

# Synthesis and Characterisation of Mixed Copper(II) Complexes with 2,2'-Bipyridine & 1,10-Phenanthroline

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Mixed chelate complexes of composition  $[\text{Cu}(\text{L})_2](\text{VO}_3)_2 \cdot n\text{H}_2\text{O}$ , where L = bipy or phen (bipy = 2,2'-bipyridine and phen = 1,10-phenanthroline),  $n = 1$  or 2 have been prepared and characterised through elemental analysis, molar conductance, magnetic susceptibility, electronic and infrared spectral data. The lattice constant and unit cell calculated with the help of powder diffraction pattern of complexes.

## INTRODUCTION

Many binary complexes of Cu(II) of 2,2'-bipyridine or 1,10-phenanthroline are reported with the different type of anion, *i.e.*  $\text{NO}_3^-$ ,  $\text{SCN}^-$ ,  $\text{ClO}_3^-$  etc.<sup>1</sup> In present investigation, we reported mixed chelate complexes of Cu(II) with two different neutral ligand containing primary and tertiary nitrogen donor atoms and new oxoanion metavanadate ( $\text{VO}_3^-$ ) which acts as anion in these complexes and its structure depends upon the hydrous or anhydrous nature of complex.

## EXPERIMENTAL

All chemicals used were of AnalaR, BDH grade. Copper metavanadate  $[\text{Cu}(\text{VO}_3)_2]$  has been prepared by the method reported in the literature<sup>2,3</sup>, and chemical composition has been checked by analysing copper as copper salicylaldehyde method and vanadium as silver vanadate method both gravimetrically by the recommended procedure<sup>4</sup>.

The complexes have been isolated by refluxing a mixture of bipy or phen ligand with copper metavanadate in molar ratio 1 : 2 in 100 ml EtOH, for *ca* 24 hrs. The product was filtered, washed with acetone 3-4 times and recrystallized by double distilled water. After recrystallisation, complexes washed with acetone and dried in vacuum over  $\text{P}_4\text{O}_{10}$  before analysis.

## RESULTS AND DISCUSSION

The analytical and physical data of the complexes are presented in Table 1. Elemental analyses were in good agreement with the proposed formula  $[\text{Cu}(\text{L})_2](\text{VO}_3)_2 \cdot n\text{H}_2\text{O}$ , where L = bipy or phen and  $n = 1$  or 2 for the complexes. These complexes show a high value of molar conductance 128.0 and 112.58  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  of bipy and phen respectively in conductivity water, it is indicating that the ionic nature of the comp-

lexes<sup>5,6</sup>. It is also supported by the IR spectral data. These complexes are paramagnetic at room temperature at 304K. The magnetic moment values ( $\mu_{\text{eff}}$ ) of complexes are 2.09 and 1.98 B.M. of bipy and phen complex respectively, which are in good agreement with the reported value of Cu(II) complexes in square planer (1.73–2.2 B.M.) corresponding to one unpaired electron.

TABLE I  
ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

Complex	Colour	% Found (Calcd.)				$\mu_{\text{eff}}$ B.M.	$\Sigma N$ $\text{ohm}^{-1}\text{cm}^2$ $\text{mol}^{-1}$
		Cu	V	N	H		
[Cu(bipy) <sub>2</sub> ](VO <sub>3</sub> ) <sub>2</sub> · H <sub>2</sub> O	Light	10.27	17.00	8.98	2.99	2.09	128.00
	Green	(10.71)	(17.18)	(9.44)	(3.06)		
[Cu(phen) <sub>2</sub> ](VO <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	Blue	9.35	15.20	7.93	1.75	1.98	112.58
		(9.66)	(15.49)	(8.51)	(1.83)		

bipy = 2,2' Bipyridine and phen = 1,10 phenanthroline.

Magnetic moment and conductance at 304K.

The electronic spectra of Cu(II) complexes showed one broad band at 685 nm for bipy complex and at 520 nm for phen complex. This absorption band may be assigned to the transition  ${}^2B_{1g} \rightarrow {}^2A_{1g}$ . The band positions suggest the square planer configuration for these complexes<sup>7–10</sup>.

The assignments of the IR spectra of the complexes have been made by comparing the spectra of the coordinated ligands with those of the free ones<sup>11</sup>. A positive shift in C=N and C=C stretching could be due to the tightening of the aromatic ring of the bidentate ligand in both the complexes<sup>12–15</sup>. The absorption due to plane motion of the ring hydrogen lies in the lower region. The negative shift of this band indicates the change in the size and polarising effect inside the coordinate molecule<sup>14</sup>. The complexes show a broad band around at 3500  $\text{cm}^{-1}$  due to OH stretching and a sharp band at 1620  $\text{cm}^{-1}$  due to H—O—H bending, indicate the presence of water of crystallisation<sup>16,17</sup>. The absorption for metavanadate ion in these complexes lies at *ca*  $\nu_5$  990,  $\nu_3$  890,  $\nu_1$  780 and  $\nu_5$  985,  $\nu_3$  875,  $\nu_1$  795  $\text{cm}^{-1}$  of bipy and phen complexes respectively, which is indicating that the ionic nature of metavanadate group present in these complexes<sup>18</sup>. The Cu—N stretching band present in these complexes around at 496–480  $\text{cm}^{-1}$ .

All the total reflections observed between 5 to 70°, the maximum intensity peak, were found at  $2\theta = 14.252$  corresponding to  $d = 7.8085 \text{ \AA}$  and at  $2\theta = 7.5225$  corresponding to  $d = 11.7423 \text{ \AA}$  for bipy and phen complexes respectively. The diffraction pattern was indexed by the inspection and trial method<sup>19,20</sup> for the tetragonal and orthorhombic crystal system. The unit cell for complexes have been found to tetragonal type

with lattice constant  $a = b = 14.8916 \text{ \AA}$  and  $c = 11.4922 \text{ \AA}$  for bipy complex, while orthorhombic type with lattice constant  $a = 20.6406 \text{ \AA}$   $b = 13.4200 \text{ \AA}$  and  $c = 11.6221 \text{ \AA}$  for phen complex. A careful comparison of the  $\sin^2 \theta$  values reveals that there is a good agreement between the calculated and the observed values (Tables 2 & 3)

TABLE 2  
X-RAY DIFFRACTION PARAMETERS OF  
 $\text{Cu}^{II}(\text{bipy})_2(\text{VO}_3)_2 \cdot \text{H}_2\text{O}$

A = B	= 0.00268;	a = b = 14.8916 $\text{ \AA}$ ;
C	= 0.0045;	c = 11.4922 $\text{ \AA}$ ;
Cell Volume	= 2548.5073 $\text{ \AA}^3$ ;	n = 4
$d_{\text{cal.}}$	= 1.54579 $\text{ gm cm}^{-3}$ ;	
$d_{\text{obs.}}$	= 1.69825 $\text{ gm cm}^{-3}$ .	

The observed values of the density of the complexes were found to be  $1.6983 \text{ g cm}^{-3}$  and  $1.4894 \text{ g cm}^{-3}$  for bipy and phen complexes respectively, these are  $n = 4$ , *i.e.* four molecules of the complex are present per unit cell (Tables 2 & 3).

TABLE 3  
X-RAY DIFFRACTION PARAMETERS OF  
 $\text{Cu}^{II}(\text{phen})_2(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$

A	= 0.001395;	a = 20.6406 $\text{ \AA}$ ;
B	= 0.0033;	b = 13.4200 $\text{ \AA}$ ;
C	= 0.0044;	c = 11.6221 $\text{ \AA}$ ;
Cell Volume	= 3219.285 $\text{ \AA}^3$	n = 4
$D_{\text{cal.}}$	= 1.35733 $\text{ gm cm}^{-3}$	
$D_{\text{obs.}}$	= 1.489286 $\text{ gm cm}^{-3}$ .	

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