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Nickel(II), Cobalt(II) and Copper(II) Complexes of 2, 2′-Diaminobiphenyl*[1]

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Nickel(II), cobalt(II) and copper(II) complexes of 2, 2′-diaminobiphenyl were prepared in an autoclave under a high pressure and a high temperature as the acetates: $Ni(C_{12}H_{12}N_2)_2(CH_3CO_2)_2$, $Co(C_{12}H_{12}N_2)_2(CH_3CO_2)_2$ and $Cu(C_{12}H_{12}N_2)(CH_3CO_2)_2$. They are sparingly soluble in water and in non-polar solvents, but are soluble in some polar solvents. The presence of a monomer complex was verified by a molecular weight determination in a methyl ethyl ketone solution for both the cobalt and copper complexes. Analytical, magnetic susceptibility, powder X-ray diffraction, diffuse reflection spectral, infrared spectral, and ESR spectral data are given, and the geometric isomerism of the complexes is discussed.

In the course of the reduction of 2, 2′-dinitrobiphenyl to 2, 2′-diaminobiphenyl with hydrogen in the presence of a nickel catalyst, some of the spent nickel catalyst occasionally forms a nickel(II) complex with the reduced amine, bis-(2, 2′-diaminobiphenyl)nickel(II) acetate, under the reducing reaction conditions of a high pressure and a high temperature in an autoclave.[1] The nickel complex thus obtained as a by-product has been reported to be soluble only in chloroform. As for this amine as a ligand, some transitional metal complexes have recently been prepared as perchlorates, thiocyanates, nitrates, or halides under atmospheric conditions by Hein and Jehn.[2] Most of their compounds, however, were solvated and showed considerable solubilities in dimethylformamide, thus making it possible to measure the electric conductivity. In the present paper we will describe the complex formation of this amine with some transition metal ions, starting from the ligand amine and the metal acetate, under a high pressure and a high temperature in an autoclave. The coordination of the acetate group to the central metal ion and the geometric isomerism will be discussed in relation to the complexes prepared.

Experimental

Reagents. *2, 2′-Diaminobiphenyl (DABP).* The diamine was prepared by the method by Baker *et al.*[1] The reduced product was recrystallized from ethanol. The results of metlting point measurement and elementary analysis agreed well with the reported and calculated values.

Metal(II) Acetate. Nickel(II), cobalt(II), and copper(II) acetate hydrates commercially available were used.

Synthesis of the Complexes. In a steel autoclave, 0.02 mol (3.7 g) of 2, 2′-diaminobiphenyl, 0.015 mol of metal acetate (3.8 g of $Ni(CH_3CO_2)_2(H_2O)_4$, 3.8 g of $Co(CH_3CO_2)_2(H_2O)_4$, or 3.0 g of $Cu(CH_3CO_2)_2(H_2O)$), 20 *ml* of ethanol, and 10 *ml* of glacial acetic acid were placed, and then nitrogen gas was introduced at a pressure at 80 atm. Then the autoclave was heated at 120°C and shaked for 4 hr. The crystals formed were filtered through a glass filter, and repeatedly washed with water and ethanol. The yield was 50—60% for the light blue nickel and dark green copper complexes, and 10% for the pink cobalt complex, on the basis of the diamine. From the filtrates of both the nickel and cobalt complexes, plate-like crystals showing the same colors as those mentioned above were separated

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*[1] Presented in part at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, April, 1966.

1) W. Baker, M. P. V. Boarland and J. F. W. McOmie, *J. Chem. Soc.*, **1954**, 1476.

2) F. Hein and W. Jehn, *Z. anorg. u. allgem. Chem.*, **341**, 244 (1965).

TABLE 1. ANALYTICAL RESULTS

Compound	Mol wt Found (Calcd.)	Elementary analysis Found/(Calcd.)%				Mdp** °C	$\mu_{eff.}$ B. M.
		C	H	N	Metal		
Ni(DABP)$_2$(OAc)$_2$	—	61.09	5.56	10.85	10.63	262—263	3.10
$C_{28}H_{30}N_4O_4Ni$	(545.0)	(61.65)	(5.54)	(10.27)	(10.77)		
Co(DABP)$_2$(OAc)$_2$	330	61.38	5.86	10.15	11.19	226—228	4.99
$C_{28}H_{30}N_4O_4Co$	(545.3)	(61.65)	(5.54)	(10.27)	(10.80)		
Cu(DABP)(OAc)$_2$	270	52.49	4.91	7.56	17.60	204	1.81
$C_{16}H_{18}N_2O_4Cu$	(365.7)	(52.56)	(4.96)	(7.66)	(17.37)		
Ni(DABP)$_2$(OAc)$_2$*	—	60.86	5.59	9.68	11.05	247—251	—
$C_{28}H_{30}N_4O_4Ni$		(61.65)	(5.54)	(10.27)	(10.77)		
Co(DABP)$_2$(OAc)$_2$*	—	60.17	6.04	9.49	10.00	199—201	—
$C_{28}H_{30}N_4O_4Co$		(61.65)	(5.54)	(10.27)	(10.80)		

* Obtained from the filtrates. ** Melting decomposition point.

after two months. The analytical results of these complexes agreed well with those of the first crops. The complexes obtained were as follows: Bis-(2, 2′-diaminobiphenyl)nickel(II) acetate, $Ni(C_{12}H_{12}N_2)_2(CH_3CO_2)_2$; Bis-(2, 2′-diaminobiphenyl)cobalt(II) acetate, $Co(C_{12}H_{12}N_2)_2(CH_3CO_2)_2$; and 2, 2′-Diaminobiphenylcopper(II) acetate, $Cu(C_{12}H_{12}N_2)(CH_3CO_2)_2$. The copper complex reacted with sodium chloride in an aqueous solution to give a greenish yellow complex, probably $Cu(C_{12}H_{12}N_2)(CH_3CO_2)Cl$ but not was enough obtained to make a complete analysis possible. The results of the elementary analyses are shown in Table 1.

Magnetic Susceptibility. To avoid magnetic contamination from the autoclave wall, samples for this measurement were prepared in a specially-made glass vessel that was fitted to the inside of the autoclave wall (Fig. 1). The finely powdered samples were measured with a Gouy balance*2 at room temperature. Cobalt(II) mercury(II) tetrathiocyanate was used as the standard paramagnetic substance. The effective magnetic moments were calculated from the values of the volume susceptibility after the correction for the diamgnetic contribution from the ligands had been made.

Molecular Weight Determination. The molecular weights of the cobalt and copper complexes in methyl ethyl ketone were determined osmometrically by the use of a Mecrolab β-pressure Osmometer, Model 301A. The nickel complex was insoluble in this solvent, so its molecular weight could not be determined directly.

Powder X-Ray Diffractometry. The powder X-ray diffraction data were recorded with finely powdered samples by the use of a Rigaku-Denki X-ray diffractometer.

Diffuse Reflection Spectra. The spectra in the ultraviolet and visible regions were measured with a Hitachi EPU-2A spectrophotometer equipped with a standard reflectance attachment.*3 The reflectance rates were calculated with the Kubelka-Munk equation.3)

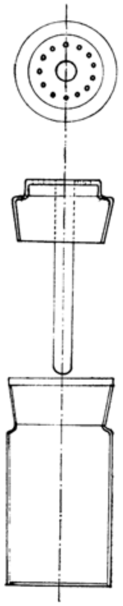

Fig. 1. The glass apparatus fitted to the inside of the autoclave wall.

Infrared Spectra. The spectra were recorded with Hitachi EPI-L, Hitachi FIS-1 and Nihon Bunko DS-402G recording spectrometers for the samples in the Nujol mulls and KBr disks.

ESR Spectra. The spectra of two copper complexes, Cu(DABP)(OAc)$_2$ and Cu(DABP)(OAc)Cl, were recorded with a JEOL JES-118 spectrometer. Manganese(II) diluted in magnesium oxide and DPPH were used for the calibration.

Results and Discussion

Chemical Properties. 2, 2′-Diaminobiphenyl acts as a ligand to form bis- and monodiamine

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*2 The authors' thanks are due to Professor Yukichi Yoshino, of the College of General Education of this University, for the use of the Gouy balance.

*3 The authors' thanks are due to Professor Masayoshi Nakahara, of Rikkyo University, for the use of the spectrophotometer and for his helfpul advice and discussion.

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

TABLE 2. THE CHARACTERISTIC INFRARED BANDS OF THE DABP-COMPLEXES AND THE RELATED COMPOUNDS, cm^{-1}

DABP	Ni-DABP	Co-DABP	Cu-DABP	Aniline	$M(An)_2X_2$*	Assignment
3400 3380	3355	3350	3180	3481	3330—3200	NH_2 asym. str.
3270 3180	3260	3250	3105	3395	3260—3190	NH_2 sym. str.
1635	1595	1590	1620	1619	1590—1560	NH_2 bend.
	1010	990	1115		1200—1000	NH_2 wag.
	1548	1546	1570			CO str.

* An=aniline; M=Pt, Pd, Cu, Ni, Co, Zn, Cd, Mn; X=Cl, Br, I.[5]

complexes. The yield of the complexes in a galss vessel fitted to the inside of the autoclave to obtain the samples for magnetic measurements was considerably less than that in the autoclave without the glass vessel. This fact showed that there must be a catalytic action of the steel autoclave wall. The first preparation of the nickel complex found unexpectedly during the reduction of 2, 2′-dinitrobiphenyl to the corresponding diamine might have been due to this catalytic effect. The complexes prepared under high pressures and at high temperatures are very stable against many kinds of solvenst and against high temperatures. They are only soluble in a few kinds of organic solvents, mainly polar ones, for instance, aniline or pyridine, that may be able to act as ligands to the central metal. The nickel complex is slightly soluble in acetone, chloroform, and tetrahydrofuran. The cobalt complex is somewhat soluble in aceton, and slightly so in chloroform. The copper complex has rather high solubilities in some polar solvents. The small solubility of the nickel complex into methyl ethyl ketone made it impossible to determine the moclecular weight directly. Their thermal stabilities were indicated by their high decomposition points. These low solubilities and high thermal stabilities suggest that these complexes are polymeric. The molecular weights of the cobalt and copper complexes determined in methyl ethyl ketone, however, were revealed as those of monomers. By analogy with the cobalt complex, the nickel complex would also be monomeric; this idea was supported by the spectroscopic data to be presented in the following section. The copper complex was more soluble and less stable than the others. It decomposed in an aqueous solution after a day or two at room temperature.

The Electronic Nature. The three complexes were all paramagnetic and all had reasonable values of effective magnetic moments. The nickel and cobalt complexes had a high-spin structure. This suggests that the nickel(II) ion is in an octahedral or tetrahedral coordination. The data on the electronic spectra (Fig. 2) supports the octahedral coordination of nickel(II).[4] As the ESR spectra of two copper(II) complexes were not identical, these two complexes were different from each other in the electronic state. The first one, prepared in the autoclave, has an anisotropy of two dimensions in its *g*-factors, while the other one, obtained from the sodium chloride solution, has one of three dimensions. The *g*-values were as follows: for the former, $g_{1(\perp)}=2.05_1$, $g_{2(\parallel)}=2.26_4$; for the latter, $g_1=2.05_6$, $g_2=2.11_6$, $g_3=2.19_4$.

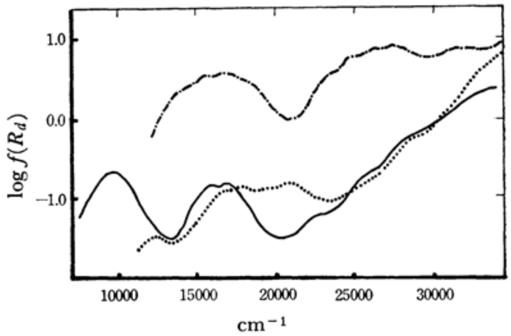

Fig. 2. The diffuse reflection spectra of the metal-DABP complexes.

—— $Ni(DABP)_2(OAc)_2$
…… $Co(DABP)_2(OAc)_2$
-·-·- $Cu(DABP)(OAc)_2$

Structural Information. The coordination of the amino group to the metals in these complexes can be clearly explained on the basis of the infrared data. The absorption bands due to the amino group of the ligand amine shifted considerably towards lower frequencies in its complexes. The degrees of shift were reasonable when the amino group was bound to a transitional metal. The characteristic feature of these amine complexes is their strong and broad NH_2-wagging bands in the 1000—1100 cm^{-1} region (Table 2). Some metal-aniline complexes, *e. g.*, $Ni(C_6H_5NH_2)_2Cl_2$ and $Co(C_6H_5NH_2)_2Cl_2$, showed similar shifts

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[4] H. Ito, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **77**, 1383 (1956).

TABLE 3. THE POWDER X-RAY DIFFRACTION DATA

Ni-DABP		Co-DABP		Cu-DABP		Ni-DABP*		Co-DABP*	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
10.40	0.21	10.49	0.21	9.56	1.00	10.13	1.00	9.99	1.00
9.38	1.00	9.48	1.00	8.85	0.26	9.67	0.43	9.53	0.38
8.59	0.12	8.59	0.13	5.38	0.24	6.35	0.27	6.28	0.10
6.13	0.30	6.17	0.17	4.98	0.08	6.26	0.30	6.01	0.10
5.96	0.24	6.08	0.13	4.79	0.08	6.05	0.08	5.51	0.14
5.76	0.09	5.81	0.11	4.42	0.14	5.56	0.16	5.36	0.19
4.84	0.09	4.88	0.09	4.29	0.15	5.39	0.27	5.14	0.10
4.77	0.09	4.77	0.09	4.18	0.14	5.19	0.08	4.98	0.19
4.52	0.21	4.53	0.13	4.04	0.14	5.02	0.12	4.75	0.10
4.14	0.15	4.14	0.09	3.45	0.08	4.77	0.08	4.67	0.10
3.71	0.12	3.72	0.11	3.20	0.21	4.65	0.08	4.30	0.10
3.60	0.15	3.35	0.11			4.31	0.13	3.92	0.19
						3.93	0.23	3.78	0.14
						3.80	0.12		

* Obtained from the filtrates.
Relative intensities were estimated by comparing the height of the peaks. Less intensity lines are omitted.

TABLE 4. THE FAR-INFRARED BANDS OF THE METAL-DABP-COMPLEXES AND DABP, cm^{-1}

DABP	Ni-DABP	Co-DABP	Cu-DABP	Ni-DABP*	Co-DABP*
486 vs	502 vs	497 vs	498 vs	498 vs	497 vs
452 w					
446 w				443 vs	440 s
433 w	431 vs	430 vs		431 vs	431 vs
426 w	423 vs	420 vs		423 vs	421 vs
	352 m Ni–N str.	344 m Co–N str.	393 s 385 s Cu–N str.	379 m 352 m Ni–N str.	367 m 345 m Co–N str.
321 sh	305 vs	302 vs	323 vs	305 vs	302 vs
314 vs					
		293 m			293 m
277 m	278 m	276 m	274 vs Cu-lig. vib.	276 w	275 m
270 m					
241 m		243 w		250 m	252 m
	224 vs Ni-lig. vib.		223 s	225 vs Ni-lig. vib.	
204 s	207 s	202 vs Co-lig. vib.		207 m	216 m
	171 vs Ni-lig. vib.			174 vs Ni-lig. vib.	204 vs Co-lig. vib.
		165 m			156 vs Co-lig. vib.
		154 vs Co-lig. vib.	145 vs Cu-lig. vib.		
	140 m				

* Obtained from the filtrates.

in their infrared spectra.[5] As for the carboxylate group, from the adopted assignments shown in the table, it may be considered that the acetate is "purely ionic." This term, however, does not mean that these complexes are of an ionic nature. The low solubility in water and the molecular weight determined establish that they are of a covalent nature. Thus, it can be concluded that the nickel and cobalt are octahedrally hexacoordinated with four nitrogens of two ligand diamines and with two oxygens of two acetate groups. The copper should be coordinated with two nitrogens of the diamine and two oxygens of two acetate groups. The almost identical infrared spectra and powder X-ray data, latters showing an isomorphism of the nickel and cobalt complexes, suggest that these two have similar octahedral structures as is shown in Table 3. There may be geometric isomers of these bis-diamineacetatometal

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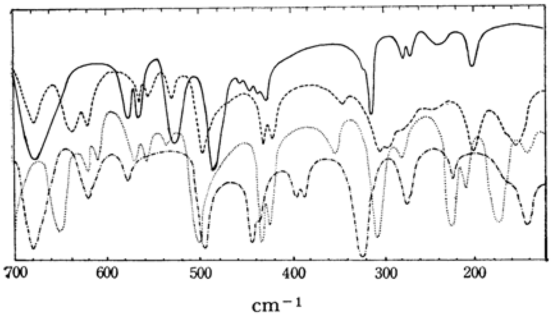
[5] M. A. J. Jungfauer and C. Curran, *Spectrochim. Acta*, **21**, 641 (1965).

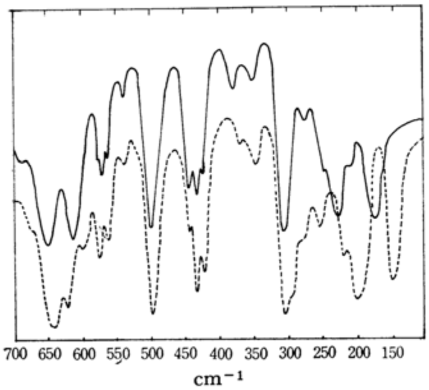
complexes, trans and cis forms. Moreover, in each isomer a conformational isomerism of biphenyl rings⁽⁶⁾ can be expected to give some differences in the infrared spectra. Because the difference could not be clearly detected in the sodium chloride region, measurement in the far-infrared region, 700—100 cm^{-1}, was attempted for the ligand amine itself and for the complexes on the assumption that the effect of the conformation isomerism might be small compared with that of the cis-trans isomerism. For the trans isomer, the effective symmetry of the skeletal structure is D_{4h} and five vibration bands due to metal-ligand vibrations are expected to appear in the far-infrared region, while for the cis isomer, the effective symmetry is C_{2v} and thirteen vibration bands become infrared-active except for the bands due to the ligand. The ligand-metal vibration bands for each complex were assigned by comparison with spectrum of the free diamine (Table 4 and Fig. 3). The appearance of three metal-ligand vibration bands for both the nickel and cobalt complexes gave much weight to the possibility of a trans structure for them. For the copper complex, a square-planar cis structure may be deduced, since two N–Cu stretching bands were observed in the spectrum, at 393 and 385 cm^{-1}.

The plate crystals of the ncikel and cobalt complexes obtained from the filtrates after they had been left for several weeks, although they gave the same analytical results as those first prepared in the autoclave, showed different X-ray powder diffraction patterns (Table 3). Their infrared spectra also showed features dissimilar to those of the former complexes; first, the NH_2-wagging band at about 1000 cm^{-1} varied in the spectra obtained with the Nujol mull and with the KBr disk. In the fomer medium the band was complex and was mainly composed of three bands, but in the latter the spectrum was almost identical with that of the first one prepared in the autoclave. Undoubtedly, the quality of the latter must be a result of the effedt of the pressure. Second, in the far-infrared region, the number of metal-ligand vibrational bands increased. The decomposing points of these complexes separated from the filtrates are lower than those of the complexes prepared directly in the autoclave. These difference in nature suggested the possibility that those from the filtrates are cis isomers, although it cannot be concluded from only these measurements whether they are cis siomers or show polymorphism of the crystals.



—— DABP
······ $Ni(DABP)_2(OAc)_2$
---- $Co(DABP)_2(OAc)_2$
–·–·– $Cu(DABP)(OAc)_2$

Fig. 3. (a)



—— $Ni(DABP)_2(OAc)_2$*
---- $Co(DABP)_2(OAc_2$*

Fig. 3. (b)

Fig. 3. The far-infrared spectra of the metal-DABP complexes.
* Obtained from the filtrates.

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6) T. Habu and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **88**, 1128 (1966).