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Cobalt(III)-Peroxo Complexes Containing 1,2-Bis(dimethylphosphino)ethane (dmpe) or 1,3-Bis(dimethylphosphino)propane (dmpp). Molecular Structures of $[Co(O_2)(dmpe)_2]B(C_6H_5)_4$ and $[Co(O_2)(dmpp)_2]BF_4 \cdot H_2O$

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Monomeric (yellow) and dimeric (red) cobalt(III)-dioxygen complexes containing 1,2-bis(dimethylphosphino)ethane (dmpe) have been prepared from $[Co(dmpe)_2]^+$ and $[Co(dmpe)_2]^{2+}$, respectively, by air oxidation. The 1,3-bis(dimethylphosphino)propane (dmpp) complex afforded only the monomeric dioxygen complex by either preparative method. The crystal structures of $[Co(O_2)(dmpe)_2]B(C_6H_5)_4$ (**1**) and $[Co(O_2)(dmpp)_2]BF_4 \cdot H_2O$ (**2**) have been determined by X-ray analysis. Crystal data for **1**; monoclinic, $P2_1/a$, a=18.011(12), b=18.761(10), c=11.455(6) Å, β=107.78(4)°, V=3686(4) Å^3, Z=4, and R=0.064. Crystal data for **2**; orthorhombic, $Pbcn$, a=14.540(5), b=13.123(4), c=13.138(2) Å, V=2507(1) Å^3, Z=4, and R=0.076. The complex ions in both **1** and **2** have a trigonal-bipyramidal coordination geometry when the O_2 group bonded to the Co atom in the side-on form at a coordination site of the trigonal plane is assumed to be a unidentate ligand. Bond lengths, Co-O (1.858(7)—1.881(4) Å) and O-O (1.414(12) and 1.425(6) Å), and O-O stretching frequencies (877 and 862 cm^{-1}) indicate that both **1** and **2** are the peroxo complexes. The monomeric dioxygen complexes react immediately with SO_2 and with concd HCl to afford $[Co(SO_4)(\text{dmpe or dmpp})_2]^+$ and *cis*-$[CoCl_2(\text{dmpe or dmpp})_2]^+$, respectively. The red dimeric *trans*-$[(dmso)(dmpe)_2Co(\mu\text{-}O_2)Co(dmpe)_2(dmso)](BF_4)_4$ (dmso=dimethyl sulfoxide) complex was isolated and characterized.

Only a few monomeric cobalt(III)-dioxygen complexes have been known, in contrast to a large number of dimeric cobalt(III)-dioxygen complexes.[1] Vaska et al.[2,3] prepared $[Co(O_2)(dpee)_2]^+$ (dpee=*cis*-$(C_6H_5)_2PCHCHP(C_6H_5)_2$) and determined the molecular structure by X-ray analysis. Gray et al.[4] studied the chemical properties, formation mechanisms, and absorption spectra of this complex in some detail. In the present paper, we report new complexes of the same type, $[Co(O_2)(\text{dmpe or dmpp})_2]^+$ (dmpe=$(CH_3)_2PCH_2CH_2P(CH_3)_2$, dmpp=$(CH_3)_2PCH_2CH_2CH_2P(CH_3)_2$). These new complexes are highly reactive to SO_2 and HCl to afford $[Co(SO_4)(\text{dmpe or dmpp})_2]^+$ and *cis*-$[CoCl_2(\text{dmpe or dmpp})_2]^+$, respectively, while $[Co(O_2)(dpee)_2]^+$ is unreactive to SO_2 and much less reactive to HCl. In order to examine their different reactivities, we have determined the molecular structures of $[Co(O_2)(dmpe)_2]^+$ and $[Co(O_2)(dmpp)_2]^+$ and compared them with that of $[Co(O_2)(dpee)_2]^+$. A new dimeric cobalt(III)-dioxygen complex, *trans*-$[(dmso)(dmpe)_2Co(\mu\text{-}O_2)Co(dmpe)_2(dmso)]^{4+}$, and two related complexes, $[Co(CO_3)(dmpe)_2]^+$ and *trans*-$[Co(H_2O)_2(dmpe)_2]^{3+}$ are also described. A preliminary report on $[Co(O_2)(dmpe)_2]^+$ has been published.[5]

Experimental

The dmpe[6] and dmpp[7] ligands were prepared according to the literatures and handled under a nitrogen atmosphere until they formed cobalt(III) complexes. All solvents used for the preparations were deoxygenated by bubbling nitrogen for 20 min immediately before use. Absorption, ^{1}H NMR and IR spectra were recorded on a Hitachi 323 spectrophotometer, a Jeol JNM-PMX 60 spectrometer and a Jasco A-3 spectrophotometer, respectively.

Preparation of Complexes. $[Co(O_2)(dmpe)_2]BF_4$ and $[Co(O_2)(dmpe)_2]B(C_6H_5)_4$ (1). The complexes were prepared by the methods reported in a previous paper.[5]

$[Co(^{18}O_2)(dmpe)_2]BF_4$. The complex was prepared by a method similar to that for $[Co(O_2)(dmpe)_2]BF_4$.[5] The complex was yielded by exposing an ethanol solution of $[Co(dmpe)_2]^+$ to $^{18}O_2$ gas (Prochem. Co., 99% pure), instead of bubbling air.

$[Co(O_2)(dmpp)_2]BF_4 \cdot H_2O$ (2). Method a). To an ethanol solution (50 cm^3) of $Co(BF_4)_2 \cdot 6H_2O$ (588 mg, 1.73 mmol) was added an ethanol solution (5 cm^3) of dmpp (707 mg, 4.31 mmol) with stirring. After stirring for 30 min, air was bubbled into the solution for 10 h. A small amount of a white precipitate (probably the phosphine oxide) was filtered off, and the filtrate was concentrated to ca. 10 cm^3 under reduced pressure. The concentrate was chromatographed using a column (ϕ 2.5 cm×20 cm) of Toyopearl TSK-GEL. By elution with ethanol, a yellow and a pink ($Co(BF_4)_2$) band appeared. The eluate containing the yellow band was collected and concentrated to ca. 20 cm^3 under reduced pressure. To the concentrate was added diethyl ether (50 cm^3), and the solution was allowed to stand at −10 °C for 10 h, yielding yellow-orange crystals which were filtered and air-dried. Yield: 384 mg(43%). Found: C, 31.79; H, 7.28%. Calcd for $C_{14}H_{38}BCoF_4O_3P_4$: C, 32.09; H, 7.30%.

Method b). The same dmpp dioxygen complex was also yielded by a method similar to that for the dmpe complex.[5] To an ethanol solution (50 cm^3) of $Co(BF_4)_2 \cdot 6H_2O$ (1.37 g, 3.71 mmol) was added an ethanol solution (5 cm^3) of dmpp (1.06 g, 6.45 mmol) with stirring. After 1 h an ethanol solution (3 cm^3) of $NaBH_4$(140 mg, 3.71 mmol) was added to the solution. The solution was stirred for 30 min, and then air was bubbled into the solution for 10 h. The resulting solution was concentrated to ca. 10 cm^3, yielding a yellow precipitate. It was dissolved in ethanol (10 cm^3), diethyl ether (30 cm^3) was added, and the solution was allowed to stand at −10 °C for 10 h to give yellow-orange crystals. Yield: 660 mg(35%).

The complex is soluble in ethanol and acetonitrile. It is also soluble in water, but slowly decomposes to give Co(II) species.

[(dmso)(dmpe)$_2$Co(μ-O$_2$)Co(dmpe)$_2$(dmso)](BF$_4$)$_4$. Air was bubbled into a dimethyl sulfoxide (dmso) solution (30 cm^3) of [Co(dmpe)$_2$](BF$_4$)$_2$[5] (1.06 g, 1.99 mmol) for 10 h. A red precipitate was obtained, filtered, and dissolved in dmso (5 cm^3). The solution was chromatographed with a column (ϕ 2.5 cm×20 cm) of Toyopearl TSK-GEL. By elution with dmso, a main red and a minor yellow (probably [Co(dmpe)$_2$]$^{2+}$) bands developed. The eluate containing the red band was collected and mixed with ethanol to give a red precipitate. It was filtered, washed with a mixture of ethanol and diethyl ether (1:1), and air-dried. Yield: 460 mg(37%). Found: C, 26.93; H, 6.28; P, 20.43%. Calcd for $C_{14}H_{38}B_2CoF_8O_2P_4S$: C, 26.82; H, 6.11; P, 19.76%. The complex is soluble in dmso, but hardly in other common solvents such as water or ethanol.

[Co(CO$_3$)(dmpe)$_2$]ClO$_4$·1.5NaClO$_4$·H$_2$O. To *trans*-[CoCl$_2$(dmpe)$_2$]ClO$_4$[8] (840 mg, 1.6 mmol) in a mixture (100 cm^3) of methanol and water (2:1) was added K_2CO_3(335 mg, 2.42 mmol) in water (2 cm^3). The color of the solution immediately changed from blue to orange-yellow. After stirring for 4 h, the solution was diluted with water (2 dm^3) and applied on a column (ϕ 5 cm×20 cm) of SP-Sephadex C-25. The column was washed thoroughly with water, and the adsorbed product was eluted with 0.2 mol dm^{-3} NaClO$_4$ to give a main yellow and a small blue band (the starting complex). The eluate containing the yellow band was collected and concentrated to ca. 30 cm^3 under reduced pressure. Further concentration was carried out in a desiccator over P_4O_{10} to afford yellow crystals, which were filtered, washed with a mixture (50 cm^3) of methanol and diethyl ether (1:1), and air-dried. Yield: 940 mg(80%). Found: C, 21.03; H, 5.38%. Calcd for $C_{13}H_{34}Cl_{2.5}CoNa_{1.5}O_{14}P_4$: C, 21.15; H, 4.91%. The complex is soluble in water, methanol and ethanol, but not in diethyl ether.

***trans*-[Co(H$_2$O)$_2$(dmpe)$_2$](ClO$_4$)$_3$·2H$_2$O.** To an aqueous solution (20 cm^3) of [Co(CO$_3$)(dmpe)$_2$]ClO$_4$·1.5NaClO$_4$·H$_2$O (2.19 g, 2.97 mmol) was added dropwise 60% perchloric acid (5 cm^3) with stirring. The solution was warmed at 50 °C for 2 h, and then concentrated slowly in a desiccator over P_4O_{10} to yield red crystals, which were filtered, washed with a mixture (100 cm^3) of ethanol and diethyl ether (1:1), and air-dried. Yield: 1.85 g(86%). Found: C, 19.52; H, 5.22%. Calcd for $C_{12}H_{40}Cl_3CoO_{16}P_4$: C, 19.76; H, 5.53%. The complex decomposes slowly to cobalt(II) species in neutral water, although it is stable in water acidified with HClO$_4$. This complex was assigned to the trans isomer from the ^{1}H NMR spectrum.

Reaction of [Co(O$_2$)(dmpe or dmpp)$_2$]$^+$ with SO$_2$. SO$_2$ gas was bubbled into an ethanol solution (50 cm^3) of [Co(O$_2$)(dmpe)$_2$]BF$_4$ (100 mg, 0.2 mmol) for 10 min. The color of the solution changed immediately from yellow to red-orange. The solution was concentrated to ca. 5 cm^3. On addition of diethyl ether (30 cm^3) the concentrate afforded an orange precipitate, which was filtered and dissolved in a mixture (2 cm^3) of acetonitrile and ethanol (1:1). The solution was applied on a column (ϕ 1.5 cm×20 cm) of Toyopearl TSK-GEL, and the adsorbed product was eluted with a mixture of acetonitrile and ethanol (1:5). The eluate containing the orange band was collected and concentrated to ca. 5 cm^3 under reduced pressure. To the concentrate was added diethyl ether (20 cm^3), and the mixture was allowed to stand at −10 °C for 10 h, yielding orange crystals of [Co(SO$_4$)(dmpe)$_2$]BF$_4$·2H$_2$O, which were filtered and washed with a mixture (20 cm^3) of diethyl ether and ethanol (2:1). Yield: 80 mg(70%). Found: C, 24.97; H, 6.31%. Calcd for $C_{12}H_{36}BCoF_4O_6P_4S$: C, 24.93; H, 6.28%. The complex was identical with that prepared from *trans*-[Co(H$_2$O)$_2$(dmpe)$_2$](ClO$_4$)$_3$·2H$_2$O and Na$_2$SO$_4$.

The [Co(O$_2$)(dmpp)$_2$]BF$_4$·H$_2$O complex reacted similarly with SO$_2$ to afford [Co(SO$_4$)(dmpp)$_2$]BF$_4$. Yield: 52%. Found: C, 29.46; H, 5.81%. Calcd for $C_{14}H_{36}BCoF_4O_4P_4S$: C, 29.49; H,

Table 1. Experimental Conditions and Refinement Details

	1	**2**
Chemical formula	$[Co(O_2)(C_6H_{16}P_2)_2][B(C_6H_5)_4]$	$[Co(O_2)(C_7H_{18}P_2)_2]BF_4\cdot H_2O$
Formula weight	710.5	524.1
Density, D_x and D_m (Mg m^{-3})	1.28, 1.25(2)	1.38, 1.41(2)
μ(Mo $K\alpha$) (mm^{-1})	0.664	0.969
Habit of crystals	Thin tabular (100)	Prisms surrounded by (100), (011), and $(00\bar{1})$
Size of specimen (mm^3)	0.1×0.5×0.5	0.4×0.5×0.6
Number of reflections and 2θ range (°) for measuring lattice parameters	20 $23<2\theta<31$	25 $40<2\theta<45$
$2\theta_{max}$ (°)	55	55
Range of h, k, and l	$-21\leqq h\leqq 18$, $0\leqq k\leqq 19$, $0\leqq l\leqq 12$	$0\leqq h\leqq 20$, $0\leqq k\leqq 17$, $0\leqq l\leqq 18$
Systematic absences	$h0l$, h odd; $0k0$, k odd	$hk0$, $h+k$ odd; $h0l$, l odd; $0kl$, k odd
Variation of $\lvert F_o\rvert$ of n standard reflections, $\sum(\lvert F_o\rvert/\lvert F_o\rvert_{initial})/n$	$n=3$ 0.96—1.00	$n=5$ 0.94—1.00
Number of reflections measured	12127	3530
Number of unique reflections observed $[\lvert F_o\rvert>3\sigma(\lvert F_o\rvert)]$	2421	2346
Absorption correction	No	0.630≦transmission factor≦0.694
R	0.064	0.076
wR	0.068	0.119
$w^{-1}=\sigma^2(\lvert F_o\rvert)+(c\lvert F_o\rvert)^2$	$c=0.015$	$c=0.03$
S	2.4	3.2
$(\Delta\rho)_{min}$ and $(\Delta\rho)_{max}$ in final difference synthesis (e Å^{-3})	−0.63, 0.62	−1.0, 1.6
$(\Delta/\sigma)_{max}$	0.5	0.8

6.36%.

Reaction of $[Co(O_2)(dmpe, dmpp, or dpee)_2]^+$ with concd HCl. Both solid and dissolved $[Co(O_2)(dmpe or dmpp)_2]^+$ in ethanol reacted immediately with concd HCl at 0 °C to afford red *cis*-$[CoCl_2(dmpe or dmpp)_2]^+$. The same *cis*-dichloro complexes were prepared from $[Co(CO_3)(dmpe or dmpp)_2]^+$ with concd HCl.[9] The $[Co(O_2)(dpee)_2]^+$ complex reacted slowly with concd HCl at 0 °C to give a mixture of red *cis*-and green *trans*-$[CoCl_2(dpee)_2]^+$. The relative yield of the trans isomer increased with the reaction temperature. The $[Co(CO_3)(dpee)_2]ClO_4$ complex[4] afforded only the *trans*-dichloro complex by reaction with concd HCl even at below 0 °C.[9]

Crystal Structure Determination. Experimental conditions are listed in Table 1. Densities of the crystals were measured by flotation in aqueous solutions of KI. Intensity measurements were performed by a Rigaku AFC-5 four-circle diffractometer with Mo$K\alpha$ radiation (λ=0.70926 Å) monochromatized by a graphite plate. A crystal of **2** was sealed in a glass capillary with the mother liquid. The space group was uniquely determined from the Laue group and systematic absences. The intensity of reflections of **1** decreased rapidly with 2θ, and most of the reflections with $2\theta>40°$ were not observed. Corrections were made for Lorentz and polarization effects. Absorption correction was applied for **2** but not for **1**. The position of Co was deduced from the Patterson function, but the structure of **1** could not be solved by the heavy atom method because the location of Co near $y=0$ or 1/2 lacked the phase-determining power for reflections with $h+k$ odd in the case of $P2_1/a$. The structure was solved by direct methods with MULTAN78.[10] Starting with the positions of Co, four P and O atoms, those of the other non-hydrogen atoms were determined from the Fourier synthesis and refined by block-diagonal least-squares with anisotropic thermal parameters using UNICS III computation program system.[11] The function minimized was $\sum w||F_o|-|F_c||^2$. Complex neutral-atom scattering factors were taken from International Tables for X-Ray Crystallography.[12] The positions of 8 among 52 H atoms were found on the difference synthesis and others were calculated. Final R was 0.064 for 2421 observed unique reflections.[13] The atomic parameters of the non-hydrogen atoms are presented in Table 2.

The general position of space group $Pbcn$ is eightfold. The Co atom of **2** must be on the fourfold position. Consequently the Co atom must lie on the twofold axis, because the complex does not have a center of symmetry. The position of the Co atom was deduced from the Patterson function and the orientation of the CoO_2P_4 octahedron around the twofold axis was determined by the R factor method, where the geometry of **1** was utilized. All of non-hydrogen atoms were found on the Fourier synthesis and all the H atoms except those of the water molecule were found on the difference synthesis. Positional disorder of the F atoms of BF_4^- was found. The B atom lies on the twofold axis. The population parameters for the two sets of F atoms, (F(1), F(2)) and (F(01), F(02)) were estimated to be 0.7 and 0.3, respectively by the trial and error method in such a way that the isotropic thermal parameters took nearly equal value. The F(01) atom could not be found on the difference synthesis so that it was omitted. Final R was 0.076 for 2346 unique reflections.

Results and Discussion

Preparation. Gray et al.[4] prepared $[Co(O_2)(dpee)_2]^+$ by two methods; one is oxidation of $[Co(dpee)_2]^+$ with O_2, and the other oxidation of $[Co(dpee)_2]^{2+}$ with air. In the present study, either oxidation of $[Co(dmpp)_2]^+$ or $[Co(dmpp)_2]^{2+}$ with air yielded $[Co(O_2)(dmpp)_2]^+$, while $[Co(O_2)(dmpe)_2]^+$ was only formed from $[Co(dmpe)_2]^+$. Oxidation of $[Co(dmpe)_2]^{2+}$ with air in dmso afforded a red complex whose chemical composition is $CoO(dmpe)_2(dmso)(BF_4)_2$. The $[Co(O_2)(dmpe or dmpp)_2]^+$ complexes are yellow in color and contain the O_2^{2-} group bonded to the Co^{3+} ion in the side-on form (vide infra). The ^1H NMR spectrum of the red complex in d_6-dmso is quite similar to that of *trans*-$[CoCl_2(dmpe)_2]^+$ [8] in the region of signals due to dmpe, and shows a singlet signal at 3.37 ppm assignable to the methyl protons of coordinated dmso.[14] In the IR spectrum the complex exhibits a strong band at 917 cm^{-1} which can be assigned to the S–O stretching vibration of dmso coordinated through the oxygen atom.[14] The *trans*-$[CoCl_2(dmpe)_2]^+$ complex shows no strong absorption in this region. Thus we assumed the red complex to be a dimeric μ-peroxo complex where the dmso and μ-peroxo groups occupy the trans positions to each other. No dimeric μ-peroxo cobalt(III) complex is formed with dpee and dmpp. Gray et al.[4] suggested that the dimeric μ-peroxo dpee complex is unstable for steric repulsions of the bulky dpee ligands with a solvent molecule coordinated at the position trans to the μ-peroxo group. The dmpe ligand is less bulky than dpee[15] and may be sterically favorable for formation of the dimeric μ-peroxo complex. The dmpp complex does not form the dimeric μ-peroxo complex. The instability of the dimeric dmpp complex will also be attributable to the steric reasons, since the six-membered dmpp chelate ring should be more bulky than the five-membered dmpe chelate ring and will have larger steric repulsions with other ligands. We have also attempted to prepare the dioxygen complex of 1, 2-bis(dibutylphosphino)ethane (dbpe) by two different methods described above. Both reactions proceeded quite similarly to those for dmpp and afforded only the monomeric dioxygen complex, $[Co(O_2)(dbpe)_2]^+$. The pure complex could not be isolated because the complex was highly soluble in common solvents, but the formation of only the monomer was confirmed by the ^1H NMR and absorption spectra. The dimeric μ-peroxo complex of bulky dbpe will also be unstable for steric reasons. Bosnich et al.[16] reported that *o*-phenylenebis(dimethylarsine) (diars) and *meso*- and *rac*-$\{(CH_3)_2AsCH_2CH_2CH_2As(C_6H_5)CH_2-\}_2$ (tetars) form both monomeric peroxo and dimeric μ-peroxo cobalt(III) complexes.

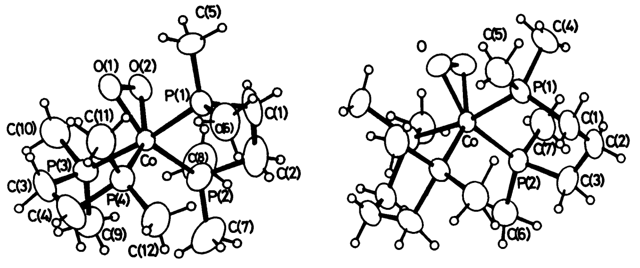
The monomeric dioxygen complexes of dmpe, dmpp and dbpe are stable in organic solvents such as alcohols

Table 2. Fractional Coordinates (×10⁴, ×10⁵ for Co, ×10³ for F) and Equivalent Isotropic Thermal Parameters

	Atom	x	y	z	B_{eq}/Å^2
(1)					
	Co	18531 (8)	49248 (7)	61991 (13)	2.6
	P(1)	1591 (2)	6083 (2)	6184 (3)	3.9
	P(2)	3077 (2)	5234 (2)	6551 (3)	4.6
	P(3)	2000 (2)	3747 (2)	6082 (3)	4.3
	P(4)	1609 (2)	4705 (2)	7935 (3)	4.2
	O(1)	894 (4)	4773 (4)	5009 (7)	4.3
	O(2)	1486 (4)	4972 (4)	4498 (6)	4.3
	C(1)	2404 (8)	6532 (7)	5784 (13)	6.7
	C(2)	3147 (7)	6206 (7)	6591 (18)	9.4
	C(3)	1455 (7)	3338 (6)	7002 (13)	6.1
	C(4)	1677 (8)	3745 (7)	8272 (13)	7.0
	C(5)	726 (7)	6336 (6)	5007 (12)	5.5
	C(6)	1573 (8)	6579 (7)	7520 (13)	6.5
	C(7)	3864 (7)	5003 (8)	7821 (13)	7.4
	C(8)	3425 (8)	4994 (8)	5260 (13)	7.5
	C(9)	2928 (7)	3312 (6)	6647 (14)	7.1
	C(10)	1570 (8)	3378 (6)	4614 (12)	6.0
	C(11)	590 (7)	4891 (7)	7829 (12)	6.2
	C(12)	2157 (8)	5062 (8)	9377 (11)	7.1
	B	4816 (7)	2500 (7)	10023 (12)	3.2
	C(13)	4692 (5)	2958 (5)	11195 (9)	2.6
	C(14)	4203 (6)	3557 (6)	11030 (11)	4.2
	C(15)	4057 (6)	3918 (6)	11969 (11)	4.6
	C(16)	4404 (7)	3712 (6)	13142 (12)	5.0
	C(17)	4889 (7)	3123 (7)	13393 (10)	4.9
	C(18)	5018 (6)	2765 (6)	12372 (9)	3.6
	C(19)	5046 (5)	3052 (5)	9059 (9)	3.0
	C(20)	4910 (6)	2922 (6)	7834 (9)	3.9
	C(21)	5155 (7)	3383 (7)	7047 (11)	6.2
	C(22)	5530 (6)	4001 (6)	7490 (12)	5.2
	C(23)	5675 (7)	4152 (7)	8675 (12)	5.6
	C(24)	5436 (7)	3684 (6)	9454 (10)	4.3
	C(25)	4027 (6)	2062 (5)	9339 (9)	2.7
	C(26)	3291 (6)	2185 (5)	9471 (9)	2.8
	C(27)	2632 (6)	1827 (6)	8834 (10)	3.7
	C(28)	2646 (6)	1294 (6)	7991 (11)	4.2
	C(29)	3367 (6)	1150 (6)	7830 (10)	4.1
	C(30)	4027 (6)	1515 (6)	8470 (10)	3.6
	C(31)	5562 (6)	1968 (5)	10573 (9)	2.9
	C(32)	6338 (6)	2186 (6)	10844 (9)	3.5
	C(33)	6965 (6)	1749 (6)	11422 (11)	4.6
	C(34)	6846 (6)	1067 (6)	11768 (10)	4.5
	C(35)	6085 (7)	831 (6)	11491 (11)	4.7
	C(36)	5454 (6)	1263 (6)	10905 (10)	3.7
(2)					
	Co	50000	16436 (7)	25000	2.5
	B	5000	6228 (11)	2500	6.1
	P(1)	3511 (1)	1481 (1)	2075 (1)	3.3
	P(2)	5244 (1)	2663 (1)	1190 (1)	3.2
	O	4803 (3)	318 (3)	2997 (3)	4.0
	C(1)	2912 (4)	2560 (5)	1499 (5)	4.4
	C(2)	3377 (4)	2982 (5)	555 (4)	4.5
	C(3)	4299 (5)	3510 (5)	794 (5)	4.7
	C(4)	3329 (5)	464 (5)	1156 (5)	4.9
	C(5)	2761 (4)	1136 (6)	3130 (5)	4.8
	C(6)	6169 (5)	3596 (5)	1179 (5)	5.2
	C(7)	5465 (5)	1901 (6)	66 (5)	5.1
	OW	1379 (3)	3649 (4)	3308 (5)	6.8
	F(1)	552 (1)	679 (1)	195 (1)	14.6
	F(2)	433 (1)	582 (1)	184 (1)	14.8
	F(02)	546 (2)	579 (2)	174 (2)	12.2

and acetonitrile, but slowly decompose in water to give cobalt(II) species. No liberation of oxygen from the complexes was observed by bubbling nitrogen into organic solutions of the complexes. Uptake of O_2 is irreversible in these complexes.

Molecular Structure. Perspective drawings of complexes **1** and **2** are shown in Fig. 1. Bond distances and bond angles are listed in Table 3. The dioxygen group in each complex coordinates to the cobalt atom in the side-on form. [$Co(O_2)(dmpe)_2$]$^+$ **1** has a pseudo twofold axis passing through the Co and the midpoint of the O(1)–O(2) bond axis, and the coordination geometry can be described as a trigonal-bipyramid when the O_2 group is regarded as a unidentate ligand. A similar trigonal-bipyramidal structure was report-



(1) (2)

Fig. 1. ORTEP drawings of the complex cations **1** and **2** with thermal ellipsoids scaled at the 50% probability level.[17] H atoms are represented by circles of radius 0.08 Å.

Table 3. Bond Distances (*l*/Å) and Angles (*ϕ*/°)

(1)

Co	-P(1)	2.222(4)	P(1)	-Co	-P(2)	86.7(1)
Co	-P(2)	2.194(4)	P(1)	-Co	-P(3)	174.4(2)
Co	-P(3)	2.234(4)	P(1)	-Co	-P(4)	95.1(2)
Co	-P(4)	2.202(4)	P(1)	-Co	-O(1)	89.8(2)
Co	-O(1)	1.866(7)	P(1)	-Co	-O(2)	86.5(2)
Co	-O(2)	1.858(7)	P(2)	-Co	-P(3)	98.1(1)
P(1)	-C(1)	1.864(16)	P(2)	-Co	-P(4)	110.5(1)
P(1)	-C(5)	1.785(12)	P(2)	-Co	-O(1)	145.9(2)
P(1)	-C(6)	1.799(15)	P(2)	-Co	-O(2)	101.3(2)
P(2)	-C(2)	1.827(14)	P(3)	-Co	-P(4)	85.9(1)
P(2)	-C(7)	1.747(12)	P(3)	-Co	-O(1)	84.6(2)
P(2)	-C(8)	1.829(17)	P(3)	-Co	-O(2)	89.7(2)
P(3)	-C(3)	1.815(16)	P(4)	-Co	-O(1)	103.6(2)
P(3)	-C(9)	1.794(12)	P(4)	-Co	-O(2)	148.2(2)
P(3)	-C(10)	1.763(13)	O(1)	-Co	-O(2)	44.6(3)
P(4)	-C(4)	1.838(14)	Co	-P(1)	-C(1)	105.2(5)
P(4)	-C(11)	1.835(14)	Co	-P(1)	-C(5)	113.6(4)
P(4)	-C(12)	1.776(12)	Co	-P(1)	-C(6)	123.9(5)
O(1)	-O(2)	1.414(12)	C(1)	-P(1)	-C(5)	105.3(6)
C(1)	-C(2)	1.50(2)	C(1)	-P(1)	-C(6)	101.2(7)
C(3)	-C(4)	1.58(2)	C(5)	-P(1)	-C(6)	105.4(6)
			Co	-P(2)	-C(2)	109.0(4)
			Co	-P(2)	-C(7)	127.0(4)
			Co	-P(2)	-C(8)	111.1(5)
			C(2)	-P(2)	-C(7)	101.2(6)
			C(2)	-P(2)	-C(8)	103.2(7)
			C(7)	-P(2)	-C(8)	102.7(7)
			Co	-P(3)	-C(3)	106.8(5)
			Co	-P(3)	-C(9)	122.9(4)
			Co	-P(3)	-C(10)	114.8(4)
			C(3)	-P(3)	-C(9)	102.0(6)
			C(3)	-P(3)	-C(10)	103.3(6)
			C(9)	-P(3)	-C(10)	104.7(6)
			Co	-P(4)	-C(4)	110.7(5)
			Co	-P(4)	-C(11)	112.1(4)
			Co	-P(4)	-C(12)	124.1(4)
			C(4)	-P(4)	-C(11)	101.6(6)
			C(4)	-P(4)	-C(12)	101.1(6)
			C(11)	-P(4)	-C(12)	104.5(6)
			Co	-O(1)	-O(2)	67.4(4)
			Co	-O(2)	-O(1)	68.0(5)
			P(1)	-C(1)	-C(2)	106.5(9)
			P(2)	-C(2)	-C(1)	110.4(9)
			P(3)	-C(3)	-C(4)	107.5(8)
			P(4)	-C(4)	-C(3)	107.3(9)

Table 3. (Continued)

(**2**)							
Co	-P(1)	2.246(2)	P(1)	-Co	-P(2)	91.1(1)
Co	-P(2)	2.208(2)	P(1)	-Co	-O	81.5(1)
Co	-O	1.881(4)	P(2)	-Co	-O	148.8(1)
P(1)	-C(1)	1.827(7)	Co	-P(1)	-C(1)	119.3(2)
P(1)	-C(4)	1.819(7)	Co	-P(1)	-C(4)	112.0(2)
P(1)	-C(5)	1.821(7)	Co	-P(1)	-C(5)	114.3(2)
P(2)	-C(3)	1.842(7)	C(1)	-P(1)	-C(4)	103.0(3)
P(2)	-C(6)	1.819(7)	C(1)	-P(1)	-C(5)	102.9(3)
P(2)	-C(7)	1.812(7)	C(4)	-P(1)	-C(5)	103.6(3)
C(1)	-C(2)	1.517(8)	Co	-P(2)	-C(3)	117.8(2)
C(2)	-C(3)	1.541(9)	Co	-P(2)	-C(6)	122.2(2)
O	-O′	1.425(6)	Co	-P(2)	-C(7)	109.2(2)
			C(3)	-P(2)	-C(6)	98.2(3)
			C(3)	-P(2)	-C(7)	103.6(3)
			C(6)	-P(2)	-C(7)	103.5(3)
			P(1)	-C(1)	-C(2)	114.2(4)
			C(1)	-C(2)	-C(3)	112.7(5)
			P(2)	-C(3)	-C(2)	115.8(4)
			P(1)	-Co	-P(1′)	169.1(1)
			O	-Co	-O′	44.6(2)
			P(2)	-Co	-P(2′)	105.5(1)

ed for $[Co(O_2)(dpee)_2]^+$.[3] The O_2 ligand and P(2) and P(4) atoms form an equatorial plane, to which the P(1)-Co-P(3) axis is approximately perpendicular. The P(2) and P(4) atoms deviate by 0.03 and −0.02 Å, respectively from the plane formed by the Co, O(1) and O(2) atoms. The P(1) and P(3) atoms are 2.22 Å distant from the plane. The O-O bond distance (1.414(12) Å) is nearly the same as the values found in $[Co(O_2)(dpee)_2]^+$ (1.420(10) Å)[3] and *Δ-cis* *β*-$[Co(O_2)($*RR*-tetars$)]^+$ (1.420 (10) Å).[18] These O-O distances are in the range of the reported values for a peroxide ion.[1] The O(1) and O(2) atoms are at essentially the same distance from the Co, and the Co-O distances (1.866(7), 1.858(7) Å) are similar to those for $[Co(O_2)(dpee)_2]^+$ (1.871(7), 1.902(7) Å)[3] and for *Δ-cis* *β*-$[Co(O_2)($*RR*-tetars$)]^+$ (1.862(6), 1.867(7) Å)[18]. These facts indicate that the Co-O and O-O distances are not greatly affected by other ligands in a complex. The dmpe chelate ring takes a gauche conformation. The average Co-P bond distance, 2.213 (4) Å, is by 0.04—0.06 Å shorter than those in *Δ*-$[Co(en)_2(dmpe)]^{3+}$ (2.256(3) Å; en=$NH_2CH_2CH_2NH_2$)[19] and *trans*(*P, N*)-$[Co(edmp)_2(dmpe)]^{3+}$ (2.277(4) Å; edmp=$(CH_3)_2PCH_2CH_2NH_2$).[20] The average P-Co-P chelate angle (86.3(1)°) is by 2—4° larger than those of *Δ*-$[Co(en)_2(dmpe)]^{3+}$ (84.2(1)°) and *trans*(*P,N*)-$[Co(edmp)_2(dmpe)]^{3+}$ (82.7(1)°). The axial Co-P bond distances in **1** are longer by ca. 0.03 Å on average than those in the equatorial plane. It may be accounted for by trans influence of the mutually trans P donating atoms.[21] Two methyl groups C(5) and C(10) of **1** are placed over and under the O_2 group. The distance from the Co atom to the midpoint of the peroxide ion is 1.73(1) Å, which is comparable with the P-CH_3 bond length.

The structure of $[Co(O_2)(dmpp)_2]^+$ (**2**) is very similar to complex **1**. Complex **2** has a crystallographic twofold axis passing through the Co atom and the midpoint of the O-O bond. The trigonal-bipyramid around the Co atom is slightly deformed. The P(2) atom deviates by 0.37 Å from the plane formed by the Co, O, and O' atoms, and the P(1) atom is apart from the plane by 2.21 Å. All the O-O, Co-O, and Co-P bond distances are slightly longer than those of complex **1**, though not significant in view of the e.s.d.'s. The six-membered chelate ring formed by dmpp adopts a chair conformation. The C(1), C(2), and C(3) atoms of the chelate skeleton are shifted by 0.89, 0.47, and 0.89 Å, respectively from the plane through the Co, P(1) and P(2) atoms. There is no short contact between the two methyl groups C(4) and C(7), although P(1)-C(4) and P(2)-C(7) bonds are axial to the six-membered ring. Interatomic distances C(4)···C(7) and P(1)···P(2) are 3.91(1) and 3.18(2) Å, respectively.

IR Spectra. In Fig. 2 are shown IR spectra of $[Co(O_2)(dmpe)_2]BF_4$ and $[Co(^{18}O_2)(dmpe)_2]BF_4$ in the O-O stretching frequency region. The medium intensity band at 877 cm^{-1} of the O_2 complex shows the isotope shift; the $^{18}O_2$ complex gives a new band at 827 cm^{-1}. Other bands remain unchanged. The value of shift agrees well with that calculated for the O-O stretching vibration ($\Delta\nu$=50 cm^{-1}). For $[Co(O_2)(dmpp)_2]^+$, a similar medium intensity band is observed at 862 cm^{-1}. The corresponding *cis*-$[CoCl_2($dmpe or dmpp$)_2]^+$ complexes show no such bands in this region. Thus the bands at 877 cm^{-1} of the dmpe and 862 cm^{-1} of the dmpp complex can be assigned to the O-O stretching vibration. Gray et al.[4] assigned the band at 909 cm^{-1} of the dpee complex to the O-O stretching vibration. These frequencies are in the range of the reported values for a peroxide ion.[1,22]

Absorption Spectra. Figure 3 shows absorption spectra of the dioxygen complexes of dmpe, dmpp and

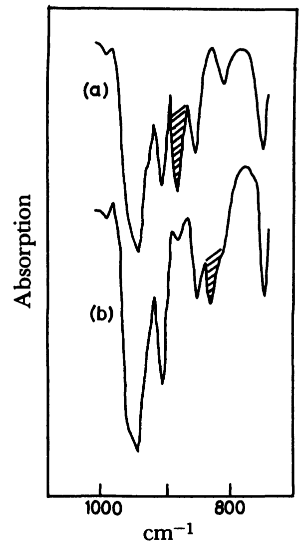


Fig. 2. IR spectra of $[Co(O_2)(dmpe)_2]BF_4$ (a) and $[Co(^{18}O_2)(dmpe)_2]BF_4$ (b).

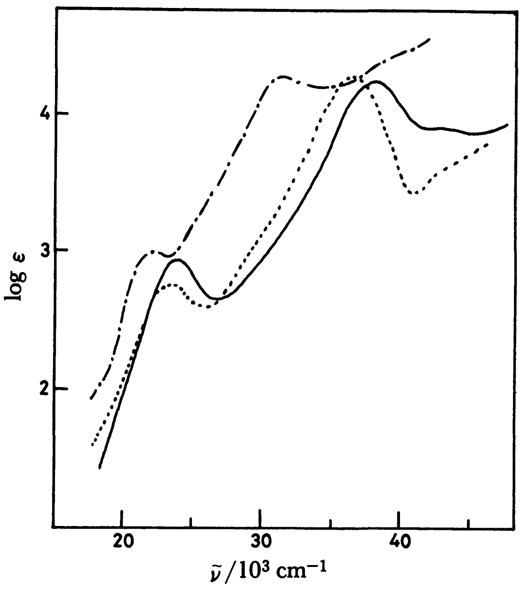


Fig. 3. Absorption spectra of $[Co(O_2)(dmpe)_2]BF_4$ (———), $[Co(O_2)(dmpp)_2]BF_4$ (·········) and $[Co(O_2)(dpee)]BF_4$ (— · — · —) in CH_3CN.

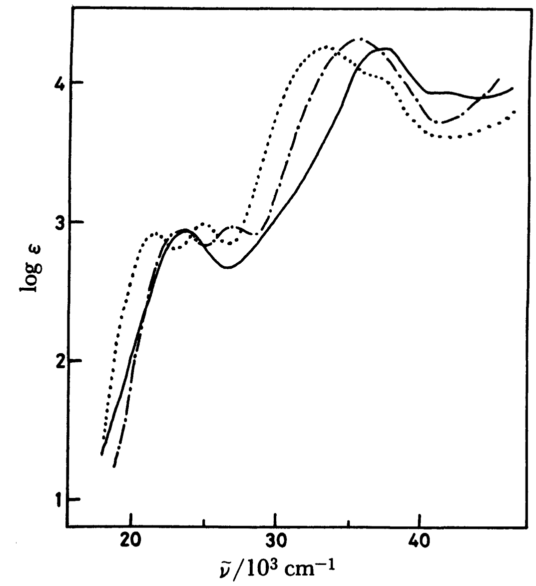


Fig. 4. Absorption spectra of $[Co(O_2)(dmpe)_2]BF_4$ (———), $[Co(CO_3)(dmpe)_2]ClO_4$ (— · — · —) and $[Co(SO_4)(dmpe)_2]BF_4$ (·········) in CH_3CN.

dpee. Gray et al.[4] assigned the band at 21000 cm^{-1} and the shoulder around 26000 cm^{-1} of the dpee complex to the first ($^1A \rightarrow {}^1T_1$) and the second ($^1A \rightarrow {}^1T_2$) ligand field bands, respectively, from a comparison with the spectrum of $[Co(CO_3)(dpee)_2]^+$ which has the same *cis*-$[CoO_2P_4]$ chromophore. The spectra of the dmpe and dmpp complexes are similar in pattern to that of the dpee complex, giving a peak at ca. 24000 cm^{-1} and a shoulder around 30000 cm^{-1} in the ligand field band region. The peak positions shift to high energy in the order of dpee<dmpp< dmpe complexes. This order coincides with the ranking of these phosphine ligands in the spectrochemical series.[23] Thus we have assigned the bands at 23750 cm^{-1} (log ε=2.95) of the dmpe complex and 23250 cm^{-1} (log ε=2.77) of the dmpp complex to the first ligand field band. It is not clear whether the shoulder absorption around 30000 cm^{-1} is the second ligand field band. In Fig. 4 are compared the spectrum of $[Co(O_2)(dmpe)_2]^+$ with those of $[Co(CO_3)(dmpe)_2]^+$ and $[Co(SO_4)(dmpe)_2]^+$. The latter two complexes exhibit two distinct absorption bands in the region of 20000 to 28000 cm^{-1} ($[Co(CO_3)(dmpe)_2]^+$ in water: 23530(2.96), 27100(2.98); $[Co(SO_4)(dmpe)_2]^+$ in CH_3CN: 21740(2.92), 25130(2.99) in cm^{-1} (log ε)). The two bands of each complex can be assigned to the ligand field bands, although the energy separation between them is much smaller than those of Co(III) amine complexes. The energy difference between the two ligand field bands in $[Co(CO_3)(dmpe)_2]^+$ (3750 cm^{-1}) is smaller than the half of the difference in $[Co(CO_3)(en)_2]^+$ (8250 cm^{-1}).[24] It is known that the energy differences between the two ligand field bands of phosphine[25] and arsine[16,26] cobalt(III) complexes are markedly reduced. No distinct band is observed for $[Co(O_2)(dmpe)_2]^+$ in the region of the second ligand field band of $[Co(CO_3)(dmpe)_2]^+$, although the first absorption bands of the two complexes are very similar both in intensity and peak position. When the shoulder around 30000 cm^{-1} of $[Co(O_2)(dmpe)_2]^+$ is assigned to the second ligand field band, the energy difference from the first ligand field band seems to be too large for a phosphine complex. Bosnich et al.[16] reported the absorption and CD spectra of an optically active peroxo tetrarsine complex, Δ-*cis* β-$[Co(O_2)(RR\text{-tetars})]^+$. The complex shows an absorption spectral pattern very similar to that of $[Co(O_2)(dmpe)_2]^+$ in the ligand field band region, and exhibits rather strong CD corresponding to the first ligand field band and fairly weak CD in the region from the absorption minimum to the high energy side. If the weak CD corresponds to the second ligand field band ($^1A \rightarrow ^1T_2$) of Co(III), such a CD pattern is acceptable as a cobalt(III) complex. The second ligand field band would be so weak that it is hidden by adjacent strong absorption, although the reason is unknown. The ligand field absorption spectra of $[Co(O_2)(dmpe)_2]^+$ and $[Co(O_2)(dmpp)_2]^+$ could be understood in the same manner as that of the tetars complex.

The peroxo-bis(diphosphine) complexes show strong absorption bands in the region of 30000 to 40000 cm^{-1}. Gray et al.4) assigned the band at 31000 cm^{-1} of $[Co(O_2)(dpee)_2]^+$ to a ligand-to-metal charge transfer transition of the type $\sigma(P) \rightarrow d\sigma^*(Co)$. The corresponding strong band is observed at 38000 cm^{-1} (log ε=4.36) and 36000 cm^{-1} (log ε=4.29) for $[Co(O_2)(dmpe)_2]^+$ and $[Co(O_2)(dmpp)_2]^+$, respectively. These bands are largely shifted to the high energy side compared with that of the dpee complex. Similar P-to-Co charge transfer bands of complexes, $[Co(en)_2(N\text{-}P)]^{3+}$ (N-P=$NH_2CH_2CH_2P(C_6H_5)_2$ or $NH_2CH_2CH_2P(CH_3)_2$)27) and *trans*-$[Co(CN)_4(P)_2]^-$ (P=$P(C_6H_5)_3$, $P(C_6H_5)_2(CH_3)$ or $P(C_6H_5)(CH_3)_2$)28) show a similar large shift to high energy by replacing a phenyl group on P with a methyl group.

The *trans*-$[(dmso)(dmpe)_2Co(\mu\text{-}O_2)Co(dmpe)_2(dmso)]^{4+}$ complex shows two medium intensity bands at 20000 cm^{-1} (log ε=2.93) and 25000 cm^{-1} (log ε=2.64) and a strong band at 36000 cm^{-1} (log ε=4.67)(Fig. 5). The former two bands can be assigned to the two ligand field transitions of cobalt(III), since the spectral pattern quite resembles that of *trans*-$[Co(dmso)_2(dmpe)_2]^{3+}$ which was generated from *trans*-$[Co(H_2O)_2(dmpe)_2]^{3+}$ in dmso. While such distinct ligand field bands of a μ-peroxo cobalt(III) complex have been observed for $[(CH_3CN)(diars)_2Co(\mu\text{-}O_2)Co(diars)_2(CH_3CN)]^{4+}$16) and $[X(cyclam)Co(\mu\text{-}O_2)(cyclam)X]^{n+}$ (X= a unidentate ligand such as H_2O or Cl^-; cyclam=1,4,8,11-tetraazacyclotetradecane),29) a large number of amine complexes such as $[(NH_3)(en)_2Co(\mu\text{-}O_2)Co(en)_2(NH_3)]^{4+}$ show a broad, unresolved spectrum in the ligand field region.30)

The *trans*-$[Co(H_2O)_2(dmpe)_2]^{3+}$ complex exhibits the first ligand field band split into two components, a shoulder around 20000 cm^{-1} (log ε = ca. 2.4) and a band at 23300 cm^{-1} (log ε = 2.80), and the second ligand field band at 27000 cm^{-1} (log ε = 2.96). The splitting of the first ligand field band can be anticipated from a *trans*-$[CoO_2P_4]$ chromophore. However, neither the present μ-peroxo complex nor *trans*-$[Co(dmso)_2(dmpe)_2]^{3+}$ show such splitting of the first ligand field band. Further studies will be needed for elucidating the absorption spectra of the cobalt(III) phosphine complexes.

Reactivity of Dioxygen Complexes. Both monomeric peroxo complexes of dmpe and dmpp in ethanol solutions react immediately with SO_2 at room temperature to afford $[Co(SO_4)(dmpe\ or\ dmpp)_2]^+$, which were isolated as the tetrafluoroborate. The $[Co(O_2)(dbpe)_2]^+$ complex also reacts with SO_2, but the sulfato complex could not be isolated because it decomposed to give Co(II) species during the course of isolation. Similar reactions have been reported for dioxygen complexes of cobalt(III). The $[Co(O_2)(diars)_2]^+$ complex reacts with SO_2, but the product (probably sulfato complex) can not be isolated because of the instability in the presence of SO_2.16) Some μ-peroxo amine complexes such as $[(en)_2Co(\mu\text{-}NH_2,\mu\text{-}O_2)Co(en)_2]^{3+}$ yield μ-sulfato complexes by reaction with SO_2.31)

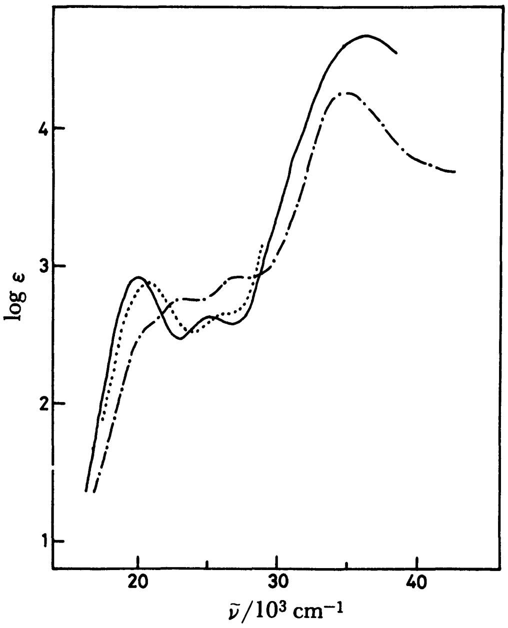


Fig. 5. Absorption spectra of $[(dmso)(dmpe)_2Co(\mu\text{-}O_2)Co(dmpe)_2(dmso)]^{4+}$ in dmso (———), and *trans*-$[Co(H_2O)_2(dmpe)_2]^{3+}$ in 0.5 mol dm^{-3} $HClO_4$ (—·—·—) and in dmso (·········).

On the other hand, $[Co(O_2)(dpee)_2]^+$ is quite inert toward SO_2. As described in Molecular Structure, the bond distances and angles of the Co–O_2 moiety are similar among the dmpe, dmpp and dpee complexes. As described previously the O_2^{2-} ion is surrounded by substituents on the axial P donor atoms of diphosphine ligands. The peroxide ion in $[Co(O_2)(dpee)_2]^+$ might be protected by the surrounding bulky phenyl groups against the attack of SO_2. Bulkiness of substituents on the axial P donor atoms in the $[Co(O_2)(diphosphine)_2]^+$ complex seems to be an important factor for the reactivity of the ligating peroxide ion. Thus the remarkable difference in reactivity toward SO_2 between the dpee complex and the other dmpe and dmpp complexes may be attributable to steric factors rather than electronic factors.

The peroxo complexes of dmpe and dmpp react instantly with concd HCl at 0 °C to afford red *cis*-$[CoCl_2(diphosphine)_2]^+$, while the same reaction of the dpee complex takes place very slowly and gives a mixture of green *trans*- and red *cis*-$[CoCl_2(dpee)_2]^+$. This indicates also the less reactivity of the dpee complex. The formation of *trans*-[CoCl$_2$(dpee)$_2$]$^+$ may be related with the fact that *cis*-[CoCl$_2$(dpee)$_2$]$^+$ in ethanol isomerizes to the trans isomer (half-life=1.07 h at 53.3 °C) much faster than does *cis*-[CoCl$_2$(dmpe)$_2$]$^+$ (half-life=148 h at 55.0 °C). Detailed isomerization studies for these dichloro complexes will be reported elsewhere.

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