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Synthesis and Characterization of Metal Complexes with Schiff Bases Obtained from *N*,*N'*-Bis(3-aminopropyl)piperazine and Salicylaldehyde Derivatives

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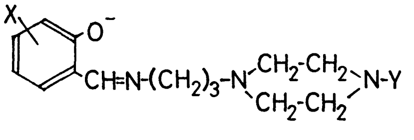
Cobalt(II), nickel(II), cobalt(III), manganese(III), and iron(III) complexes have been synthesized with Schiff bases (abbreviated as X-sal-prpi) derived from *N*,*N'*-bis(3-aminopropyl)piperazine and salicylaldehyde derivatives. On the basis of electronic spectra, infrared spectra, and magnetic data, the structures of the metal complexes are discussed. Complexes of the type Co^{II}(X-sal-prpi) are five-coordinated, and M^{III}(X-sal-prpi)ClO$_4$ consist of six-coordinated [M(X-sal-prpi)]$^+$ and free ClO$_4^-$ ions, the ligands X-sal-prpi being quinquidentate in the former and sexadentate in the latter.

It was previously reported that the ligands X-salen-pip (Ia) with four donor atoms form cobalt(II) and nickel(II) complexes of the type M(X-salen-pip)$_2$, in which X-salen-pip serve as terdentate ligands, one of the four donor atoms not being bound to the metal ions.[1] It is now interesting to examine metal complexes with the similar ligands X-sal-prpi (Ib) having six donor atoms and compare the results with those of X-salen-pip.† The present paper describes synthesis and characterization of some 3d metal complexes with these new ligands, *i.e.*, Schiff bases obtained from *N*,*N'*-bis(3-aminopropyl)piperazine and salicylaldehyde derivatives.



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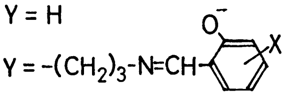
a: Y = H

b: 

Experimental

Materials. The Schiff bases H(X-sal-prpi) (X=H, 5-Cl, 5-Br) were synthesized in the following way. *N*,*N'*-Bis(3-aminopropyl)piperazine (0.5 mol) was added gradually to a solution of X-salicylaldehyde (1 mol) in ethanol (300 ml), the reaction vessel being placed in an ice bath. The solution was stirred for 30 min. A yellow crystalline precipitate was collected by filtration and recrystallized from ethanol to give yellow crystals. Elemental analysis agreed with the empirical formulae of the compounds. Mp 76 (X=H), 106 (X=5-Cl), 113 °C (X=5-Br).

Ni(X-sal-prpi) (X=H, 5-Cl, 5-Br). To a solution of nickel(II) acetate tetrahydrate (10 mmol) in ethanol (100 ml) was added a Schiff base H(X-sal-prpi) (11 mmol) and the mixture was heated with stirring on a water bath at about 70 °C for 10 min, followed by addition of sodium acetate trihydrate (12.5 mmol); a green precipitate appeared in 30 min. The reaction was continued for 3 h and a green crystalline precipitate was collected by filtration and washed with hot methanol. Attempts to recrystallize the products from such solvents as chloroform and benzene have not been successful.

Co(X-sal-prpi) (X=5-Cl, 5-Br). These cobalt(II) complexes were prepared as red crystals in a manner similar to the corresponding nickel(II) complexes. Recrystallization was carried out from methanol.

[Co(X-sal-prpi)]ClO$_4$ (X=H, 5-Cl, 5-Br). Cobalt(II) acetate tetrahydrate (10 mmol) was added to a solution of H(X-sal-prpi) (11 mmol) in ethanol (100 ml), and the brown solution was heated on a water bath at about 65 °C for 10 min. Sodium acetate trihydrate (12.5 mmol) and sodium perchlorate (10 mmol) were added to the solution, and the reaction was continued for 3 h. A brown precipitate was recrystallized from methanol to give brown crystals. Molar conductivities (Λ/Ω^{-1} cm^2 mol^{-1}): 98.5 (X=H); 88.1 (X=5-Cl); 84.0 (X=5-Br).

[Mn(X-sal-prpi)]ClO$_4$ and [Fe(X-sal-prpi)]ClO$_4$ (X=H, 5-Cl, 5-Br). These complexes were prepared in a manner similar to the corresponding cobalt(III) complexes. The manganese(III) complexes were obtained as dark green crystals by recrystallization of the crude products from methanol or chloroform. The iron(III) complexes were isolated as dark brown crystals, recrystallization being carried out from ethanol. Λ/Ω^{-1} cm^2 mol^{-1}: 98.7 (X=H, Mn^{3+}); 102.2 (X=5-Cl, Mn^{3+}); 98.8 (X=5-Br, Mn^{3+}); 95.0 (X=H, Fe^{3+}); 89.4 (X=5-Br, Fe^{3+}).

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

Measurements. Electronic absorption spectra of the complexes were measured on a Shimadzu MPS-50L spectrophotometer. The absorption maxima of the metal complexes in solution are almost coincident with those of the same complexes in the solid state. Infrared spectra were recorded as Nujol mulls using a Hitachi 215 infrared spectrophotometer. Magnetic measurements at room temperature were carried out by the Gouy method using CoHg(SCN)$_4$ as a calibrant. Conductivity measurements with methanolic solutions were carried out using a calibrated Toa-Electronics CG 201 PL conductivity cell and a Toa-Electronics Model CM-1DB conductivity bridge. The concentration of the solutions was 1/2000 mol dm^{-3}. The conductivity measurement with [Fe(5-Cl-sal-prpi)]ClO$_4$ was not carried out because of its low solubility in appropriate solvents.

Results and Discussion

Bivalent Metal Complexes. With cobalt(II) and nickel(II), complexes of the type M^{II}(X-sal-prpi) were isolated (Table 1). Since the nickel(II) complex is diamagnetic and shows a d-d band at 16.1 × 10^3 cm^{-1}, it is presumed that the nickel(II) ion in this complex

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† For X=H, these ligands are abbreviated as salen-pip and sal-prpi, respectively.

Table 1. Analytical data of metal complexes of the types M(X-sal-prpi) and [M(X-sal-prpi)]ClO_4

Compound	Mp/°C	Found, % C	H	N	Calcd, % C	H	N	μ[a]
Ni(sal-prpi)	dec	61.66	6.58	12.13	61.96	6.50	12.04	dia
Co(5-Cl-sal-prpi)	206	54.16	5.22	10.52	53.94	5.28	10.49	4.58
Co(5-Br-sal-prpi)	232	46.03	4.61	8.84	46.25	4.53	8.99	4.50
Co(sal-prpi)ClO_4	235	50.58	5.48	9.89	51.02	5.35	9.92	dia
Co(5-Cl-sal-prpi)ClO_4	206	45.16	4.83	8.33	45.48	4.75	8.54	dia
Co(5-Br-sal-prpi)ClO_4	232	40.13	4.31	7.66	39.88	3.90	7.75	dia
Fe(sal-prpi)ClO_4	214	51.28	5.45	10.00	51.30	5.38	9.97	5.94
Fe(5-Cl-sal-prpi)ClO_4	244	45.70	4.40	9.13	45.70	4.47	8.88	5.98
Fe(5-Br-sal-prpi)ClO_4	236	39.97	3.89	8.10	40.05	3.92	7.79	5.93
Mn(sal-prpi)ClO_4	dec	51.09	5.54	9.98	51.39	5.39	9.99	5.07
Mn(5-Cl-sal-prpi)ClO_4[b]	98[c]	35.92	3.59	6.41	35.95	3.48	6.45	4.95
Mn(5-Br-sal-prpi)ClO_4[b]	85[c]	32.97	3.16	5.95	32.61	3.16	5.85	4.96

a) μ: BM at room temperature. b) 2 $CHCl_3$ adduct. c) The low melting point may be due to the inclusion of the chloroform molecules.

Table 2. Main d-d absorption bands of Co(X-sal-prpi) and [M(X-sal-prpi)]ClO_4

Compound	Solvent	ν (log ε)
Co(5-Cl-sal-prpi)	$CHCl_3$	7.8(0.7)sh, 9.3(0.8), 12.0(0.7)sh, 18.2(1.5)
Co(5-Br-sal-prpi)	$CHCl_3$	7.8(0.7)sh, 9.3(0.8), 12.2(0.75)sh, 18.1(1.5)
[Co(sal-prpi)]ClO_4	CH_3OH	16.0(2.25)sh, 20.0(2.75)
[Co(5-Cl-sal-prpi)]ClO_4	CH_3OH	16.0(2.3)sh, 20.0(2.8)
[Co(5-Br-sal-prpi)]ClO_4	CH_3OH	15.9(2.3)sh, 20.0(2.8)
[Mn(sal-prpi)]ClO_4	CH_3OH	16.2(2.75)
[Mn(5-Cl-sal-prpi)]ClO_4	CH_3OH	15.9(2.77)
[Mn(5-Br-sal-prpi)]ClO_4	CH_3OH	15.7(2.77)

ν: 10^3 cm^{-1}. sh: Shoulder.

is planar four-coordinated. This complex does not show a sharp melting point, and is probably polymeric. From the experimental data so far available, it is difficult to draw a definite conclusion about its precise structure.

Contrary to the nickel(II) complex, the cobalt(II) complexes Co(X-sal-prpi) show sharp melting points. They are paramagnetic (Table 1), and their electronic spectra have d-d bands typical of the five-coordinated cobalt(II) complexes, as shown in Fig. 1 and Table 2. It is thus found that five of the six donor atoms in the ligands are coordinated to cobalt(II) ion.

Infrared C=N frequencies of the cobalt(II) complexes are at lower frequencies than those of the free ligands (Table 3), and appear as a single peak, implying that the two imine nitrogen atoms of the ligands are coordinated to the metal ion. Similarly, infrared bands of the free ligands at about 1560—1570 cm^{-1}, which are usually ascribed to C–O vibrations, appear as a single peak and are shifted toward appreciably lower frequencies as the ligands are bound to the cobalt(II) ion, implying that the two phenolic oxygen atoms of the ligands are bound to the cobalt(II) ion. These facts lead to the presumption that only one of the two tertiary nitrogen atoms of the ligands is bound to the cobalt(II) ion in these complexes.

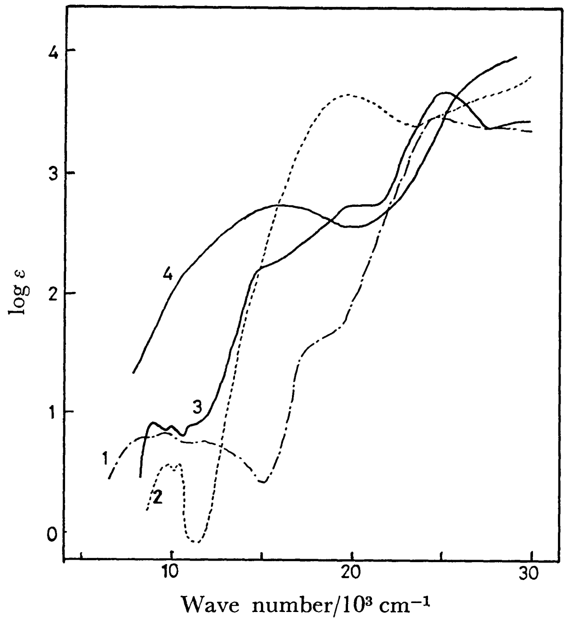

Fig. 1. Electronic absorption spectra: 1, Co(5-Cl-sal-prpi), in chloroform; 2, [Fe(sal-prpi)]ClO_4, in methanol; 3, [Co(sal-prpi)]ClO_4, in methanol; 4, [Mn(sal-prpi)]ClO_4, in methanol.

Table 3. Main infrared absorption bands of M(X-sal-prpi) and [M(X-sal-prpi)]ClO$_4$

Compound	ν(C=N) cm^{-1}	ν(C–O) cm^{-1}
H(sal-prpi)	1635	1565
H(5-Cl-sal-prpi)	1625	1570
H(5-Br-sal-prpi)	1625	1560
Ni(sal-prpi)	1615	1540
Co(5-Cl-sal-prpi)	1618	1518
Co(5-Br-sal-prpi)	1618	1512
[Co(sal-prpi)]ClO$_4$	1620	1540
[Co(5-Cl-sal-prpi)]ClO$_4$	1618	1520
[Co(5-Br-sal-prpi)]ClO$_4$	1618	1520
[Mn(sal-prpi)]ClO$_4$	1610	1545
[Mn(5-Cl-sal-prpi)]ClO$_4$	1600	1530
[Mn[5-Br-sal-prpi)]ClO$_4$	1600	1525
[Fe(sal-prpi)]ClO$_4$	1610	1545
[Fe(5-Cl-sal-prpi)]ClO$_4$	1610	1530
[Fe(5-Br-sal-prpi)]ClO$_4$	1610	1527

Tervalent Metal Complexes. With manganese(III), iron(III), and cobalt(III), complexes of the type M$^{\text{III}}$(X-sal-prpi)ClO$_4$ were isolated. The perchlorate ion in these complexes is not coordinated, since a broad infrared band due to the free perchlorate ion appears at about 1040 to 1110 cm^{-1}.[2] This is borne out by their electric conductivities, which are found to be in the range between 89 and 103 Ω^{-1} cm^2 mol^{-1}, showing that they are 1:1 electrolytes.[3] As shown in Table 3, stretching C=N and C–O frequencies of the complexes lie at lower frequencies than those of the free ligands, and each of them appears as a single peak, implying that the two imine nitrogen atoms and two phenolic oxygen atoms are bound to the metal ion.

The cobalt(III) complexes are diamagnetic. Judging from the general tendency of the cobalt(III) ion, the low spin cobalt(III) complexes obtained in the present work are reasonably assumed to be six-coordinated. Their electronic absorption spectra, which are similar to each other, are also in agreement with this view. Examination of the model shows that in the most favourable structure the four nitrogen atoms occupy the coordination sites at the corners of the square, the two oxygen atoms being *trans* to each other. The d-d band at about 14 to 21×10^3 cm^{-1}, which is assigned to the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition in the O_h symmetry scheme, is found to be composed of two components, as may be seen in Fig. 1 and Table 2. The significant band splitting seems to support the *trans*-configuration.[4]

The manganese(III) and iron(III) complexes are of a high spin type (Table 1). Infrared spectra of M(X-sal-prpi)ClO$_4$, M being Mn(III) and Fe(III), are similar to those of Co(X-sal-prpi)ClO$_4$ in the whole region from 650 to 4000 cm^{-1}. All the infrared bands are almost coincident with the corresponding bands of the cobalt(III) complexes. It is thus very likely that the coordination mode of the multidentate ligands X-sal-prpi is similar in the manganese(III), iron(III), and cobalt(III) complexes.

The manganese(III) complexes exhibit a broad d-d band at about 16×10^3 cm^{-1}, which may be assigned, in the octahedral group, to the $^5T_{2g} \leftarrow {}^5E_g$ transition.[5]

In the spectra of the iron(III) complexes some feeble, sharp spin-forbidden d-d bands appear at about 10×10^3 cm^{-1}. However, most of the spin-forbidden bands are hidden under an intense metal-to-ligand charge transfer band, whose maximum occurs at 19.5 (X=H), 19.1 (X=5-Cl), and 19.2×10^3 cm^{-1} (X=5-Br).

All these findings combined show that the manganese(III) and iron(III) complexes most probably have a configuration similar to that of the corresponding cobalt(III) complexes, namely a *trans*-six-coordinated (N)$_4$(O)$_2$ configuration.

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