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Characterization and thermal behaviour of Cu(II) chelates of Schiff bases derived from aminopyridines

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Abstract

Complexes of copper(II) with Schiff bases derived from 3-amino- and 2-amino-pyridine and its derivatives with salicylaldehyde and *o*-hydroxynaphthaldehyde have been synthesized. The compounds have been characterized by elemental analysis, IR and electronic absorption spectra and differential thermal analysis. The data show the formation of two different types of compound with 1:1 and 1:2 metal–ligand stoichiometries and different thermal properties.

INTRODUCTION

Schiff bases derived from the reaction of aromatic aldehydes and aliphatic or aromatic amines represent an important series of widely studied organic ligands [1–5]. Osipov et al. [6] have studied the luminescent and photochemical properties of Cu(II) complexes of Schiff bases derived from some substituted salicylaldehydes and 2-aminopyridine; they demonstrated that the copper complexes have a tetrahedral or pyramidal structure. Yamada and Yamanouchi [7] have studied complexes of Cu(II), Zn(II), Pd(II), Co(II) and Ni(II) with the same Schiff bases; they found that the copper complexes have a planar configuration. In addition, complexes of Co(II), Ni(II), Cu(II), Th(II) and UO_2 with salicylaldene-2-aminopyridine have been investigated [8]. In these compounds, the molecules of the Schiff base, not its anion, are coordinated to the metal ions studied. In the reaction of *N*-2-pyridylsalicylaldimine with copper(II) nitrate, the tridentate Schiff base ligand is coordinated to three different copper atoms in such a way that the phenolic oxygen is bridged to two of these copper atoms and the pyridine nitrogen atom is coordinated to the third one [9,10] Császár and Balog [11] have studied the

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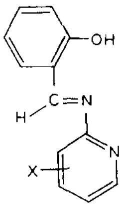
synthesis and structure of nickel complexes of salicylaldene-3-aminopyridine. Recently, Cu(II), Ni(II) and Co(II) complexes of salicylaldene-2-aminopyridine were synthesized and the copper complex was shown to have an octahedral structure [12].

In this paper, we report the synthesis of copper(II) complexes with Schiff bases derived from the condensation of 3-amino- and 2-aminopyridine and its derivatives with salicylaldehyde and *o*-hydroxynaphthaldehyde. The resulting complexes were studied by elemental analysis, differential thermal analysis, and IR and electronic absorption spectroscopy. The data obtained indicate the formation of 1 : 1 and 2 : 1 ligand–metal stoichiometries which have different thermal properties.

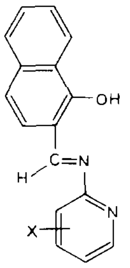
EXPERIMENTAL

Synthesis

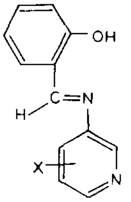
Schiff bases were prepared by mixing stoichiometric amounts of analytically pure salicylaldehyde or *o*-hydroxynaphthaldehyde with the corresponding aminopyridine in absolute ethanol. The mixtures were heated under reflux on a water bath until the appearance of shining yellow crystals. The crude products were recrystallized from ethanol. The ligands prepared have the following formulae:



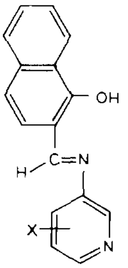
$L_1 : X = H$
$L_4 : X = 4 - CH_3$
$L_5 : X = 6 - CH_3$



$L_6 : X = H$
$L_9 : X = 4 - CH_3$
$L_{10} : X = 6 - CH_3$



L_2



L_7

The complexes were prepared by the reaction of the Schiff bases with copper acetate or chloride in acetone or alcohol. The reaction mixture was refluxed for about 1 hr. The solid complexes which separated out were filtered, washed with ethanol and dried in a desiccator.

Apparatus

The IR absorption spectra were obtained on a model 2000 Perkin–Elmer spectrophotometer using KBr discs. Solid electronic absorption spectra were measured in Nujol mull using a 2560-Beckman spectrophotometer from 200 to 750 nm. Differential thermal analysis of the prepared samples (20–25 mg) was carried out at a heating rate of 10 °C min^{-1} in air using a Shimadzu XD-30 thermal analyser. X-ray powder diffraction patterns of the Cu Kα line were carried out using a Shimadzu XD-3 diffractometer.

RESULTS AND DISCUSSION

All the complexes are stable at room temperature and non-hygroscopic in nature. They decompose at 250 °C and are almost insoluble in water but partially soluble in polar solvents (dimethyl sulphoxide and dimethylformamide). Two types of complex were obtained depending on the counter-anion of the copper salt. The analytical data reported in Table 1 suggest that the reaction of the ligands with $Cu(CH_3COO)_2$ produces complexes of the type $Cu(L)_2$ and $Cu(L)_2 \cdot H_2O$. However, the reaction with $CuCl_2 \cdot 2H_2O$ gave complexes of formulae $CuLCl \cdot H_2O$.

IR and electronic absorption spectra

The tentative assignments of some of the important bands of the Schiff bases and their corresponding metal complexes are recorded in Table 2. The bands in the region 1285–1274 cm^{-1} for the salicylaldehyde Schiff bases and 1319–1300 cm^{-1} for the naphthaldehyde analogue are ascribed to the phenolic and naphthalenic C–O stretching vibration respectively [13]. This band is found in the 1330–1290 cm^{-1} region in the IR spectra of L_1–L_4 complexes and in the 1390–1350 cm^{-1} region for the L_5–L_{10} complexes. The higher frequency shift observed for the C–O bond in going from a hydrogen-bonded structure to a covalent metal-bonded structure may be due to a higher mesomeric interaction in the latter complexes, activated by the presence of the metal ion [14]. The absence of any measurable absorption in the IR region characteristic of OH (3650–3590 cm^{-1}) has been attributed to the existence of intramolecular hydrogen bonding [15]. For the same reason, some of the Schiff bases of this study exhibit thermochromism and photochromism [16–18]. In the ligand spectra the strong band appearing at about 1540 cm^{-1} is assigned to the ν(C=N) stretching mode. In the metal complexes, this band shifts to a lower frequency region, indicating the formation of a coordination bond between the nitrogen of the azomethine group and the metal ion. This accords with previous assignments for the ν(C=N) mode of Schiff base complexes [11,13,19].

The electronic absorption spectra of the copper complexes were studied in Nujol mull. The shift in the bands and the change in colour indicate complex formation. As seen from Table 2, it is expected that the copper(II) complexes obtained in the present work have a square-planar geometry, as demonstrated by the appearance of only one band in the electronic spectra

TABLE 1

Analytical data for the copper complexes

Complex	Colour	H (%)		C (%)		N (%)		Cl (%)		Cu (%)	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$Cu(L_1)_2$	Reddish brown needles	3.93	3.70	62.93	62.11	12.22	11.85	–	–	13.87	13.73
$Cu(L_2)_2$	Shining green crystals		3.85		62.30		11.90	–	–		13.80
$Cu(L_4)_2 \cdot H_2O$	Yellowish brown needles	4.40	4.18	62.07	62.01	11.13	11.11	–	–	12.63	13.10
$Cu(L_5)_2 \cdot H_2O$	Yellowish brown powder		4.10		62.15		11.20	–	–		12.97
$Cu(L_6)_2$	Yellowish brown powder	3.61	3.65	68.89	68.70	10.03	10.40	–	–	11.39	11.37
$Cu(L_7)_2$	Shining green sheets		3.70		68.75		10.14	–	–		11.49
$Cu(L_9)_2 \cdot H_2O$	Reddish brown crystals	5.00	4.87	67.59	67.62	9.27	9.09	–	–	10.50	10.25
$Cu(L_{10})_2 \cdot H_2O$	Reddish brown crystals		5.10		67.90		8.98	–	–		10.51
$Cu\ L_1Cl \cdot H_2O$	Shining violet crystals	3.52	3.40	45.86	45.70	8.90	9.10	11.29	11.40	20.21	20.60
$Cu\ L_2Cl \cdot H_2O$	Brown powder		3.35		45.60		9.22		11.35		20.44
$Cu\ L_4Cl \cdot H_2O$	Deep brown crystals	4.82	4.50	47.41	47.43	8.50	8.40	10.78	10.26	19.29	19.19
$Cu\ L_5Cl \cdot H_2O$	Shining brown crystals		4.57		47.60		8.47		10.49		19.51
$Cu\ L_6Cl \cdot H_2O$	Green crystals	3.56	3.17	52.76	52.46	7.68	7.55	9.74	9.89	17.44	17.96
$Cu\ L_7Cl \cdot H_2O$	Brown crystals		3.40		52.38		7.60		8.40		17.18
$Cu\ L_9Cl \cdot H_2O$	Green powder	4.25	4.30	53.96	53.80	7.40	7.60	9.38	9.40	16.79	16.48
$Cu\ L_{10}Cl \cdot H_2O$	Brown crystals		4.35		54.10		7.57		9.25		16.25

TABLE 2

IR and electronic spectral data for Cu(II)–Schiff base complexes

Formula	IR spectra (cm^{-1}) [a]				Electronic spectra (nm)
	ν(C=C)	ν(C=N)	ν(C–O)	δ(OH)	
$Cu(L_1)_2$	1602 s	1528 m	1320 m	1180 s	> 750,410,300
	1583 m			1148 s	
	1569				
$Cu\ L_1Cl \cdot H_2O$	1604 s	1522 m	1290 m	1182 s	> 750,420,370
	1580 m			1147 m	
$Cu(L_2)_2$	1607 vs	1520 m	1330	1180 m	> 750,570,390
	1571 m			1140 m	
$Cu\ L_2Cl \cdot H_2O$	1605 s	1515 m	1315 m	1175 m	> 750,550,420,300
	1570 m			1147 m	
$Cu(L_4)_2 \cdot H_2O$	1605 m	1530 m	1320 m	1190 m	700,400,300
	1590 m			1149 m	
$Cu\ L_4Cl \cdot H_2O$	1604 m	1523 m	1300 m	1185 m	750,550,300
	1583 m			1147 m	
$Cu(L_5)_2 \cdot H_2O$	1606 m	1524 m	1370 m	1201 m	715,590,385
	1583 m			1150 m	
$Cu\ L_5Cl \cdot H_2O$	1610 s	1537 m	1380 m	1185 m	750,575,376
	1590 m			1140 m	
$Cu(L_6)_2$	1609 m	1528 m	1358 m	1175 m	750,600,400
	1593 m			1150 m	
	1553 m				
$Cu\ L_6Cl \cdot H_2O$	1611 m	1530 m	1365 m	1175 m	700,430
	1598 m			1150 m	
	1555 m				
$Cu(L_7)_2$	1610 m	1528 m	1365 m	1179 m	> 750,420,300
	1596 s			1134 m	
$Cu\ L_7Cl \cdot H_2O$	1613 m	1530 m	1375 m	1184 m	750,570,450,310
	1600 m			1142 w	
$Cu(L_9)_2 \cdot H_2O$	1610 m	1530 m	1390 m	1185 m	750,575,470,415
	1595 m			1150 m	
	1580 m				
$Cu\ L_9Cl \cdot H_2O$	1619 m	1530 m	1380 m	1190 m	710,440,320
	1608 m			1155 m	
	1580 m				
$Cu(L_{10})_2 \cdot H_2O$	1611 m	1529 m	1350 m	1182 m	750,570,480
	1590 m		1380 m	1152 w	
	1560 m				
$Cu\ L_{10}Cl \cdot H_2O$	1613 m	1530 m	1350 m	1184 m	
	1594 m		1370 m	1165 m	700,625,588,480
	1560 m				

[a] m, medium; s, strong; vs, very strong; w, weak.

at around 700 nm, with a shoulder at about 550 nm [20]. This is in agreement with previous studies on copper complexes of Schiff bases [5,12]. Some complexes of this type are also known to form associated species in the solid state, yielding five-coordinate copper(II) complexes [7].

Thermal study

The DTA curves (Fig. 1) in the temperature range 30–500 °C for all the metal complexes show that they are thermally stable up to 160 °C. The data indicate some thermal effects, such as those due to a phase change of some type or a lattice rearrangement. Thus, it is possible to distinguish between various types of behaviour as found in the DTA curves. The one and two sharp exothermic peaks appearing for the complexes $Cu(L_2)_2$ and $Cu(L_6)_2$, respectively, before melting are most probably correlated with rearrangements of the molecular lattice [21]. The exothermic peaks lying at 220–290 °C for all the complexes were assigned to melting. This is followed by broad, more or less strong exothermic peaks located at 440–520 °C, corresponding to partial and complete decomposition of the complex [22].

The DTA curve of the complex $Cu(L_1)_2$ (Fig. 1(a)), however, shows an endothermic peak at 165 °C, corresponding to melting of the complex. The sharp exothermic peak at 200 °C is most probably correlated with the vaporization of the complex under investigation which often occurs after melting [23].

The substituted pyridines used in our study have a relatively narrow range of basicity, but their effect on the difference in the thermal stability of the final solid complexes is quite large. Thus, the substituted pyridines are listed in order of decreasing basicity as follows 3-aminopyridine > 6-methyl-2-aminopyridine > 2-aminopyridine > 4-methyl-2-aminopyridine. It is also apparent that the 4-methyl- and 2-aminopyridine ligands have a pronounced effect on the thermal stability of the copper(II) complexes (see Fig. 1(b) and Table 3). In our view this effect is not a result of the basicity of the ligand

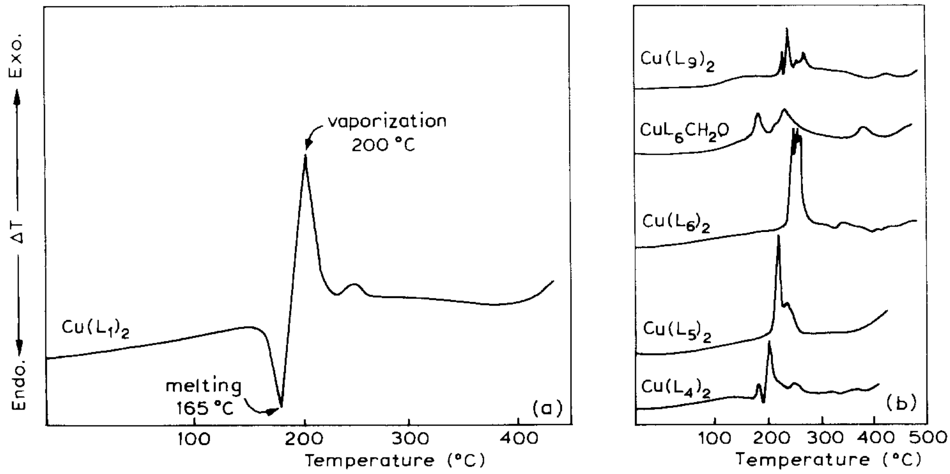


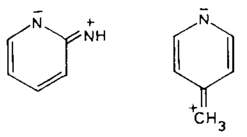
Fig. 1. DTA curves for the copper(II) complexes.

TABLE 3

DTA peaks and their assignments for some Cu(II) complexes

Complex	DTA peaks (° C)		Assignments
	Endo.	Exo.	
$Cu(L_1)_2$	165	–	Melting
		200	Vaporization
		452	Partial decomposition
$Cu(L_2)_2$	–	240	Lattice rearrangement
		290	Melting
		460	Partial decomposition
$Cu(L_4)_2 \cdot H_2O$	–	175	Melting
		200	Vaporization
		452	Partial decomposition
$Cu(L_5)_2 \cdot H_2O$	–	220	Melting
		240	Lattice rearrangement
		460	Partial decomposition
$Cu(L_6)_2$	–	240–250	Lattice rearrangement
		260	Melting
		340	Vaporization
		520	Partial decomposition
$Cu\ L_6Cl \cdot (H_2O)$	–	190	Melting
		240	Vaporization
		520	Partial decomposition
$Cu(L_9)_2 \cdot H_2O$	–	230	Melting
		240	Vaporization
		520	Partial decomposition

and thus can only be due to the existence of resonance structures of the type



This would agree with the high frequency shift observed for the C–O bond in the IR spectra. This means that when the pyridine contains methyl and amino groups in positions 4 and 2, the complexes are less thermally stable and decompose more easily (452° C) than those containing substituent groups in positions 6 and 3 (460° C) [24]. The relatively more thermally stable complexes, $Cu(L_4)_2 \cdot H_2O$ and $Cu(L_9)_2 \cdot H_2O$, showed only a single exothermic peak each at 452° C and 520° C respectively. This is attributed to the difference in the aldehyde moiety: [salicylaldehyde in $Cu(L_4)_2 \cdot H_2O$; 2-hydroxy-1-naphthaldehyde in $Cu(L)_9)_2 \cdot H_2O$].

The brown complex obtained by heating the green form of $Cu(L_2)_2$ at 240° C no longer shows the DTA peak at 290° C displayed by the green modification (Fig. 2). Moreover, the X-ray diffraction pattern of the brown

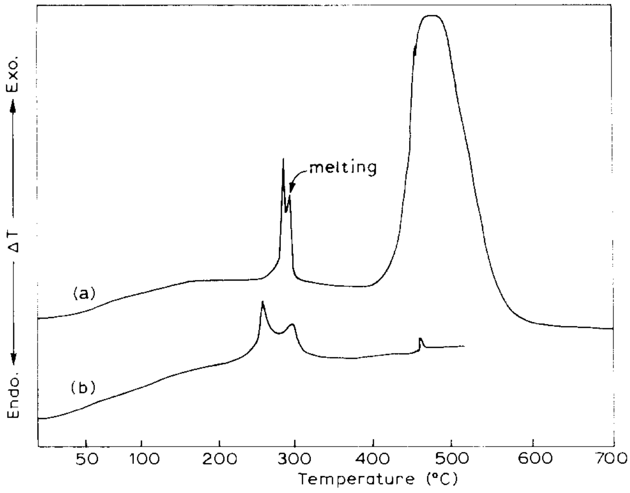


Fig. 2. DTA curves of $Cu(L_2)_2$ complex: curve a, before heating; curve b, after heating.

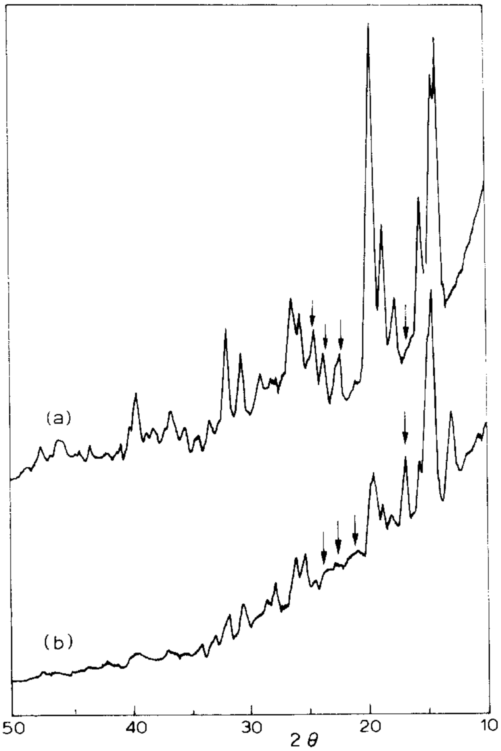


Fig. 3. X-ray powder diffraction pattern of $Cu(L_2)_2$ complex: curve a, before heating; curve b, after heating.

form (Fig. 3) is different from that of the green form. This indicates that the green modification is irreversibly transformed to the brown in the solid state at 240 °C [25]. From its numerous lower intensity reflections, the X-ray pattern of the brown form (Fig. 3, curve b) suggests a lower degree of symmetry and crystallinity, compared with the green form [26,27].

REFERENCES

1 R. Holm, G.W. Everett and A. Chakravorty, in F.A. Cotton (Ed.), Progr. Inorg. Chem., Interscience Publication, New York, Vol. 7, 1966.
2 L. Sacconi, Coord. Chem. Rev., 1 (1966) 126.
3 S. Yamada, Coord. Chem. Rev., 1 (1966) 415.
4 R.L. Dutta and G.P. Sengupta, J. Indian Chem. Soc., 48 (1971) 83.
5 F.A. Aly, M. Gaber, R.M. Issa and F.A. El-Said, Bull. Soc. Chim. Fr., 4 (1988) 661.
6 O.A. Osipov, V.I. Minkin, D.Sh. Verkhovodova and M.I. Knyazhanskii, Russ. J. Inorg. Chem., 12 (1967) 814.
7 S. Yamada and K. Yamanouchi, Bull. Chem. Soc. Jpn., 42 (1969) 2562.
8 M.R. Mahmoud and M.T. El-Haty, J. Inorg. Nucl. Chem., 24 (1980) 349.
9 W.E. Hatfield and F.L. Bunger, Inorg. Chem., 8 (1969) 1194.
10 J. Drummond and J.S. Wood; J. Chem. Soc., Dalton, Trans, (1972) 365.
11 J. Császár and J. Balog, Acta Chim. (Budapest), 87 (1975) 321.
12 R.K. Parashar, R.C. Sharma, A. Kumar and G. Mohan, Inorg. Chim. Acta, 151 (1988) 201.
13 J.E. Kovacic, Spectrochim. Acta, Part A, 23 (1967) 183.
14 M.R. Mahmoud, I.M. Issa, M.S. Elmelliegy and A.S. Elgyar, Monatsh. Chem., 109 (1978) 861.
15 S.P. Hendricks; D.R. Wulf, G.E. Hilbert and U. Liddel, J. Am. Chem. Soc., 58 (1936) 1991.
16 G.M.J. Schmidt, Acta Crystallogr., 10 (1957) 793.
17 M.D. Cohen, G.M.J. Schmidt and S. Flavian, J. Chem. Soc., (1964) 2041.
18 E. Hadjoudis, J. Petro and J. Xexakis, Mol. Cryst. Liq. Cryst., 93 (1983) 73.
19 V.H. Kulkarni, B.R. Patil and B.K. Prabhakar, Monatsh. Chem., 108 (1977) 1305.
20 A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1968.
21 M. Natarajan and E.A. Secco, Can. J. Chem., 59 (1981) 2685.
22 M. Gaber, M.M. Ayad and M.I. Ayad, Thermochim. Acta, 176 (1990) 21.
23 C.F. Bell and D.R. Rose, Inorg. Chem., 7 (1968) 325.
24 R. Lozano; M. Martinez, A. Martinez and A.D. Lopez, Polyhedron, 2 (1983) 977.
25 A. Takeuchi and S. Yamada, Rev. Roum. Chim., 22 (1977) 781.
26 T.F. Zafiropoulos, A.G. Galinos and S.P. Perlepes, J. Coord. Chem., 13 (1984) 197.
27 M.M. Abou Sekkina, S.E. Morsi and A.E. El-Geassy; Bull. National Research Centre (Egypt), 2 (1977) 18.