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Synthesis and Properties of Bis(N-phenyl-β-mercapto-thiocinnamamido)Pd(II)[1]

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Bis(N-phenyl-β-mercaptothiocinnamamido)Pd(II) was prepared and its chemical properties were investigated. It was revealed that the complex is coordinated with two sulfur atoms of the ligand and capable of containing two pyridine molecules when it is recrystallized from its pyridine solution. These pyridine molecules do not coordinate with the central palladium ion, but were supposed to be included as clathrate and probably interact with the protons of the thioamido groups of the ligands.

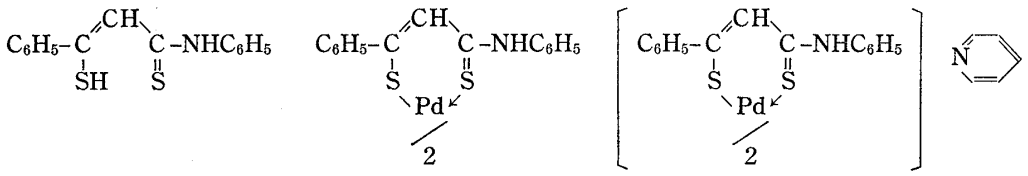
Keywords——dithio palladium complex; thioamido group; infrared spectra; NMR spectra; thermogravimetric analysis; pyridine clathrate; hydrogen bond

Sulfur-containing chelating agents are sometimes very useful for the analytical chemistry on account of their high selectivity towards metal ions and their ability to coordinate strongly with various metal ions. Accordingly, we have been interested in dithio chelating agents.

Studies on bidentate dithio chelating agents are one of the most attractive subjects in the coordination chemistry and many ligands have hitherto been reported with their metal complexes, which are briefly divided into the following three groups, 1,1-, 1,2- and 1,3-dithio complexes which involves 4-, 5- and 6-membered chelating ring, respectively.

The 1,1- and 1,2-dithio chelating agents have widely been studied with various metal chelates and reviewed.[3–5] Although no 1,3-dithio chelating agents have been isolated till recently, Martin, *et al.*[6] have succeeded in preparing O-ethylthioacetothioacetate (OEt–SacSacH) which is the only example ever reported.

Recently we have also succeeded in preparing a new 1,3-dithio chelating agent, N-phenyl-β-mercaptothiocinnamamide (LH).[1] In this paper, we deal with the palladium complex of this ligand (PdL_2) and its pyridine adduct (PdL_2py_2).



LH PdL_2 PdL_2py_2

Experimental

Materials——N-Phenyl-β-mercaptothiocinnamamide (LH): LH was prepared by the procedure reported in ref. 1.

Bis(N-phenyl-β-mercaptothiocinnamamido)Pd(II) (PdL_2): To 2 mmol of LH in 100 ml of EtOH 1 mmol of palladium ammonium chloride in 100 ml of water was added with stirring. The orange-red

1) Previous paper: S. Kitagawa and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **26**, 1021 (1978).
2) Location: *Yoshida, Shimoadachi-cho, Sakyo-ku, Kyoto, 606, Japan.*
3) R. Eisenberg, *Prog. Inorg. Chem.*, **12**, 295 (1970).
4) J.A. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968).
5) D. Coucouvanis, *Prog. Inorg. Chem.*, **11**, 233 (1969).
6) A.R. Hendrickson and R.L. Martin, *Aust. J. Chem.*, **25**, 257 (1972).

precipitate was filtered, washed with MeOH and recrystallized from acetone, mp 302° (dec.). Yield 80%. *Anal.* Calcd. for $C_{30}H_{24}N_2PdS_4$: C, 55.73; H, 3.72; N, 4.33; S, 19.81; Pd, 16.41. Found: C, 55.36; H, 3.89; N, 4.20; S, 19.07; Pd, 19.09.

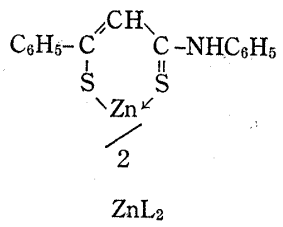
Bis(N-phenyl-β-mercaptothiocinnamamido)Pd(II) Dipyridine (PdL_2py_2): PdL_2 was recrystallized from pyridine. The obtained orange-red product was washed with MeOH and dried *in vacuo* at room temperature, mp 302° (dec.). Yield 85%. *Anal.* Calcd. for $C_{40}H_{34}N_4PdS_4$: C, 59.70; H, 4.23; N, 6.97; S, 15.92; Pd, 13.18. Found: C, 59.69; H, 4.37; N, 7.00; S, 15.81; Pd, 13.04.

Apparatus——Electronic spectra were recorded on a Shimadzu multiconvertible spectrophotometer Model Double-40. Infrared (IR) absorption measurements were carried out as KBr disks with a Hitachi IR spectrophotometer Model EPI-S2. Molecular weight estimation by vapour pressure osmometry were performed in pyridine with a Mechrolab vapour pressure osmometer Model 301A using triphenylphosphine as a standard substance. Magnetic susceptibility measurements were carried out by the Gouy method at room temperature (25±1°). Thermogravimetric analysis (TGA) was done with a Rigaku thermogravimetric analyzer Model MP 803. Nuclear magnetic resonance (NMR) spectra in dimethylsulfoxide (DMSO) were measured on a Varian A-60 spectrophtometer at 60 MHz with tetramethylsilane as an internal standard. Mass spectra were recorded with a Hitachi RMU-6C mass spectrometer.

Results and Discussion

Although LH coordinates easily with a number of transition metal ions, they have a very low solubility to organic solvents except DMSO and pyridine which give a little better solubility to the chelates. Most of the chelates, however, decompose gradually in pyridine and these properties make it difficult to study their chemical properties. Since PdL_2 is the most stable in pyridine, it was taken up first for the investigation of the properties of the metal chelates.

The NMR data of PdL_2 are presented in Table I compared with those of LH and the corresponding zinc chelate, ZnL_2.[7] All the expected signals of PdL_2 were detected except that of the NH proton which is supposed to disappear because of the proton exchange for the water molecule in DMSO-d_6. Actually, the NH signal of LH at δ 8.89 in $CDCl_3$ disappear in DMSO-d_6 as shown in Table I. Similarly, that of ZnL_2 at δ 8.28 in $CDCl_3$ vanishes by the addition of DMSO-d_6 to the solution. The lower shift of the methine signal is not observed on chelation, while the C=C stretching vibration in IR spectrum shows a lower shift on chelation.



ZnL_2

Table I. Nuclear Magnetic Resonance Data (δ ppm)

Compound	Solvent	Proton		
		–NH–	C_6H_5–	=CH–
LH	$CDCl_3$	8.89	7.37	6.70
	DMSO-d_6	n.o.[a]	7.52	7.10
PdL_2	DMSO-d_6	n.o.	7.52	7.08
ZnL_2	$CDCl_3$	8.28	7.31	6.85

a) Not observed.

The IR spectrum of PdL_2 is presented in Fig. 1 and listed in Table II, compared with those of LH. The SH stretching of LH disappears in PdL_2, which shows that the ligand chelates with palladium ion with its SH group. The C=C stretching vibration at 1560 cm^{-1} in LH shifts to lower frequency on chelation, which seems to indicate the π-delocalization of the C=C bond.

7) S. Kitagawa and H. Tanaka, "in preparation."

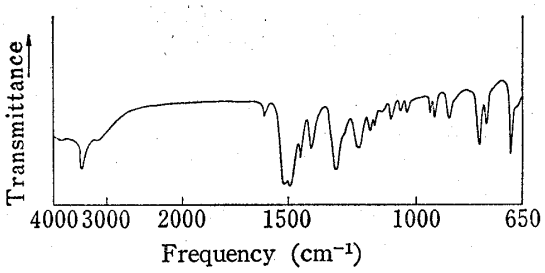


Fig. 1. The Infrared Spectrum of of PdL_2

Table II. Partial Infrared Spectra (cm^{-1})

Assignment	LH	PdL_2
ν(NH)	3240	3250
ν(SH)	2200	—
ν(C=C)	1560	1510
NCS I	1500	1490
NCS II	1310	1310
NCS III	1200	1170

Rao, *et al.*[8] reported that in compounds with >N–C=S unit, strong vibration coupling effects by ν(C–N), ν(C=S) and δ(NH) are possible and three characteristic bands due to the mixed vibrations appear in the regions, 1395—1570, 1260—1420 and 960—1140 cm^{-1} which were tentatively designated as the "NCS I, II and III band," respectively, among which Rao, *et al.* supposed that the NCS III band is mainly due to ν(C=S). In PdL_2 strong absorptions are seen at 1490, 1310 and 1170 cm^{-1} which are supposed to be the NCS I, II and III band, respectively. Although the NCS I and II bands show very little shift on chelation, the NCS III band moves to 30 cm^{-1} lower frequency on chelation, which seems to exhibit that LH chelates with its sulfur atom of the thiocarbonyl group, not the nitrogen atom. Actually, the ν(NH) of LH shifts only slightly on chelation.

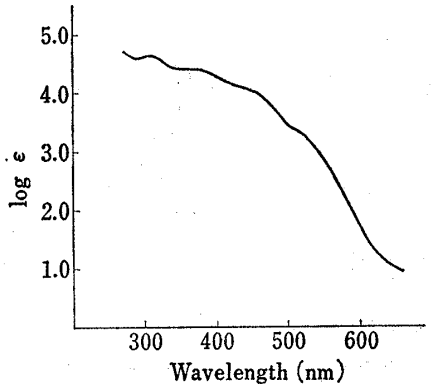


Fig. 2. The Electronic Spectrum of PdL_2 in DMSO

Table III. The Electronic Spectra of LH in EtOH and PdL_2 in DMSO nm (ε)

LH	PdL_2	Assignment
	528sh (1510)	d–π
	452sh (10100)	d–π or π–π
	372sh (25000)	
347 (15600)	310 (40100)	π–π
256sh (10600)		
229sh (17800)		

Below 270 nm of PdL_2 was unable to be measured because of the absorption of the solvent.

The electronic spectrum of PdL_2 in DMSO is reproduced in Fig. 2 and listed in Table III with that of LH in EtOH. Taking these molar absorbances into account, the band below 372 nm may be assigned as π-π band and that at 452 nm, as π-π or d-π band. Martin, *et al.*[9] reported that Pd(OEt–SacSac)$_2$ exhibits a band at 523 nm (ε: 900) and that its ε value is sufficiently low to be assigned as a ligand field transition. Although PdL_2 displays a similar band at 528 nm (ε: 1510), it should be assigned as a d-π band from its ε value.

PdL_2 produces a pyridine–containing complex which was confirmed by its elemental analysis to accord with PdL_2py_2. With repect to the interaction of pyridine molecules with PdL_2, following two cases seem to be available: 1) pyridine molecules directly coordinate to the central palladium ion and 2) pyridine molecules are included in the crystals of PdL_2 as clathrate, although both cases have never been reported with dithio palladium complexes.

The NMR spectra of PdL_2 and PdL_2py_2 in DMSO-d_6 are similar and the spectrum of PdL_2 in pyridine-d_5 does not show paramagnetic shift and broadening. Moreover, the

8) C.N.R. Rao and R. Venkataraghvan, *Spectrochim. Acta*, **18**, 541 (1962).
9) A.R. Hendrickson and R.L. Martin, *Inorg. Chem.*, **12**, 2582 (1973).

electronic spectra of both complexes, PdL_2 and PdL_2py_2 are similar except those in the ultraviolet region where PdL_2py_2 shows the extra absorptions typical of pyridine[10] at 246, 253, 257 and 262 nm as seen Fig. 3.

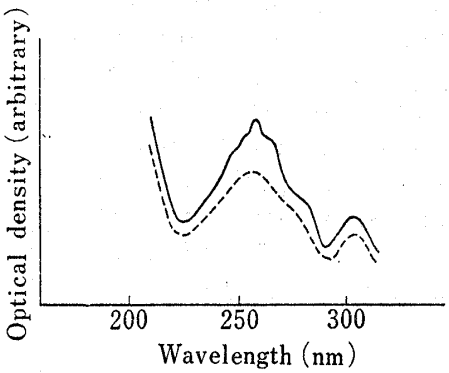


Fig. 3. The Electronic Spectral Difference between PdL_2 and PdL_2py_2 in EtOH.

----: PdL_2.
——: PdL_2py_2.

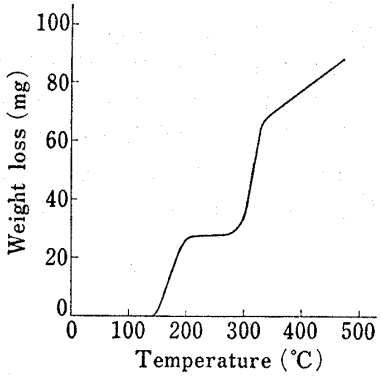


Fig. 4. Thermogravimetric Analysis of PdL_2py_2

There have been no reports with pyridine adducts of dithio metal chelates with six-membered ring, but Livingston, *et al.* reported some those of nickel chelates of β-thioketo-ester[11] and monothio-β-diketones[12] where pyridine molecules coordinate to the central nickel ions forming octahedral complexes. They noted that these adducts are unstable and easily lose the pyridine molecules when they are exposed to air at room temperature. The pyridine adduct, PdL_2py_2, however, are very stable on exposure to air. So as to examine its stability against heating, TGA was carried out and the results are shown in Fig. 4 and Table IV. The

Table IV. The Possible Decomposition Reaction of PdL_2py_2 in TGA

	Reaction		Weight loss (%) Calcd.	Weight loss (%) Found	Dissociation temperature (°C)
1st Stage	PdL_2py_2(s)	PdL_2(s)+2Pyridine(g)	19.7	19.6	147
2nd Stage	PdL_2(s)	PdL(s)+L(g)	41.8	33.6	295
3rd Stage	PdL(s)	PdO(s)+L(g)	67.6	—	363

s: solid, g: gas.

first stage of the weight loss is supposed to be the dissociation of two pyridine molecules. The dissociation begins at a fairly high temperature, 147°, which reveas PdL_2py_2 is very stable against heating in contrast with the adducts reported by Livingston, *et al.*

These data obtained from NMR, electronic spectra and TGA all exclude the first assumption and support the second assumption that the pyridine molecules in PdL_2py_2 are included as clathrate. Moreover, an additional result supporting this was obtained by magnetic susceptibility measurements which reveals that PdL_2py_2 is diamagnetic in solid state as well as PdL_2.

PdL_2, as mentioned before, shows very low solubility in various organic solvents, but it shows better solubility in pyridine. This fact led us to the consideration that the difference

10) H.U. Daeniker, *Helv. Chim. Acta*, **35**, 1955 (1952).
11) S.H.H. Chaston, S.E. Livingston, T.N. Lockyer, V.A. Pickles, and J.S. Shannon, *Aust. J. Chem.*, **18**, 678 (1965).
12) S.H.H. Chaston, S.E. Livingston, and T.N. Lockyer, *Aust. J. Chem.*, **19**, 1401 (1966).

in solbility may be caused by the thioamido groups of PdL_2. As is shown in Chart 1, the electron shift seems to occure on the complex formation with metal ion and this causes the decrease of electron density at the nitrogen atoms. The induced positive property seems to enable that the thioamido protons associate with proton accepting solvents by forming hydrogen bond. Actually, Saito, *et al.*[13] proposed such an electron migration in formamide. Furthermore, Chikuma, *et al.*[14] reported that the hydrogen bond between the secondary amido proton and pyridine was suggested from the extrathermodynamic analysis for the pyridine adduct formation of Ni(II) chelate of thio-β-diketones and related amides.

So as to examine the existence of hydrogen bond, we performed the molecular weight estimation of PdL_2 in pyridine by vapour pressure osmometry, but it gave 637 versus 804, the theoretical value of PdL_2py_2. This result may be considered that the interaction of pyridine with thioamido protons is too weak to be detected in solution.

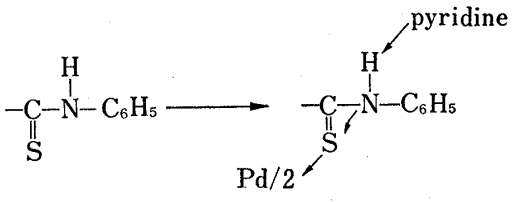


Chart 1. The Electron Migration Process

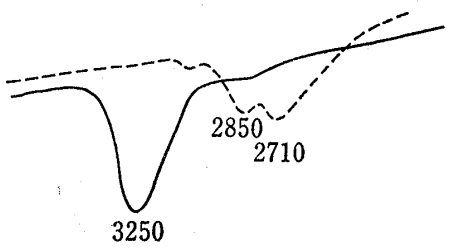


Fig. 5. The NH Stretching Bands of PdL_2 and PdL_2py_2 (cm^{-1})
——: PdL_2.
– – –: PdL_2py_2.

The IR spectra of PdL_2 and PdL_2py_2 in KBr disks, however, show clearly different absorptions with respect to their NH bands as shown in Fig. 5. PdL_2 exhibits a strong absorption at 3250 cm^{-1}, while PdL_2py_2 shows two absorptions with medium intensity at 2850 and 2710 cm^{-1}. This shift to lower frequency is likely due to the hydrogen bond between pyridine molecules and the thioamido protons because pyridine shows no absorption in this region and the latter returns to the former after PdL_2py_2 is heated and the pyridine molecules are completely expelled.

These experimental data gave us a plausible idea that pyridine molecules interact weakly with the thioamido groups of PdL_2 in solution, but that they interact fairly strongly with those in solid state, producing the pyridine clathrate, PdL_2py_2.

13) H. Saito, Y. Tanaka, and K. Nukada, *J. Am. Chem. Soc.*, **93**, 1077 (1971).
14) M. Chikuma, A. Yokoyama, and H. Tanaka, *J. Inorg. Nucl. Chem.*, **36**, 1243 (1974).