

# SPECTROPHOTOMETRIC STUDY OF NEW SCHIFF BASE COMPLEXES WITH SOME METAL IONS IN METHANOL SOLUTION

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**ABSTRACT:** The complexation reactions between *N,N'*-3,6-dioxa-1,8-octanebis (salicylaldimine) [saldioxen(I)] and Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) were studied spectrophotometrically in methanol solution at 25°C. The stoichiometry of the complexes were obtained as 2:1 and 1:1 saldioxen-metal ion using mole ratio method. The formation constants of the complexes were determined, and found to follow the Irving-Williams, rule for the cations of the first transition series. IR spectroscopy and other evidence indicated that, in 2:1 complexes, the coordination takes place through the azomethin nitrogen atoms only, whereas in 1:1 complexes, metal ion coordinated with ligand through two azomethin groups and the phenolic oxygen atoms.

**KEY WORDS:** Complexation, Schiff base, *N,N'*-3,6-dioxa-1,8-octanebis (salicylaldimine)

## INTRODUCTION

The ability of Schiff bases derived from salicylaldehyde as poly-dentate ligands to form very stable complexes with different cations is well known [1]. Their complexes have been known since the mid-nineteenth century [2], and before the general preparation of Schiff base ligands themselves [3]. However, there was no comprehensive, systematic study until the preparative work of Pfeiffer and associates was reported [4,5].

Transition metal complexes of Schiff base ligands

have contributed significantly to the development of transition metal chelate chemistry [6-8] and complexes of these ligands with some cations play a major role as speculative models in bio-inorganic chemistry and enzymatic studies [9]. However, despite extensive scientific reports on the synthesis, characterization and crystalline structure of the transition metal-salen complexes [10-12], very little is known about the nature of the different species and their formation equilibrium in solution [13].

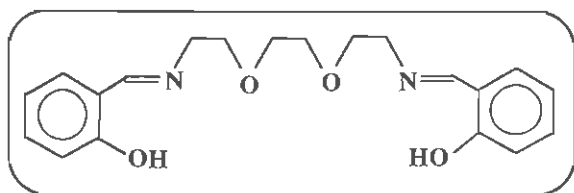
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In this paper we report the spectrophotometric study of a new Schiff base, *N,N'*-3,6-dioxa-1,8-octane bis(salicylalimine) [saldioxen (I)] with some of transition metals in methanol solution in order to evaluate the formation constants of their complexes. Moreover, we have synthesized these complexes with regard to the resulting stoichiometry and characterized by melting point, conductivity and IR spectroscopy.



(I)

## EXPERIMENTAL

Reagent grade acetate salts of manganese, cobalt, nickel, copper, zinc, cadmium and mercury (all from Merck, Darmstadt, Germany) were all of highest commercial purity available and were used without further purification. Spectroscopic grade methanol (Merck) was used as received. Saldioxen (I) was synthesized, purified and dried by the method described below. The chemicals used for preparing the saldioxen were of reagent grade salicylaldehyde (from Fluka) and 1,8-diamino-3,6-dioxaoctan (Merck).

All UV-Vis spectra were obtained on a Philipps Pu 8750 spectrophotometer, the absorbance measured on a Philipps Pu 8675 vis spectrophotometer at  $25 \pm 1^\circ\text{C}$ . Conductivity measurements were carried out with a Metrohm 660 conductometer. Melting points were determined in open capillary tubes in a Buchi 510 oil circulating melting point apparatus. Infrared spectra (in KBr) of the ligand and complexes were recorded on a Perkin Elmer 781 spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX-250 in pure  $\text{CDCl}_3$  using TMS as an internal standard. Mass spectra were determined on a Shimadzu GCMS-QP 1000 EX instrument at 70 eV.

The formation constants of the resulting 2:1 complexes between the saldioxen and metal ions used were determined by the absorbance measurements, at  $\lambda_{\text{max}}$  of each saldioxen-metal ion complex, [14,15] in solutions of varying concentrations of the metal ions ( $4 \times 10^{-6}$ – $8 \times 10^{-5}$  M) added to a fixed concentration

of saldioxen ( $4 \times 10^{-5}$  M) in methanol [16]. In contrast in determination of the formation constants of 1:1 complexes, varying concentrations of the saldioxen ( $5 \times 10^{-6}$ – $1 \times 10^{-4}$  M) were added to fixed concentration of metal ions ( $4 \times 10^{-5}$  M) in methanol. Attainment of equilibrium was checked by observing the point at which change in the spectra occurred after several hours. When a metal ion,  $\text{M}^{2+}$ , reacts with a Schiff base ligand, L, to form a 1:1 complex,



the formation constant is given as

$$K_f = \frac{[\text{ML}]}{[\text{M}][\text{L}]} \quad (2)$$

The mass balance equations for [L] and [M] are given by

$$C_L = [\text{L}] + [\text{ML}] \quad (3)$$

$$C_M = [\text{M}] + [\text{ML}] \quad (4)$$

where  $C_L$ ,  $C_M$ , [L], [M] are the total concentration of the ligand, total concentration of the metal ion, concentration of the free ligand and concentration of the uncomplexed metal ion, respectively. Substitution of equations (3) and (4) into equation (2) and rearrangement, yields (5)

$$K_f [\text{L}]^2 + (1 + K_f(C_M - C_L)) [\text{L}] - C_L = 0 \quad (5)$$

In order to form a 2:1 complex between a metal ion and a ligand,



the overall formation constant, K (or  $\beta_2$ ) is given as;

$$K = \frac{[\text{ML}_2]}{[\text{M}][\text{L}]^2} \quad K = \beta_2 \quad (7)$$

The mass balance equations for [L] and [M] are given by

$$C_L = [\text{L}] + 2[\text{ML}_2] \quad (8)$$

$$C_M = [\text{M}] + [\text{ML}_2] \quad (9)$$

Substitution of equations (8) and (9) into equation (7) and rearrangement, yields (10)

$$K[\text{L}^3] + (2KC_M - KC_L) [\text{L}]^2 + [\text{L}] - C_L = 0 \quad (10)$$

For the evaluation of the formation constants from the absorbance-mole ratio data, a non-linear least-squares curve fitting program by a multi-dimensional Newton method was used. The program is based on the iterative adjustment of the calculated values of the absorbance to the observed values by

using either the Wentworth matrix technique [17] or the Pawell procedure [18]. Adjustable parameters are formation constants and the molar absorptivities of all complexes  $\epsilon_L$ ,  $\epsilon_{ML}$  and  $\epsilon_{ML_2}$ . The free ligand concentration [L] was calculated from equations (5) or (10). Once the value of [L] had been obtained, the concentration of all other species involved were calculated from the corresponding mass balance equations (3) or (8) and (4) or (9) by using the estimated value of the formation constant at the current iteration step of the program. Refinement of the parameters is continued until the sum-of-squares of the residuals between calculated and observed values of the absorbance for all experimental points is minimized. The output of the program used is comprised of refined parameters, the sum-of-squares and the standard deviation of the data as well as the distribution of the species.

### Synthesis of saldioxen

Saldioxen was synthesized by mixing salicylaldehyde and 1,8-diamino-3,6-dioxaoctane in 2:1 molar ratio in methanol and then the reaction mixture was refluxed with stirring for about 15 h. After the reaction was complete, the solvent was evaporated to give a yellow oil, which was crystallized by petroleum ether (60-80°C) to give a yellow crystalline solid in 94% yield (3.34 g). m.p. = 46°C,  $R_f = 0.56$  ( $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{OH}/97:3$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 250 MHz)  $\delta$  3.59(s, 4H), 3.71 (s, 8H), 6.87(d t, 2H,  $J_1 = 7.5$  Hz,  $J_2 = 1.0$  Hz), 6.93 (d, 2H,  $J = 8.25$  Hz), 7.23(d, 1H,  $J = 1.5$  Hz), 7.26(dd, 1H,  $J_1 = 3.25$  Hz,  $J_2 = 1.5$  Hz), 7.31(dd, 2H,  $J_1 = 7.25$  Hz,  $J_2 = 1.63$  Hz), 8.32(s, 2H), 13.39(s, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 62.9 MHz)  $\delta$  59.01, 70.56, 96.12, 116.97, 118.65, 131.31, 132.17, 161.19, 166.36; IR(KBr), 650 (m), 742(w), 765(vs), 850(s), 870(w), 925(m), 970(m), 1040(s), 1062(s), 1125(vs), 1162(s), 1235(m), 1255(w), 1280(s), 1325(m), 1342(m), 1408(w), 1450(s), 1470 (m), 1500(m), 1510(s), 1587(m), 1615(m), 1645(vs), 2890(s), 2920(s), 3020(m), 3450(br, s)  $\text{cm}^{-1}$ ; Ms,  $m/z = 358$  ( $\text{M}^+ + 2$ , 3.5), 357 ( $\text{M}^+ + 1$ , 12.6), 356 ( $\text{M}^+$ , 23.2), 210(23.0), 192(18.9), 164(19.4), 150 (18.0), 149(72.1), 148(41.3), 135(53.1), 121(44.3), 107 (base peak), 91 (25.4), 78(24.3), 77(74.8), 65(33.7), 51 (38.5), 43 (24.0), 41 (19.1), UV( $\text{CH}_3\text{OH}$ ):  $\lambda_{\text{max}}$  221( $\epsilon = 51220$ ), 254( $\epsilon = 1820$ ), 315( $\epsilon = 5840$ ).

### Synthesis of 2:1 saldioxen-metal ion complexes

A solution of related transition metal acetate salt (0.01 mol) in methanol (30 mL) was added dropwise (30 min) to a solution of saldioxen (0.02 mol) in methanol (40 mL). The mixture was stirred at room temperature for one h, and let stand overnight (pH 7.2). Then the precipitate formed was filtered, washed with cold methanol and dried in vacuum at room temperature. Complexes were recrystallized from dichloromethane.

### Synthesis of 1:1 saldioxen-metal ion complexes

A solution of saldioxen (0.01 mol) in methanol (25 mL) was added dropwise (30 min) to a solution of transition metal acetate salt (0.01 mol) in methanol (30 mL). The mixture was stirred at room temperature for one h, and let stand overnight (pH 5.7). The resulting adduct was then filtered, washed with cold methanol and dried in vacuum at room temperature. Consequently complexes were recrystallized from dichloromethane.

## RESULTS AND DISCUSSION

The electronic absorption spectra of saldioxen ( $1.52 \times 10^{-4}$  M) in the presence of increasing amounts metal ion in methanol solution at 25°C for  $\text{Ni}^{2+}$  ion is shown in Fig. 1. The corresponding spectra for the other metal ions are very similar to that of  $\text{Ni}^{2+}$  ion and thus are not included. As it is seen, in the spectra of the ligand, the absorption bands appeared at 221, 254 and 315 nm. Addition of various concentrations of the  $\text{Ni}^{2+}$  ion to saldioxen solution results in a decrease in the absorption band at 315 nm and appearance of two strong absorptions at 238 and 364 nm, indicating the presence of a new saldioxen species, presumably due to the formation of saldioxen- $\text{Ni}^{2+}$  complex. The wavelength of 364 nm for  $\text{Ni}^{2+}$  ion was selected as the most convenient wavelength for further studies. The selected wavelength for other metal ions are shown in Table 1. Moreover, the existence of well defined isobestic points, formed at the same time, in the spectra of saldioxen upon titration with  $\text{Ni}^{2+}$  ion (Fig. 1), also with other metal ions, further supports the occurrence of a simple complexation equilibrium in solution.

In order to determine the stoichiometry of reac-

Table 1: Stability constants of saldioxen complexes with different metal ions in methanol solution at 25°C

Cation	$\lambda_{\max}(\text{nm})$	Log $K_f^a$	
		1:1	2:1
Mn <sup>2+</sup>	358	4.54 ± 0.03	8.36 ± 0.05
Co <sup>2+</sup>	354	5.45 ± 0.04	9.39 ± 0.03
Ni <sup>2+</sup>	364	6.07 ± 0.02	9.45 ± 0.04
Cu <sup>2+</sup>	364	6.38 ± 0.05	9.99 ± 0.02
Zn <sup>2+</sup>	357	6.29 ± 0.02	10.32 ± 0.04
Cd <sup>2+</sup>	362	6.32 ± 0.04	—
Hg <sup>2+</sup>	390	7.28 ± 0.03	—

a) In 2:1 complexes,  $K_f = \beta_2$

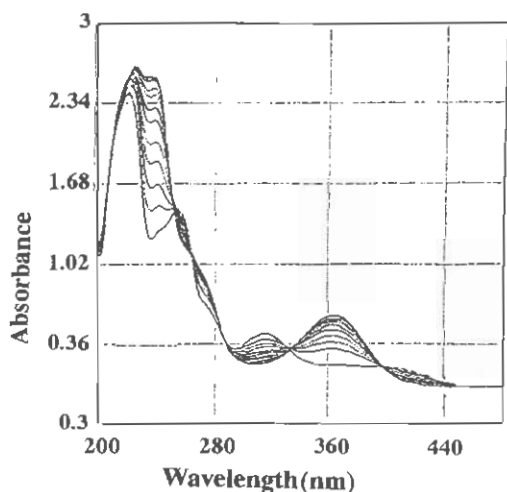


Fig. 1: Absorption spectra of  $1.24 \times 10^{-4} \text{ M}$  saldioxen in methanol at various concentrations of  $\text{Ni}^{2+}$  ions. Molar ratio of  $\text{Ni}^{2+}$ : saldioxen vary from the bottom to the top spectrum are 0.00, 0.12, 0.24, 0.36, 0.48, 0.60, 0.72, 0.84, 0.96, 1.08, 1.20 and 1.32:1.

tions, the mole ratio method was used. The formation constants of the resulting complexes were determined as described in the experimental section. Figs. 2 and 3 show the plots of absorbance vs. metal ion: saldioxen mole ratio in methanol solution for all of the metal ions, obtained at  $\lambda_{\max}$  of each complex. The plots are clearly indicative of the formation of a 2:1 saldioxen-metal ion complex in the case of  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$  ions (Fig. 2) and a 1:1 complex in the case of  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  ions (Fig. 3).

Fig. 4 shows the plots of absorbance vs. saldioxen: metal ion mole ratio in methanol solution for  $\text{Mn}^{2+}$ ,

$\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$  ions obtained at  $\lambda_{\max}$  of each complex. The plots indicate that in all the metal

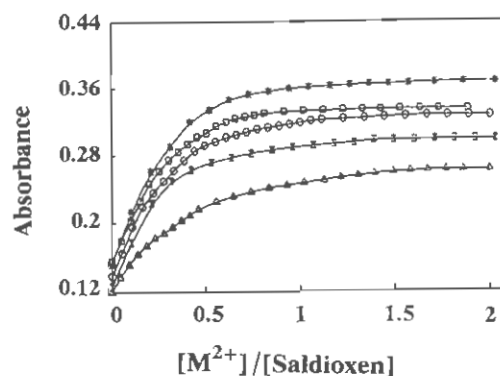


Fig. 2: Plots of absorbance vs. molar ratio of metal ion: saldioxen in methanol solution at 25°C and  $\lambda_{\max}$  of each complex.  $\Delta$ ,  $\text{Mn}^{2+}$ ;  $\times$ ,  $\text{Co}^{2+}$ ;  $\circ$ ,  $\text{Ni}^{2+}$ ;  $\square$ ,  $\text{Cu}^{2+}$ ;  $*$ ,  $\text{Zn}^{2+}$ .

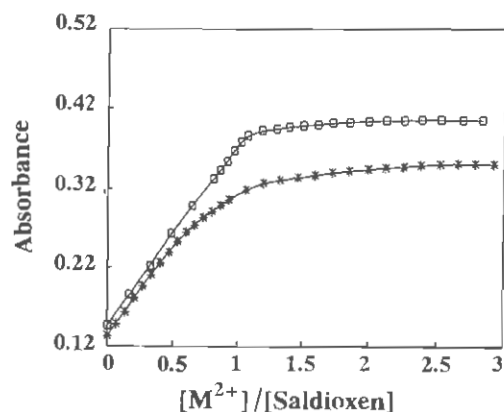


Fig. 3: Plots of absorbance vs. molar ratio of metal ion: saldioxen in methanol solution at 25°C and  $\lambda_{\max}$  of each complex.  $*$ ,  $\text{Cd}^{2+}$ ;  $\square$ ,  $\text{Hg}^{2+}$ .

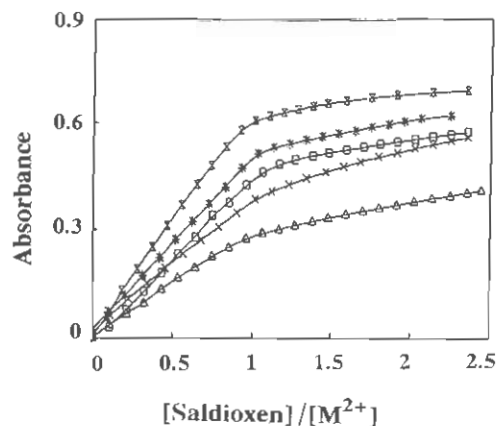


Fig. 4: Plots of absorbance vs. molar ratio of saldioxen: metal ion in methanol solution at 25°C and  $\lambda_{\max}$  of each complex.  $\Delta$ ,  $\text{Mn}^{2+}$ ;  $\times$ ,  $\text{Co}^{2+}$ ;  $\square$ ,  $\text{Ni}^{2+}$ ;  $*$ ,  $\text{Zn}^{2+}$ ;  $\times$ ,  $\text{Cu}^{2+}$ .

ions used, ML complex was formed. With regard to the difference between stoichiometry obtained by the two types of titrations, it is suggested that during the titration of a fixed concentration of ligand with varying amounts of the metal ion, the ligand is in excess compared to the metal ion. Thus two ligands were coordinated with one metal ion giving  $ML_2$  complex. Whereas in titrating a constant amount of the metal ion with varying concentrations of the ligand, the metal ion is in excess and thus the ML complex is formed. As it is seen in plots of mole ratio (Fig. 4), in none of the metal ions, the 1:1 complex is converted to the 2:1 complex by the addition of further amounts of ligand to metal ion in methanol solution. In order to confirm the above results, the complexes were characterized by IR spectroscopy.

In all cases studied, the resulting absorbance-mole ratio data from Figs. 2, 3 and 4 showed the best computer fitting to the 2:1, 1:1 and 1:1 saldioxen-metal ion stoichiometry, respectively. Two of the computer fittings of the mole ratio data (for  $ML_2$  and ML systems) are shown in Figs. 5 and 6. The fair agreement between the observed and calculated absorbances further supports the occurrence of a 2:1 and 1:1 complexation between the saldioxen and metal ion used in methanol solution respectively. The formation constants of all corresponding complexes and their  $\lambda_{max}$  values are listed in Table 1. As is seen, among the metal ions used, the stability of the resulting 2:1 saldioxen complexes vary in the order  $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$  and the sequence of the formation constant of 1:1 saldioxen complexes with the cations of the first transition series (i.e.,  $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ ) follows the Irving-Williams series, [19] which generally holds for the equilibrium constants of transition metals. However, among 1:1 complexes of cations  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Hg^{2+}$ , saldioxen- $Hg^{2+}$  complex in methanol solution shows the highest stability, which probably is due to the proper size of  $Hg^{2+}$  ion that favors a suitable spatial fit [20] with flexible donating atoms of the ligand (azomethin nitrogen atoms and phenolic oxygen atoms).

In the synthesis of 1:1 complexes, the pH of the reaction mixture was acidic whereas in the case of 2:1 complexes it was neutral. These results indicated that

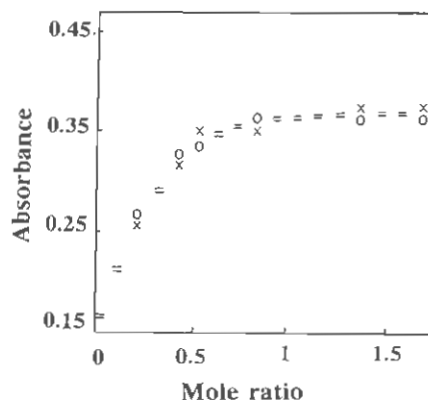


Fig. 5: computer fit of the plot of absorbance vs. molar ratio  $Cu^{2+}$ : saldioxen obtained at 364 nm and 25°C: (x), experimental points; (o), calculated points; (=), experimental and calculated points are the same within the resolution of the plot.

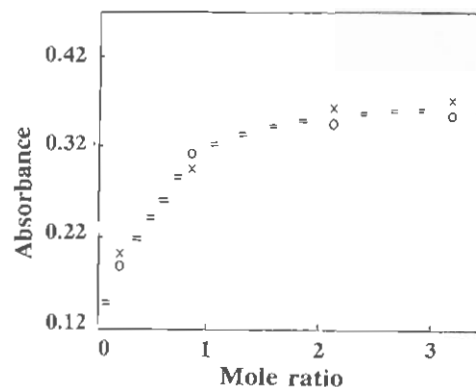


Fig. 6: computer fit of the plot of absorbance vs. molar ratio  $Cd^{2+}$ : saldioxen obtained at 364 nm and 25°C: (x), experimental points; (o), calculated points; (=), experimental and calculated points are the same within the resolution of the plot.

in the 1:1 complexes, the Schiff base was ionised by removal of the phenolic protons whereas in the of 2:1 complexes, the Schiff base was unionised.

Melting point and millimolar conductance of the ligand and both types of complexes in dichloromethane are reported in Table 2. The conductance data for 1:1 saldioxen-metal ion complexes were different from those of 2:1 complexes. The low molar conductivities of these complexes as for the other complexes [1,21-24] indicated their non-electrolytic behavior.

In Table 2, the significant IR frequencies for the free saldioxen and its related complexes are given along with the appropriate assignments. A strong

Table 2: Melting point, conductivity and selected IR frequencies ( $\text{cm}^{-1}$ ) of the ligand and metal complexes.

Compound	Stoichiometry	m.p. (°C)	$\Lambda_M$ ( $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ )	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})$
Saldioxen	—	46	3.34	1645	1280
Saldioxen-Mn	1:1	171	5.78	1622	1298
Saldioxen-Mn	2:1	78	8.56	1615	1282
Saldioxen-Co	1:1	111	5.72	1620	1325
Saldioxen-Co	2:1	84	8.92	1620	1280
Saldioxen-Ni	1:1	110	4.98	1633	1305
Saldioxen-Ni	2:1	93	7.86	1625	1280
Saldioxen-Cu	1:1	108	4.65	1620	1325
Saldioxen-Cu	2:1	69	9.28	1625	1285
Saldioxen-Zn	1:1	96	4.46	1625	1315
Saldioxen-Zn	2:1	184	8.73	1630	1280
Saldioxen-Cd	1:1	121	4.27	1630	1315
Saldioxen-Hg	1:1	56	5.62	1625	1310

absorption band at  $1645\text{ cm}^{-1}$  was assigned [25] to C=N stretching frequency in the free ligand which shifts to a lower frequency at about  $1625\text{ cm}^{-1}$  in both type 1:1 and 2:1 complexes ( $\Delta\nu\ 12\text{-}30\text{ cm}^{-1}$ ). It has been suggested [26-28] that a shift to lower frequency occurs due to the reduction of electron density in the azomethin link as the nitrogen coordinates to the metal ion.

A sharp absorption band at  $1280\text{ cm}^{-1}$  assignable [25] to C-O stretching vibration in the free saldioxen which shifts to a higher frequency at about  $1320\text{ cm}^{-1}$  in the 1:1 complexes ( $\Delta\nu\ 18\text{-}45\text{ cm}^{-1}$ ). Whereas this same band in the 2:1 complexes does not show an appreciable shift compared to the free saldioxen (Table 2). A strong absorption band at  $1600\text{ cm}^{-1}$  due to acetate anion is present in the 2:1 complexes. However, this band was not seen in the 1:1 complexes.

As it is shown in Table 2, the IR spectra of the 1:1 complexes, in which there are a lowering in the C=N stretching frequency and an increase in the C-O stretching vibration suggest that a coordination bond has been formed between the metal ion and two azomethin groups of the ligands and the phenolic oxygen atoms. The IR data belonging to the 2:1 complexes showed that the C=N stretching vibration was lower than that of the free ligand while the C-O absorption in the spectra of the complexes was unchanged or slightly increased in frequency ( $\Delta\nu\ 0\text{-}5\text{ cm}^{-1}$ ). These

indicate that the coordination takes place through the azomethine nitrogen atoms only. In these adducts, saldioxen coordinates the respective metal ions acting as bidentate ligand, so that the shift of the C=N band in the adducts is of the same order as found for ligands which do not contain salicylaldehyde OH group [29,30].

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