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# Synthesis And Spectroscopic Studies Of Trinuclear $N_4$ Schiff Base Complexes

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**Abstract:** Several amben type reduced Schiff bases have been prepared from the reaction of 2-aminobenzaldehyde with various diamines. The trinuclear copper (II) – vanadium (II) complexes of the Schiff bases in the form of their sulphate salt have been prepared from the mononuclear copper (II) complexes. The mononuclear copper(II) complexes and vanadyl sulphate reacts in the molar ratio of 2:1 to form the trinuclear complexes. The complexes are obtained as green colored powders and soluble in DMF, DMSO, acetone, acetonitrile, ethanol and methanol. These solid complexes are characterized by metal, C,H&N contents, conductivity measurements, infrared and electronic spectral studies. The details of these spectral and physical studies are discussed below.

**Key words:** Schiff base, vanadium complexes, trinuclear complexes, copper-vanadium complexes, 2-aminobenzaldehyde.

## Introduction:

Many Schiff bases and their complexes have been widely studied because of their industrial and biological applications.[1-3] Schiff base compounds (–RC=N–) are usually formed by the condensation of a primary amine with an active carbonyl. The cross-linking agents can also be derived from metal complexes with O, N or S ligands. For example, salicylates or anthranilates and aliphatic or aromatic amines can form strong five- or six-membered chelate rings which are able to produce metal containing cross-linking agents with the required properties.[4–7] Synthesis of oxovanadium(IV) complexes of Schiff bases derived by the condensation of 2-aminobenzaldehyde with various diamines (1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane) are characterized by elemental analysis, spectral data and electrochemical studies.[8] Rajavel and Krishnan[9] have reported the synthesis and characterization of oxovanadium(IV) complexes of the Schiff bases derived by the condensation of 2-aminobenzaldehyde with various diamines such as 1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane and discussed the elemental analysis, electrochemical studies and spectral data of the complexes. Erdal Canpolat et al[10] have reported the synthesis and characterization of a new 5-bromosalicylidene–*p*-aminoacetophenoneoxime and its complexes with Co(II), Ni(II), Cu(II) and Zn(II). Jian-ning Liu et al. [11] have reported synthesis and characterization of metal complexes of Cu(II), Ni(II), Zn(II), Co(II), Mn(II) and Cd(II) with tetradentate Schiff bases[12]. The present paper aims to prepare and characterize the Schiff base complexes derived from diamines and 2-aminobenzaldehyde.

## Experimental:

All chemicals used in this work are of A.R. quality. All the solvents used are of high purity and distilled in the laboratory before use. Conductivities of compounds are determined on Systronics direct reading conductivity bridge provided with conventional dip type platinised platinum electrodes. The cell constant is checked by measuring the specific conductance of aqueous solution of KCl at different concentrations of whose specific conductivity was known. The electronic spectra of the complexes in acetonitrile are recorded in HITACHI UV - 2001 spectrophotometer. IR spectra are recorded on Jasco - IR - 700 Double beam spectrophotometer in the range 4000 - 400 $cm^{-1}$ using KBr pellets and the complexes are analyzed for metal content[14], C, H & N.

### Synthesis Of Ligands:

The ligands are prepared by the reaction of 2-aminobenzaldehyde with various diamines such as 1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane and 1,2-diaminobenzene.

### Synthesis Of 2-Aminobenzaldehyde:

2-Aminobenzaldehyde is prepared by the reduction of 2-nitrobenzaldehyde using ferrous sulphate in an ammoniacal medium[15]. The product is then separated by steam distillation. 2-aminobenzaldehyde as obtained is converted into the tetraamines by condensing it with the appropriate diamine[16-18]. These ligands are then used for the synthesis of mononuclear complexes. By using these mononuclear complexes, trinuclear complexes are prepared.

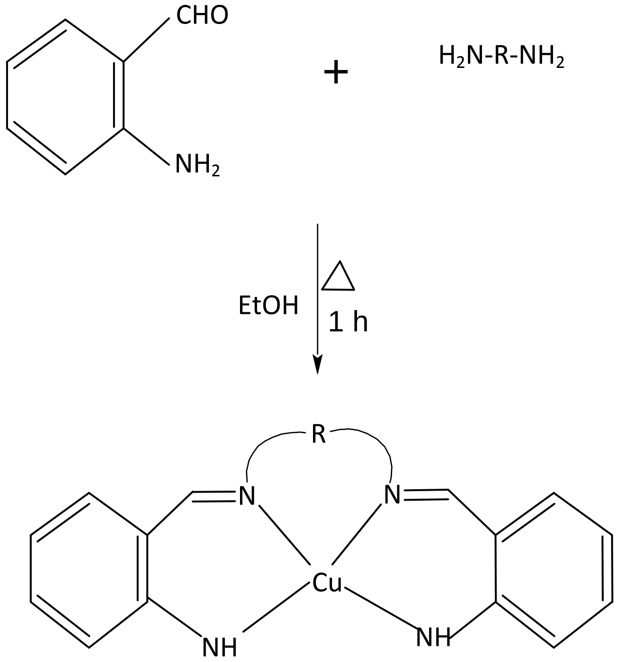
### Synthesis Of Mononuclear Complexes[17,19,20]:

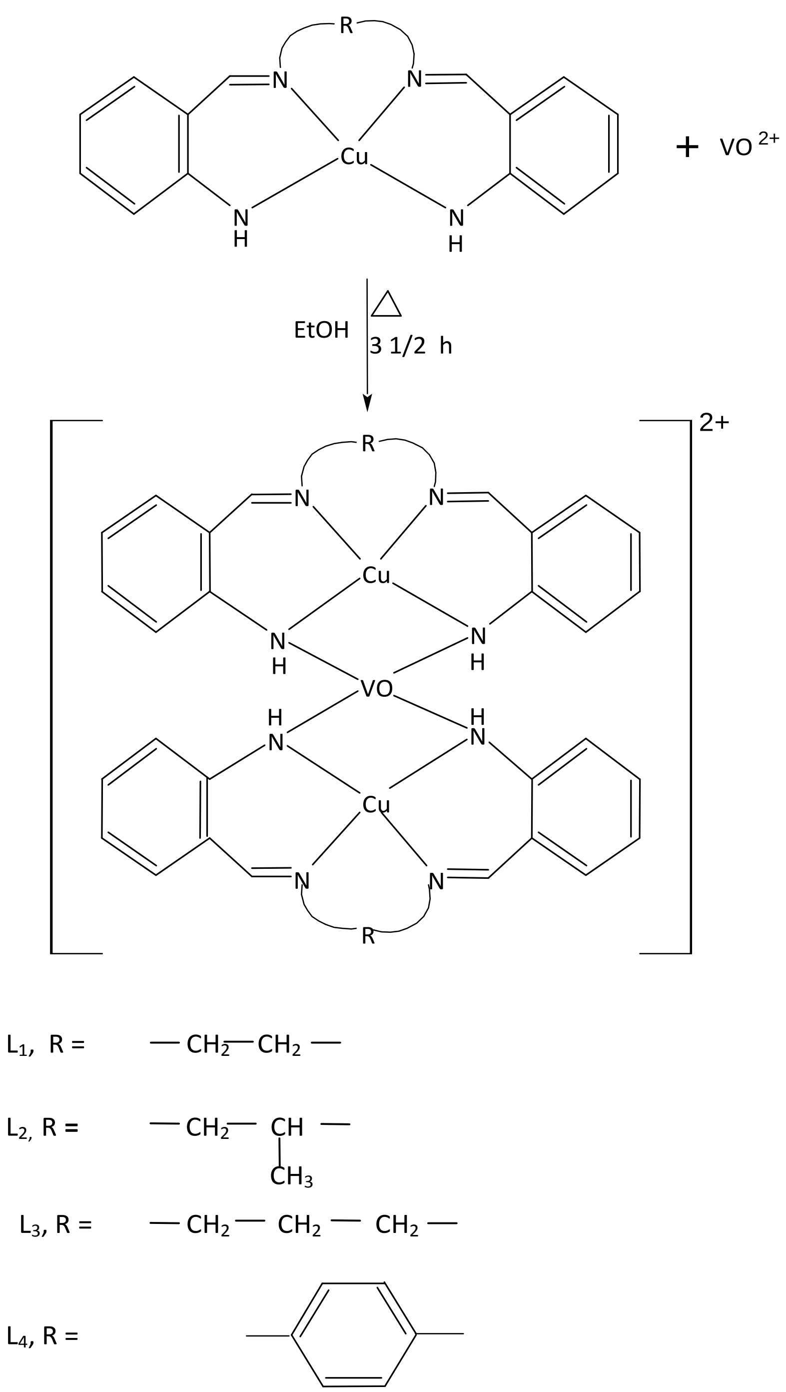
1 mole of the ligand ($L_1$) dissolved in absolute ethanol is taken and a sample of 1 mole of copper(II) perchlorate hexahydrate in ethanol is added slowly and stirred well. The reaction mixture is refluxed for 1½ hours. The solution is allowed to cool slowly. The complex deposited as a brown colored solid is filtered and dried. Similar procedure was followed for the preparation of all complexes using the ligands $L_2$, $L_3$ and $L_4$.

### Preparation Of Trinuclear Copper (Ii)-Oxovanadium(Iv) Complexes:

To the solution of 2 moles of mononuclear complex ($CuL_1$) dissolved in 30 mL of absolute ethanol, a solution containing 1 mole of vanadyl sulphate trihydrate dissolved in 25 mL of ethanol is added drop wise, during which time the colour of the solution changed from dark brown to green. The reaction mixture is refluxed for about 3½ hours. The mixture is allowed to cool and dark green colored solid formed is filtered off (scheme). A similar procedure was followed for the synthesis of trinuclear complexes using the mononuclear complexes $CuL_2$, $CuL_3$ and $CuL_4$.

**Scheme**





## Elemental Analysis:

The metal, C, H and N contents of the trinuclear copper(II)- oxovanadium(IV) complexes are given in Table I. It is known that the tetradentate Schiff base ligands (amben, ambpn, ambtn and ambphen) bind to divalent copper ions as diimines by losing one proton each from the two primary amine groups[19]. Hence the mononuclear copper (II) complex is formed as a neutral complex[17]. But when two mononuclear copper moieties combined with the third metal ion $VO^{2+}$, the trinuclear copper(II)-oxovanadium(IV) complex is formed as a dicationic species. The bond formed between the $VO^{2+}$ ion added and the two nitrogen atoms of the –NH groups involve the nitrogen (imine) lone pair of electrons. The observed metal, C, H and nitrogen contents agreed with such a formulation with a sulphate as counter ion as seen in the data reproduced in Table I.

## Conductivity Studies:

Conductivity studies on coordination compounds and the interpretation of the data in terms of possible structures date back to the commencement of systematic studies in coordination chemistry. The conductivity of the copper(II)-oxovanadium(IV) complexes are measured in acetonitrile solutions and the data are tabulated in

Table II. The copper(II)-vanadium(IV) complexes presently reported are electrolytes confirming the ionic structure proposed. It is found that the complexes in their sulphate form exhibit a 1:1 type electrolytic behaviour in solution. The results are compared with the literature values[21] in arriving at this conclusion. Thus the anion (i.e.) sulphate ion is present as a counter ion in solution.

**Infrared Spectral Studies:**

The infrared spectra of the complexes are recorded as KBr discs in the 4000 – 400 cm$^{-1}$ region. The important peaks are indicated in Table III. The striking feature common to all the spectra of the complexes is a broad band at 3400-3450 cm$^{-1}$. This band is assigned to –NH stretching frequency[22]. Commonly, the Schiff base complexes contain the characteristic strong band at 1600 – 1610 cm$^{-1}$ which is assigned to C=N bond stretches[23]. This band is present in all the spectra of the complexes indicating the presence of this group. The bands due to the vibrations of the aromatic ring are found in the 1450-1600 cm$^{-1}$ region. The other bands fall in the finger print region. When the spectra of the complexes are examined, it is found that the bands typically assigned to the -NH group is shifted to lower frequencies compared to the mononuclear copper(II) complexes, which are used as ligands for the preparation of these complexes. This shift is indicative of the involvement of the -NH group in binding to V = O group. Another feature observed in the IR spectra of the complexes is a strong band observed in the 1100 cm$^{-1}$ region. This strong band is ascribable to $ClO_4^-$ or $SO_4^{2-}$ ions[24]. Since the mononuclear complex is a neutral one and in the formation of the trinuclear complex, the metal salt used is vanadyl sulphate, sulphate ion is expected to be present as counter ion. The observation of the bands ascribable to the sulphate ion is in conformity with the elemental analysis and conductivity data. A further examination of the infrared spectra of the trinuclear copper(II)- oxovanadium(IV) complexes reveal a peak in the 960 – 980 cm$^{-1}$ region. This peak is typical of oxometal species and is assigned to V=O stretching of the vanadyl group[25]. The V=O stretching frequency is indicative of the ligand σ- and π-bonding[26]. Strong π bonding by the ligand is expected to shift the V=O stretching to lower frequencies. The position of the band observed in the present complexes indicates minimal π bonding. Thus the infrared spectra of the copper(II)-oxovanadium(IV) trinuclear complexes indicate the presence of sulphate ion as a counter ion, in addition to indicating the presence of vanadyl group. These bands are not observed in the mononuclear copper(II) complexes show the formation of trinuclear copper(II)- oxovanadium(IV) complexes.

**Table –I : Analytical data of trinuclear complexes**

| Complex | Molecular formulae | Found (Calculated) % | | | | |
|---|---|---|---|---|---|---|
| | | C | H | N | Cu | V |
| $[VO(CuL_1)_2]SO_4$ | $C_{32}H_{32}N_8Cu_2VOSO_4$ | 47.22<br>(46.94) | 3.81<br>(3.92) | 13.82<br>(13.69) | 15.35<br>(15.52) | 6.34<br>(6.23) |
| $[VO(CuL_2)_2]SO_4$ | $C_{34}H_{36}N_8Cu_2VOSO_4$ | 48.63<br>(48.34) | 4.25<br>(4.26) | 13.35<br>(13.23) | 15.12<br>(15.01) | 6.15<br>(6.02) |
| $[VO(CuL_3)_2]SO_4$ | $C_{34}H_{36}N_8Cu_2VOSO_4$ | 48.96<br>(48.34) | 4.13<br>(4.26) | 13.44<br>(13.23) | 14.98<br>(15.01) | 5.91<br>(6.02) |
| $[VO(CuL_4)_2]SO_4$ | $C_{40}H_{32}N_8Cu_2VOSO_4$ | 53.84<br>(53.93) | 3.50<br>(3.59) | 11.98<br>(12.25) | 13.01<br>(13.89) | 5.39<br>(5.38) |

**Table –II : Conductance data of the mononuclear and trinuclear complexes**

| Complex | Molar conductance (S cm$^2$ mol$^{-1)}$ | Type of electrolyte |
|---|---|---|
| $CuL_1$ | 68 | Non-electrolyte |
| $CuL_2$ | 61 | Non-electrolyte |
| $CuL_3$ | 76 | Non-electrolyte |
| $CuL_4$ | 74 | Non-electrolyte |
| $[VO(CuL_1)_2]SO_4$ | 145 | 1:1 |
| $[VO(CuL_2)_2]SO_4$ | 151 | 1:1 |
| $[VO(CuL_3)_2]SO_4$ | 143 | 1:1 |
| $[VO(CuL_4)_2]SO_4$ | 138 | 1:1 |

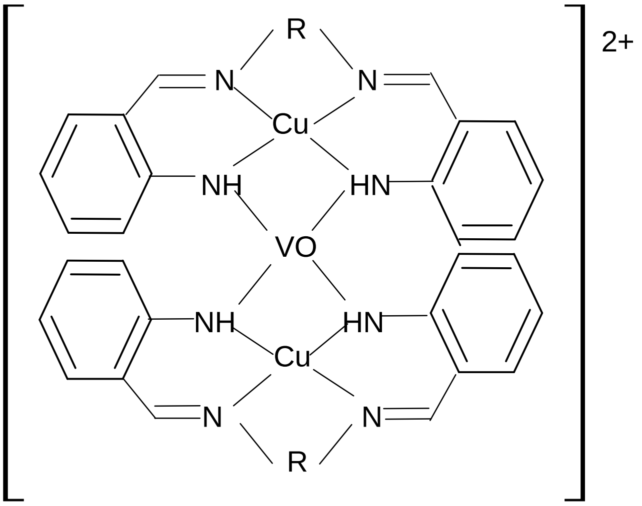
**Table III Infrared spectral data of mono and trinuclear complexes**

| Complex | -NH stretching $cm^{-1}$ | C=N $cm^{-1}$ | $SO_4^{2-}$ $cm^{-1}$ | V=O $cm^{-1}$ |
|---|---|---|---|---|
| $CuL_1$ | 3454 | 1608 | - | - |
| $CuL_2$ | 3451 | 1606 | - | - |
| $CuL_3$ | 3450 | 1610 | - | - |
| $CuL_4$ | 3456 | 1618 | - | - |
| $[VO(CuL_1)_2]SO_4$ | 3446 | 1606 | 1119 | 968 |
| $[VO(CuL_2)_2]SO_4$ | 3420 | 1606 | 1118 | 971 |
| $[VO(CuL_3)_2]SO_4$ | 3426 | 1610 | 1117 | 965 |
| $[VO(CuL_4)_2]SO_4$ | 3424 | 1618 | 1119 | 975 |

## Electronic Spectral Studies:

In acetonitrile solution, the spectra of the complexes contain two absorption bands at ~270 nm and 297 nm. These bands are due to the n → π* and π → π* intraligand charge transfer transitions[27]. The electronic spectra of all the complexes show a high energy absorption band with maxima at ~260 nm which can be assigned to benzenoid π → π* transition[28]. The spectra of the some of the complexes also exhibit a peak at ca. 350 nm which is attributed to the transition arising from the π-electrons present in the imine group[29]. The trinuclear complexes display a shoulder in the 550 - 575 nm region. This is characteristic for copper(II) ion, which may be assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$ transition suggesting square planar geometry[30]. Several schemes have been advanced to interpret the electronic spectra of oxovanadium(IV) complexes[31]. Three band spectrum has been predicted for five-coordinate oxovanadium(IV) complexes possessing square - pyramidal geometry. Ballhausen and Gray[32] proposed the energy level scheme for $[VO(H_2O)_5]^{2+}$. In this model, the unpaired electron resides in a largely non-bonding $d_{xy}$ orbital (Z-axis is taken as the vanadyl bond) with lobes pointing between the equatorial ligands. Pandey et al[33] recorded the electronic spectra of some oxovanadium(IV) complexes and found that three bands are observed in the regions 925-833 nm, 696-641 nm and 476-450 nm. These bands are assigned to $^2B_2 \rightarrow E$, $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2A_1$ transitions respectively. The spectra of the presently studied complexes in acetonitrile solution contain weak absorption peaks in the 893 nm, ~ 730 nm and 470-490 nm regions which are assigned to the d-d transitions within the $VO^{2+}$ ion in a five coordinate square pyramidal structure. The transitions involved in these absorptions are $^2B_2 \rightarrow E$, $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2A_1$. Hence the electronic spectra of the complexes prepared in the present study confirm the presence of copper(II) and oxovanadium(IV) ions in the complexes.

The structure proposed for the trinuclear copper(II)-oxovanadium(IV) complexes in accordance with the data presented is shown below.



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