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Preparation and Characterization of *cis*- and *trans*- [RhCl$_2$(dmap)$_2$]$^+$ (dmap=1,3-bis(dimethylarsino)propane), and X-Ray Structure Analyses of These Complexes and *trans*-[CoCl$_2$(dmap)$_2$]$^+$

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The *cis*- and *trans*- [RhCl$_2$(dmap)$_2$]$^+$ (dmap=1,3-bis(dimethylarsino)propane) complexes were prepared by reaction of RhCl$_3$·3H$_2$O with dmap, and the molecular structures of these complexes were determined by the single crystal X-ray diffraction method. Crystal data and final R values are: *trans*-[RhCl$_2$(dmap)$_2$]ClO$_4$ (**1**), monoclinic, Cc, a=20.018(4), b=10.229(1), c=12.972(2) Å, β=99.98(2)°, V=2616(1) Å^3, Z=4, R=0.034 for 1298 observed unique reflections. *cis*-[RhCl$_2$(dmap)$_2$]PF$_6$ (**2a**), orthorhombic, Pca2$_1$, a=14.699(2), b=9.367(2), c=19.640(9) Å, V=2704(1) Å^3, Z=4, R=0.086 for 1284 reflections. *cis*-[RhCl$_2$(dmap)$_2$]CF$_3$SO$_3$ (**2b**), orthorhombic, Pca2$_1$, a=14.700(3), b=9.381(4), c=19.644(8) Å, V=2709(2) Å^3, Z=4, R=0.088 for 1094 reflections. The Rh-As distances in the linear As-Rh-As groups are 2.442(4)—2.454(4) Å (av 2.446(4) Å) for (**1**), 2.345(4) and 2.484(6) (av 2.415(6) Å) for (**2a**), and 2.389(10) and 2.441(10) Å (av 2.415(10) Å) for (**2b**), while those in the linear As-Rh-Cl groups are 2.385(3) and 2.370(4) Å (av 2.378(4) Å) for (**2a**), and 2.387(4) and 2.367(5) Å (av 2.377(5) Å) for (**2b**). The molecular structure of *trans*-[CoCl$_2$(dmap)$_2$]ClO$_4$ (**3**) was also determined by the X-ray method. Crystal data and the final R value are: orthorhombic, Pccm, a=8.018(2), b=8.428(1), c=18.716(3) Å, V=1265 Å^3, Z=2, R=0.095 for 1072 reflections. A series of *trans*-[RhX$_2$(dmap)$_2$]$^+$ (X=Cl, Br, I) were prepared and their absorption spectra were compared with one another and with those of related complexes.

In previous papers, we discussed the trans influence of a phosphine ligand on the rhodium(III)-ligand bond on the basis of X-ray crystal structure analyses of *trans(Cl,Cl),cis(P,P)*- and *cis(Cl,Cl),trans(P,P)*-[RhCl$_2$(edpp)$_2$]$^+$[1] (edpp=(2-aminoethyl)diphenylphosphine, NH$_2$CH$_2$CH$_2$P(C$_6$H$_5$)$_2$), *fac*-[Rh(edmp)$_3$]$^{3+}$[2] (edmp=(2-aminoethyl)dimethylphosphine, NH$_2$CH$_2$CH$_2$P(CH$_3$)$_2$), *trans-(Cl,Cl),cis(P,P)*-[RhCl$_2$(edmp)$_2$]$^+$,[2] and *trans*-[RhCl$_2$(dmpe)$_2$]$^+$[2] (dmpe=1,2-bis(dimethylphosphino)ethane, (CH$_3$)$_2$PCH$_2$CH$_2$P(CH$_3$)$_2$).

This paper describes the preparation and characterization of *cis*- and *trans*-[RhCl$_2$(dmap)$_2$]$^+$, and the X-ray crystal structure analyses of these complexes in order to confirm the geometrical structures and to use the results as the basis of a comparison of the trans influence of As with that of P in related complexes. The crystal structure of the trans-complex could be determined straightforwardly. However, the structure determination of the cis-complex was difficult because of the poor quality of the crystals. In order to improve the reliability of the molecular structural data for the cis-complex, both the PF$_6^-$ and the CF$_3$SO$_3^-$ salts were examined. A series of *trans*-[RhX$_2$(dmap)$_2$]$^+$ (X=Cl, Br, I) were also prepared and their absorption spectra were compared with one another and with those of related complexes. The X-ray structure analysis of *trans*-[CoCl$_2$(dmap)$_2$]$^+$ was also carried out in order to confirm the previous assignment.[3]

Experimental

The dmap ligand was prepared by the literature method,[3,4] and handled under an atmosphere of nitrogen until it formed air-stable rhodium(III) and cobalt(III) complexes. The *trans*-[CoCl$_2$(dmap)$_2$]ClO$_4$ complex (**3**) was prepared as described previously.[3] Absorption spectra were obtained with a Hitachi 323 or a Hitachi U-3400 spectrophotometer. ^{1}H NMR spectra were recorded on a Hitachi R-90H spectrometer using TMS as an internal reference.

Preparation of Complexes. *cis*-[RhCl$_2$(dmap)$_2$]PF$_6$ (2a) and *trans*-[RhCl$_2$(dmap)$_2$]CF$_3$SO$_3$. A deaerated ethanol solution (100 cm^3) of RhCl$_3$·3H$_2$O (0.55g, 2.09 mmol) was heated to reflux. To this solution was added a deaerated ethanol solution (8 cm^3) of dmap (2.02 g, 8.01 mmol). The mixture was refluxed for 7 h to give a yellow solution together with a small amount of orange precipitate. The reaction mixture was cooled to room temperature and the excess of dmap was oxidized by bubbling air through the solution. After filtering off the precipitate, the filtrate was evaporated to dryness under reduced pressure. The orange-yellow residue was mixed with water (100 cm^3) and the solution was filtered. The yellow filtrate was applied on a column (ϕ3 cm×70 cm) of SP-Sephadex C-25 (Na$^+$ form). By elution with 0.05 mol dm^{-3} NaCl, a lemon yellow (the cis isomer) and then a dark yellow (the trans isomer) band developed successively and highly charged species remained at the top of the column. The eluate containing the faster-moving band was collected and evaporated to dryness under reduced pressure. The residue was extracted with ethanol (3×20 cm^3) and the solvent was removed under reduced pressure. The residue was dissolved in hot water (90 °C, 90 cm^3), and to this solution was added a solution of NH$_4$PF$_6$ (1.0 g) in water (10 cm^3). The mixture was allowed to stand first at room temperature and then overnight in a refrigerator to yield yellow crystals. They were collected by filtration, washed with water, and dried in air. Yield: 0.46 g (27%). Found: C, 20.22; H, 4.45;

Cl, 8.63%. Calcd for $[RhCl_2(dmap)_2]PF_6$=$C_{14}H_{36}As_4Cl_2F_6PRh$: C, 20.43; H, 4.41 ; Cl, 8.62%. ^{1}H NMR ($C_6D_5NO_2$) δ=1.74 (6H, s, $AsCH_3$), 1.86 (6H, s, $AsCH_3$), 1.90 (12H, s, $AsCH_3$), and 2.0—2.5 (12H, m, $-CH_2-$). The complex is soluble in acetonitrile and nitromethane, and slightly soluble in ethanol and methanol, but insoluble in water and diethyl ether.

From the slower-moving band, *trans*-$[RhCl_2(dmap)_2]CF_3SO_3$ was isolated by a similar method, $NaCF_3SO_3 \cdot H_2O$ (1 g in 10 cm^3 of water) being used instead of NH_4PF_6. Yield: 0.58 g (34%). Found: C, 21.55; H, 4.44; Cl, 8.61; S, 4.00%. Calcd for $[RhCl_2(dmap)_2]CF_3SO_3$=$C_{15}H_{36}As_4Cl_2F_3O_3SRh$: C, 21.79; H, 4.39; Cl, 8.57; S, 3.88%. ^{1}H NMR (CD_3OD) δ=1.58 (24H, s, $AsCH_3$) and 2.0—2.4 (12H, m, $-CH_2-$). The complex is soluble in acetonitrile, nitromethane, and ethanol, and slightly soluble in water.

***trans*-$[RhCl_2(dmap)_2]ClO_4$ (1).** This complex was prepared from *trans*-$[RhCl_2(dmap)_2]CF_3SO_3$ and $LiClO_4$ by the same method as that for *trans(Cl,Cl),cis(P,P)*-$[RhCl_2(edmp)_2]ClO_4$[2)] and subjected to X-ray structure determination.

***cis*-$[RhC_2(dmap)_2]CF_3SO_3$ (2b).** A solution (ca. 10 cm^3) of *cis*-$[RhCl_2(dmap)_2]PF_6$ (ca 0.05 g) in acetonitrile-methanol (1 : 10 v/v) was applied on a column (ϕ1 cm×2 cm) of SP-Toyopearl 650 M (Li^+ form). The complex was eluted with an acetonitrile-methanol (1 : 10 v/v) solution of 0.1 mol dm^{-3} $LiCF_3SO_3$, and the eluate was evaporated to dryness. The residue was shaken with water (15 cm^3) and filtered to leave yellow microcrystals. Single crystals for X-ray analysis were obtained by recrystallization from acetonitrile-methanol (1 : 3 v/v).

***trans*-$[RhBr_2(dmap)_2]CF_3SO_3$.** To an aqueous solution (20 cm^3) of *trans*-$[RhCl_2(dmap)_2]CF_3SO_3$ (0.25 g, 0.30 mmol) was added a large excess of KBr (9.5 g, 80 mmol), and the mixture was refluxed for 29 h. An orange yellow crystalline solid which precipitated was filtered while the solution was still hot. The product was extracted with 5 cm^3 of acetonitrile. The solution was mixed with water (20 cm^3), and the mixture was heated to boiling. A hot aqueous solution (2 cm^3) of $NaCF_3SO_3 \cdot H_2O$ (1 g) was added to this solution. The mixture was allowed to stand for crystallization and evaporation of the acetonitrile first at room temperature and then in a refrigerator overnight. The orange yellow crystals were collected by filtration, washed with water, and dried in air. Yield: 0.11 g (40 %). Found: C, 19.77; H, 3.96%. Calcd for $[RhBr_2(dmap)_2]CF_3SO_3$=$C_{15}H_{36}As_4Br_2F_3O_3SRh$: C, 19.67; H, 3.96%.

***trans*-$[RhI_2(dmap)_2]CF_3SO_3$.** To an ethanol solution (20 cm^3) of *trans*-$[RhCl_2(dmap)_2]CF_3SO_3$ (0.20 g, 0.24 mmol) was added a large excess of NaI (8 g, 53 mmol), and the mixture was refluxed for 7 h. The solution was evaporated to dryness under reduced pressure, and the residue was shaken with dichloromethane until the extracts were colorless (ca. 60 cm^3). The combined extracts were evaporated to dryness under reduced pressure. The residue was dissolved in methanol (100 cm^3) and the solution was applied on a column (ϕ2.5 cm×20 cm) of SP-Toyopearl 650 M (Na^+ form). The products were eluted with 0.1 mol dm^{-3} $NaCF_3SO_3 \cdot H_2O$ in methanol. The eluate containing the red band was collected and evaporated to dryness under reduced pressure. The residue was dissolved in a mixture of acetonitrile (25 cm^3) and water (50 cm^3). The solution was heated to boiling for a

Table 1. Crystal Data, Experimental Conditions and Refinement Details

	1	**2a**	**2b**	**3**
Chemical formula	*trans*-$[RhCl_2(As_2C_7H_{18})_2]ClO_4$	*cis*-$[RhCl_2(As_2C_7H_{18})_2]PF_6$	*cis*-$[RhCl_2(As_2C_7H_{18})_2]CF_3SO_3$	*trans*-$[CoCl_2(As_2C_7H_{18})_2]ClO_4$
Formula weight	777.4	822.9	827.0	733.4
Space group	Cc	$Pca2_1$	$Pca2_1$	Pccm
D_m and D_x/Mg m^{-3}	1.99(2), 1.97	2.02(2), 2.02	2.02(2), 2.03	2.02(2), 1.93
μ(Mo $K\alpha$)/mm^{-1}	5.98	5.77	5.77	6.24
Color of crystals	Orange	Yellow	Yellow	Green
Size of specimen/mm^3	Sphere of 0.35(5) mm in diameter	0.40×0.40×0.55	Sphere of 0.40(5)mm in diameter	0.13×0.14×0.17
Laue group	$2/m$	mmm	mmm	mmm
Range of h	0—25 (0—19)	0—19 (−5—5)	0—19 (0—14)	0—10
k	0—13 (−9—9)	0—12 (−3—3)	0—12 (−9—9)	−10—10
and l	−16—16 (−12—12)	−24—0 (−7—0)	−25—25 (−18—18)	−22—22
Systematic absences	hkl, $h+k$ odd; $h0l$, l odd	$h0l$, h odd; $0kl$, l odd	$h0l$, h odd; $0kl$, l odd	$h0l$, l odd; $0kl$, l odd
Possible space group	Cc or C2/c	$Pca2_1$ or Pcam	$Pca2_1$ or Pcam	Pcc2 or Pccm
Variation of five standard reflections $\sum(\lvert F_o\rvert/\lvert F_o\rvert_{initial})/5$	1.00—1.01	0.99—1.01	0.99—1.00	0.99—1.00
Number of reflections measured	4443	3267	6959	5620
Number of reflections observed $[\lvert F_o\rvert>3\sigma(\lvert F_o\rvert)]$	2103	1381	3055	3070
Transmision factor, A	0.23—0.25	0.14—0.28	0.20—0.22	0.37—0.47
Number of unique reflections, R_{int}	1298 (0.021)	1284 (0.009)	1094 (0.030)	1072 (0.036)
Final R value	0.034	0.086	0.088	0.095
$(\Delta/\sigma)_{max}$ for nonhydrogen atoms	0.46	0.37	0.95	0.37
$\Delta\rho$/e Å^{-3}	−1.05. 0.52	−2.28, 1.96	−0.98, 1.64	−1.29, 1.40

while to evaporate the acetonitrile, and allowed to stand at room temperature to yield reddish brown crystals. They were collected by filtration, washed with ice-cold water, and dried in air. Yield: 0.19 g (78%). Found: C, 17.89; H, 3.59%. Calcd for $[RhI_2(dmap)_2]CF_3SO_3$=$C_{15}H_{36}As_4F_3O_3ISRh$: C, 17.84; H, 3.59%.

Crystal Structure Determinations. Experimental conditions and refinement informations are listed in Table 1. Intensities were measured up to 2θ=55° using graphite monochromatized Mo*Kα* radiation (λ=0.71073 Å) on a Rigaku four-circle diffractometer AFC-5 by the θ-2θ scan technique at a scan rate of $6^\circ\,\mathrm{min}^{-1}$ in θ. In order to avoid the error due to strong absorption by As, crystals were ground into spheres whenever possible and intensity data of equivalent reflections in the region of 2θ less than 40° (**1**), 15° (**2a**), 40° (**2b**), and 55° (**3**) were also collected. Lattice constants were determined from 20—25 2θ values (20°<2θ<30°).The structures were solved by the Patterson-Fourier method. The

Table 2. Fractional Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (×10)

Atom	x	y	z	B_{eq}/(Å^2×10)
		1		
Rh	0	2498(5)	2500	23
As(1)	−846(1)	741(1)	2191(1)	32
As(2)	−914(1)	4093(1)	2072(1)	31
As(3)	918(1)	911(1)	2921(1)	31
As(4)	825(1)	4282(1)	2806(1)	32
Cl(1)	30(2)	2410(4)	686(3)	40
Cl(2)	17(2)	2564(4)	4317(2)	37
Cl	2462(7)	−2466(3)	4926(12)	54
O(1)	2156(10)	−3369(16)	5201(17)	150
O(2)	2523(21)	−1211(13)	5136(29)	151
O(3)	2155(9)	−2509(15)	3784(10)	98
O(4)	3141(8)	−2780(16)	4715(13)	103
C(1)	−1646(8)	997(14)	1290(11)	42
C(2)	−1157(9)	33(18)	3387(13)	54
C(3)	−633(9)	−719(14)	1357(12)	46
C(4)	−1722(8)	3623(15)	1088(13)	45
C(5)	−1263(11)	4890(18)	3151(12)	67
C(6)	−741(8)	5478(14)	1176(11)	39
C(7)	−2057(8)	2312(14)	1415(13)	48
C(8)	1776(8)	1584(14)	3753(12)	41
C(9)	687(8)	−618(14)	3700(12)	44
C(10)	1263(8)	119(16)	1714(13)	46
C(11)	1736(9)	3842(15)	3813(14)	56
C(12)	1124(10)	5081(16)	1565(14)	56
C(13)	497(8)	5839(12)	3431(12)	39
C(14)	2058(9)	2750(17)	3403(16)	61
		2a		
Rh	879(1)	2374(2)	0$^{a)}$	30
As(1)	−595(2)	1312(3)	−9(5)	46
As(2)	315(2)	4740(4)	−72(6)	80
As(3)	1007(3)	2428(10)	1190(2)	113
As(4)	985(3)	2086(8)	−1255(3)	93
Cl(1)	2394(4)	3274(11)	−78(13)	94
Cl(2)	1483(5)	31(10)	−72(13)	91
P	−2581(15)	2884(19)	−2479(12)	116
F(1)	−1602(26)	2125(48)	−2541(27)	178
F(2)	−2012(19)	4198(38)	−2285(20)	124
F(3)	−2635(30)	3030(52)	−3175(32)	211
F(4)	−2992(21)	1263(54)	−2787(23)	155
F(5)	−2855(29)	2273(44)	−1752(26)	185
F(6)	−3499(21)	3312(43)	−2435(22)	144
C(1)	−1597(24)	2325(43)	223(21)	65
C(2)	−1115(36)	773(63)	−949(31)	104
C(3)	−753(25)	−328(46)	513(24)	62
C(4)	2191(36)	1899(63)	−1569(33)	108
C(5)	626(36)	3124(70)	−2035(35)	111
C(6)	395(33)	−141(61)	−1516(31)	94
C(7)	−564(32)	−382(59)	−1301(30)	91
C(8)	−303(24)	5713(46)	558(25)	62
C(9)	−616(25)	5115(44)	−926(20)	54
C(10)	1270(27)	6263(52)	188(25)	85
C(11)	257(32)	4171(64)	1561(33)	100
C(12)	2253(29)	3276(55)	1383(27)	84
C(13)	525(57)	1312(136)	1873(69)	248
C(14)	191(32)	5547(59)	1187(28)	87
		2b		
Rh	880(2)	2371(3)	0$^{a)}$	31
As(1)	−595(2)	1311(4)	38(5)	44
As(2)	323(3)	4738(4)	9(7)	82
As(3)	1019(4)	2359(11)	1238(3)	117
As(4)	967(4)	2132(10)	−1209(3)	96
Cl(1)	2395(7)	3337(15)	−47(15)	95
Cl(2)	1484(8)	42(13)	173(7)	57
S	−2552(21)	2861(29)	−2418(15)	154
C(1)	−1664(38)	2648(55)	−225(28)	78
C(2)	−694(46)	−351(73)	−510(30)	92
C(3)	−1002(45)	616(66)	1112(32)	94
C(4)	2165(41)	1574(63)	−1598(34)	84
C(5)	441(55)	3310(84)	−1916(46)	137
C(6)	619(53)	115(75)	−1695(35)	113
C(7)	−532(47)	−403(73)	−1180(35)	99
C(8)	−514(59)	5321(95)	816(39)	141
C(9)	−387(37)	5517(64)	−681(28)	73
C(10)	1290(46)	6337(66)	295(33)	111
C(11)	243(65)	4205(102)	1653(47)	165
C(12)	2284(54)	2624(84)	1515(46)	129
C(13)	−18(98)	765(149)	1700(67)	276
C(14)	439(60)	5616(91)	1223(49)	153
C(15)	−3148(33)	1468(53)	−2759(26)	55
O(1)	−1494(36)	2797(46)	−2563(26)	113
O(2)	−2635(35)	2752(47)	−1693(26)	127
O(3)	−3123(29)	3913(44)	−2711(22)	98
		3		
Co	0	0	0	38
As	1419(2)	−1481(2)	880(1)	49
Cl(1)	2077(6)	1800(6)	0	46
Cl(2)	5000	5000	2500	73
O(1)	3745(57)	4217(52)	2185(26)	163
O(2)	4403(95)	3524(60)	2334(45)	111
O(3)	5699(88)	4900(215)	3140(33)	149
C(1)	3482(29)	−3611(28)	0	53
C(2A)$^{b)}$	3648(31)	−2178(33)	596(14)	34
C(3A)$^{b)}$	539(36)	−3222(37)	1476(18)	45
C(4A)$^{b)}$	2395(36)	−128(44)	1793(15)	46
C(2B)$^{b)}$	1921(39)	−3687(31)	384(16)	44
C(3B)$^{b)}$	−46(49)	−2322(35)	1569(16)	47
C(4B)$^{b)}$	3290(31)	−849(32)	1262(17)	38

a) This parameter was used to define the origin of the unit cell along z and is listed without e.s.d.
b) Population parameters of the disordered carbon atoms 0.5.

Table 3. Selected Bond Lengths (l/Å) and Bond Angles (ϕ/°)

	1	**2a**	**2b**
Rh-As(1)	2.454(4)	2.385(3)	2.387(4)
Rh-As(2)	2.442(4)	2.370(4)	2.367(5)
Rh-As(3)	2.442(4)	2.345(4)	2.441(10)
Rh-As(4)	2.447(4)	2.484(6)	2.389(10)
Rh-Cl(1)	2.366(4)	2.386(7)	2.406(11)
Rh-Cl(2)	2.352(3)	2.372(9)	2.383(13)
As(1)-Rh-As(2)	89.1(1)	94.1(1)	94.4(2)
As(1)-Rh-As(3)	91.2(2)	95.1(1)	92.5(3)
As(1)-Rh-As(4)	178.8(1)	90.2(2)	92.3(3)
As(1)-Rh-Cl(1)	86.9(1)	174.3(2)	177.5(3)
As(1)-Rh-Cl(2)	94.3(1)	87.3(2)	87.3(3)
As(2)-Rh-As(3)	179.6(1)	93.9(1)	91.5(3)
As(2)-Rh-As(4)	89.8(2)	93.7(2)	96.5(3)
As(2)-Rh-Cl(1)	86.9(1)	89.6(2)	88.1(3)
As(2)-Rh-Cl(2)	95.1(1)	173.0(2)	171.2(5)
As(3)-Rh-As(4)	89.9(1)	170.4(2)	170.3(2)
As(3)-Rh-Cl(1)	92.8(1)	88.9(2)	87.8(3)
As(3)-Rh-Cl(2)	85.1(1)	92.8(2)	79.8(4)
As(4)-Rh-Cl(1)	93.3(1)	85.2(2)	87.0(4)
As(4)-Rh-Cl(2)	85.6(1)	79.4(3)	92.1(4)
Cl(1)-Rh-Cl(2)	177.7(1)	88.5(3)	90.3(4)

	3
Co-As	2.359(2)
Co-Cl(1)	2.253(5)
As-Co-Cl(1)	90.0(1)

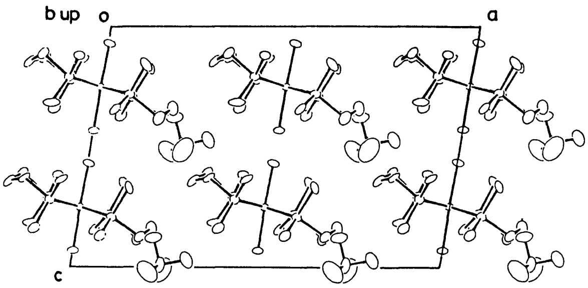


Fig. 1. The crystal structure of *trans*-[RhCl$_2$(dmap)$_2$]ClO$_4$ (**1**) along *b*.

function, $\sum w||F_o|-|F_c||^2$ was minimized using block-diagonal least squares. Atomic scattering factors were taken from International Tables for X-ray crystallography.5) The calculations were carried out on a FACOM M380R computer at Keio University with the computation program system UNICS-III.6) The final atomic parameters are listed in Table 2 and the bond lengths and bond angles involving the Co or Rh atom in Table 3.7) Experimental details are as follows:

(**1**) Systematic absences indicated that the space group is Cc or C2/c. D_m suggested that Z=4. At first, the space group was assumed to be C2/c. The position of the Rh atom on a twofold axis was derived from the Patterson function, and all the non-hydrogen atoms were located in the Fourier syntheses and refined anisotropically. However, the R-value ceased to decrease at 0.14. When the space group was changed to Cc, the R-value decreased to 0.055. As seen from Fig. 1, the complex cation has an approximate twofold axis parallel to b. The Cl atom of the ClO$_4^-$ ion lies nearly on (1/4, −1/4, 1/2), where there is a center of symmetry if the space group is C2/c. The space group C2/c is still possible if the complex cation has rigorous twofold symmetry and the ClO$_4^-$ ion exhibits orientational disorder around the center of symmetry. However, an indication of such orientational disorder of the ClO$_4^-$ was not recognized in the refinement based on the space group Cc. In this context the space group C2/c was again checked; the R value, however, could not be reduced to less than 0.14. $\Delta\rho$ in the final difference synthesis was less than 0.6 e Å^{-3}. Consequently, the space group was determined to be Cc. The positions of the hydrogen atoms were calculated and fixed in the refinement with B=7.0 Å^2.

(**2a**) Systematic absences indicated the space group to be Pca2$_1$ (No. 29) or Pcam [$ba\bar{c}$ setting of Pbcm (No. 57)]. D_m led to Z=4. Assuming the space group to be Pca2$_1$, the structure was solved. Carbon atoms were refined isotropically to avoid non-positive definite matrices for the thermal parameters. All other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were finally introduced in the structure analysis. When the sign of $\Delta F''$ was inverted, the R value did not change significantly. The relatively large R value of 0.086 may be due to the poor crystallinity. The B_{eq} values of the As atom from 5 to 11 Å^2 suggest positional disorder. The complex cation could not be accommodated in any of the twofold positions in space group Pcam due to the lack of symmetry.

(**2b**) The crystal structure is isomorphous with that of (**2a**) and by utilizing the atomic coordinates of (**2a**) as a starting set, the structure could be refined in the same manner. The F atoms in the CF$_3$SO$_3^-$ ion could not be located in the difference synthesis and were therefore not included in the refinement.

(**3**) Systematic absences suggested the space group Pcc2 (No.

27) or Pccm (No. 49). Since $Z=2$, the Co atom is required to lie at a special position. At first, the space group was assumed to be Pccm with Co located at 2a with site symmetry 2/m. A Cl-Co-Cl bond axis and a bisector of the As-Co-As chelate angle lie on a mirror plane. Non-hydrogen atoms were found from Fourier or difference synthesis and refined anisotropically. In the Fourier maps of the dmap ligand, an indication of the superposition of two conformations emerged. The space group Pcc2 was then tried locating the Co atom on the twofold axis. However, the disorder of the dmap ligand could not be deleted and therefore the centrosymmetric space group, Pccm was adopted and the carbon atoms except C(1) were split into two possible positions A and B with weight of 1/2 each. All the non-hydrogen atoms were refined anisotropically, and H atoms were not introduced.

Results and Discussion

By reaction of $RhCl_3 \cdot 3H_2O$ with dmap in ethanol, $[RhCl_2(dmap)_2]^+$ was formed, and the complex was separated into the cis- and trans-isomers by column chromatography on SP-Sephadex. The structures of the isomers were assigned on the basis of the ^1H NMR spectra. The isomer obtained from the slower-moving dark yellow band gives only one resonance attributable to the As-CH_3 protons, and is assigned as the trans-isomer. The four methyl groups should be in equivalent environments because of rapid puckering of the chelate rings on the NMR time scale. On the other hand, the isomer obtained from the faster-moving lemon yellow band exhibits three resonances in the As-CH_3 region and is assigned as the cis-isomer. These assignments were confirmed by X-ray structure determination of the isomers (vide infra). In general, a trans isomer is eluted faster than the corresponding cis isomer in ion-exchange column chromatography. The present complex is an exception to this elution order.

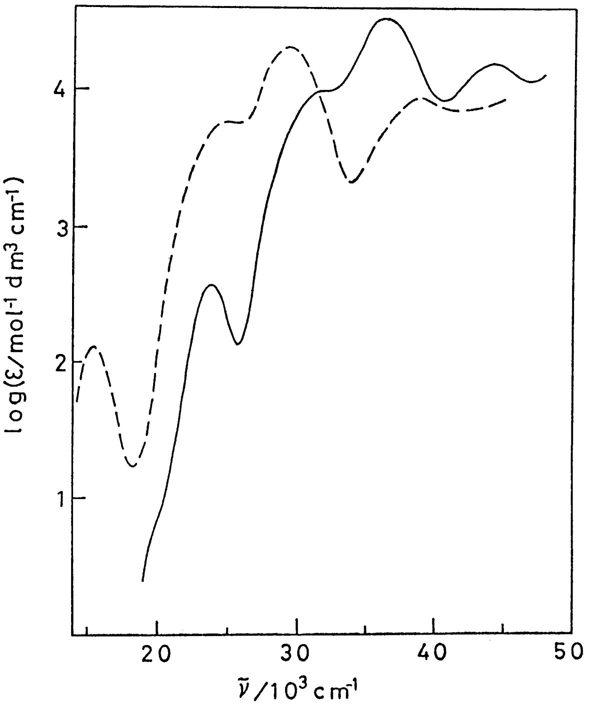


Fig. 2. Absorption spectra of *trans*-$[RhCl_2(dmap)_2]CF_3SO_3$ (——) in methanol and *trans*-$[CoCl_2(dmap)_2]ClO_4$ (----) in acetonitrile.

Figure 2 compares the absorption spectrum of *trans*-$[RhCl_2(dmap)_2]^+$ with that of *trans*-$[CoCl_2(dmap)_2]^+$,[3] and the data are given in Table 4. Both spectra are quite similar in pattern, although all of the bands of the rhodium(III) complex are shifted by 5200—8200 cm^{-1} toward higher energy compared to the corresponding bands of the cobalt(III) complex. The low energy absorption band at 23900 cm^{-1} of the rhodium(III) complex can be assigned to be the split component (I_a) of the first absorption band, $^1A_{1g} \rightarrow {}^1T_{1g}$ (O_h). In the analogous phosphine complex, *trans*-$[RhCl_2(dmpp)_2]^+$ (dmpp=1,3-bis(dimethylphosphino)propane) the I_a component lies at 25330 cm^{-1}.[8] Thus the spectrochemical series for the group 5B (15) elements can be determined to be P>As. The same order has been reported for the trans-dichloro cobalt(III) complexes.[3,9] The I_b and second absorption bands of *trans*-$[MCl_2(dmap)_2]^+$ (M=Rh, Co) are hidden by the strong charge-transfer bands.

The *trans*-$[RhBr_2(dmap)_2]^+$ and *trans*-$[RhI_2(dmap)_2]^+$ complexes were prepared by substitution reactions from the *trans*-dichloro complex and potassium bromide or sodium iodide. The configuration was retained in the reactions as indicated by the absorption spectra. The absorption spectra of *trans*-$[RhX_2(dmap)_2]^+$ (X=Cl, Br, I) are shown in Fig. 3. The spectral patterns of the complexes are similar, although the I_a component of the diiodo complex is observed as a shoulder because of the overlap with the Rh-I charge-transfer band. In this series, the energy of the I_a component decreases in the order Cl>Br>I. The spectra show a shoulder at the low energy side of the I_a band and the absorption is assigned as a spin-forbidden transition. The shoulder becomes more pronounced as X proceeds from Cl through Br to I. All of the complexes show an intense band at ca. 36500 cm^{-1}, and

Table 4. Absorption Spectral Data (in Methanol)

Complex	$\tilde{\nu}/10^3$ cm^{-1} (log ε/mol^{-1} dm^3 cm^{-1})
trans-$[RhCl_2(dmap)_2]CF_3SO_3$	23.9(2.56) 32(4.0)$^{a)}$ 36.5(4.52) 44.3(4.18)
trans-$[RhBr_2(dmap)_2]CF_3SO_3$	19.5(1.1)$^{a)}$ 22.7(2.49) 28.8(3.74) 35.8(4.47)
trans-$[RhI_2(dmap)_2]CF_3SO_3$	18(1.4)$^{a)}$ 21.5(2.7)$^{a)}$ 25.1(3.75) 36(4.4)
cis-$[RhCl_2(dmap)_2]PF_6$	28.5(3.25)$^{a)}$ 34.7(4.27) 40.3(4.41) 47(4.1)$^{a)}$

a) Shoulder.

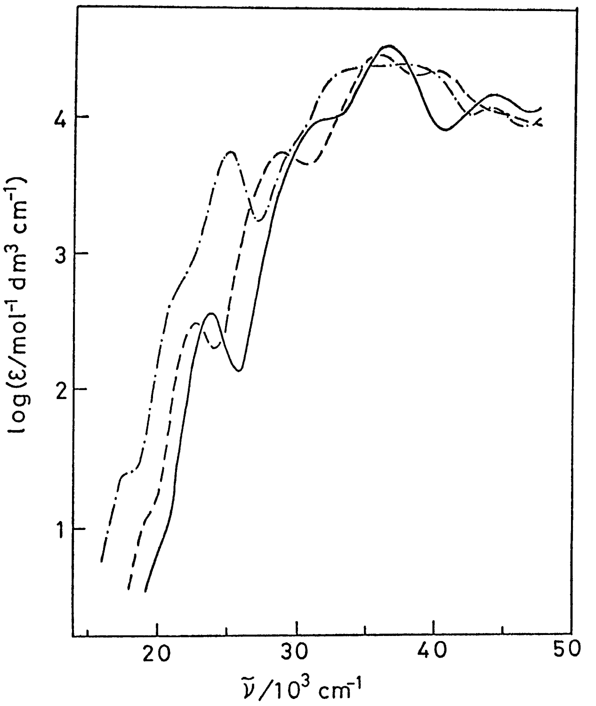


Fig. 3. Absorption spectra of *trans*-[RhCl$_2$(dmap)$_2$]CF$_3$SO$_3$ (——), *trans*-[RhBr$_2$(dmap)$_2$]CF$_3$SO$_3$ (----), and *trans*-[RhI$_2$(dmap$_2$]CF$_3$SO$_3$ (—•—) in methanol.

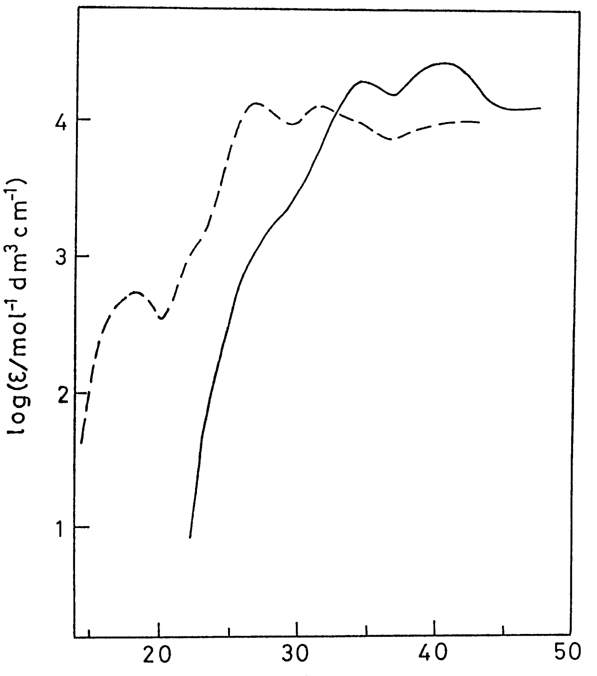


Fig. 4. Absorption spectra of *cis*-[RhCl$_2$(dmap)$_2$]PF$_6$ (——) in methanol and *cis*-[CoCl$_2$(dmap)$_2$]ClO$_4$ (----) in acetonitrile.

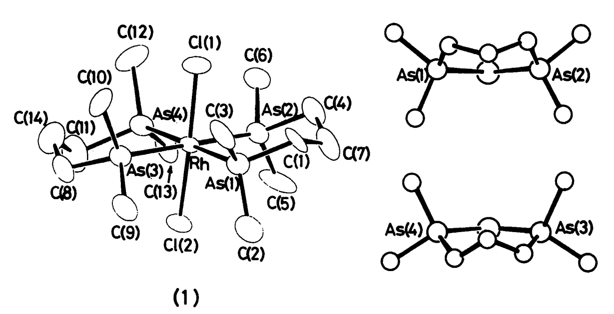


Fig. 5. The molecular structure of the *trans*-[RhCl$_2$(dmap)$_2$]$^+$ complex cation (**1**) and edge-on views of the six-membered dmap chelate rings.

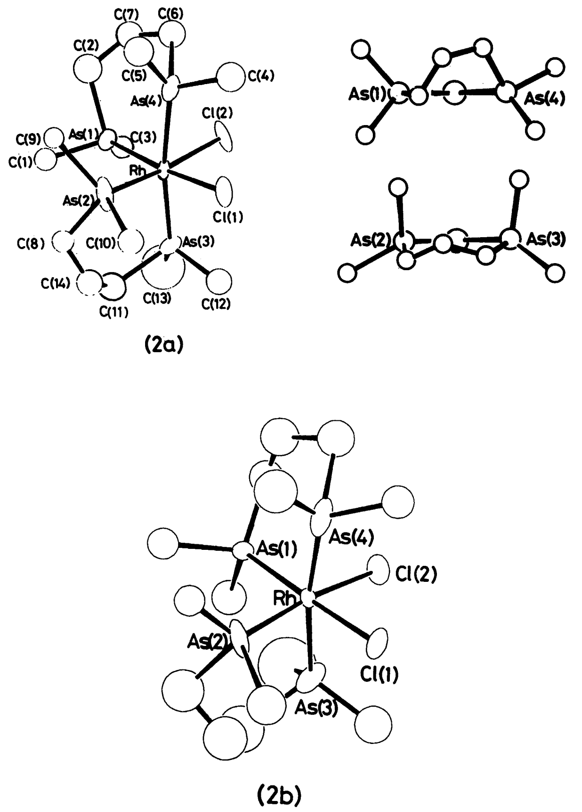
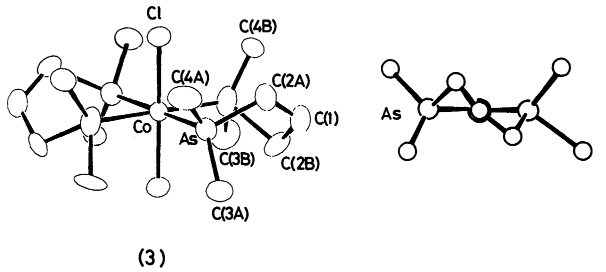


Fig. 6. The molecular structures of the PF$_6^-$ (**2a**) and CF$_3$SO$_3^-$ (**2b**) salts of *cis*-[RhCl$_2$(dmap)$_2$]$^+$.

the band may be assigned as the Rh–As charge-transfer transition, since this band remains constant when the halogen in the complex is changed.

Figure 4 compares the absorption spectrum of *cis*-[RhCl$_2$(dmap)$_2$]$^+$ with that of *cis*-[CoCl$_2$(dmap)$_2$]$^+$. The spectral patterns are similar to each other. The band at 18700 cm^{-1} of the cobalt(III) complex has been assigned as the first absorption band.[3] The shoulder at ca. 28500 cm^{-1} of the rhodium(III) complex can also be assigned as the first absorption band, since the ratio of the positions ($\tilde{\nu}_{\mathrm{Rh}}/\tilde{\nu}_{\mathrm{Co}}$=28500/18700=1.52) is very close to the spectrochemical parameter for rhodium-(III), 1.56 given by Shimura (the parameter for cobalt(III) is 1.00).[10] The ratio for the trans complexes is also 1.52.

Structures of *trans*- and *cis*-[RhCl$_2$(dmap)$_2$]$^+$ and *trans*-[CoCl$_2$(dmap)$_2$]$^+$. Molecular structures of the complex cations (**1**), (**2a**) and (**2b**), and (**3**) are shown in



(3)

Fig. 7. The molecular structure of the *trans*-$[\mathrm{CoCl_2(dmap)_2}]^+$ complex cation (**3**). Co, Cl, and C(1) atoms lie on a mirror plane. There is also a twofold axis passing through the Co atom and perpendicular to the mirror plane. Although the ligand dmap has two possible conformations (δ and λ-skew boat forms with possibility 50%), only one of them was drawn for clarity. The other conformation is the mirror image. The chair forms could not be assigned becaused of too small angles for C(2A)-C(1)-C(2A′) and C(2B)-C(1)-C(2B′).

Figs. 5, 6, and 7, respectively. The structure determinations confirmed the assignments based on the ^{1}H NMR and absorption spectra. Isomerization of *cis*-$[\mathrm{CoCl_2(dmap)_2}]^+$ to the trans isomer precluded the isolation of the cis isomer in a crystalline form suitable for X-ray analysis.³⁾

The six-membered chelate ring of dmap takes the chair form in *trans*-$[\mathrm{RhCl_2(dmap)_2}]\mathrm{ClO_4}$, and the skew conformation in the Co complex. The chelate rings take the chair form in (**2b**), and one of them a distorted skew conformation in (**2a**). The different conformations indicate the flexibility of the dmap chelate rings in the crystal field.

A detailed discussion of the lengthening of mutually trans Rh-As bonds in terms of the trans influence of As on the Rh-As bond length is limited by the low accuracy of the structural data for *cis*-$[\mathrm{RhCl_2(dmap)_2}]^+$. If the standard $\mathrm{Rh^{III}}$-As bond length,not affected by trans influence, is taken from the mean Rh-As distance along the linear Cl-Rh-As groups in (**2a**), 2.378(4) Å, and (**2b**), 2.377(5) Å, the lengthening of Rh-As by the trans influence of As can be estimated to be ca. 0.07 Å in comparison with the mean Rh-As distance of 2.446(4) Å in (**1**). The two Rh-As bond distances along the linear As-Rh-As group in both (**2a**) and (**2b**) differ substantially, 2.345(4) and 2.484(6) Å for (**2a**), and 2.389(10) and 2.441(10) Å for (**2b**). We have no explanation for these differences at present. However, these Rh-As bonds average 2.415 Å, which is longer by ca. 0.04 Å than the mean Rh-As distance along the linear Cl-Rh-As group. The trans influence of P on the Rh-P bond length was found to be 0.05—0.09 Å in the *trans*-$[\mathrm{RhCl_2(dmpe)_2}]^+$ complex.²⁾ The strength of the trans influence of As seems to be almost the same as that of P in the rhodium(III) complexes. The trans influence (0.02—0.04 Å) of As on the Rh-Cl bond length is smaller than that of As on the Rh-As bond length (0.04—0.07 Å). The Co-As bond distance in (**3**), 2.359(2) Å, is a little longer than that in *trans*-$[\mathrm{CoCl_2(diars)_2}]\mathrm{Cl}$ (diars=*o*-phenylenebis(dimethylarsine)), 2.334(2) Å.¹¹⁾ These bond distances are longer than that (2.302(1) Å) in $[\mathrm{Co(acac)_2\{NH_2CH_2CH_2As(CH_3)_2\}}]^+$,¹²⁾ suggesting that the trans influence of As on the Co-As bond distance is 0.03—0.06 Å. The difference (ca. 0.09 Å) between the Rh-As and Co-As bond lengths in the present complexes, (**1**) and (**3**), is a little smaller than that (ca. 0.11 Å) between the Rh-Cl and Co-Cl bonds, but fairly larger than that (ca. 0.05 Å) between the Rh-P and Co-P bond lengths in *trans*(*Cl*,*Cl*),*cis*(*P*,*P*)-$[\mathrm{MCl_2(edpp)_2}]^+$ (M=Rh¹⁾, Co¹³⁾) and *fac*-$[\mathrm{M(edmp)_3}]^{3+}$ (M=Rh²⁾, Co¹⁴⁾). The Rh(III) center seems to have a particularly strong affinity for P.

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