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Metal Complexes with Schiff Bases Obtained from Salicylaldehyde Derivatives and 2-Aminoethylpyridine

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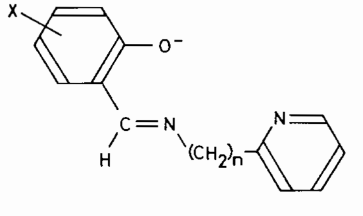
Cobalt(II), cobalt(III), nickel(II), copper(II) and palladium(II) complexes with N-2-(2-pyridyl)ethyl-ring-substituted salicylideneiminates (abbreviated as X-Sal-2-Epy) were synthesized. In addition to Co^{III} *(H-Sal-2-Epy)*$_3$*, the complexes of the formula* M^{II}*(X-Sal-2-Epy)*$_2 \cdot nH_2O$ *were obtained in crystals. The cobalt(III) complex is diamagnetic and has an electronic absorption spectrum typical of the six-coordinate, octahedral cobalt(III) complex. The cobalt(II) complexes in the solid state show electronic spectra typical of the six-coordinate cobalt(II) complexes. Electronic spectra also indicate that the nickel(II) complexes in the solid state and in non-donor solvents are six-coordinate, octahedral. In the cobalt(II) and nickel(II) complexes, the ligand X-Sal-2-Epy functions as terdentates, while in the cobalt(III) complex it acts as a bidentate ligand. The results are compared with those reported previously for related ligands.*

Introduction

In a previous paper, the present authors studied the synthesis and structure of bis(N-2-pyridyl-ring-substituted salicylideneiminato)metal(II) complexes[1] and compared the results with those about bis(N-2-pyridylmethylsalicylideneiminato)metal(II) complexes.[2] As extension of these studies, various metal complexes with N-2-(2-pyridyl)ethyl-ring-substituted salicvlideneiminates (Ic, abbreviated as X-Sal-2-Epy) have been synthesized and their structure has been examined in the present work. The results are compared with those of the corresponding complexes with ligands Ia and Ib (abbreviated as X-Sal-2-py and X-Sal-2-Mpy, respectively), in order to see the effect of the steric condition on the structure of the metal complexes.



Ia : n=0 , Ib : n=1 , Ic : n=2

Experimental

Materials

Bis[N-2-(2-pyridyl)ethyl-ring-substituted salicylideneiminato]metal(II), $M(X\text{-}Sal\text{-}2\text{-}Epy)_2 \cdot nH_2O$

The metal complexes of this type newly prepared in the present work are shown in Table I. The preparation methods are similar to those previously reported for other related complexes.[1] One of the typical methods is given for $Cu(H\text{-}Sal\text{-}2\text{-}Epy)_2$ as an example.

To an aqueous solution of copper(II) acetate hydrate (0.005 mol) were added an ethanolic solution of N-2-(2-pyridyl)ethylsalicylideneimine (0.01 mol) and an aqueous solution of sodium carbonate (0.003 mol). The resulting solution was heated with stirring at about 60° C for about 30 min. A brown, crystalline precipitate obtained was recrystallized from organic solvents, such as chloroform, ethanol and acetone, to give pure crystals of the complex.

The other metal complexes of this type were prepared in a similar way. All these metal complexes are insoluble in water, but soluble in methanol, ethanol, chloroform, acetone and benzene. The cobalt(II) complexes are oxidized gradually in the atmosphere, particularly in solution.

Tris[N-2-(2-pyridyl)ethylsalicylideneiminato] cobalt(III), $Co(H\text{-}Sal\text{-}2\text{-}Epy)_3$

To an ethanolic solution of the Schiff base (0.03 mol) were added an aqueous solution of cobalt(II) acetate tetrahydrate (0.01 mol) and sodium carbonate (0.01 mol). The resulting solution was heated at about 60° C for about 1 hr, and was allowed to stand for a few days at room temperature. A green, crystalline precipitate was recrystallized from ethanol, chloroform or acetone to give green crystals. Addition of aqueous hydrogen peroxide accelerates the reaction. Found: C, 68.65;

TABLE I. Analytical Data of Metal Complexes of the Type $M(X\text{-Sal-2-Epy})_2 \cdot nH_2O$.[a]

M	X	n	Calcd., %			Found, %			Color	μ
			C	H	N	C	H	N		
Co	H	2	63.75	5.35	10.62	63.80	5.10	10.68	r.o.	4.8
	5-Br	1	49.07	3.82	8.18	49.91	3.80	8.02	red	4.8
	5-NO_2	0	56.10	4.04	14.02	55.70	3.89	14.09	r.o	4.9
Ni	H	2	61.68	5.55	10.28	61.87	5.57	10.60	green	3.2
	5-Br	1	49.11	3.83	8.18	49.90	3.73	8.09	green	3.2
	5-Cl	1	56.42	4.40	9.40	56.25	4.69	9.11	green	3.0
	5-NO_2	0	56.12	4.04	14.03	55.96	3.94	13.81	y.b.	3.4
Cu	H	0	65.42	5.10	10.90	65.40	5.17	10.72	y.b.	1.9
	5-Br	0	50.05	3.60	8.34	49.78	3.51	8.46	o.g.	1.9
Pd	H	0	60.35	4.70	10.06	60.25	4.64	9.99	yellow	dia.

[a] μ: at room temperature in B.M. r.o.: red–orange; y.b.: yellow–brown; o.g.: olive-green.

H, 5.35; N, 11.44%. Calcd. for $C_{42}H_{39}N_6O_3Co$: C, 68.44; H, 5.32; N, 11.82%.

Measurements

Electronic absorption spectra of these metal complexes in solution and in nujol were measured on a Shimadzu MPS-50L spectrophotometer. In Table II are listed only those data for which Beer's law was confirmed to hold. Infrared spectra were measured with a Hitachi EPI-S2 and a Hitachi EPI-L infrared spectrophotometer using the nujol mull technique.

TABLE II. Main Absorption Maxima of Complexes of the Type $M(X\text{-Sal-2-Epy})_2 \cdot nH_2O$.[a]

M	X	n	Solvent	ν (logε)
Co	H	2	nujol	10.5
			CH_2Cl_2	10.4 (0.90)
			pyridine	10.4 (0.92)
	5-Br	1	nujol	10.5
			$CHCl_3$	10.5 (0.93)
			pyridine	10.4 (0.95)
	5-NO_2	0	nujol	10.2
			$CHCl_3$	10.4 (0.97)
			pyridine	10.2 (1.31)
Ni	H	2	nujol	10.8, 17.9
			$CHCl_3$	10.8 (1.32), 17.9 (1.23)
			pyridine	10.6 (1.16), 17.5 (1.15)
	5-Br	1	nujol	10.8, 17.8
			$CHCl_3$	10.9 (0.86), 17.6 (1.22)
			pyridine	10.8 (1.18), 17.6 (1.15)
	5-NO_2	0	nujol	10.9, 17.9sh
			$CHCl_3$	11.0 (1.27), 18.0 (1.75)
			pyridine	11.0 (1.31), 18.0 (1.35)
Cu	H	0	nujol	17.1, 22sh
			$CHCl_3$	17.1 (2.05), 22.0 (2.6)sh
	5-Br	0	$CHCl_3$	16.7 (2.05), 21.6 (2.6)sh
Pd	H	0	$CHCl_3$	25.3 (3.82)

[a] ν: 10^3 cm^{-1}; sh: shoulder.

Magnetic measurements were carried out at room temperature by the Gouy method using $CoHg(SCN)_4$ as a standard.

Results and Discussion

The Cobalt Complexes

Since $Co(H\text{-Sal-2-Epy})_3$ is diamagnetic, it is presumed that this cobalt(III) complex is a spin-paired, six-coordinate complex. This presumption is borne out by its electronic absorption spectrum, which has absorption bands at 16.4 kK (logε 2.27) and 25.7 kK (logε 3.98), as shown in Figure 1. It is thus evident that the ligand H-Sal-2-Epy in this complex functions as a bidentate ligand.

As may be seen in Figure 1 and Table II, the electronic spectra of all the cobalt(II) complexes in the

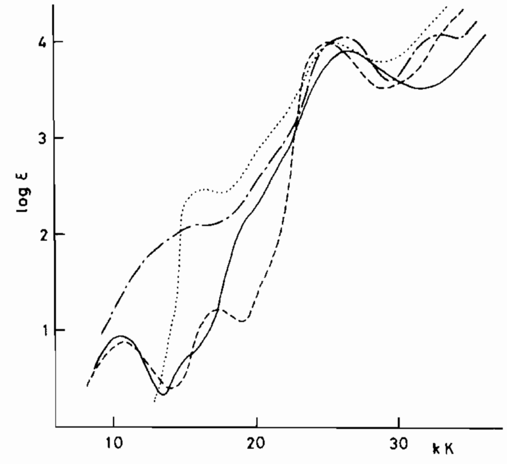


Figure 1. Electronic Absorption Spectra of Metal Complexes in Chloroform. 1, $Co(5\text{-Br-Sal-2-Epy})_2 \cdot H_2O$, (——); 2, $Ni(5\text{-Br-Sal-2-Epy})_2 \cdot H_2O$, (– – – – –); 3, $Cu(5\text{-Br-Sal-2-Epy})_2$, (— — —); 4, $Co(H\text{-Sal-2-Epy})_3$, (· · · · ·).

solid state are similar to each other and have main features typical of octahedral cobalt(II) complexes, differing entirely from those of tetrahedral cobalt(II) complexes.[3] Their magnetic moments fall in the range of magnitude expected for spin-free, octahedral cobalt (II) complexes (Table I). It is, therefore, considered that the cobalt(II) ion assumes a six-coordinate, octahedral geometry, the ligands in the cobalt(II) complexes functioning as terdentate ligands with the pyridine nitrogen atom bound to the cobalt(II) ion.

The same octahedral configuration is retained in pyridine and in non-donor solvents, since their spectra in pyridine and in non-donor solvents are essentially similar to those in the solid state.

It was proposed that the infrared absorption bands due to the pyridine ring deformations, which appear at about 400 cm^{-1} and 600 cm^{-1} are sensitive to the stereochemistry of the complexes and could be used to determine whether the pyridine nitrogen atom is coordinated or not.[2,4] For the complexes obtained in the present work, however, bands of other origins are superposed over the bands around 400 cm^{-1}, making reliable band assignment difficult in this region. The band around 600 to 650 cm^{-1}, which may tentatively be assigned to the pyridine ring vibrations, are listed in Table III. Representative curves in this region are shown in Figure 2. Inspection of Figure 2 and Table III indicates that the pyridine ring vibrations in the cobalt (II) complexes are shifted toward higher frequencies than those in the free ligands, Co(H-Sal-2-Epy)$_3$ and Pd(H-Sal-2-Epy)$_2$. It may be reasonable to assume that the ligand in the latter two complexes functions as a bidentate, the pyridine nitrogen atom not being bound with the metal ions. These data seem to be in agreement with the conclusion derived above that the ligands in the cobalt(II) complexes function as terdentate ligands, with the pyridine nitrogen atoms bound to the cobalt(II) ion.

TABLE III. Infrared Absorption Bands tentatively assigned to Vibrations of In-plane Pyridine-ring Deformation in M^{II}(X-Sal-2-Epy)$_2$·nH$_2$O (Type A), Co(H-Sal-2-Epy)$_3$ (Type B) and the Free Schiff Bases.

M	X	n	ν, cm^{-1}
(free ligand)	H	0	631
	5-Br	0	631
(Type A)			
Co	H	2	644
	5-Br	1	640
	5-NO$_2$	0	645
Ni	H	2	644
	5-Br	1	640
	5-NO$_2$	0	646
Cu	H	0	632
	5-Br	0	635
Pd	H	0	630
(Type B)			
Co	H	0	630

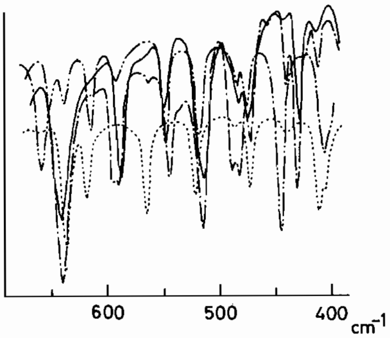


Figure 2. Infrared Spectra of Metal Complexes. 1, Co(5-Br-Sal-2-Epy)$_2$·H$_2$O, (——); 2, Ni(5-Br-Sal-2-Epy)$_2$·H$_2$O, (————); 3, Cu(5-Br-Sal-2-Epy)$_2$, (——·——); 4, free ligand, (5-Br-Sal-2-Epy)H, (-----).

The Nickel(II) and Copper(II) Complexes

Since electronic absorption spectra of the Ni(X-Sal-2-Epy)$_2$ type complexes in the solid state are essentially the same as those in non-donor solvents, the configurations of the nickel(II) complexes in the solid state are regarded to be retained in non-donor solvents. As may be seen in Figure 1 and Table II, the electronic spectra clearly indicate that the nickel(II) ion assumes a six-coordinate, octahedral configuration in all the nickel(II) complexes obtained, the ligands being terdentates in all of them. The infrared spectra in the region from 400 cm^{-1} to 4000 cm^{-1} of these nickel(II) complexes are remarkably similar to those of the corresponding cobalt(II) complexes, showing similarity in the structure between the nickel(II) and cobalt(II) complexes. In agreement with this also seem to be their infrared bands around 630 cm^{-1} to 650 cm^{-1}, which are found to be shifted toward higher frequencies, as compared with those of the free ligands and the palladium(II) complex (Table III).

The same octahedral configurations are found to be retained in the pyridine solutions, since their spectra in pyridine are essentially similar to those in non-donor solvents and in the solid state.

Complexes of the type Cu(X-Sal-2-Epy)$_2$ show a comparatively broad *d–d* band with main maximum at about 17 kK (X = H) and 16.5 kK (X = 5-Br). The spectra, for instance, their intensity and frequency of the band maxima, seem to be very similar to those of bis(N-arylsalicylideneminato)copper(II) complexes.[5]

Now we may compare the three ligands Ia, Ib and Ic, in connection with their coordinating ability. The difference between the ligands X-Sal-2-py and X-Sal-2-Epy is apparent particularly in the configuration of their cobalt(II) complexes. Most of the cobalt(II) complexes with the former ligands are tetrahedral,[1] while the latter ligands do not form tetrahedral cobalt (II) complexes, but those with an octahedral configuration are obtained. Thus comparison of the structures of the cobalt(II) complexes indicates that the tendency of X-Sal-2-Epy to act as a terdentate ligand is higher than that of X-Sal-2-py, which normally behaves as a bidentate. This is ascribed probably to the steric condition.

Approximate Dq values of the nickel(II) complexes with these ligands can be estimated from their *d–d* band maxima given in Table II. It is interesting to note that the 10 Dq value increases in the following order: X-Sal-2-py (9.5 kK) < X-Sal-2-Mpy (9.8 kK) < X-Sal-2-Epy (10.8 kK). This order is in agreement with the order found as to *d–d* band maxima of the corresponding copper(II) complexes, as may be seen in Table II.

Acknowledgement

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