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ADDUCTS OF BIS(O,O'-DIETHYL DITHIOPHOSPHATO)COBALT(II) WITH SOME AMINES AND TRIPHENYLPHOSPHINE

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The 1:1 triphenylphosphine, hexamine, piperazine, pyrazine, and benzothiazole adducts, as well as the 2:1 benzothiazole and benzimidazole adducts of bis(O,O'-diethyl dithiophosphato)-cobalt(II) were obtained as crystalline solids, which were hardly oxidized in air, but partially dissociated in their solutions.

Bis(O,O'-diethyl dithiophosphato)nickel(II), which is stable in air, is in a square planar form, and amines or such kinds of ligands can attack the complex easily from apical direction, to form 1:1 and 2:1 adducts.$^{1-5)}$ On the other hand, as bis(O,O'-diethyl dithiophosphato)cobalt(II) ($Co(dtp)_2$) is in a tetrahedral form, the deformation of the original complex is indispensable, when some ligands bond to the complex to make their adducts. Moreover, the complex, $Co(dtp)_2$, is extremely air sensitive and without air-shielding synthetic process,$^{6)}$ it is oxidized easily and only the cobalt(III) complex is obtained. Probably this is why its adducts were not investigated until now. But when its adducts were obtained, we found that they were very stable in their solid states and could be kept in air many months at room temperature without being oxidized.

For an example, the hexamine adduct was prepared as follows. The benzene solution of $Co(dtp)_2$ was obtained by extracting it from the mixture of concentrated aqueous solution of cobalt(II) chloride and Na(dtp) with benzene. After the addition of a little excess of hexamine, the solution was stirred, and its solvent was evaporated off. From the residue, the adduct was extracted with the hot mixture of benzene and ligroin, and was recrystallized from the same solvent. The other adducts were also synthesized by the same technique, although the solvent should be selected from benzene, toluene, petroleum ether, petroleum benzine, ligroin, and their mixture, depending on their solubilities.

When these adducts were dissolved into water, they decomposed and pink colored hexaaquacobalt(II) solution was obtained except in the case of 1:1 piperazine one, where some green basic salt precipitated.

The chemical formulae and the results of their elemental analysis are as follows. Co(dtp)$_2$(tp): Found: Co, 8.52; C, 45.24; H, 5.10%; Calcd for $\mathrm{CoC_{26}H_{35}O_4P_3S_3}$: Co, 8.52; C, 45.15; H, 5.10%. Co(dtp)$_2$(hx): Found: Co, 10.27; C, 29.74; H, 5.69; N, 10.01%; Calcd for $\mathrm{CoC_{14}H_{32}O_4N_4P_2S_4}$: Co, 10.35; C, 29.52; H, 5.66; N, 9.84%. Co(dtp)$_2$(pp): Found: Co, 11.57; C, 27.85; H, 5.76; N, 5.43%; Calcd for $\mathrm{CoC_{12}H_{30}O_4N_2P_2S_4}$: Co, 11.43; C, 27.96; H, 5.87; N, 5.43%. Co(dtp)$_2$(pr): Found: Co, 11.50; C, 28.30; H, 4.73; N, 5.49%; Calcd for $\mathrm{CoC_{12}H_{24}O_4N_2P_2S_4}$: Co, 11.57; C, 28.29; H, 4.75; N,5.50%. Co(dtp)$_2$(bt): Found: Co, 10.34; C, 32.03; H, 4.47; N, 2.48%; Calcd for $\mathrm{CoC_{15}H_{25}O_4NP_2S_5}$: Co, 10.44; C, 31.91; H, 4.46; N, 2.48%. Co(dtp)$_2$(bt)$_2$: Found: Co, 8.41; C, 37.82; H, 4.33; N, 3.96%; Calcd for $\mathrm{CoC_{22}H_{30}O_4N_2P_2S_6}$: Co, 8.42; C, 37.76; H, 4.32; N, 4.00%. Co(dtp)$_2$(bi)$_2$: Found: Co, 8.64; C, 39.86; H, 4.85; N, 8.44%; Calcd for $\mathrm{CoC_{22}H_{32}O_4N_4P_2S_4}$: Co, 8.85; C, 39.70; H, 4.85; N, 8.42%.7)

Some spectral and magnetic properties of the obtained adducts, the colors of

Table. Spectral and magnetic properties of the adducts, Co(dtp)$_2$·L$_n$

n	L7)	Color7)		Magnetic moment (B.M.)	Reflectance spectra (10^3 cm^{-1})	IR spectra ν(Co-N) (cm^{-1})
		Solid	Benzene solution			
1	tp	g	g-bl	4.5	15.6 16.9	
1	hx	bl	bl	4.3	15.6 17.7	360
1	bt	g-bl	g	4.5	16.0 17.2	365
1	pp	r-v	bl	5.1	15.7 17.0 18.5 19.6	379
1	pr	y	g	5.0	16.3 17.4 18.3 19.3	435
2	bt	y-br	g	5.0	16.1 17.9 18.6 20.0	359
2	bi	r-v	bl	5.0	16.1 17.0 18.9 20.5	380

their crystals as well as of their benzene solutions, their magnetic moments of solids (with Gouy balance), the wavenumbers of the absorption maxima of diffuse reflectance spectra of their solids (14200---25000 cm^{-1}), and the wavenumbers of ν(Co-N) band, are shown in Table.

These adducts are devided into two groups. The first group includes the 1:1 adducts of triphenylphosphine, hexamine, and benzothiazole. Their magnetic moments are 4.3---4.5 B.M., and in their reflectance spectra of solids, two peaks are observed, assigned as $^4A'_2(P) \leftarrow {}^4A'_2(F)$ (higher wavenumber one), and $^4E''(P) \leftarrow {}^4A'_2(F)$ of the penta-coordinated trigonal bipyramidal cobalt(II) complexes.[8,9] The 1:1 adducts of piperazine and pyrazine, as well as 2:1 adducts of benzothiazole and benzimidazole make the second group. Their magnetic moments are 5.0---5.1 B.M., and four peaks are observed in their reflectance spectra. (One of the two peaks is splitted into three, and then four peaks in total are observed.) They are assigned as $^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$, and $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$, respectively, of the octahedral cobalt(II) complexes.[10] Piperazine and pyrazine likely work as a bidentate with their two nitrogen atoms in their solid adducts, therefore, their adducts are likely in the polymer form.

The benzene solution of the hexamine adduct, which is probably the most stable one in these products, gives five peaks in the absorption spectra of 7100---28000 cm^{-1} region. The absorption maxima (shown by the wavenumbers and $\log\varepsilon$ in parentheses) are 9090(0.91), 12100(1.09), 15900(1.80), 17200(1.76) for 0.01 M solution, and 26100(3.17) for 0.0002 M one. The spectral pattern resembles that of penta-coordinated trigonal-bipyramidal cobalt(II) complexes.[8] However, the absorption coefficients of the bands in visible region do not obey Beer's law, and they increase when the solution is diluted, moreover, the peak of 15900 cm^{-1} broadens, and the maximum shifts to about 15000 cm^{-1}, which corresponds with the peak of the free tetrahedral $Co(dtp)_2$.[6] These facts show that the adduct is in equilibrium between the free $Co(dtp)_2$ and penta-coordinated adduct in the solution. The solutions of other adducts give almost the same pattern as that of the hexamine adduct. Even the hexa-coordinated adducts in their solid states, also give the spectral pattern of the penta-coordinated cobalt(II) in their solutions, due to their dissociation.

Their infrared spectra show some characteristic bands. For examples, ν(P-S) and the mixture of ν(P-S) and ν(P-O) appear at about 800, 680, and 570 cm^{-1}, and ν(Co-S) at about 275 cm^{-1}.[11] The ν(Co-N) bands for amine adducts are not unambiguous, and their peaks shown in Table are tentatively assigned ones.

To clarify the structure of these adducts, the X-ray structure analysis is in progress in our laboratory.

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7) Abbreviations for the names of the ligands are as follows; tp: triphenylphosphine, hx: hexamine, pp: piperazine, pr: pyrazine, bt: benzothiazole, bi: benzimidazole. Abbreviations for the names of colors are as follows; g: green, bl: blue, r: red, v: violet, y: yellow, br: brown.

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