Synthesis and structural characterization of Cu(II) and Ni(II) complexes of antipyrine schiff base derivatives

S Abdul Samath, K Jeyasubramanian, S Thambidurai
& S K Ramalingam*

School of Chemistry, Madurai Kamaraj University,
Madurai 625 021

The terfunctional schiff base ligands acetylaceton-4-aminoantipyrine, salicylal-4-aminoantipyrine and 2-hydroxy-1-naphthal-4-aminoantipyrine react with Cu(II) and Ni(II) metal ions in different stoichiometric ratios and at various pH values to yield complexes with different bonding features such as (i) neutral bidentate - coordination via. $>C=O$ and $>C=\ddot{N}$-, (ii) neutral terdentate - coordination via. $>C=O$, $=CH-NH-$ and quinonoid $=O$: from -OH, (iii) monovalent bidentate - coordination via. $>C=N$-, and -O- from -OH and (iv) monovalent terdentate - coordination via. $>C=N$, $>C=O$ and -O- from -OH.

The classical coordination chemistry of biologically active antipyrine with transition metals and lanthanides has been extensively studied[1-9]. In all the reported cases, the coordination possibilities of the schiff base ligands AcAAP, SAAP and HNAAP are restricted to terdentately bound complexes. Nevertheless, these ligands are also capable of behaving as neutral bidentates in their deprotonated form to coordinate with metal(II) ions.

In this note, we report the possibilities of these systems forming metal complexes by making use of different reaction conditions such as (i) the pH of the reaction solution (acidic, neutral or alkaline) and (ii) variable stoichiometries of substrates.

Experimental

All the chemicals and solvents used were of reagent grade. The ligands acetylaceton-4-aminoantipyrine (AcAAP), salicylal-4-aminoantipyrine (SAAP) and 2-hydroxy-1-naphthal-4-aminoantipyrine (HNAAP) were prepared by the condensation of 4-aminoantipyrine (AAP) with acetylacetone, salicylaldehyde or 2-hydroxy-1-napthaldehyde according to the literature method[5,8].

Preparation of complexes

Under acidic conditions (pH = 5-6)

A solution of hydrated metal(II) salt (0.01 mol) and the schiff base ligand in acetone were refluxed for 15-20 min in appropriate molar ratios. The solid product thus obtained upon cooling was filtered, washed with warm benzene, water and finally dried over $CaCl_2$ in a desiccator.

Under neutral conditions (pH = 7)

An ethanolic solution of the schiff base ligand was added to an equimolar aqueous solution of sodium acetate. To this solution, an ethanolic solution of metal(II) salt in appropriate molar ratio was added and boiled for 15 to 20 min. The pH of the reaction solution was monitored by an aq.solution of sodium acetate and ethanol using a pH meter. The precipitated solid product thus obtained was purified as described above.

Under alkaline conditions (pH 8-9)

The preparation of the complexes was achieved by adopting the same procedure described above in ethanol medium. The pH of the solution was rendered alkaline (8-9) using either NaOH (1N) or dil. NH_4OH. In most of the cases, the metal complexes precipitated within minutes, which were filtered, washed with cold ethanol and dried at room temperature. The physical measurements were carried out, as reported earlier[8].

Results and discussion

A consequence of the monobasic nature of the ligands AcAAP - Acetylaceton-4-aminoantipyrine, SAAP-salicylal-4-aminoantipyrine and HNAAP-2-hydroxy-1-naphthal-4-aminoantipyrine with the metals Mn(II), Co(II), Ni(II) and Cu(II) at alkaline $pH(\sim 8$-9$)$ due to deprotonation of -OH into O-, is that the possibilities o coordination at the metal ion increase. Thus a second ligand such as an anion, or another molecule of the ligand itself, can enter the coordination sphere resulting in a 4 or 6 coordination geometry around the metal ion. Furthermore, 1:1 and 2:1 metal - ligand stoichiometries, can lead to the formation of complexes of the type [MLX] and [ML]$_2$X$_2$ respectively at alkaline pH (~ 8-9$)$ when NaOH (1N) is added. Interestingly, the same monobasic terdentate ligand at pH (~ 8-9$)$ when NH_4OH is added, can form complexes of the type [ML$_2$] irrespective of the concentration of the substrates.

The IR spectra of these complexes viz. [MLX], [ML]$_2$X$_2$ and [ML$_2$] show no bands ~ 3200 cm^{-1} suggesting the absence of intra-ligand hydrogen

Table 1—Characterization data of representative nickel(II) or copper(II) complexes of acetylacetone-4-aminoantipyrine (AcAAP)

Compound	Found (Calc.), %				Electronic spectral bands (cm^{-1})				Magnetic moment
	M	C	H	N	v_1	v_2	v_3	v_4	μ (BM)
AcAAP	—	67.2(67.6)	6.4(6.3)	14.9(14.8)	—	—	—	—	—
[Ni(AcAAP)Cl$_2$]^a	14.3(14.2)	46.7(46.4)	4.4(4.4)	10.2(10.2)	9000	16000	—	22800	3.09
[Ni(AcAAP)Cl]$_2$Cl$_2$^{a}	14.5(14.2)	46.13(46.4)	4.4(4.4)	10.3(10.2)	8350	10340	14850	22800	2.16
[Cu(AcAAP)Cl]$_2$Cl$_2$	15.3(15.2)	46.1(45.9)	4.4(4.3)	10.6(10.0)	9060	11000	15600	23000	1.33
[Ni(AcAAP)(H$_2$O)Cl$_2$]^{b*}	13.9(13.6)	44.7(44.5)	4.1(4.2)	10.0(9.7)	9040	15500	—	23600	2.89
[Ni(AcAAP)$_2$]^c	9.8(9.4)	61.5(61.3)	5.9(5.7)	13.5(13.4)	—	12200	15000	23600	Dia
[Ni(AcAAP)Cl]^d	15.7(15.5)	51.1(50.8)	4.9(4.8)	11.3(11.1)	9000	—	16500	23400	2.93
[Ni(AcAAP)]$_2$Cl$_2$^{e}	15.5(15.5)	50.6(50.8)	4.7(4.8)	11.6(11.1)	8160	10640	15200	24000	2.21
[Cu(AcAAP)]$_2$Cl$_2$	16.8(16.6)	51.0(50.1)	4.7(4.7)	11.1(10.0)	9640	11200	15500	22800	1.41

^{a} - neutral bidentate - coordination via. C=O (pyrazolone ring) and C=N-, monomer

^{b} - neutral terdentate - monomer, coordination via. C=O, C=N- and -OH

^{c} - monobasic bidentate - coordination via -O- of -OH and C=N-

^{d} - monobasic terdentate - coordination via. C=O, C=N and -O- of -OH, monomer

^{e} - monobasic terdentate - coordination via. C=O, C=N and -O- of -OH, dimer

$*$ - conversion of -O- to =O a resulting resonance from C = N- to NH

bond[10,11], consequent to deprotonation. The stretching frequency observed at 1680 cm^{-1} for AcAAP (1658 cm^{-1} for SAAP and 1640 cm^{-1} for HNAAP) attributed to free pyrazole >C=O group[12] gets shifted to lower frequencies in the spectra of [MLX] and [ML]$_2$X$_2$ type complexes, whereas this band gets retained in the spectra of the [ML$_2$] type complexes. The other band at 1520 cm^{-1} corresponding to >C=N̈- shifts to higher region[13] in all the above complexes.

The monobasic nature of the coordinated ligand under alkaline pH is confirmed by the PMR spectra of the Ni(II) complexes (square planar; $\lambda = 700$ nm)[14] wherein the -OH peak originally present in the ligand at 13.50 δ (ppm) is conspicuous by its absence.

In neutral pH, the ligands behave as neutral terdentates and lead to the formation of the complexes of the type [MLX$_2$(H$_2$O)]. The coordination of the functional group -OH in its deprotonated form (=Ö: quinonoid) can yield such octahedral complexes irrespective of the stoichiometries of the substrates. The complexes show a new IR band appearing ~3300 cm^{-1} (instead of 3200 cm^{-1} which is characteristic of intramolecular hydrogen bond) assignable to vN-H vibrations. The hydrogen bonding arrangement (O--H....N) changes the >C=N to >N−H due to the tautomeric conversion of enolimine to ketoneamine. The IR bands at 1620-1610 and 1570-1535 cm^{-1} corresponding to v-N-H[15] and =O:→M[16] frequencies confirm the above tautomerism.

The in situ generation of acid prevents the deproto-

nation of -OH group and the ligands offer new possibilities yielding two types of complexes such as nonelectrolytic mononuclear complex [MLX$_2$] and 1:1 electrolytic dinuclear complex -[MLX]$_2$X$_2$.

These complexes show a broad band ~3600 cm^{-1} instead of 3200 cm^{-1} in the complexes, showing the non-involvement of -OH group on coordination.

The magnetic moments of the nickel(II) complexes (1,4) and (6) at room temperature are in the range 2.89 to 3.09 BM. These values are consistent with high spin d^8 complexes. On the other hand, the nickel(II) complexes of the types (2,7) and the copper(II) complexes (3,8) show magnetic moments in the ranges 2.16 to 2.21 and 1.3 to 1.41 BM respectively. These values are lower than that predicted for low spin d^8 and d^9 metal ion respectively. The data indicate that all these complexes are probably dimeric similar to that found for the distinctly dimeric copper(II) acetate monohydrate with the attendent metal-metal interaction. The exchange interaction between the metal ions might occur through the phenoxide bridge (7 and 8) or through halide bridge (2 and 3).

While the Ni(II) complexes, 1,5 and 6 show a broad absorption band in the region 16500-16000 cm^{-1} assignable to $^3T_1(F)--->$ $^3T_2(F)$ in a tetrahedral geometry, 4 exhibits two bands of lower intensity in the regions 15500-15000 and 23500 cm^{-1} assignable to $^3A_{2g}\rightarrow^3T_{1g}$ and $^3A_{2g}\rightarrow^3T_{1g}(P)$ respectively in an octahedral geometry. Also the presence of an additional band below 10000 cm^{-1} confirms the octahedral geometry for the latter Ni(II) compelx 4. The molars con-

Scheme 1
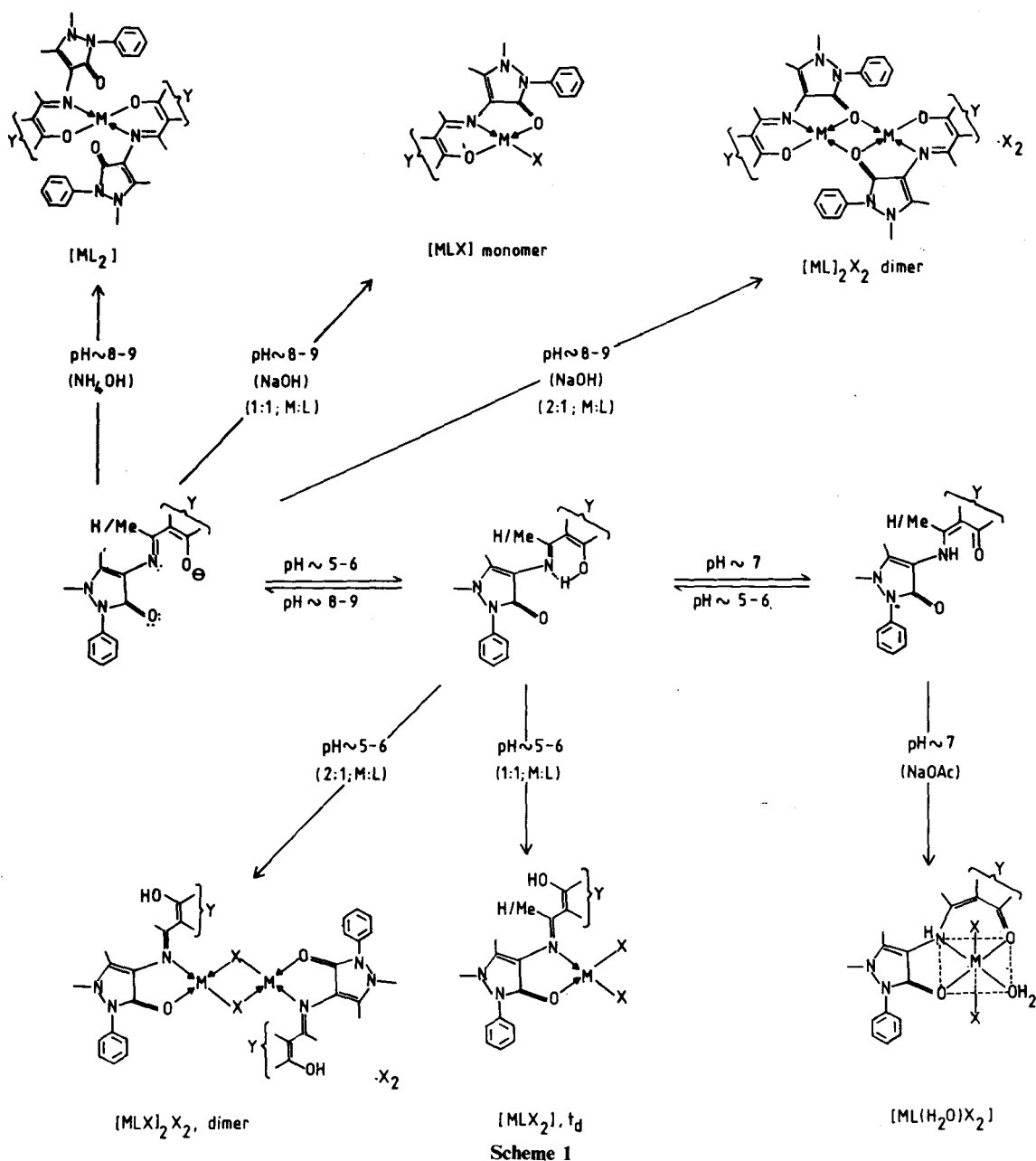
where M = Mn(II), Co(II), Ni(II) and Cu(II);

X = Br or CL;

Y = alicyclic, AcAAP; phenyl, SAAP and naphthyl; HNAP.

ductance data[17] are in accord with a 1:1 composition for complexes (2,3,7 and 8) and a nonelectrolytic structure for the rest.

The analytical results of C, H, N and M (Table 1) of the complexes are in good agreement with the assigned structural formula. The overall reaction pattern is given in Scheme 1

Acknowledgement

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