

Synthesis and Thermal Decomposition of the Coordination Polymer of 4,4'-bipyridine and Oxalate Anion with Cu (II) and VO(IV)

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Abstract: The coordination polymer $\{[\text{Cu}(\text{VO})_2(\text{C}_{10}\text{H}_8\text{N}_2)_{2.5}(\text{C}_2\text{O}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}]\}_n$ has been obtained and characterized on the basis of elemental analysis, by electronic and IR spectra, molecular electrical conductivity and thermal analysis. The electronic spectrum shows the presence of VO(IV) species of C_{4v} symmetry and Cu (II) in octahedral surrounding. The molar conductivity value in DMSO proves that the heteronuclear oxalate-compound is non-electrolyte. IR spectrum proves the presence of the coordinated 4,4'-dipyridyl and of the oxalate anion as a bisbidentate and bidentate ligand. Thermal analysis shows that decomposition occurs in three steps, the last one being the release of the oxalate chains. Based on these methods, a polymeric structure is proposed.

Keywords: 4,4'-bipyridine; anion oxalate; copper; vanadium; IR; VIS, thermal analysis.

1. Introduction

Synthesis and properties of transition metals complexes with carboxylates is extensively studied. In numerous works dealing coordination polymers, 4,4'-bipyridine has been extensively used in the construction of framework structures. Also, the interest in hetero-metal polynuclear complexes containing these types of ligands has risen in recent years. [1]

Structurally, the oxalate anion is well-known for its chelating coordination mode and for its symmetric bis-chelating bridging mode [2] its coordination to two metal ions affords a wide variety of polynuclear compounds with special magnetic properties. [3]

A number of Cu(II)-VO(IV) complexes with a bridging oxalato group have been synthesized [4] and the interest in the coordination chemistry of oxalate is largely due to the ability of this ion to generate homo- and heteropolynuclear complexes with various nuclearities or dimensionalities is well known. [5]

In this present paper we describe the synthesis and characterization of mixed ligand complex containing copper (II) and oxovanadium (IV) with 4,4'-bipyridine and oxalate anion.

2. Experimental

2.1. Synthesis of the complex

30 ml solution containing 10 mmol $\text{VO}(\text{C}_2\text{O}_4)$ was treated with 0.5 g (2.5mmol) $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and 0.78 g (5 mmol) 4,4'-dipyridyl dissolved in 20 ml water

and further, with 0.19 g (2.5 mmol) $\text{CH}_4\text{N}_2\text{S}$ dissolved in 10 ml water, under vigorous stirring.

The obtained mixture was heated to 75°C for three hours, and after cooling to room temperature, the green product was separated by filtration, washed with hot water and dried over CaCl_2 . Yield 1.4 g

Anal. Calc. for $\text{C}_{29}\text{H}_{30}\text{N}_5\text{CuV}_2\text{O}_{16}$ (MW 870.01g/mol)
%: C 40.04; H 3.48; N 8.05; V 11.71; Cu 7.30. Found %:
C 38.94 ; H 2.66; N 7.71 ; V 11.39; Cu 6.96.

IR (KBr) ν / cm^{-1} : 3420m, 3089 m, 3063 m, 1664 vs, 1644s, 1622s, 1487 m, 1413 s, 1353 m, 1310 m, 1257 m, 1213 m, 1015w, 987 s, 810 vs, 539 m, 486m, 424 m. UV-Vis: $\lambda_{\text{max}} = 796 \text{ nm}$ ($\epsilon = 57.1 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$).

2.2. Physical Measurements

Analytical data were obtained by a Perkin Elmer model 240C elemental analyzer for C, N, and H and for metal ions with GBC SENSAA apparatus. Electronic absorption spectrum of the complex was recorded on freshly prepared DMSO solutions on a Lambda 12 Perkin-Elmer spectrophotometer. Electric conductivity was measured in DMSO solution with a WTW LF 340 -A conductometer. IR spectrum in range $4000\text{cm}^{-1} - 400\text{cm}^{-1}$ was recorded on KBr pellet with a Jasco FT/IR - 430 Spectrometer. The thermal analysis were performed by a TGA/SDTA 851- LF 1100 Mettler apparatus. The mass of the investigated sample was 49.7189 mg. The measurements were made between room temperature and 750°C, at a heating rate of 5 °C/min, in ceramic crucibles under static atmosphere of air, with $\alpha\text{-Al}_2\text{O}_3$ as reference substance.

3. Results and discussion

The compound $\{[\text{Cu}(\text{VO})_2(\text{C}_{10}\text{H}_8\text{N}_2)_{2.5}(\text{C}_2\text{O}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}]\}_n$ has been obtained from aqueous solution as microcrystalline green powder, insoluble in water and in common polar organic solvents like C_1 - C_5 alcohols, acetone, acetonitrile and chloroform and slight soluble in dimethylsulphoxide. The low molar conductivity value of $23.02 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ measured on 10^{-4} M DMSO solution leads to the conclusion that compound is non-electrolyte. [6]

Experiments have shown that the nature of the product depends on the initial vanadium to copper and vanadium to oxalate ratio, temperature and the reaction time. Thus, the above compound has been obtained starting from vanadium to copper ratio of 2:1 and vanadium to oxalate of 1:1.5. This compound has been obtained using thiourea as sulfure source. Although the resulted compound did not contain sulfur, it could not be obtained in the absence of thiourea for reasons which remain unclear until now. Typical synthesis method is given in the experimental section. The molecular formulas of the obtained compound has been established on the basis of elemental analysis and some properties, as it results from the data below presented.

3.1. Electronic absorption spectrum

The electronic absorption spectrum of the compound is given in Figure 1.

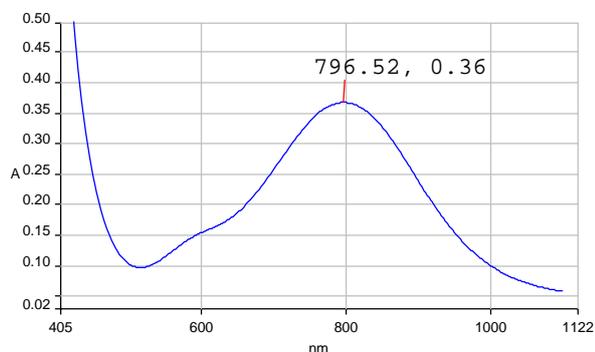
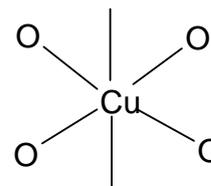


Fig. 1. VIS spectrum in DMSO of the complex

In the visible region of the spectrum, a large asymmetric band at 796 nm is observed. This can be the envelope of two other bands at lower and higher wave lengths respectively. The model suggested by Ballhausen and Gray [7] for oxovanadium (IV) ion having C_{4v} symmetry and that of the copper (II) ion in a distorted octahedral geometry [8] could explain these bands. The spectrum of copper (II) ion might be superimposed on that of VO (IV) in this region. According to Lever [7], the shoulder at near 600 nm was assigned to a ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ transition. This band is characteristic for carboxylates containing CuO_4 planar chromophore units and among these copper-copper interaction occurs so that each copper ion has an octahedral symmetry.

Its asymmetric shape may be explained as follows:



3.2. Infrared spectrum

The infrared spectrum of the obtained compound is very complex. However, specific bands attributable to the ligands can be identified. The broad band centered at 3420 and that at 3089 and 3063 cm^{-1} can be assigned to OH stretching modes of water molecules that are linked by hydrogen bonds. [9]

The IR spectrum displays the characteristic bands corresponding to the bidentate oxalato ligand: $\nu_{\text{as}}(\text{CO})$ at 1709 and 1664 cm^{-1} ; $\nu_{\text{s}}(\text{CO})$ at 1413 and 1257 cm^{-1} and that of $\delta(\text{OCO})$ at 762 cm^{-1} and the bisbidentate oxalato ligand: $\nu_{\text{as}}(\text{CO})$ at 1644 cm^{-1} ; $\nu_{\text{s}}(\text{CO})$ at 1353 and 1310 cm^{-1} and $\delta(\text{OCO})$ at 810 cm^{-1} . [10]

Typical stretching vibrational modes associated with the terminal $\text{V}=\text{O}$ and $\text{V}-\text{O}$ bonds are at 987 and 486 cm^{-1} .

In the complex, bands which appear at 1457, 1488 and 1622 cm^{-1} , can be tentatively assigned to the skeletal vibrations of the aromatic dipyridyl rings. The pyridine 'breathing' frequency appearing at 993 cm^{-1} in free ligand is shifted to 1015 cm^{-1} for the complex. This splitting proves the coordination of 4,4'-bpy to the metal atom by nitrogen.

In spectrum of the complex appears a medium band at 539 cm^{-1} which is attributed to combinations of MO with oxalate C-C stretching vibration.

4. Thermal Analysis

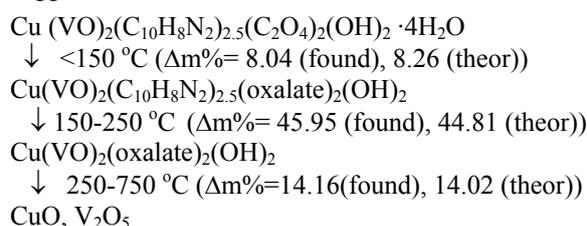
The thermal decomposition of the investigated complex proceeds in three temperature ranges:

- I.: below 150 °C
- II.: between 150 and 250 °C
- III.: between 250 and 750 °C

Below 150 °C as usually it could be suppose that the water molecules release the solid matrix.

At higher temperature two (150-250, 250-750 °C) steps could be observed on the TG curve.

According to the losses of mass in the case of the compound, the release of the bipyridil moiety could be suggested in the first step, while the change of the oxalate and the hydroxid anion take place in the second step. In these case the following decomposition scheme are suggested:



5. Conclusion

The compound $\{[\text{Cu}(\text{VO})_2(\text{C}_{10}\text{H}_8\text{N}_2)_{2.5}(\text{C}_2\text{O}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}]\}_n$ has been obtained.

The nature of the resulted compound depend on the initial vanadium to copper and vanadium to oxalate ratio, as well as on the nature of the used ligands.

The electronic spectrum shows the presence of VO(IV) has a distorted square pyramidal environment and Cu^{II} ion has a distorted octahedral environment.

IR spectrum proves the presence of the coordinated 4,4'-bipyridine and of the oxalate anion act as bisbidentate and bidentate ligand.

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