April, 1994] *Bull. Chem. Soc. Jpn.,* ***67****, 1013—1023(1994)* 1013

# Preparation and Characterization of Iridium(III) Complexes Containing (2-Aminoethyl)dimethylphosphine (edmp) or (2-Aminoethyl)diphenylphosphine (edpp). Structures of *fac*-[Ir(edmp)$_3$]Cl$_3$·5H$_2$O and *trans*(*Cl*,*Cl*),*cis*(*P*,*P*)-[IrCl$_2$(edpp)$_2$]BF$_4$ and Comparisons of Their Properties with Those of the Cobalt(III) and Rhodium(III) Analogs

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(Received October 12, 1993)

The iridium(III) complexes containing (2-aminoethyl)dimethylphosphine (edmp) or (2-aminoethyl)diphenylphosphine (edpp) were prepared. Crystal structures of *fac*-[Ir(edmp)$_3$]Cl$_3$·5H$_2$O (**2**), *trans(Cl,Cl),cis(P,P)*-[IrCl$_2$(edpp)$_2$]BF$_4$ (**3**), and $\Delta$(*lel*$_3$)- and $\Lambda$(*ob*$_3$)-[Ir(*R*,*R*-chxn)$_3$](NO$_3$)$_3$·3H$_2$O (**4** and **5**; chxn=*trans*-1,2-cyclohexanediamine) were determined by single-crystal X-ray diffraction. Crystal data and final *R* values are: for **2**, FW=703.7, triclinic, $P\bar{1}$, $a=11.718(2)$, $b=13.199(1)$, $c=9.482(1)$ Å, $\alpha=91.44(1)$, $\beta=105.86(1)$, $\gamma=90.53(1)$°, $V=1410.0(2)$ Å$^3$, $D_x=1.66$ Mg m$^{-3}$, and $Z=2$, $R=0.039$ for 5410 reflections. For **3**, FW=808.5, triclinic, $P\bar{1}$, $a=11.465(1)$, $b=13.694(1)$, $c=10.049(1)$ Å, $\alpha=94.764(6)$, $\beta=92.197(8)$, $\gamma=102.807(8)$°, $V=1530.5(2)$ Å$^3$, $D_x=1.75$ Mg m$^{-3}$, and $Z=2$, $R=0.035$ for 5978 reflections. For **4**, FW=774.9, hexagonal, $P6_3$, $a=13.005(1)$, $c=10.221(2)$ Å, $V=1497.1(3)$ Å$^3$, $D_m=1.71(2)$, $D_x=1.72$ Mg m$^{-3}$, and $Z=2$, $R=0.020$ for 1063 reflections. For **5**, hexagonal, FW=774.9, $P6_3$, $a=13.359(1)$, $c=9.848(2)$ Å, $V=1522.0(3)$ Å$^3$, $D_m=1.70(2)$, $D_x=1.69$ Mg m$^{-3}$, and $Z=2$, $R=0.015$ for 1105 reflections. The average Ir–N bond length of 2.167(6) Å in **2** is longer by 0.077(6) Å than those in **4** and **5**. The structural data of the corresponding cobalt(III) and rhodium(III) complexes show that the order of the strength of the trans influence of the –PMe$_2$ group in edmp is Co$^{\mathrm{III}}$<Ir$^{\mathrm{III}}$<Rh$^{\mathrm{III}}$. In **3**, the elongation of the metal–nitrogen bond length by the trans influence of the –PPh$_2$ group in edpp is smaller than that of the –PMe$_2$ group in **2**, and the elongation is nearly the same as those in the corresponding cobalt(III) and rhodium(III) complexes. The absorption spectra of the two series of complexes, *fac*-[M(edmp)$_3$]$^{3+}$ and *trans*(*Cl*,*Cl*),*cis*(*P*,*P*)-[MCl$_2$(edpp)$_2$]$^+$ (M=Co$^{\mathrm{III}}$, Rh$^{\mathrm{III}}$, and Ir$^{\mathrm{III}}$) are compared and Shimura's spectrochemical parameters for iridium(III) are discussed.

In a series of papers,[1—5)] we reported the preparation and characterization of cobalt(III) and rhodium(III) complexes containing (2-aminoethyl)dimethylphosphine (edmp) or (2-aminoethyl)diphenylphosphine (edpp). The X-ray analyses revealed that due to the trans influence of the phosphorus donor atom the metal–nitrogen bond trans to the phosphorus atom is elongated, and that the elongations of the Rh–N bonds are larger than those of the corresponding Co–N bonds.[1—4)] From their absorption spectra, the spectrochemical series of the ligands were determined for both cobalt(III) and rhodium(III) as dmpe > edmp > en≥edpp > Me$_4$-en (dmpe = 1,2-bis(dimethylphosphino)ethane; en = 1,2-ethanediamine; Me$_4$-en = *N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethanediamine), and Shimura's spectrochemical parameter[6)] for rhodium(III) was discussed.[1)]

In order to complete phosphine complexes of the Co$^{\mathrm{III}}$–Rh$^{\mathrm{III}}$–Ir$^{\mathrm{III}}$ series and to compare absorption spectra and trans influence of the phosphorus donor atom among these complexes, the title iridium(III) complexes have been prepared, the absorption spectra measured, and the structures determined by single-crystal X-ray diffraction. To obtain a standard Ir–N bond length the crystal structures of $\Delta$(*lel*$_3$)- and $\Lambda$(*ob*$_3$)-[Ir(*R*,*R*-chxn)$_3$](NO$_3$)$_3$·3H$_2$O (chxn = *trans*-1,2-cyclohexanediamine) have also been determined.

## Experimental

All preparative procedures were performed under an atmosphere of nitrogen until air-stable iridium(III) complexes were formed. All solvents used in the preparations of ligands and complexes were bubbled with nitrogen for 20 min immediately before use.

**Preparation of Ligands.** For the preparation of edmp, the previous method[3)] was modified as follows. Instead of chloroform, diethyl ether was used for the extraction of edmp, since edmp with unpurified chloroform causes precipitation of its hydrochloride salt. Before use edmp was purified by distillation under reduced pressure (bp 52—55 °C, 3.4 kPa). The edpp was prepared and purified according

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to the literature method.[7)]

**Preparation of Complexes.** $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ (coe= cyclooctene) was prepared by the literature method.[8)]

***trans(Cl, Cl), trans(P, P)*- $[IrCl_2(edmp)_2]PF_6$ (1).** To a deaerated aqueous solution (20 cm$^3$) of $K_3[IrCl_6]$ (755 mg, 1.45 mmol) was dropwise added edmp (0.86 g, 8.2 mmol), and the mixture was refluxed with stirring for 40 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was washed with diethyl ether (50 cm$^3$×2) and extracted with boiling ethanol (50 cm$^3$) to remove KCl. The extract was evaporated to dryness under reduced pressure, and the greenish-yellow residue was dissolved in water (100 cm$^3$). The solution was applied on a short column ($\phi$ 3 cm×3.5 cm) of SP-Toyopearl 550C (Na$^+$ form) and adsorbed products were eluted with a 0.05 mol dm$^{-3}$ aqueous NaCl solution (200 cm$^3$) in order to remove highly charged species. The eluate was evaporated to dryness under reduced pressure, and the residue was shaken with boiling ethanol (50 cm$^3$) to extract the complexes. The solvent was removed from the extract under reduced pressure, and the residue was dissolved in water (150 cm$^3$). The solution was applied on a column ($\phi$ 3 cm×15 cm) of SP-Toyopearl 550C, and the adsorbed products were eluted with a 0.04 mol dm$^{-3}$ aqueous NaCl solution, the eluate being monitored by the absorption of UV-light (340 nm). After elution of the fastest moving band, a fraction containing the main band was collected. The eluate was evaporated to dryness under reduced pressure. The residue was extracted with ethanol (50 cm$^3$), and the volume of the extract was reduced to 5 cm$^3$. A saturated ethanol solution (1 cm$^3$) of $NH_4PF_6$ was added, and the mixture was allowed to stand in a refrigerator overnight. Pale yellow crystals were collected and dried in air. Yield: 82 mg (0.132 mmol, 9.0%). Found: C, 15.63; H, 3.92; N, 4.52%. Calcd for $C_8H_{24}Cl_2F_6IrN_2P_3$: C, 15.54,; H, 3.91; N, 4.53%. $^1$H NMR (dmso-$d_6$) $\delta$=1.63 (t, $J$=4.1 Hz, 3H: $P\text{–}C\underline{H}_3$), 2.2—2.7 (m, 1H; $P\text{–}C\underline{H}_2\text{–}$), 3.31 (s, 1H, $N\text{–}C\underline{H}_2\text{–}$), 5.60 (s, 1H; $\text{–}N\underline{H}_2$). $^{13}$C NMR (dmso-$d_6$) $\delta$=5.98 (t, $J$=17.6 Hz; $P\text{–}\underline{C}H_3$), 27.11 (t, $J$=15.5; $P\text{–}\underline{C}H_2\text{–}$), 45.03 (s; $N\text{–}\underline{C}H_2\text{–}$). $^{31}$P NMR (dmso-$d_6$) $\delta$=−3.26 (s).

***fac*-$[Ir(edmp)_3]Cl_3\cdot 5H_2O$ (2).** The edmp (0.75 g, 7.1 mmol) ligand was added dropwise with stirring to a dichloromethane suspension (50 cm$^3$) of $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ (1.00 g, 1.12 mmol) giving a yellow solution. Chlorine gas (50%v in Ar) was bubbled into the solution for 5 min, which resulted in a white precipitate, and the mixture was stirred for 2 h. After bubbling nitrogen through the mixture for 10 min to remove excess chlorine, the mixture was evaporated to half volume under reduced pressure. The white precipitate was collected by filtration, washed with diethyl ether (25cm$^3$×2), and dried in vacuo. The crude product was recrystallized from an aqueous–ethanol (1 : 5) mixture (30 cm$^3$) to form colorless crystals, which were collected by filtration and dried in air. Yield: 222 mg (0.315 mmol, 14.1%). Found: C, 20.43; H, 6.84; N, 5.80%. Calcd for $C_{12}H_{46}Cl_3IrN_3O_5P_3$: C, 20.47; H, 6.59; N, 5.97%. $^1$H NMR ($D_2O$) $\delta$=1.91 (d, $J$=10.4 Hz, 3H: $P\text{–}C\underline{H}_3$), 2.06 (d, $J$=10.1 Hz, 3H: $P\text{–}C\underline{H}_3$), 2.2—2.3 (m, 1H; $P\text{–}C\underline{H}_2\text{–}$), 2.35—2.45 (m, 1H: $P\text{–}C\underline{H}_2\text{–}$), 2.8—2.95 (m, 2H; $\text{–}N\underline{H}_2$), 3.05—3.25 (m, 2H; $N\text{–}C\underline{H}_2\text{–}$). $^{13}$C NMR ($D_2O$) $\delta$=13.65 (d, $J$=38.1 Hz; $P\text{–}\underline{C}H_3$), 16.46 (d, $J$=38.1 Hz, $P\text{–}\underline{C}H_3$), 35.80 (d, $J$=41.2 Hz; $P\text{–}\underline{C}H_2\text{–}$), 45.95 (s; $N\text{–}\underline{C}H_2\text{–}$). $^{31}$P NMR ($D_2O$) $\delta$=−5.93 (s).

Crystals suitable for X-ray analysis were obtained by slow cooling of an aqueous–ethanol (1 : 5) solution from 50 °C to 20 °C.

***trans(Cl,Cl),cis(P,P)*-$[IrCl_2(edpp)_2]BF_4$ (3).** The edpp (2.12 g, 9.25 mmol) ligand was added dropwise with stirring to an ethanol suspension (30 cm$^3$) of $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ (1.77 g, 1.98 mmol). The resulting yellow solution was filtered and the filtrate was evaporated to dryness under reduced pressure. The orange residue was stirred in diethyl ether (50 cm$^3$) giving a yellow precipitate, which was collected by filtration. The product was dissolved in dichloromethane (40 cm$^3$), and to the filtered solution was added edpp (217 mg, 0.95 mmol). Chlorine gas (50%v in Ar) was bubbled slowly into the solution for 5 min. After bubbling with nitrogen for 10 min to remove excess chlorine gas, the mixture was evaporated to dryness under reduced pressure. The brownish yellow oily residue was stirred in diethyl ether (50 cm$^3$) giving a yellow precipitate, which was collected on a filter and washed with diethyl ether (25 cm$^3$×2). The product was extracted with ethanol (20 cm$^3$), and a saturated ethanol solution of $LiBF_4$ (5 cm$^3$) was added to the extract. The mixture was allowed to stand in a refrigerator overnight, and the yellow microcrystals were collected by filtration and dried in air. Yield: 1.35 g (1.67 mmol, 42.3%). Found: C, 41.36; H, 4.00; N, 3.42%. Calcd for $C_{28}H_{32}BCl_2F_4IrN_2P_2$ : C, 41.55; H, 3.96; N, 3.46%. $^{13}$C NMR ($CD_3CN$) $\delta$=31.08 (filled-in doublet; $P\text{–}\underline{C}H_2\text{–}$), 42.76 (s; $N\text{–}\underline{C}H_2\text{–}$), 128.43 (dd; $P\text{–}\underline{C}_1$), 128.56 (t; *m*-$\underline{C}$), 131.76 (s; *p*-$\underline{C}$), 133.97 (t; *o*-$\underline{C}$). $^{31}$P NMR ($CD_3CN$) $\delta$=−3.60 (s).

Crystals of **3** for X-ray analysis were grown from a solution in a mixture of acetonitrile and methanol (1 : 1).

**$\Delta$(*lel*$_3$)- and $\Lambda$(*ob*$_3$)-$[Ir(R,R\text{-}chxn)_3](NO_3)_3\cdot 3H_2O$ (4 and 5).** Preparation, separation, and characterization of diastereomeric $[Ir(chxn)_3]^{3+}$ were reported previously.[9)] Crystals suitable for X-ray analyses of both complexes were grown from aqueous solutions.

**Measurements.** Absorption spectra were measured at 24 °C on a Hitachi U-3410 spectrometer. $^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded at 23 °C on a Hitachi R-90HS (at 90.02, 22.66, and 36.46 MHz, respectively) or a JEOL GX400 (at 399.8, 100.5, and 161.9 MHz, respectively) spectrometer. Tetramethylsilane (TMS) or sodium [1,2-$^2$H$_4$]-trimethylsilylpropionic acid (TSP) was used as an internal reference for $^1$H and $^{13}$C NMR spectra, and 85% $H_3PO_4$ as an external reference for $^{31}$P NMR spectra.

**Crystal Structure Determination.** Crystal data and experimental conditions are listed in Table 1. The X-ray intensities were measured at 23 °C with graphite monochromatized Mo $K\alpha$ radiation ($\lambda$=0.71073 Å) on an automated Rigaku four-circle diffractometer AFC-5 at Keio University. The $\theta$–$2\theta$ scan technique was employed. The lattice constants were determined from $2\theta$ values in the range from 20 to 30°. Absorption correction was made by the Gauss numerical integration method.[10)] The structures of **2** and **3** were solved by the heavy atom method using the SHELXS-86 program.[11)] Non-hydrogen atoms were located in Fourier syntheses and were refined anisotropically. All the H atoms were included in the structure factor calculations except for those in the disordered chelate rings, and those for the crystal solvents. Crystals of **4** and **5** are isostructural with the

Table 1. Crystal Data, Experimental Conditions, and Refinement Details

| | **2** | **3** | **4** | **5** |
|---|---|---|---|---|
| Isomer | *fac* | *trans(Cl,Cl),cis(P,P)* | $\Delta(lel_3)$ | $\Lambda(ob_3)$ |
| Chemical formula | $[Ir(C_4H_{12}NP)_3]Cl_3\cdot 5H_2O$ | $[IrCl_2(C_{14}H_{16}NP)_2]BF_4$ | $[Ir(C_6H_{14}N_2)_3](NO_3)_3\cdot 3H_2O$ | $[Ir(C_6H_{14}N_2)_3](NO_3)_3\cdot 3H_2O$ |
| Formula weight | 703.7 | 808.5 | 774.9 | 774.9 |
| Crystal system | Triclinic | Triclinic | Hexagonal | Hexagonal |
| Space group and $Z$ | $P\bar{1}$, 2 | $P\bar{1}$, 2 | $P6_3$, 2 | $P6_3$, 2 |
| Lattice constants $a$/Å | 11.718(2) | 11.465(1) | 13.005(1) | 13.359(1) |
| $b$/Å | 13.199(1) | 13.694(1) | | |
| $c$/Å | 9.482(1) | 10.049(1) | 10.221(2) | 9.848(2) |
| $\alpha$/deg. | 91.44(1) | 94.764(6) | | |
| $\beta$/deg. | 105.86(1) | 92.197(8) | | |
| $\gamma$/deg. | 90.53(1) | 102.807(8) | | |
| $V$/Å$^3$ | 1410.0(2) | 1530.5(2) | 1497.1(3) | 1522.0(3) |
| $D_m$ and $D_x$/Mg m$^{-3}$ | —, 1.66 | —, 1.75 | 1.71(2), 1.72 | 1.70(2), 1.69 |
| $\mu$(Mo $K\alpha$)/mm$^{-1}$ | 5.19 | 4.67 | 4.51 | 4.43 |
| Color of crystals | Colorless | Yellow | Colorless | Colorless |
| Size of specimen/mm$^3$ | $0.3\times0.3\times0.4$ | $0.15\times0.25\times0.55$ | Diameter 0.33 | Diameter 0.47 |
| Laue group | $\bar{1}$ | $\bar{1}$ | $6/m$ | $6/m$ |
| $2\theta_{max}$/deg. | 55 | 55 | 55 | 55 |
| Range of $h,k$, and $l$ | $-15\leq h\leq 15$ | $-14\leq h\leq 14$ | $-16\leq h\leq 16$ | $-17\leq h\leq 17$ |
| | $0\leq k\leq 17$ | $-17\leq k\leq 17$ | $0\leq k\leq 16$ | $0\leq k\leq 17$ |
| | $-12\leq l\leq 12$ | $-13\leq l\leq 0$ | $0\leq l\leq 13$ | $0\leq l\leq 12$ |
| Variation of five standard reflections $\Sigma(\lvert F_o\rvert/\lvert F_o\rvert_{initial})/5$ | 0.990—1.002 | 0.931—1.003 | 1.000—1.030 | 0.996—1.007 |
| Number of reflections measured | 6740 | 7426 | 3799 | 3888 |
| Number of reflections observed $[\lvert F_o\rvert>3\sigma(\lvert F_o\rvert)]$ | 5621 | 6319 | 3271 | 3428 |
| Transimisson factor | 0.15—0.33 | 0.21—0.56 | 0.34—0.36 | 0.23—0.25 |
| Number of unique reflections, $R_{int}$ | 5410 (0.020) | 5978 (0.012) | 1063 (0.023) | 1105 (0.014) |
| Number of parameters refined | 252 | 475 | 192 | 192 |
| $R$ | 0.039 | 0.035 | 0.020 | 0.015 |
| $wR$ | 0.049 | 0.041 | 0.022 | 0.020 |
| $S$ | 2.1 | 1.7 | 1.1 | 1.1 |
| $(\Delta/\sigma)_{max}$ for nonhydrogen atoms | 0.04 | 0.11 | 0.27 | 0.27 |
| $\Delta\rho$/e Å$^{-3}$ | −3.29, 3.33 | −2.35, 2.00 | −0.55, 0.49 | −0.75, 0.26 |

$Co^{III}$ and $Rh^{III}$ chxn complexes,[12—14] and the refinements were carried out straightforwardly. Complex neutral-atom scattering factors[15] were used. The calculations were carried out at Keio University using the computation program system UNICS-III[16] on a FACOM M780/10 computer or using the CRYSTAN-GM software[17] on a SUN-SPARC2 workstation. The atomic parameters are listed in Table 2, the selected bond lengths and angles in Table 3, and hydrogen bond distances in Table 4.[18]

Some experimental details are given below.

**2:** A crystal was sealed in a capillary tube with mother liquor to prevent efflorescence. There exist two possible positions of the C(12) atom, A and B, indicating the conformational disorder of the five-membered chelate ring. H atoms bonded to the C(11) and C(12) atoms were not introduced. The counter $Cl^-$ ion occupies two possible positions with 50% probability each. Crystal solvents were all assigned to water molecules based on the interatomic distances.

**3:** There are two possible positions for the C(4) atom, indicating the conformational disorder of the edpp chelate ring.

## Results and Discussion

**Preparation and Characterization of the Iridium(III) Complexes. $[IrCl_2(edmp)_2]^+$:** In our previous papers[1,3] it was reported that *fac*-$[M(edmp)_3]^{3+}$ (M=$Co^{III}$ and $Rh^{III}$) was prepared by a reaction of $[CoCl_2(en)_2]^+$ or $RhCl_3\cdot 3H_2O$ with an excess of edmp in a fairly good yield. However, a similar reaction using an excess of edmp and $K_3[IrCl_6]$ or $IrCl_3\cdot 3H_2O$ in water did not give the tris(edmp)iridium(III) complex. Reaction between $K_3[IrCl_6]$ and an excess of edmp in boiling water for 40 h gave a greenish yellow solution whose $^{31}$P NMR spectrum showed a number of peaks, indicating the presence of many kinds of species in the reaction mixture. In the reaction with $(NH_4)_2[IrCl_6]$, a similar result was obtained, except for the fact that just after the addition of the ligand a color change occurred by reduction of $Ir^{IV}$ to $Ir^{III}$.

These reaction mixtures were, after removal of KCl (or $NH_4Cl$), applied on a cation-exchange (SP-Toyopearl or SP-Sephadex) column. By monitoring the absorption of UV-light (340 nm) of the eluate, more than

Table 2. Fractional Coordinates and Equivalent Isotropic Temperature Factors

| Atom | $x$ | $y$ | $z$ | $B_{eq}/Å^2$ [a)] | PP[b)] |
|---|---|---|---|---|---|
| **2** | | | | | |
| Ir | 0.21380(2) | 0.21128(2) | 0.23763(3) | 1.8 | |
| Cl(1) | −0.0762(2) | 0.6285(2) | 0.2280(2) | 4.5 | |
| Cl(2) | −0.1151(2) | −0.0329(2) | 0.1476(2) | 3.9 | |
| Cl(3) | 0.4816(4) | 0.9469(5) | 0.1659(8) | 6.8 | 0.5 |
| Cl(4) | 0.3684(6) | −0.2449(5) | 0.1724(6) | 6.9 | 0.5 |
| P(1) | 0.1364(2) | 0.3684(1) | 0.2537(2) | 2.8 | |
| P(2) | 0.1905(2) | 0.1552(1) | 0.4546(2) | 2.6 | |
| P(3) | 0.4095(2) | 0.2570(2) | 0.3281(2) | 2.8 | |
| N(1) | 0.0358(5) | 0.1739(5) | 0.1098(6) | 2.7 | |
| N(2) | 0.2530(5) | 0.0537(4) | 0.2047(6) | 2.7 | |
| N(3) | 0.2472(5) | 0.2390(4) | 0.0266(6) | 2.4 | |
| C(1) | 0.1789(8) | 0.4696(6) | 0.1533(9) | 4.0 | |
| C(2) | 0.141(1) | 0.4294(7) | 0.427(1) | 6.0 | |
| C(3) | −0.0199(8) | 0.3447(7) | 0.169(1) | 5.4 | |
| C(4) | −0.0396(8) | 0.2614(8) | 0.061(1) | 5.4 | |
| C(5) | 0.2753(8) | 0.2111(7) | 0.6292(8) | 3.8 | |
| C(6) | 0.0412(7) | 0.1467(7) | 0.4737(9) | 3.8 | |
| C(7) | 0.2428(8) | 0.0252(6) | 0.4556(9) | 3.9 | |
| C(8) | 0.2144(8) | −0.0174(6) | 0.3017(9) | 3.9 | |
| C(9) | 0.5112(7) | 0.1658(7) | 0.425(1) | 4.2 | |
| C(10) | 0.453(1) | 0.3717(8) | 0.443(1) | 6.2 | |
| C(11) | 0.4508(9) | 0.281(1) | 0.162(1) | 7.4 | |
| C(12A) | 0.377(2) | 0.232(1) | 0.037(2) | 3.0 | 0.5 |
| C(12B) | 0.361(2) | 0.292(2) | 0.030(2) | 3.9 | 0.5 |
| O(1) | 0.8116(8) | 0.2777(7) | 0.647(1) | 8.3 | |
| O(2) | −0.2411(8) | 0.3085(8) | 0.353(1) | 8.5 | |
| O(3) | 0.534(1) | 0.4444(8) | 0.862(2) | 13.2 | |
| O(4) | 0.697(1) | 0.4922(9) | 0.215(2) | 11.6 | |
| O(5) | 0.292(1) | 0.856(1) | 0.832(1) | 15.4 | |
| **3** | | | | | |
| Ir | 0.25279(2) | 0.32138(1) | 0.18143(2) | 2.6 | |
| Cl(1) | 0.4165(1) | 0.4527(1) | 0.2651(2) | 4.5 | |
| Cl(2) | 0.0665(1) | 0.2181(1) | 0.1014(1) | 3.8 | |
| P(1) | 0.3541(1) | 0.2671(1) | 0.0071(1) | 2.5 | |
| P(2) | 0.2737(1) | 0.2201(1) | 0.3488(1) | 2.9 | |
| N(1) | 0.2166(4) | 0.4251(3) | 0.0443(5) | 3.7 | |
| N(2) | 0.1500(5) | 0.3864(4) | 0.3230(5) | 5.1 | |
| C(1) | 0.3219(5) | 0.3463(4) | −0.1237(5) | 3.6 | |
| C(2) | 0.3057(5) | 0.4454(4) | −0.0577(6) | 3.8 | |
| C(3) | 0.1973(6) | 0.2752(4) | 0.4863(6) | 4.4 | |
| C(4A) | 0.0896(9) | 0.3085(7) | 0.4203(9) | 3.8 | 0.6 |
| C(4B) | 0.218(2) | 0.391(1) | 0.470(2) | 5.6 | 0.4 |
| C(5) | 0.3048(4) | 0.1385(3) | −0.0739(5) | 2.8 | |
| C(6) | 0.1936(5) | 0.1076(4) | −0.1424(5) | 3.1 | |
| C(7) | 0.1526(5) | 0.0083(4) | −0.1967(5) | 3.8 | |
| C(8) | 0.2219(6) | −0.0586(4) | −0.1820(7) | 4.7 | |
| C(9) | 0.3309(6) | −0.0302(4) | −0.1149(8) | 5.7 | |
| C(10) | 0.3731(5) | 0.0687(4) | −0.0625(7) | 4.6 | |
| C(11) | 0.5158(4) | 0.2844(3) | 0.0215(5) | 3.0 | |
| C(12) | 0.5777(5) | 0.2787(5) | −0.0962(6) | 4.2 | |
| C(13) | 0.7003(6) | 0.2889(5) | −0.0886(7) | 5.1 | |
| C(14) | 0.7626(5) | 0.3043(4) | 0.0348(7) | 4.7 | |
| C(15) | 0.7032(5) | 0.3078(4) | 0.1493(6) | 4.0 | |
| C(16) | 0.5804(5) | 0.2984(4) | 0.1434(5) | 3.4 | |
| C(17) | 0.4222(5) | 0.2197(4) | 0.4212(5) | 3.2 | |
| C(18) | 0.4693(5) | 0.1356(4) | 0.3997(6) | 4.0 | |
| C(19) | 0.5842(6) | 0.1373(5) | 0.4493(7) | 5.1 | |
| C(20) | 0.6515(6) | 0.2214(5) | 0.5208(7) | 5.5 | |
| C(21) | 0.6044(6) | 0.3039(5) | 0.5454(6) | 5.1 | |

Table 2. (Continued)

| Atom | $x$ | $y$ | $z$ | $B_{eq}/\text{Å}^2$ a) | PP b) |
|---|---|---|---|---|---|
| C(22) | 0.4895(6) | 0.3044(4) | 0.4961(5) | 4.0 | |
| C(23) | 0.2016(5) | 0.0872(3) | 0.3314(5) | 3.1 | |
| C(24) | 0.1812(6) | 0.0317(4) | 0.2060(5) | 3.9 | |
| C(25) | 0.1329(6) | −0.0713(4) | 0.1955(6) | 4.5 | |
| C(26) | 0.1045(5) | −0.1190(4) | 0.3096(7) | 4.4 | |
| C(27) | 0.1224(6) | −0.0655(5) | 0.4303(6) | 4.8 | |
| C(28) | 0.1714(6) | 0.0371(4) | 0.4428(6) | 4.2 | |
| B | 0.0007(7) | 0.5723(6) | 0.2540(8) | 4.9 | |
| F(1) | 0.1007(5) | 0.6030(4) | 0.3224(7) | 13.4 | |
| F(2) | −0.0466(5) | 0.6411(3) | 0.2121(7) | 11.4 | |
| F(3) | −0.0740(6) | 0.5031(5) | 0.3106(7) | 13.7 | |
| F(4) | 0.0187(8) | 0.5162(7) | 0.1444(8) | 17.2 | |
| **4** | | | | | |
| Ir | 1/3 | 2/3 | 0 | 2.0 | |
| N(1) | 0.2166(4) | 0.5208(4) | −0.1137(5) | 2.6 | |
| N(2) | 0.3390(4) | 0.5375(4) | 0.1149(5) | 2.6 | |
| C(1) | 0.2353(5) | 0.4191(5) | −0.0753(6) | 3.1 | |
| C(2) | 0.2422(4) | 0.4188(4) | 0.0728(6) | 2.5 | |
| C(3) | 0.2607(7) | 0.3187(6) | 0.1207(8) | 4.7 | |
| C(4) | 0.1600(7) | 0.1983(5) | 0.0650(8) | 5.6 | |
| C(5) | 0.1640(7) | 0.2029(7) | −0.0874(9) | 5.6 | |
| C(6) | 0.1407(6) | 0.3015(6) | −0.1293(8) | 4.0 | |
| N(3) | 0.6057(5) | 0.5175(5) | 0.0971(6) | 4.2 | |
| O(1) | 0.5555(6) | 0.5265(7) | 0.1950(6) | 7.9 | |
| O(2) | 0.5737(5) | 0.5315(5) | −0.0127(7) | 5.8 | |
| O(3) | 0.6848(6) | 0.4920(7) | 0.1103(7) | 7.8 | |
| O(W) | 0.7997(6) | 0.5061(6) | −0.1399(6) | 6.7 | |
| **5** | | | | | |
| Ir | 1/3 | 2/3 | 0 | 1.7 | |
| N(1) | 0.2165(3) | 0.5200(3) | 0.1108(4) | 2.4 | |
| N(2) | 0.3506(3) | 0.5441(3) | −0.1127(4) | 2.3 | |
| C(1) | 0.1877(4) | 0.4145(4) | 0.0284(5) | 2.8 | |
| C(2) | 0.3000(4) | 0.4337(3) | −0.0343(5) | 2.5 | |
| C(3) | 0.2805(5) | 0.3313(4) | −0.1223(7) | 3.8 | |
| C(4) | 0.2242(6) | 0.2201(4) | −0.0380(8) | 5.2 | |
| C(5) | 0.1099(6) | 0.2012(5) | 0.0162(17) | 7.1 | |
| C(6) | 0.1283(5) | 0.3030(5) | 0.1107(8) | 4.2 | |
| N(3) | 0.4821(4) | 0.0955(4) | −0.1047(5) | 3.5 | |
| O(1) | 0.4730(4) | 0.0529(3) | 0.0139(6) | 4.4 | |
| O(2) | 0.5065(5) | 0.1979(4) | −0.1170(6) | 6.3 | |
| O(3) | 0.4693(5) | 0.0374(4) | −0.2086(4) | 5.5 | |
| O(W) | 0.4941(6) | 0.2906(5) | 0.1457(5) | 6.0 | |

a) $B_{eq}=(8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$. b) Population parameter.

10 bands were detected. From the main band, which was the second one eluted with a 0.04 mol dm$^{-3}$ aqueous NaCl solution, pale yellow crystals were obtained as the PF$_6$ salt, although the yield was rather poor (5—9%).

The structure of the complex was determined by X-ray analysis to be *trans(Cl, Cl), trans(P, P)*-[IrCl$_2$(edmp)$_2$]PF$_6$ (**1**). The crystal structure was previously communicated.[19] The geometrical structure was also assigned on the basis of $^1$H and $^{13}$C NMR spectra. The complex in dmso-$d_6$ shows one kind of resonance for each of the P–$\underline{CH_3}$, P–$\underline{CH_2}$–, N–$\underline{CH_2}$–, and –N$\underline{H_2}$ groups, suggesting the *trans(Cl, Cl)*-structure. Further, any resonance for the P-C$\underline{H_3}$ in $^1$H NMR and the P–$\underline{C}$H$_3$ and P–$\underline{C}$H$_2$– groups in $^{13}$C NMR spectra show a triplet peak, owing to the virtual coupling of $^2J_{P,P}$ for two mutually trans P atoms in the complex.[20]

In our previous studies of Co$^{III}$ and Rh$^{III}$ complexes, only the *trans(Cl, Cl), cis(P, P)*-isomer was obtained among five possible geometrical isomers for [MCl$_2$(edmp)$_2$]$^+$ (Fig. 1), and no other isomers were indicated in column chromatography.[1,5] For the Ir$^{III}$ complex, however, many unknown complexes together with a small amount of other isomers were always yielded in preparations with various ratios of the ligand to metal. There was a minor band first eluted with a 0.04 mol dm$^{-3}$ aqueous NaCl solution. In the $^{31}$P NMR spectrum of this band only one singlet resonance at $\delta=-0.03$ was observed, and in the $^1$H NMR spectrum one kind of doublet peak appeared in the

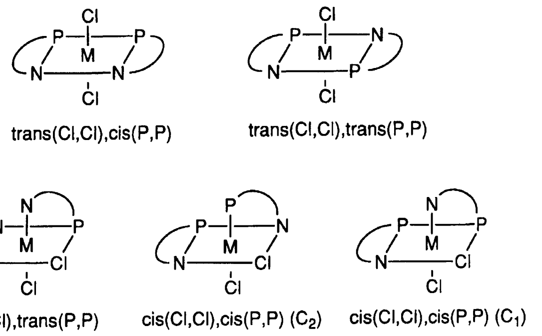
Table 3. Selected Bond Lengths ($l$/Å) and Bond Angles ($\phi$/deg.)

| | | | |
|---|---|---|---|
| **2** | | | |
| Ir–P(1) | 2.289(2) | Ir–N(1) | 2.152(5) |
| Ir–P(2) | 2.288(2) | Ir–N(2) | 2.167(6) |
| Ir–P(3) | 2.288(2) | Ir–N(3) | 2.181(6) |
| P(1)–Ir–P(2) | 96.12(7) | P(1)–Ir–P(3) | 97.32(7) |
| P(2)–Ir–P(3) | 95.83(7) | P(1)–Ir–N(1) | 83.3(2) |
| P(1)–Ir–N(2) | 169.3(2) | P(1)–Ir–N(3) | 93.6(2) |
| P(2)–Ir–N(1) | 95.7(2) | P(2)–Ir–N(2) | 83.2(2) |
| P(2)–Ir–N(3) | 170.2(2) | P(3)–Ir–N(1) | 168.3(2) |
| P(3)–Ir–N(2) | 93.4(2) | P(3)–Ir–N(3) | 83.3(2) |
| N(1)–Ir–N(2) | 86.1(2) | N(1)–Ir–N(3) | 85.0(2) |
| N(2)–Ir–N(3) | 87.2(2) | | |
| **3** | | | |
| Ir–Cl(1) | 2.365(1) | Ir–Cl(2) | 2.356(1) |
| Ir–P(1) | 2.301(1) | Ir–P(2) | 2.305(1) |
| Ir–N(1) | 2.152(5) | Ir–N(2) | 2.142(6) |
| Cl(1)–Ir–Cl(2) | 167.64(4) | | |
| Cl(1)–Ir–P(1) | 94.02(4) | Cl(1)–Ir–P(2) | 94.54(4) |
| Cl(1)–Ir–N(1) | 85.4(1) | Cl(1)–Ir–N(2) | 86.1(2) |
| Cl(2)–Ir–P(1) | 93.93(4) | Cl(2)–Ir–P(2) | 92.48(4) |
| Cl(2)–Ir–N(1) | 86.2(1) | Cl(2)–Ir–N(2) | 84.6(2) |
| P(1)–Ir–P(2) | 105.28(4) | P(1)–Ir–N(1) | 83.1(1) |
| P(1)–Ir–N(2) | 171.3(2) | P(2)–Ir–N(1) | 171.6(1) |
| P(2)–Ir–N(2) | 83.4(2) | N(1)–Ir–N(2) | 88.3(2) |
| **4** | | | |
| Ir–N(1) | 2.092(4) | Ir–N(2) | 2.081(6) |
| N(1)–Ir–N(2) | 83.3(2) | | |
| **5** | | | |
| Ir–N(1) | 2.100(3) | Ir–N(2) | 2.085(5) |
| N(1)–Ir–N(2) | 82.3(2) | | |

Table 4. Hydrogen Bond Lengths ($l$/Å)

| | |
|---|---|
| **2** | |
| N(2)$\cdots$Cl(2$^{i}$) | 3.293(6) |
| N(3)$\cdots$Cl(1$^{ii}$) | 3.246(6) |
| N(3)$\cdots$Cl(2$^{i}$) | 3.290(6) |
| **3** | |
| N(1)$\cdots$F(4) | 2.99(1) |
| N(1)$\cdots$F(2$^{iii}$) | 3.114(8) |
| N(2)$\cdots$F(1) | 3.140(8) |
| **4** | |
| N(1)$\cdots$O(2$^{iv}$) | 3.125(10) |
| N(1)$\cdots$O(3$^{v}$) | 3.137(9) |
| N(2)$\cdots$O(1) | 3.004(11) |
| N(2)$\cdots$O(w$^{vi}$) | 2.972(8) |
| **5** | |
| N(1)$\cdots$O(2$^{iv}$) | 2.992(8) |
| N(1)$\cdots$O(3$^{v}$) | 2.942(8) |
| N(2)$\cdots$O(1) | 3.144(10) |
| N(2)$\cdots$O(w$^{vi}$) | 3.203(6) |

Symmetry codes: (i) $-x$, $-y$, $-z$; (ii) $-x$, $1-y$, $-z$; (iii) $-x$, $1-y$, $z$; (iv) $-x+y$, $1-x$, $z$, (v) $1-x$, $1-y$, $z-1/2$, (iv) $1-x$, $1-y$, $z+1/2$.


trans(Cl,Cl),cis(P,P) trans(Cl,Cl),trans(P,P)

cis(Cl,Cl),trans(P,P) cis(Cl,Cl),cis(P,P) ($C_2$) cis(Cl,Cl),cis(P,P) ($C_1$)

Fig. 1. The five possible geometrical isomers of $[MCl_2(N\text{-}P)_2]^+$ (M=Co$^{III}$, Rh$^{III}$, or Ir$^{III}$; N–P= edmp or edpp).

$P-C\underline{H}_3$ region ($\delta=2.09$ (d, $J=14.9$ Hz) in $D_2O$). Thus, the band might contain the *trans(Cl, Cl), cis-(P, P)*-isomer,[1] but the complex could not be isolated because of the very poor yield. The *trans(P,P)*-structure would be sterically favored, but electronically disfavored owing to the strong trans influence of the phosphino donor group.[21] All of the *trans-(Cl, Cl)*-isomer of $[MCl_2(\text{edmp or edpp})_2]^+$ (M=Co$^{III}$ and Rh$^{III}$) so far obtained are the *cis(P,P)*-isomer, indicating the preference of the electronic factor. The reason why the *trans(Cl, Cl),trans(P,P)*-isomer was obtained in this iridium(III) study is not obvious.

***fac*-[Ir(edmp)$_3$]$^{3+}$.** The tris(edmp)iridium(III) complex, $[Ir(edmp)_3]Cl_3$, was obtained as a white precipitate by oxidizing a dichloromethane solution containing $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ and an excess of edmp with chlorine in a yield of 15%. The complex in $D_2O$ shows one singlet peak in the $^{31}$P NMR spectrum, and can be recrystallized from aqueous–ethanol (1 : 5). From the filtrate of the reaction mixture, a yellow product was obtained. However, the $^{31}$P NMR spectrum of the product shows a number of resonances, none of which corresponds to that of $[Ir(emdp)_3]^{3+}$. The species contained in this product are unknown.

The geometrical configuration of $[Ir(edmp)_3]^{3+}$ was assigned on the basis of $^{1}$H and $^{13}$C NMR spectra. The $^{13}$C NMR spectrum in $D_2O$ exhibits two, one, and one kinds of resonances for the P–$\underline{C}H_3$, P–$\underline{C}H_2$–, and N–$\underline{C}H_2$– groups, respectively. In the $^{1}$H NMR spectrum in $D_2O$, the P–$C\underline{H}_3$ and P–$C\underline{H}_2$– groups show two doublet peaks and two multiplet peaks, respectively. Thus the complex can be assigned to the *fac*($\mathbf{C}_3$) configuration. The assignment was confirmed by X-ray analysis.

Figure 2(a) shows a perspective view of the complex cation in *fac*-$[Ir(edmp)_3]Cl_3\cdot 5H_2O$ (**2**). The complex ion has approximate $\mathbf{C}_3$ symmetry, and can be designated as the *lel*$_3$-isomer, since the C–C bonds in the chelate rings are nearly parallel to the pseudo-$C_3$ axis of the complex ion. The structure is similar to *fac*-$[Co(edmp)_3]^{3+}$3) and *fac*-$[Rh(edmp)_3]^{3+}$.1) The Ir–P bond lengths (av. 2.289(2) Å) in **2** are shorter than those in **1** (av. 2.325(4) Å)19) and in *trans*-$[IrCl(dmpe)_2(C(O)OCH_3)]FSO_3$ (av. 2.343(2) Å),23) both of which have the two –$PMe_2$ groups in the trans positions. On the other hand, the Ir–N bond lengths in **2** (av. 2.167(6) Å) are considerably longer than those in **1** (av. 2.097(10) Å). The variations in bond lengths are attributed to the trans influence of the –$PMe_2$ group. Similar discussions have been made for *fac*-$[Co(edmp)_3]^{3+}$ and *fac*-$[Rh(edmp)_3]^{3+}$, where as a standard the M(Co$^{III}$ or Rh$^{III}$)–N bond length in $[M(en)_3]^{3+}$ or $[M(chxn)_3]^{3+}$ was used.1) To obtain the standard Ir$^{III}$–N bond length crystals of $\Delta$(*lel*$_3$)-[Ir(*R*,*R*-chxn)$_3$]$(NO_3)_3\cdot 3H_2O$ (**4**) and $\Lambda$(*ob*$_3$)-[Ir(*R*,*R*-chxn)$_3$]$(NO_3)_3\cdot 3H_2O$ (**5**) were analyzed by X-ray diffraction. The perspective views are depicted in Fig. 2(b) and (c). The Table 5, the M–N bond lengths of the related complexes are collected. The strength of the trans influence is measured with the value of $\Delta$(M–N) = M–N (in a certain complex) − M–N (in $[M(chxn)_3]^{3+}$), and the $\Delta$(M–N) values are plotted against the averaged M–N length of the *lel*$_3$- and *ob*$_3$-$[M(chxn)_3]^{3+}$ complexes in Fig. 3. The $\Delta$(M–N) values for *fac*-$[M(edmp)_3]^{3+}$ are Co$^{III}$ (0.064(13) Å) $<$ Ir$^{III}$ (0.077(6) Å) $<$ Rh$^{III}$ (0.098(12) Å), therefore, the strength of trans influence of the –$PMe_2$ group in edmp is Co$^{III}$ < Ir$^{III}$ < Rh$^{III}$. The same conclusion is obtained when the M–N bond length in $[M(en)_3]^{3+}$ is used as a standard. The order of the metal ions for the trans influence of edmp is apparently different from that for the spectrochemical series, Co$^{III}$ < Rh$^{III}$ < Ir$^{III}$ (vide infra).6) The reason why the trans influence of the –$PMe_2$ group on Ir$^{III}$ is weaker than that on Rh$^{III}$ remains unknown. Further studies including theoretical ones will be needed.

***trans(Cl,Cl),cis(P,P)*-$[IrCl_2(edpp)_2]^+$.** By a procedure similar to the one for *fac*-$[Ir(edmp)_3]^{3+}$, preparation of an iridium(III) complex containing edpp was attempted by oxidation of the corresponding iridium(I) complex with chlorine. Addition of an excess of edpp to an ethanol suspension of $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ gave a yellow solution, from which a yellow precipitate was obtained by evaporation of the solvent and washing the residue with diethyl ether. The precipitate was rather stable in nitrogen, and assumed to be $[Ir(edpp)_2]Cl$ (the $^{31}$P NMR spectrum shows two resonances which could be assigned to the *cis*- and *trans*-isomers). The product was dissolved in dichloromethane containing a small amount of edpp, and the solution was then oxidized by chlorine. Pale yellow crystals were obtained in a yield of 50% by concentration of the mixture followed by addition of $LiBF_4$. The $^{31}$P NMR spectrum of the product in $CD_3CN$ shows that it is a single isomer. In the oxidation the addition of an excess edpp was necessary, otherwise the product became a mixture of several species and the yield of the desired complex was extremely poor. Elemental analysis of the product indicates that it is not $[Ir(edpp)_3](BF_4)_3$, but $[IrCl_2(edpp)_2]BF_4$, although a preparative procedure similar to the one for $[Ir(edmp)_3]^{3+}$ was performed. Because of the phenyl groups on the P atom of edpp, $[Ir(edpp)_3]^{3+}$ is anticipated to have a large steric hinderance for both *fac*- and *mer*-isomers. This may be the reason why $[Ir(edpp)_3]^{3+}$ is not formed in the presence of an excess of edpp. For the preparation of $[IrCl_2(edpp)_2]^+$, the ligand substitution reaction used for the corresponding Rh$^{III}$ complex2) was also attempted. An ethanol solution containing $IrCl_3\cdot 4H_2O$ and a large excess of edpp, or an aqueous-ethanol solution containing $K_3[IrCl_6]$ and edpp, was refluxed for more than 2 d. The $^{31}$P NMR spectrum indicated that the reaction mixture contained a number of species. The product was insoluble in water, and cation-exchange column chromatography could not be carried out for the separation of the complexes.

The $^{13}$C NMR spectrum of $[IrCl_2(edpp)_2]BF_4$ in $CD_3CN$ shows a filled-in doublet and a singlet peak for the P–$\underline{C}H_2$– and N–$\underline{C}H_2$–, respectively, and the *o*-$\underline{C}$, *m*-$\underline{C}$, *p*-$\underline{C}$, and the P–$\underline{C}_1$ of the phenyl group exhibit one kind of resonance. Thus, the geometry of the complex can be assigned to trans(Cl,Cl),cis(P,P). The structure was confirmed by X-ray analysis.

A perspective view of the complex cation in *trans(Cl,Cl),cis(P,P)*-$[IrCl_2(edpp)_2]BF_4$ (**3**) is presented in Fig. 2(d). The structure resembles those of *trans(Cl,Cl),cis(P,P)*-$[MCl_2(edpp)_2]^+$ (M = Co$^{III}$ and Rh$^{III}$),2,4) and has approximate $\mathbf{C}_2$ symmetry. The Ir–P bond lengths (av. 2.303(2) Å) are rather shorter than those in *trans*-$[IrCl_2(dppe)_2]Cl$ (av. 2.395(7) Å, dppe = 1,2-bis(diphenylphosphino)ethane),28) and the Ir–N bond lengths (av.

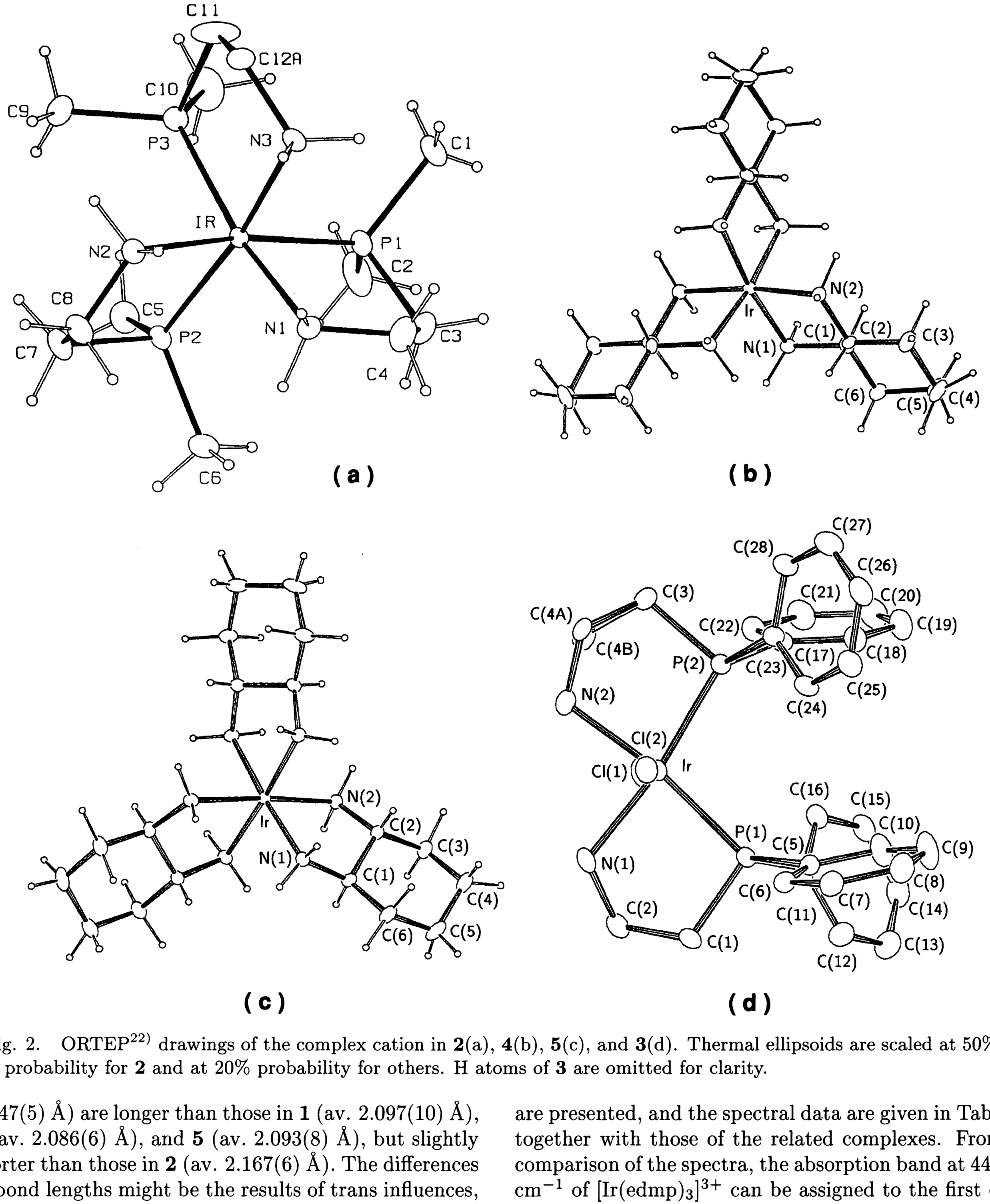


Fig. 2. ORTEP[22] drawings of the complex cation in **2**(a), **4**(b), **5**(c), and **3**(d). Thermal ellipsoids are scaled at 50% probability for **2** and at 20% probability for others. H atoms of **3** are omitted for clarity.

2.147(5) Å) are longer than those in **1** (av. 2.097(10) Å), **4** (av. 2.086(6) Å), and **5** (av. 2.093(8) Å), but slightly shorter than those in **2** (av. 2.167(6) Å). The differences in bond lengths might be the results of trans influences, whose order is $-PMe_2 > -PPh_2 \gg -NH_2$. In contrast to the complexes of edmp, the elongation of the M–N bond ($\Delta$(M–N)) due to the trans influence of the $-PPh_2$ group in edpp is nearly the same, 0.047—0.057 Å, for $Co^{III}$, $Rh^{III}$, and $Ir^{III}$ (see Table 5 and Fig. 3). The trans influence of the $-PPh_2$ group in edpp may not be so strong as to reveal the differences among these metal ions.

**Absorption Spectra.** In Fig. 4, the absorption spectra of *fac*-$[M(edmp)_3]^{3+}$ (M=$Co^{III}$, $Rh^{III}$, and $Ir^{III}$) are presented, and the spectral data are given in Table 6 together with those of the related complexes. From a comparison of the spectra, the absorption band at 44600 $cm^{-1}$ of $[Ir(edmp)_3]^{3+}$ can be assigned to the first d–d absorption band, $^1A_1 \rightarrow {}^1A_2$, $^1E$. The ratio of the wave number of this band to that of the cobalt(III) complex, $\sigma_{Ir}/\sigma_{Co}$, is 1.88. This value corresponds well to the spectrochemical parameter for iridium(III), $m_{Ir}=1.90$, given by Shimura.[6] The parameter for the rhodium(III) complex ($m_{Rh}=1.56$, obsd, $\sigma_{Rh}/\sigma_{Co}=1.57$) was previously discussed.[1] A shoulder appearing around 36100 $cm^{-1}$ in the iridium(III) complex can be assigned to the spin-forbidden d–d absorption band.

Figure 5 shows the absorption spectra of *trans(Cl,Cl)*,

Table 5. Averaged M–N Bond Lengths ($l$/Å) in Some $M^{III}$ Complexes (M=Co, Rh, and Ir)[a)]

| Complex (M= | $Co^{III}$ | $Rh^{III}$ | $Ir^{III}$) |
|---|---|---|---|
| *lel*$_3$-$[M(en)_3]^{3+}$ | 1.964(2)[24)] | 2.060(8)[25)] | |
| *lelob*$_2$-$[M(en)_3]^{3+}$ | 1.969(12)[26)] | 2.068(2)[27)] | 2.081(8)[27)] |
| *lel*$_3$-$[M(chxn)_3]^{3+}$ | 1.977(2)[12)] | 2.076(8)[13)] | 2.087(6)[b)] |
| *ob*$_3$-$[M(chxn)_3]^{3+}$ | 1.976(2)[12)] | 2.070(3)[14)] | 2.093(6)[b)] |
| *fac*-$[M(edmp)_3]^{3+}$ | 2.041(13)[3)] | 2.171(12)[1)] | 2.167(6)[b)] |
| *trans(Cl,Cl),cis(P,P)*-$[MCl_2(edpp)_2]^+$ | 2.024(8)[4)] | 2.125(4)[2)] | 2.147(6)[b)] |

a) Superscripts in the table show the reference numbers and b) denotes this work.

Table 6. Absorption Spectral Data[a)]

| Complex | $\sigma/10^3$ cm$^{-1}$ (log ($\varepsilon$/mol$^{-1}$ dm$^3$ cm$^{-1}$)) | | | | | |
|---|---|---|---|---|---|---|
| *fac*-$[Co(edmp)_3]Br_3{\cdot}3H_2O$ | | 23.7 (2.68) | | 30.2 (2.36) | 39.8 (4.42) | |
| *fac*-$[Rh(edmp)_3]Cl_3{\cdot}4H_2O$ | | 37.3 (3.27) | | | 47.4 (4.69) | |
| *fac*-$[Ir(edmp)_3]Cl_3{\cdot}5H_2O$ | 36.1 (2.0)$^{sh}$ | 44.6 (3.24) | | | | |
| *trans(Cl,Cl),cis(P,P)*-$[CoCl_2(edmp)_2]Cl$ | | 16.6 (2.14) | 23.8 (2.2)$^{sh}$ | | 29.7 (3.39) | 39.4 (4.31) |
| *trans(Cl,Cl),cis(P,P)*-$[RhCl_2(edmp)_2]PF_6$ | | 25.5 (2.34) | | | 37.7 (3.59) | 47.0 (4.72) |
| *trans(Cl,Cl),trans(P,P)*-$[IrCl_2(edmp)_2]PF_6$ | 25.0 (1.10)$^{sh}$ | 30.28 (2.00) | | | 40.17 (3.44) | 47.3 (4.27) |
| *trans(Cl,Cl),cis(P,P)*-$[CoCl_2(edpp)_2]Cl{\cdot}2H_2O$ | | 15.9 (2.03) | 21.5 (2.1)$^{sh}$ | 27.5 (3.7)$^{sh}$ | 31.9 (4.26) | 39.7 (4.16) |
| *trans(Cl,Cl),cis(P,P)*-$[RhCl_2(edpp)_2]Cl{\cdot}2EtOH$ | | 24.45 (2.22) | 29.0 (2.0)$^{sh}$ | 33.6 (3.8)$^{sh}$ | 39.1 (4.35) | |
| *trans(Cl,Cl),cis(P,P)*-$[IrCl_2(edpp)_2]BF_4$ | 25.21 (1.62) | 29.06 (2.26) | 33.6 (2.5)$^{sh}$ | (36.1 (3.39)$^{sh}$ | 37.3 (4.10)$^{sh}$) | |

a) Solvents; see captions of Figs. 4, 5, and 6.

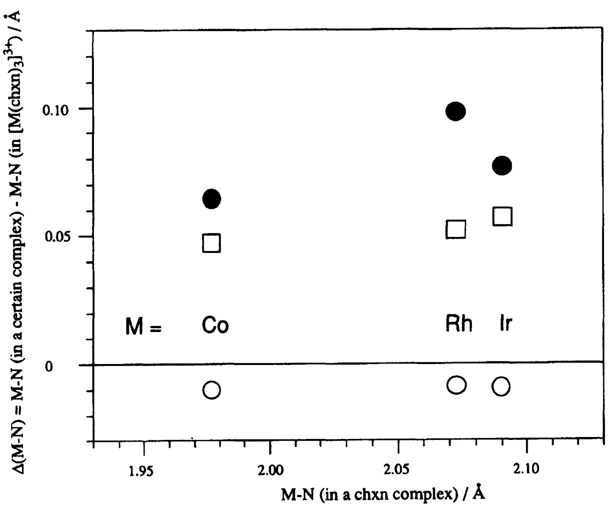


Fig. 3. Δ(M−N) versus a standard M–N bond length in $[M(chxn)_3]^{3+}$ listed in Table 5. ●=*fac*-$[M(edmp)_3]^{3+}$; □ = *trans(Cl,Cl),cis(P,P)*-$[MCl_2(edpp)_2]^+$; ○=*lel*$_3$- or *lelob*$_2$-$[M(en)_3]^{3+}$.

*cis(P,P)*-$[MCl_2(edpp)_2]^+$ (M=$Co^{III}$, $Rh^{III}$, and $Ir^{III}$). The spectral patterns are similar to one another, except for the fairly strong spin-forbidden d–d band around 25210 cm$^{-1}$ of the iridium(III) complex. The spectra are shifted to higher energy in the order $Co^{III}$<$Rh^{III}$<

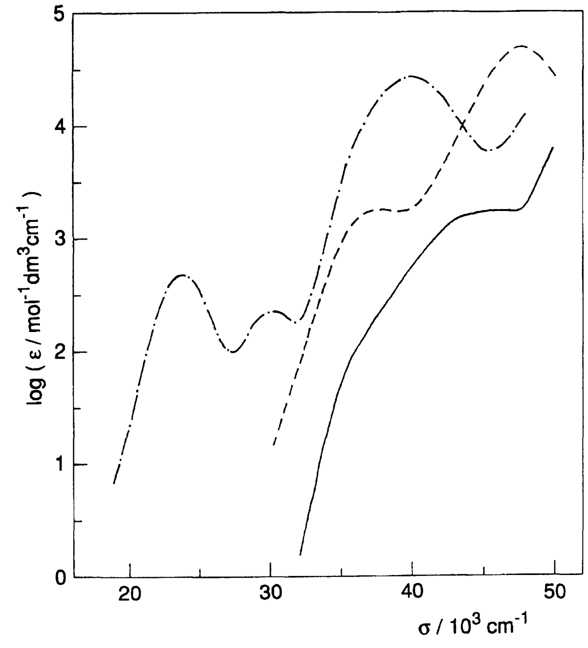


Fig. 4. Absorption spectra of *fac*-$[M(edmp)_3]^{3+}$ (M=$Co^{III}$ (–••–), $Rh^{III}$ (---), and $Ir^{III}$ (—)) in $H_2O$.

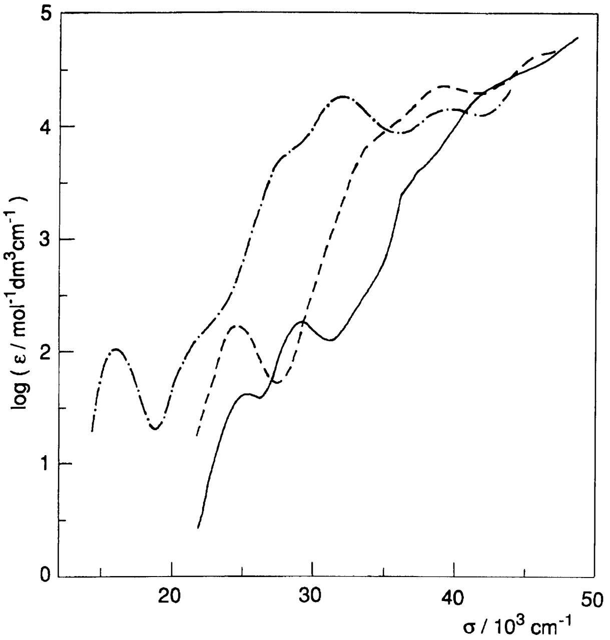


Fig. 5. Absorption spectra of *trans(Cl, Cl), cis(P, P)*-$[\text{MCl}_2(\text{edpp})_2]^+$ (M=$\text{Co}^{\text{III}}$ (-··-), $\text{Rh}^{\text{III}}$ (---), and $\text{Ir}^{\text{III}}$ (——)) in $\text{CH}_3\text{CN}$.

$\text{Ir}^{\text{III}}$. The $\text{I}_\text{a}$ component of the first d–d band is observed at 15900 $\text{cm}^{-1}$ for $\text{Co}^{\text{III}}$, 24450 $\text{cm}^{-1}$ for $\text{Rh}^{\text{III}}$, and 29060 $\text{cm}^{-1}$ for $\text{Ir}^{\text{III}}$. The ratios of the wave numbers of the bands, $\sigma_{\text{Rh}}/\sigma_{\text{Co}}$ and $\sigma_{\text{Ir}}/\sigma_{\text{Co}}$, are 1.54 and 1.83, respectively. Shimura reported[6] that for mixed halogeno complexes the empirical reduced parameter $\alpha$ should be introduced for the estimation of the wave number of the first d–d band. The $\alpha$ values given for the *trans(Cl, Cl)*-$[\text{MCl}_2(\text{L})_4]$-type complexes are;

$$\text{for L} = \text{N};\ \text{M} : \text{Co} = 0.96\ (\alpha_{\text{Co,N}}),$$
$$\text{Rh} = 0.94\ (\alpha_{\text{Rh,N}}),\ \text{Ir} = 0.92\ (\alpha_{\text{Ir,N}}),$$
$$\text{for L} = \text{P};\ \text{M} : \text{Co} = 0.90\ (\alpha_{\text{Co,P}}),$$
$$\text{Rh} = 0.88\ (\alpha_{\text{Rh,P}}),\ \text{Ir} = 0.84\ (\alpha_{\text{Ir,P}}).$$

For the complex having three different ligating atoms no $\alpha$ value is given. However, the value for the *trans(Cl, Cl), cis(P, P)*-$[\text{MCl}_2(\text{P})_2(\text{N})_2]$-type complex can be estimated by the average ($\alpha_{\text{M,N,P}}$) of $\alpha_{\text{M,N}}$ and $\alpha_{\text{M,P}}$, since the holohedrized symmetry[29] of this complex ($D_{4h}$) is the same as that of *trans*-$[\text{MCl}_2(\text{L})_4]$. The estimated averaged values are: $\alpha_{\text{Co,N,P}}=0.93$, $\alpha_{\text{Rh,N,P}}=0.91$, and $\alpha_{\text{Ir,N,P}}=0.88$. With these reduced parameters the ratios of the wave numbers of the first d–d bands are calculated as

$$m'_{\text{Rh}} = (\alpha_{\text{Rh,N,P}}/\alpha_{\text{Co,N,P}})m_{\text{Rh}} = 1.53 \text{ and}$$
$$m'_{\text{Ir}} = (\alpha_{\text{Ir,N,P}}/\alpha_{\text{Co,N,P}})m_{\text{Ir}} = 1.80.$$

These values agree with the observed ones within the deviation of ±2%.

In Fig. 6 are compared the absorption spectrum of *trans(Cl, Cl), trans(P, P)*-$[\text{IrCl}_2(\text{edmp})_2]\text{PF}_6$ with those of *trans(Cl, Cl), cis(P, P)*-isomers of the rhodium(III) and cobalt(III) complexes. Unlike the spectra in Figs. 4 and 5, the $\text{I}_\text{a}$ component of the $\text{Ir}^{\text{III}}$ complex (30280 $\text{cm}^{-1}$, $\log\varepsilon=2.00$) has appreciably less intensity than those of the $\text{Co}^{\text{III}}$ (16600 $\text{cm}^{-1}$, $\log\varepsilon=2.14$) and $\text{Rh}^{\text{III}}$ (25500 $\text{cm}^{-1}$, $\log\varepsilon=2.34$) complexes. The less intense d–d band of the iridium(III) complex might be the effect of the geometrical structure. The *trans(Cl, Cl), trans-(P, P)*-structure has a centrosymmetry, and the d–d transition is symmetrically forbidden, while it is allowed in the *trans(Cl, Cl), cis(P, P)*-structure with no center of symmetry.

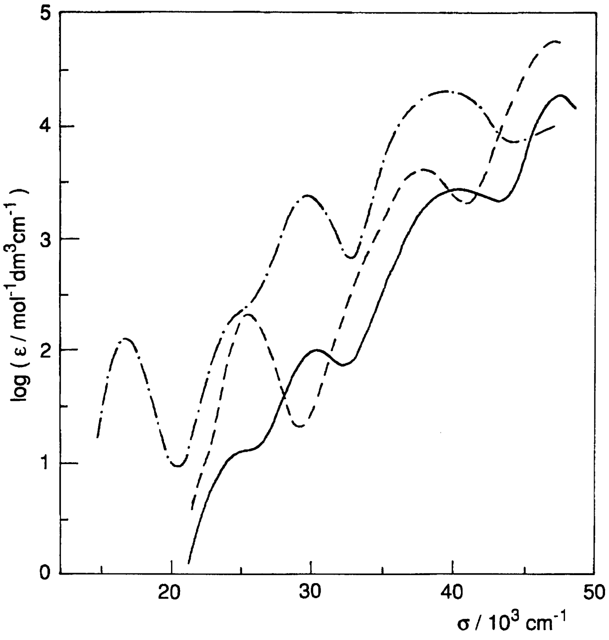


Fig. 6. Absorption spectra of *trans(Cl, Cl), trans(P, P)*-$[\text{IrCl}_2(\text{edmp})_2]^+$ in water (——), *trans(Cl, Cl), cis(P, P)*-$[\text{RhCl}_2(\text{edmp})_2]^+$ in methanol(---), and *trans(Cl, Cl), cis(P, P)*-$[\text{CoCl}_2(\text{edpp})_2]^+$ in methanol (-··-).

Acknowledgements are made to Ministry of Education, Science, and Culture for providing generous fellowship supports for M.R. and K.P.S. to work as exchange students at Nagoya University. We wish to thank Professor Hideo Yamatera (Daido Institute of Technology) for his kind supply of $\text{K}_3[\text{IrCl}_6]$.

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