Asian Journal of Chemistry Vol. 14, No. 1 (2002), 489–492

Synthetic and Antimicrobial Studies of Hexacoordinated Ternary Complexes of Mn(II) and Cu(II)

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Some new ternary complexes of Mn(II) and Cu(II) with isonitrosoacetophenone isonicotinoyl hydrazone (INAPIH)/4-chloroisonitrosoacetophenone isonicotinoyl hydrazone (ClINAPIH) as primary and 1-(*o*-methoxy anilinomethyl) benzimidazole (MAMB) as secondary ligand have been synthesised and their structural features have been studied on the basis of analytical, spectral and conductance data. Analytical data suggest 1 : 1 : 1 (M-L/L′-L″) stoichiometric composition for the isolated ternary complexes (where $M = Mn^{2+}/Cu^{2+}$, L = deprotonated INAPIH, L′ = deprotonated ClINAPIH and L″ = MAMB). The complexes show 1 : 1 electrolytic nature. IR spectra confirm the tridentate and bidentate behaviour of the hydrazone (INAPIH/ClINAPIH) and Mannich base (MAMB) respectively. Electronic spectral data propose octahedral stereochemistry for the complexes. The complexes show increased antimicrobial activity than the corresponding ligands.

Key words: Mn(II), Cu(II), ternary complexes, spectral, antimicrobial agents.

INTRODUCTION

A broad spectrum of biological activity is reported to be associated with a number of heterocyclic compounds[1–4]. A large number of transition metal complexes of a variety of acid hydrazides and the corresponding hydrazones have been synthesised[5, 6]. A thorough survey of the literature reveals that the ternary complexes of Mn(II) and Cu(II) with isonitrosoacetophenone isonicotinoyl hydrazone/4-chloroisonitrosoacetophenone isonicotinoyl hydrazone as primary and 1-(*o*-methoxy anilinomethyl) benzimidazole (MAMB) as secondary ligand have not been studied so far. Here, we report the synthesis and characterization of these compounds. The complexes have been screened for their antimicrobial activity.

EXPERIMENTAL

All the reagents used were of AnalaR grade. Conductivity measurements were carried out on Toshniwal conductivity bridge. IR spectra were recorded on Beckmann IR-20 spectrophotometer. Magnetic susceptibility was measured at 300 ± 1 K on a Gouy's balance using $Hg(Co(NCS)_4]$ as calibrant. Isonicotinic

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hydrazide and benzimidazole were procured from Aldrich Ctemical Co. Inc., USA.

Preparation of ligand: Isonitrosoacetophenone and 4-chloroisonitrosoacetophenone were prepared by the reported procedure[7]. INAPIH and ClINAPIH were synthesised by condensing isonitrosoacetophenone/4-chloroisonitrosoacetophenone with isonicotinic acid hydrazide for 40–45 min in ethanol. MAMB was obtained by refluxing an equimolecular mixture of benzimidazole and *o*-methoxy aniline with formalin (40%) using ethanol as solvent.

Preparation and isolation of complexes: Aqueous ethanolic solution of respective metal salt (0.01 mol) and INAPIH/ClINAPIH (0.01 mol) dissolved in ethanol, were mixed in 1 : 1 molar ratio and stirred on a magnetic stirrer for *ca.* 45 min. To it, an excess of ethanolic solution of MAMB was added dropwise with constant stirring. The separated crystalline complexes were filtered, washed with ethanol, acetone and dry ether and dried *in vacuo* over P_4O_{10}.

RESULTS AND DISCUSSION

Analytical data (Table-1) suggested 1 : 1 : 1 stoichiometric composition of the ternary complexes. The complexes are soluble in common organic solvents, DMSO and DMF. The molar conductance values (Table-1) in acetone at the concentration 10^{-3} M show 1 : 1 electrolytic nature of the complexes. The complexes are stable and non-hygroscopic.

TABLE-1
ANALYTICAL, CONDUCTANCE AND MAGNETIC MOMENT DATA OF METAL COMPLEXES

Complexes (Colour)	Analysis %, Found (Calcd.)					Ω^{-1} (cm^2 $mole^{-1}$)	μ_{eff} (B.M.)
	M	C	H	N	Cl		
$[CuLL''(H_2O)]Cl$ (Green)	9.92 (9.98)	54.14 (54.63)	4.37 (4.39)	15.27 (15.38)	5.51 (5.56)	65.4	2.04
$[CuL'L''(H_2O)]Cl$ (Green)	9.54 (9.46)	51.43 (51.82)	4.05 (4.02)	14.47 (14.59)	10.64 (10.56)	58.6	2.06
$[CuLL''(H_2O)]NO_3$ (Green)	9.51 (9.58)	52.06 (52.44)	4.17 (4.21)	16.99 (16.88)	—	63.2	2.02
$[CuL'L''(H_2O)]NO_3$ (Green)	9.02 (9.11)	50.26 (49.85)	3.84 (3.87)	15.88 (16.04)	5.04 (5.08)	61.8	2.05
$[CuLL''(H_2O)]OAc$ (Green)	9.67 (9.62)	56.03 (56.31)	4.72 (4.69)	14.70 (14.83)	—	64.5	2.04
$[CuL'L''(H_2O)]OAc$ (Green)	9.06 (9.14)	53.12 (53.52)	4.35 (4.31)	14.01 (14.10)	5.06 (5.10)	59.4	2.02
$[MnLL''(H_2O)]Cl$ (Grey)	8.70 (8.74)	55.06 (55.38)	4.42 (4.45)	15.71 (15.59)	5.68 (5.64)	60.8	5.90
$[MnL'L''(H_2O)]Cl$ (Brown)	8.23 (8.29)	52.10 (52.50)	4.03 (4.07)	14.78 (14.85)	10.60 (10.69)	59.7	5.91

where L = $C_{14}H_{11}N_4O_2$. L' = $C_{14}H_{10}N_4O_2Cl$, L'' = $C_{15}H_{15}N_3O$ and OAc = acetate

Magnetic and electronic spectral studies: The magnetic moments of Cu(II) complexes lie in the range 2.02–2.06 B.M. The spectra of these complexes exhibit a single broad band at 18,200–18,400 cm^{-1} which may be assigned to $^2E_g \rightarrow {}^2T_{2g}$ transition, characteristic of Cu(II) ion in the tetragonally distorted octahedral environment.

Magnetic moment values of the present Mn(II) complexes (5.90 and 5.91 B.M.) indicate $^6A_{1g}$ as ground state for d^5 configuration in high spin octahedral stereochemistry. The electronic spectra of the Mn(II) complexes exhibit three bands at 16,650–16,500, 19,650–19,500 and 24,580–23,450 cm^{-1} which are assignable to the transitions $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4E_g$, $^4A_{1g}(G)$ transitions respectively, suggesting an octahedral stereochemistry.

From a careful comparison of the infrared spectra of metal complexes with those of ligands, it is inferred that the band attributable to the OH stretching frequency of NOH group present in INAPIH/ClINAPIH is absent in the complexes. This observation suggests that the proton of NOH group is replaced by the metal ion. Further, the shift of ν(N—O) (*ca.* 1015 cm^{-1}) band to higher frequency band[8] (1045–1035 cm^{-1} indicates the bond formation of the metal with nitrogen of oximino group. A positive shift of 20–30 cm^{-1} in ν(C═N) vibrations (*ca.* 1,615 cm^{-1} in INAPIH/ClINAPIH) implies the participation of azomethine nitrogen in complexation. A sharp band is seen in the range 1665-1660 cm^{-1} in the spectra of hydrazones, which may be due to ν(C═N) (amide-I band). Further, two additional bands observed at 1510–1505 (w) and 1325–1320 (sh) cm^{-1} in the hydrazones may be regarded as amide-II and amide-III bands[9] respectively. In the complexes, these bands have been located at 1650, 1530 and 1310 cm^{-1} suggesting the coordination of carbonyl oxygen.

A weak band is noticed at 3330 cm^{-1} in MAMB, characteristic of ν(N—H). This band is, however, missing in the spectra of the ternary complexes and instead of it, a new band appears at *ca.* 3300 cm^{-1} which indicates the involvement of nitrogen of CH_2—NH in coordination. It seems to be justified by the negative shift (15–20 cm^{-1}) of ν(CH_2—N) vibrations in the complexes (2800 cm^{-1} in MAMB). ν(C═N) of benzimidazole ring (present in MAMB) existing at 1575 cm^{-1} gets shifted to lower frequency band (*ca.* 1540 cm^{-1}) in the complexes suggesting the involvement of nitrogen of ν(C═N).

Two non-ligand medium intensity bands existing at 500–515 and 410–425 cm^{-1} in the spectra of complexes may tentatively be assigned as ν(M—O) and ν(M—N) vibrations respectively. The appearance of broad band around 3420 cm^{-1} and somewhat weaker bands around 850 and 700 cm^{-1} in the complexes, assigned to OH stretching, rocking and wagging vibrations[10] respectively confirms the presence of coordinated water. Further, weight loss in the complexes at 160-180°C corresponds to a coordinated water molecule.

Antimicrobial studies: The antimicrobial activity of the ligands and synthesised ternary complexes was evaluated by the paper-disc plate method[11]. The compounds were screened against *S. aureus* and *E. coli*. The results indicated that the metal complexes are more active in comparison to the organic ligands. The increased activity of the complexes may be due to their increased liophilic nature.

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(*Received*: 3 October 2001; *Accepted*: 23 November 2001) AJC-2528