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Dimethylsulfoxide Clathrates of Metal Complexes of β-Mercaptothiocinnamamide Derivatives

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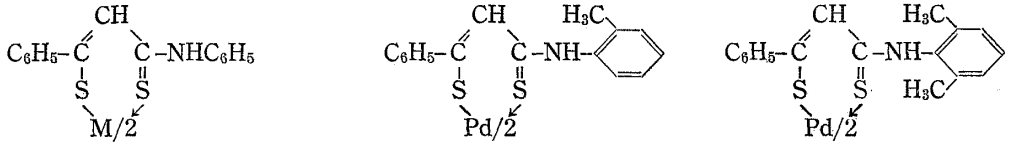
Dimethylsulfoxide (DMSO) clathrates of some dithio metal complexes, bis(N-phenyl-β-mercaptothiocinnamamido)metal(II)bidimethylsulfoxide($ML_2(DMSO)_2$, M: Pt^{2+}, Pd^{2+}, Ni^{2+}), bis{N-(2-methylphenyl)- and bis{N-(2,6-dimethylphenyl)-β-mercaptothiocinnamamido}palladium(II)bidimethylsulfoxide ($PdL'_2(DMSO)_2$ and $PdL_2''(DMSO)_2$, respectively) were prepared. From the results of infrared spectra and magnetic susceptibility measurements, these DMSO molecules were supposed to interact with the thioamido protons of the ligands by forming hydrogen bonds.

Keywords——dimethylsulfoxide clathrates; dithio metal complexes; thioamido group; infrared spectra; NH stretching band; magnetic susceptibility measurement; hydrogen bond

In the previous papers,[2,3] we reported the synthesis and properties of bis{N-phenyl-, bis{N-(2-methylphenyl)- and bis{N-(2,6-dimethylphenyl)-β-mercaptothiocinnamamido}-palladium(II) (PdL_2, $PdL^{2'}$ and PdL''_2, respectively) and their pyridine clathrates (PdL_2py_2, PdL'_2py_2 and PdL''_2py_2, respectively). These clathrates found to be diamagnetic by magnetic susceptibility measurements and their ν_{NH} absorptions appeared in the 2850—2700 cm^{-1} region, about 400—500 cm^{-1} lower than those of their original complexes. The lowering of ν_{NH} seemed to be due to the formation of hydrogen bonds. Therefore, it was supposed that in these clathrates pyridine molecules interacted with the thioamido protons of the ligands. Supporting this assumption, the N-methylated palladium complex, bis(N-methyl-, N-phenyl-β-mercaptothiocinnamamido)palladium (II) ($Pd(MeL)_2$) did not give a pyridine clathrate.[4]



ML_2 (M=Pt^{2+}, Pd^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}) PdL'_2 PdL''_2

$Pd(MeL)_2$ disulfide (I)

Chart 1

Similar dimethylsulfoxide (DMSO) clathrates of these dithio metal complexes were obtained by the recrystallization from DMSO. Their elemental analyses showed that these clathrates contained two DMSO molecules (Table I). The clathrates were found to be dia-

1) Location: *Yoshida, Shimoadachi-cho, Sakyo-ku, Kyoto, 606, Japan.*
2) S. Kitagawa and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **26**, 1026 (1978).
3) S. Kitagawa and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **26**, 2793 (1978).
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Table I. Analytical Data of the Obtained DMSO Clathrates

Compound	mp (°C)	Calcd. (%)			Found (%)		
		C	H	N	C	H	N
$PtL_2(DMSO)_2$	>280	45.79	4.04	3.14	45.86	3.91	3.01
$PdL_2(DMSO)_2$	264	50.87	4.49	3.49	50.36	4.73	3.49
$NiL_2(DMSO)_2$	217	54.04	4.77	3.71	55.13	4.86	4.10
$PdL'_2(DMSO)_2$	275	52.05	4.82	3.37	51.93	5.01	3.37
$PdL''_2(DMSO)_2$	>280	53.15	5.13	3.26	53.88	5.20	3.49

magnetic and their ν_{NH} were lowered similarly to the pyridine clathrates as shown in Fig. 1 and Table II, although the DMSO clathrates displayed an additional absorption around 3150 cm^{-1}. This band may be that of $\nu_{O\cdots H}$.

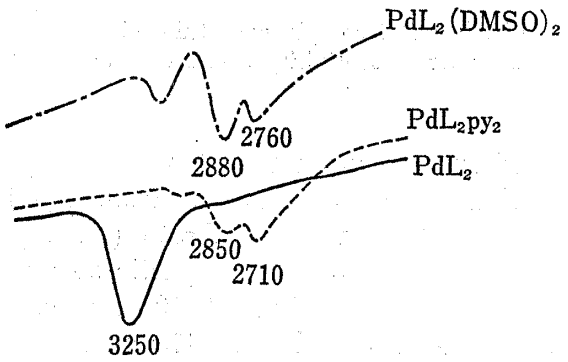

Fig. 1. NH Stretching Bands of PdL_2, PdL_2py_2 and $PdL_2(DMSO)_2$ (cm^{-1})

From these observations, DMSO molecules in the clathrates are also likely to interact with the thioamido protons of the ligands.

It is well-known that metal ions such as Pt^{2+} and Pd^{2+}, which are soft acid, coordinate strongly with sulfur atom through not only σ-bonding but also π-bonding. These strong bondings cause electron migration from the nitrogen- to the sulfur-atom of the thioamido group. Therefore, the thioamido protons which become more positive are able to form strong hydrogen bonds with pyridine and DMSO.

Table II. ν_{NH} Bands of the Complexes (cm^{-1})

Compound	ν_{NH}		$\nu_{O\cdots H}$
PtL_2	3220		
PdL_2	3250		
NiL_2	3250		
PdL'_2	3250		
PdL_2''	3310		
PtL_2py_2	2830	2700	
PdL_2py_2	2850	2710	
PdL'_2py_2	2850	2720	
PdL''_2py_2	2850	2710	
$PtL_2(DMSO)_2$	2880	2780	3150
$PdL_2(DMSO)_2$	2880	2760	3150
$NiL_2(DMSO)_2$	2880	2790	3180
$PdL'_2(DMSO)_2$	2950	2770	3150
$PdL''_2(DMSO)_2$	2900	2760	3130

With respect to this clathrate formation, the central metal ions of the original complexes are divided into the following three groups. 1) Both pyridine- and DMSO-clathrate are possible: Pt^{2+},Pd^{2+}. 2) Only DMSO clathrate is possible: Ni^{2+}. 3) Neither is possible: Co^{2+}, Zn^{2+}.

$NiL_2(DMSO)_2$ was isolated, but NiL_2 decomposed in pyridine into non-metal-containing disulfide (I)[5] instead of NiL_2py_2. Ligand field stability of NiL_2 is lower than those of PtL_2 and PdL_2. Therefore, it may likely occur that pyridine molecules coordinate with Ni^{2+} from the axial directions, which dissociate NiL_2. On the contrary ,DMSO which is a weaker base than pyridine dose not dissociate NiL_2 and gives $NiL_2(DMSO)_2$.

PtL_2 and PdL_2 yielded both pyridine- and DMSO-clathrate. On the other hand, CoL_2 and ZnL_2 formed neither clathrate.

These differences are supposed to depend on the stability of the complexes against bases. Therefore, the stability of the metal complexes, ML_2, seems to be PtL_2, $PdL_2 > NiL_2 > CoL_2$, ZnL_2.

Experimental

DMSO clathrates were synthesized by recrystallization of their original complexes from DMSO. Infrared measurements were carried out as potassium bromide disks with a Hitachi Infrared Spectrophotometer Model EPI-S2. Magnetic susceptibility measurements were done by the Gouy method at room temperature ($20 \pm 1°$).

5) S. Kitagawa and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **26**, 1629 (1978).

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Bovine Liver β-Acetylhexosaminidase. Purification by Hydrophobic Affinity Chromatography and Heterogeneity

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Bovine liver β-acetylhexosaminidase A (Hex A) and B (Hex B) were purified by hydrophobic affinity chromatography. Octyl Sepharose CL-4B was more effective than Phenyl Sepharose CL-4B as an adsorbent. Both the crude and the purified preparations of Hex A and Hex B exhibited extensive heterogeneity when focused on a polyacrylamide gel plate with pH gradient; Hex A gave at least ten bands with pI's ranging from 5.0 to 7.0, and Hex B at least fourteen bands with pI's ranging from 6.5 to 8.5.

Stepwise elution with increasing pH from a CM-cellulose column resulted in rough separation of Hex A and Hex B into overlapping classes.

Keywords——β-acetylhexosaminidase; bovine liver; hydrophobic affinity chromatography; isoelectric focusing; polymorphism of enzyme; isozyme

β-Acetylhexosaminidase from bovine liver consists of two main components, acetylhexosaminidase A and B (Hex A and Hex B),[2] like many other mammalian visceral acetylhexosaminidases. Previously, the bovine liver enzymes were purified by affinity chromatography using CH-Sepharose 4B substituted with *p*-aminophenyl β-acetylglucosaminide and the corresponding 1-thio-glycoside as affinity adsorbent, in which multiplicity of Hex B was suggested on the basis of its behaviour in affinity chromatography.[2b]

1) Location: *2-2-1, Miyama, Funabashi-shi, Chiba, 274, Japan.*
2) *a*) T.J. Langley and F.R. Jevons, *Arch. Biochem. Biophys.*, **128**, 312 (1968); *b*) M. Tanaka, S. Kyosaka, and S. Murata, *Chem. Pharm. Bull.* (Tokyo), **26**, 1188 (1978).