

Synthesis and Properties of New Oxovanadium (IV) –copper (II) Complexes Containing Sulfide and 4,4'- bipyridine as Ligands

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Abstract: The present paper describes the preparation and characterization of V-Cu complex in which sulfide anions and 4,4'-bipyridine act as ligands. As sulfide source, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ has been used. The nature of the resulted compound depend strongly on the copper (II) to vanadium and metal to sulfide ratio as well as on the nature of the used ligand. The nature of the obtained compound with formula: $[\text{CuVOS}_2(4,4'\text{-dpy})(\text{OH})_2\cdot 2\text{H}_2\text{O}]_n$ has been established on the basis of elemental analysis, spectral properties. The electronic spectrum shows the presence of VO (IV) species of C_{4v} symmetry and Cu (II) in octahedral surrounding. The IR spectrum proves the presence of the coordinated 4,4'-bipyridine and presence of the vanadyl ion.

Keywords: 4,4'-bipyridine, copper, vanadium, sulfide anions, IR, VIS.

1. Introduction

The pharmacological and therapeutic agents available for the treatment of Wilson and Menkes diseases recently have been reviewed. Most of these pharmaceuticals are complexes of zinc or molybdenum which can act as ligands toward copper(II) ions. Also, MoS_4^{2-} and the oxy analogues, $\text{MoO}_x\text{S}_{4-x}^{2-}$, are involved as intermediates in the Cu-Mo antagonism that afflicts ruminants. MoS_4^{2-} is also clinically used for the removal of excess Cu from Wilson's disease patients. Only a few reports deal with V/Cu/S complexes.[1] These complexes were obtained from a reaction system containing thiovanadate in the manner used for Mo-S-Cu complexes. In most of these complexes, the structural motif of a four-membered heterocycle M_2S_2 was emphasised.

Sulfide and polysulfide complexes represent an important field of basic and applied inorganic chemistry. The chemistry of soluble sulfido transition metal complexes has been attracting significant attention, owing to their structures and properties with relevance to certain metalloenzymes. G.Christou [2] surveyed the reactivity of vanadyl containing materials in order to understand the pathways by which vanadyl impurities in crude oil are reduced/aggregated/sulfided to vanadium sulfides.

Binary or ternary vanadium sulfides may represent new materials with special magnetic and electro-optical [3] properties, and metal complexes containing vanadium-sulfur bonds can represent precursors for such systems. Müller and al. obtained trinuclear heterometallic V-Cu-S compounds $(\text{PPh}_3)_4\text{Cu}_3(\text{VS}_4)$ and $(\text{PPh}_3)_4\text{Cu}_3(\text{VS}_4)\cdot 2\text{CH}_2\text{Cl}_2$ [4]

Here we report on the synthesis of V-Cu complex in which sulfide anions and 4,4'-bipyridine act as ligands. Some spectral properties of the obtained complex are also presented.

2. Experimental

2.1. $[\text{CuVOS}_2(\text{C}_{10}\text{H}_8\text{N}_2)(\text{OH})_2\cdot 2\text{H}_2\text{O}]_n$. 0.25 g (1.25 mmol) $\text{Cu}(\text{CH}_3\text{COO})_2\cdot \text{H}_2\text{O}$ in 10 ml water was mixed with 0.39 g (2.5 mmol) 4,4'-dipyridyl and the obtained blue solution was mixed with 0.29 g(2,5 mmol) NH_4VO_3 and further with 0.3 g (1.25 mmol) $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ dissolved in 5 ml water. The obtained mixture was vigorous stirred for 1 hour and then heated to 80°C for two hours. After cooling to room temperature, the green product was separated, washed with hot water and dried in air. Anal. Calc. for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{S}_2\text{CuVO}_5$ (MW 420.851g/mol): C 28.53; H 3.35; N 6.65; S 15.23; V 12.10; Cu 15.09 %. Found :C 28.20; H 2.96; N 6.30; S 14.83; V 11.92; Cu 14.74%. IR (KBr) ν/cm^{-1} : 3437m, 1612s, 1417m, 1111s, 966vs, 836s, 815s, 548vs, 421w. $\Lambda_{\text{max}}=960\text{nm}$ ($\epsilon=1061\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$).

2.2. Physical Measurements

Analytical data were obtained by a Perkin Elmer model 240C elemental analyzer for C, N, and H and contain of the metal ions was determined with GBC SENSAA apparatus. Electronic absorption spectrum of the complex, recorded on freshly prepared MeCN solution was measured with Lambda 12 Perkin-Elmer spectrophotometer. Electric conductivity was measured in acetonitrile solution with a WTW LF 340 – A conductometer. IR spectrum in range 4000cm^{-1} - 400cm^{-1} was recorded on KBr pellet with a Perkin-Elmer 16PC FT-IR Spectrometer.

3. Results and Discussion

The heterometallic complex $[\text{CuVOS}_2(\text{C}_{10}\text{H}_8\text{N}_2)(\text{OH})_2 \cdot 2\text{H}_2\text{O}]_n$ has been obtained from aqueous solution as microcrystalline powder. The stoichiometry of the product depends on the initial vanadium to copper and metal to sulfide ratio. Thus, the change of the V:S ratio was obtained sulphur of copper.

The above compound has been obtained starting from vanadium to copper ratio of 1:2 and vanadium to sulfide anion of 1:2. Out of these values, mixtures of sulfides were obtained. The molecular formula of the obtained compound has been established on the basis of elemental analyses and some properties, as it results from the data below presented.

The complex is insoluble in water and in common polar organic solvents (i.e. $\text{C}_1\text{-C}_5$ alcohols, acetone and chloroform), lightly soluble in dimethylformamide, dimethylsulphoxide and acetonitril. The low molar conductivity value $40 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ of compound was measured on 10^{-3} M MeCN solution leads to the conclusion that compound is non-electrolyte. [5]

3.1. Electronic absorption spectrum

The electronic absorption spectrum of the compound is given in Fig. 1. In the visible region of the spectrum, a large band centered at 959 nm and with shoulders at 950 nm and at 975 nm was observed.

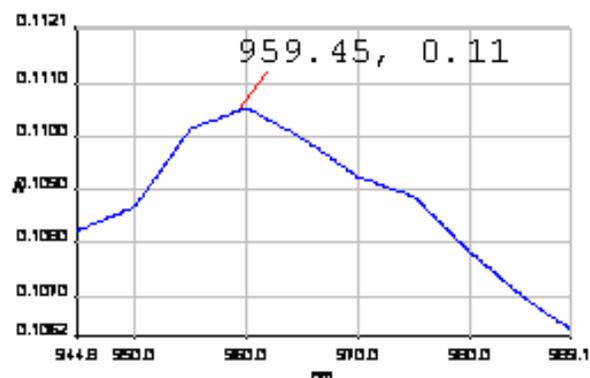


Fig. 1. VIS spectrum in MeCN of the complex.

The model suggested by Ballhausen and Gray[6] for oxovanadium(IV) ion having C_{4v} symmetry and that of the copper(II) ion in a distorted octahedral geometry [7] could explain these bands. In terms of Ballhausen and Gray's molecular orbit Scheme, the π -bonding between the vanadium $3d_{xy}$, $3d_{yz}$ orbitals and the oxygen $2p_x$, $2p_y$, orbitals in $\text{V}=\text{O}$ bond is largely enhanced when ligand coordination.[6]

3.2. Infrared spectrum

The infrared frequencies and their assignments are given in Table 1.

The $\nu(\text{OH})$ band at 3437 cm^{-1} shows the presence of coordinating water.

IR spectrum of the free ligand is characterized, in part, by prominent bands appearing at approximately 1596 and 1074 cm^{-1} due to $\nu(\text{CN})$ stretching modes, at 1531 cm^{-1} due to $\nu(\text{CC})$ and at 809 cm^{-1} due to $\delta(\text{CH})$ stretching mode. Some of them are shifted as a result of the coordination:

- the $\nu_s(\text{C-N})$ bands in the free ligand appear at 1596 and 1074 cm^{-1} are shifted to higher frequencies at 1612 and 1077 cm^{-1} upon complexation
- the $\nu_s(\text{CC})$ band in the ligand appears at 1531 cm^{-1} and in the complex this band appears at 1536 cm^{-1} .
- the $\delta(\text{CH})$ band in the ligand appears at 809 cm^{-1} and in the complex this band appear at 815 cm^{-1} .

The absence of absorption in the 2400 cm^{-1} , region where N-H stretching is expected, shows that 4,4-dpy is not protonated.

Thus, the very prominent absorption at 966 cm^{-1} is characteristic for the vanadyl stretching mode $\nu(\text{V}=\text{O})$. [8]

A new band appears at 554 cm^{-1} due to $\nu(\text{S-S})$ stretching.

TABLE 1. Characteristic bands in the IR spectrum of the complex

Ligand	Complex	Assignment cm^{-1}	
4,4'-dipyridyl			
	3437	$\nu_s(\text{H}_2\text{O})$	
	1596	1612	$\nu_s(\text{CN})$
	1531	1536	$\nu(\text{CC})$
	1074	1077	$\nu_s(\text{C-N})$
	993	1014	breathing
		966	$\nu_s(\text{V}=\text{O})$
	809	815m	$\delta(\text{CH})$
		554	$\nu_s(\text{S-S})$

ν_s = very strong; m = moderate; w = weak; ν_{asym} = asymmetric and ν_{sym} = symmetric

4. Conclusion

The elemental analyses data, VIZ and IR spectroscopy prove the reproducible character of the synthesis method and, at same time, the good definite nature of the new compound obtained.

The copper (II) ion is a d^9 system while VO^{2+} is a d^1 system. The copper (II) ion is softer than vanadium (IV) on the basis of the Hard-Soft Acid-Base model and prefers the more sulfur donors. The vanadium (IV) center prefers nitrogen and sulfur donors to about the same degree.

The electronic spectrum shows the presence of $\text{VO}(\text{IV})$ species of C_{2v} symmetry and $\text{Cu}(\text{II})$ in octahedral surrounding.

The IR spectrum proves the presence of the coordinated 4,4'-bipyridine and presence of the vanadyl ion and presence of the sulfide anions.

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