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Pd(II) Complexes with 2,2′-Diaminobiphenyl

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The new palladium(II) complexes with 2,2′-diaminobiphenyl (DABP) have been synthesized under various conditions. The hexa-coordinated palladium complex, $[Pd(DABP)_2Cl_2]$, has been prepared under a high pressure. The square planar diamagnetic complexes, $[Pd(DABP)_2]X_2$ ($X=Cl$, Br), have been synthesized under atmospheric pressure. As to the $[Pd(DABP)_2]Cl_2$ complexes, two isomers, the yellow complex and the yellow-green complex, are obtained according to the temperature at which the complexes are synthesized. Both the complexes, the yellow and the yellow-green complexes, are similar with respect to the powder X-ray diffraction pattern and the IR spectra in the region from 4000 cm^{-1} to 200 cm^{-1}, but are somewhat different with respect to the stability to air, the thermal stability, and the solubility in chloroform.

Stereochemical and preparative studies of the 2,2′-diaminobiphenyl (DABP)-metal complexes have been reported.[2,3)] The compounds subjected to these studies were prepared under an atmospheric pressure. The present author has reported that the Ni(II), Co(II), and Cu(II) complexes with 2,2′-diaminobiphenyl synthesized under a high pressure differ from those complexes prepared under the atmospheric pressure with respect to the spectroscopic behavior and melting or decomposing points.[4)] The present paper aims to throw light upon the effect that the preparative conditions may have on the coordination of the ligand to the central metal atom or the other properties in the case of Pd(II)-DABP complexes.

Experimental

Materials. 2,2′-diaminobiphenyl (DABP) was prepared as has been previously reported.[4)] Commercially-available $PdCl_2$ and $PdBr_2$ were used.

Syntheses of Compounds. *$[Pd(DABP)_2]Cl_2$ (I) and (II):*

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[2)] F. McCollough, Jr., and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **78**, 714 (1956); T. Habu and J. C. Bailar, Jr., *ibid.*, **88**, 1128 (1966).

[3)] F. Hein and W. Jehn, *Z. Anorg. Allg. Chem.*, **341**, 244 (1965).

[4)] S. Onaka, T. Iwamoto, Y. Sasaki, and S. Fujiwara, This Bulletin, **40**, 1398 (1967).

TABLE 1. ANALYTICAL RESULTS

Compound	Elemental analysis Found/(Calcd) % C	H	N	Mdp[a)] °C
[Pd(DABP)$_2$]Cl$_2$ (I) (yellow compound)	52.72	4.72	9.72	132—133
$C_{24}H_{24}N_4Cl_2Pd$	(52.81)	(4.43)	(10.27)	
[Pd(DABP)$_2$]Cl$_2$ (II) (yellow-green compound)	52.45	4.66	9.92	136.5—137
$C_{24}H_{24}N_4Cl_2Pd$	(52.81)	(4.43)	(10.27)	
[Pd(DABP)$_2$]Br$_2$ (III)	44.66	3.81	8.56	
$C_{24}H_{24}N_4Br_2Pd$	(45.42)	(3.81)	(8.83)	

a) Melting or decomposing point is uncorrected.

0.004 mol (0.74 g) of DABP was dissolved into 50 m*l* of ethanol. This solution was slowly dropped into a solution which contained 0.0014 mol (0.25 g) of $PdCl_2$ in 100 m*l* of ethanol below 50°C. The mixture was stirred for 2 hr under the same condition. The resulting yellow precipitates (I) were collected on a glass filter (4 *G*), washed with absolute ethanol, and then dried *in vacuo* for 24 hr at 80°C. (If the temperature is raised to 130°C in drying the precipitates, the compound turns grey-brown). Yield: 80%, based on $PdCl_2$. On the other hand, if the ethanol solution of DABP is dropped into the ethanol solution of $PdCl_2$ at a refluxing temperature, yellow-green precipitates (II) are obtained. (Yield: 80%, based on $PdCl_2$) The yellow-green product (II) is also obtainable by treating the yellow product (I) with an ethanol solution of DABP at a refluxing temperature for a few hours. This compound (II) is thermally more stable than the compound (I). The decomposing points for these compounds are shown in Table 1. Both the compounds are hygroscopic and turn grey-brown when left in air for a few hours. The yellow product is more stable than the yellow-green product in air. The solubility of the yellow-green product to chloroform is higher than that of the yellow product. The solubility of these compounds to methanol and water suggests the monomeric structure.[2,3)]

[Pd(DABP)$_2$]Br$_2$ (III): Only a yellow product was obtained under the atmospheric pressure in the temperature region from 80°C to room temperature with the manner described above. Yield: 42%, based on $PdBr_2$.

[Pd(DABP)$_2$Cl$_2$] (IV): In a steel autoclave, 0.01 mol (1.8 g) of palladium chloride, 0.02 mol (3.7 g) of DABP, 20 m*l* of ethanol, and 3 m*l* of concentrated hydrochloric acid were placed, and nitrogen gas was introduced at a pressure of 80 atm. Then the autoclave was heated at 120°C and shaken for 2 hr. A mixture of the yellow and grey powders was thus obtained. The yellow powder that was carefully separated from the grey powder was subjected to infrared measurement.

The results of the elemental analyses are shown in Table 1.

Magnetic Susceptibility.[5)] The finely-powdered samples were measured with a Gouy balance at room temperature. The complexes prepared under the atmospheric pressure are diamagnetic.

Powder X-Ray Diffractometry. The powder X-ray diffraction data were obtained as has been previously described.[4)] The results are shown in Table 2.

TABLE 2. THE POWDER X-RAY DIFFRACTION DATA

[Pd(DABP)$_2$]Cl$_2$ (I) (yellow product) 2θ, °	I/I_0	[Pd(DABP)$_2$]Cl$_2$ (II) (yellow-green product) 2θ, °	I/I_0
9.0	1.0	9.0	1.0
12.9	0.12	12.9	0.20
13.2	0.16	13.2	0.20
18.4	0.12	18.4	0.17
20.4	0.12	20.4	0.20
22.7	0.10	22.7	0.17
25.6	0.21	25.6	0.23
29.0	0.10	29.0	0.12

Relative intensities were calculated by comparing the height of the peaks. rad: CuKα_1.
Less intensity lines are excluded.

Diffuse Reflection Spectra.[6)] The reflection spectra in the ultraviolet and visible regions were measured with a Shimazu MP-S-50L apparatus equipped with a standard reflectance attachment. The reflectance rates were calculated by means of the Kubelka-Munk equation.[7)]

Infrared Spectra. The infrared spectra were recorded with a Hitachi EPI-G2 spectrometer and a Hitachi EPI-L spectrometer for the samples in the Nujol mulls from 4000 cm^{-1} to 200 cm^{-1}. The results are shown in Fig. 1, in Fig. 3, and in Table 3.

Discussion

The magnetic measurements show that the complexes (I), (II), and (III) synthesized under atmospheric pressure are square planar. The coordination of the amino group to the palladium metal can be clearly explained on the basis of the infrared data. The absorption bands due to the amino group of the ligand amine are considerably shifted toward lower frequencies in its complexes. The far-infrared spectra of the compounds (I), (II), and (III) form additional evidence of the coordination of the amino group. It is expected that the participation of the halogen atoms in the coordination may cause remarkable shifts of the bands in the far-infrared region, depending on the halogen atoms.[8)] As is shown in Fig. 1, the far-infrared spectrum of the compound (III) is almost the

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5) The author's thanks are due to Professor Yukichi Yoshino, of the College of General Education of this University, for the use of the Gouy balance.

6) The author's thanks are due to Professor Sadao Yoshikawa, of Department of Applied Chemistry, Faculty of Engineering of this University, for the kind permission to use the reflectance spectrometer.

7) P. Kubelka and F. Munk, *Z. tech. Physik*, **12**, 593 (1931).

8) J. Hiraishi, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, **24A**, 819 (1968).

TABLE 3. THE CHARACTERISTIC INFRARED AND THE FAR-INFRARED BANDS OF THE DABP-COMPLEXES, cm^{-1}

DABP	$[Pd(DABP)_2]Cl_2$ (I)	$[Pd(DABP)_2]Cl_2$ (II)	$[Pd(DABP)_2]Br_2$ (III)	Assignment
3400, s	3360, s	3380, m	3380, s	NH_2 asym. str.
3380, s		3360, s		
3270, m				
3180, s	3150, m	3150, m	3140, s	NH_2 sym. str.
1635, vs	1615, s	1615, s	1610, vs	NH_2 bend.
	1585, vs	1575, s	1570, vs	
	1050, m	1050, s	1045, s	NH_2 wag.
486, vs				
452, w	458, w	456, w	455, w	
446, w	442, s	440, s	440, s	
433, w	432, m	429, s	427, m	
426, w				
	410, m	410, m	412, m	Pd-N str.
			405, w, sh	
321, sh	332, s	330, s	325, vs	
314, vs	314, s	313, s	310, vs	
277, m				
270, m				
204, s	225, m	235, m	230, m	

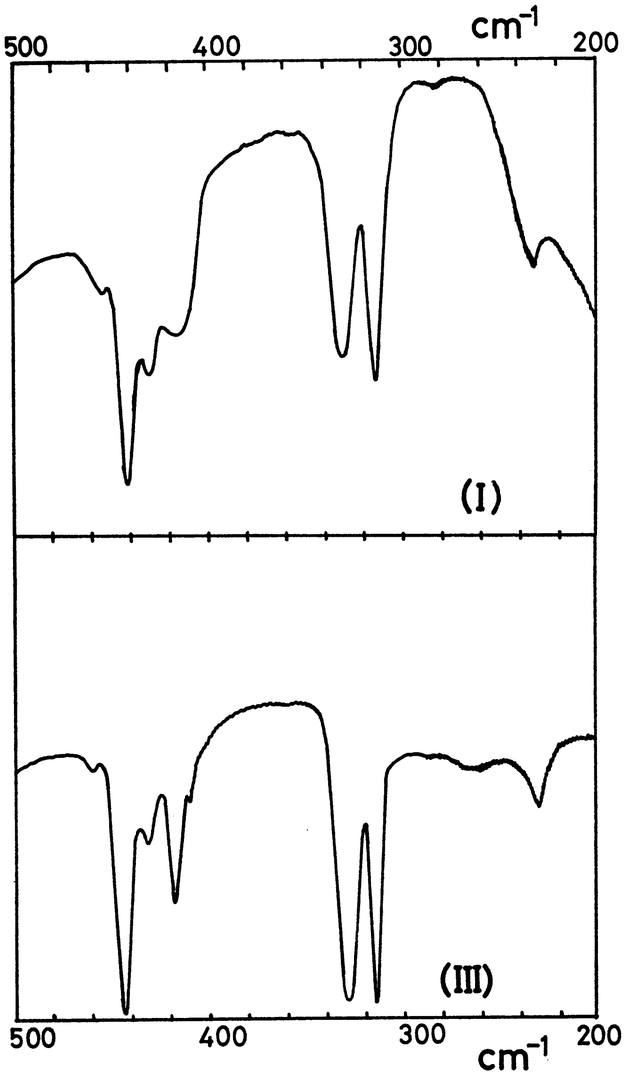
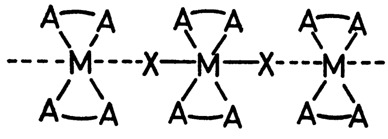


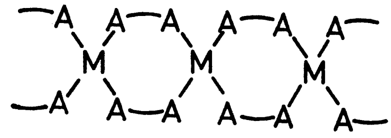
Fig. 1. The far-infrared spectra of DABP-Pd complexes. (I): $[Pd(DABP)_2]Cl_2$, (III): $[Pd(DABP)_2]Br_2$

same as that of compound (I) or (II), and bands which are assignable to a Pd–N stretching vibration with a reasonable intensity are observed at 410 cm^{-1} for compounds (I) and (II) and at 412 cm^{-1} for compound (III).[4,8,9] Therefore, the amine, DABP, acts as a bidentate ligand in these compounds.

Measurements of the powder X-ray diffraction analyses and the diffuse reflectance spectra of compounds (I) and (II) are made in order to clarify further the difference between the compounds (I) and (II). Compounds (I) and (II) give almost the same diffraction pattern, as is shown in Table 2. No serious differences are observed in the diffuse reflectance spectra of the compounds (I) and (II), as is shown in Fig. 2. Therefore, we may exclude the possibility that either the compound (I) or the compound (II) is a structural isomer, such as Vauquelin-type compounds or halogen-bridged compounds, as is shown below by (a),[10] or a diamine-bridged polynuclear complex, as is shown below by (b). Moreover, the



(a)



(b)

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[9] M. A. J. Jungbauer and C. Curran, *Spectrochem. Acta*, **21**, 641 (1965).

[10] H. Reihlen and E. Flohr, *Chem. Ber.*, **67**, 2010 (1934).

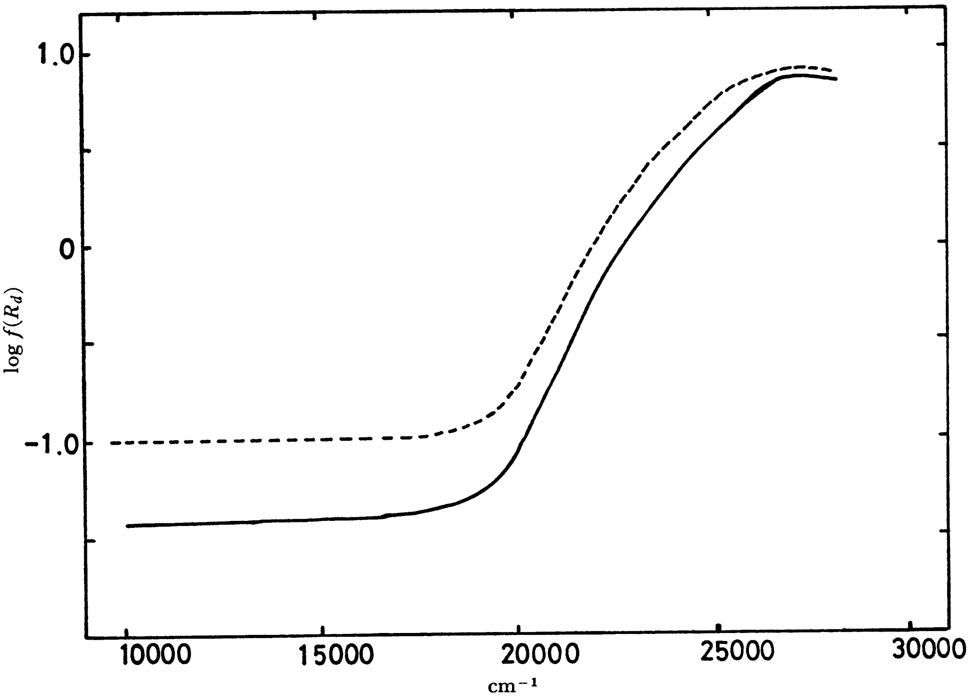

Fig. 2, The diffuse reflection spectra of the DABP-Pd complexes.
—— $[Pd(DABP)_2]Cl_2$ (I) ---- $[Pd(DABP)_2]Cl_2$ (II)

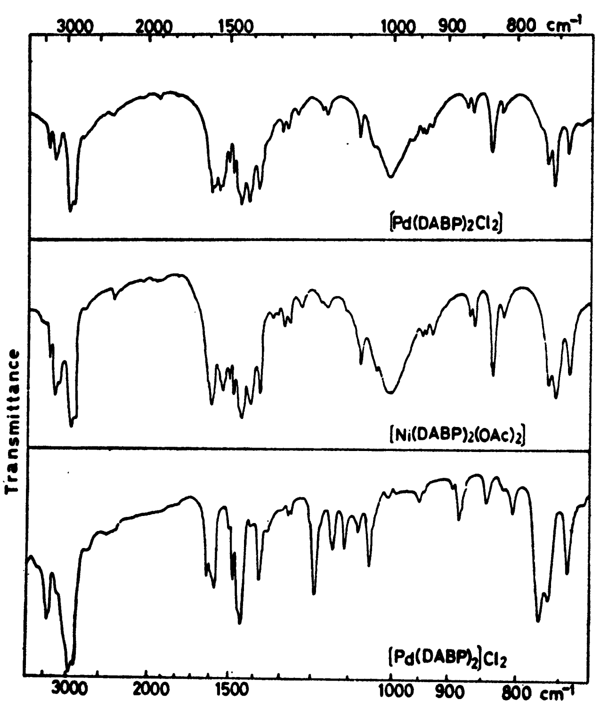

Fig. 3. IR spectra of Pd(II) complexes with DABP.

possibility that this isomerism is caused by the crystal dichroism[11] may be ruled out because of the size of the crystals: the fine precipitates (I) and (II) pass through a 3G-glass filter. It is well known that optically-active isomers are possible if the 2,2'-diaminobiphenyl is coordinated to a metal ion,[2-4] because the coordination with a metal ion prevents the rotation of the phenyl rings. As the compounds (I) and (II), however, show no optical activity, they may be racemic mixtures or of the meso form. A possible origin of this isomerism of these two compounds may be a conformational difference arising from the diamine which does not affect the optical activity.

The yellow compound (IV) synthesized under a high pressure gives a infrared spectrum which strikingly resembles that of $[Ni(DABP)_2(OAc)_2]$, as is shown in Fig. 3. Analytically-pure samples of the compound (IV) have not yet been obtained, though the infrared spectrum of Fig. 3 is clear evidence of the formation of a hexa-coordinated complex $[Pd(DABP)_2Cl_2]$.

It can be concluded that the preparative conditions have an important effect on the coordination of ligands to a metal atom, on the chemical behavior, and on the color of the compounds in the case of Pd-DABP complexes.

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[11] S. Yamada, H. Yoneda, and R. Tsuchida, *Nippon Kagaku Zasshi*, **69**, 145 (1948).