

Syntheses and Structure of Bis(*O,O'*-diethyl dithiophosphato)bis-(hexamethylenetetramine)cadmium(II) and Related Adducts

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The title complex was synthesized, and the crystal structure was determined by means of the X-ray diffraction technique. The crystal is monoclinic; space group $P2_1/n$, $a=16.310(3)$, $b=6.777(1)$, $c=14.576(3)$ Å, $\beta=96.13(1)^\circ$, $Z=2$, $D_x=1.58$, $D_m=1.55(3)$ g cm⁻³, $\mu(\text{Mo } K\alpha)=1.12$ mm⁻¹. The molecule has a center of symmetry, and a distorted octahedron is formed around the central cadmium atom; two *O,O'*-diethyl dithiophosphato ions (dtp) act as bidentate ligands, and each ligand forms a four-membered chelate ring with its two sulfur atoms on the equatorial plane, while two hexamethylenetetramine molecules are coordinated to the metal atom by their nitrogen atoms from the axial direction. Related adducts, $\text{Cd(II)(dtp)}_2 \cdot X_n$, where X is a donor and $n=1$ or 2, were also synthesized, and their structures were compared with those of the corresponding $\text{Co(II)(dtp)}_2 \cdot X_n$ -type complexes.

The present authors have reported in another paper¹⁾ that the phosphine or amine adducts of bis(*O,O'*-diethyl dithiophosphato)cobalt(II) (hereafter, abbreviated as Co(II)(dtp)_2 ; the same types of abbreviations are used for related adducts) are very stable in air; however, the original Co(II)(dtp)_2 is easily oxidized. We have attempted to obtain similar types of adducts of other metals in order to compare them with the corresponding cobalt(II) complexes. As the electron paramagnetic resonance spectra, especially that of the single crystal, is expected to be effective in clarifying the stabilization mechanism, we have tried to synthesize adducts that are isostructural to the cobalt(II) analogues and contain a diamagnetic metal atom. Thus, the present authors have synthesized adducts containing cadmium(II) and compared their properties and structures with those of the corresponding cobalt(II) adducts. From their chemical compositions, the general features of their infrared spectra, and then X-ray powder diffraction patterns, the adducts of cobalt(II) and of cadmium(II) are found to resemble each other, and some of them are isostructural, as will be shown later. In the other paper,¹⁾ we have suggested the octahedral structure for some adducts from the magnetic as well as the visible spectroscopic results; however, no structural analysis has been carried out. In this connection, the structure of $\text{Cd(II)(dtp)}_2(\text{hex})_2$ (where hex=hexamethylenetetramine), which is expected to be octahedral, was determined by the X-ray diffraction technique. Another reason for the selection of the hex adduct in the present study was to examine the effect of such a bulky ligand on the coordination bond. In fact, the structure analysis of the metal complex involving this amine had been carried out only for $\text{Mn(II)Cl}_2(\text{hex})_2(\text{H}_2\text{O})_2$.²⁾ As cadmium(II) is a diamagnetic metal, the ¹H-NMR technique is easily applicable to the adducts. The results of the study revealed that the adducts are not completely dissociated, even in a solution.

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Experimental

Synthesis of Bis(O,O'-diethyl dithiophosphato)cadmium(II) Adducts, Cd(II)(dtp)₂·X_n (Where X is a Donor, and n=1 or 2). All the chemicals used were the GR- or EP-grade reagents of Wako Pure Chemicals Co., Ltd., and no further purification was necessary. Na(dtp) was obtained from phosphorus pentasulfide by the method of Livingstone.³⁾ The adducts were synthesized as follows:

Synthesis of Cd(II)(dtp)₂ (1): Into about 400 cm³ of ethanol, 9.12 g (40 mmol) of hydrated cadmium(II) chloride ($\text{CdCl}_2 \cdot 2.5 \text{H}_2\text{O}$) and 16.6 g (80 mmol) of Na(dtp) were added, and the mixture was refluxed for 1 h. After cooling, the deposited crude complex was filtered off and recrystallized from ethanol. Yield: 18 g (93%).

Synthesis of Cd(II)(dtp)₂(hex) (2): Into about 35 cm³ of benzene, 1.93 g (4 mmol) of **1**, and 0.56 g (4 mmol) of hex were dissolved. After filtration, the filtrate was left standing for a while and then filtered once more to remove the white turbid. To the filtrate, 5 cm³ of benzene was added, and the mixture was left standing in a desiccator containing hexane for several days. A crystalline product came out. Yield: 0.6 g (25%). Found: Cd, 18.00; C, 27.20; H, 5.19; N, 9.07%. Calcd for $\text{CdC}_{14}\text{H}_{32}\text{N}_4\text{O}_4\text{P}_2\text{S}_4$: Cd, 18.04; C, 26.99; H, 5.18; N, 8.99%.

Synthesis of Cd(II)(dtp)₂(hex)₂ (3): Into 70 cm³ of chloroform, 3.15 g (6.97 mmol) of **1** and 1.95 g (13.9 mmol) of hex were added, and the mixture was refluxed for 1 h. After cooling, it was filtered off, and the filtrate was left standing for several days in hexane vapor. Crystallines were thus precipitated. Yield: 2.9 g (55%). (It was also obtained from the evaporation residue of a mixed solution of the starting materials by repeated recrystallizations from diisopropyl ether.) Found: Cd, 14.76; C, 31.55; H, 5.80; N, 14.65%. Calcd for $\text{CdC}_{20}\text{H}_{44}\text{N}_8\text{O}_4\text{P}_2\text{S}_4$: Cd, 14.73; C, 31.48; H, 5.81; N, 14.68%.

Synthesis of Cd(II)(dtp)₂(PPh₃) (4) (Where PPh₃=Triphenylphosphine): Into 30 cm³ of chloroform, 0.97 g, (2.0 mmol) of **1** and 1.05 g (4.0 mmol) of PPh₃ were added, and the mixture was refluxed for 30 min. The solvent was evaporated off, and from the residue the product was extracted by ligroine. The extracted solution was ice-cooled, and the crystals came out. The crude product was recrystallized from benzene containing PPh₃. Yield: 1.25 g (84%). Found: Cd, 15.07; C, 42.42; H, 4.73%. Calcd for CdC_{26} -

$\text{H}_{35}\text{O}_4\text{P}_3\text{S}_4$, Cd, 15.09; C, 41.49; H, 4.74%.

Synthesis of $\text{Cd(II)}(\text{dtp})_2(\text{pip})$ (5**)** (Where *pip*=Piperazine): This complex was synthesized by the same procedure as that for **4**, 0.8 g (1.7 mmol) of **1** and 0.45 g (5.2 mmol) of pip being used. Toluene was employed in place of benzene for the extraction. Yield: 0.45 g (48%). Found: Cd, 19.66; C, 25.43; H, 5.28; N, 5.20%. Calcd for $\text{CdC}_{12}\text{H}_{30}\text{N}_2\text{O}_4\text{P}_2\text{S}_4$: Cd, 19.75; C, 25.33; H, 5.32; N, 4.92%.

Synthesis of $\text{Cd(II)}(\text{dtp})_2(\text{pyr})$ (6**)** (Where *pyr*=Pyrazine): Into 30 cm³ of chloroform, 0.8 g (1.7 mmol) of **1** and 0.4 g (5.0 mmol) of pyrazine were dissolved, after which the solution was evaporated using a rotary vacuum evaporator under 80 °C. The residue was recrystallized from 1,2-dichloroethane-ligroine (20/7=v/v). Yield: 0.35 g (38%). Found: Cd, 19.89; C, 25.62; H, 4.23; N, 4.71%. Calcd for $\text{CdC}_{12}\text{H}_{24}\text{N}_2\text{O}_4\text{P}_2\text{S}_4$: Cd, 19.97; C, 25.60; H, 4.30; N, 4.98%.

Synthesis of $\text{Cd(II)}(\text{dtp})_2(\text{bzt})_2$ (7**)** (Where *bzt*=Benzothiazole): The synthesis procedure for **6** was applied, starting from 0.8 g (1.7 mmol) of **1**, and 0.5 g (3.7 mmol) of bzt. The recrystallization solvent used was ligroine-toluene (1/1=v/v). Yield: 0.75 g (60%). Found: Cd, 14.97; C, 35.07; H, 4.00; N, 3.72%. Calcd for $\text{CdC}_{22}\text{H}_{30}\text{N}_2\text{O}_4\text{P}_2\text{S}_6$: Cd, 14.92; C, 35.08; H, 4.02; N, 3.72%.

Synthesis of $\text{Cd(II)}(\text{dtp})_2(\text{bza})_2$ (Where *bza*=Benzylamine): The crude product was synthesized by the same method as **6**, starting from 0.8 g (1.7 mmol) of **1** and 0.5 g (4.9 mmol) of bza. The product was extracted with ligroine and it was deposited by ice cooling. Yield: 0.69 g (52%). Found: Cd, 16.00; C, 37.71; H, 5.43; N, 4.13%. Calcd for $\text{CdC}_{22}\text{H}_{38}\text{N}_2\text{O}_4\text{P}_2\text{S}_4$: Cd, 16.17; C, 38.01; H, 5.22; N, 4.03%.

X-Ray Measurements. **Powder X-Ray Diffraction Patterns:** They were recorded on the diffractometer, Model DX-GO-F of GEOL, in the range from 6° to 30° in 2 θ , Cu K α radiation being used.

Single-crystal X-Ray Analysis: The single-crystal specimen of **3** for the X-ray study was grown from a chloroform-hexane solution kept in hexane vapor for several days. The crystal was shaped into a sphere ($\phi=0.34$ mm) and covered by cyanoacrylate resin to prevent decomposition by atmospheric moisture. The crystallographic data are: $\text{CdC}_{20}\text{H}_{44}\text{N}_8\text{O}_4\text{P}_2\text{S}_4$, F.W.=763.21, monoclinic, space group $\text{P2}_1/\text{n}$, ** $a=16.310(3)$, $b=6.777(1)$, $c=14.576(3)$ Å, $\beta=96.13(1)^\circ$, $Z=2$, $D_x=1.58$, $D_m=1.55(3)$ g cm⁻³, $\mu(\text{Mo K}\alpha)=1.12$ mm⁻¹. The reflections with 2 θ less than 60° were collected on a Rigaku automated four-circle diffractometer with Mo K α radiation, θ -2 θ scan technique being employed. Of 4670 reflections measured, 3654 independent reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the structure refinement. The intensities were corrected for Lorentz and polarization factors, but no correction was made for absorption and extinction. The calculations were carried out mainly on the FACOM 230-48 computer at The Institute for Solid State Physics, The University of Tokyo, and partly on HITAC 8700/8800 computer at The Computer Center of The University of Tokyo, using the local version of UNICS program.⁴⁾ The atomic-scattering factors were taken from Ref. 5.⁵⁾

Structure Determination: The structure was solved by the heavy-atom method. All the non-hydrogen atoms except for ethyl carbon atoms were deduced from a three-dimensional Patterson map, while the carbon atoms were located by successive Fourier syntheses. Their positional and thermal parameters were refined by the block-diagonal least-squares method. The positions of all the hexamethylene-

tetramine hydrogen atoms as well as of four ethyl hydrogen atoms were obtained from a difference Fourier synthesis; they were also refined. In the final cycle of the refinement with anisotropic temperature factors for all the non-hydrogen atoms, all the parameter shifts were less than one-third of the corresponding standard deviations. The final R value becomes 0.030.⁶⁾

¹H-NMR Measurement. The ¹H-NMR spectra of their chloroform-*d* solutions were recorded on a JEOL JNM-MH-100 NMR spectrometer, using TMS as the internal standard.

Results and Discussion

The final atomic parameters for **3** are listed in Table 1,⁷⁾ while the interatomic distances, as well as the bond angles of the complex, are tabulated in Table 2. A perspective drawing of the adduct and the numbering scheme of the atoms are shown in Fig. 1, while Fig. 2 presents a projection of the structure along *b*.

The crystal consists of discrete molecules, and each

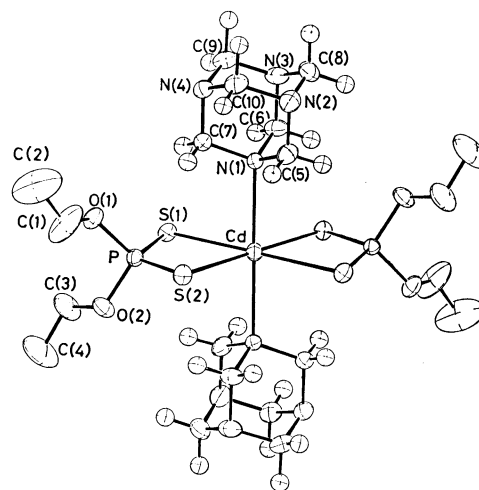


Fig. 1. A perspective drawing of the title compound with the numbering scheme of atoms.

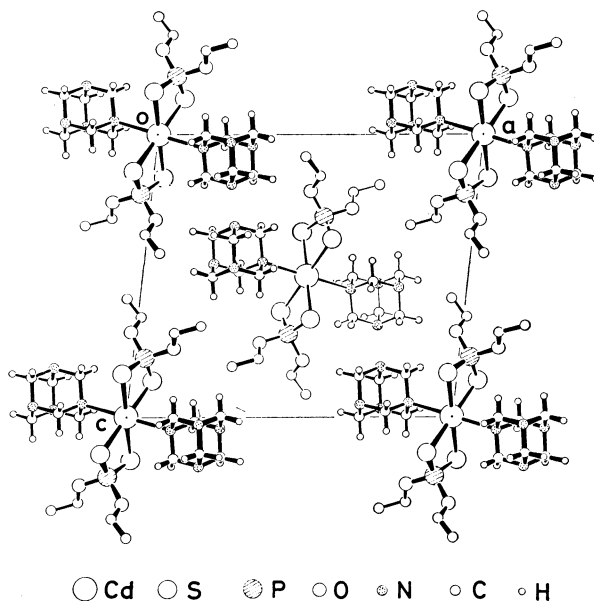


Fig. 2. Crystal packing diagram projected along *b*.

** Systematic absence of the reflections were 0*k*0 for $k=\text{odd}$ and $h0l$ for $h+l=\text{odd}$.

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}/\text{\AA}^2$ a)	Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}/\text{\AA}^2$ a)
Cd	0	0	0	3.19	C(1)	-116(3)	2152(8)	3536(3)	10.63
S(1)	282.6(4)	-2258.4(8)	1530.5(4)	3.35	C(2)	424(4)	2859(9)	4197(5)	14.60
S(2)	-665.1(4)	2134.5(8)	1281.7(4)	3.37	C(3)	-1175(2)	-2783(6)	2960(3)	7.90
P	-354.1(3)	-161.1(8)	2083.5(4)	3.00	C(4)	-1954(3)	-3268(8)	3178(4)	12.49
O(1)	175(1)	474(3)	3019(1)	4.44	C(5)	1444(2)	3709(4)	37(2)	4.13
O(2)	-1192(1)	-987(3)	2399(1)	4.67	C(6)	2087(2)	530(4)	170(2)	4.22
N(1)	1403(1)	1725(3)	470(1)	2.98	C(7)	1577(2)	2025(4)	1488(2)	3.91
N(2)	2242(2)	4681(3)	276(2)	4.76	C(8)	2881(2)	3381(5)	-20(2)	5.85
N(3)	2892(1)	1430(4)	414(2)	5.02	C(9)	3013(2)	1733(4)	1421(2)	4.91
N(4)	2373(1)	2968(3)	1748(1)	3.89	C(10)	2380(2)	4876(4)	1281(2)	4.70
Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}}/\text{\AA}^2$	Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}}/\text{\AA}^2$
H(3-1)	-85(3)	-253(7)	349(4)	12.0(17)	H(7-1)	156(2)	72(4)	178(2)	2.3(6)
H(3-2)	-99(3)	-392(8)	258(3)	11.3(16)	H(7-2)	110(2)	296(4)	166(2)	2.4(6)
H(4-1)	-187(3)	-449(6)	346(3)	7.1(11)	H(8-1)	343(2)	411(5)	14(2)	3.4(7)
H(4-2)	-232(4)	-348(9)	267(4)	14.3(19)	H(8-2)	277(2)	328(5)	-66(2)	4.4(8)
H(5-1)	130(1)	357(4)	-60(2)	1.8(5)	H(9-1)	354(2)	235(4)	163(2)	4.0(7)
H(5-2)	105(2)	448(4)	21(2)	1.6(5)	H(9-2)	294(2)	48(4)	175(2)	3.1(7)
H(6-1)	198(2)	39(4)	-43(2)	2.1(6)	H(10-1)	289(2)	545(4)	144(2)	3.4(7)
H(6-2)	206(2)	-76(4)	48(2)	2.5(6)	H(10-2)	196(2)	559(4)	152(2)	2.0(5)

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

cadmium atom is at the center of symmetry. A couple of dtp ligands are coordinated to the central metal atom by their two sulfur atoms, forming four-membered chelate rings on the equatorial plane. On the other hand, two hex molecules are coordinated to the central metal atom by their nitrogen atoms from the axial direction. Thus, the cadmium(II) atom takes a six-coordinate distorted octahedral configuration.

The Cd-S distances of the present adduct are 2.704(1) and 2.682(1) Å, slightly longer than those in Cd(II) (*i*-Pr₂dtp)₂ (where *i*-Pr₂dtp = *O,O'*-diisopropyl dithiophosphato group) (2.486(7)–2.590(8) Å.⁸⁾) This is probably because of the fact that the former is in an octahedral configuration, while the latter is in tetrahedral configuration. In the present adduct, the two P-S distances in the ligand are about the same, *ca.* 1.98 Å, and intermediate between the single bond (2.09 Å) and the double bond (1.87 Å),⁹⁾ indicating that the double bond is delocalized. The four-membered ring formed by Cd, S(1), S(2), and P atoms is almost planar. In the present complex, the S(1)–Cd–S(2) bond angle is 77.09(2)°, smaller than those of common *O,O'*-dialkyl dithiophosphato complexes and of their adducts,^{10–24)} including the Co(Me₂dtp)₂(PPh₃) (where Me₂dtp = *O,O'*-dimethyl dithiophosphato group; PPh₃ = triphenylphosphine) reported in the other paper,¹⁾ although there are some exceptions.^{13,16)}

The apparent C–C distances of the ethyl groups of the present adduct were found to be 1.323(8) and 1.382(7) Å, shorter than the common C–C single bond length (1.50 Å). This is probably a result of the fact that the carbon atoms are not fixed, but have large

thermal parameters, as is shown in Table 2.

The Cd–N(1) distance is 2.595(2) Å, longer than the common Cd–N distances (about 2.3 Å) in cadmium(II) complexes.²⁵⁾ Similar phenomenon has also been observed in Mn(II)Cl₂(hex)₂(H₂O)₂, where Mn–N is 2.40 Å.²⁾ In the present case, this is probably attributable to the repulsion between the hydrogen atoms of the hex and the sulfur atoms of the dtp ligand. As is shown in Table 2, H(7-1)⋯S(1), H(7-2)⋯S(2), H(5-1)⋯S(1'), and H(6-1)⋯S(2') are all about 2.9 Å. They are shorter than the sum of the van der Waals radii of H and S atoms (3.05 Å), suggesting a strong repulsion. Thus, the long Cd–N distance of this adducts is probably attributable to the hindrance caused by the bulky ligand. As was shown in another paper, the Co–P distance of Co(II)(Me₂dtp)₂(PPh₃) is also large, because of the bulky ligand.¹⁾ In the case of smaller ligands, the metal–nitrogen distances of the amine adducts, for example, the Ni–N distances of Ni(II)(dtp)₂·X_n-type adducts, are not unusually long (2.06–2.11 Å);^{19–23)} they are not much longer than the sum of the coordination radii (2.00 Å).

In the free hex molecule, all the C–N bonds are equivalent; their length is 1.476(2) Å. In contrast, the average distance between carbon and nitrogen atoms bonded to the metal atom in the present adduct is 1.488(5) Å, and the mean length of the other N–C bonds is 1.464(5) Å. This observation suggests that electrons flow from the ligand into the metal through the coordinated nitrogen atom. The same type of elongation of the C–N bond of hex has also been reported for its adducts of borane²⁷⁾ and iodine.²⁸⁾

The powder X-ray diffraction pattern of **2** was compared with that of the same type of Co(II) adduct. The diffraction patterns are shown in Fig. 3a. The peak positions, as well as their intensities, correspond with each other, except for some weak peaks. Their infrared spectra in the 400–4000 cm^{-1} region are also similar. Thus, the cadmium(II) and cobalt(II) adducts are likely to be isostructural, exhibiting a five-

coordinate trigonal bipyramidal configuration.

The powder X-ray diffraction patterns of **1**, **2**, **3**, and hex were compared with each other, but no coincidence between them were recognized. This fact indicates that **2** and **3** are not mixtures, but different kinds of compounds.

The adduct **5** and Co(II)(dtp)₂(pip), as well as **6** and Co(II)(dtp)₂(pyr), are found to be isostructural with one another, and the structure of **5** resembles that of **6**; the diffraction patterns of **5**, **6**, and Co(II)-

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

Interatomic distance ($\text{\AA}$)			
Cd-S(1)	2.704(1)	N(2)-C(5)	1.467(4)
Cd-S(2)	2.682(1)	N(2)-C(8)	1.464(4)
Cd-N(1)	2.595(2)	N(2)-C(10)	1.464(4)
P-S(1)	1.982(1)	N(3)-C(6)	1.457(3)
P-S(2)	1.979(1)	N(3)-C(8)	1.465(4)
P-O(1)	1.593(2)	N(3)-C(9)	1.474(4)
P-O(2)	1.590(2)	N(4)-C(7)	1.461(3)
O(1)-C(1)	1.471(5)	N(4)-C(9)	1.458(4)
C(1)-C(2)	1.323(8)	N(4)-C(10)	1.462(3)
O(2)-C(3)	1.465(4)		
C(3)-C(4)	1.382(7)	S(1)···H(7-1)	2.89(3)
N(1)-C(5)	1.490(3)	S(2)···H(7-2)	2.93(3)
N(1)-C(6)	1.482(3)	S(1')···H(5-1)	2.93(2)
N(1)-C(7)	1.493(3)	S(2')···H(6-1)	2.92(3)
Bond angle ($^\circ$)			
S(1)-Cd-S(2)	77.09(2)	C(5)-N(1)-C(6)	107.4(2)
S(1)-Cd-N(1)	88.24(4)	C(6)-N(1)-C(7)	107.4(2)
S(2)-Cd-N(1)	89.08(4)	C(7)-N(1)-C(5)	106.6(2)
Cd-S(1)-P	83.05(2)	C(5)-N(2)-C(8)	107.6(2)
Cd-S(2)-P	83.69(3)	C(8)-N(2)-C(10)	108.1(2)
S(1)-P-S(2)	115.85(4)	C(10)-N(2)-C(5)	108.4(2)
S(1)-P-O(1)	106.40(7)	C(6)-N(3)-C(8)	107.7(2)
S(1)-P-O(2)	111.66(8)	C(8)-N(3)-C(9)	107.4(2)
S(2)-P-O(1)	111.97(7)	C(9)-N(3)-C(6)	108.8(2)
S(2)-P-O(2)	105.87(7)	C(7)-N(4)-C(9)	108.2(2)
O(1)-P-O(2)	104.6(1)	C(9)-N(4)-C(10)	108.3(2)
P-O(1)-C(1)	118.2(2)	C(10)-N(4)-C(7)	108.5(2)
O(1)-C(1)-C(2)	115.3(5)	N(1)-C(5)-N(2)	112.6(2)
P-O(2)-C(3)	119.2(2)	N(1)-C(6)-N(3)	112.7(2)
O(2)-C(3)-C(4)	111.3(4)	N(1)-C(7)-N(4)	112.8(2)
Cd-N(1)-C(5)	111.9(1)	N(2)-C(8)-N(3)	113.0(3)
Cd-N(1)-C(6)	110.3(1)	N(3)-C(9)-N(4)	112.4(2)
Cd-N(1)-C(7)	113.1(1)	N(4)-C(10)-N(2)	112.2(2)

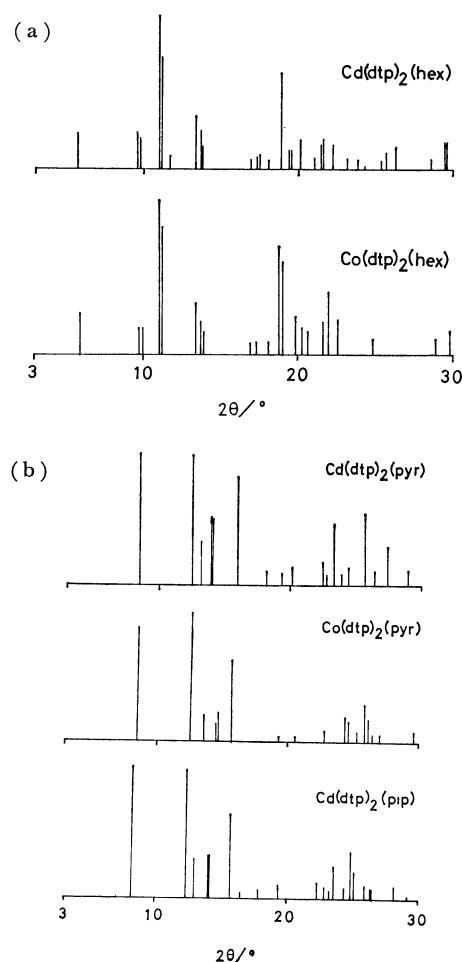


Fig. 3. Powder X-ray diffraction patterns of a) hexamethylenetetramine adducts, and b) pyrazine and piperazine adducts.

TABLE 3. ^1H -NMR DATA OF $\text{Cd(II)(dtp)}_2 \cdot X_n$ -TYPE ADDUCTS (IN δ , SOLVENT = CHLOROFORM- d)

	Ethyl protons of dtp		Ligand in Adducts		Free ligand	
[Cd(II)(dtp) ₂]	4.30	1.42				
[Cd(II)(dtp) ₂ (hex)]	4.19	1.39	4.82		4.73	
Cd(II)(dtp) ₂ (PPh ₃)	4.15	1.36	7.44		7.17	7.14
[Cd(II)(dtp) ₂ (pip)]	4.20	1.42	3.11	1.96	2.83	2.00
[Cd(II)(dtp) ₂ (pyr)]	4.25	1.40	8.78	8.67	8.55	
[Cd(II)(dtp) ₂ (bzt) ₂]	4.23	1.37	9.28	8.38	8.85	8.08
			7.99	7.51	7.88	7.41
[Cd(II)(dtp) ₂ (bza) ₂]	4.18	1.37	7.37	4.08	7.30	3.84
			2.67		1.44	

dtp: *O,O'*-Diethyl dithiophosphato ligand; hex: hexamethylenetetramine; PPh₃: triphenylphosphine; pip: piperazine; pyr: pyrazine; bzt: benzothiazole; bza: benzylamine.

(dtp)₂(pyr) are shown in Fig. 3b. These cobalt(II) adducts are expected to have an octahedral configuration,¹⁾ where two nitrogen atoms of the ligand act as donor atoms, and the ligand bridges two metal atoms. Therefore, the corresponding cadmium(II) adducts may have the same structure. The **4** and **7** adducts are not exactly isostructural to the corresponding Co(II)(dtp)₂ adducts, but each pair of adducts is likely to have structures resembling each other.

The chemical shifts of the ¹H-NMR of **1** and its adducts in a chloroform-*d* solution, together with those of the free ligands, are shown in Table 3. As expected, the signals of the dtp ethyl protons are shifted to a higher magnetic field by the formation of the adducts. On the other hand, the signals of the amine or phosphine protons of the adducts appear in a lower magnetic field than those of the corresponding ligands. This fact shows that the amine or phosphine molecules form bonds with the complex, even in a solution, or at least in equilibrium with the bonded form. Thus, the electrons appear to flow from the amine or phosphine to the dtp ligand through the central metal atom.

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