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Metallation of tetradentate N_2O_2 Schiff base with Mn(II), Co(II), Cu(II) and Zn(II): synthesis, characterization and formation constants measurement

Research Article

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Abstract: Four Schiff base ligands, salabza- $H_2 = N,N'$ -bis(salicylidene)-2-aminobenzylamine, were synthesized by condensation of one mole of 2-aminobenzylamine and two moles of salicylaldehyde and/or two moles of substituted salicylaldehyde (5-OMe, 5-Br, 5-NO₂). All the four Schiff bases and their Mn(II), Co(II), Cu(II) and Zn(II) complexes are characterized by UV-Vis, FT–IR, ¹H NMR spectroscopy, mass spectrometry and elemental analysis. The formation constants and the Gibbs free energies were measured spectrophotometrically for 1:1 complexes in methanol in constant ionic strength (I = 0.1 mol dm⁻³ NaClO₄) and at 25 °C. The data refinement was carried out with the SQUAD program. The trend of formation constants of H_2L^1 with M(II) follows the order: Mn(II) (3.97) < Zn(II) (4.30) < Co(II) (4.89) < Cu(II) (5.73)

Also, the trend of formation constants of ligand toward a given metal (for example Mn) is as follows:

 H_2L^1 (p-OMe) (3.97) > H_2L^2 (p-H) (3.65) > H_2L^3 (p-Br) (3.37) > H_2L^4 (p-NO₂) (3.04)

Keywords: Schiff base • Formation constant • Transition metals

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1. Introduction

Schiff bases are very important tools for the inorganic chemists as these are widely used in designing molecular ferromagnets [1,2], in catalysis [3,4], in biological modeling applications [5,6], and as liquid crystals [7,8]. Schiff base complexes are once again topical in connection with self-assembling cluster complexes [9-15]. Schiff base complexes are known to be biologically important and serve as catalysts in various chemical and photochemical reactions [16-20].

In view of recent interest in the energetic of the metal ligand bonding in metal chelates involving N, O donor ligand, we tried to study Schiff base complexes derived from N,N'-bridged tetradentate ligands involving N_2O_2 donor atoms [21-28]. There are some title Schiff

bases and Cu(II) and Mn(III) complexes, which were previously synthesized [29-33] but comprehensive studies on complexation not achieved. The present report describes the synthesis and characterization of four Schiff bases and their complexation by Mn(II), Co(II), Cu(II) and Zn(II) metals. These compounds were characterized by elemental analysis, FT–IR, ¹H NMR, Mass and UV-Vis techniques. The effect of the nature of the equatorial substituents on the ligand upon the UV-Vis bands was studied. Also, the thermodynamic studies of complex formation of the ligands with the metals were described.

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Scheme 1. Schematic representation of the ligands and labels.

2. Experimental Procedure

2.1. Reagents

2.2. Physical measurements

The electronic absorption spectra were recorded using a Perkin-Elmer Lambda 2 spectrophotometer, while IR spectra were recorded by Shimadzu FTIR–8300 infrared spectrophotometer. The NMR spectra were recorded on a Bruker Avance DPX–250 spectrometer in CDCl₃ or DMSO– d_6 solvent using TMS as an internal standard at 250 MHz. The mass spectra were obtained on a Perkin-Elmer R MU–6E instrument (electron ionization mode-70 electron volt). The elemental analysis was carried out by Thermo Finnigan-Flash-1200.

2.3. Synthesis of the ligand

2-aminobenzylamine (1.0 mmol) in methanol (20 mL) was added drop-wise with continuous stirring to a warm methanolic solution of appropriate salicylaldehyde (2.0 mmol). After a few minutes, microcrystalline solids appeared, which were subsequently isolated *via* filtration. The isolated precipitates were washed with small amounts of cold methanol and dried in vacuum oven (Scheme 1).

2.4. Synthesis of the complexes

The manganese(II) and cobalt(II) complexes were prepared under ambient conditions. To a hot solution of the ligands (1.0 mmol) in appropriate solvent (for H_2L^1 , H_2L^2 and H_2L^3 chloroform and for H_2L^4 in CH_3OH 10 mL: DMF 10 mL) a hot methanolic solution of M(OAc)₂ (1.0 mmol, M = Mn, Co, Cu and Zn) was added dropwise. The reaction mixture was refluxed for 2h. The colored solution was cooled and evaporated to yield colored powders or crystals. The products were washed with water and methanol and dried under vacuum.

*H*₂*L*¹: ¹H NMR (250 MHz, CDCl₃, 25°C): δ = 12.78 (s, 1H, OH'), 12.64 (s, 1H, OH), 8.52 (s, 1H, N=CH⁷), 8.42 (s, 1H, N=CH⁷), 7.41 (dd, 7.4 and 1.6 Hz, 1H, H¹⁰), 7.38 (d, 1.6 Hz, 1H, H¹¹), 7.35 (d, 1H, 1.5 Hz, H⁸), 7.31 (dd, 7.4 and 1.5 Hz, 1H, H¹¹), 7.01 (s, 2H, H^{6,6'}), 6.88 (d, 2.5 Hz, 2H, H^{4,4'}), 6.68 (d, 2.5 Hz, 2H, H^{3,3}), 4.94 (s, 2H, CH₂), 3.83 (s, 3H, OCH₃'), 3.73 (s, 3H, OCH₃) ppm.

*H*₂*L*²: ¹H NMR (250 MHz, CDCl₃, 25°C): δ = 13.32 (s, 1H, OH'), 13.11 (s, 1H, OH), 8.56 (s, 1H, N=CH⁷), 8.47 (s, 1H, N=CH⁷), 7.41 (t, 7.6 Hz, 1H, H¹⁰), 7.38 (d, 7.6 Hz, 1H, H¹¹), 7.30 (t, 7.6 Hz, 1H, H⁹), 7.20 (d, 7.6 Hz, 1H, H⁸), 7.15 (d, 7.5 Hz, 2H, H^{6.6'}), 7.06 (d, 7.5 Hz, 2H, H^{3.3'}), 6.96 (t, 7.5 Hz, 2H, H^{4.4'}), 6.85 (t, 7.5 Hz, 2H, H^{5.5'}), 4.96 (s, 2H, CH₂) ppm.

*H*₂*L*³: ¹H NMR (250 MHz, CDCl₃, 25°C): δ = 13.23 (s, 1H, OH'), 13.04 (s, 1H, OH), 8.50 (s, 1H, N=CH⁷), 8.36 (s, 1H, N=CH⁷), 7.50 (s, 2H, H^{6,6'}), 7.40 (d, 6.9 Hz, 1H, H¹¹), 7.34–7.26 (m, 2H, H⁹, H¹⁰), 7.13 (d, 7.2 Hz, 1H, H⁸), 6.95 (d, 8.6 Hz, 2H, H^{4,4}), 6.82 (d, 8.6 Hz, 2H, H^{3,3'}), 4.94 (s, 2H, CH₂) ppm.

*H*₂*L*⁴: ¹H NMR (250 MHz, DMSO–*d*₆, 25°C): δ = 14.40 (s, 1H, OH'), 14.00 (s, 1H, OH), 8.98 (s, 1H, N=CH⁷), 8.82 (s, 1H, N=CH⁷), 8.35–8.19 (m, 2H, H^{10,11}), 8.03 (dd, 9.5 and 3.0 Hz, 2H, H^{4,4}), 7.45 (s, 2H, H^{6,6'}), 7.39–7.35 (m, 1H, H⁹), 7.09 (d, 9.2 Hz, 1H, H⁸), 6.66 (d, 9.5 Hz, 2H, H^{3,3'}), 5.02 (s, 2H, CH₂) ppm.

ZnL¹: ¹H NMR (250 MHz, DMSO– d_6 , 25°C): δ = 8.46 (s, 1H, N=CH⁷), 8.39 (s, 1H, N=CH⁷), 7.38 (t, 8.1 Hz, 1H, H¹⁰), 7.28–7.18 (m, 1H, H⁹), 7.02–6.82 (m, 2H, H^{8.11}), 6.69 (s, 2H, H^{6.6}), 6.60 (d, 9.2 Hz, 2H, H^{4.4}), 6.51 (d, 9.2 Hz, 2H, H^{3.3}), 4.66 (s, 2H, CH₂), 3.66 (s, 3H, OCH₃), 3.63 (s, 3H, OCH₃) ppm.

ZnL²: ¹H NMR (250 MHz, DMSO– d_6 , 25°C): δ = 8.50 (s, 1H, N=CH⁷), 8.43 (s, 1H, N=CH⁷), 7.79 (d, 7.6 Hz, 1H, H¹¹), 7.42–7.11 (m, 3H, H⁸, H⁹, H¹⁰), 6.96 (d, 6.9 Hz, 2H, H^{6.6}), 6.62 (d, 6.9 Hz, 2H, H^{3.3}), 6.51 (t, 6.9 Hz, 2H, H^{4.4}), 6.41 (t, 6.9 Hz, 2H, H^{5.5}), 4.70 (s, 2H, CH₂) ppm.

ZnL³: ¹H NMR (250 MHz, DMSO– d_6 , 25°C): δ = 8.49 (s, 1H, N=CH⁷), 8.43 (s, 1H, N=CH⁷), 7.56 (s, 2H, H^{6,6°}), 7.45–7.19 (m, 4H, H⁸, H⁹, H¹⁰, H¹¹), 6.61 (d, 9.1 Hz, 2H, H^{4,4°}), 6.53 (d, 9.1 Hz, 2H, H^{3,3°}), 4.68 (s, 2H, CH₂) ppm.



Figure 1. Spectrophotometric titration of H_2L^2 (5.0×10⁻⁵ mol dm⁻³) with various amounts of $Zn(OAc)_2$ H_2O (5×10⁻⁶ -1×10^{-4} mol dm⁻³) in methanol, at I = 0.10 mol dm-3 (NaClO₄) and at 25°C.

ZnL⁴: ¹H NMR (250 MHz, DMSO– d_6 , 25°C): δ = 8.73 (s, 1H, N=CH⁷), 8.68 (s, 1H, N=CH⁷), 8.09–7.98 (m, 2H, H^{10,11}), 7.93 (s, 2H, H^{6,6}), 7.50–7.28 (m, 2H, H^{8,9}), 6.75 (d, 9.5 Hz, 2H, H^{4,4}), 6.66 (d, 9.5 Hz, 2H, H^{3,3}), 4.78 (s, 2H, CH₂) ppm.

2.5. Equilibrium measurements

Complexes were obtained from the reaction of the metals with the Schiff base donors according to Eq. 1

 $H_2L^x + M(OAc)_2$ [ML^x] + 2HOAc (1) The formation constant measurements were carried

out by spectrophotometric titrations of the ligands with various concentrations of the metal ion at constant ionic strength (0.10 mol dm⁻³ NaClO₄) and at $25.0(\pm 0.1)^{\circ}$ C. The interaction of NaClO₄ with the ligands and metals in methanol was negligible. In a typical measurement, 3 mL solution of ligand (5×10⁻⁵ mol dm⁻³) in methanol was titrated with methanolic solution of M(OAc), (5×10⁻⁶ -1×10⁻⁴ mol dm⁻³). The metal concentrations were varied till 2.0 fold in excess. UV-vis spectra were recorded in the range 300-500 nm about 5 min after each addition. The absorption measurements were monitored at various wavelengths in the 350-410 nm regions where the difference in absorption between the ligands and the product was the largest after the equilibrium was attained. As an example, the variation of the electronic spectra for [H₂L²] titrated with various concentrations of Zn(II) acetate at 25°C in MeOH is shown in Fig. 1. The same procedure was followed for other systems.

3. Results and Discussion

The analytical and physical data for the complexes are given in Table 1. The analytical data show that the metal complexes involve 1:1 metal to ligand ratio and the complexes are also associated with one or two molecules of water or methanol.

Table 1. Characteristic and analytical data of Schiff bases and their complexes.

	Color	M.P(°C)	Yield		Found (Calcd.)	
				С	н	Ν
H ₂ L ¹	Orange	116	94	70.47 (70.75)	5.74 (5.68)	7.17 (6.92)
H_2L^2	Yellow	107	89	76.16 (76.34)	5.45 (5.49)	8.43 (8.48)
H_2L^3	Yellow	146	100	51.68 (51.67)	3.20 (3.30)	6.02 (5.74)
H_2L^4	Yellow	247	83	59.67 (60.00)	3.88 (3.84)	13.44 (13.33)
MnL1•2CH ₃ OH	Brown	113	71	58.92 (59.17)	5.78 (5.56)	5.18 (5.52)
MnL ² • 2H ₂ O	Green	162	89	59.77 (60.15)	4.78 (4.81)	6.63 (6.68)
MnL ³ •2H ₂ O	Green	155	77	43.34 (43.70)	2.91 (3.14)	4.59 (4.85)
$MnL^4 \bullet H_2O$	Brown	>250	89	51.54 (51.34)	3.29 (3.28)	11.14 (11.40)
CoL1•H ₂ O	Brown	168	58	59.49 (59.36)	4.50 (4.76)	6.39 (6.02)
CoL ² •2H ₂ O	Green	172	72	59.22 (59.58)	4.47 (4.76)	6.49 (6.62)
CoL ³ •H ₂ O	Brown	>250	51	44.43 (44.79)	2.66 (2.86)	5.25 (4.97)
CoL ⁴ •2H ₂ O	Brown	>250	47	48.79 (49.14)	3.92 (3.53)	10.87 (10.91)
$CuL^1 \bullet H_2O$	Brown	>250	87	58.43 (58.78)	4.47 (4.72)	5.62 (5.96)
$CuL^2 \bullet H_2O$	Green	>250	90	61.45 (61.53)	4.13 (4.43)	6.53 (6.83)
CuL ³ •CH ₃ OH	Green	>250	68	45.59 (45.42)	2.78 (3.12)	5.11 (4.82)
$CuL^4 \bullet 0.5 H_2O$	Green	>250	97	51.73 (51.38)	3.04 (3.08)	11.35 (11.41)
$ZnL^1 \bullet CH_3OH$	Yellow	280	58	59.36 (59.33)	4.66 (4.98)	6.01 (5.77)
$ZnL^2 \bullet 2H_2O$	Yellow	>250	42	58.97 (58.69)	4.48 (4.69)	6.71 (6.52)
ZnL³•2H ₂ O	Yellow	>250	44	43.22 (42.93)	2.88 (3.09)	4.39 (4.77)
ZnL4•2CH ₃ OH	Yellow	>250	50	50.20 (50.43)	3.98 (4.05)	10.23 (10.23)

	<i>m</i> /e
H_2L^1	390, 240, 196, 168, 151, 123, 91, 57
H_2L^2	330, 313, 210, 137, 180, 118, 91, 69
H_2L^3	488, 289, 209, 180, 152, 118, 91, 57
H_2L^4	420, 403, 396, 314, 255, 209, 180, 152, 118, 91, 57
MnL ¹	443, 430, 256, 237, 213, 185, 167, 149, 111, 85, 57
MnL ²	383, 222, 194, 167, 149, 129, 97, 71, 55
MnL ³	541, 368, 313, 240, 180, 135, 97, 57
MnL ⁴	473, 237, 126, 97, 73, 57
CoL ¹	446, 208, 148, 121, 97, 71, 55
CoL ²	387, 328, 266, 250, 209, 180, 152, 121, 91, 51
CoL ³	545, 289, 180, 91
CoL ⁴	477, 237, 192, 166, 129, 91, 71, 55
CuL ¹	451, 388, 314, 239, 196, 168, 151, 111, 83, 57
CuL ²	391, 240, 210, 180, 149, 133, 113, 97, 71, 55
CuL ³	550, 213, 149, 98, 64
CuL ⁴	482, 133, 98, 80, 64
ZnL ¹	453, 437, 391, 239, 151, 106, 83, 57
ZnL ²	394, 368, 314, 283, 236, 211, 195, 166, 118, 97, 79, 52
ZnL³	552, 369, 313, 236, 152, 118, 57
ZnL⁴	482, 452, 436, 267, 207, 166, 129, 107, 91, 55

Table 2. Mass spectral data of the Schiff bases and their complexes.

3.1.¹H NMR spectra

In the ¹H NMR spectra of the ligands, the phenolic proton was seen at 12–15 ppm. These high frequency orthophenolic hydrogens in all Schiff base are attributed to the presence of intramolecular hydrogen bonding. The ¹H NMR of the ligands provides compelling evidence of the presence of two azomethine groups. Due to different chemical environments two signals were recorded for azomethine proton. The phenol ring proton signals resolve in the range 6–8 ppm and CH₂ proton was seen at 4.5–5.0 ppm. A singlet was seen at 3.60–3.90 ppm that was assigned to those Schiff bases and their complexes that have OMe group.

By comparing the ¹H NMR spectra of the Schiff base ligands to those of the corresponding zinc complexes, it is noted that there is an upfield shift in the frequency of azomethine protons confirming coordination of the metal ion to both groups. In all the complexes, no signal is recorded for the phenolic hydrogen in the 12–15 ppm region, as in the case of the Schiff base indicating deprotonation of the orthohydroxyl group [34,35].

3.2. Mass spectra

The mass spectra of all compounds show an intense molecular ion peak $[ML^x]^+$ (Table 2).





3.3. Electronic spectra

With aim to obtain information about the type of the electronic transition and interaction liable to exist in solutions, the electronic spectra of ligand and their complexes were measured in DMF solvent (Fig. 2).

Generally, the recorded spectra of ligands displayed two main absorption bands (Table 3). The first band was observed in the 260–262 nm range as a broad and/or a shoulder band. This band can be ascribed to the π – π * transitions of the benzenoid system of the compounds strongly overlapped with n– π * electronic transition that involves the nonbonding electrons of the azomethine nitrogen atom. A similar assignment was described by Jaffe *et al.* [36].

The longer wavelength band(s) in the recorded spectra of the ligands observed in the range 316–355 nm can be ascribed to the transition within the whole molecule essentially as intramolecular charge transfer (CT) interaction. The CT bands seem to originate from the aryl moiety, whereas, the positive charge azomethine carbon atom is the acceptor center.

Generally, it is evident that addition of a metal ion to the ligand solution causes distinguishable changes in the visible absorption spectra of the ligand. This behavior suggests an instantaneous complex formation in solution from the reaction of each of the ligands under investigation with each of the used metal ions.

Bands due to the $n-\pi^*$ transition of the C=N chromophores occur between 260–262 nm as ligands shifts to lower energy upon complexation [37]. In the ultraviolet region, the bands observed in the range 267–299 nm in spectra of metal complexes can be ascribed to an intraligand electronic transition, because bands in these regions are sensitive enough to the type of metal ion used.

The longer wavelength band(s) of each free ligand at 316–355 nm has acquired a red shift on complex

	$\pi \rightarrow \pi^{*}$ (benzene ring and C=N)	Intramolecular CT transition	Charge Transfer
	λ _{max} /nm (ε / M ⁻¹ cm ⁻¹)	λ _{max} /nm (ε / M ⁻¹ cm ⁻¹)	λ _{max} /nm (ε / M ⁻¹ cm ⁻¹)
H_2L^1	262 (21250) ^{sh}	355 (12802)	
H_2L^2	260 (29730)	327 (17533)	
H_2L^3	261 (29834) ^{sh}	325 (17777)	
H_2L^4	261 (25114)	316 (22730)	
MnL ¹	268 (18673)		331 (8888) ^{sh} 440 (4346)
MnL ²	267 (18916)		320 (11783) ^{sh} 412 (4593)
MnL³	267 (16537)		326 (7518) ^{sh} 410 (3376) ^{sh}
MnL ⁴	267 (17890)		394 (33807)
CoL ¹	287 (10353)		425 (3187)
CoL ²	284 (18184)		396 (5236)
CoL ³	285 (11350)		390 (5502)
CoL ⁴	299 (5258)		381 (11242)
CuL ¹	268 (22199)		420 (9961) 458 (7135) ^{sh}
CuL ²	270 (25985)		380 (12902) 412 (10543) ^{sh}
CuL ³	268 (23827)		388 (8901) 420 (7311) ^{sh}
CuL ⁴	272 (6632)		378 (7822)
ZnL ¹	269 (10641)		404 (7171)
ZnL ²	273 (9453)		378 (7314)
ZnL ³	286 (9924) ^{sh}		377 (12338)
ZnL ⁴	267 (16545)		375 (35071)
sh shou	Ilder		

Table 3. Electronic spectra data of Schiff bases and their complexes in DMF solvent.

formation with the metal ion. A new band was observed at longer wavelengths (in the range of 370–460 nm) in case of the complex solution. This behavior can be explained as follows.

The longer wavelength band observed in the spectrum of the free ligands can be assigned to an intramolecular CT transition liable to take place within the solute molecule. Thus the red shift observed in the λ_{max} of this band on complex formation with the divalent transition metal ions Mn(II), Co(II), Cu(II) and Zn(II) can be interpreted based on the principle of an expected easier CT transition within the complexed Schiff bases rather than within the free ones. This is due to the positive charge of the coordinating metal ions. On the other hand, these bands strongly overlap with an intermolecular transition from the ligands molecules to the vacant orbitals localized on the coordinated metal ions, *i.e.*, LMCT.

3.4. IR spectra

To reach a conclusive idea about the structure of the metal chelates with the ligands studied, infrared spectra of the free ligands and their complexes were recorded. The IR spectra of the free ligands and the complexes exhibit various bands in the 400–4000 cm⁻¹ regions. Important IR absorption frequencies of ligands and their complexes along with their assignments are listed in Table 4. The IR spectra of complexes exhibit absorption around 3400 cm⁻¹ that is attributed to the presence of lattice and coordinated water [38]. The weak bands at 2800–3100 cm⁻¹ are related to C–H vibrations.

A strong band in the region 1610–1635 cm⁻¹ is observed in the IR spectra of all ligands, which may be assigned to the stretching vibration of the azomethine group [39]. Generally these bands shifted to lower frequencies on complexation. Thus, it suggests that coordination of each of the ligands under investigation with the metal ions studied takes place through the nitrogen azomethine. However, the shift of these bands

	υ _{ο-н}	υ _{с-н}	υ _{c=N}	υ _{c=c}	υ c-o	υ _{M-N}	υ _{м-0}
H ₂ L ¹	3425	3009 2835	1635 1609	1566 1489	1161		
H_2L^2	3445	3055 2881	1632 1612	1566 1481	1149		
H_2L^3	3414	3067 2912	1635 1616	1562 1473	1176		
H_2L^4	3425	3055 2920	1620 1610	1578 1485	1176		
MnL ¹	3421	3032 2854	1620 1608	1543 1465	1161	771	675
MnL ²	3445	3046 2854	1623 1608	1539 1446	1141	763	621
MnL ³	3433	3056 2920	1620 1605	1527 1454	1172	756	648
MnL ⁴	3441	3065 2932	1620 1608	1554 1466	1099	752	650
CoL ¹	3441	3024 2854	1620 1608	1535 1466	1157	752	678
CoL ²	3437	3055 2931	1612 1608	1535 1450	1153	756	617
CoL ³	3441	3032 2851	1620 1608	1520 1454	1165	756	636
CoL ⁴	3441	3044 2920	1613 1608	1551 1470	1099	756	644
CuL ¹	3441	3065 2920	1631 1608	1531 1466	1034	783	667
CuL ²	3441	3035 2920	1623 1608	1531 1443	1145	756	602
CuL³	3441	3024 2854	1627 1608	1515 1454	1168	768	636
CuL ⁴	3441	3074 2932	1612 1601	1551 1462	1107	756	652
ZnL ¹	3433	3032 2843	1623 1608	1542 1473	1157	794	671
ZnL ²	3425	3036 2920	1630 1610	1531 1446	1149	756	698
ZnL³	3425	3065 2920	1630 1610	1524 1454	1169	756	636
ZnL ⁴	3433	3054 2920	1620 1601	1551 1481	1103	756	640

to lower frequencies reveals that the bond order of the -C=N- linkage is lowered upon their coordination to metal ion.

The two bands appeared in the IR spectra of the free ligands and the corresponding metal chelates in the regions $1520-1580 \text{ cm}^{-1}$ and $1445-1485 \text{ cm}^{-1}$ are assigned to C=C stretching vibrations of the aromatic systems. The observed shifts to lower frequencies may be due to the involvement of C=C band in some mesomeric interaction upon the formation of chelate rings.

Furthermore, the phenolic C–O stretching vibrations appeared at 1145–1175 cm⁻¹ in the spectra of the ligands and was found to have an appreciable shift to

lower frequency in the IR spectra of the corresponding metal chelates confirming its coordination to the metal ion [40-42]

The coordination mode of ligands is further supported by the new frequencies occurring in the 600-795 cm⁻¹ range and which have been assigned to M–O and M–N, respectively [43].

	Mn	Zn	Co	Cu
H ₂ L ¹	3.97 (± 0.04)	4.30 (± 0.01)	4.89 (± 0.03)	5.73 (± 0.10)
H_2L^2	3.65 (± 0.03)	3.90 (± 0.03)	4.36 (± 0.02)	5.54 (± 0.03)
H_2L^3	3.37 (± 0.04)	3.54 (± 0.02)	3.79 (± 0.02)	5.10 (± 0.02)
H_2L^4	3.04 (± 0.07)	3.34 (± 0.02)	3.67 (± 0.13)	4.88 (± 0.07)

Table 5. The formation constants, log K, for the complexes of ligands with M(II), in methanol at 25°C (I = 0.10 mol dm⁻³).

Table 6. The free energy, ΔG°, for the complexes of ligands with M(II), in methanol at 25°C (I = 0.10 mol dm⁻³).

	Mn	Zn	Co	Cu
H ₂ L ¹	-22.65 (± 0.10)	-24.52 (± 0.03)	-27.90 (± 0.07)	-32.70 (± 0.25)
H_2L^2	-20.82 (± 0.07)	-22.24 (± 0.07)	-24.88 (± 0.05)	-31.60 (± 0.07)
H_2L^3	-19.22 (± 0.10)	-20.19 (± 0.05)	-21.62 (± 0.05)	-29.09 (± 0.05)
H_2L^4	-17.33 (± 0.17)	-19.05 (± 0.05)	-20.93 (± 0.32)	-27.83 (± 0.17)

3.5. The formation constant and the thermodynamic free energy calculations

The formation constant of the various Schiff bases with the metal ions were calculated using SQUAD program [44,45], designed to calculate the best value for the formation constant of the proposed equation model (Eq. 1) by employing a non-linear, least-squares approach. Also the free energy change ΔG° of the complexes formed were calculated from $\Delta G^{\circ} = -RT \ln K$ at 25°C.

3.6. Metal effect

The formation constant and the free energy parameter for the metal-ligand complexes are presented in Tables 5 and 6. On the basis of the results, the formation of the complexes follows the sequence below:

Mn(II) < Zn(II) < Co(II) < Cu(II)

This is in agreement with the general order of the stability of the complexes of these metal ions which has been reported before [46]. The electronegativity (Pauling Scale) of the transition metals selected, 1.55, 1.88, 1.90 and 1.65 for manganese, cobalt, copper and zinc respectively, helps us to interpret the above trend in the formation of complexes. The above trend also is confirmed by considering the M(II)-O and M(II)-N bond distances [47,48]. Mean metal ligand bond distances for isothiocyanate, pyridine, imidazole, water, and chloride, bound to Mn, Co, Cu and Zn in their +2 oxidation states have been investigated by See et al. [47], and were as follows: Mn > Zn > Co ≈ Cu. The order of bond distances is in agreement with the electronegativity order. The more electronegative the metal is, the more it withdraws electrons and therefore the formation constants are higher [49].

Moreover ligand fields have additional stabilization that confirms this trend. $Mn(II)-d^5$ and $Zn(II)-d^{10}$ have

no ligand field stabilization, but Co(II)-d⁷ and Cu(II)-d⁹ have additional ligand field stabilization energy due to Jahn-Teller effect. Also, Cu(II)-d⁹ has more Jahn-Teller effect than Co(II)-d⁷.

3.7. The electronic effect of para substituted Schiff base ligands

The stability of each metal complexed with the different ligands used decreases according to the sequence:

5-OMe > 5-H > 5- Br > 5- NO₂

This is somewhat in agreement with decreasing electron-releasing character of the substituents in the same direction, which results in a decrease in the basicity of the azomethine nitrogen and, the phenolic oxygen groups of the ligand and, consequently, the tendency toward complex formation is expected to decrease. For example, the 5-OMe substituted ligand has the tendency to act as a good σ -donor as a result of the high electron releasing power of the OMe groups in the para position in HL1 relative to that of the non-substituted HL2 and electron-withdrawing groups in para position HL³, HL⁴. The withdrawing functional groups makes the Schiff base a poor donor ligand and decreases the formation constants while the electron donor group increases the formation constants. Therefore, the ligands having Br and NO₂ groups have the smallest formation constant while the ligands with OMe group have the highest [50,51].

4. Conclusion

Using a tetradentate N_2O_2 Schiff base ligand system, we have succeeded in preparing four coordinate Mn(II), Co(II), Cu(II) and Zn(II) complexes containing 2-aminobenzylamine and substituted salicylaldehyde.

By considering the formation constants and the ΔG° of the complex formation for Schiff base as donor and

the M(II) as acceptor, the following conclusions were drawn:

1. The formation constant for a given Schiff bases (H_2L^1) changes according to the following trend:

Mn(II) (3.97) < Zn(II) (4.30) < Co(II) (4.89) < Cu(II) (5.73) 2. The formation constants for a given M(II) (Mn) acceptor toward the Schiff base donors changes according to the following trend:

5-OMe (3.97) > 5-H (3.65)> 5- Br (3.37)> 5- NO₂ (3.04)

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