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Preparation and Molecular Structures of $[Co(S_2O\text{-}S,S')(Me_2PCH_2CH_2PMe_2)_2]ClO_4$ and $[Co(S_2PMe_2)_2(Me_2PCH_2CH_2PMe_2)]BF_4$

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The reaction of elemental sulfur S_8 with $[Co(dmpe)_2](BF_4)_2$ in a mixture of methanol and benzene gave a novel *S*,*S'*-coordinated disulfur oxide cobalt(III) complex, $[Co(S_2O\text{-}S,S')(dmpe)_2]ClO_4$ (**1**), and a dimethyldithiophosphinato complex, $[Co(S_2PMe_2)_2(dmpe)]BF_4$ (**2**). The molecular structures of these complexes were determined by X-ray structure analyses. Crystal data for complex **1**: monoclinic, $P2_1/n$, $a=14.702(3)$, $b=11.645(1)$, $c=14.333(2)$ Å, $\beta=109.90(2)°$, $V=2307.4(2)$ Å^3, $D_x=1.55$, $D_m=1.54(3)$ g cm^{-3}, $Z=4$, $R=0.039$ for 4542 reflections. Crystal data for complex **2**: orthorhombic, $Pnc2$, $a=13.383(3)$, $b=12.333(2)$, $c=13.742(3)$ Å, $V=2268.1(8)$ Å^3, $D_x=1.60$, $D_m=1.59(2)$ g cm^{-3}, $Z=4$, $R=0.075$ for 2060 reflections. The central sulfur atom of the S–$\underline{S}$–O group in complex **1** exerts a larger trans influence than does the terminal sulfur.

The oxidative addition of elemental sulfur to planar-type complexes of d^8-metal ions, such as Ir^+ or Rh^+, is a convenient method for preparing octahedral disulfur (S_2^{2-}) complexes.[1)] Attempts to prepare cobalt(III) disulfur complexes from Co(I) (d^8) complexes, $[CoCl(PPh_3)_3]$[2)] and $[Co(dmpe)_2]^+$ (dmpe=1,2-bis(dimethylphosphino)ethane: $(CH_3)_2PCH_2CH_2P(CH_3)_2$)[3)] were all unsuccessful, affording insoluble, unknown black products. Here, we describe reactions of elemental sulfur with a Co(II) (d^7) complex, $[Co(dmpe)_2]^{2+}$, the method being similar to that for Co(III)-dioxygen complexes in our previous studies.[4)] The main products were found to be $[Co(S_2O)(dmpe)_2]^+$ and $[Co(S_2PMe_2)_2(dmpe)]^+$ by X-ray crystal-structure analyses.

Experimental

The $[Co(dmpe)_2](BF_4)_2$[3)] complex, which is fairly unstable to oxygen, was handled under an atmosphere of nitrogen. Methanol and benzene used as solvents were deoxygenated by bubbling nitrogen and dried over Molecular Sieves. Elemental sulfur was recrystallized from benzene. Absorption spectra were recorded on a JASCO UVIDEC spectrophotometer. X-Ray photoelectron spectra were measured on a VG Scientific ESCA LAB MK II System at Institute for Molecular Science (Okazaki). The binding energies for the S-2p, P-2p, Co-2p, and C-1s electrons were measured. The charging effect was corrected by adjusting the C-1s peak values to 285.00 eV as an internal standard.

Reaction between Elemental Sulfur and $[Co(dmpe)_2](BF_4)_2$. A yellow $[Co(dmpe)_2](BF_4)_2$ complex was obtained by reaction of dmpe and $Co(BF_4)_2 \cdot 6H_2O$ (2 : 1 molar ratio) in methanol (yield>90%).[3)] To a suspension of $[Co(dmpe)_2](BF_4)_2$ (1 g, 1.9 mmol) in methanol (200 cm^3) was added a solution of S_8 (0.5 g, 1.9 mmol) in benzene (100 cm^3). The yellow suspension was stirred at room temperature for two weeks, gradually giving a reddish-brown solution. The solution was evaporated to dryness under reduced pressure. The brown residue was washed with benzene (200 cm^3×3), stirred with 1 dm^3 of water for a while, and filtered. The brown aqueous filtrate was applied on a column (2 cm×50 cm) of SP-Sephadex C-25 (Na^+ form), and the adsorbed products were eluted with a 0.2 mol dm^{-3} Na_2SO_4 aqueous solution. An orange, and then brown, band were eluted as the major products. Each eluate of the orange and brown bands was evaporated under reduced pressure to a small volume (ca. 20 cm^3). Methanol (ca. 20 cm^3) was added to the concentrate to precipitate Na_2SO_4, which was filtered off. For the orange complex, the filtrate was evaporated again to dryness under reduced pressure. The residue was dissolved in water (20 cm^3), and $NaB(C_6H_5)_4$ (1 g) was added. Orange crystals were deposited immediately, collected by filtration and recrystallized from CH_2Cl_2 and $(C_2H_5)_2O$. Yield: 0.28 g (20%). Found: C, 56.76; H, 7.03%. Calcd for $[Co(S_2O)(dmpe)_2]B(C_6H_5)_4=C_{36}H_{52}OBS_2P_4Co$: C, 57.00; H, 6.91%. For the brown complex, the filtrate gave brown crystals by addition of $NaBF_4$ (2 g). They were collected by filtration and recrystallized from hot water. Yield: 0.26 g (25%). Found: C, 21.96; H, 5.26%. Calcd for $[Co\{S_2P(CH_3)_2\}_2(dmpe)]BF_4=C_{10}H_{28}P_4S_4BF_4Co$: C, 21.99; H, 5.17%. The orange complex is soluble in methanol and CH_2Cl_2, but insoluble in water and diethyl ether. The brown complex is soluble in water, methanol, and CH_2Cl_2, but insoluble in diethyl ether.

Crystal Structure Determination. $[Co(S_2O)(dmpe)_2]ClO_4$. No single crystal suitable for X-ray analysis was obtained for $[Co(S_2O)(dmpe)_2]B(C_6H_5)_4$ (thin plates). The complex was stirred in water–methanol (1 : 1) with QAE-Sephadex A-25 (ClO_4^- form) for 2 h. The resulting orange solution was filtered and concentrated to nearly dryness under reduced pressure to yield orange crystals, which were recrystallized from hot methanol. Found: C, 25.89; H, 5.79%. Calcd for $[Co(S_2O)(dmpe)_2]ClO_4=C_{12}H_{32}O_5P_4S_2ClCo$: C, 26.75; H, 5.99%. Crystal data: monoclinic, $P2_1/n$, $a=14.702(3)$, $b=11.645(1)$, $c=14.333(2)$ Å, $\beta=109.90(2)°$, $V=2307.4(2)$ Å^3, $D_x=1.55$, $D_m=1.54(3)$ g cm^{-3}, $Z=4$, μ (Mo $K\alpha$)$=1.325$ mm^{-1}. A prismatic crystal of approximate dimensions 0.55×0.25×0.15 mm^3 was used for X-ray analysis. The intensities were measured with graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.71073$ Å) on a Rigaku four-circle diffractometer AFC-5. No absorption correction was applied. The calculations were carried out on a HITAC M-680H computer at the computer center of Institute for Molecular Science (Okazaki) with the program system UNICS III.[5] The structure was solved by the usual heavy-atom method; the position of the Co atom was deduced by a Patterson synthesis, and all the non-hydrogen atoms were located by a subsequent Fourier synthesis. The positions of all the hydrogen atoms were identified in subsequent difference-Fourier maps. The structure was refined by block-diagonal least-squares method with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogen atoms. The final R was 0.039 for 4542 reflections. The atomic parameters of non-hydrogen atoms are listed in Table 1.[6]

[Co(S₂PMe₂)₂(dmpe)]BF₄. Crystal data: orthorhombic, $Pnc2$, $a=13.383(3)$, $b=12.333(2)$, $c=13.742(3)$ Å, $V=2268.1(8)$ Å^3, $D_x=1.60$, $D_m=1.59(2)$ g cm^{-3}, $Z=4$, μ (Mo $K\alpha$)$=1.413$ mm^{-1}. A dark brown prismatic crystal with approximate dimensions $0.3\times0.4\times0.5$ mm^3 was used for X-ray analysis. Diffraction data were collected on a Rigaku AFC-5 diffractometer with Mo $K\alpha$ radiation up to $2\theta_{\max}=55°$ by the θ–2θ scan technique. 3445 independent reflections were measured, of which 2060 reflections were obtained with $|F_o|>3\sigma(|F_o|)$. Three standard reflections showed no significant intensity variation. The lattice constants were determined from 20 2θ values ($20<2\theta<30°$). The structure analysis was carried out on a FACOM M780/10 computer at Keio University. Absorption correction was made by a numerical-integration method (transmission factor, 0.606—0.694). Laue group mmm and systematic absences ($0kl$, $k+l$ odd; $hk0$, k odd) indicated the space group $Pn2b$ (a, −c, b setting of $Pnc2$, No. 30) or $Pnmb$ (b, a, −c setting of $Pmna$, No. 53). The reflection indices were transformed in subsequent calculations to accord with the standard cell setting of the space groups. Density of the crystal suggested $Z=4$. Assuming the centrosymmetric space group $Pmna$ and the Co atom on a twofold axis, the structure could not be solved. The Patterson function suggested that the Co atoms lie on twofold axes even in the space group $Pnc2$. The structure was solved utilizing the metal-ligand vectors observed in the Patterson function. For one of the two independent complex cations, there exists orientational disorder of the S_2PMe_2 ligands. Two possible sets of the positions for the S(01), S(02), and P(01) atoms were labeled as A and B, and the occupation factors were estimated to be 0.85 and 0.15, respectively, for the A and B sets. The disorder suggests that the $\Delta(\Lambda)$- and $\Lambda(\Delta)$-complexes lie on the Co(2) site with possibility of 85 and 15%, respectively, while the Co(1) site is occupied only by the $\Lambda(\Delta)$-complex. There exists complicated disorder of the BF_4 anions. The B(1) atom was located on a twofold axis and ten possible positions of F around B(1) were introduced in the refinement. The position of B(2) was not fixed on a twofold axis to avoid large thermal parameter, and six possible F positions around B(2) were considered. H atoms were not included in the refinement. The polar direction of the c axis could not be assigned, because the R factor was not significantly altered when the sign of $\Delta f''$ was changed from positive to negative. The function $\Sigma w||F_o|-|F_c||^2$ was minimized with $w^{-1}=\sigma^2(|F_o|)+(0.015|F_o|)^2$ by block-diagonal least squares. The final R was 0.075 for 2060 reflections. The number of parameters was 266. The structure model of $Pnc2$ cannot be transferred into that of the centrosymmetric space group $Pncm$ (bca setting of $Pmna$, No. 53), because a mirror plane perpendicular to the c-axis does not exist in the arrangement of the Co atoms, as can be seen from Fig. 5. On the other hand, the Co(1) and Co(2) complexes are approximately related to the center of symmetry at (1/4, 0, 3/8). If the inversion center was crystallographic, the space group $Pnc2$ became $Pnca$ (cab setting of $Pbcn$, No. 60), and additional systematic absences were caused: $hk0$, h odd. Among 132 $hk0$ reflections with h odd, 32 reflections were observed [$|F_o|>3\sigma(|F_o|)$]. The observations indicate that the structure model cannot be transferred into that of $Pnca$. The atomic parameters are listed in Table 2.[6]

Table 1. Positional Parameters ($\times10^4$) and Equivalent Isotropic Temperature Factors ($\times10$ Å^2) of $[Co(S_2O)(dmpe)_2]ClO_4$

Atom	x	y	z	B_{eq}
Co	2959.9(2)	2488.5(3)	6063.2(2)	20
Cl	8455.3(6)	2582.4(7)	6862.5(6)	44
S(1)	3303.4(5)	1469.9(6)	7509.3(5)	35
S(2)	3461.7(5)	3200.5(6)	7622.9(5)	31
P(1)	1402.9(5)	2494.4(5)	5962.6(5)	27
P(2)	2598.6(5)	4126.4(5)	5222.4(5)	26
P(3)	4487.2(5)	2482.0(5)	6044.6(5)	26
P(4)	2741.1(5)	1006.4(5)	4993.5(5)	26
O(1)	8629(2)	2739(3)	5959(2)	67
O(2)	9038(2)	1689(2)	7410(2)	78
O(3)	8735(3)	3611(3)	7403(2)	106
O(4)	7496(2)	2337(4)	6673(3)	118
O(5)	4480(1)	3592(2)	8005(2)	45
C(1)	692(2)	1196(3)	5797(3)	45
C(2)	1163(2)	3174(3)	6997(2)	42
C(3)	724(2)	3382(3)	4912(2)	37
C(4)	1303(2)	4459(3)	4942(2)	40
C(5)	2742(2)	4225(3)	4015(2)	37
C(6)	3164(2)	5441(3)	5832(2)	44
C(7)	5328(2)	1559(3)	6957(2)	36
C(8)	5197(2)	3775(3)	6130(2)	40
C(9)	4464(2)	1840(3)	4876(2)	35
C(10)	3864(2)	759(3)	4718(2)	38
C(11)	1846(2)	1049(3)	3753(2)	41
C(12)	2565(3)	−399(3)	5452(3)	49

Results and Discussion

A number of octahedral S_x^{2-} ($x=2-8$) complexes of Rh(III) and Ir(III) have been prepared by oxidative addition reactions of elemental sulfur to the respective planar Rh(I) and Ir(I) complexes.[1] In the reaction of sulfur with $[Co^{II}(dmpe)_2](BF_4)_2$, however, $[Co^{III}(S_2)(dmpe)_2]^+$ was not obtained, but $[Co^{III}(S_2O)(dmpe)_2]^+$ and $[Co^{III}(S_2PMe_2)_2(dmpe)]^+$ (vide infra) were isolated. No band indicative of the S_2^{2-} complex and no oxidation reaction were observed in the course of column chromatography. The S_2^{2-} complex might be air-sensitive and would be oxidized to the S_2O^{2-} one during the reaction and the treatment of the reaction mixtures. The S_2O^{2-} complex is stable in air. However, an orange CH_2Cl_2 solution of $[Co(S_2O)(dmpe)_2]ClO_4$ turned yellow immediately upon the addition of a stoi-

Table 2. Positional Parameters ($\times 10^4$) and Equivalent Isotropic Temperature Factors ($\times 10$ Å^2) of $[Co(S_2PMe_2)_2(dmpe)]BF_4$

Atom	x	y	z	B_{eq}	Occupancy
Co(1)	0	0	0[b)]	14	
Co(2)	5000	0	7430(2)	27	
S(1)	126(3)	1370(3)	1178(3)	35	
S(2)	1697(3)	−58(4)	102(3)	34	
S(01A)	4811(3)	−1459(3)	6278(3)	23	0.85
S(02A)	3250(2)	106(3)	7350(3)	20	0.85
P(1)	1611(3)	899(4)	1274(3)	36	
P(2)	−31(3)	−1236(3)	−1191(3)	26	
P(01A)	3415(3)	−892(4)	6167(4)	32	0.85
P(02)	5023(4)	1227(3)	8584(3)	32	
C(1)	1763(17)	67(20)	2513(14)	73	
C(2)	2548(9)	1961(11)	1267(13)	28	
C(3)	1028(11)	−2244(16)	−1188(18)	58	
C(4)	−1135(16)	−2149(23)	−1187(19)	85	
C(5)	46(20)	−504(12)	−2319(10)	54	
C(01)	3120(11)	−52(15)	5095(9)	37	
C(02)	2637(18)	−2240(28)	6329(32)	102	
C(03)	3970(15)	2029(15)	8728(16)	53	
C(04)	6011(13)	2171(15)	8735(19)	52	
C(05)	5449(15)	382(29)	9757(13)	99	
B(1)[a)]	0	5000	−40(16)	27	
B(2)[a)]	5256(34)	4847(47)	7322(32)	54	0.5
S(01B)[a)]	5344(19)	−1498(22)	6234(25)	37	0.15
S(02B)[a)]	3215(16)	−219(16)	7220(15)	21	0.15
P(01B)[a)]	6590(11)	−893(12)	6140(11)	4	0.15
F(B1)1[a)]	846(23)	4526(26)	555(23)	39	0.3
F(B1)2[a)]	788(23)	5195(26)	428(25)	45	0.3
F(B1)3[a)]	102(26)	4796(20)	−997(16)	28	0.3
F(B1)4[a)]	373(26)	5214(29)	−959(28)	26	0.2
F(B1)5[a)]	926(27)	4205(29)	29(29)	26	0.2
F(B1)6[a)]	732(31)	5737(33)	417(31)	31	0.2
F(B1)7[a)]	63(45)	5977(42)	433(38)	53	0.2
F(B1)8[a)]	1132(66)	5677(71)	−445(65)	36	0.1
F(B1)9[a)]	657(64)	4724(66)	−960(66)	36	0.1
F(B1)10[a)]	84(51)	4365(46)	−920(43)	14	0.1
F(B2)1[a)]	5519(19)	5863(21)	7209(19)	67	0.5
F(B2)2[a)]	4427(20)	5799(20)	6981(19)	67	0.5
F(B2)3[a)]	5623(39)	5431(39)	6840(35)	89	0.3
F(B2)4[a)]	5432(37)	5727(40)	8123(36)	82	0.3
F(B2)5[a)]	5472(46)	4140(52)	7863(45)	65	0.2
F(B2)6[a)]	5806(36)	5018(47)	7584(42)	57	0.2

a) The atoms refined isotropically. b) This parameter was used to define the origin of the unit cell along z and is listed without esd.

chiometric amount of an oxidizing agent such as *m*-chloroperbenzoic acid. Although the yellow species would be a $S_2O_2^{2-}$ complex, it was unstable and could not be isolated.

For the formation of $[Co(S_2PMe_2)_2(dmpe)]^+$, the P–C bond cleavage of dmpe must take place. Details concerning this reaction are unknown at present. This dimethyldithiophosphinato complex is stable in the solid state and in water and common organic solvents.

The XPS spectrum of $[Co(S_2O)(dmpe)_2]ClO_4$ shows two kinds of peaks in the S-2p binding energy region. The chemical shifts of the binding energy of core-electrons reflect the oxidation state or the net charge of an atom. Thus the higher energy peak (165.26 eV) can be assigned to the oxidized central sulfur atom of the S_2O group and the lower energy peak (162.98 eV) to the terminal sulfur one. The S-2p binding energy of $[Co(S_2PMe_2)_2(dmpe)]BF_4$ (162.55 eV) is similar to that of $[Co(S_2CNMe_2)(NH_2CH_2CH_2NH_2)_2](ClO_4)_2$ (162.7 eV).[7)] The phosphorus atoms of $S_2PMe_2^-$ and dmpe in the present two complexes give similar chemical shifts in the P-2p energy region: a broad peak at 131.87 eV of $[Co(S_2PMe_2)_2(dmpe)]BF_4$ and a peak at 131.68 eV of $[Co(S_2O)(dmpe)_2]ClO_4$. Thus, these phosphorus atoms are suggested to have similar net charges. The Co-2p binding energy of the S_2O complex (780.34 eV) is a little higher than that of the S_2PMe_2 complex (779.98 eV). These Co-2p binding energies are within those of the region of Co(III) complexes (778—782 eV).[8)]

The absorption spectrum of $[Co(S_2O)(dmpe)_2]^+$ in the d–d transition energy region (15000—24000 cm^{-1}) is similar to that of $[Co(S_2CNMe_2)(dmpe)_2]^{2+}$,[9)] as shown in Fig. 1. The S_2O complex shows a new band at 28500 cm^{-1}, which can be assigned to an intraligand transition of the S_2O moiety or a ligand(S_2O)-to-metal(Co) charge-transfer. The similarity in the spectral pattern between the S_2O and dimethyldithiocarbamato complexes also suggests the oxidation state of Co(III)–S_2O^{2-}.

Although the absorption spectral pattern of $[Co(S_2PMe_2)_2(dmpe)]^+$ is similar to that of $[Co(S_2CNMe_2)_2(dmpe)]^+$,[9)] in the d-d band region, the spectrum of the former complex is shifted to the lower energy side than that of the latter one (Fig. 2). The

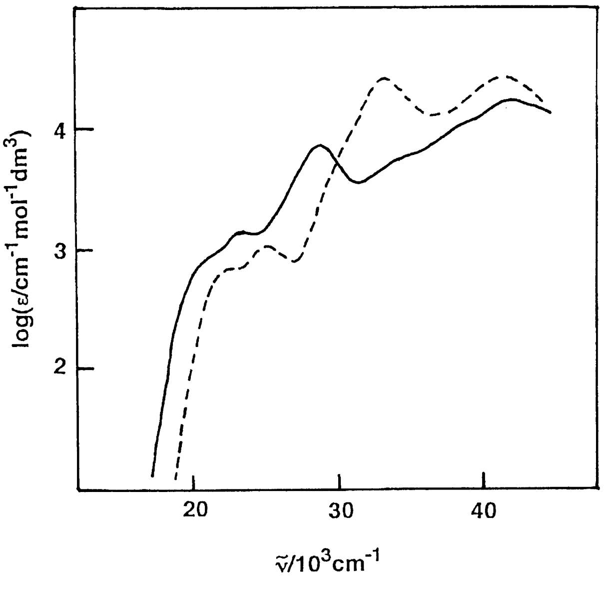

Fig. 1. Absorption spectra of $[Co(S_2O)(dmpe)_2]ClO_4$ (—) and $[Co(dtc)(dmpe)_2](BF_4)_2$ (---) in CH_3CN solution.

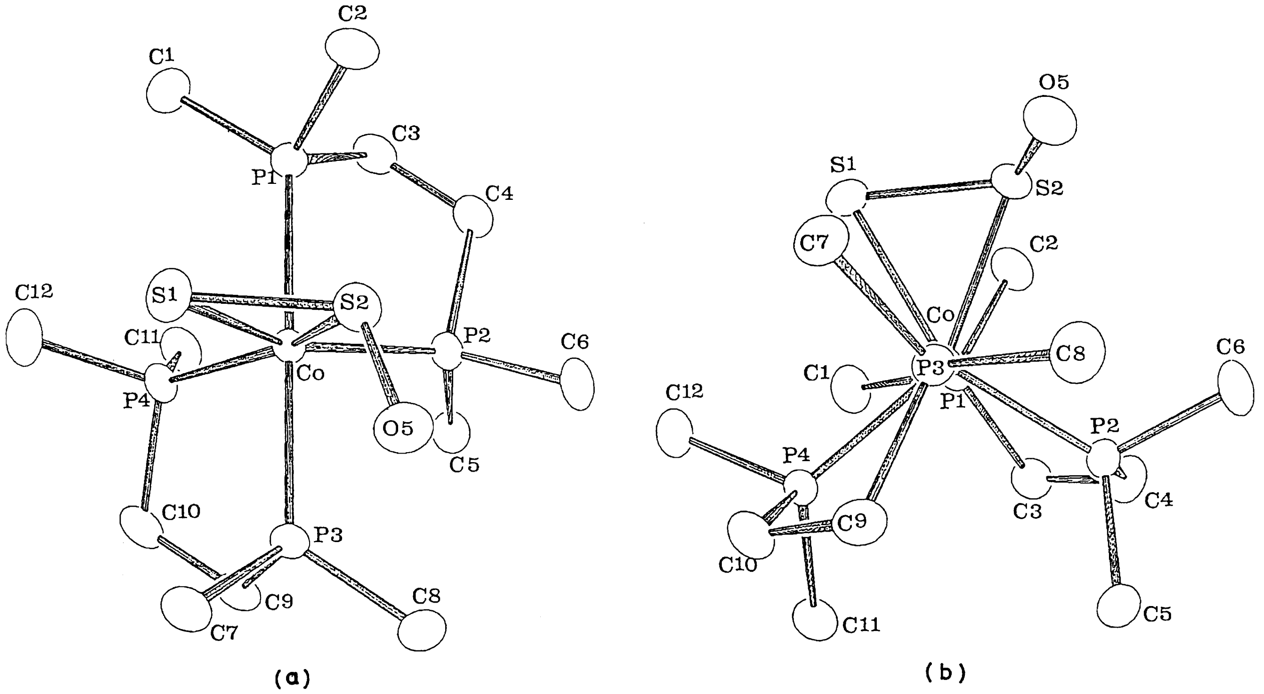

Fig. 3. Perspective views of $[Co(S_2O)(dmpe)_2]^+$.

ligand field strength of $S_2PMe_2^-$ should be less than that of $S_2CNMe_2^-$. The first d–d band of analogous $[Co(S_2PPh_2)_3]$ is also observed at lower energy (13000 cm^{-1})[10] than that of $[Co(S_2CNMe_2)_3]$ (15300 cm^{-1}).[7]

The ^1H NMR spectra of the S_2O and S_2PMe_2 complexes were measured, but signals are complicated and could not be analyzed.

Crystal Structure of $[Co(S_2O\text{-}S,S')(dmpe)_2]ClO_4$. Perspective views of the complex ion are shown in Fig. 3. The selected bond distances and angles are listed in Table 3. The S_2O group is coordinated to the Co ion via both sulfur atoms, in the side-on mode. The two Co–S bond lengths differ apparently; the Co–S(2) bond (2.290(1) Å) bonded to the oxygen atom is longer than the terminal Co–S(1) one (2.260(1) Å). The S(2) atom has a pyramidal geometry. The S–S–O angle of 114.2(1)° is similar to that (118°) of the disulfur monoxide S_2O molecule.[11] The S(1)–S(2) bond distance of 2.029(1) Å is similar to that of elemental sulfur S_8 (2.06 Å),[11] and is much longer than that of the S_2O molecule (1.882 Å),[11] the length of which is almost the same as that of the S_2 molecule (1.89 Å).[11] Thus, the S–S bond of coordinated S_2O can be regarded as being a single bond, while the S–S bond of the S_2O molecule as a double bond. The coordinated S_2O group can be considered as S_2O^{2-} and the Co atom as Co(III) as indicated by the absorption and XPS spectra of $[Co(S_2O)(dmpe)_2]^+$. Mononuclear complexes containing S_2O-*S,S'* are known for Ir,[12] Mn,[13] and Nb,[14] and an X-ray structure analysis has been reported for the Mn complex.[13] The bond distances and bond angles of the S_2O^{2-} and those of the related complexes are listed in Table 4. The Mn–S_2O moiety is very similar to the Co–S_2O one in the structural parameters, and the Mn metal may be regarded as Mn(III).

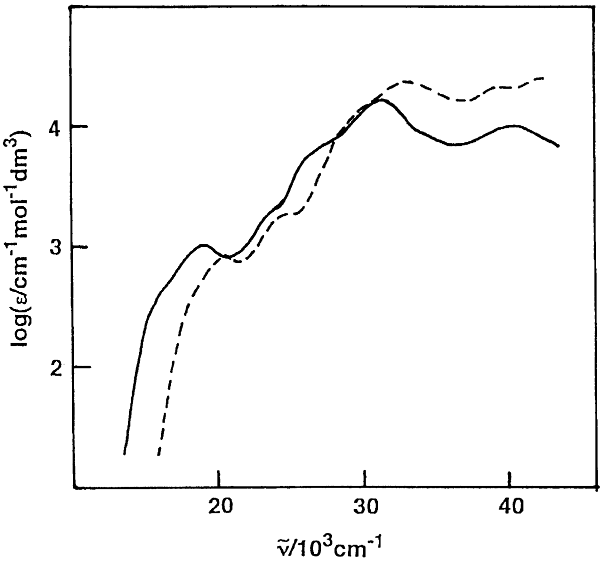

Fig. 2. Absorption spectra of $[Co(S_2PMe_2)_2(dmpe)]BF_4$ (—) and $[Co(dtc)_2(dmpe)]BF_4$ (- - -) in CH_3CN solution.

The S(2) atom is chiral and has a *R*(*S*) configuration in the $\Delta(\Lambda)$-complex. The stereospecific configuration of the S(2) atom appears to arise from the difference in magnitude of the steric repulsion between the P-methyl groups (C(2) or C(7)) and the oxygen atom (O(5)) as shown in Fig. 3b.

The coordination geometry around the Co(III) ion is very similar to that in $[Co(O_2)(dmpe)_2]B(C_6H_5)_4$.[4]

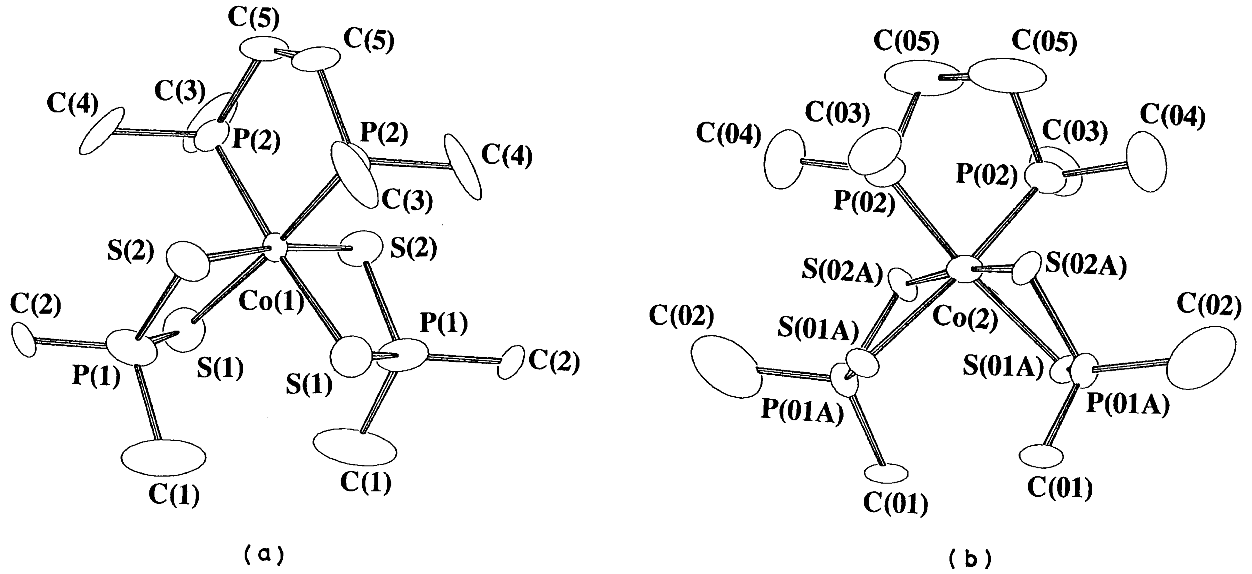

Fig. 4. Perspective views of $[Co(S_2PMe_2)_2(dmpe)]^+$.

Table 3. Bond Distances (l/Å) and Angles (ϕ/°) of $[Co(S_2O)(dmpe)_2]ClO_4$

Co–S(1)	2.290(1)	Co–S(2)	2.260(1)
Co–P(1)	2.244(1)	Co–P(2)	2.222(1)
Co–P(3)	2.255(1)	Co–P(4)	2.258(1)
S(1)–S(2)	2.029(1)	S(2)–O(5)	1.480(2)
P(1)–C(1)	1.807(3)	P(1)–C(2)	1.818(4)
P(1)–C(3)	1.819(3)	P(2)–C(4)	1.818(4)
P(2)–C(5)	1.817(3)	P(2)–C(6)	1.818(3)
P(3)–C(7)	1.815(3)	P(3)–C(8)	1.812(3)
P(3)–C(9)	1.824(3)	P(4)–C(10)	1.846(4)
P(4)–C(11)	1.817(3)	P(4)–C(12)	1.815(3)
C(3)–C(4)	1.509(4)	C(9)–C(10)	1.509(4)
S(1)–Co–S(2)	52.96(3)	S(1)–Co–P(1)	88.03(3)
S(1)–Co–P(2)	150.91(3)	S(1)–Co–P(3)	95.47(3)
S(1)–Co–P(4)	98.93(3)	S(2)–Co–P(1)	92.57(4)
S(2)–Co–P(2)	99.14(3)	S(2)–Co–P(3)	91.25(3)
S(2)–Co–P(4)	151.09(3)	P(1)–Co–P(2)	84.97(3)
P(1)–Co–P(3)	175.90(3)	P(1)–Co–P(4)	93.00(3)
P(2)–Co–P(3)	92.96(3)	P(2)–Co–P(4)	109.60(3)
P(3)–Co–P(4)	84.35(3)	Co–S(1)–S(2)	62.75(3)
Co–S(2)–S(1)	64.29(3)	Co–S(2)–O(5)	115.3(1)
S(1)–S(2)–O(5)	114.2(1)	Co–P(1)–C(1)	122.5(1)
Co–P(1)–C(2)	115.2(1)	Co–P(1)–C(3)	103.7(1)
C(1)–P(1)–C(2)	102.0(2)	C(1)–P(1)–C(3)	103.7(1)
C(2)–P(1)–C(3)	102.9(2)	Co–P(2)–C(4)	109.6(1)
Co–P(2)–C(5)	119.2(1)	Co–P(2)–C(6)	118.5(1)
C(4)–P(2)–C(5)	103.0(1)	C(4)–P(2)–C(6)	101.4(2)
C(5)–P(2)–C(6)	102.8(2)	Co–P(3)–C(7)	115.5(1)
Co–P(3)–C(8)	102.0(1)	Co–P(3)–C(9)	107.8(1)
C(7)–P(3)–C(8)	102.0(1)	C(7)–P(3)–C(9)	102.4(1)
C(8)–P(3)–C(9)	103.4(2)	Co–P(4)–C(10)	109.5(1)
Co–P(4)–C(11)	122.2(1)	Co–P(4)–C(12)	116.6(1)
C(10)–P(4)–C(11)	101.4(2)	C(10)–P(4)–C(12)	100.7(2)
C(11)–P(4)–C(12)	103.5(1)	P(1)–C(3)–C(4)	107.7(2)
P(2)–C(4)–C(3)	111.2(2)	P(3)–C(9)–C(10)	107.8(2)
P(4)–C(10)–C(9)	111.0(2)		

However, the Co–P(4) and other three Co–P bonds in the S_2O^{2-} complex are longer, respectively, by ca. 0.04 and ca. 0.02 Å than the corresponding ones in the O_2^{2-} complex. Thus, the trans influence of the central sulfur atom of the S_2O group is larger than that of the terminal sulfur, and seems to have a similar strength to that of the phosphino groups.

Crystal Structure of $[Co(S_2PMe_2)_2(dmpe)]BF_4$. Perspective views of the two crystallographically independent complexes are shown in Fig. 4. The crystal structure is given in Fig. 5. The bond distances and angles of the complex ion are listed in Table 5. The Co atoms lie on two fold axes along c. The Co(1) complex ion is not disordered but the Co(2) complex ion is done to be $85\Delta(\Lambda):15\Lambda(\Delta)$. Although the crystal consists of three kinds of complex ions, their structures

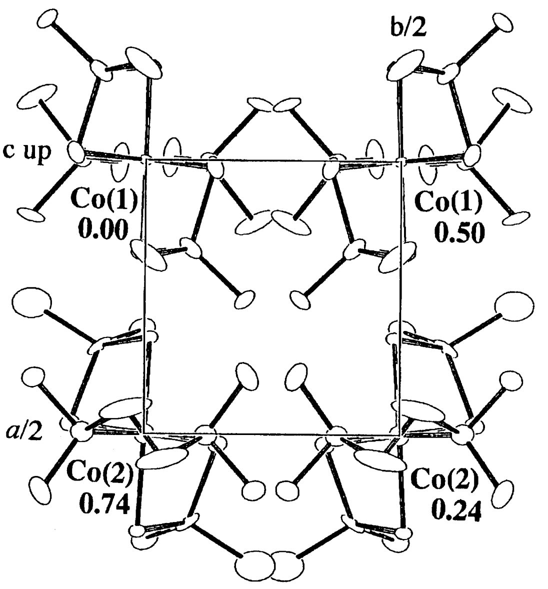

Fig. 5. Crystal packing of $[Co(S_2PMe_2)_2(dmpe)]BF_4$.

Table 4. Selected Bond Distances (l/Å) and Angles (ϕ/°) of $[Co(S_2O)(dmpe)_2]^+$ and Its Related Complexes

Complex	S–S	M–S	S–M–S
$[Co(S_2O\text{-}S,S')(dmpe)_2]^+$	2.029(1)	2.260(1)$^{a)}$ 2.290(1)$^{b)}$	52.96(3)
$[Mn(\eta^5\text{-}C_5Me_5)(S_2O\text{-}S,S')(CO)_2]^{c)}$	2.013(8)	2.328(5)$^{a)}$ 2.400(5)$^{b)}$	50.4(2)
$[Ir(S_2)(dppe)_2]^{+,\ d)}$	2.066(6)	2.406(5)	50.8(2)
$[Ir(S_2O_2\text{-}S,S')(dppe)_2]^{+,\ e)}$	2.041	2.407	50.2

a) $\underline{\mathrm{S}}$–S–O. b) S–$\underline{\mathrm{S}}$–O. c) Ref. 13. d) dppe=$Ph_2PCH_2CH_2PPh_2$, W. D. Bonds and J. A. Ibers, *J. Am. Chem. Soc.*, **94**, 3413 (1972). e) G. Schmid and G. Ritter, *Chem. Ber.*, **108**, 3008 (1975).

Table 5. Bond Distances (l/Å) and Angles (ϕ/°) of $[Co(S_2PMe_2)_2(dmpe)]BF_4$

Co(1)–S(1)	2.346(4)	Co(1)–S(2)	2.277(4)
Co(1)–P(2)	2.237(4)	Co(2)–S(01A)	2.410(4)
Co(2)–S(02A)	2.348(3)	Co(2)–P(02)	2.192(4)
Co(2)–S(01B)	2.515(30)	Co(2)–S(02B)	2.421(21)
S(1)–P(1)	2.075(6)	S(2)–P(1)	2.000(6)
S(01A)–P(01A)	2.001(6)	S(02A)–P(01A)	2.051(7)
S(02B)$^{b)}$–P(01B)	2.038(25)	P(1)–C(1)	1.998(21)
P(1)–C(2)	1.813(14)	P(2)–C(3)	1.885(18)
P(2)–C(4)	1.858(25)	P(2)–C(5)	1.797(15)
P(01A)–C(01)	1.844(16)	P(01A)–C(02)	1.974(32)
P(02)–C(03)	1.733(20)	P(02)–C(04)	1.774(19)
P(02)–C(05)	2.002(25)	S(01B)–P(01B)	1.831(30)
C(5)–C(5$^{a)}$)	1.249(30)	C(05)–C(05$^{b)}$)	1.527(54)
S(1)–Co(1)–S(2)	87.4(1)	C(1)–P(1)–C(2)	107.8(8)
S(1)–Co(1)–P(2)	175.5(1)	Co(1)–P(2)–C(3)	115.7(6)
S(1)–Co(1)–P(2$^{a)}$)	90.7(1)	Co(1)–P(2)–C(4)	115.2(8)
S(2)–Co(1)–P(2)	92.4(2)	Co(1)–P(2)–C(5)	106.7(5)
S(01A)–Co(2)–S(02A)	84.6(1)	C(3)–P(2)–C(4)	101.4(9)
S(01A)–Co(2)–P(02)	172.8(1)	C(3)–P(2)–C(5)	106.9(7)
S(01A)–Co(2)–P(02$^{b)}$)	87.6(1)	C(4)–P(2)–C(5)	110.7(9)
S(02A)–Co(2)–P(02)	90.5(1)	S(01A)–P(01A)–S(02A)	104.5(3)
S(01B)–Co(2)–S(02B)	91.2(9)	S(01A)–P(01A)–C(01)	117.2(5)
S(01B)–Co(2)–P(02)	167.7(7)	S(01A)–P(01A)–C(02)	100.9(10)
S(01B)–Co(2)–P(02$^{b)}$)	88.2(7)	S(02A)–P(01A)–C(01)	105.8(5)
S(02B)–Co(2)–P(02)	100.2(5)	S(02A)–P(01A)–C(02)	111.1(10)
Co(1)–S(1)–P(1)	84.9(2)	C(01)–P(01A)–C(02)	116.8(11)
Co(1)–S(2)–P(1)	88.5(2)	Co(2)–P(02)–C(03)	117.7(7)
Co(2)–S(01A)–P(01A)	83.5(2)	Co(2)–P(02)–C(04)	123.2(6)
Co(2)–S(02A)–P(01A)	84.0(2)	Co(2)–P(02)–C(05)	103.1(7)
Co(2)–S(01B)–P(01B)	85.0(12)	C(03)–P(02)–C(04)	102.6(9)
Co(2)–S(02B$^{b)}$)–P(01B)	83.4(8)	C(03)–P(02)–C(05)	115.9(10)
S(1)–P(1)–S(2)	99.7(2)	C(04)–P(02)–C(05)	92.0(9)
S(1)–P(1)–C(1)	107.2(6)	S(01B)–P(01B)–S(02B$^{b)}$)	109.8(12)
S(1)–P(1)–C(2)	117.4(5)	P(2)–C(5)–C(5$^{a)}$)	119.6(12)
S(2)–P(1)–C(1)	112.2(7)	P(02)–C(05)–C(05$^{b)}$)	95.6(14)
S(2)–P(1)–C(2)	112.5(5)		

Symmetry code: a) $-x$, $-y$, z. b) : $1-x$, $-y$, z.

are essentially the same to form a distorted octahedron. The dmpe ligand takes a gauche conformation, and the structural parameters are nearly the same as those of dmpe found in the above S_2O^{2-} complex, $[Co(dmpe)(en)_2]^{3+}$,[15] and $[Co(dtc)(dmpe)_2]^{2+}$.[16] Recently, the crystal structure of $[Cr(S_2PMe_2)_3]$ was reported[17] and its S–P bond length (av 2.010(2) Å) and S–P–S angle (av 106.23(7)°) are almost the same as those of the present Co(III) complex.

The differences in bond distances between the Co(1)–S(1) (2.346(4) Å) and Co(1)–S(2) (2.277(4) Å), between Co(2)–S(01A) (2.410(4) Å) and Co(2)–S(02A) (2.348

(3) Å), and between Co(2)–S(01B) (2.515(30) Å) and Co(2)–S(02B) (2.421(21) Å) are attributable to a trans influence induced by dmpe. The average Co–S bond distance in the $S_2PMe_2^-$ complex (2.386 Å) is significantly longer than those in $[Co(dtc)(dmpe)_2](BF_4)_2$16) (av 2.275(2) Å) and $[Co(pipdtc)\{P(OMe)_3\}_4](BF_4)_2$18) (av 2.288(3) Å, pipdtc = piperidyldithiocarbamate). The longer Co–S bond in the $S_2PMe_2^-$ complex than that in the $S_2CNMe_2^-$ is in line with that $S_2PMe_2^-$ has weaker ligand field strength than $S_2CNMe_2^-$ as seen in the absorption spectra in Fig. 2.

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