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Syntheses, Structure, and Properties of Several Bis(*O,O'*-dialkyl dithiophosphato)cobalt(II) Adducts[1)]

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Several amine or phosphine adducts of bis (*O,O'*-dialkyl dithiophosphato)cobalt(II), which were hardly oxidized in air at room temperature, were obtained as crystalline solids. The crystal and molecular structure of one adduct, $Co(Me_2dtp)_2$(triphenylphosphine) (Me_2dtp= *O,O'*-dimethyl dithiophosphato group), was determined by means of the X-ray diffraction method. The crystal is monoclinic: space group $P2_1/n$, $a=26.712(4)$, $b=9.495(1)$, $c=11.180(5)$ Å, $\beta=95.43(3)°$, $Z=4$, $D_x=1.495$, $D_m=1.45$ g cm^{-3}, μ(Mo $K\alpha$)$=1.17$ mm^{-1}, and the final R value obtained is 0.062 for 4466 observed reflections. The coordinated atoms around the cobalt atom are in a trigonal bipyramidal configuration. The approximate first formation constants of the adducts, $K=[Co(II)(R_2dtp)_2\cdot X]/\{[Co(II)(R_2dtp)_2][X]\}$ (R=alkyl group, and X=donor) in solution, were obtained by means of the spectrophotometric as well as the NMR technique.

Dithioacid ions, such as *N,N*-dialkyl dithiocarbamate, *O*-alkyl dithiocarbonate, and *O,O'*-dialkyl dithiophosphate ions, are able to make four-membered chelates with 3d transition metals. Among them, the *O,O'*-dialkyl dithiophosphato chelates have various properties different from those of common Werner-type complexes. For example, bis(*O,O'*-diethyl dithiophosphato)nickel(II) (abbreviated as $Ni(II)(Et_2dtp)_2$ hereafter; the related complexes are also shown by the same type of abbreviation) is typical, and many studies have already been published about the complex itself as well as its adducts.[2—5)] On the other hand, only a few publications are to be found about $Co(II)(Et_2dtp)_2$, although Cavell and others[6)] have reported the isolation of $Co(II)(Et_2dtp)_2$, and Jørgensen[7,8)] claimed the formation of its ethanol adducts in solution. This is probably because of the low stability of the complex. By way of studying sulfur-coordinated metal complexes, we found that, contrary to $Co(II)(R_2dtp)_2$ (R=alkyl group), some amine or phosphine adducts of them were very stable when once obtained in their solid state; they could be kept in air at room temperature for many months without any decomposition or air-oxidation.

As $Co(II)(Et_2dtp)_2$ is in a tetrahedral configuration, the geometry of the originally bonded Et_2dtp must be seriously affected by the formation of its adducts, while in the case of $Ni(II)(Et_2dtp)_2$, which is originally in a square planar form, the positions of the ligands are not much moved by the coordination of additional ligands. The adduct of the $Co(II)(R_2dtp)_2\cdot X_n$ type (where X= donor) will exhibit either a trigonal bipyramidal or a square pyramidal coordination around the central metal atom. In order to elucidate the geometry of the adduct, we have determined the crystal and molecular structure by means of the X-ray diffraction method.

Although the $Co(II)(R_2dtp)_2\cdot X_n$ adducts ($n=1$ or 2) are very stable in their solid states, they are easily hydrolyzed with water and are turned into hexaaquacobalt(II) ions in a dilute aqueous solution. The R_2dtp ligands are bonded strongly to the cobalt(II) atom in the complexes in a non-polar organic solvent, although a rapid broadening of the R_2dtp alkyl proton peak due to the ligand-exchange reaction between the two chelates is observed in their NMR spectra when the cobalt(II) complexes or their adducts in solution are added to a solution of the R_2dtp complexes of other diamagnetic metal ions, such as zinc(II) or cadmium(II).

On the other hand, the donor, X, of the $Co(II)(R_2dtp)_2\cdot X$ adduct is shown to be labile in an organic solvent, and the equilibrium,

$$Co(II)(R_2dtp)_2 + X = Co(II)(R_2dtp)_2\cdot X$$

is attained soon after they are dissolved. Therefore, when more of the donor is added to a solution of the adduct, it shows more resistivity to air-oxidation. A quantitative study of the equilibrium will be presented in the later part of this paper.

Experimental

Synthesis of Adducts. All the chemicals used were GR-grade from Wako Pure Chemicals Co., Ltd., and were used without any further purification. The $Co(II)(R_2dtp)_2\cdot X_n$ ($n=1$ or 2) were synthesized as follows.

Synthesis of Co(II)(Et₂dtp)₂(hexamethylenetetramine). The benzene solution of cobalt(II)$(Et_2dtp)_2$ was obtained by extracting it from a mixture of cobalt(II) chloride hexahydrate (0.7 g, 3 mmol) and $Na(Et_2dtp)$ (1.2 g, 6 mmol) in a concentrated aqueous solution with benzene. After the addition of an excess of hexamethyleneteramine (0.9 g, 6.4 mmol), the obtained mixture was stirred for several min, after which the supernatant fluid was separated and evaporated by the use of a vacuum rotary evaporator. From the residue, the adduct was extracted with a hot mixture of benzene and ligroine (1/1=v/v); crystals came out when it was cooled. Found: Co, 10.27; C, 29.74; H, 5.69; N, 10.01%. Calcd for $CoC_{14}H_{32}O_4P_2S_4$: Co, 10.35; C, 29.52; H, 5.66; N, 9.84%. Yield, 1.3 g (77%).

Synthesis of Co(II)(Et₂dtp)₂(triphenylphosphine). Six tenth of a gram (2.5 mmol) of cobalt(II) chloride hexahydrate, 1.1 g

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(5.4 mmol) of Na(Et_2dtp), about 20 cm^3 of a benzene solution containing 1.5 g (5.7 mmol) of triphenylphosphine, and 1 cm^3 of water were mixed and stirred for several min, after which benzene layer was separated and dried with anhydrous sodium sulfate. The solution was evaporated, and the residue was recrystallized from ligroine. Found: Co, 8.52; C, 45.24; H, 5.10%. Calcd for $CoC_{26}H_{35}O_4P_3S_3$: Co, 8.52; C, 45.15; H, 5.10%. Yield, 1.1 g (64%).

Synthesis of Co(II)(Me_2dtp)$_2$(triphenylphosphine) (Where Me=CH_3). This complex was synthesized in almost the same way as the Co(II)(Et_2dtp)$_2$(triphenylphosphine) described above by using 0.6 g (2.5 mmol) of cobalt(II) chloride hexahydrate and 0.9 g (3.0 mmol) of Na(Me_2dtp). As the complex is more sensitive to air oxidation than Et_2dtp derivative, it was recrystallized from benzene–hexane (1/1=v/v) mixed solvent under a nitrogen atmosphere. Found: Co, 9.20; C, 41.16; H, 4.27%. Calcd for $CoC_{22}H_{27}O_4P_3S_3$: Co, 9.27; C, 41.58; H, 4.29%. Yield 0.8 g (50%).

Synthesis of Cobalt(II)(Et_2dtp)$_2$(benzothiazole)$_2$. This adduct was synthesized in the same way as was used for the triphenylphosphine adduct of Co(II)(Et_2dtp)$_2$, starting from 0.47 g (2 mmol) of cobalt(II) chloride hexahydrate, 0.83 g (4 mmol) of Na(Et_2dtp), and 0.81 g (6 mmol) of benzothiazole. Recrystallized from ligroine. Found: Co, 8.41; C, 37,82; H, 4.33; N, 3.96%. Calcd for $CoC_{22}H_{30}O_4N_2P_2S_6$: Co, 8.42; C, 37.76; H, 4.32; N, 4.00%. Yield, 0.75 g (54%).

Synthesis of Co(II)(Et_2dtp)$_2$(benzothiazole). This adduct was obtained by the same method as was the bis adduct described above, except that a lower molar ratio of benzothiazole to cobalt(II) chloride was employed. For example, from 0.7 g (3 mmol) of cobalt(II) chloride hexahydrate, 1.25 g (6 mmol) of Na(Et_2dtp), and 0.81 g (6 mmol) of benzothiazole, the mono-adduct was obtained as a blue green solid in a low yield. From the mother liquor, the bis-adduct was obtained, too. Found: Co, 10.34; C, 32.03; H, 4.47; N, 2.48%. Calcd for $CoC_{15}H_{25}NP_4S_5$: Co, 10.44; C, 31.91; H, 4.46; N, 2.48%. Yield, 0.4 g (24%).

Synthesis of Co(II)(Et_2dtp)$_2$(benzimidazole). The crude product was obtained by mixing and stirring 0.95 g (4 mmol) of cobalt(II) chloride hexahydrate, 1.7 g (8 mmol) of Na(Et_2dtp), about 10 cm^3 of an acetone solution containing 0.9 g (8 mmol) of benzimidazole, 20 cm^3 of benzene, and 1 cm^3 of water, and by then evaporating the fluid. The residue containing the crude adduct was recrystallized from benzene. Found: Co, 8.64; C, 39.86; H, 4.85; N, 8.44%. Calcd for $CoC_{22}O_4N_4P_2S_4$: Co, 8.85; C, 39.70; H, 4.85; N, 8.42%. Yield, 1.6 g (73%).

Synthesis of Co(II)(Et_2dtp)$_2$(piperazine). This adduct was synthesized, using 2-propanol in place of benzene as the solvent, by means of the method used for the benzimidazole adduct mentioned above. We started with 0.71 g (3 mmol) of cobalt(II)chloride hexahydrate, 1.25 g (6 mmol) of Na(Et_2dtp), and 0.5 g (6 mmol) of piperazine. Recrystallized from ligroine. Found: Co, 11.57; C, 27.85; H, 5.76; N, 5.43%. Calcd for $CoC_{12}H_{30}O_4N_2P_2S_4$: Co, 11.43; C, 27.96; H, 5.87; N, 5.43%. Yield, 0.95 g (62%).

Synthesis of Co(II)(Et_2dtp)$_2$(pyrazine). To about 20 cm^3 of a benzene solution containing 0.16 g (2 mmol) of pyrazine, 1 cm^3 of water, 0.4 g (2 mmol) of Na(Et_2dtp), and 0.24 g (1 mmol) of cobalt(II) chloride hexahydrate were added, after which the mixture was stirred for several min. The adduct was then precipitated, filtered, and washed with water. Recrystallized from the benzene–ligroine mixture (1/1=v/v). Found: Co, 11.50; C, 28.30; H, 4.73; N, 5.49%. Calcd for $CoC_{12}H_{24}O_4N_2P_2S_4$: Co, 11.57; C, 28.29; H, 4.75; N, 5.50%. Yield, 0.7 g (69%).

Attempt to Synthesize the 4,4′-Bipyridine Adduct of Co(II)(Et_2dtp)$_2$. Although many kinds of synthetic techinques have been applied to obtain the adduct, they have not been successful. It was found that the addition of 4,4′-bipyridine to a solution of Co(II)(Et_2dtp)$_2$ rather accelerated the air oxidation of the complex.

X-Ray Measurement. The single crystal of bis(*O,O′*-dimethyl dithiophosphato)(triphenylphosphine)cobalt(II) used for the X-ray measurement was a parallelepiped $0.28\times 0.35\times 0.39$ mm^3 in size. All the edges of the crystal were ground off beforehand. The crystallographic data are: $CoC_{22}H_{27}O_4P_3S_4$, F. W.=635.55, monoclinic, space group $P2_1/n$,** $a=26.712(4)$, $b=9.495(1)$, $c=11.180(5)$ Å, $\beta=95.43(3)°$, $Z=4$, $D_x=1.495$, $D_m=1.45$ g cm^{-3}, μ(Mo $K\alpha$)=1.17 mm^{-1}. The reflections within the range of $2\theta<55°$ were collected on a Rigaku automated four-circle diffractometer, with Mo $K\alpha$ radiation (0.7107 Å), the ω scan technique being employed. In total, 4466 independent reflections with $|F_o|>3\sigma(|F_o|)$ among the 6819 measured ones were used for the structure refinement. The intensities were corrected for Lorentz and polarization factors, but no correction was made for absorption and extinction. No decrease in the intensities attributable to the decomposition of the sample was recognized during the intensity measurement.

The calculations were mainly carried out on the FACOM 230-48 computer at The Institute for Solid State Physics, The University of Tokyo, but a part of them were done on the HITAC 8800/8700 computer at The Computer Center of The University of Tokyo, using the local version of the UNICS program.[9] The atomic-scattering factors were taken from the tables.[10]

Structure Determination. The structure was solved by the heavy-atom method. The positions of the Co, P, and S atoms were deduced from three-dimensional Patterson maps, while all the other non-hydrogen atoms were located by successive Fourier syntheses. Their positional and thermal parameters were refined by the block-diagonal least-squares method. Then the positions of all the hydrogen atoms, except one, were obtained from a difference Fourier synthesis, they were also refined. The coordinates of the H atom, H(1-2), that could not be located by the difference synthesis, was supplied by calculation. The isotropic temperature factor of 10.0 $Å^2$ was assumed for it. Anisotropic temperature factors were assumed for all non-hydrogen atoms. In the last cycle of the refinement, all the parameter shifts were less than one-third of the corresponding standard deviations. The final *R* value was 0.062 for 4466 reflections.[11]

Other Measurements. The megnetic moments of the solid products were measured using a Gouy balance at room temtemperature (20—15 °C).

The infrared absorption spectra were obtained by a Nujol and hexachloro-1,3-butadiene mull procedure using a 403G-type infrared spectrophotometer of JASCO, Ltd.

The visible spectra were recorded on Hitachi EPS-3- and Hitachi 124-type spectrophotometers. The reflectance spectra of the solid adducts were measured by a Hitachi 124-type spectrophotometer using an attachment. The temperatures of the sample solution and of the cell chamber were kept constant by circulating thermostated water through using a Haake F 4391 thermostat.

The ^{1}H-NMR spectra were obtained using a JEOL JNM-MH-100 (100 MHz) NMR spectrometer (TMS as the internal standard).

** The systematic absence of the reflections were those of $0k0$ (where k=odd) and those of $h0l$ (where $h+l$=odd).

TABLE 1. FINAL ATOMIC COORDINATES ($\times 10^4$ FOR NON-HYDROGEN ATOMS, AND $\times 10^3$ FOR HYDROGEN ATOMS) AND ISOTROPIC TEMPERATURE FACTORS (B/Å^2), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	B_{eq}/Å^2 a)	Atom	x	y	z	B_{iso}/Å^2
Co	1455.9(3)	2253.9(7)	4684.1(7)	3.99	H(1-1)	137(3)	−81(10)	916(8)	12.5(27)
S(1)	1766.1(6)	118(2)	5453(2)	5.82	H(1-2)	169	−107	804	10.0
S(2)	648.0(6)	1361(2)	5507(2)	5.15	H(1-3)	127(3)	−198(8)	819(6)	8.4(19)
S(3)	1447.4(5)	4320(1)	5810(1)	3.85	H(2-1)	75(2)	−313(7)	488(5)	6.3(15)
S(4)	2363.7(6)	3218(2)	4301(2)	5.15	H(2-2)	110(4)	−196(10)	446(9)	14.0(31)
P(1)	1103.5(7)	−107(2)	6146(1)	4.85	H(2-3)	55(2)	−178(6)	440(5)	5.8(14)
P(2)	2085.1(5)	4827(1)	5115(1)	3.20	H(3-1)	258(2)	699(7)	409(6)	7.1(17)
P(3)	996.4(5)	2285(1)	2577(1)	3.28	H(3-2)	248(2)	598(8)	312(5)	8.0(18)
O(1)	1132(2)	−16(5)	7568(4)	7.12	H(3-3)	220(3)	724(9)	319(7)	11.2(25)
O(2)	901(2)	−1655(4)	5973(4)	5.58	H(4-1)	213(2)	646(7)	708(5)	6.7(16)
O(3)	1945(1)	6117(4)	4256(3)	3.76	H(4-2)	266(3)	657(9)	754(7)	11.5(25)
O(4)	2495(1)	5419(4)	6102(3)	4.33	H(4-3)	239(3)	749(7)	630(6)	7.6(18)
C(1)	1360(3)	−1063(8)	8312(5)	6.63	H(6)	163(2)	461(5)	214(4)	3.8(11)
C(2)	781(3)	−2232(6)	4801(6)	5.24	H(7)	201(2)	548(7)	68(5)	6.8(16)
C(3)	2327(3)	6773(8)	3622(6)	5.79	H(8)	191(2)	448(6)	−123(5)	5.1(13)
C(4)	2375(2)	6607(7)	6842(5)	5.16	H(9)	149(2)	259(5)	−142(4)	3.6(11)
C(5)	1297(2)	2958(5)	1287(4)	3.05	H(10)	106(2)	150(7)	−6(5)	6.5(15)
C(6)	1569(2)	4194(5)	1447(5)	3.88	H(12)	157(2)	−5(6)	192(5)	6.1(15)
C(7)	1785(2)	4797(6)	486(5)	4.64	H(13)	134(2)	−233(5)	152(4)	3.9(11)
C(8)	1735(2)	4167(6)	−622(5)	4.40	H(14)	52(2)	−326(5)	151(4)	3.8(11)
C(9)	1467(2)	2949(6)	−786(5)	4.25	H(15)	−15(2)	−169(6)	199(5)	5.6(14)
C(10)	1249(2)	2332(6)	168(5)	3.87	H(16)	7(2)	62(6)	239(4)	4.7(12)
C(11)	815(2)	495(5)	2152(4)	3.25	H(18)	15(2)	288(7)	77(6)	7.4(17)
C(12)	1194(2)	−441(6)	1913(5)	4.31	H(19)	−51(2)	430(7)	64(6)	7.1(16)
C(13)	1075(3)	−1834(6)	1636(5)	5.06	H(20)	−70(2)	557(5)	223(4)	4.2(12)
C(14)	595(3)	−2315(6)	1629(5)	5.23	H(21)	−18(2)	555(6)	388(5)	5.1(13)
C(15)	223(2)	−1413(7)	1886(5)	5.08	H(22)	55(2)	416(6)	405(5)	5.3(13)
C(16)	326(2)	−8(6)	2143(5)	4.25					
C(17)	414(2)	3313(5)	2442(4)	3.05					
C(18)	90(2)	3335(7)	1410(5)	4.54					
C(19)	−338(2)	4168(8)	1339(5)	5.13					
C(20)	−431(2)	5012(6)	2280(6)	4.26					
C(21)	−110(2)	5013(6)	3295(4)	4.27					
C(22)	314(2)	4178(5)	3392(4)	3.69					

a) The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{eq}=(4/3)(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{13}ac\cos\beta)$. The B_{ij}'s are defined by: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$.

Results and Discussion

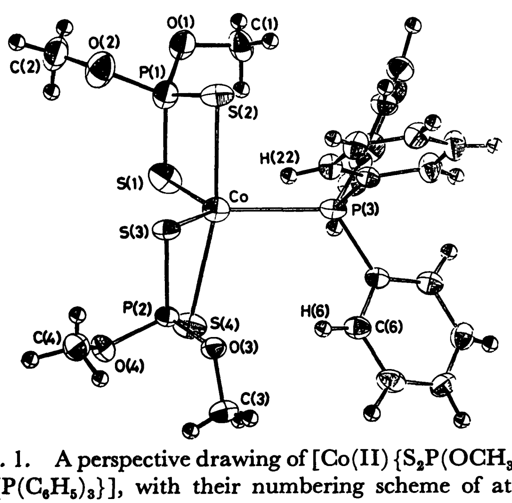

Fig. 1. A perspective drawing of $[Co(II)\{S_2P(OCH_3)_2\}_2\{P(C_6H_5)_3\}]$, with their numbering scheme of atoms. (A part of the numbering scheme is shown; see text.)

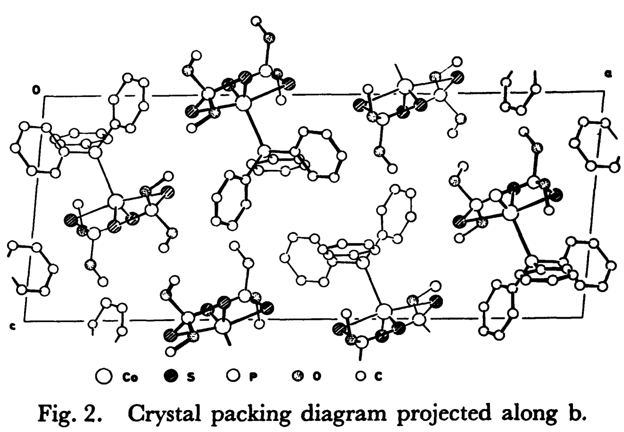

Fig. 2. Crystal packing diagram projected along b.

The crystal structure of bis(O,O'-dimethyl dithiophosphato)(triphenylphosphine)cobalt(II) will now be summarized. The final atomic parameters are listed in Table 1,[12] while the interatomic distances as well as bond angles are given in Table 2. A perspective drawing of the complex and a partial numbering scheme of the atoms are shown in Fig. 1. The remaining

TABLE 2. INTERATOMIC DISTANCES AND BOND ANGLES, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Interatomic distance l/Å			
Co–S(1)	2.325(2)	C(6)–C(7)	1.390(8)
Co–S(2)	2.569(2)	C(7)–C(8)	1.370(8)
Co–S(3)	2.333(2)	C(8)–C(9)	1.363(8)
Co–S(4)	2.664(2)	C(9)–C(10)	1.391(8)
Co–P(3)	2.551(2)	C(10)–C(5)	1.380(7)
S(1)–P(1)	2.010(3)	C(11)–C(12)	1.392(8)
S(2)–P(1)	1.941(2)	C(12)–C(13)	1.388(8)
P(1)–O(1)	1.586(5)	C(13)–C(14)	1.362(10)
P(1)–O(2)	1.572(4)	C(14)–C(15)	1.363(9)
O(1)–C(1)	1.399(9)	C(15)–C(16)	1.386(8)
O(2)–C(2)	1.429(7)	C(16)–C(11)	1.390(7)
S(3)–P(2)	1.997(2)	C(17)–C(18)	1.376(7)
S(4)–P(2)	1.960(2)	C(18)–C(19)	1.385(9)
P(2)–O(3)	1.580(4)	C(19)–C(20)	1.363(8)
P(2)–O(4)	1.582(4)	C(20)–C(21)	1.356(7)
O(3)–C(3)	1.438(8)	C(21)–C(22)	1.379(8)
O(4)–C(4)	1.452(7)	C(22)–C(17)	1.389(7)
P(3)–C(5)	1.831(5)	S(3)···H(22)	2.95(5)
P(3)–C(11)	1.818(5)	S(2)···H(22)	3.11(6)
P(3)–C(17)	1.830(5)	S(4)···H(6)	3.24(5)
C(5)–C(6)	1.383(7)	S(4)···C(6)	3.776(6)
Bond angle ϕ/°			
S(1)–Co–S(3)	123.75(6)	Co–P(3)–C(11)	108.9(2)
S(1)–Co–P(3)	118.36(6)	Co–P(3)–C(17)	114.4(2)
S(3)–Co–P(3)	117.40(5)	C(5)–P(3)–C(11)	104.2(2)
S(1)–Co–S(2)	82.05(6)	C(11)–P(3)–C(17)	105.9(2)
S(3)–Co–S(4)	81.55(5)	C(17)–P(3)–C(5)	100.4(2)
S(2)–Co–S(4)	168.32(6)	P(3)–C(5)–C(6)	117.3(4)
S(2)–Co–P(3)	89.28(5)	P(3)–C(5)–C(10)	123.7(4)
S(4)–Co–P(3)	102.31(5)	C(10)–C(5)–C(6)	119.0(5)
S(1)–P(1)–S(2)	109.04(10)	C(5)–C(6)–C(7)	120.0(5)
S(1)–P(1)–O(1)	114.9(2)	C(6)–C(7)–C(8)	120.5(5)
S(1)–P(1)–O(2)	110.9(2)	C(7)–C(8)–C(9)	119.8(5)
S(2)–P(1)–O(1)	107.4(2)	C(8)–C(9)–C(10)	120.4(5)
S(2)–P(1)–O(2)	115.5(2)	C(9)–C(10)–C(5)	120.3(5)
O(1)–P(1)–O(2)	99.1(2)	P(3)–C(11)–C(12)	117.8(4)
P(1)–O(1)–C(1)	122.3(5)	P(3)–C(11)–C(16)	123.4(4)
P(1)–O(2)–C(2)	121.1(4)	C(16)–C(11)–C(12)	118.6(5)
S(3)–P(2)–S(4)	111.61(9)	C(11)–C(12)–C(13)	119.8(5)
S(3)–P(2)–O(3)	105.2(2)	C(12)–C(13)–C(14)	121.0(6)
S(3)–P(2)–O(4)	111.9(2)	C(13)–C(14)–C(15)	119.6(6)
S(4)–P(2)–O(3)	113.6(2)	C(14)–C(15)–C(16)	120.9(6)
S(4)–P(2)–O(4)	109.4(2)	C(15)–C(16)–C(11)	120.0(5)
O(3)–P(2)–O(4)	104.9(2)	P(3)–C(17)–C(18)	122.7(4)
P(2)–O(3)–C(3)	119.8(4)	P(3)–C(17)–C(22)	118.4(4)
P(2)–O(4)–C(4)	119.9(3)	C(22)–C(17)–C(18)	118.7(4)
Co–S(1)–P(1)	86.50(8)	C(17)–C(18)–C(19)	120.5(5)
Co–S(2)–P(1)	81.39(8)	C(18)–C(19)–C(20)	120.1(5)
Co–S(3)–P(2)	86.58(7)	C(19)–C(20)–C(21)	120.0(5)
Co–S(4)–P(2)	78.57(7)	C(20)–C(21)–C(22)	121.0(5)
Co–P(3)–C(5)	121.6(2)	C(21)–C(22)–C(17)	119.8(5)

numberings are: the phenyl carbons of the triphenylphosphine ligand are C(5)–C(10), C(11)–C(16), and C(17)–C(22) for those of the I, II, and III phenyl groups respectively, where C(5), C(11), and C(17) are bonded to P(3). The numbering of each hydrogen atom is the same as that of the phenyl carbon atom to which it is bonded. The hydrogen atoms of the methyl groups of Me_2dtp ligands are numbered H(n-1—3), where n is the number of the bonded methyl carbon atom. The arrangement of the molecules in a unit cell is shown in Fig. 2 (projection along the b axis).

The crystal consists of discrete molecules of [Co(II)-

TABLE 3. SPECTRAL AND MAGNETIC PROPERTIES OF THE ADDUCTS, $[Co(II)(Et_2dtp)_2L_n]$ (Et_2dtp=DIETHYL DITHIOPHOSPHATO LIGAND), IN THEIR SOLID STATE

n	L	Color		Reflectance spectra $\nu/10^3$ cm^{-1}				Magnetic moment μ/BM$^{a)}$
		Solid	Benzene solution					
1	PPh_3	Green	Greenish blue	15.6	16.9			4.5
1	hex	Blue	Blue	15.6	17.7			4.5
1	bzt	Greenish blue	Green	16.0	17.2			4.5
1	pip	Red violet	Blue	15.7	17.0	18.5	19.6	5.1
1	pyr	Yellow	Green	16.3	17.4	18.3	19.3	5.0
2	bzt	Yellow brown	Green	16.1	17.9	18.6	20.0	5.0
2	bzi	Red violet	Blue	16.1	17.0	18.9	20.5	5.0

PPh_3=Triphenylphosphine, hex=hexamethylenetetramine, bzt=benzothiazole, pip=piperazine, pyr=pyrazine, bzi=benzimidazole. a) 1 BM=9.274078(36)$\times 10^{-24}$ J T^{-1}.

$\{S_2P(OCH_3)_2\}_2(PPh_3)]$, where PPh_3 means $P(C_6H_5)_3$, and no intermolecular interactions were observed except for van der Waals interaction. The central metal atom in this complex has a trigonal bipyramidal environment; two sulfur atoms of each Me_2dtp ligand are coordinated to the central metal from both the axial and equatorial directions. The phosphorus atom of the PPh_3 ligand is coordinated in the equatorial plane. As is shown in Fig. 1, Co, S(1), S(3), and P(3) atoms are almost on a plane, although the Co atom is deviated to the S(4) direction by about 0.097 Å from the S(1)–S(3)–P(3) plane. The bond angles around the Co atom on the equatorial plane (1 ∠S–Co–S and 2 ∠S–Co–P) are all about 120°. Although the ∠S(2)–Co–P(3) is almost rectangular, the ∠S(4)–Co–P(3) angle is 102.31(5)°. The Co–S(1) and Co–S(3) are about 2.33 Å, while Co–S(2) and Co–S(4) are about 2.6 Å; the latter are longer than the former. The two P–S bond distances in each Me_2dtp ligand also differ from each other; that for S(2) or S(4) atom, which coordinates to the Co atom from the axial direction, is shorter than the other. As the common P=S bond distance is about 1.92 Å, while that of P–S about 2.10 Å,[13] the double-bond character of the $-PS_2-$ moiety of the Me_2dtp ligand is localized rather to the P–S(axial) bond. The Co–P(3) bond distance is 2.551(2) Å; this is probably the longest Co–P distance of metal complexes ever reported. This may be due to the steric hindrance between the bulky ligands.

As will be described below, the magnetic as well as the spectral properties suggest that $Co(II)(Et_2dtp)_2(PPh_3)$, $Co(II)(Et_2dtp)_2$(hexamethylenetetramine), and $Co(II)(Et_2dtp)_2$(benzothiazole) have structures similar to that of $Co(II)(Me_2dtp)_2(PPh_3)$, whose crystal structure has been determined. Elemental analyses show that they are all 1 : 1 adducts with the general formula of $Co(II)(R_2dtp)_2\cdot X$. As may be seen from Table 3, their magnetic moments at room temperature range from 4.3 to 4.5 BM. The reflectance spectra of their solids give two peaks which can assigned to the $^4A'_2(P)\leftarrow{}^4A'_2(F)$ (higher wave number peak) and $^4E''(P)\leftarrow{}^4A'_2(F)$ of the pentacoordinated trigonal bipyramidal cobalt(II) complexes.[14,15]

Another group of adducts are the 1 : 1 adducts of piperazine and pyrazine, as well as the 2 : 1 adducts of benzothiazole and benzimidazole. As is shown in Table 3, their magnetic moments are 5.0—5.1 BM, and two peaks (one of them splits into three peaks) are observed in their reflectance spectra. They can be identified as $^4A_{2g}(F)\leftarrow{}^4T_{1g}(F)$ and $^4T_{1g}(P)\leftarrow{}^4T_{1g}(F)$ respectively of the octahedral cobalt(II) complexes.[16,17] In the 1 : 1 adducts of piperazine and pyrazine, these amines are likely to function as bidentate ligands with their two nitrogen atoms; consequently, the complexes may be polymeric. The splitting of the spectral peaks may be attributable to some deviation from an exact octahedral coordination.

The infrared spectra of all of these adducts show some characteristic bands; for example, ν(P–S) and a mixture of ν(P–S) and ν(P–O) appeared at about 800, 680, and 570 cm^{-1}, and ν(Co–S), at about 275 cm^{-1}.[18] The ν(Co–N) bands of amine adducts are rather ambiguous, although some peaks are found in the near-360 cm^{-1} region in their far-infrared spectra.

The visible absorption spectra of the benzene solution of $Co(II)(Et_2dtp)_2$(hexamethylenetetramine), which is the most stable in the series of adducts, gives five peaks in the region of 7100—28000 cm^{-1}. The absorption maxima given by the wave numbers with the log ε values in parentheses, are 9090(0.91), 12100(1.09), 15900(1.80), and 17200(1.76) for a 0.01 mol dm^{-3} solution, and 26100(3.17) for 0.0002 mol dm^{-3} one. The spectral pattern resembles that of pentacoordinated trigonal bipyramidal cobalt(II) complexes.[14] However, the absorption coefficients of the bands in the visible region do not obey Beer's law for they increase when the solution is diluted; moreover, the peak at 15900 cm^{-1} is broadened, and the maximum shifts to about 15000 cm^{-1}, which corresponds to the peak of the free $Co(II)(Et_2dtp)_2$.[6] This observation indicates that $Co(II)(Et_2dtp)_2$ and the pentacoordinated adduct are in equilibrium in the solution. The solutions of other adducts also show almost the same pattern as that of the hexamethylenetetramine adduct. Even the hexacoordinated adducts in their solid states also give a spectral pattern similar to that of pentacoordinated cobalt(II) in their solution; this is a result of partial dissociation. Therefore, the equilibrium studies described below take into account only the 1 : 1 adduct formation process; the second-step association is assumed to be negligible

TABLE 4. FORMATION CONSTANTS OF 1 : 1 ADDUCTS, $[Co(II)(R_2dtp)_2 \cdot X]$

R	X	Solvent	T/°C	From spectra		From ^{1}H-NMR		
				ε_1	log K	δ_A	δ_B	log K
C_2H_5	PPh_3	CCl_4	30	103	1.6_1	12.8	7.2_5	1.5_7
CH_3	PPh_3	C_6H_6	25	94	1.9			
C_2H_5	bzt	CCl_4	30	73	2.2_1	97.7	8.8_4	2.2_2
C_2H_5	hex	$CHCl_3$	30	56	3.4	26.5	4.7_6	a)
C_2H_5	pyr	$CHCl_3$	30			88.5	8.5_7	2.2_5

PPh_3=Triphenylphosphine, bzt=benzothiazole, hex=hexamethylenetetramine, pyr=pyrazine. a) The formation constant is too high to obtain by this method.

compared to the first one.

Although the $Co(II)(Et_2dtp)_2$ or $Co(II)(Me_2dtp)_2$ in carbon tetrachloride or in a benzene solution is gradually air-oxidized, the solutions were spectrophotometrically stable for 2 h after dissolution when the concentration was of the order of 3×10^{-3} mol dm^{-3}. Thus, practically, the absorbance of the solution did not change during the period of the measurement. After mixing a solution of $Co(II)(R_2dtp)_2$, or $Co(II)(R_2dtp)_2(PPh_3)$ with PPh_3, the equilibrium was attained in several min. All the other adducts also behaved in the same way. Therefore, the absorbance measurement of the mixture could be started about 7 min after mixing and could be finished in about 1 h. A series of the spectra of the mixture of $Co(II)(Me_2dtp)_2(PPh_3)$ and PPh_3 are shown in Fig. 3. Two isosbestic points are found, and the wavelengths of the absorption maxima of these spectra are kept at about 662 nm in the mixing-ratio region.

The same type of spectra posessing two isosbestic points were observed in the $Co(II)(Et_2dtp)_2$–PPh_3, and $Co(II)(Et_2dtp)_2$–benzothiazole systems. In the case of the $Co(II)(Et_2dtp)_2$–hexamethylenetetramine system, the hexamethylenetetramine adduct itself could not be used as the starting material because the formation constant of the adduct is too high. In this case, the PPh_3 adduct rather than the free complex was used as the starting material. Since the formation constant of the hexamethylenetetramine adduct is about 200 times that of PPh_3, the co-existence of the phosphine due to the use of its adduct was expected to be outside the range of experimental error. The isosbestic points were found in this system when $[Co(II)(Et_2dtp)_2] = 3.0 \times 10^{-3}$ mol dm^{-3}, and [hexamethylenetetramine] $= 0$—6.0×10^{-3} mol dm^{-3}.

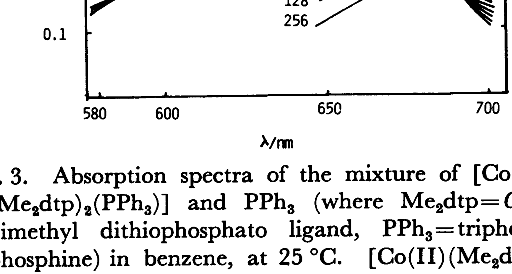

Fig. 3. Absorption spectra of the mixture of $[Co(II)(Me_2dtp)_2(PPh_3)]$ and PPh_3 (where Me_2dtp=*O,O'*-dimethyl dithiophosphato ligand, PPh_3=triphenylphosphine) in benzene, at 25 °C. $[Co(II)(Me_2dtp)_2(PPh_3)]$ added was always 2.00×10^{-3} mol dm^{-3}, and the concentration ratio of $[PPh_3]/[Co(II)(Me_2dtp)_2(PPh_3)]$ (originally added, mol/mol) are shown by numbers in the figure.

The apparent formation constants of the adducts, $K = [Co(II)(R_2dtp)_2 \cdot X]/\{[Co(II)(R_2dtp)_2][X]\}$, where $R = CH_3$ or C_2H_5, $X = PPh_3$, benzothiazole, or hexamethylenetetramine are listed in Table 4. That of the pyrazine adduct was not obtained because of its low solubility.

The formation constant, K, was calculated as follows. Let the total concentration of Co(II) be m_0, and let that of the donor X be d, while x is the concentration of the $Co(II)(R_2dtp)_2 \cdot X$ adduct.*** Then, $[Co(II)(R_2dtp)_2]$ and [X] in the solution are given by $m_0 - x$ and $d - x$ respectively. As the wavelength of the maximum absorption does not change in the concentration region, while the isosbestic points are retained, the absorbance can be written as $A = \varepsilon_1 x + \varepsilon_2(m_0 - x)$, where ε_1 stands for the absorption coefficient of the $Co(II)(R_2dtp)_2 \cdot X$ adduct, and ε_2, that of the free complex, $Co(II)(R_2dtp)_2$. From these relations, the following equation can be derived:

$$\frac{1}{m_0K[X](\varepsilon_1-\varepsilon_2)} + \frac{1}{m_0(\varepsilon_1-\varepsilon_2)} = \frac{1}{A-\varepsilon_2 m_0}.$$

Therefore, when $d \gg x$; *i.e.* $[X] \fallingdotseq d$, a linear relationship exists between $1/d$ and $1/(A - \varepsilon_2 m_0)$. From the gradient of the line and the intercept, the values of $1/\{m_0K(\varepsilon_1-\varepsilon_2)\}$ and $1/\{m_0(\varepsilon_1-\varepsilon_2)\}$ respectively can be known. Then, the ε_1 and K of each adduct can be calculated. The ε_2 of $Co(II)(Et_2dtp)_2$ was determined from the absorbance of the complex, extracted by the organic solvent from a mixture of cobalt(II) chloride and $Na(Et_2dtp)$ in aqueous solution; the concentration of Co(II) was estimated by titration after decomposing the ligand. The ε_2 of $Co(II)(Et_2dtp)_2$ and that of $Co(II)(Me_2dtp)_2$ were almost the same; *i.e.*, 315 mol^{-1} dm^3. This is slightly smaller than that reported by Jørgensen,[8b)] although he stated that his result might be a little too high.

These apparent first-order adduct formation constants were also obtained from the ^{1}H-NMR paramagnetic

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*** m_0, d, and x are in mol dm^{-3} units, accordingly, K is in mol^{-1} dm^3 units.

shifts of the donor protons caused by the addition of the $Co(II)(R_2dtp)_2 \cdot X$ adduct to the solution of a donor. The broadening of the peak by the addition of the adduct was not much, indicating that the exchange rate of the donors between the free state and that in the adduct is high. The paramagnetic shifts of the proton peak of the donor protons can thus be expected to be given by the weighed average of the chemical shifts of the proton of the donor in the free and bonded states. The most probable species existing in the solution is the 1 : 1 adduct, and the fraction of the 2 : 1 adduct or the higher ones can be expected to be low, even in such relatively concentrated solution of a donor.

Therefore, in this case, too, only the first step was considered, and the adduct formation constant was obtained by the use of the equation: $K=[Co(II)(R_2dtp)_2 \cdot X]/\{[Co(II)(R_2dtp)_2]\cdot[X]\}$. The calculations were as follows. The chemical shift of a proton of a donor, X, in a free state is denoted by δ_B; that in an adduct, by δ_A, and that of the observed, by δ_o. As in the case of the spectrophotometric method, m_o, d, and x are defined as the total concentration of Co(II), the total concentration of the donor, and the concentration of the existing adduct, respectively. Since d is enough larger than m_0 and x in the NMR measurement, too, we use the approximation of $[X] \fallingdotseq d$. Therefore, we have $K=x/\{(m_0-x)d\}$. On the other hand, $\delta_o = \delta_B + x(\delta_A - \delta_B)/d$. From these relations, we obtain:

$$d = (\delta_A - \delta_B)\{m_o/(\delta_o - \delta_B)\} - (1/K).$$

From this linear relation between d and $m_o/(\delta_o - \delta_B)$, δ_A was obtained from its gradient. Next, the δ_o's of a series of samples with different d values, but with the same $m_o/d(\equiv a)$, were measured. The equation can be rewritten as: $1/\Delta = [1/\{\alpha(\delta_A - \delta_B)\}][1+(1/K)(1/d)]$, where $\Delta = \delta_o - \delta_B$. When a is kept constant, there is a linear relationship between $1/\Delta$ and the formation constant, K, which was obtained from the gradient. The proton peaks used for the calculations were those of the phenyl ortho protons for the PPh_3 adduct, and the methine proton at the 2-position for the benzothiazole adduct. In the case of hexamethylenetetramine or the pyrazine adduct, a single peak in the ^1H-NMR was used. The obtained results, the δ_A, δ_B, and log K values, are listed in Table 4, also; they agreed well with those obtained from spectrophotometry.

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