,1-tris(diphenylphosphinomethyl)ethane (pptp) have been studied extensively,[1)] relatively few investigations have been reported on those with the dimethyl analogue (mmtp),[2—4)] and its cobalt(III) complex has never been known. The mmtp ligand is less bulky and more basic than pptp, and therefore the ligand can be expected to form stable complexes even with such small and hard metal ions as Co(III). This paper deals with the preparation and characterization of cobalt(III) complexes containing mmtp, and the crystal structure of $[Co(mmtp)_2][Co(CN)_6]\cdot 2.25H_2O$ determined by X-ray analysis. Only three, $[Co(Me_2PCH_2CH_2PMe_2)_3]^{3+}$,[5,6)] $[Co\{o\text{-}C_6H_4(PMe_2)_2\}_3]^{3+}$,[6)] and $[Co\{o\text{-}C_6H_4(PPh_2)_2\}_3]^{3+}$,[6)] have been known so far for the Co(III)–phosphine complexes of the $[CoP_6]^{3+}$ type, and no X-ray structure analysis has been reported.

Experimental

All the operations were performed by standard Schlenk techniques under an argon atmosphere when free mmtp was handled. All solvents used for the preparation of the ligand and complexes were made oxygen-free by bubbling argon for 20 min immediately before use. Absorption, and ^1H and ^{13}C NMR spectra were recorded on a Hitachi U3400 spectrophotometer, and a Hitachi R-90H spectrometer, respectively.

Preparation of mmtp. The ligand was prepared according to the literature method.[3b)] Crude undistilled mmtp was used for the preparation of $[CoCl_3(mmtp)]$, from which other complexes were derived.

Preparation of Cobalt(III) Complexes. $[CoCl_3(mmtp)]$. To a solution of *trans*-$[CoCl_2(py)_4]Cl\cdot 6H_2O$[7)] (3.0 g, 6.2 mmol) in dry pyridine (60 cm^3) was added mmtp (1.48 g, 5.85 mmol) dropwise with stirring. After stirring for 3 h, a red precipitate which formed was collected by filtration and washed with pyridine, ethanol and then diethyl ether. Yield: 1.20 g (ca. 50%). Found: C, 31.65; H, 6.35%. Calcd for $[CoCl_3(mmtp)]$=$C_{11}H_{27}P_3Cl_3Co$: C, 31.64; H, 6.52%. The complex is soluble in CH_3OH, DMSO, and DMF, and less soluble in C_2H_5OH, CH_2Cl_2, and $CHCl_3$. The complex is also soluble in H_2O and CH_3CN, but changes the color from red to yellow.

$[CoBr_3(mmtp)]$. To an aqueous solution (30 cm^3) of $[CoCl_3(mmtp)]$ (0.42 g, 1.0 mmol) was added $AgNO_3$ (0.51 g, 3.0 mmol). After stirring for a while, the precipitate of AgCl was filtered off, and the filtrate was applied on a column (ϕ 2.5 cm×10 cm) of SP-Sephadex C-25 (Na^+ form). The column was washed thoroughly with water, and then the adsorbed complex was eluted with a 1 mol dm^{-3} KBr aqueous solution, giving a single red band. The red eluate was evaporated to dryness under reduced pressure, and the residue was mixed with ethanol to extract the complex. The red extract was evaporated again to dryness under reduced pressure, and the red complex was extracted with dichloromethane. The extract was allowed to stand in air to give red crystals. Yield: 0.35 g (63%). Found: C, 24.08; H, 4.66%. Calcd for $[CoBr_3(mmtp)]$=$C_{11}H_{27}P_3Br_3Co$: C, 23.98; H, 4.96%. The solubility of this complex is similar to that of $[CoCl_3(mmtp)]$.

$[Co(CN)_3(mmtp)]$. A methanol solution (30 cm^3) of $[CoCl_3(mmtp)]$ (0.42 g, 1.00 mmol) was stirred with NaCN (0.15 g, 3.00 mmol) for 3 h. The resulting yellow solution was evaporated to dryness under reduced pressure, and the complex was extracted with methanol from the residue. The yellow extract was allowed to stand in air to give yellow crystals. Yield: 0.14 g (36%). Found: C, 43.15; H, 7.20; N, 10.88%. Calcd for $[Co(CN)_3(mmtp)]$=$C_{14}H_{27}N_3P_3Co$: C, 43.20; H, 6.99; N, 10.81%. The complex is soluble in H_2O, CH_3OH, DMSO, and DMF, less soluble in C_2H_5OH, and insoluble in CH_2Cl_2 and $CHCl_3$.

$[Co(mmtp)_2](BF_4)_3$. Pure distilled mmtp (0.25 g, 1.00 mmol) was added to a methanol solution (30 cm^3) of $[CoCl_3(mmtp)]$ (0.42 g, 1.00 mmol) which had been made oxygen-free with argon. The solution was stirred for 3 h, evaporated to 3 cm^3 under reduced pressure, and then mixed with diethyl ether (100 cm^3) to give a yellow precipitate. It was collected by filtration, washed with diethyl ether until the characteristic odor of mmtp disappeared, and recrystallized from methanol (3 cm^3) by addition of $LiBF_4$ (0.5 g, 5 mmol). The yellow precipitate was collected by filtration and washed with methanol and diethyl ether. Yield: 0.64 g (78%). Found: C, 32.07; H, 6.64%. Calcd for $[Co(mmtp)_2](BF_4)_3$=$C_{22}H_{54}B_3F_{12}P_6Co$: C, 32.07; H,6.61%. The complex is soluble in H_2O, CH_3CN, DMSO, and DMF, but insoluble in CH_3OH, C_2H_5OH, CH_2Cl_2, and $CHCl_3$.

$[Co(NH_3)_3(mmtp)](BF_4)_3$. Ammonia was condensed (30 cm^3) onto solid $[CoCl_3(mmtp)]$ (0.40 g, 0.96 mmol) in a Schlenk tube, giving a red solution. The solution turned yellow on slow evaporation of ammonia at room temperature. The yellow residue was mixed with 30 cm^3 of methanol, and the mixture was dissolved with a minimum amount of water (pH2, HCl). On addition of $LiBF_4$ (0.5 g, 5 mmol) the solution yielded a yellow precipitate, which was collected by filtration and washed with methanol and diethyl ether. Yield: 0.35 g (59%). Found: C, 21.36; H, 5.91; N, 6.63%. Calcd for $[Co(NH_3)_3(mmtp)](BF_4)_3$=$C_{11}H_{36}N_3B_3F_{12}P_3Co$: C, 21.22; H, 5.83; N, 6.75%. The solubility of the complex is similar to that of $[Co(mmtp)_2](BF_4)_3$.

$[Co(dien)(mmtp)](BF_4)_3$. A mixture of $[CoCl_3(mmtp)]$ (0.21 g, 0.50 mmol) and 3-azapentane-1,5-diamine (dien; 0.05 g, 0.50 mmol) in methanol (30 cm^3) was stirred at room temperature for 3 h, and then $LiBF_4$ (0.30 g, 3 mmol) was added. The yellow precipitate which formed was collected by filtration and washed with methanol and diethyl ether. Yield: 0.29 g (86%). Found: C, 26.99; H, 6.05; N, 6.44%. Calcd for

Table 1. Fractional Coordinates (×10^4) and Equivalent Isotropic Temperature Factors (×10)

Atom	x	y	z	$B_{eq}/Å^2$	Atom	x	y	z	$B_{eq}/Å^2$
Co(1)	7500(2)	3893(2)	2497(3)	17	C(18)	8406(8)	5685(23)	2142(11)	28
Co(01)	5239(1)	−32(2)	4997(3)	15	C(19)	7381(8)	1499(23)	3590(11)	30
Co(A)	2266(1)	1105(2)	0[a]	20	C(20)	8037(8)	957(24)	2777(11)	31
Co(B)	5000(2)	4987(6)	2493(3)	20	C(21)	7681(7)	7061(20)	3177(9)	18
P(1)	6776(2)	4070(7)	2720(3)	27	C(22)	7352(7)	5117(23)	3912(10)	24
P(2)	7337(2)	5293(6)	1767(3)	27	C(01)	5987(6)	−2697(18)	4972(18)	27
P(3)	7282(2)	2283(6)	1874(3)	24	C(02)	6306(6)	−3821(20)	5109(11)	27
P(4)	8211(2)	4090(6)	2273(3)	20	C(03)	6231(7)	−1529(20)	5197(9)	20
P(5)	7717(2)	2292(6)	3114(3)	27	C(04)	5609(9)	−3097(26)	5297(12)	42
P(6)	7669(2)	5277(6)	3248(2)	23	C(05)	5843(8)	−2414(24)	4328(11)	32
P(01)	5978(1)	6(5)	5001(6)	27	C(06)	6270(8)	585(25)	5607(11)	35
P(02)	5305(3)	−1701(8)	5643(4)	47	C(07)	6236(9)	797(28)	4416(13)	45
P(03)	5341(2)	−1591(8)	4309(4)	54	C(08)	4894(7)	−2781(21)	5785(10)	21
P(04)	4523(2)	26(7)	4715(3)	24	C(09)	5514(8)	−1533(24)	6328(11)	34
P(05)	5278(2)	1884(6)	4495(3)	27	C(010)	4837(11)	−2724(32)	4240(15)	63
P(06)	5018(2)	1174(6)	5754(3)	26	C(011)	5401(8)	−1108(25)	3508(11)	32
N(1A)	1627(7)	657(20)	955(9)	34	C(012)	4500(6)	2701(18)	4967(17)	25
N(2A)	2928(6)	1717(18)	−883(8)	27	C(013)	4175(6)	3794(19)	5068(15)	29
H(3A)	1619(7)	558(22)	−929(10)	45	C(014)	4227(6)	1437(17)	5081(12)	21
N(4A)	2964(8)	1527(24)	890(11)	55	C(015)	4783(6)	2850(19)	4497(9)	14
N(5A)	2535(6)	−1609(17)	29(17)	46	C(016)	4731(9)	2620(27)	5616(12)	43
N(6A)	1996(5)	3877(17)	17(17)	37	C(017)	4136(6)	−1168(19)	4920(13)	27
N(1B)	5527(8)	5118(23)	3596(10)	49	C(018)	4415(8)	93(25)	3947(11)	33
N(2B)	4429(6)	5061(19)	1486(8)	25	C(019)	5394(7)	1779(22)	3726(10)	24
N(3B)	5390(8)	2450(24)	2097(11)	53	C(020)	5643(8)	3105(23)	5216(10)	35
N(4B)	4605(6)	7577(19)	2792(8)	28	C(021)	5386(9)	1988(27)	6278(12)	41
N(5B)	4314(8)	3603(25)	3118(12)	57	C(022)	4602(8)	427(25)	6208(11)	34
N(6B)	5666(6)	6569(19)	1868(9)	32	C(1A)	1865(7)	883(22)	618(10)	24
C(1)	6568(9)	3768(27)	1556(12)	38	C(2A)	2696(6)	1497(16)	−563(8)	7
C(2)	6225(9)	3672(27)	1053(13)	44	C(3A)	1866(7)	743(21)	−551(10)	23
C(3)	6424(6)	3781(21)	2132(9)	17	C(4A)	2655(10)	1311(30)	549(14)	55
C(4)	6810(7)	5099(23)	1471(10)	26	C(5A)	2433(6)	−648(17)	34(17)	24
C(5)	6917(8)	2791(25)	1307(11)	32	C(6A)	2102(6)	2822(19)	30(19)	28
C(6)	6594(8)	5764(25)	2915(12)	35	C(1B)	5329(6)	5057(21)	3159(9)	16
C(7)	6521(9)	3057(27)	3246(12)	41	C(2B)	4632(7)	5068(24)	1853(10)	27
C(8)	7407(9)	6970(26)	1862(12)	40	C(3B)	5268(11)	3427(33)	2318(15)	59
C(9)	7626(8)	4908(25)	1124(11)	35	C(4B)	4762(6)	6577(18)	2714(8)	10
C(10)	7687(7)	1468(20)	1419(9)	21	C(5B)	4592(6)	4095(19)	2884(8)	14
C(11)	7048(8)	901(23)	2188(11)	29	C(6B)	5414(10)	5925(29)	2089(13)	49
C(12)	8402(7)	3874(21)	3505(9)	20	O(1)	1305(4)	1576(11)	2042(5)	7
C(13)	8839(9)	3918(27)	3828(12)	41	O(2)	8216(6)	3361(17)	75(13)	62
C(14)	8610(8)	3463(24)	2832(11)	30	O(3)	5980(5)	686(15)	2636(7)	29
C(15)	8148(7)	2754(22)	3631(10)	25	O(4)[b]	6819(14)	3385(41)	−22(36)	90
C(16)	8227(8)	5195(23)	3521(11)	30	O(5)[b]	3491(10)	778(31)	1774(14)	29
C(17)	8474(7)	3307(21)	1682(9)	18	O(6)[b]	3278(13)	1093(42)	1918(19)	58

a) This parameter was used to define the origin of the unit cell along z and is listed without esd. b) Population parameters of the disordered H_2O 0.5.

$[\mathrm{Co(dien)(mmtp)}](\mathrm{BF_4})_3=\mathrm{C_{15}H_{40}N_3B_3F_{12}P_3Co}$: C, 26.70; H, 5.98; N, 6.23%. The solubility of the complex is similar to that of $[\mathrm{Co(mmtp)_2}](\mathrm{BF_4})_3$.

$[\mathrm{Co(tacn)(mmtp)}](\mathrm{BF_4})_3$. A slurry of 1,4,7-triazacyclononane trihydrochloride (tacn·3HCl; 0.24 g, 1.00 mmol) in ethanol (30 cm^3) was neutralized with KOH, cooled, and filtered.8) The ethanolic filtrate was added to a methanol solution (30 cm^3) of $[\mathrm{CoCl_3(mmtp)}]$ (0.42 g, 1.00 mmol), and the solution was stirred for 3 h. On addition of $\mathrm{LiBF_4}$ (0.5 g, 5 mmol) the solution gave a yellow precipitate, which was collected by filtration and washed with methanol and diethyl ether. Yield: 0.15 g (21%). Found: C, 29.09; H, 6.55; N, 6.09%. Calcd for $[\mathrm{Co(tacn)(mmtp)}](\mathrm{BF_4})_3=\mathrm{C_{17}H_{42}N_3B_3F_{12}P_3Co}$: C, 29.14; H, 6.04; N, 6.00%. The complex is soluble in $\mathrm{H_2O}$, DMSO, and DMF, slightly soluble in $\mathrm{CH_3CN}$, and insoluble in $\mathrm{CH_3OH}$, $\mathrm{C_2H_5OH}$, $\mathrm{CH_2Cl_2}$, and $\mathrm{CHCl_3}$.

$[\mathrm{Co(ttcn)(mmtp)}](\mathrm{NO_3})_3\cdot\mathrm{H_2O}$. A methanol solution (50 cm^3) containing $\mathrm{AgNO_3}$ (0.28 g, 1.67 mmol) and $[\mathrm{CoCl_3(mmtp)}]$ (0.23 g, 0.56 mmol) was refluxed for 1 h, and the precipitate of AgCl was filtered off. To the filtrate was added 1,4,7-trithiacyclononane (ttcn; Aldrich Chem. Co., Inc.; 0.10 g, 0.55 mmol), and the solution was refluxed for 30 min. Cooling of the solution yielded orange-yellow crystals, which were collected by filtration and washed with methanol and diethyl ether. Yield: 0.26 g (76%). Found: C, 29.13; H, 5.91; N, 6.03%. Calcd for $[\mathrm{Co(ttcn)(mmtp)}](\mathrm{NO_3})_3\cdot\mathrm{H_2O}=\mathrm{C_{17}H_{41}N_3S_3O_{10}P_3Co}$: C, 29.35; H, 5.94; N, 6.04%. The solubility of the complex is similar to that of $[\mathrm{Co(tacn)(mmtp)}](\mathrm{BF_4})_3$.

Crystal Structure Determination. A 1 mol dm^{-3} aqueous solution of $[\mathrm{Co(mmtp)_2}](\mathrm{BF_4})_3$ (50 cm^3) was slowly mixed with a 1 mol dm^{-3} aqueous solution of $\mathrm{K_3[Co(CN)_6]}$ (50 cm^3). After several days the yellow rectangular prismatic crystals were formed. Found: C, 39.85; H, 7.36; N, 9.95%. Calcd for $[\mathrm{Co(mmtp)_2}][\mathrm{Co(CN)_6}]\cdot4\mathrm{H_2O}=\mathrm{C_{28}H_{62}N_6O_4P_6Co}$: C, 39.54; H, 7.35; N, 9.88%. The crystals effloresce when removed from the mother liquor. The crystal for data collection was coated with manicure.

Crystal data of $[\mathrm{Co(mmtp)_2}][\mathrm{Co(CN)_6}]\cdot x\mathrm{H_2O}$ (2.25 water molecules were identified in the analysis): orthorhombic, $Pca2_1$, $a=31.579(5)$, $b=10.521(1)$, $c=23.458(3)$ Å, $V=7794(2)$ Å^3, $Z=8$, $D_m=1.48(2)$ g cm^{-3}, $D_x=1.40$ g cm^{-3}. A yellow crystal of approximate dimensions 0.45×0.50×0.33 mm^3 was used for X-ray analysis. Diffraction data were collected up to $2\theta_{\max}=60°$ with graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.71069$ Å) on a Rigaku AFC-5R diffractometer at the Institute for Molecular Science. The ω scan technique was employed. 11597 reflections were measured, of which 4196 reflections were observed with $|F_o|>3\sigma(|F_o|)$. Variation of $|F_o|$ of three standard reflections was $0.958<\sum(|F_o|/|F_o|_{\mathrm{initial}})/3<1.002$. The diffraction intensities were corrected for the decay. The lattice constants were determined from 50 2θ values ($25°<2\theta<30°$). The structure analysis was carried out on a FACOM M780/10 computer at Keio University using the computation program system UNICS-III.9) Absorption correction was made assuming a spherical crystal shape (transmission factor, $0.646<A<0.651$). Laue group mmm and systematic absences $0kl$, l odd; $h0l$, h odd indicated the space group $Pca2_1$ (No. 29) or $Pcam$ (b, a, $-c$ setting of $Pbcm$, No. 57). $Pca2_1$ is a subgroup of $Pcam$.10) The Patterson function could be analyzed based on the space group $Pca2_1$, but not on $Pcam$. Starting with two Co atoms, other non-hydrogen atoms were located on Fourier or difference syntheses. In order to reduce the number of parameters, C, N, and O atoms were refined isotropically, and H atoms were not included in the refinement. A total of the occupancy factors of the water molecules in an asymmetric unit is 4.5, which is smaller than the expected value of 8 based on the elemental analysis. However, the final difference synthesis showed no prominent peak ($-0.64<\Delta\rho<0.96$ e Å^{-3}). These facts suggest positional disorder of the water molecules and/or the partial occupations by efflorescence. The function, $\sum w||F_o|-|F_c||^2$, was minimized with $w^{-1}=\sigma^2(|F_o|)+(0.015|F_o|)^2$ by the block-diagonal least squares. $R=0.084$ was obtained for 4196 reflections. Number of parameters is 442. Complex neutral-atom scattering factors were used.11) R factors did not alter significantly when the sign of $\Delta f''$ was changed from positive to negative. Therefore, the polar direction of the c axis could not be assigned. The atomic parameters are listed in Table 1.12) The structure model of $Pca2_1$ cannot be transferred into that of the centrosymmetric space group $Pbcm$.

Results and Discussion

Syntheses and Chemical Properties. Two methods have been reported for the preparation of mmtp2a,3b) In this study the ligand was prepared by the method of Whitesides et al.,3b) and the crude oily product was used without distillation for the preparation of $[\mathrm{CoCl_3(mmtp)}]$. The complex was easily formed by reaction of *trans*-$[\mathrm{CoCl_2(py)_4}]\mathrm{Cl}$7) with mmtp in dry pyridine. The product was hardly soluble in this solvent and analytically pure. This complex is a good starting material for other mmtp complexes including $[\mathrm{Co(mmtp)_2}]^{3+}$.

All of the complexes obtained in this study are stable both in the solid state and in solution, except the $\mathrm{Cl^-}$, $\mathrm{Br^-}$, and $\mathrm{NH_3}$ complexes in particular solvents. The red $[\mathrm{CoX_3(mmtp)}]$ ($\mathrm{X=Cl^-}$ and $\mathrm{Br^-}$) complexes are stable in such solvents as $\mathrm{CH_3OH}$, $\mathrm{C_2H_5OH}$, $\mathrm{CH_2Cl_2}$, $\mathrm{CHCl_3}$, DMSO, and DMF, but turn yellow rapidly when dissolved in $\mathrm{H_2O}$ and $\mathrm{CH_3CN}$. These yellow solutions show the first d–d band at higher energy than those of the complexes in $\mathrm{CH_2Cl_2}$. The high energy shift of the d–d band indicates that the halide ions in the complexes are easily replaced by solvents, $\mathrm{H_2O}$ and $\mathrm{CH_3CN}$. The $[\mathrm{Co(NH_3)_3(mmtp)}](\mathrm{BF_4})_3$ complex, which is only mixed Co(III)-phosphine complex with ammonia to our knowledge, is stable in neutral or weakly acidic aqueous solutions. However, the complex is unstable in fairly strong acids and, in particular, in basic solutions. For example, a yellow solution of the complex in 10^{-3} mol dm^{-3} aqueous ammonia (pH ca. 10) fades rapidly and becomes turbid to give a brown unknown precipitate. In 1 mol dm^{-3} hydrochloric acid the complex slowly changes the color from yellow to orange. The spectrum changes with isosbestic points as shown in Fig. 1, and the final product shows the first d–d band at 21000 cm^{-1}. Since $[\mathrm{Co(NH_3)_3(mmtp)}]^{3+}$ and $[\mathrm{CoCl_3(mmtp)}]$ show the first d–d band at 24200 and 20100 cm^{-1}, respectively, the product can be assigned to $[\mathrm{CoCl_2(NH_3)(mmtp)}]^+$ on the basis of the rule of average environment for ligand field bands.13)

In general, Co(III)-NH$_3$ bonds are known to be very stable in acidic solutions. The [Co(NH$_3$)$_3$(mmtp)]$^{3+}$ complex is a rare example, in which the ammonia ligands are easily replaced by Cl$^-$ ions in hydrochloric acid.

Other [CoX$_3$(mmtp)]$^{n+}$ (X$_3$=(CN)$_3$, mmtp, dien, tacn, and ttcn) complexes are stable even in 6 mol dm^{-3} hydrochloric acid. The stability of [Co(mmtp)$_2$](BF$_4$)$_3$ is remarkable, in contrast to [Co(dmpe)$_3$](ClO$_4$)$_3$ (dmpe=(CH$_3$)$_2$PCH$_2$CH$_2$P(CH$_3$)$_2$) which liberates one dmpe in solution containing excess Cl$^-$ ions to give *trans*-[CoCl$_2$(dmpe)$_2$]$^+$.5) Attempts to prepare analogous Co(III) complexes with 1,1,1-tris(diphenylphosphinomethyl)ethane (pptp) were unsuccessful. For example, a green solution of *trans*-[CoCl$_2$(py)$_4$]Cl in pyridine turned red similar in color to [CoCl$_3$(mmtp)] by addition of pptp, but the green starting complex was recovered by evaporation of the solvent. The ligand might be too bulky to form stable octahedral complexes with a small Co(III) ion.

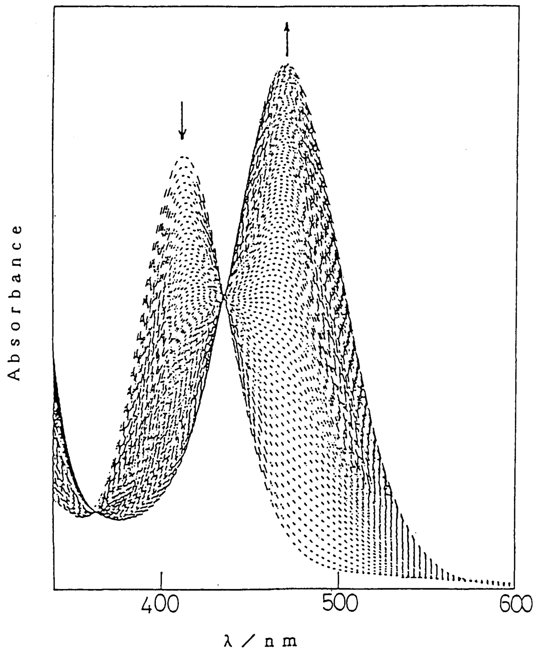

Fig. 1. Change in absorption spectrum of [Co(NH$_3$)$_3$(mmtp)]$^{3+}$ in a 1 mol dm^{-3} HCl aqueous solution at 25 °C (60 min intervals). Trends of spectral changes with time are shown by arrows.

Crystal Structure of [Co(mmtp)$_2$][Co(CN)$_6$]·2.25H$_2$O. Two crystallographically independent complex ions are in the unit cell, but their structures are very similar to each other. Perspective views of the complex cations are shown in Fig. 2. The selected bond distances and angles are given in Table 2. Both Co atoms are surrounded by six phosphorus atoms in a slightly distorted octahedron. The Co–P bond distances are 2.291(9)—2.357(7) Å (av 2.331 Å). These distances are exceedingly long for Co(III)–phosphine complexes, except the Co(III)–P(C$_6$H$_5$)$_3$ and –P(C$_6$H$_{11}$)$_3$ bonds in the [Co(dimethylglyoximato)$_2$(alkyl)(phosphine)]-type complexes.14) The longest Co–P distances found in our previous studies are 2.295(3) and 2.294(3) Å of two mutually *trans* Co–P bonds in [Co(edmp)$_2$(dmpe)]Br$_3$·3H$_2$O (edmp=NH$_2$CH$_2$CH$_2$P(CH$_3$)$_2$).15) The distances found in a large number of other analogous Co(III)–phosphine complexes are in the range of 2.20 to 2.27 Å.16)

The average Co–P distance of [Co(mmtp)$_2$]$^{3+}$ (2.331(9) Å) is longer than the average Cr–P distance of [Cr(mmtp)$_2$] (2.287(1) Å) which is the Cr(0) complex of the same low-spin d^6-type.3a) The shorter Cr–P distance may be attributed to the stronger π-back bonding interaction between the Cr(0) (filled dπ) and P (vacant 3d) atoms than that in the Co(III)–P bonds. The dπ orbital energy of Cr(0) will be much higher than that of Co(III),17) and thus the orbitals will be able to interact more effectively with the vacant 3d orbitals of P to strengthen the Cr–P bonds. On the other hand, the average Cr(III)–P distance in [CrCl$_3$(mmtp)] (2.456(2) Å)3a) is longer by 0.125(9) Å than the Co(III)–P distance in [Co(mmtp)$_2$]$^{3+}$. This difference is similar in magnitude to that in M–N distance, 0.114(4) Å, between [Cr(en)$_3$]$^{3+}$ (av 2.078(4) Å)18) and [Co(en)$_3$]$^{3+}$ (av 1.964(2) Å)19) (en=NH$_2$CH$_2$CH$_2$NH$_2$), both of which would

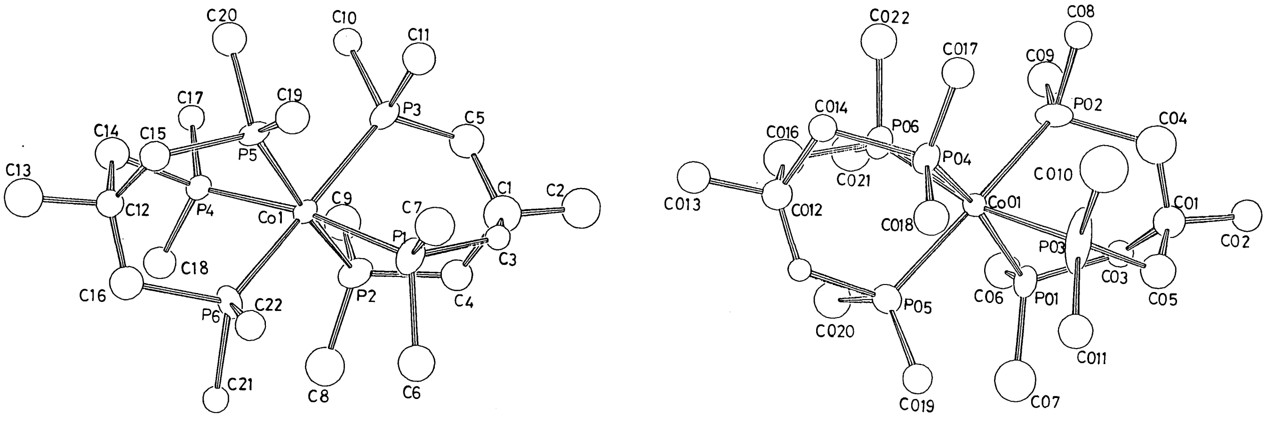

Fig. 2. Perspective views of [Co(mmtp)$_2$]$^{3+}$ cations projected along the C$_2$ axis.

Table 2. Selected Bond Distances (l/Å) and Angles (ϕ/°) of $[Co(mmtp)_2][Co(CN)_6]\cdot 2.25H_2O$

Co(1)–P(1)	2.353(9)	Co(1)–P(2)	2.317(9)
Co(1)–P(3)	2.341(8)	Co(1)–P(4)	2.315(9)
Co(1)–P(5)	2.324(8)	Co(1)–P(6)	2.347(8)
Co(01)–P(01)	2.334(4)	Co(01)–P(02)	2.329(10)
Co(01)–P(03)	2.324(10)	Co(01)–P(04)	2.357(7)
Co(01)–P(05)	2.338(8)	Co(01)–P(06)	2.291(9)
P(1)–C(3)	1.797(21)	P(1)–C(6)	1.928(27)
P(1)–C(7)	1.818(29)	P(2)–C(4)	1.815(23)
P(2)–C(8)	1.792(28)	P(2)–C(9)	1.809(27)
P(3)–C(5)	1.839(27)	P(3)–C(10)	1.874(23)
P(3)–C(11)	1.790(25)	P(4)–C(14)	1.934(26)
P(4)–C(17)	1.814(23)	P(4)–C(18)	1.814(25)
P(5)–C(15)	1.887(24)	P(5)–C(19)	1.752(26)
P(5)–C(20)	1.902(26)	P(6)–C(16)	1.877(26)
P(6)–C(21)	1.885(22)	P(6)–C(22)	1.859(24)
P(01)–C(03)	1.860(22)	P(01)–C(06)	1.801(28)
P(01)–C(07)	1.800(32)	P(02)–C(04)	1.933(29)
P(02)–C(08)	1.757(24)	P(02)–C(09)	1.746(27)
P(03)–C(05)	1.807(26)	P(03)–C(010)	1.995(35)
P(03)–C(011)	1.956(27)	P(04)–C(014)	1.953(22)
P(04)–C(017)	1.817(22)	P(04)–C(018)	1.835(27)
P(05)–C(015)	1.865(20)	P(05)–C(019)	1.844(24)
P(05)–C(020)	2.416(25)	P(06)–C(016)	1.800(29)
P(06)–C(021)	1.896(29)	P(06)–C(022)	1.865(26)
P(1)–Co(1)–P(2)	84.2(3)	P(1)–Co(1)–P(3)	84.9(3)
P(1)–Co(1)–P(4)	170.3(2)	P(1)–Co(1)–P(5)	101.9(3)
P(1)–Co(1)–P(6)	90.3(3)	P(2)–Co(1)–P(3)	86.2(3)
P(2)–Co(1)–P(4)	89.5(3)	P(2)–Co(1)–P(5)	170.6(4)
P(2)–Co(1)–P(6)	102.2(2)	P(3)–Co(1)–P(4)	102.0(3)
P(3)–Co(1)–P(5)	87.2(2)	P(3)–Co(1)–P(6)	169.9(4)
P(4)–Co(1)–P(5)	85.4(3)	P(4)–Co(1)–P(6)	83.9(3)
P(5)–Co(1)–P(6)	85.1(3)	Co(1)–P(1)–C(3)	114.6(7)
Co(1)–P(1)–C(6)	114.6(9)	Co(1)–P(1)–C(7)	122.3(10)
Co(1)–P(2)–C(4)	114.5(8)	Co(1)–P(2)–C(8)	120.4(10)
Co(1)–P(2)–C(9)	111.2(9)	Co(1)–P(3)–C(5)	115.2(9)
Co(1)–P(3)–C(10)	119.1(7)	Co(1)–P(3)–C(11)	116.9(9)
Co(1)–P(4)–C(14)	116.6(8)	Co(1)–P(4)–C(17)	125.2(8)
Co(1)–P(4)–C(18)	116.8(8)	Co(1)–P(5)–C(15)	115.2(8)
Co(1)–P(5)–C(19)	124.3(9)	Co(1)–P(5)–C(20)	115.7(8)
Co(1)–P(6)–C(16)	116.2(8)	Co(1)–P(6)–C(21)	123.8(7)
Co(1)–P(6)–C(22)	116.8(8)		
P(01)–Co(01)–P(02)	85.5(3)	P(01)–Co(01)–P(03)	82.9(3)
P(01)–Co(01)–P(04)	163.7(4)	P(01)–Co(01)–P(05)	86.2(2)
P(01)–Co(01)–P(06)	107.0(3)	P(02)–Co(01)–P(03)	84.7(3)
P(02)–Co(01)–P(04)	106.7(3)	P(02)–Co(01)–P(05)	166.7(4)
P(02)–Co(01)–P(06)	86.6(4)	P(03)–Co(01)–P(04)	87.5(3)
P(03)–Co(01)–P(05)	104.6(4)	P(03)–Co(01)–P(06)	166.3(3)
P(04)–Co(01)–P(05)	83.5(3)	P(04)–Co(01)–P(06)	84.9(3)
P(05)–Co(01)–P(06)	85.9(2)	Co(01)–P(01)–C(03)	114.6(7)
Co(01)–P(01)–C(06)	121.4(10)	Co(01)–P(01)–C(07)	117.2(11)
Co(01)–P(02)–C(04)	110.1(9)	Co(01)–P(02)–C(08)	123.0(9)
Co(01)–P(02)–C(09)	123.8(10)	Co(01)–P(03)–C(05)	116.3(9)
Co(01)–P(03)–C(010)	111.6(11)	Co(01)–P(03)–C(011)	119.8(9)
Co(01)–P(04)–C(014)	110.8(7)	Co(01)–P(04)–C(017)	123.6(7)
Co(01)–P(04)–C(018)	117.1(9)	Co(01)–P(05)–C(015)	115.1(7)
Co(01)–P(05)–C(019)	116.8(8)	Co(01)–P(05)–C(020)	97.5(6)
Co(01)–P(06)–C(016)	118.8(10)	Co(01)–P(06)–C(021)	124.5(9)
Co(01)–P(06)–C(022)	115.1(9)		

involve no π-bonding between the metal and nitrogen atoms. Thus the M–P bonds in $[CrCl_3(mmtp)]$ and $[Co(mmtp)_2]^{3+}$ would not involve effective π-bonding interaction either. The difference in bond distance between these Cr(III) and Co(III) complexes is attributable to the difference in bond strength due to σ-bonding between the metal and donor atoms.

The chelate angles of mmtp are a little smaller than

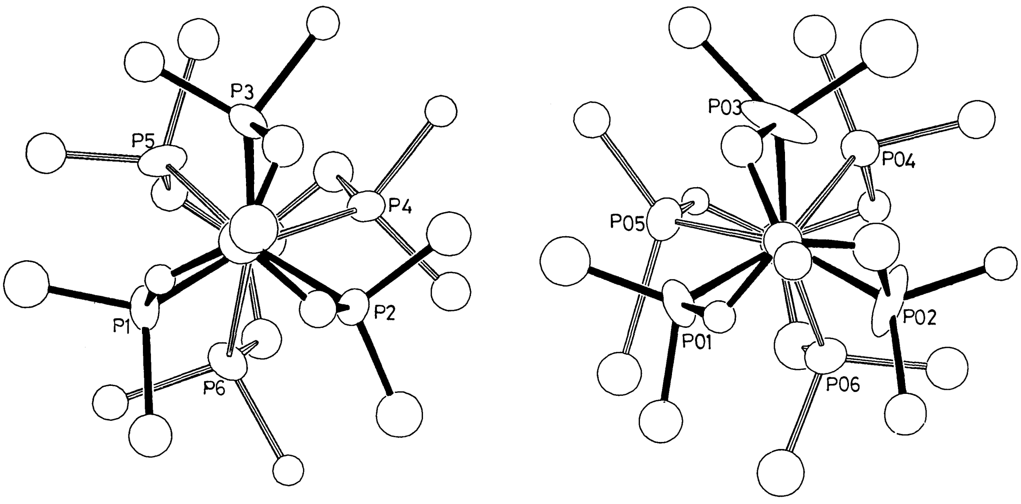

Fig. 3. Perspective views of $[Co(mmtp)_2]^{3+}$ cations projected along the C_3 axis.

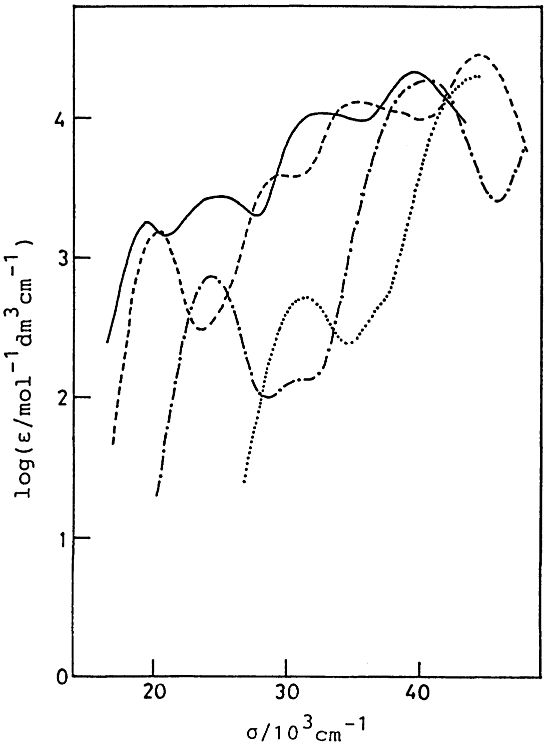

Fig. 4. Absorption spectra of $[CoCl_3(mmtp)]$ in CH_2Cl_2 (– – –), $[CoBr_3(mmtp)]$ in CH_2Cl_2 (——), $[Co(NH_3)_3(mmtp)](BF_4)_3$ in H_2O (—•—), and $[Co(CN)_3(mmtp)]$ in H_2O (······).

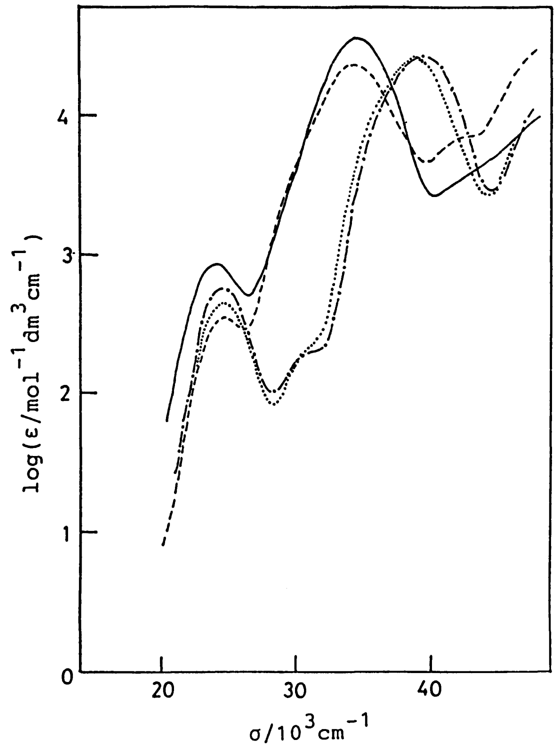

Fig. 5. Absorption spectra of $[Co(mmtp)_2](BF_4)_3$ (——), $[Co(tacn)(mmtp)](BF_4)_3$ (—•—), $[Co(dien)(mmtp)](BF_4)_3$ (······), and $[Co(ttcn)(mmtp)](BF_4)_3$ (– – –) in H_2O.

the octahedral angle, 82.9(3)—86.2(3)° (av 84.8°). The *cis* P–Co–P angles formed by two mmtp ligands are classified into two groups, 86.2(2)—90.3(3)° (av 87.9°) and 101.9(3)—107.0(3)° (av 104.1°). The three small and three large angles are arranged alternatively when viewed from the direction of the chemical C_3 axis, and the complex ion forms a twisted octahedron along this axis (Fig. 3). The twist structure is chiral and yields a pair of enantiomers. In addition to this twist, the mmtp–Co moiety is also twisted to afford another chirality. For $[Co(mmtp)_2]^{3+}$, a pair of enantiomers and a meso isomer are possible with respect to the twist of this moiety. The two mmtp ligands in each of two complex ions in the unit cell have the same chirality, and the two complex ions are enantiomeric with each other, although the structures are slightly different (Fig. 3). Thus the crystal forms a pseudo-racemate. The structure, in which the coordinate bonds are twisted along

Table 3. Absorption Spectral Data

Complex	$\sigma/10^3\ \mathrm{cm^{-1}}$ $(\log(\varepsilon/\mathrm{cm^{-1}\,mol^{-1}\,dm^3}))$			
$[\mathrm{CoBr_3(mmtp)}]^{a)}$	19.3 (3.24),	24.4 (3.43),	32.6 (4.06),	39.6 (4.34)
$[\mathrm{CoCl_3(mmtp)}]^{a)}$	20.1 (3.18),	29.5 (3.58),	35.2 (4.11)	
$[\mathrm{Co(NH_3)_3(mmtp)}](\mathrm{BF_4})_3{}^{b)}$	24.2 (2.87),	31.4 (2.12),	40.5 (4.33)	
$[\mathrm{Co(CN)_3(mmtp)}]^{b)}$	31.0 (2.74),	36 $(2.5)^{\mathrm{sh}}$,	44.0 (4.49)	
$[\mathrm{Co(mmtp)_2}](\mathrm{BF_4})_3{}^{b)}$	24.0 (2.92),	34.8 (4.56)		
$[\mathrm{Co(dien)(mmtp)}](\mathrm{BF_4})_3{}^{b)}$	24.4 (2.77),	31.3 (2.29),	39.5 (4.43)	
$[\mathrm{Co(tacn)(mmtp)}](\mathrm{BF_4})_3{}^{b)}$	24.4 (2.65),	30.7 (2.32),	38.9 (4.41)	
$[\mathrm{Co(ttcn)(mmtp)}](\mathrm{BF_4})_3{}^{b)}$	24.5 (2.54),	34.4 (4.38),	42.5 (3.86)	
$[\mathrm{Co(dmpe)_3}](\mathrm{ClO_4})_3{}^{c,d)}$	26.0 (2.97),	30.5 $(3.3)^{\mathrm{sh}}$		
fac-$[\mathrm{Co(edmp)_3}]^{3+\ b,e)}$	23.7 (2.68),	30.2 (2.36),	39.8 (4.42)	
$[\mathrm{Co(CN)_6}]^{3-\ f)}$	32.1			
$[\mathrm{Co(NH_3)_6}]^{3+\ f)}$	21.0			
$[\mathrm{Co(dien)_2}]^{3+\ f)}$	21.8			
$[\mathrm{Co(tacn)_2}]^{3+\ g)}$	21.8			
$[\mathrm{Co(ttcn)_2}]^{3+\ h)}$	21.0			

sh: shoulder. Solvents: a) CH_2Cl_2. b) H_2O. c) $(CH_3)_2SO$. d) Ref. 5. e) Ref. 16a. f) Y. Shimura, *Bull. Chem. Soc. Jpn.*, **61**, 693 (1988). g) D. Ventur, K. Wieghardt, B. Nuber, and J. Weiss, *Z. Anorg. Allg. Chem.*, **551**, 33 (1987). h) H.-J, Kupper, A. Neves, C. Pomp, D. Ventur, K. Wieghardt, B. Nuber, and J. Weiss, *Inorg. Chem.*, **25**, 2400 (1986).

the C_3 axis and two mmtp ligands have the same chirality, seems to result from relaxation of stric repulsions between the methyl groups of two mmtp ligands. However, three or four short C···C contacts from 3.08(3) to 3.32(4) Å still remain. The crowded structure of $[Co(mmtp)_2]^{3+}$ will be one of the reasons for the exceedingly long Co–P distance in this complex.

The structure of the complex anion, $[Co(CN)_6]^{3-}$ (av Co–C: 1.886(35) Å, C–N: 1.157(43) Å) is almost the same as that in $[Co(NH_3)_6][Co(CN)_6]$ (av Co–C: 1.894(1) Å, C–N: 1.157(2) Å),[20] but the esd values of the present complex are large.

Absorption Spectra. Absorption spectra of $[CoX_3(mmtp)]^{n+}$ are shown in Figs. 4 and 5, and the spectral data in Table 3. These mmtp complexes have approximate C_3 symmetry, and exhibit a symmetrical absorption band with medium intensity in the lower energy region. These bands can be assigned to the first d–d band. The second d–d band is observed as a shoulder for the NH_3, CN^-, dien, and tacn complexes, while those of other complexes are hidden by charge transfer bands. The spectra of $[CoX_3(mmtp)]^{3+}$ (X_3=$(NH_3)_3$, dien, or tacn) are very similar to that of *fac*-$[Co(edmp)_3]^{3+}$ in the whole region,[16a] although the second d–d bands of the mmtp complexes are fairly weak compared with that of $[Co(edmp)_3]^{3+}$. The $[CoBr_3(mmtp)]$ complex shows a band at 24400 cm^{-1} with intensity similar to that of the first d–d band. The band will not be the ligand field band, but the charge-transfer band (Br^- to Co(III)) corresponding to the one at 29500 cm^{-1} of $[CoCl_3(mmtp)]$. The halogeno-Co(III) complexes containing phosphine ligands such as *trans*-$[CoBr_2(dmpe)_2]^+$ and -$[CoCl_2(dmpe)_2]^+$ show similar bands at 24000 cm^{-1} ($\log\varepsilon$=3.35) and 26100 cm^{-1} ($\log\varepsilon$=3.70), respectively.[21]

The first d–d band of $[Co(mmtp)_2]^{3+}$ is observed at 24000 cm^{-1}, which is a little lower energy than those of $[CoX_3(mmtp)]^{3+}$ (X_3=$(NH_3)_3$, dien, and tacn) (24200—24400 cm^{-1}). Since the bands of these $[CoX_3(mmtp)]^{3+}$ are at higher energy than those of the $[CoN_6]^{3+}$-type complexes of NH_3, dien, and tacn (21000—21800 cm^{-1}), it is apparent that the ligand field strength of mmtp is stronger than those of these ammine and amine ligands. This result is in accord with the conclusion obtained from our spectral studies that the ranking of the $-P(CH_3)_2$ group is higher than that of the $-NH_2$ group in the spectrochemical series.[5] The estimated value for the first d–d band of $[Co(mmtp)_2]^{3+}$ from the spectral data of $[CoX_3(mmtp)]^{n+}$ and $[CoX_6]^{m+}$ based on the Yamatera rule[22] is in the range of 27000 (X_3=dien and tacn) to 29900 cm^{-1} (X_3=$(CN)_3$). The values are appreciably larger than the observed value of 24000 cm^{-1}, and seem to indicate that the less bulkiness of the X ligand, the larger the estimated band energy. The small observed value for $[Co(mmtp)_2]^{3+}$ is in acoord with the long Co–P distance which might arise from the crowded structure of this complex ion.

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