

The Preparation and Characterization of Divalent Copper, Nickel, Cobalt and Manganese Complexes of Some Schiff Base Ligands

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ABSTRACT. Co(II), Mn(II), and Cu(II) Complexes of Schiff bases which are derived from the condensation of 3-amino-1,2,4-triazole and salicylaldehyde (L_1), p-hydroxy benzaldehyde (L_2) and vaniline (L_3), have been prepared and investigated by spectrophotometric, conductometric and analytical measurements. L_1 is coordinated through the iminic nitrogen and phenolic oxygen atoms. L_2 and L_3 are bonded through the imino nitrogen and one ring nitrogen atoms as bidentate ligands. Most of these complexes behave as a non-electrolyte while some as a 1:1 electrolyte. The structural configurations have been proposed by the corresponding electronic transition.

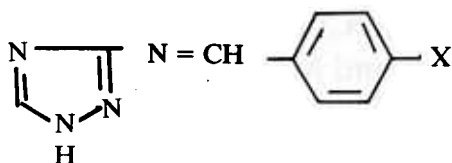
Introduction

Schiff bases are important ligands in chemistry, because of their biological aspects and their application in the field of colour photography^[1-3]. It was therefore of interest to try to study the complexing properties of the Schiff bases derived from 3-amino-1,2,4-triazole and salicylaldehyde (L_1); p-hydroxybenzaldehyde (L_2); and vaniline (L_3) with Co(II), Mn(II), Ni(II) and Cu(II). In the present paper we report on the preparation and characterization of these complexes. The composition and stability constants of chelates formed in solution as well as the proposed structures are elucidated from the spectral behaviour of the chelates.

Experimental

1 – Materials and Solutions

All the chemicals used were of analytical grade reagents. Schiff bases were prepared by condensation of equimolar quantities of the amine and the aldehydes in dry ethanol^[4]. The solid ligands obtained were recrystallized from ethanol. The elemental analysis confirmed the suggested structure of these compounds. The ligands prepared have the formula:



$x = o\text{-OH}$ (L_1); $p\text{-OH}$ (L_2) $P\text{-OH}$, $m\text{-OCH}_3$ (L_3).

Stock solutions (1×10^{-2} mol. dm^{-3}) of the ligands and the metal salts $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were prepared by dissolving accurately weighed amount of each in ethanol. The metal solutions are standardized by recommended methods of analysis^[5]. Solutions for absorbance and conductance measurements of the desired concentration were obtained by accurate dilution of the stock solutions with ethanol.

II. Synthesis of Solid Complexes

The solid complexes were prepared by mixing ethanolic solutions of calculated amounts of the ligand and metal salt. The resulting solution was refluxed for ≈ 1 hr. The solid complexes which precipitated were filtered off, washed with ethanol, recrystallized from ethanol and dried. Microanalysis of C, H and N was undertaken by the microanalytical unit, Cairo University (see Table 1).

The conductance values were measured at $25 \pm 0.1^\circ\text{C}$ with a WPA CM 25 conductivity meter. The electronic spectra in the UV and visible regions were recorded on a Shimadzu 240 spectrophotometer using 1 cm matched silica cells. The infrared spectra were recorded ($4000\text{-}200\text{ cm}^{-1}$) on a Perkin-Elmer 599 B spectrophotometer as KBr disks.

Results and Discussion

The formation of the complexes in ethanolic solution is established on the bases of the shifts in the absorption maxima of the ligands^[6].

The band of the free ligands at λ_{max} 335 (L_1), 330 (L_2) or 325 (L_3) nm is red shifted to 405-415 nm (L_1), 348-435 nm (L_2) and 365-375 nm (L_3) on complexation to the metals (Fig. 1). Due to the electron withdrawing character of 1,2,4-triazole ring^[7], it is suggested that, the free ligand is assigned to excitation of π -electrons of exocyclic and cyclic $\text{C} = \text{N}^{[3]}$ influenced by the intramolecular charge transfer (CT) originating

TABLE 1. Analytical data, % calculated (found), colour, decomposition temperature (°C) and molar conductivity, M ($\text{ohm}^{-1} \cdot \text{mole}^{-1} \cdot \text{cm}^2$) of the Schiff bases complexes ($L_1 - L_3$).

Complex	% C	% H	% N	Molar conductivity M	Colour	Decomposition temperature	% Cl
L₁ - Complexes							
[C ₉ H ₇ N ₄ O Mn Cl H ₂ O]	36.57 (36.09)	3.07 (3.20)	18.96 (18.72)	38.43	buff	> 320	11.16 (10.98)
[(C ₉ H ₇ N ₄ O) ₂ Co (H ₂ O) ₂]	46.06 (45.92)	3.86 (3.75)	23.87 (24.05)	50.63	blueish - violet	> 320	
[(C ₉ H ₇ N ₄ O) ₂ Ni (H ₂ O) ₂]	46.09 (45.81)	3.86 (3.95)	23.88 (23.72)	49.93	pale green	> 320	
[C ₉ H ₇ N ₄ O ₂ Cu (H ₂ O)]NO ₃	30.99 (30.49)	3.81 (3.22)	20.08 (20.18)	81.10	deep green	225	
L₂ - Complexes							
[C ₉ H ₈ N ₄ O Mn Cl ₂]	34.42 (34.09)	2.57 (2.68)	17.84 (17.52)	45.09	buff	> 320	22.59 (22.42)
[(C ₉ H ₈ N ₄ O) ₂ Mn Cl ₂]Cl	43.04 (42.83)	3.21 (3.31)	22.31 (22.52)	49.34	beige	> 320	14.11 (14.03)
[C ₉ H ₈ N ₄ O Co Cl H ₂ O]Cl	32.17 (32.29)	3.00 (2.88)	16.67 (16.89)	73.44	violet	> 320	20.98 (20.22)
[C ₉ H ₈ N ₄ O Ni Cl H ₂ O]Cl	32.19 (31.88)	3.00 (3.09)	16.68 (16.91)	69.05	greenish - yellow	> 320	20.99 (20.34)
[C ₉ H ₈ N ₄ O Cu NO ₃ (H ₂ O) NO ₃]	27.45 (27.52)	2.56 (2.62)	21.34 (21.00)	90.73	greenish - brown	225	
[(C ₉ H ₈ N ₄ O) ₂ Cu NO ₃ (H ₂ O)]NO ₃	37.15 (36.72)	3.11 (2.93)	24.06 (24.09)	97.62	pale brown	320	
L₃ - Complexes							
[C ₁₀ H ₁₀ N ₄ O ₂ Mn Cl ₂]	34.91 (34.43)	2.93 (2.78)	16.28 (16.51)	40.96	greenish - yellow	> 320	20.61 (20.27)
[(C ₁₀ H ₁₀ N ₄ O ₂) ₂ Co Cl (H ₂ O)]Cl	41.11 (40.98)	3.80 (3.62)	19.18 (19.03)	65.93	green	> 320	11.77 (11.24)
[(C ₁₀ H ₁₀ N ₄ O ₂) ₂ Ni Cl (H ₂ O)]Cl	41.13 (41.29)	3.80 (3.72)	19.19 (19.12)	65.90	pale green	> 320	11.78 (11.53)
[C ₁₀ H ₁₀ N ₄ O ₂ Cu NO ₃ (H ₂ O)]NO ₃	28.34 (28.83)	2.85 (3.12)	19.83 (19.99)	90.76	greenish - brown	> 320	

from the aryl moiety to the nitrogen hetero ring^[8]. Hence, the observed red shift which confirms the complex formation can be attributed to the expected easier (CT) in the complexed ligand as a result of the high positive charge of the coordinated metal ion which facilitates this transition.

The composition of the complexes formed in ethanolic solution between each of Co(II), Mn(II), Ni(II) and Cu(II) and Schiff bases $L_1 - L_3$, is determined by the spec-

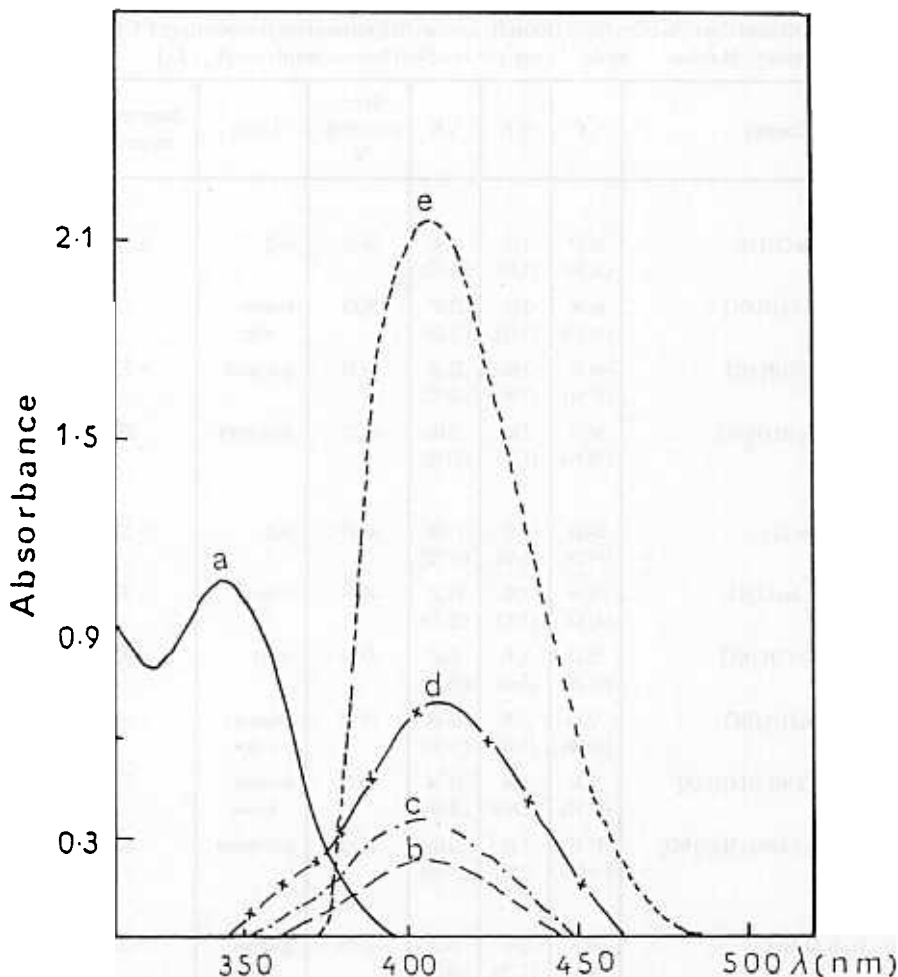


FIG. Spectra of 1×10^{-4} mol. dm^{-3} of L_1 (a), 1.2×10^{-3} mol. dm^{-3} of Li with 6×10^{-4} mol. dm^{-3} Mn(II) (b), Co(II) (c), Ni(II) (d) and Cu(II) (e).

trophotometric molar ratio and continuous variation method^[9] at λ_{max} of each complex (Fig. 2, 3).

The same concentration of the ligand as in the test solution is used as a blank in all the measurements. The results show that Co(II) and Ni(II) form 1:2 complex $[\text{M}(\text{II}) : \text{L}]$ with L_1 ; L_3 and 1:1 formation with L_2 . Mn(II) and Cu(II) form 1:1 and 1:2 complexes with L_2 , while 1:1 complex was formed with L_1 and L_3 .

The conductometric titration results of 25 ml of 1×10^{-3} mol. dm^{-3} metal ion solution against (1×10^{-2} mol. dm^{-3}) ligand solution (Fig. 4 as a representative example) are in accordance with the results obtained from the spectroscopic measurements.

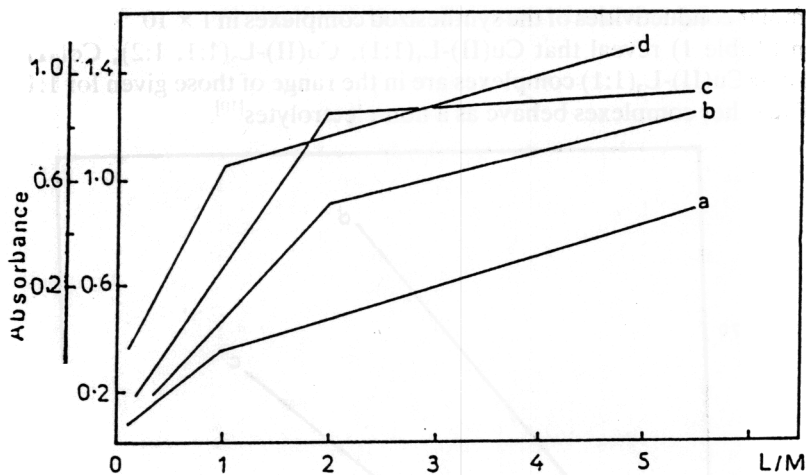


FIG. 2. Molar ratio method for $M-L_3$ chelates :

- a - Mn(II), $\lambda = 370$ nm, $Mn(II) = 1 \times 10^{-4}$ mol. dm^{-3}
- b - Co(II), $\lambda = 375$ nm, $Co(II) = 1 \times 10^{-4}$ mol. dm^{-3}
- c - Ni(II), $\lambda = 365$ nm, $Ni(II) = 1 \times 10^{-4}$ mol. dm^{-3}
- d - Cu(II), $\lambda = 368$ nm, $Cu(II) = 1 \times 10^{-4}$ mol. dm^{-3}

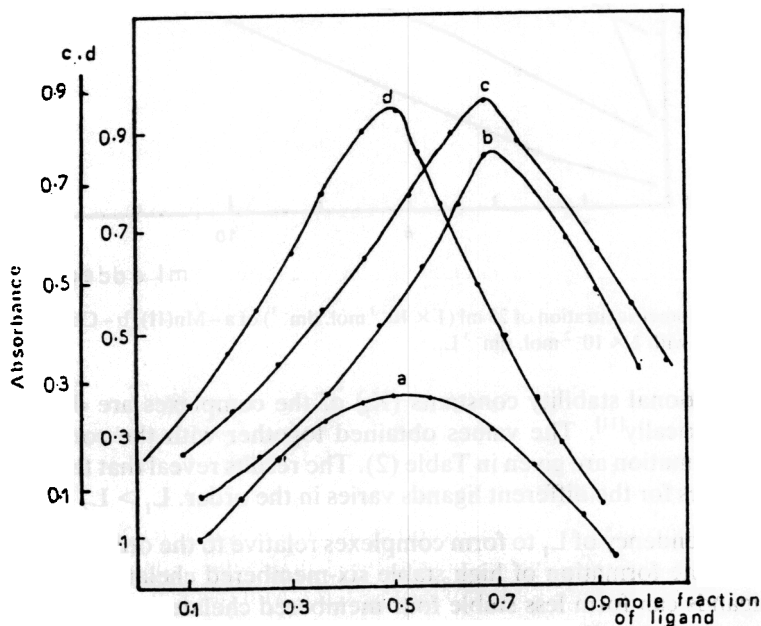


FIG. 3. Job's continuous variation method for $M-L_3$ chelates :

- a - Mn(II), $\lambda = 370$ nm, total concentration = 2×10^{-4} mol. dm^{-3}
- b - Co(II), $\lambda = 375$ nm, total concentration = 1×10^{-4} mol. dm^{-3}
- c - Ni(II), $\lambda = 365$ nm, total concentration = 1×10^{-4} mol. dm^{-3}
- d - Cu(II), $\lambda = 368$ nm, total concentration = 2×10^{-4} mol. dm^{-3}

The molar conductivities of the synthesized complexes in 1×10^{-3} mol. dm^{-3} DMF solution (Table 1) reveal that Cu(II)-L₁(1:1), Cu(II)-L₂(1:1, 1:2); Co(II), Ni(II)-L₃(1:2) and Cu(II)-L₃(1:1) complexes are in the range of those given for 1:1 electrolytes. The other complexes behave as a non-electrolytes^[10].

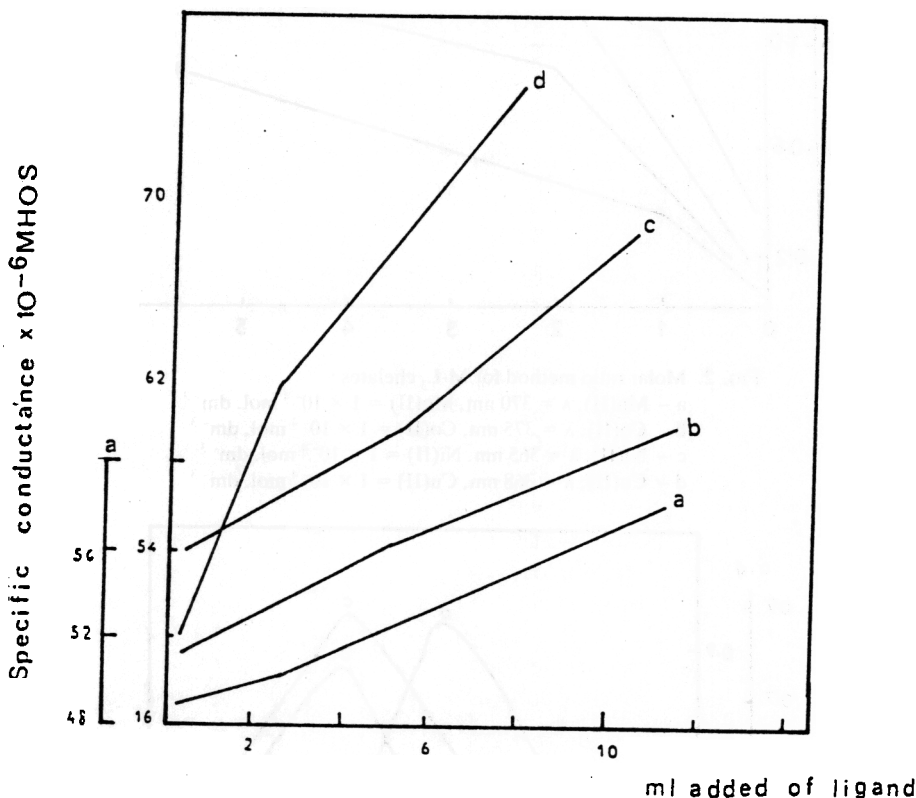


FIG. 4. Conductometric titration of 25 ml (1×10^{-3} mol. dm^{-3}) of a - Mn(II), b - Co(II), c - Ni(II) and d - Cu(II) with 1×10^{-2} mol. dm^{-3} L₁.

The conditional stability constants (K_f) of the complexes are determined spectrophotometrically^[11]. The values obtained together with the corresponding free energy of formation are given in Table (2). The results reveal that the stability of the metal chelates for the different ligands varies in the order. L₁ > L₂ > L₃.

The high tendency of L₁ to form complexes relative to the other ligands can be attributed to the formation of high stable six-membered chelate ring. On the other hand, ligands can form less stable four-membered chelate ring. Moreover, the results given in Table (2), show that the stability of the metal chelates for the same ligand are in agreement with the general order of stability of these metal ion complexes^[12]. Comparison of the principal ir bands of the free ligands with their metal complexes Table (3), show the following :

TABLE 2. The stability constants (K_F , $L \text{ mol}^{-1}$) and energy of formation ($-\Delta G$, $K \text{ cal mol}^{-1}$) for Cu(II), Ni(II), Co(II) and Mn(II) - Schiff base complexes.

Metal ion	M:L ratio	L_1		L_2		L_3	
		K_F	ΔG	K_F	ΔG	K_F	ΔG
Cu(II)	1:1	9.92×10^6	9.60	4.44×10^6	9.12	2.43×10^6	3.76
	1:2	-	-	2.65×10^{11}	15.67	-	-
Ni(II)	1:1	-	-	1.66×10^6	8.54	-	-
	1:2	9.89×10^{12}	17.83	-	-	4.26×10^{11}	15.94
Co(II)	1:1	-	-	6.65×10^5	7.99	-	-
	1:2	5.60×10^{12}	17.50	-	-	1.88×10^{11}	15.47
Mn(II)	1:1	2.59×10^6	8.80	-	-	1.10×10^6	8.29
	1:2	-	-	-	-	-	-

L_1 (x = o-OH), L_2 (x = p-OH) and L_3 (x = p-OH, m-OCH₃)

(1) The free ligand L_1 shows a broad band at 3050 cm^{-1} which is assigned to the intramolecular hydrogen bonded $\nu_{\text{O-H}}$ stretching. The disappearance of this band in the ir spectra of L_1 complexes indicates that the o-OH group is taking part in complexation. This is supported by the lowering of the phenolic $\nu_{\text{C-O}}$ stretching of L_1 on complexation. The band observed at 3200 cm^{-1} in the spectra of ligands L_2 and L_3 can be ascribed to the ν_{OH} stretching of p-OH group of the aldehydic moiety. The presence of broad band in the ir spectra of all complexes in the region $3350\text{-}3500 \text{ cm}^{-1}$, except of Mn(II) with L_2 & L_3 , suggests the presence of coordinated water molecules^[13]. On the other hand, the phenolic $\nu_{\text{C-O}}$ stretching of the ligands L_2 and L_3 does not show a marked shift on complexation, a result which excludes a coordination through the oxygen atom of the p-OH group.

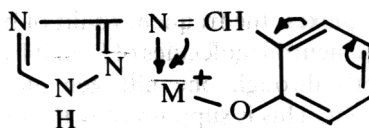
(2) The free ligands show two bands in the regions $1605\text{-}1615 \text{ cm}^{-1}$ and $1670\text{-}1672 \text{ cm}^{-1}$. Due to electron withdrawing character of the triazole ring^[7], the high frequency band can be assigned to the stretching vibration of the central azomethine $\nu_{\text{C=N}}$ and the lower frequency is due to the stretching of the ring $\nu_{\text{C=N}}$. Thus, in L_1 complexes, the ring $\nu_{\text{C=N}}$ does not show a marked shift while the central azomethine $\nu_{\text{C=N}}$ shows a blue shift. This suggests that L_1 is coordinated to the metal ion through the central azomethine nitrogen atom. This leads to electronic shifts from ring nitrogen atoms towards the azomethine nitrogen atom. On the other hand, for L_2 and L_3 complexes, the frequency shift of both ring $\nu_{\text{C=N}}$ and central $\nu_{\text{C=N}}$ suggests that the neutral molecules of L_2 and L_3 are coordinated to the metal ion as bidentate ligands through one nitrogen atom of triazole ring and the azomethine nitrogen atom. This is supported by the elemental analysis of the solid complexes formed (Table 1).

(3) New bands appear in the region $465\text{-}320 \text{ cm}^{-1}$ may be assigned to $\nu_{\text{M-N}} \leftarrow \text{N}^{[14,15]}$. Thus, according to the previously discussed results, the structural formula of 1:1 of M:L chelates are as follows :

TABLE 3. Infrared spectral band assignments (cm^{-1}) in the region 4000-200 cm^{-1} of Schiff base triazoles and their complexes.

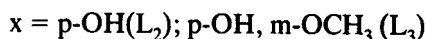
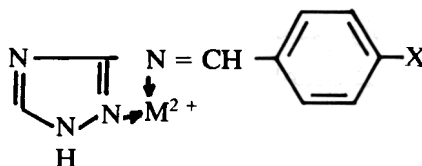
Compound	νOH	$\nu\text{C}=\text{N}$	$\nu\text{C}-\text{O}$	$\nu\text{M}-\text{N}$
L_1 (x = o-OH)	3050	1670 1601	1285	-
L_1 - Cu(II)	3300 (br)	1660	1270	460 (w)
L_1 - Ni(II)	3400 (br)	1660 1580 sh	-	359 (vs)
L_1 - Co(II)	3500 (br)	1675 1560		395 (m)
L_1 - Mn(II)	3460 (br)	1675	1270	392 (m)
L_2 (x = p-OH)	3200	1672 1615	1260 (s)	-
L_2 - Cu(II)	3350 (br)	1675 1610	1300 (w)	460
L_2 - Ni(II)	3400 (br)	1650 (br) 1600	1300 (m)	460
L_2 - Co(II)	3400 (br)	1655 1600	1300 (m)	460
L_2 - Mn(II)	3400	1675 (s) 1610	1300	460 (s)
L_3 (vanilin)	3200 (br)	1672 1605	1300	-
L_3 - Cu(II)	3400 (br, s)	1600 (s)	-	460
L_3 - Ni(II)	3400 (br)	1675 (br) 1610	1310 (s)	390
L_3 - Co(II)	3450 (br)	1680 1620	1300 (m)	395
L_3 - Mn(II)	3400	1675 1610 (s)	1310 (s)	465

br = broad, vs = very strong, w = weak, s = strong and m = medium.



I

$\text{M}-\text{L}_1$ (1:1)



The electronic spectra of the synthesized complexes in DMF are consistent with tetrahedral geometry for 1:1 complexes, but spectra of the 1:2 (M:L) complexes can be interpreted in terms of an octahedral geometry. The bands centered at about 16000 cm^{-1} in the spectra of 1:1 complexes are similar to those of other tetrahedral complexes. The spectra of 1:2 complexes show a strong band at around 27000 cm^{-1} consistent with octahedral geometry. The observed strong band in the region $30000\text{-}28570 \text{ cm}^{-1}$ in the spectra of all complexes are due to $\pi\text{-}\pi^*$ transition within the central C = N group.

References

- [1] Cohen, A.L. and Witkop, B., Umlagerungen in der chemie der Aminosäuren und peptide. *Angew. Chem.* **73**: 253 (1961).
- [2] Hubbard, P., *Proc. Natl. Phys. Lab.*, London (Symp, No. 8) **1**: 151 (1958).
- [3] Cordes, H.E. and Jencks, P.W., *Biochemistry* **1**: 773 (1972).
- [4] Mahmoud, R.M., Abdel-Hamid, R. and Abdel-Goad, F.A., Electronic Spectra and Acidity Constants of Hetero-Aromatic Schiff Bases Derived from 2-amino-5-phenyl-1,3,4-thiadiazole and various Aromatic Aldehydes, *Z. phys. Chemie, Leipzig* **262**(3), 551-560 (1981).
- [5] Scott, W. and Furman, H., *Standard Methods of Chemical Analysis*, 6th edition, Van Nostrand, New York (1962).
- [6] Person, B.W., A Criterion for Reliability of Formation Constants of Weak Complexes, *J. Am. Chem. Soc.* **87**: 167 (1965).
- [7] Elderfield, C.R., *Heterocyclic Compounds*, Wiley, New York (1961).
- [8] Yoe, H.J. and Jones, L.A., *Ind. Eng. Chem.*, (Anal. Edit.) **16**: 111 (1944).
- [9] Job, P., *Ann. Chem. Phys.* **9**: 113 (1928).
- [10] Geary, J.W., *Coord. Chem. Rev.* **7**: 81 (1971).
- [11] Issa, I.M., Issa, R.M. and Abdalla, S.M., Studies on Manganese (IV) Complexes with Tellurate I. Spectrophotometric study in strongly alkaline solutions, *Egypt, J. Chem.* **14**: 25 (1971).
- [12] Irving, H. and Williams, P.J.R., The Stability of Transition-metal Complexes, *J. Chem. Soc.*, 3192 (1953).
- [13] Theriot, J.L., Carlisle, O.G. and Hu, J.H., Oxovanadium (IV) Complexes of N-salicylidene Amino Acids with ANOMAIIOUS Magnetic Properties, *J. Inorg. Nucl. Chem.* **31**: 3303 (1969).
- [14] Fabrtti, A.G., Franchino, C.G. and Peyronel, G., Tin (IV) tetrahalide complexes of 2,5-disubstituted 1,3,4-thiadiazoles. *Spectrochimica Acta*, **36A**, 517-520 (1980).
- [15] Nakamot, K., *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York (1970).

تحضير وتشخيص متراكبات النحاس والنيكل والكوبلت والمنجنيز الثائية التكافؤ مع بعض قواعد شيف

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المستخلص . تم تحضير متراكبات الكوبلت والمنجنيز والنيكل والنحاس مع قاعدة شيف المشتقة من ٣ - أمين - ١،٢،٤ - ترايزول والساليسلدهيد (L_1) ، باراهيدروكسي بنزالدهيد (L_2) والفانيلين (L_3) ، وتمت دراسة المتراكبات باستعمال القياسات الطيفية والتوصيلية والتحليلية . وقد وجد أن (L_1) يرتبط بذرتي النيتروجين الأميني والأكسجين الفينيلي ، بينما (L_2) ، (L_3) ترتبط بذرة النيتروجين الأميني وأحد ذرات النيتروجين الحلقي كليجاندا ثنائي المخلب .

معظم هذه المتراكبات تسلك مسلك لا إلكتروليات بينما البعض يسلك مسلك إلكتروليت (١:١) .

هذا وبدراسة الانتقالات الإلكترونية أمكن اقتراح التركيب البنائي للمتراكبات