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Cobalt(II) and Nickel(II) Complexes with Schiff Bases Obtained from Salicylaldehyde Derivatives and *N*-(2-Aminoethyl)-piperazine[1]

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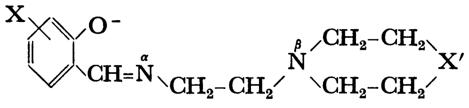
Synopsis. Cobalt(II) and nickel(II) complexes have been synthesized with Schiff bases derived from ring-substituted salicylaldehydes and *N*-(2-aminoethyl)-piperazine. Bis-(Schiff base)-metal(II complexes have been isolated. All of them have an octahedral structure, in which the Schiff bases are terdentate. The results are compared with those for complexes of related ligands.

It was reported previously that ligands of the type Ia formed bis(Schiff base)-complexes with cobalt(II) and nickel(II), the structure of which was planar, tetrahedral, octahedral or penta-coordinate, depending upon X as well as upon the metal ion.[2,3] Ligands of the type Ib, abbreviated as X-salen-pip, contain another nitrogen atom in the heterocyclic ring and might function as a quadridentate ligand. It seems interesting to explore such a possibility, and at the same time to examine if there is any significant electronic effect of the introduced NH group on the donor strength of the β nitrogen atom in the same ligand.



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(a) $X'=CH_2$, (b) $X'=NH$

In the present work, cobalt(II) and nickel(II) complexes with ligands of the type Ib were synthesized and the structure was examined mainly on the basis of spectral and magnetic data. The results were discussed in comparison with those for the corresponding complexes with ligands Ia.

Experimental

Materials. The nickel(II) complexes were prepared by the following method. A solution of nickel(II) chloride hexahydrate (0.01 mol) in ethanol (50 ml) was added to a solution of X-salicylaldehyde (0.022 mol) and *N*-(2-aminoethyl)-piperazine (0.022 mol) at 60 °C. To the resulting solution was added a solution of sodium carbonate in a small amount of water or potassium ethoxide (0.008 mol) in ethanol, and the mixture was stirred at 60 °C for about 3 h. After cooling the precipitate was collected and recrystallized from pyridine or methanol to yield olive-green microcrystals. These nickel(II) complexes are soluble in hot pyridine, slightly soluble in methanol, and insoluble in benzene and chloroform.

The cobalt(II) complexes were prepared in orange microcrystals by a method similar to that for the corresponding nickel (II) complexes. Recrystallization was carried out from pyridine. They are soluble in hot pyridine and almost insoluble in the common organic solvents.

Analytical data of the complexes prepared in the present work are shown in Table 1.

Measurements. Electronic absorption spectra were measured on a Shimadzu MPS-50L spectrophotometer. Magnetic measurements were carried out at room temperature by the Gouy method using $CoHg(SCN)_4$ as a calibrant.

Results and Discussion

Cobalt(II) complexes of the type $Co(X\text{-salen-pip})_2$ were obtained in the present work, X being 5-Cl, 5-Br, and 5-NO_2. These complexes in the solid state show very similar spectra, which have one d-d band at about 10500 cm^{-1} (Table 2). The band maximum is comparatively close to those of the corresponding cobalt(II) complexes of ligands Ia, which were concluded to be octahedral.[3] The octahedral structure, therefore, is assigned to the present cobalt(II) complexes. In these complexes the ligands are considered to function as a terdentate ligand. In view of the results of the previous studies, it seems most likely that the β nitrogen atom, in addition to the phenolic oxygen and the imine nitrogen atom, is coordinated to the cobalt(II) ion.

These cobalt(II) complexes are of a high-spin type, the values of the magnetic moments at room temperature being 4.6 to 4.8 BM. These values, particularly the lowest value (4.6 BM) for the complex with X=5-NO_2, may appear to be too low for the expected stereochemistry. A similar phenomenon was reported for

TABLE 1. ANALYTICAL DATA OF METAL COMPLEXES OF THE TYPE $M(X\text{-salen-pip})_2\cdot nH_2O$

M(II)	X	*n*	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	μ[a]
Co	5-Cl	0.5	51.92	5.87	13.96	51.66	5.69	13.99	4.8
	5-Br	1	44.65	5.19	12.02	44.80	4.92	12.16	4.7
	5-NO_2	1	49.44	5.75	17.75	49.49	5.31	17.52	4.6
Ni	H	0	59.67	6.93	16.06	59.48	6.88	15.92	3.2
	5-Cl	0	52.73	5.79	14.19	52.19	5.74	14.04	3.2
	5-Br	1	44.66	5.19	12.02	44.84	4.88	12.05	3.1
	5-NO_2	0	50.91	5.59	13.70	51.13	5.58	13.74	3.0

a) μ: BM at room temperature.

Table 2. Main d-d absorption band maxima of $M(X\text{-salen-pip})_2 \cdot nH_2O$ in Nujol mulls

M(II)	X	n	ν, kK
Ni	H	0	10.5, 17.5
	5-Cl	0	10.5, 17.5
	5-Br	1	10.5, 17.6
	$5\text{-}NO_2$	0	10.7, 17.5
Co	5-Cl	0.5	10.3
	5-Br	1	10.2
	$5\text{-}NO_2$	1	10.3

octahedral cobalt(II) complexes with ligands of the type Ia and was ascribed to a partial oxidation of the solid.[3]

Nickel(II) complexes of the type $Ni(X\text{-salen-pip})_2$ were obtained in the present work. Since they are only slightly soluble in appropriate solvents, Nujol mull spectra have been measured. The d-d band maxima are shown in Table 2. These complexes exhibit spectra, which are typical of the octahedral nickel(II) complex. The d-d bands at about 10.1—10.4 kK may be assigned to a transition $^3T_{2g} \leftarrow {}^3A_{2g}$ in the scheme of the O_h ligand field symmetry. No absorption bands appear in the lower frequency region, where the five-coordinate and the tetrahedral species are expected to absorb.

They are paramagnetic with magnetic moments of 3.0 to 3.3 BM at room temperature. It is, therefore, presumed that these nickel(II) complexes may have an octahedral structure.

Thus the ligands in these complexes are found to function as a terdentate ligand with the β nitrogen atom bound to the nickel(II) ion. This result differs from that reported previously for ligands of the type Ia. All the nickel(II) complexes of the ligands Ia are diamagnetic and planar in the solid state.[3] The difference in this respect between the ligands Ia and Ib may be ascribed to the electronic factor, since the steric condition is very similar for the ligands of the two types. It is rather surprising that such an apparently slight difference in the ligands gives rise to a remarkable difference in the structure of their nickel(II) complexes.

References

1) Presented, in part, at the 25th National Symposium on Coordination Chemistry, Tokyo, October, 1975.

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3) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, **4**, 943 (1965); L. Sacconi, M. Ciampolini, and G. Speroni, *Inorg. Chem.*, **4**, 1116 (1965).