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Metal Complexes of Schiff Bases Obtained from Substituted Salicylaldehydes and 2-Aminopyridine Derivatives[1]

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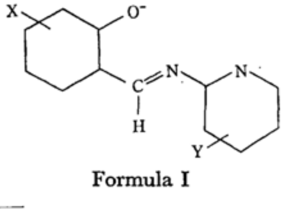
Numerous metal complexes (abbreviated as $M(X\text{-}SAL\cdot R)_2\cdot nH_2O$) of Schiff bases obtained from substituted salicylaldehydes and 2-aminopyridine derivatives were prepared as crystals, where X=H, 5,6-benzo, 5-Cl, 5-Br, 5-NO_2 and 3-CH_3O, R=2-pyridyl, 2-(3-methylpyridyl), 2-(4-methylpyridyl) and 2-(6-methylpyridyl), and M=Co(II), Ni(II), Cu(II), Zn(II) and Pd(II). It is concluded, mainly from the electronic absorption spectra, that the cobalt(II) complexes are tetrahedral, with one exception, which has an octahedral configuration with two water molecules coordinated to the cobalt(II) ion. The nickel(II) complexes are octahedral, and the copper(II) and the palladium(II) complexes are planar. In these metal complexes, the Schiff bases are bidentate, except bis(*N*-2-(6-methylpyridyl)-salicylideneiminato)nickel(II), in which the ligand functions as a terdentate.

Ligands represented by Formula I[*1] contain three atoms capable of coordinating to one metal ion, but the steric condition does not seem to be favorable for them to act as terdentate ligands. However, there still remains a possibility that these ligands behave as terdentate ligands, and it seems interesting to examine in what compounds this may, in fact, occur. The present work concerns the preparation of Schiff base complexes with some transition metal ions and examination of their structure in relation to the coordination mode of these ligands.



Formula I

Experimental

Materials. Schiff base metal complexes newly prepared in the present work are shown in Tables 1, 2 and 3. The cobalt(II) complexes with the ligands

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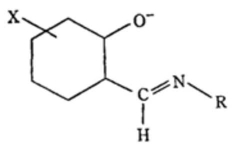
[1] Presented, in part, at the 18th Symposium on Coordination Chemistry, Kyoto, October, 1968.

[*1] Abbreviated as X-SAL·2-Py for Y=H and as X-SAL·CH_3-Py for Y=CH_3.



Formula II

represented by Formula II[*2] were prepared as previously reported,[2,3] either from cobalt(II) acetate tetrahydrate, substituted salicylaldehydes and amines, or from bis(substituted salicylaldehydato)cobalt(II) and amines. One of the typical methods is given below for Co(H-SAL·2-Py)$_2$ as an example. To a solution of cobalt(II) acetate tetrahydrate (0.005 mol) in ethanol (10 m*l*) was added a solution of a Schiff base (0.01 mol) in ethanol (10 m*l*). The reaction was continued at about 65°C for about one hour. When the solution was cooled, crude product of the complex separated out. The pure compound was obtained as red crystals by recrystallization of the crude product from such solvents as chloroform, acetone, ethanol and benzene.

TABLE 1. ANALYTICAL DATA OF Co(X-SAL·2-Py)$_2$

X	Calcd %			Found %			μ*
	C	H	N	C	H	N	
H	63.58	4.00	12.49	63.55	3.73	12.28	4.39
5,6-Benzo	69.44	4.01	10.12	69.28	3.77	9.86	4.17
5-Cl	55.19	3.09	10.73	54.61	2.77	10.58	4.31
5-Br	47.24	2.64	9.18	46.85	2.46	8.88	4.47
5-NO$_2$	53.05	2.97	15.47	52.54	2.59	15.46	4.51
3-CH$_3$O	60.82	4.32	10.91	60.48	4.11	11.30	4.35

* μ: magnetic moment in Bohr magneton at room temperature

The other cobalt(II) complexes were obtained in a similar way. Nickel(II), copper(II) and zinc(II) complexes given in Tables 2 and 3, were prepared by methods similar to those for the cobalt(II) complexes described above. Some of the cobalt(II) and nickel(II) complexes were obtained as dihydrate, which may be recrystallized from benzene or chloroform without decomposition.

TABLE 2. ANALYTICAL DATA OF M(X-SAL·2-Py)$_2$

M	X	Calcd %			Found %		
		C	H	N	C	H	N
Cu*	H	62.94	3.96	12.23	63.31	3.77	12.11
	5,6-Benzo	68.87	3.97	10.04	68.49	3.73	9.70
	3-CH$_3$O	60.30	4.09	11.21	60.28	4.29	10.82
Zn**	H	62.69	3.95	12.19	63.42	3.42	11.91
	5,6-Benzo	68.64	3.96	10.01	69.28	3.59	9.56
Pd**	H	57.52	3.62	11.18	57.97	3.24	11.08
	5,6-Benzo	63.92	3.69	9.32	62.94	3.42	9.86

* The Cu(II) complexes are brown or dark-brown.
** The Zn(II) and the Pd(II) complexes are orange.

Palladium(II) complexes given in Table 2, were prepared by a method similar to that previously reported.[4]

All these complexes are insoluble in water, but soluble in methanol, ethanol, chloroform, dichloromethane and benzene, except Co(5-NO$_2$-SAL·2-Py)$_2$, which is almost insoluble in these organic solvents.

Measurements. The electronic absorption spectra of these complexes in solution and in the solid state were determined with a Shimadzu QR-50 and a Shimadzu MPS-50L spectrophotometer. In Tables 4 and 5 are listed only those data of the solution spectra, for which Beer's law was confirmed to hold.

The X-ray powder diagrams were obtained with a Toshiba ADX-103 diffractometer. The magnetic moments were determined at room temperature by the Gouy method using CoHg(SCN)$_4$ as a standard.

TABLE 3. ANALYTICAL DATA OF M(H-SAL·Y-Py)$_2$(H$_2$O)$_n$

M	Y	*n*	Colour		C,%	H,%	N,%	μ
Co	3-CH$_3$	2	brown	calcd	60.35	5.06	10.83	
				found	60.19	4.97	10.68	4.79
	4-CH$_3$	0	red	calcd	64.87	4.61	11.64	
				found	64.51	4.55	11.45	4.38
	6-CH$_3$	0	red	calcd	64.87	4.61	11.64	
				found	64.61	4.55	11.76	4.42
Ni	3-CH$_3$	2	green	calcd	60.38	5.07	10.83	
				found	59.91	4.88	10.81	3.10
	4-CH$_3$	2	green	calcd	60.38	5.07	10.83	
				found	60.31	4.96	11.02	3.17
	6-CH$_3$	0	orange	calcd	64.90	4.61	11.64	
				found	64.73	4.63	11.83	3.25
Cu	3-CH$_3$	0	dark-green	calcd	64.25	4.56	11.53	
				found	64.53	4.26	11.45	—

Results and Discussion

Cobalt(II) and Zinc(II) Complexes. The complexes of the type Co(X-SAL·2-py)$_2$ are paramagnetic with magnetic moments ranging from 4.17 to 4.50 B.M., the values which lie in the range expected for tetrahedral cobalt(II) complexes of a high-spin type. The octahedral cobalt(II) complexes with the related Schiff bases are known to have magnetic moments near 5.0 B.M.,[2] which are evidently larger than the values for the tetrahedral complexes.

The electronic absorption spectra of these cobalt(II) complexes in the solid state and in non-donor solvents, as shown in Fig. 1 and Table 4, are typical

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[*2] Abbreviated as X-SAL·R.

2) S. Yamada, *Coordin. Chem. Rev.*, **1**, 415 (1966).

3) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, "Progress in Inorganic Chemistry," Vol. VII, ed. by F. A. Cotton, Interscience Publishers, New York, N. Y. (1966), p. 83.

4) S. Yamada, H. Nishikawa and K. Yamasaki, This Bulletin, **36**, 483 (1963); S. Yamada and K. Yamanouchi, This Bulletin, **42**, 2543 (1969).

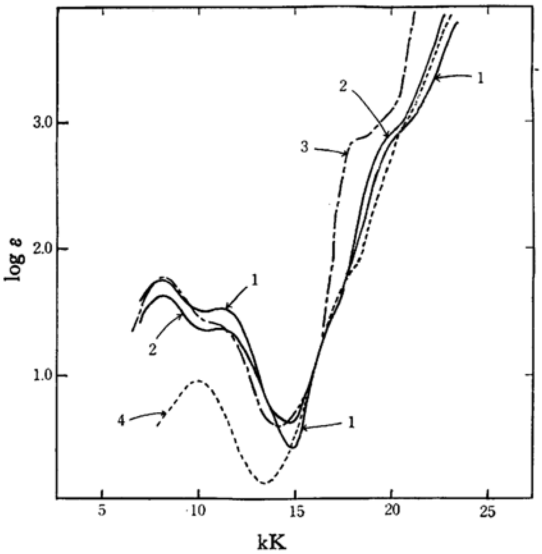

Fig. 1. Electronic absorption spectra of Co(X-SAL·R)$_2$ in solution.
1 X=H, R=Ph, in chloroform
2 X=H, R=2-Py, in chloroform
3 X=5,6-benzo, R=2-Py, in chloroform
4 X=H, R=2-Py, in pyridine

TABLE 4. SPECTRAL DATA OF Co(X-SAL·2-Py)$_2$

X	State	ν (log ε)	ν (log ε)
H	solid	8.1	10.7 sh
	chloroform	8.1(1.62)	11.0(1.37) sh
	pyridine	9.9(0.96)	
5,6-Benzo	solid	8.2	11.0 sh
	chloroform	8.2(1.76)	11.0(1.36) sh
	pyridine	10.1(1.21)	
5-Cl	solid	8.2	11.1 sh
	chloroform	8.2(1.77)	11.1(1.48) sh
5-Br	solid	8.2	11.0 sh
	chloroform	8.2(1.60)	11.0(1.34) sh
5-NO$_2$	solid	8.0	10.8 sh
	chloroform	insoluble	
3-CH$_3$O	solid	8.2	11.3
	chloroform	8.2(1.67)	11.4(1.48)

ν: 10^3 kK
sh: shoulder

of the tetrahedral cobalt(II) complex and different from that of the octahedral complex.[2,5] It is, therefore, concluded that the complexes of the type, Co(X-SAL·2-Py)$_2$, are tetrahedral with a high-spin. It is to be noted that the spectrum of Co-H-SAL·2-Py)$_2$ is quite similar to that of Co(H-SAL·Ph)$_2$,[*3] which was previously concluded to be tetrahedral.[2] The absorption band at about 8.1 kK with a small shoulder at about 11 kK may be assigned to the transition $^4T_1 \leftarrow {}^4A_2$. It is also found that the configuration of these cobalt(II) complexes is tetrahedral, irrespective of the nature of the substituent X.

In all these cobalt(II) complexes, the ligands X-SAL·2-Py are found to act as bidentate ligands and not as terdentate ligands, the nitrogen atom in the heterocyclic ring not being bound with the metal ion. It is considered that the steric condition is not favorable for these ligands to act as terdentate ligands.

For R=4-CH$_3$-Py and 6-CH$_3$-Py, complexes of the type Co(H-SAL·R)$_2$ were obtained. It is concluded, from the electronic spectra, that they are tetrahedral with a high-spin. On the contrary, for R=3-CH$_3$-Py, a similar method yielded Co(H-SAL·R)$_2$(H$_2$O)$_2$ instead of Co(H-SAL·R)$_2$. The electronic spectra, as shown in Table 5, indicate that this complex in the solid state and in non-donor solvents consists of octahedral cobalt(II) with the two water molecules bound to the cobalt(II) ion. The magnetic moment of 4.79 B. M. for this complex may be understood on the basis of the octahedral configuration, although the value seems to be a little too low.

The electronic spectra, as shown in Tables 4 and 5, and Fig. 1, also indicate that, when dissolved in pyridine, these cobalt(II) complexes exist as bis-(pyridine)-complexes Co(X-SAL·R)$_2$(*py*)$_2$, where *py* denotes a pyridine molecule. This behavior is similar to that with the corresponding complexes for R=phenyl and substituted phenyl groups.[2]

It is known that the complexes of the type Zn(X-SAL-R)$_2$, in general, take a similar configuration to that of the corresponding cobalt(II) complexes. It may be, therefore, reasonable to assume that the zinc(II) complexes prepared in the present work also take a tetrahedral configuration. This seems to agree with the finding that the X-ray powder diagram of Zn(H-SAL·2-Py)$_2$ is quite similar to that of Co(H-SAL·2-Py)$_2$, showing that these two complexes are isomorphous with each other.

Complexes of Nickel(II) and Other Metal Ions. For R=2-Py, all the methods, which have been applicable to the synthesis of complexes of the other ions, proved to be unsuccessful for isolating the nickel(II) complexes of the type Ni(X-SAL·2-Py)$_2$. Thus those methods only yielded crystals of nickel(II) complexes with a complicated composition.

For R=3-CH$_3$-Py and 4-CH$_3$-Py, the nickel(II) complexes of the type Ni(H-SAL·R)$_2$(H$_2$O)$_2$ were obtained. They are all of a high-spin type with a magnetic moment ranging between 3.10 and 3.17 B.M. The electronic absorption spectra indicate, as shown in Fig. 2 and Table 5, that these nickel(II) complexes are octahedral in the solid state and in non-doner solvents. It is most likely that the two water molecules are bound with the nickel(II) ion.

[*3] The notation Ph represents a phenyl group.

5) S. Yamada, *Coordin. Chem. Rev.*, **2**, 83 (1967).

Heating these complexes at about 100°C for many hours gave rise to neither decomposition nor loss of the water molecules. This indicates that the linkage of the water moleculrs with the nickel(II) ion may be considerably strong.

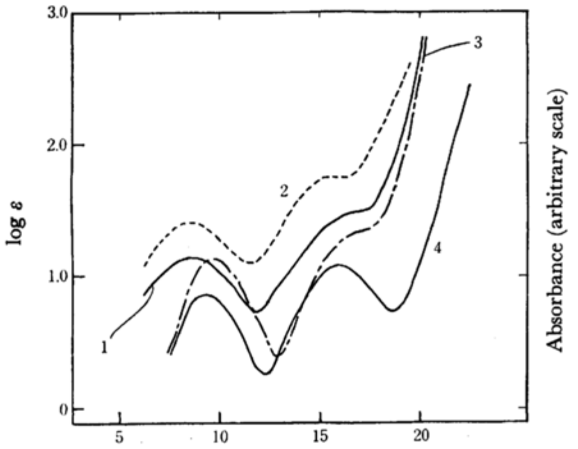

Fig. 2. Electronic absorption spectra of Ni(H-SAL·R)$_2$(H$_2$O)$_n$ in
1 R=6-CH$_3$-Py, n=0, in chloroform
2 R=6-CH$_3$-Py, n=0, solid
3 R=6-CH$_3$-Py, n=0, in pyridine
4 R=4-CH$_3$-Py, n=2,in chloroform

Table 5. Spectral data of M(H-SAL·Y-Py)$_2$(H$_2$O)$_n$

M	Y	n	State	ν (log ε)	ν (log ε)
Co	3-CH$_3$	2	solid	9.6	
			dichloro-methane	9.7(0.93)	
	4-CH$_3$	0	solid	8.0	9.9 sh
			chloroform	8.3 (1.75)	10.4(1.51) sh
	6-CH$_3$	0	solid	7.9	10.6 sh
			chloroform	8.2 (1.75)	10.6(1.46) sh
			pyridine	10.0(0.95)	
Ni	3-CH$_3$	2	solid	9.5	16.2
			dichloro-methane	9.4 (0.88)	16.0 (1.05)
	4-CH$_3$	2	solid	9.5	16.3
			chloroform	9.3 (0.86)	15.9 (1.08)
	6-CH$_3$	0	solid	8.1	15.2 sh
			chloroform	8.2 (1.13)	15.7 (1.45)sh
			pyridine	9.8 (1.13)	16.8 (1.28)sh

ν: 10^{3}kK
sh: shoulder

For R=6-CH$_3$-Py the nickel(II) complex Ni(H-SAL·R)$_2$ was obtained. This complex is paramagnetic with a magnetic moment of 3.25 B.M., which corresponds to a moment expected for the nickel(II) complex of a high-spin type. The electronic spectra indicate, as shown in Fig. 2 and Table 5, that this nickel(II) complex is octahedral in the solid state and in non-doner solvents. Since Beer's law holds for this as well as the other complexes, the association of the planar molecules in solution may be excluded for this complex. The band maxima lie in much lower frequency regions than the mixima of the related nickel(II) complexes, as may be seen in Table 5. The low frequency of the d–d band maxima, together with the comparatively high magnetic moment, seems to indicate that the configuration of Ni(H-SAL·6-CH$_3$-Py)$_2$ may be considerably distorted from the regular octahedron. It is to be noted that the ligand in this complex functions as a terdentate ligand with the nitrogen atom in the heterocyclic ring coordinated to the nickel(II) ion. It is also concluded, from the electronic spectrum, that this nickel(II) complex, when dissolved in pyridine, forms an octahedral pyridine adduct Ni(N-SAL·6-CH$_3$-Py)$_2$-(*py*)$_2$ in which the ligand H-SAL·6-CH$_3$-Py acts as a bidentate ligand.

The palladium(II) ion is similar to the nickel(II) ion in the sense that both ions have a d^8 configuration. Difference between these two ions, however, is remarkable in some respects; the palladium(II) ion forms stable quadri-coordinated planar complexes with various ligands, and the tendency of the palladium(II) ion to take coordination number exceeding four is much lower than that of the nickel-(II) ion. In the present work, the complexes of the type Pd(X-SAL·2-Py)$_2$ were obtained. Since the complexes of the type Pd(X-SAL·R)$_2$ so far obtained are known to have a square-planar con-

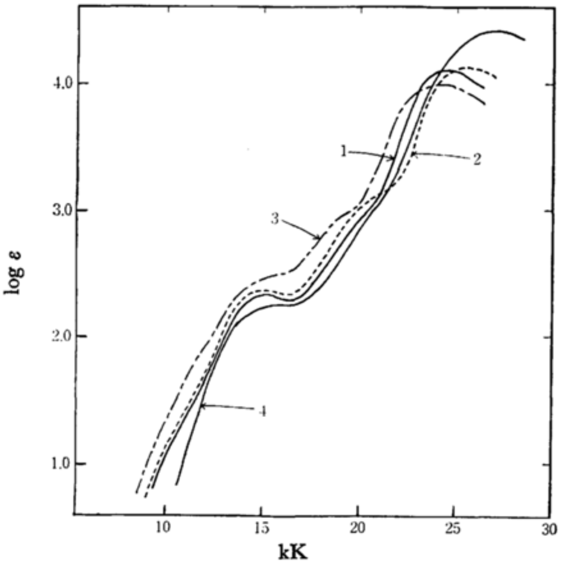

Fig. 3. Electronic absorption spectra of Cu(X-SAL·R)$_2$ in solution.
1 X=H, R=Ph, in chloroform
2 X=H, R=2-Py, in chloroform
3 X=3-CH$_3$O, R=2-Py, in chloroform
4 X=H, R=3-CH$_3$-Py, in dichloromethane

figuration for R=*n*-alkyl and aryl groups, it is most likely that the palladium(II) complexes may also be planar. In fact, the electronic spectrum of Pd(H-SAL·2-Py)$_2$ in solution is similar to that of Pd(H-SAL·Ph)$_2$ in solution, with a band at about 23.6 kK (log ε 3.8).

In contrast to the nickel(II) complexes, the copper(II) complexes of the type Cu(X-SAL·R)$_2$ were readily obtained as crystals. Since, for R=*n*-alkyl and aryl groups, the complexes of the type Cu(X-SAL·R)$_2$ so far obtained, in general, are known to take an essentially planar configuration,*[4] it is expected that the copper(II) complexes obtained in the present work may also be planar. This seems to agree with the finding that the electronic absorption spectrum of Cu(H-SAL·2-Py)$_2$ is quite similar to that of Cu(H-SAL·Ph)$_2$, which was previously concluded to be planar, as shown in Fig. 3. The spectra of the other copper(II) complexes prepared in the present work are also found to be quite similar to the spectrum of Cu(H-SAL·2-Py)$_2$.

It is found that the ligands of the types X-SAL·2-Py and H-SAL·CH$_3$-Py function as bidentate ligands in the metal complexes prepared in the present work, with the exception of one nickel(II) complex, in which the ligand might act as a terdentate ligand. The steric condition does not seem to be favorable for these ligands to function as terdentate ligands, since in this case there should be formed the unstable four-membered ring containing the metal ion and the nitrogen atom in the pyridine ring. In this connection, it is interesting to note that for R=(2-pyridyl)-methyl Oehmke and Bailar[6] obtained a compound of a formula Ni(H-SAL·R)$_2$, in which the nickel(II) ion has coordination number six. The steric condition is obviously favorable for this ligand to act as a terdentate ligand.

Support of this work by the Ministry of Education is gratefully acknowledged.

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*[4] Some complexes are also known to form associated species in the solid state, yielding five-coordinated copper(II) complexes.

6) R. W. Oehmke and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **27**, 2209 (1965).