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Studies on some Trinuclear Schiff base Complexes

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Abstract: Some Copper(II)-Manganese(II) trinuclear complexes of Schiff bases derived from 2-aminobenzaldehyde and diamines are reported and characterized based on their elemental analyses, conductivity studies, IR, UV-Visible, ESR spectroscopy and cyclic voltammetric studies. The complexes are found to have the formula $[Mn(CuL)_2](CH_3COO)_2$. The elemental analyses data confirms the formation of trinuclear complexes. The important IR spectral bands corresponding to the active groups in the mononuclear and the trinuclear complexes under investigation are studied. All the trinuclear complexes are 1:2 electrolytes. The formation of trinuclear complexes is also confirmed by ESR and cyclic voltammetric studies.

Keywords: Schiff base, Cu(II) complexes, 2-aminobenzaldehyde, Mn(II) complexes.

Introduction

Schiff base ligands are considered "privileged ligands" because they are easily prepared by the condensation between aldehydes and imines. Schiff base ligands are able to coordinate with different metals[1-5] and to stabilize them in various oxidation states. The Schiff base complexes have been used in catalytic reactions[6] and as models for biological systems[7,8]. Many copper complexes of Schiff bases were prepared[9-14]. It has been reported that the structure of the substituent bonded to the imino nitrogen affects the coordination geometry of the complex[15]. During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donors[16-21]. This may be attributed to their stability, biological activity[22], and potential applications in many fields such as oxidation catalyst[23], electrochemistry[24].

The present study deals with the preparation of some trinuclear Schiff base complexes with copper and manganese. The solid complexes have been synthesized and studied by elemental, IR, UV-Visible, ESR spectral and cyclic voltammetric studies.

Experimental:

1. Materials and Physical measurements:

All chemicals used in the present investigation are of Analar grade from BDH used as received without further purification. The solvents were of spectroscopic pure from BDH.

The instrumental techniques used for the characterization of the complexes are Infrared spectral studies, Electronic spectral studies, Conductivity studies, Variable temperature electron spin resonance spectral studies and cyclic voltammetric studies. Jasco - IR - 700 Double beam spectrophotometer is used for recording the infrared spectra of the complexes in the range 4000 - 400 cm^{-1}. The spectra are taken by dispersing the solid substance in KBr disc. The samples are ground to a fine powder and mixed with KBr and then ground again to mix thoroughly. The KBr - sample mixture is then pressed into a thin disc.

The electronic spectra of the complexes in acetonitrile are recorded in HITACHI UV - 2001 spectrophotometer. In the present study, the conductance is measured using a Systronics direct reading conductivity bridge provided with conventional dip type platinised platinum electrodes. The ESR spectra of the complexes are recorded on a JEOL spectrometer equipped with variable - temperature facility operating at X-band frequencies. The spectra are recorded at room temperature and at liquid nitrogen temperature in ethanol. Cyclic voltammetric studies on complexes are carried out using a Model ECDA - 001, Basic electrochemistry system.

2. Preparation of Schiff bases [25-29]:

The Schiff base ligands used are prepared by mixing 2-aminobenzaldehyde with various diamines in the molar ratio of 2:1 in ethanol medium. The diamines used are 1,2-diaminoethane,1,2-diaminopropane and1,3-diaminopropane. Since 2-aminobenzaldehyde undergoes self-condensation it could not be stored. It is freshly prepared as and when required [26].

3. Preparation of trinuclear Copper (II)-Manganese (II) complexes:

To prepare the trinuclear complexes, mononuclear copper(II) complexes are prepared first [28-30]. The mononuclear copper(II) complex (CuL_1) is dissolved in 40 mL of hot ethanol. To this solution, a sample of 0.5609 g of manganese(II) acetate tetrahydrate in 25 mL of absolute ethanol is added drop wise and stirred well. The color of the solution changed from dark brown to brownish pink. The reaction mixture is refluxed for 3½ hours and allowed to cool. The brownish pink colored solid formed is filtered and dried. A similar procedure is adopted for the synthesis of trinuclear complexes using the mononuclear complexes CuL_2 and CuL_3.

Results and Discussion:

1. Elemental analyses:

The copper, manganese and nitrogen[31] contents of the trinuclear complexes have been estimated and tabulated in **Table-I.**

It is expected that the trinuclear copper(II)-manganese(II) complexes are formed by the reaction of the mononuclear copper(II) complexes and manganous salt in the molar ratio of 2:1. The mononuclear copper(II) complexes binds to the manganese(II) ion through the nitrogen atoms of the –NH groups in the mononuclear complex which has lone pair of electrons. Hence the complexes formed should be dicationic. The elemental analysis agrees well with such a formulation with acetate as the counter ion.

2. Conductivity Studies:

Conductance data are used to obtain the information about the nature of the complex in solution. The molar conductance of the complexes is determined at room temperature in acetonitrile. The values are tabulated in **Table-II.**

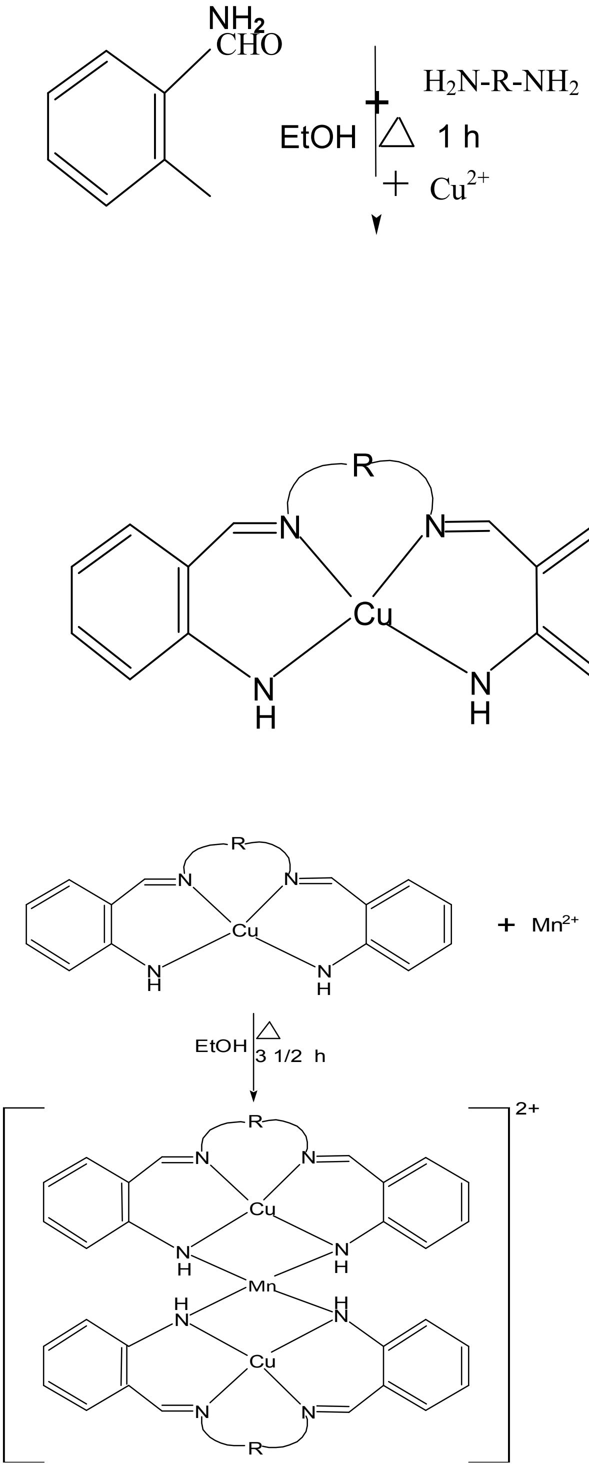
The complexes of the trinuclear copper(II)-manganese(II) complexes reported are electrolytes. The molar conductance values of the complexes are compared with the ranges given by Geary[32] suggest that they are 1:2 electrolytes. The mononuclear copper(II) complexes are neutral and the complexes presently reported are electrolytes confirming the formation of dicationic complexes. This is supported by the elemental composition data.

3. Infrared spectral studies:

The infrared spectra of the trinuclear complexes are recorded in the 4000-400cm^{-1} region and compared with the spectra of the mononuclear copper(II) complexes. The important peaks are tabulated in Table-III.

The coordination environment of the metal ions has been inferred from the infra red spectral data. In the trinuclear complexes, a sharp band around 3425-3440cm^{-1} is assigned for –NH group[33]. When the IR spectra of the trinuclear complexes are compared with the spectra of the mononuclear complexes, a downward shift of the –NH stretching vibration is found in the trinuclear complexes. This shift to lower energy of the band is due to the reduction of electron density in the –NH group. This indicates that the coordination of the mononuclear copper complexes to the manganese(II) ion added through the –NH group. In the spectra, a strong band at 1600cm^{-1} is assigned to C=N stretching of the azomethine group[34]. On comparison of the spectra of the mononuclear complexes with the trinuclear, the band position of the C=N group in the trinuclear complex is unshifted. The spectra of the trinuclear complexes show additional bands at 1520, 1340 and 700cm^{-1}. These bands can be assigned υ_{asym} (CO), $\delta(CH_3)$ and δ(COO) respectively indicating the presence of acetate ion in the complexes[35,36,37].

SCHEME



L_1, R = $-CH_2-CH_2-$

L_2, R = $-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-$

L_3, R = $-CH_2-CH_2-CH_2-$

Table –I : Analytical data of the complexes

Complex	Molecular formula	Found (Calculated) %		
		Copper	Manganese	Nitrogen
$[Mn(CuL_1)_2](CH_3COO)_2$	$C_{32}H_{32}N_8Cu_2MnC_4H_6O_4$	14.96(15.34)	6.52(6.64)	12.9(13.53)
$[Mn(CuL_2)_2](CH_3COO)_2$	$C_{34}H_{36}N_8Cu_2MnC_4H_6O_4$	14.62(14.84)	6.73(6.42)	13.12(13.08)
$[Mn(CuL_3)_2](CH_3COO)_2$	$C_{34}H_{36}N_8Cu_2MnC_4H_6O_4$	14.71(14.84)	6.36(6.42)	12.94(13.08)

Table-II: Conductance data of the mononuclear and trinuclear complexes

Complex	Molar conductance $\Lambda_m(Scm^2\ mol^{-1})$	Type of Electrolyte
CuL_1	68	Non-electrolyte
CuL_2	61	Non-electrolyte
CuL_3	76	Non-electrolyte
$[Mn(CuL_1)_2](CH_3COO)_2$	243	1:2
$[Mn(CuL_2)_2](CH_3COO)_2$	231	1:2
$[Mn(CuL_3)_2](CH_3COO)_2$	258	1:2

Table-III: Infrared spectral data of mononuclear and trinuclear complexes

Complex	-NH stretching cm^{-1}	C=N cm^{-1}	CH_3COO^- cm^{-1}
CuL_1	3454	1608	-
CuL_2	3451	1618	-
CuL_3	3450	1612	-
$[Mn(CuL_1)_2](CH_3COO)_2$	3436	1615	1528, 1340, 710
$[Mn(CuL_2)_2](CH_3COO)_2$	3426	1602	1559, 1338, 706
$[Mn(CuL_3)_2](CH_3COO)_2$	3430	1606	1520, 1349, 702

4. Electronic spectral studies:

Electronic transitions occur when electrons within the molecule or ion move from one energy level to another. The electronic spectra are concerned with the energy difference between the ground state and the excited electronic state. The energy required for the promotion of an electron from one orbital to another corresponds to the absorption bands in the near IR, visible and UV regions of the spectrum.

An examination of the spectra of the complexes indicates the presence of the bands in the UV region assignable to the transitions associated with the ligand. The spectra of all the complexes possess a high energy absorption band with maxima at 260nm which can be assigned to benzenoid $\pi \rightarrow \pi^*$ transition[38]. The band at 238nm present in the complexes is also attributable to the band of the benzene ring[39]. At low energies, the complexes exhibit a band in the case of $[Mn(CuL_1)_2]^{2+}$ and a shoulder in other two complexes at 350nm which is indicative of $\pi \rightarrow \pi^*$ transition originating mainly in the azomethine group[30]. The other bands in the UV region are assigned to the $n \rightarrow \pi^*$ transition of the ligand. In these complexes, a shoulder located in the range 520-560nm is assigned to the characteristic band of the copper(II) ion. The shoulder in this region suggests that the copper(II) is in the square planar geometry[40]. It is seen that the visible region of the spectrum is dominated by an absorption band centered at 480nm. This feature is assigned as being due to the ligand → manganese charge transfer transition[41]. In general, the manganese complexes show absorption in the visible regions at 400-480nm as band and at 560-600nm as shoulders[42]. The band is assigned to the L→ Mn charge transfer band and is found in the present complexes.

Table IV ESR spectral data of mono and trinuclear complexes

Complex		g_{II}	$g_{\perp}$	g_{ave}	A_{II} (mT)
CuL_1	RT	2.119	2.010	2.065	8.673
	LNT	2.219	1.980	2.109	19.33
CuL_2	RT	-	-	-	-
	LNT	2.203	1.988	2.096	18.922
CuL_3	RT	2.148	2.032	2.090	8.462
	LNT	2.249	2.000	2.124	16.02
$[Mn(CuL_1)_2](CH_3COO)_2$	RT	2.109	2.011	2.060	7.854
	LNT	2.196	1.975	2.085	19.02
$[Mn(CuL_2)_2](CH_3COO)_2$	RT	2.065	1.877	1.971	9.366
	LNT	2.005	-	-	9.740
$[Mn(CuL_3)_2](CH_3COO)_2$	RT	2.114	2.008	2.061	7.084
	LNT	2.226 (Cu)	2.039	2.132	19.28
		2.047(Mn)	1.994	2.023	3.047

5. Variable temperature ESR spectural studies:

The ESR spectra of the complexes are recorded in ethanol at room temperature and at liquid nitrogen temperature in the X band. The g_{II}, $g_{\perp}$ and A_{II} values are calculated and are presented in **Table-IV.**

At room temperature, the spectra of $[Mn(CuL_1)_2]^{2+}$ and $[Mn(CuL_3)_2]^{2+}$ complexes exhibit a 4 line hyperfine splitting signals which rare due to the interaction between the single d-electron of the copper and the copper-63 nuclear spin. But the $[Mn(CuL_2)_2]^{2+}$ complex shows a 6 line spectrum which is attributable to the manganese(II) ion. The four line hyperfine for the copper(II) ion is absent in this complex. At liquid nitrogen temperature, the ESR spectrum of $[Mn(CuL_1)_2]^{2+}$ complex shows the hyperfine splitting lines for the copper nucleus with the g values $g_{II} = 2.196$ and $g_{\perp} = 1.975$ and the hyperfine coupling constant value is $A_{II} = 19.02$mT. The spectrum exhibits some of the hyperfine splitting lines for the manganese nucleus but they are not well resolved and the g values could not be calculated. But the spectrum of $[Mn(CuL_3)_2]^{2+}$ complex exhibits two sets of hyperfine lines for the copper(II) and manganese(II) nuclei. The signal for the interaction of the electron with ^{63}Cu (I=3\2) nucleus appears as 4 line signals at the g values of $g_{II} = 2.226$ and $g_{\perp}=2.039$ and the hyperfine coupling constant $A_{II} = 19.28$mT and the 6 line hyperfine coupling to manganese and the spin Hamiltonian parameters are $g_{II} = 2.047$ and $g_{\perp} = 1.994$ and the A_{II} value of 3.047 mT in addition to the copper hyperfine signals. The presence of the two separate resonances for the copper(II) and manganese(II) nuclei suggest that the interaction between the terminal copper and the central manganese is weak. If there is a strong interaction between the metal ions, a septet of sextets is expected for the presently studied complexes. But the spectra of the complexes show two separate resonances for the individual ions. Hence interaction between the metal ions is weak[43]. But the frozen ethanol glass spectrum of $[Mn(CuL_2)_2]^{2+}$ complex seems to consists of only 6 line hyperfine and each line appears to be split into 3 lines for the manganese(II) nucleus at the g values of $g_{II} = 2.005$ and $A_{II} = 9.740$mT and it is seen that the $g_{\perp}$ line is getting overlapped. The hyperfine signal due to the copper nucleus is found to be absent.

6. Cyclic voltammetric studies:

The electrochemical behavior of the copper(II)-manganese(II) trinuclear complexes are studied by cyclic voltammetry. In the trinuclear complexes, the two copper atoms are found as the terminal copper centers and the manganese is the central one. Hence two reductions waves are expected for the reduction of Cu(II)→ Cu(I) and Mn(II)→ Mn(I) at different potentials. This electron transfer process can occur in two steps which is indicated as,

$Cu^{II}Mn^{II}Cu^{II} \leftrightarrow Cu^{I}Mn^{II}Cu^{I} \leftrightarrow Cu^{I}Mn^{I}Cu^{I}$

In all the complexes, the reduction potential corresponding to the reduction of Cu(II)→ Cu(I) is present in the -0.630 to -0.680 V range[44]. The reduction of Mn(II)→ Mn(I) is found to appear in the range of -0.960 V[45].

Conclusion:

The results of this investigation support the suggested structure of the trinuclear metal complexes. The IR and UV spectral studies suggest that the lone pair of electrons in the -NH groups is used to bind to the metal ions. The comparison of the IR spectra of the mononuclear and trinuclear complexes show the presence of acetate ions in the trinuclear complexes. Conductivity measurements indicate that the mononuclear complexes are non-electrolytes and the trinuclear complexes are dicationic. Cyclic voltammetric studies show the redox potentials for the copper(II), and manganese(II) ions, thus confirming the presence of these metal ions in the trinuclear complexes.

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