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Syntheses of a New Series of Transition Metal Chelates of Diphenylphosphinothioylthiourea Anion

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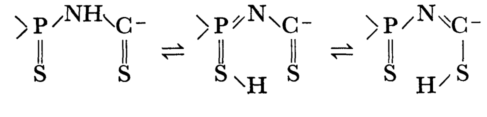
New thiourea derivatives, 3-diphenylphosphinothioyl-1-phenylthiourea (PTTU-A), 3-diphenylphosphinothioyl-1,1-diethylthiourea (PTTU-B), and 3-diphenylphosphinothioyl-1,1-dimethylthiourea (PTTU-C) were found to behave as bidentate ligands with transition metal ions such as Ni(II), Pd(II), Co(II), and Cu(II) to give a series of novel metal chelates. The structures of these complexes are discussed on the basis of magnetic susceptibilities, infrared spectra, electronic spectra, powder X-ray diffraction patterns and elemental analyses. Tentative assignments of two metal-sulfur stretching vibrations in the far infrared spectra were made for Ni-PTTU and Pd-PTTU, which have square-planar configurations. However, the structures of the Cu-PTTU complexes could not be determined by these methods because of the instability of the complexes. They were confirmed by electronic and ESR spectroscopies.

In recent years, chelate complexes with sulfur-donor ligands have been extensively studied as an interesting topic in the field of coordination chemistry and many reports have been published on the properties and reactivities of such complexes as the metal chelates of dithiocarbamates, dithioacetylacetonates, and dithiolates.[1] However, no chelate complexes which have a P=S→M structure have been synthesized so far except for metal dialkyldithiophosphinates.[2]

Thus, it is of considerable interest to synthesize chelate compounds possessing an enolizable P=S bond in the ligand. A part of this work has been described previously[3]



These new chelate rings are important as a unit of polynuclear complexes, and are interesting in connection with the model complexes of enzymatic system such as ferredoxin which is a metal complex with ligands containing sulfur as donor atoms.

The new thiourea derivatives, diphenylphosphinothioylthioureas, PTTU-A, PTTU-B, and PTTU-C, can act as sulfur-donor chelating reagents because their structures include both enolizable P=S and C=S bonds. In view of this the reactions of PTTU with transition metal halides such as nickel(II) chloride hexahydrate, palladium(II) chloride, cobalt(II) chloride hexahydrate, and copper(II) chloride dihydrate, were investigated.

Experimental

Syntheses of Ligands. Diphenylphosphinothioylthioureas were prepared by the reaction of diphenylphosphinothioyl isothiocyanate with amines. A typical procedure is described for the preparation of 3-diphenylphosphinothioyl-1,1-diethylthiourea (PTTU-B). A solution of diethylamine (0.51 g, 7.0 mmol) in 50 m*l* of ether was added to a solution of diphenylphosphinothioyl isothiocyanate (2.0 g, 7.3 mmol) in 50 m*l* of ether with stirring at room temperature. An exothermic reaction took place and white crystals of 3-diphenylphosphionothioyl-1,1-diethylthiourea (PTTU-B) were precipitated in quantitative yield. Mp 125—127°C, IR (KBr disk): 3120(ν NH), 1555(δ NH), and 1475(Amide II) cm^{-1}. Found: C, 58.75; H, 6.01; N, 7.83; S, 18.50%. Calcd: C, 58.60; H, 6.07; N, 8.04; S, 18.40%. 3-Diphenylphosphinothioyl-1-phenylthiourea (PTTU-A): White prisms, mp 143—145°C, IR(KBr disk): 3290, 3220, 3160, 3125(ν NH), 1620, and 1570(δ NH) cm^{-1}. Found: C, 61.85; H, 4.62; N, 7.38; S, 16.90%. Calcd: C, 61.94; H, 4.65; N, 7.60; S, 17.40%. Dimethylammonium salts of 3-diphenylphosphinothioyl-1,1-dimethylthiourea (PTTU-C): When a 40% aqueous solution of dimethylamine (1.30 g, 11.5 mmol) and diphenylphosphinothioyl isothiocyanate (1.35 g, 4.9 mmol) were mixed, an exothermic reaction took place. By a treatment similar to that described above, white crystals of a dimethylammonium salt of 3-diphenylphosphinothioyl-1,1-dimethylthiourea (PTTU-C) were obtained in almost quantitative yield. Mp 118—120°C (lit,[4] 119—121°C), IR (Nujol): 3290, 3240 (ν NH) and 1530 (δ NH) cm^{-1}.

Syntheses of Copmlexes.. A typical procedure is described for the preparation of bis[3-diphenylphosphinothioyl-1,1-diethylthioureato]nickel (Ni-PTTU-B): A solution of PTTU-B (1.4 g, 4.0 mmol) in 10 m*l* of dichloromethane was allowed to react with nickel(II) chloride hexahydrate (0.95 g, 2.0 mmol) in 40 m*l* of ethanol at room temperature with stirring for an hour. Dark green needles of Ni-PTTU-B precipitated, which were recrystallized from dichloromethane-ethanol. Ni-PTTU-B was accordingly obtained in a nearly quantitative yield. The Ni(II) and Pd(II) complexes of PTTU-A(Ni-PTTU-A and Pd-PTTU-A), Pd(II) and Co(II) complexes of PTTU-B (Pd-PTTU-B and Co-PTTU-B) and the Ni(II), Pd(II), and Co(II) complexes of PTTU-C (Ni-PTTU-C, Pd-PTTU-C and Co-PTTU-C) were prepared in a similar way.

Ni-PTTU-A: Dark green needles, mp 193°C (dec.). Found: C, 57.9; H, 4.4; N, 6.6; S. 16.0; Ni, 7.3%. Calcd: C, 57.7; H, 4.1; N, 7.1; S, 16.2; Ni; 7.4%.

Pd-PTTU-A: Orange-yellow prisms, mp 215°C (dec.). Found: C, 53.3; H, 3.6; N, 6.0; S, 14.5%. Calcd: C, 54.3; H, 3.8; N, 6.7; S, 15.2%.

Pd-PTTU-A: Reddish-brown prisms, mp 254°C (dec.).

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[1] G. N. Shrauzer, *Accounts. Chem. Res.*, **2**, 72 (1969); S. E. Livingstone, *Quart. Rev.*, **19**, 386 (1965); R. Mason, E. D. McKenzie, G. Robertson, and G. A. Rusholme, *Chem. Commun.*, **1968**, 1673; H. H. Wickmann and A. H. Trozzolo, *Inorg. Chem.*, **7**, 63 (1968); O. Siiman and J. Fresco, *ibid.*, **8**, 1846 (1969).

[2] C. K. Jϕrgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

[3] I. Ojima, T. Iwamoto, T. Onishi, N. Inamoto, and K. Tamaru, *Chem. Commun.*, **1969**, 1501.

[4] A. Schmidpeter and H. Groeger, *Chem. Ber.*, **100**, 3052 (1967).

Found: C, 47.8; H, 3.7; N, 3.9; S, 17.2%. Calcd: C, 47.4; H, 3.4; N, 4.3; S, 19.5%.

Ni-PTTU-B: Dark green needles, mp 200°C (dec.). Found: C, 49.0; H, 4.8; N, 6.7; S, 15.8%. Calcd: C, 51.0; H, 5.0; N, 7.0; S, 16.0%.

Co-PTTU-B: Bright green needles, mp 205—206°C. Found: C, 54.1; H, 5.2; N, 7.2; S, 16.8%. Calcd: C, 54.2; H, 5.4; N, 7.4; S, 17.0%.

Ni-PTTU-C: Dark green needles; mp 188—190°C (dec.). Found: C, 50.0; H, 4.7; N. 8.0; S, 18.2%. Calcd: C, 51.7; H, 4.6; N, 8.0; S, 18.4%.

Pd-PTTU-C: Orange-yellow prisms, mp 209—211°C (dec.). Found: C, 46.6; H, 3.8; N, 8.0; S, 16.8%. Calcd: C, 48.4; H, 4.3; N, 7.5; S, 17.2%.

Co-PTTU-C: Bright bluish-green needles, mp 194—195°C (dec.). Found: C, 49.8; H, 4.4; N, 7.8; S, 17.9%. Calcd: C, 51.6; H, 4.6; N, 8.0; S, 18.4%.

Measurements. The infrared spectra of these complexes in the region 4000—700 cm^{-1} were measured using KBr disks with a 402 *G* spectrophotometer (Japan Spectroscopic Co., Ltd). The far infrared spectra in the region 700—200 cm^{-1} were obtained with a Hitachi EPI-L spectrophotometer. Samples were mixed with paraffin or fused polyethylene or mulled in Nujol. Electronic spectra were recorded on a Hitachi EPS-S spectrophotometer. An ESR spectrometer JEOL Model JES-118 X band was used. Molecular weights were ebullioscopically determined with a Hitachi-Perkin-Elmer Model 115.

Results and Discussion

Syntheses of the Complexes and Their Magnetic Properties. First, PTTU-A was allowed to react with nickel(II) chloride hexahydrate in dichloromethane - ethanol solution under reflux for an hour to give dark green needles of Ni-PTTU-A in 60—70% yield. In the same manner, the reaction of PTTU-A with palladium(II) chloride was performed and reddish-brown prisms were obtained (Pb-PTTU′-A). The bis-phosphinothioylthioureato-metal structure of Ni-PTTU-A was confirmed on the basis of elemental analysis, UV spectrum, and magnetic susceptibility. However, for Pd-PTTU-A, elemental analysis and infrared spectra showed that the ligands have decomposed during the syntheses. In order to prevent thermal decomposition of the product, PTTU-A was allowed to react with palladium(II) chloride in dichlorometahne - ethanol at room temperature for 3 hr with stirring. Yellowish-orange prisms of Pd-PTTU-A were obtained in 90% yield. When Pd-PTTU-A was heated in dichloromethane ethanol under reflux for one hour, the reddish-brown prisms were obtained and on the basis of the melting point, infrared spectra, elemental analysis, and powder X-ray diffraction patterns were found to be identical with the Pd-PTTU′-A prepared as above.

The powder X-ray diffraction patterns of these complexes are shown in Fig. 1. By comparison of these spectra, it was found that Pd-PTTU′-A has a simpler structure than that of Ni-PTTU-A and Pd-PTTU-A. This suggests that in the Pd-PTTU′-A the six membered chelate rings remain intact, but the aniline group is lost. The structure of Pd-PTTU′-A, therefore, was suggested to be the one shown in Scheme 1.

An attempt to obtain crystalline Co-PTTU-A was unsuccessful, but its formation in solution was observed by UV spectrum, as shown in Fig. 2. It is suggested that the central cobalt(II) (d^7) has a tetrahedral configuration.

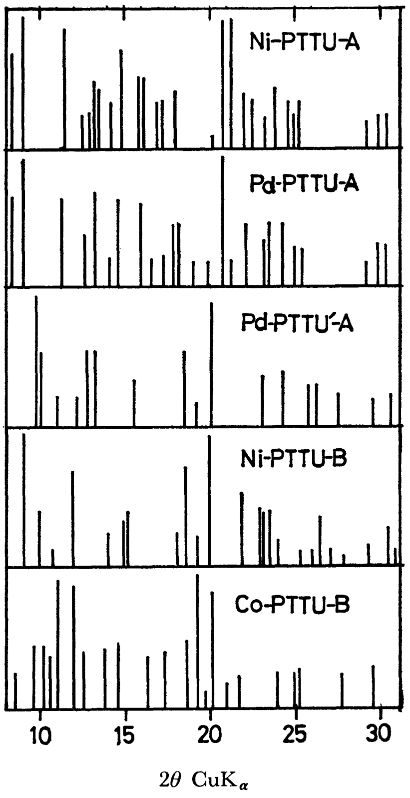
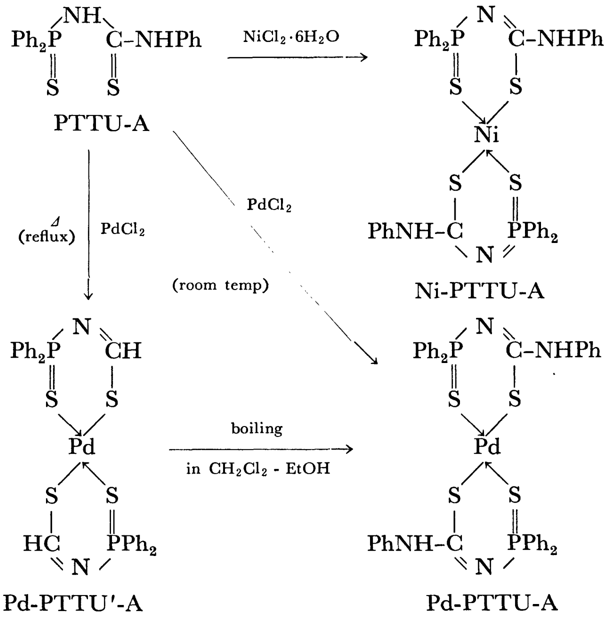


Fig. 1. The powder X-ray diffraction patterns of M-PTTU.



Scheme 1

Similarly, the nickel(II), palladium(II), and cobalt(II) complexes of PTTU-B and PTTU-C were obtained by the reaction of the corresponding PTTU with transition metal halides in dichloromethane-ethanol at room temperature with stirring for 1—2 hr as shown in Scheme 2. In contrast with Co-PTTU-A, Co-

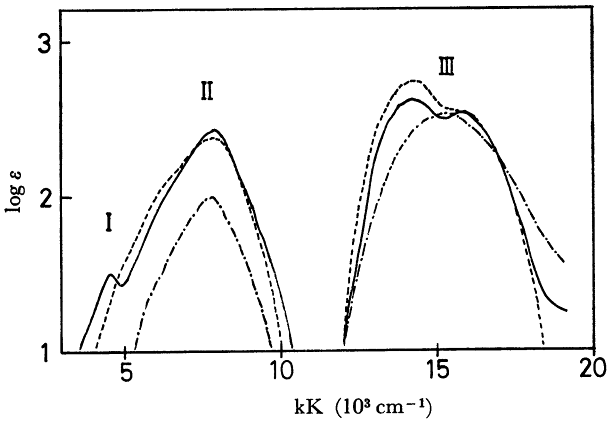
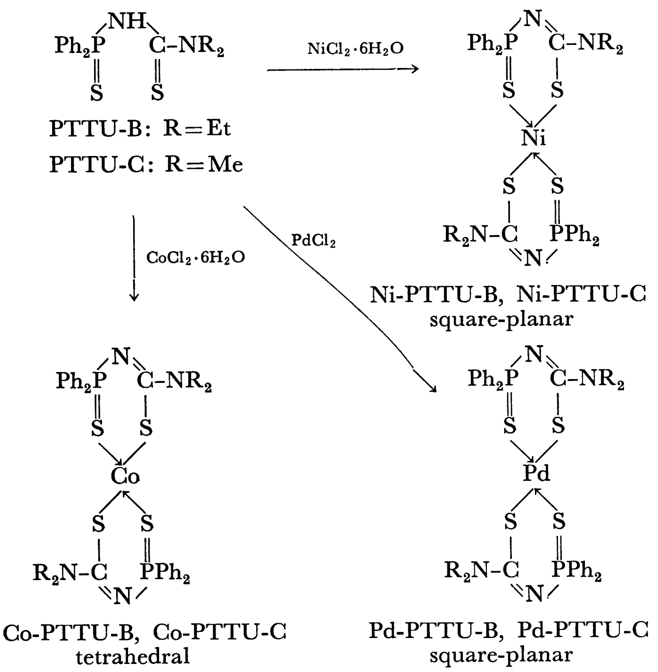


Fig. 2. The electronic spectra of Co-PTTU.



Scheme 2

PTTU-B and Co-PTTU-C were obtained as crystalline substances and a tetrahedral configuration was suggested on the basis of the magnetic susceptibility and electronic spectrum.

All these complexes have the same metal : ligand ratio (1 : 2). They are soluble in organic solvents such as benzene, chloroform, dichloromethane etc., but their solubilities in benzene were not high enough to determine their molecular weights except in the case of Co-PTTU. The molecular weights of Co-PTTU-B and Co-PTTU-C were ebullioscopically determined in benzene to be 751 and 678 (the calculated values for the monomers are 753 and 698), respectively. Except Co-PTTU, they are all diamagnetic at room temperature, which suggests that the complexes of Ni(II) and Pd(II) have square-planar configurations. Their crystal structures seem to be isomorphous according to the powder X-ray diffraction patterns as shown in Fig. 1. The effective magnetic moment of Co-PTTU-B, $\mu_{\mathrm{eff}}=4.50$ B.M. ($\chi_g=11.9\times 10^{-6}$ cgsemu) at 297°K, and that of Co-PTTU-C, $\mu_{\mathrm{eff}}=5.00$ B.M. ($\chi_g=16.3\times 10^{-6}$ cgsemu) at 297°K, correspond to the high spin state ($S=2/3$) of d^7 Co-(II) in a tetrahedral configuration. The powder X-ray diffraction pattern of Co-PTTU-B was quite different from those of Ni-and Pd-PTTU-B as shown in Fig. 1.

Electronic Spectra of Complexes. The electronic spectra of Ni-PTTU-A, Ni-PTTU-B and Ni-PTTU-C displayed an absorption band in the region of 17 kK and suggested a square-planar configuration of the central nickel(II) ions (d^8). The tetrahedral configurations for Co-PTTU-B and Co-PTTU-C. were suggested on the basis of the effective magnetic moment as described above. Moreover, the absorption bands appearing in the region 3-20 kK in the electronic spectra of Co-PTTU-A, Co-PTTU-B, and Co-PTTU-C can be assigned to Td symmetry. The absorption band III in the visible region and band II at 7.87 kK can be assigned to the transition from $^4A_2$ to $^4T_1$ (P) and from $^4A_2$ to $^4T_1$ (F), respectively. The values of $|Dq/B|$ and E/B were obtained by the use of the Tanabe-Sugano diagram according to the assignment mentioned above. Values of B and $10\,D_q$ were calculated to be 684 and 4790 cm^{-1}, respectively. It might be appropriate to assign the samll peak I, appearing in the spectrum of Co-PTTU-B at 4.65 kK, to the transition from $^4A_2$ to $^4T_2$ (the energy of this transition corresponds to $10\,Dq$). The value of Racah's electron repulsion parameter B corresponds to 60% of the free ions, thus reflecting the covalency of the cobalt-sulfur bonds. The value of Dq corresponds to 50% of that derived in the case of $[\mathrm{Co(H_2O)_6}]^{2+}$ with $\mathrm{O_h}$ symmetry. This shows the adequacy of these assignments although the value of $Dq(\mathrm{Td})/Dq(\mathrm{Oh})$ was slightly larger than 4/9. The values of B and Dq thus obtained are in reasonable agreement with those reported for several tetrahedral cobalt(II) complexes.[5] It is of interest that the cobalt(II) ion in Co-PTTU-A, Co-PTTU-B, and Co-PTTU-C has a tetrahedral configuration in contrast to the bis-dithioacetylacetonato-cobalt(II), which has a square-planar configuration.[6]

Infrared Spectra. The infrared spectra of the complexes were measured in the region 4000—200 cm^{-1}. In the far infrared spectra of the chelates with a square-planar structure, two metal-sulfur stretching vibrations were expected to appear in the region 500—200 cm^{-1},

Table 1. Characteristic bands in the infrared spectra of Ni-PTTU and Pd-PTTU (cm^{-1})

	νP=S	νM-S(ν_{I})	νM-S(ν_{II})
Ni-PTTU-A	584	417	358
Pd-PTTU-A	582	412	336
Pd-PTTU-A	586	401	334
Ni-PTTU-B	580	391	340
Pd-PTTU-B	579	380	329
Ni-PTTU-C	579	404	344
Pd-PTTU-C	576	394	334

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5) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier Pub. Co., Amsterdam (1968), pp. 322—328.

6) R. Beckett and B. F. Hoskins, *Chem. Commun.*, **1967**, 909.

as previously reported.[7] The bands appearing in the region 420—320 cm^{-1} that are most sensitive to the metal ion are tentatively assigned in Table 1 to these vibrations because of the covalent nature of metal-sulfur bond and the mass effect. The assignment of P=S stretching bands is also given in Table 1.

The strong bands appearing in the region 650—590 cm^{-1} in the spectra of the ligands can be assined to P=S stretching vibrations (PTTU-A: 635, 607 cm^{-1}, PTTU-B: 594 cm^{-1}, PTTU-C: 650, 632 cm^{-1}). When the chelate rings were formed, these bands shifted to lower frequencies by 20—70 cm^{-1}, and appeared in the region 585—575 cm^{-1}. The bands assigned to the NH stretching vibrations of Ni-PTTU-A and Pd-PTTU-A appeared at 3260 and 3250 cm^{-1}, respectively. The medium-to-strong bands observed in the region 1200—1350 cm^{-1} may be due to the thiourea structure of the ligands, and considerable changes were observed, as shown in Fig. 3, when the complexes were formed. In the case of Pd-PTTU'-A in particular, large changes were observed in these bands (Fig. 3) together with the absence of a NH stretching band between 3500 and 3000 cm^{-1}. This suggests that the aniline group has been lost.

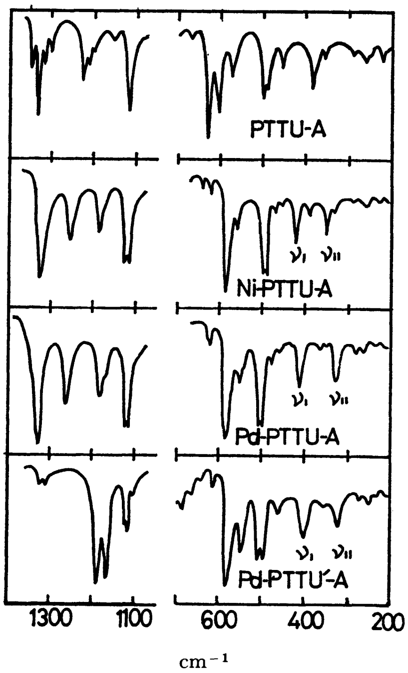

Fig. 3. The infrared and far infrared spectra of M-PTTU-A.

Synthesis of Cu-PTTU-B and Its ESR Spectra. When PTTU (2 eqiv.) and copper (II) chloride dihydrate (1 eqiv.) were reacted, a spontaneous reduction occurred and white grey prisms were precipitated. The structure was not clear, but the infrared spectrum suggests that the PTTU ligand remains although decomposition occurred in the other site. The copper contained in this complex was found on the basis of the magnetic susceptibility (diamagnetic) to be univalent.

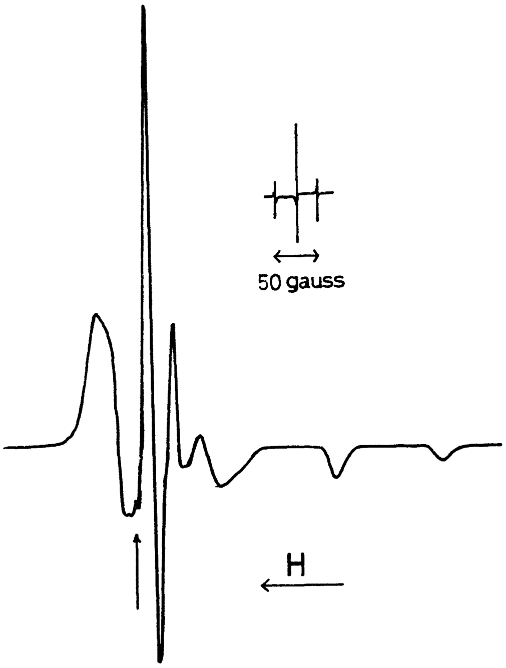

Fig. 4. ESR spectrum of Cu-PTTU-B in CH_2Cl_2 - EtOH solution frozen at 77°K. The arrow indicates the resonance field for DPPH (g=2.00354).

Fig. 5. ESR spectrum of Cu-PTTU in CH_2Cl_2 - EtOH solution at 15°C. The arrow indicates the resonance field for DPPH (g=2.00354).

The decomposition of Cu-PTTU-A and Cu-PTTU-C was so rapid that the initial formation of divalent complex could not be detected. In the case of PTTU-B, however, the formation of Cu-PTTU-B was observed in the presence of excess ligands (*ca.* 10 eqiv.) in CH_2Cl_2-EtOH solution by use of ESR spectroscopy, both at room temperature and in glassy state at 77°K. A broad absorption band was observed at 560 nm in the electronic spectrum. The observed ESR spectra of Cu-PTTU-B are shown in Figs. 4 and 5. The sample was prepared just before a measurement in a quartz tube by mixing PTTU-B in dichloromethane (10^{-1} mol/l) and copper (II) chloride dihydrate in ethanol

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[7] I. Ojima, T. Onishi, T. Iwamoto, N. Inamoto, and K. Tamaru, *Inorg. Nucl. Chem. Lett.*, **6**, 65 (1970), and references therein.

(10^{-2} mol/l). The deep violet color due to the formation of Cu-PTTU-B gradually disappeared at room temperature, but decomposition was completely suppressed at 77°K. The values of $g_{//}$, $g_{\perp}$, $|A_{//}|$ and $|A_{\perp}|$ obtained from the spectrum are 2.111, 2.026, 135×10^{-4} cm^{-1}, and 30×10^{-4} cm^{-1}, respectively. Similarly, the values of g_0 and $|A_0|$ are 2.060 and 60.1×10^{-4} cm^{-1}, respectively. Furthermore, the bonding parameter α^2 [8] was calculated to be 0.53 by the method proposed by Kivelson.[9] These values correspond precisely with those of CuS_4 type complexes, on the basis of the classification performed by Taminaga and Fujiwara, as shown in Tables 2 and 3.[10] An average of $g_{//}$ and $g_{\perp}$, 2.053 is in good agreement with g_0, 2.060, and an average of $|A_{//}|$ and $|A_{\perp}|$, 6.5×10^{-3} cm^{-1}, agrees with A_0, 6.0×10^{-3} cm^{-1}. These facts suggest that the species detected by ESR at room temperature is identical with the species existing at 77°K, and that the formation of a copper(II) complex by decomposition of the ligand did not occur.

TABLE 2. ESR PARAMETERS OF COPPER(II) COMPLEXES

Ligand	Type	g_0[a]	$g_{//}$	$g_{\perp}$	$\lvert A_0\rvert$[a]	$\lvert A_{//}\rvert$	$\lvert A_{\perp}\rvert$
					($\times 10^4$ cm^{-1})		
glycine	CuO_2N_2	2.129	2.252	2.068	69	196	5
L-alanine	CuO_2N_2	2.131	2.260	2.067	69	184	12
dith. dieth.	CuS_4	2.047	2.108	2.017	76	139	44
8-mercapt.	CuN_2S_2	2.075	2.158	2.034	63	114	38
PTTU-B	CuS_4	2.060	2.111	2.026	60	135	30

a) From solution at room temperature.

TABLE 3. BONDING PARAMETERS, α^2, OF COPPER(II) COMPLEXES

Type	Ligand	α^2	Type	Ligand	α^2
CuO_4	oxal.	0.84	CuN_2S_2	8-mercapt.	0.54
CuO_2N_2	L-alanine	0.84	CuS_4	dieth. dith.	0.55
CuN_4	dipyr.	0.80	CuS_4	PTTU-B	0.53

Abbreviation; oxal.: oxalic acid, dipyr.: 2,2′-dipyridyl, 8-mercapt.: 8-mercaptoquinoline, dieth.dith.: diethyldithiocarbamic acid, PTTU-B: 3-diphenylphosphinothioyl-1,1-diethylthiourea.

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8) $\alpha^2=-A_{//}/P+(g_{//}-2.0023)+3/7(g_{\perp}-2.0023)+0.04$ with the orbital parameter $p=2\gamma\beta\beta_N(r^{-3})\sim 0.36$ cm^{-1}

9) D. Kivelson and R. Neiman, *J. Chem. Phys.*, **35**, 149 (1961).

10) I. Taminaga and S. Fujiwara, *Spectroscopy Lett.*, **2**, 127 (1969).