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Infrared Absorption Spectra of Molecular Complexes of Pyridine. Part V

Molecular Complexes with Cu-, Co-, Ni- and Mn-Dihalides*

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Synopsis

The infrared spectra in the rock salt region of CuCl_2 , CuBr_2 , CoCl_2 , CoBr_2 , NiCl_2 , NiBr_2 and MnCl_2 complexes of pyridine have been observed by the KBr pressed disc method. The infrared absorption bands corresponding to the C-H stretching vibrations diminished in intensity and the diminution has been discussed qualitatively. A tentative assignment of absorptions is presented. The spectra are insensitive to a spatial structure of the complex.

I. Introduction

In previous papers⁽¹⁾ of this series, infrared studies on pyridine complexes of bivalent zinc, cadmium and mercury halides, and of halogens have been described. In this paper infrared spectra of pyridine complexes of bivalent copper, cobalt, nickel and manganese are reported.

The infrared spectra of the complexes in the previous paper⁽¹⁾ were much the same as regards the pyridine absorptions. This shows that the pyridine spectra are insensitive to the spatial structures of the complexes. Thus, it may be anticipated that the infrared spectra of Cu-, Co-, Ni- and Mn-dihalides complexes are similar to those of Zn-, Cd- and Hg-dihalide complexes.

II. Experimental

The complex was prepared by mixing ethyl alcohol solutions of pyridine and of the metal halide under continual stirring. The complexes show colors characteristic of the metal ions.

Analyses:

$\text{CuCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$	Found:	C, 42.36; H, 3.65; N, 9.27,
	Calcd:	C, 41.03; H, 3.45; N, 9.57,

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(1) F. Watari and S. Kinumaki, *Sci. Rep. RITU*, **A 14** (1962), 64, 129.

CuBr ₂ ·2C ₅ H ₅ N	Found:	C, 31.80; H, 2.90; N, 6.94.
	Calcd:	C, 31.48, H, 2.62; N, 7.35,
CoCl ₂ ·2C ₅ H ₅ N	Found:	C, 41.92; H, 3.76; N, 9.42,
	Calcd:	C, 41.69; H, 3.48; N, 9.73,
CoBr ₂ ·2C ₅ H ₅ N	Found:	C, 32.02; H, 2.72; N, 7.07,
	Calcd:	C, 31.87; H, 2.66; N, 7.44,
NiCl ₂ ·2C ₅ H ₅ N	Found:	C, 41.92; H, 3.63; N, 9.47,
	Calcd:	C, 41.73; H, 3.48; N, 9.74,
NiBr ₂ ·4C ₅ H ₅ N	Found:	C, 44.77; H, 3.89; N, 9.80,
	Calcd:	C, 44.92; H, 3.68; N, 10.28,
MnCl ₂ ·2C ₅ H ₅ N	Found:	C, 42.50; H, 3.75; N, 9.80,
	Calcd:	C, 42.27; H, 3.52; N, 9.87.

The analytical values show that, except NiBr₂ complex which has a NiBr₂/C₅H₅N ratio of 1/4, the complexes are in the ratio of MeX₂/C₅H₅N 1/2.

The spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer with a NaCl optics. The complexes were examined as potassium bromide discs.

All the complexes dissolve in pyridine so slightly that a change from the pure pyridine spectrum was not perceptible on solution spectra.

III. Results and discussion

The C-H absorptions around 3000 cm⁻¹ of the complexes diminished in intensity. In addition, the rock salt optics has poor resolution. So detailed discussion on the C-H stretching modes is not of value. The intensity diminution of the C-H stretching vibrations is interpreted as follows. The infrared intensity is proportional to $|\partial\mu/\partial Q|^2$ ⁽²⁾, where μ is a dipole moment of a whole molecule and Q a normal coordinate corresponding to a molecular vibration under study. A dipole moment of a donor-acceptor complex in general is large because of electron transfer from a donor molecule to an acceptor, and the moments of skeletal parts and of a donor-acceptor bond rule the dipole moment of the complex. The C-H stretching vibrations have so much higher frequencies that there is essentially no mixing with other vibrations of pyridine, and their normal coordinates effectively consist only of the C-H stretching coordinates. The C-H stretching will not have large influence on an electronic structure of pyridine as a donor molecule, by which, therefore, a change of the dipole moment will be small. There is another reason why the C-H stretching brings about a change in the dipole moment, which is a direct effect through a change of a C-H bond moment resulting from the hydrogen stretching vibration. But the change of the C-H bond moment is small because of its small moment. Thus, the C-H stretching causes the dipole moment to change in smaller amount than in pyridine itself vibrating in the molecule with a larger moment than pyridine has. So the C-H stretchings of the complex diminished in

(2) A. M. Thorndike, A. J. Wells and E. B. Wilson, Jr., J. Chem. Phys., **15** (1947), 157.

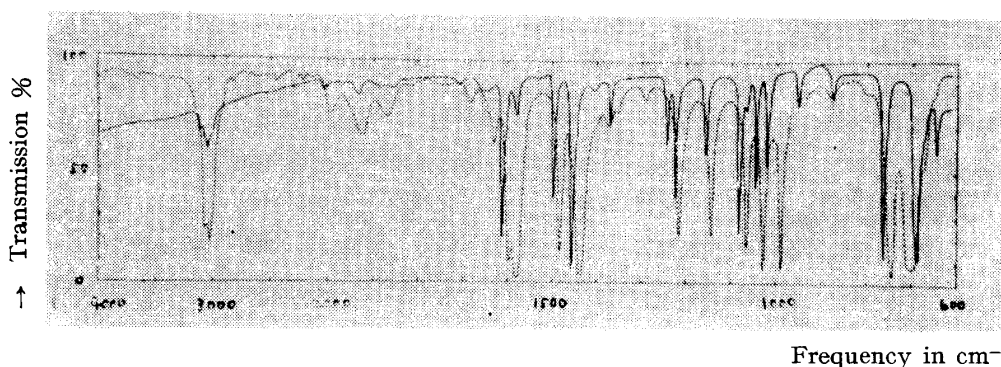


Fig. 1. Infrared absorption spectra of $\text{CuCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ complex (full line) in a KBr disc and liquid pyridine (broken line) in a cell of a path length of 30μ .

intensity, compared with pyridine itself.

A spectrum in the 1700 cm^{-1} to 600 cm^{-1} region of CuCl_2 complex is shown in Fig. 1. Spectra of the other complexes in this region are much the same as those of CuCl_2 complex and also those of ZnX_2 , CdX_2 and HgX_2 complexes described in Part IV⁽¹⁾ of this series. X-ray diffraction studies have shown that the structure of $\text{CuCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ ⁽³⁾ and $\text{HgCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ ⁽⁴⁾ consists of square coplanar units formed by two N atoms of pyridine molecules and two Cl atoms aggregated into chains perpendicular to the square unit by weaker Cu-Cl bonds. Cobalt dichloride dipyridine complex exists in two modifications: the β -modification (blue form) contains discrete molecules with a tetrahedral disposition of bonds about a cobalt atom⁽⁵⁾, and the α -modification (violet form)⁽³⁾ contains a chain structure which complete distorted octahedra about each cobalt. Cobalt dichloride-pyridine complex obtained here is blue and belongs to the β -modification. In spite of various spatial structures of the complexes, the above facts indicate that, so far as infrared spectra in the rock salt region are concerned, the pyridine spectrum of the complex is insensitive to their spatial structures.

As seen from Fig. 1, the complex absorptions have a good correspondence with the pyridine absorptions. In Table 1 are listed the assignment of pyridine absorptions by Lord⁽⁶⁾, and the correspondence between absorptions of the pyridine and the complex. There are slight differences among shifts of a pyridine band of the complexes. On account of the absence of influence from the spatial structures of the complexes, these differences are suggestive of differences in strength of a nitrogen-metal bond. This bond shows absorptions in the far infrared region and the quantitative discussion must be left till far infrared study.

The band located at 1069 cm^{-1} of pyridine has been assigned as ν_{18a} and ν_{18b} ⁽⁶⁾. There appear two bands around 1060 cm^{-1} and 1080 cm^{-1} in the complex spectrum,

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(4) D. Grdenic and I. Krstanovic, *Ark. Kemi*, **27** (1955), 143.

(5) G. B. Bokai, T. I. Malinowski and A. V. Ablov, *Kristallografiya*, **1** (1956), 49.

(6) L. Corrsin, B. J. Fax and R. C. Lord, *J. Chem. Phys.*, **21** (1953), 1170.

Table 1. Infrared absorptions of pyridine complexes with CuCl_2 , $-\text{Br}_2$, CoCl_2 , $-\text{Br}_2$, NiCl_2 , $-\text{Br}_2$ and MnCl_2

$\text{C}_5\text{H}_5\text{N}$	CuCl_2	CuBr_2	CoCl_2	CoBr_2	NiCl_2	NiBr_2	MnCl_2	Assignment
605	643		630		631		610	ν_{6a}
701	688	686	688	(686 693*	686	(698 702*	690	ν_{11}
744	759	755	757	(748 757*	755	(756 769*	752	ν_{10b}
886	871	865	875		870		875	ν_{10a}
945	948	944	953		945	985		ν_5
992	(1010 1017*	1016	1013	1012	1013	1007	1008	ν_1
1031	1043	1042	1042	1042	1041	1037	1037	ν_{12}
	1062	1060	1067		1061		1057	ν_{18a}
1069	1079	1078	1082	1064	1080	1070	1078	ν_{18b}
1148	1152	1152	1152	1156	1149	1148	1154	ν_{15}
1220	1221	1220	1221	1213	1219	(1214 1218*	1221	ν_{9a}
	1241	1238	1241	1238	1240	1234	1237	ν_3
1355	1400		1403		1403		1395	$\nu_{6a} + \nu_{10b}$
1374	1367	1362	1365		1363		1364	ν_{14}
1443	1452	1442	1450	1444	1449	1442	1448	ν_{19b}
1488	1492	1491	1492	1484	1492	1483	1492	ν_{19a}
	1577	1573	1578		1577		1576	ν_{8b}
1585	1609	1606	1607	1604	1607	1597	1605	ν_{8a}
1599	1640		1645		1638		1637	$\nu_1 + \nu_{6a}$

* Observed as a doublet.

of which the lower absorption is very weak. Vibrational spectra of pyridinium salts⁽⁷⁾ have shown one band in this region, which has been assigned to ν_{18b} . But ν_{12} , which appeared at 1031 cm^{-1} in the case of pyridine⁽⁶⁾, was not assigned in the pyridinium salts spectra, and a band at 1030 cm^{-1} was assigned to ν_{18a} . On one hand, in the 1000 cm^{-1} to 1100 cm^{-1} region there are three bands in mono-deuterated benzene⁽⁸⁾, based on which assignments the pyridinium salts absorptions were assigned: they were assigned as ν_{12} , 1007 cm^{-1} ; ν_{18a} , 1031 cm^{-1} ; ν_{18b} , 1076 cm^{-1} . Here, if the 1031 cm^{-1} band is assigned to ν_{12} , following Lord⁽⁶⁾, the lower weak absorption in the 1060 cm^{-1} to 1080 cm^{-1} region of the pyridine complex should be ascribed to ν_{18a} as in the case of $\text{C}_6\text{H}_5\text{D}$ ⁽⁸⁾, and the 1080 cm^{-1} band to ν_{18b} . In the former cases of Zn-, Cd- and Hg-halide complexes this splitting of the 1060 cm^{-1} band of pyridine was not detected. It will result from a small shift of the 1060 cm^{-1} band which occurs on complex formation.

Two absorptions at 1355 cm^{-1} and at 1374 cm^{-1} of pyridine have been assigned by Lord⁽⁶⁾ as $\nu_{6a} + \nu_{10b}$ and ν_{14} respectively. It seems that two absorptions around 1360 cm^{-1} and 1400 cm^{-1} of the complex correspond to the two bands of pyridine. But there should be found the combination band, $\nu_{6a} + \nu_{10b}$, of the complex at 1400 cm^{-1} . Therefore, they may rather be assigned as ν_{14} , the band at 1360 cm^{-1} ;

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$\nu_{6a} + \nu_{10b}$ the band at 1400 cm^{-1} .

The band located at 1220 cm^{-1} of pyridine has been assigned to ν_3 and ν_{9a} ⁽⁶⁾. The ν_3 and ν_{9a} vibrations of $\text{C}_6\text{H}_5\text{D}$ ⁽⁸⁾ have been assigned as 1292 cm^{-1} and 1176 cm^{-1} respectively. Paralleled with $\text{C}_6\text{H}_5\text{D}$ the band located around 1240 cm^{-1} of the complex can be assigned as ν_3 , though it does not correspond to any absorptions of pyridine.