

Cu(II), Ni(II), Co(II) and Mn(II) Complexes of Arylidene-2-Amino-4-Methyl Pyrimidine

A. A. GAD, A. A. GABR* AND M. A. EL-TAHER

Department of Chemistry
Faculty of Science, Aswan, Egypt

A number of chelate complexes of Cu(II), Ni(II), Co(II) and Mn(II) with some heterocyclic Schiff bases derived from 2-amino-4-methyl pyrimidine and salicylaldehyde (L_1), *p*-hydroxy benzaldehyde (L_2) and vanillin (L_3) have been prepared. The stoichiometry and the structure of the complexes were studied using elemental analysis, conductivity measurements, electronic and i.r. spectra.

INTRODUCTION

The preparation of coordination compounds from heterocyclic Schiff bases with metal ions has drawn much attention due to its importance in biological, pharmacological and antileukemic areas.¹⁻⁴ The complexes of arylidene-2-amino-4-methyl-1,3-pyrimidine with Cu(II), Ni(II), Co(II) and Mn(II) were prepared in order to investigate the coordination behaviour of these ligands towards the divalent metal ions.

EXPERIMENTAL

All chemicals used in this study were of reagent grade. Arylidene-2-amino-4-methyl-1,3-pyrimidine, L_1 - L_3 were prepared according to the method described previously.³

The 1 : 1 and 1 : 2 ($M^{2+} : L$) chelates of Cu(II), Ni(II), Co(II) and Mn(II) were prepared by mixing the appropriate quantities of alcoholic solutions of metal salt and the ligand. The reaction mixture was then refluxed for *ca.* 2 hrs. The solid chelates which precipitated were filtered off, washed with ethanol and dried in vacuo over silica gel. The solid chelates obtained were analysed for their carbon, hydrogen and nitrogen contents.

Stock solutions (10^{-2} mol dm⁻³) of the ligands, Cu(NO₃)₂.6H₂O, NiCl₂.6H₂O, CoCl₂.6H₂O and MnCl₂.4H₂O were prepared by dissolving the requisite amount in pure ethanol solutions for electronic spectra and conductivity measurements of the desired concentrations were obtained by accurate dilution of the stock solution with ethanol. The absorption spectra of the metal chelates in solutions were determined on a Shimadzu-UV/Vis. 240 recording Spectrophotometer using 1 cm matched silica cells. The i.r. spectra were recorded on a Perkin-Elmer 599 B Spectrophotometer as the KBr pellets (4000-200 cm⁻¹). The conductance measurements were carried out on a WPA CM 25 conductivity meter at 25°C ± 0.1°C.

TABLE I

THE STABILITY CONSTANTS (K_f , L mole⁻¹) AND ENERGY OF FORMATION ($-\Delta G$, K. 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	—	—	2.07 × 10 ⁶	8.67	7.31 × 10 ⁶	9.42
	1 : 2	4.05 × 10 ¹¹	15.93	6.69 × 10 ⁹	13.49	3.54 × 10 ¹¹	15.85
Ni(II)	1 : 1	5.85 × 10 ⁶	9.29	1.64 × 10 ⁶	8.53	5.7 × 10 ⁶	9.27
	1 : 2	3.86 × 10 ¹⁰	14.53	5.07 × 10 ⁹	13.32	1.74 × 10 ¹⁰	14.06
Co(II)	1 : 1	1.80 × 10 ⁶	8.59	3.06 × 10 ⁵	7.53	1.64 × 10 ⁶	8.53
	1 : 2	9.72 × 10 ⁹	13.71	2.20 × 10 ⁹	12.82	6.94 × 10 ⁹	13.51
Mn(II)	1 : 1	8.99 × 10 ⁵	8.17	1.10 × 10 ⁵	6.92	3.06 × 10 ⁵	7.53
	1 : 2	5.07 × 10 ⁹	13.32	1.03 × 10 ⁶	11.00	1.69 × 10 ⁸	11.29

RESULTS AND DISCUSSION

Results of elemental analyses reveal that the reaction of the Schiff base (L₁) with Cu(NO₃)₂ gives compound of the stoichiometry M(L₁)₂.nH₂O while with NiCl₂, CoCl₂ and MnCl₂ give compounds of the stoichiometry (ML₁)X.nH₂O and M(L₁)₂.nH₂O where X = Cl⁻¹ and n = 1 and 2. The ligands L₂ and L₃ with all metals affords compounds of the type M(HL)(X + 1).nH₂O and M(HL)₂(X + 1).nH₂O where HL = neutral ligand, X = Cl⁻ or NO₃⁻ and n = 1, 2, 3 and 4.

Results of conductometric titration of 25 ml of 10 × 10⁻³ mol dm⁻³ metal ion solutions against (1 × 10⁻² mol dm⁻³) of each ligand solution support the stoichiometries suggested on the basis of elemental analysis.

The molar conductivities of the solid complexes in DMF indicate that the metal chelates of L₁ behave as nonelectrolytes except 1 : 1 (M : L₁), M = Ni(II) behaves as 1 : 1 electrolyte. Chelates of L₂ and L₃ behave as 1 : 1 electrolytes except in case of Co(II)-L₂, Co(II)-L₃ (1 : 1) and Mn(II)-L₃ (1 : 1) behave as nonelectrolytes, while those of Cu(II)-L₂ (1 : 1 and 1 : 2), Cu(II)-L₃ (1 : 2) and Ni(II)-L₃ (1 : 1 and 1 : 2) chelates behave as 1 : 2 electrolytes.⁵

The composition of the complexes in ethanolic solution have also been computed from spectrophotometric molar ratio and continuous variation methods^{6,7} at λ_{max} of each complex. In all measured solutions, the blank has been a solution of the ligand of the same concentration as in solution of the chelate. The representative results shown in figures 1 and 2 are in

good accordance with those obtained from the conductometric titration method.

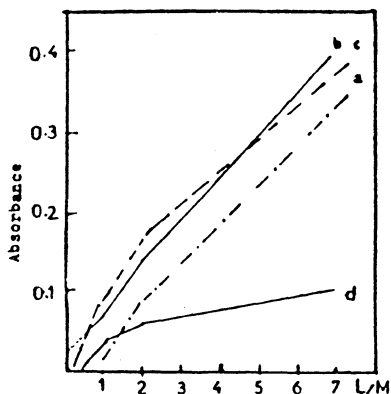


Fig. 1 Molar ratio method for M-L₁ chelates

- (a) Cu(II), $\lambda=395-400$ nm, Cu(II) = 2×10^{-4} mol dm⁻³
 (b) Ni(II), $\lambda=395-400$ nm, Ni(II) = 8×10^{-4} mol dm⁻³
 (c) Co(II), $\lambda=390$ nm, Co(II) = 4×10^{-4} mol dm⁻³
 (d) Mn(II), $\lambda=385$ nm, Mn(II) = 2×10^{-4} mol dm⁻³

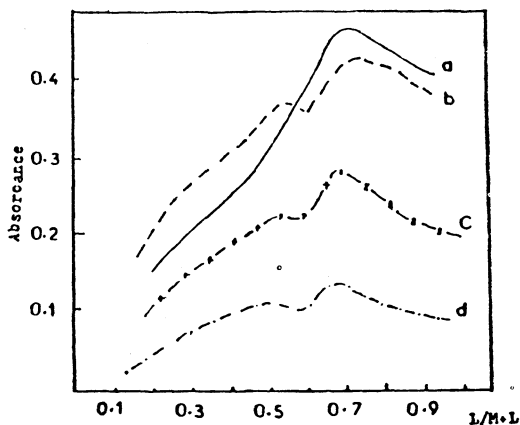


Fig. 2. Jobs continuous variation method for M-L₁ chelates

- (a) Cu(II), $\lambda=395-400$ nm, Total concn. = 2×10^{-3} mol dm⁻³
 (b) Ni(II), $\lambda=395-400$ nm, Total concn. = 2×10^{-3} mol dm⁻³
 (c) Co(II), $\lambda=390$ nm, Total concn. = 2×10^{-3} mol dm⁻³
 (d) Mn(II), $\lambda=385$ nm, Total concn. = 2×10^{-3} mol dm⁻³

The results of the spectrophotometric methods can be also utilized in calculating the apparent stability of the metal chelates⁸. Table 1 shows that the stability runs in the following order

$$L_1 > L_3 > L_2$$

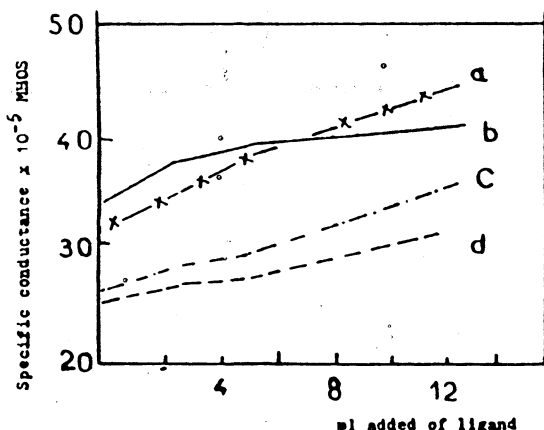


Fig. 3. Conductometric titration of 25 ml (1×10^{-3} mol dm^{-3}) (a) Cu(II), (b) Ni(II), (c) Co(II) and (d) Mn(II) with 1×10^{-2} mol dm^{-3} L_1

The high tendency of L_1 to form complexes relative to the others can be attributed to the formation of high stable six-membered chelate ring through the imine nitrogen and phenolic oxygen atoms. L_2 and L_3 are bounded through the imine nitrogen and one ring nitrogen atoms, and formed less stable four-membered chelate ring. Furthermore, the results reveal that the stability of the metal chelates for the same ligand are in agreement with the general order of the stability of these metal ion complexes⁹.

Definite evidence for the structure and coordination sites of the ligands under investigation is obtained from the i.r. data (Table 2) as discussed below:

(i) The free ligand L_1 show a strong band at 2812 cm^{-1} which is assigned to the intramolecular hydrogen bonded $o\text{-OH}$ in the molecule. The disappearance of this band in the i.r. spectra of L_1 complexes indicates that the $o\text{-OH}$ group is taking part in complexation. This is supported by a red shift observed in the phenolic $\nu\text{C—O}$ stretching. The band observed in the range $3400\text{--}3190 \text{ cm}^{-1}$ of the ligands L_2 & L_3 can be ascribed to the νOH stretching of $p\text{-OH}$ group of the aldehydic moiety. The presence of this broad band in the i.r. spectra of all the complexes suggests the presence of coordinated water molecules¹⁰. On the other hand, the phenolic $\nu\text{C—O}$ stretching of the ligands L_2 & L_3 does not show a marked shift on complexation which excludes a coordination through the oxygen atom of $p\text{-OH}$ group.

(ii) The three free ligands show two bands in the regions $1665\text{--}1620 \text{ cm}^{-1}$ and $1575\text{--}1520 \text{ cm}^{-1}$. One can assign the shorter frequency band to the stretch vibration of azomethine $\nu\text{C=N}$ and the longer frequency one

TABLE 2

IR SPECTRAL BAND ASSIGNMENTS (ν cm^{-1}) IN THE REGION 4000–200 cm^{-1} OF SCHIFF BASE METHYL PYRIMIDINE AND THEIR COMPLEXES

Compound	νOH	$\nu\text{C}=\text{N}$	$\nu\text{C}-\text{O}$	$\nu\text{M}-\text{N}$	$\nu\text{M}-\text{Cl}$
$\text{L}_1(\text{X}=\textit{o}\text{-OH})$	2812 s	1665 s 1550 s	1250 w	—	—
$\text{L}_1\text{-Cu(II)}$	3300 w, b	1650 s 1605 s	1275 w	460 w	—
$\text{L}_1\text{-Ni(II)}$	3200 s, b	1650 s 1590 s	1275 w	430 m, b	1220 s
$\text{L}_1\text{-Co(II)}$	3200 s, b	1655 s 1600 s	1270 w	450 m	1225 s
$\text{L}_1\text{-Mn(II)}$	3190 s	1660 s 1595 s	1270 w	435 s	1225 s
$\text{L}_2(\text{X}=\textit{p}\text{-OH})$	3200 s	1620 s 1530 s	1290 m	—	—
$\text{L}_2\text{-Cu(II)}$	3200 s, b	1655 s 1600 s	1290 m	455 w	—
$\text{L}_2\text{-Ni(II)}$	3300 s, b	1655 s 1590 s	1280 s	450 w	1210 s
$\text{L}_2\text{-Co(II)}$	3200 s, b	1670 m 1600 m	1280 s	430 w	1215 s
$\text{L}_2\text{-Mn(II)}$	3190 s	1655 s 1590 s	1280 m	430 w, b	1210 m
$\text{L}_3(\text{X}=\textit{p}\text{-OH}, \textit{m}\text{-OCH}_3)$	3200 s, b	1625 s 1575 s	1280 s	—	—
$\text{L}_3\text{-Cu(II)}$	3300 s, b	1630 m, b 1590 s	1270 vw	425 w	—
$\text{L}_3\text{-Ni(II)}$	3400 s	1660 vw 1625 s	1270 w	420 vw	1230 m
$\text{L}_3\text{-Co(II)}$	3300 s, b	1650 w 1625 s	1280 w	420 w	1230 m
$\text{L}_3\text{-Mn(II)}$	3400 s	1660 s 1590 s	1275 w	420, 445 w	1230 m

to the stretching of $\nu\text{C}=\text{N}$ within the ring^{11,12}. In complexes of L_1 , blue shift of the ring $\nu\text{C}=\text{N}$ and red shift of the azomethine $\nu\text{C}=\text{N}$ stretching are observed, this indicate that the coordination takes place through the azomethine nitrogen atom and $o\text{-OH}$ group where a stable six-membered ring can be formed. On the other hand, for L_2 and L_3 complexes, a marked red shift observed in the stretching of $\nu\text{C}=\text{N}$ of azomethine and the ring, this suggests that the coordination takes place through the two nitrogen atoms of azomethine group and hetero ring.

(iii) The new bands appearing in the $460\text{--}420\text{ cm}^{-1}$ and in the $230\text{--}210\text{ cm}^{-1}$ regions may be assigned to $\nu\text{M}\text{--}\text{N}$ frequency^{13,14}, and $\nu\text{M}\text{--}\text{Cl}$ ¹⁵ respectively. For the nitrate complexes a new band at *ca.* 1380 cm^{-1} may be tentatively assigned to the coordinated NO_3^- group in the solid complexes¹⁴.

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