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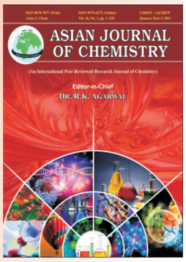

EPR Spectral, Magnetic and Electrochemical Studies of Copper-Vanadyl Trinuclear Complexes

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In this paper, we report the synthesis and characterization of several amben- and amben-type ligands and their copper-vanadium trinuclear complexes, which are derived from 2-aminobenzaldehyde and several diamines. The complexes are characterized by variable temperature EPR spectral, magnetic studies and cyclic voltammetric studies. The complexes are found to have the formula $[VO(CuL)_2]SO_4$. The EPR spectral and magnetic studies suggest the weak interaction between the terminal copper ions and the central oxovanadium(IV) ion. Cyclic voltammetric studies confirm the presence of copper and vanadium ions in the complexes.

Keywords: Schiff base complexes, Vanadium complexes, Trinuclear complexes, *o*-Aminobenzaldehyde.

INTRODUCTION

Vanadium is actually known as a trace element, essential for higher organisms although deficiency symptoms in humans have not yet been clearly identified[1]. The coordination chemistry of vanadium is of great current interest because of the discovery of its presence in abiotic as well as in biotic systems[2,3]. Another important impetus to the coordination chemistry of vanadium in the context of medical application has arisen from the ability of vanadium complexes to promote the insulin mimetic activity in pathophysiological state of diabetes mellitus in humans[4-7]. This biological and catalytic relevance of vanadium has promoted the synthesis of model vanadium compounds containing O, N donor ligands. Schiff bases which are condensation products of primary amines and aldehydes/ketones and their metal complexes have a variety of applications in biological, clinical and analytical fields[8]. It has been reported that the structure of the substituent bonded to the imino nitrogen affects the coordination geometry of the complex[9]. Several trinuclear Schiff base complexes derived from 2-amino benzaldehyde and diamines are reported[9-11].

The present study aims to prepare trinuclear copper-vanadyl Schiff base complexes and characterize the prepared complexes by using EPR spectral, magnetic and cyclic voltammetric studies.

EXPERIMENTAL

All chemicals used in the present study are of AR grade and used as received without further purification. The solvents are of spectroscopic pure. All the trinuclear complexes prepared are characterized by elemental analysis, IR and UV spectral studies, conductivity studies and reported by Annapoorani *et al.*[11]. In the present paper, the complexes are characterized by Variable temperature electron paramagnetic resonance spectral studies, magnetic measurements and cyclic voltammetric studies. The EPR 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. The hyperfine coupling constant values ($A_{\parallel}$) are directly measured from the spectra. The two major components of g-tensor, $g_{\parallel}$ and $g_{\perp}$ values are computed from the spectra. Since the operating frequency ν of the EPR spectrum is known, from the knowledge of the field values $H_{\parallel}$ and $H_{\perp}$, the g values have been calculated using the following relations.

$$g_{\parallel} = \frac{h\nu}{\beta H_{11}} \qquad g_{\perp} = \frac{h\nu}{\beta H_{\perp}}$$

Magnetic susceptibilities of solid compounds are measured from 79 to 296 K on a vibrating sample magnetometer Model-155 at USIC, University of Roorkee. The corrections for the diamagnetism are estimated from Pascal's constants[12]. Cyclic voltammetric studies on complexes are carried out using a Model ECDA-001, Basic electrochemistry system. HPLC grade acetonitrile solvent is employed for the cyclic voltammetric studies with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. A three electrode configuration is used, comprising glassy carbon or platinum working electrode, platinum wire counter electrode and Ag/AgCl reference electrode. Hydrogen gas is bubbled through the solution before starting the experiment.

Synthesis of Schiff bases: The Schiff bases used in the present study are prepared by reacting 2-aminobenzaldehyde with various diamines such as 1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane and 1,2- diaminobenzene (2:1 molar ratio) in ethanol[11]. The resulting reaction mixture was refluxed for 1 h. The yellow solid precipitate of Schiff base obtained is filtered, washed with distilled water, dried, recrystallized from ethanol and finally preserved in a desiccator. Yield: 58 %. Since 2-aminobenzaldehyde easily undergoes self condensation it could not be stored. It is prepared by the reduction of 2-nitrobenzaldehyde as and when required.

Preparation of copper(II)-vanadium(IV) trinuclear complexes {[VO(CuL$_1$)$_2$]SO$_4$, [VO(CuL$_2$)$_2$]SO$_4$, [VO(CuL$_3$)$_2$]SO$_4$, [VO(CuL$_4$)$_2$]SO$_4$}: The trinuclear complexes are prepared by refluxing mononuclear complexes with vanadyl sulphate in ethanol medium for 3.5 h[11]. The mononuclear complexes (CuL$_1$, CuL$_2$, CuL$_3$ and CuL$_4$) are prepared by refluxing various Schiff base ligands such as amben, ambpn, ambtn and amphen with copper perchlorate in ethanol medium for 1 h[9].

RESULTS AND DISCUSSION

Variable temperature EPR spectral studies: Variable temperature EPR spectral data (Table-1) has been used to indicate the overall couplings in copper(II)-oxovanadium(IV) trinuclear complexes and the spectra can be compared with the mononuclear copper complexes. The magnetic interactions involving the orbital angular momentum of the unpaired electron are the sole cause for the deviation of g-values from the free electron value of 2.002319. Thus larger the expectation value of the orbital angular momentum L, the greater is the shift in the g value. All the metal complexes containing an unpaired electron are expected to exhibit hyperfine splitting lines in the EPR spectra arising from the interaction of the unpaired electron with the metal nucleus. If more than one nucleus is present, the spectra could exhibit hyperfine splitting lines due to the interaction of the electron with all the nuclei.

EPR spectra of the copper(II)-oxovanadium(IV) trinuclear complexes in ethanol solution at room temperature exhibits a 4 line hyperfine signal for the interaction of the electron with the ^{63}Cu (I = 3/2) nucleus. At liquid nitrogen temperature, the hyperfine coupling of the electron to the ^{51}V (I = 7/2) has also been seen in [VO(CuL$_3$)$_2$]SO$_4$ complex. The spectrum of this complex exhibits two sets of hyperfine splitting signals for the interactions of electron with the copper(II) and oxovanadium(IV) nuclei. The signal for the interaction of the electron with ^{63}Cu (I = 3/2) nucleus appears as a 4 line hyperfine splitting with the following spin Hamiltonian parameters, $g_{II} = 2.453$, $g_\perp = 2.094$ and the hyperfine coupling constant (A_{II}) value of 11.019 mT and an 8 line hyperfine signal attributable to the coupling of unpaired electron with the nuclear spin of ^{51}V(I = 7/2) nucleus at the g values of $g_{II} = 2.027$ and $g_\perp = 2.022$ and the hyperfine coupling constant $A_{II} = 6.887$ mT. But the other three complexes exhibit only four line splitting for the copper nucleus. In all the complexes, the g_{II} values are greater than $g_\perp$ values suggest that the unpaired electron is localized in the $d_{x^2-y^2}$ orbital in the copper(II) ion[13,14]. The EPR spectra of the complexes taken in ethanol solutions, at room temperature show only a four line hyperfine splitting due to the interaction with copper atoms. This indicates that the two copper centers are very weakly coupled, if at all. The coupling between the copper and vanadium centers is also weak as indicated by the observation of the resonances of the individual ions separately[15]. Based on these observations, it can be suggested that there is a weak interaction between the terminal copper(II) and oxovanadium(IV) nuclei, which is also shown by magnetic susceptibility measurements.

Variable temperature magnetic susceptibility studies: Variable temperature magnetic susceptibility studies are performed on powdered samples of the trinuclear copper(II)-oxovanadium(IV) complex derived from 1,3-*bis*(2-aminobenzylideneamino)propane in the temperature range of 79 to 296 K. The magnetic susceptibilities are tabulated in Table-2.

The magnetic interaction between metal centers in the trinuclear species was explained by Kahn[16].

For an ABA trinuclear species, the spin Hamiltonian in zero field may be written as

$$H = -\frac{J}{2}\left(S^2 - S_{A1}^2 - S_{A2}^2 - S_B^2\right) - \frac{J'-J}{2}\left(S'^2 - S_{A1}^2 - S_{A2}^2\right)$$

TABLE-I
EPR SPECTRAL DATA OF MONO AND TRINUCLEAR COMPLEXES

Complexes		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
CuL$_4$	RT	-	-	-	-
	LNT	2.280	1.994	2.107	19.078
[VO(CuL$_1$)$_2$]$^{2+}$	RT	2.124	2.011	2.067	7.828
	LNT	2.214	1.990	2.102	19.146
[VO(CuL$_2$)$_2$]$^{2+}$	RT	-	-	-	-
	LNT	2.218	2.002	2.110	18.820
[VO(CuL$_3$)$_2$]$^{2+}$	RT	2.124	2.012	2.067	7.442
	LNT	2.453 (Cu)	2.094	2.273	11.019
		2.027(V)	2.022	2.025	6.887
[VO(CuL$_4$)$_2$]$^{2+}$	RT	2.225	2.005	2.113	18.490
	LNT	2.230	1.999	2.115	18.939

where S_{A_1}, S_{A_2} and S_B are the local spins, J and J′ are the interaction parameters and $S' = S_{A_1} + S_{A_2}$ and $S' = S' + S_B$

The relative energsies in zero field are expressed as,

$$E(S,S') = -\frac{J}{2}S(S+1) - \frac{J'-J}{2}S'(S+1)$$

S' varies by an integer value from 0 to $2S_A$ and for each S' values, S varies by an integer value from $|S'-S_B|$ to $S' + S_B$.

By applying the simplified Van Vleck formula, the magnetic susceptibility for an ABA trimer is,

$$\chi = \frac{N\beta^2}{3kt}\,\frac{\sum\limits_{S'=0}^{2S_A}\ \sum\limits_{S=|S'-S_B|}^{S'+S_B} g_{s,s'}^{2}\ S(S+1)\,(2S+1)\ \exp\left[-E\,(S,S')/\,kT\right]}{\sum\limits_{S'=0}^{2S_A}\ \sum\limits_{S'=|S'-S_B|}^{S'+S_B} (2S+1)\,\exp\left[-E\,(S,S')\,/\,kT\right]}$$

In the presently studied complex, the central V(IV) ion is linked to two Cu(II) ions through the nitrogen atom. The copper atom is in a square planar environment and the vanadium atom is in square pyramidal geometry. Since there is no direct interaction between the metal centers, the interaction between them is expected to be weak[17]. An acceptable fitting of the curve for the determination of the interaction constants J and J' is not obtained. The g values obtained are also not acceptable and a larger deviation is observed between the experimental and the calculated values. The magnetic moment values vary slowly as the temperature increases in the present case. If the interaction is strong, then the magnetic moment is expected be constant[18]. The slow variation of the magnetic moment indicates that the interaction is weak. The weak interaction between the metal centers is already observed in EPR spectral study.

TABLE-2
MAGNETIC SUSCEPTIBILITY VALUES
FOR TRINUCLEAR COMPLEX

Temperature (K)	$\chi_m T$ (cm^3 mol^{-1} K)
79	0.1597
90	0.1674
100	0.1723
110	0.1675
120	0.1743
130	0.1758
140	0.1786
150	0.1822
170	0.1842
190	0.1869
210	0.1952
230	0.2068
250	0.2188
270	0.2157
296	0.2183

Cyclic voltammetric studies: The macrocyclic ligands are known to stabilize unusual oxidation states of the transition metal ions. One of the ways in which this can be checked is to measure the redox potentials of the complexes. This is usually accomplished by employing electrochemical techniques such as polarography and cyclic voltammetry. To check the possibility of any such effect in the copper(II)-oxovanadium(IV) complexes, they are subjected to cyclic voltammetric studies. The redox properties of the complexes are investigated in acetonitrile solution at a glassy carbon/platinum electrode using tetrabutylammonium perchlorate as the supporting electrolyte, using a Ag/AgCl reference electrode. A platinum wire is served as the counter electrode. The cathodic and anodic peak potentials (E_{pc} and E_{pa}) obtained from the cyclic voltammograms are tabulated in Table-3. In the presently studied copper(II)-oxovanadium(IV) trinuclear complexes, the two copper atoms are in the terminal position and V=O group is in the central position. The terminal copper(II) ions are expected to undergo reduction to copper(I) and central V(IV) are reduced to V(III) and then to V(II) and oxidized to V(V). This electron transfer process can be represented as follows.

$$\begin{tikzcd} \mathrm{Cu^{II}\,V^{IV}\,Cu^{II}} \arrow[r, leftrightharpoons, "2e^-"] \arrow[d, leftrightharpoons, "e^-"] & \mathrm{Cu^{I}\,V^{IV}\,Cu^{I}} \arrow[r, leftrightharpoons, "e^-"] & \mathrm{Cu^{I}\,V^{III}\,Cu^{I}} \arrow[r, leftrightharpoons, "e^-"] & \mathrm{Cu^{I}\,V^{II}\,Cu^{I}} \arrow[r, leftrightharpoons, "e^-"] & {} \\ \mathrm{Cu^{II}\,V^{V}\,Cu^{II}} & & & & \end{tikzcd}$$

TABLE-3
CYCLIC VOLTAMMETRIC DATA
OF TRINUCLEAR COMPLEXES

Complex	E_{pa} (V)	E_{pc} (V)
$[VO(CuL_1)_2]SO_4$	-0.075	-
	-0.530	-0.590
$[VO(CuL_2)_2]SO_4$	+0.175	-
	-0.670	-0.570
	-1.2	-1.025
(Oxidation)	+0.145	+0.190
$[VO(CuL_3)_2]SO_4$	+0.120	+0.215
	-0.120	-0.310
	-0.610	-0.500
$[VO(CuL_4)_2]SO_4$	-0.550	-0.420
	-1.040	-0.690

It is observed that all the complexes exhibit one quasi reversible peak in the range of -0.500 to -0.650 V. The peak difference (DE_p) is 70 mV. Trinuclear copper(II) complexes also show peak in this region and was assigned to the reduction of two terminal copper centers. The same two terminal copper centers are present in the presently studied complexes and hence this peak may be due to the reduction of Cu(II)→Cu(I)[19]. In cathodic sweep, the quasi reversible wave occurring at -0.100 to -0.350 V is attributed to the reduction of $V^{IV} \rightarrow V^{III}$ and the wave at -1 V is for the reduction of $V^{III} \rightarrow V^{II}$. The oxidation peak for the oxidation of $V^{IV} \rightarrow V^{V}$ is found in the + 0.250 V range only in some of the complexes. This is also a quasi-reversible one. These assignments have been supported by Dutton *et al.*[20]. They investigated the redox properties of $V^{IV}O$(tsalen) (tsalen is N,N'-ethylene *bis*(thiosalicylidene-aminate). This complex shows two quasi reversible waves at - 0.24 and -1.29 V and are assigned to the reduction of $V^{IV} \rightarrow V^{III}$ and $V^{III} \rightarrow V^{II}$, respectively. An irreversible anodic wave at + 0.5 V is probably due to the $V^{IV} \rightarrow V^{V}$. The oxidation of $V^{IV} \rightarrow V^{V}$ is commonly observed in the 0.0 to + 1 V region for the oxovanadium(IV) complexes[21]. Since the reduction potential for both the copper and vanadium ions are present in the trinuclear copper(II) -oxovanadium(IV) complexes, the cyclic voltammetric studies of these complexes confirm the presence of these two metal ions.

Conclusion

EPR spectral and magnetic susceptibility studies suggest that there is a weak interaction between the terminal copper ions and the central oxovanadium(IV) ion. Cyclic voltammetric studies show the redox potentials for the copper(II) and oxovanadium(IV) ions, thus confirming the presence of these metal ions in the trinuclear complexes. Based on the above observations, the structure for the trinuclear complexes has been proposed (Fig. 1).

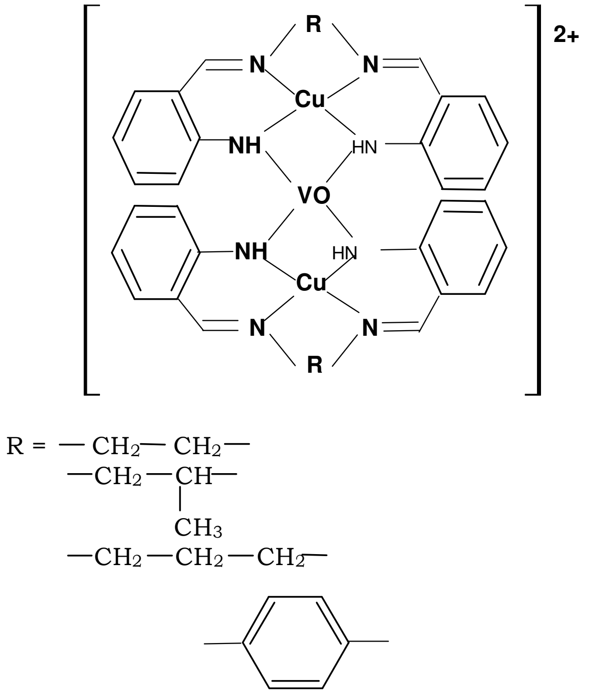

Fig. 1. Proposed structure of the trinuclear complexes

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