

SYNTHESIS, CHARACTERISATION AND THERMAL PROPERTIES OF $[\text{Cu}(\text{VO})_2(\text{C}_2\text{O}_4)_3(4,4'\text{-bpy})_2\cdot 2\text{H}_2\text{O}]$ A 2D POLYMER

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The heterometallic complex $[\text{Cu}(\text{VO})_2(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{C}_2\text{O}_4)_3\cdot 2\text{H}_2\text{O}]$ has been prepared and characterised by electronic and IR spectra, molecular electrical conductivity and thermal behaviour. A polymeric structure is proposed with oxalate and 4,4'-dipyridine acting as bridging ligands and VO(IV) of C_{4v} symmetry and Cu(II) in octahedral surrounding the oxalate anion V_{4h} .

Keywords: 4,4'-bipyridine, copper, IR, oxalate ligand, thermal analysis, vanadium, UV-Vis

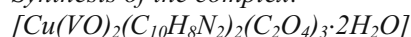
Introduction

Oxalate anion is one of the most studied ligand capable to bridge metal ions and to create inorganic polymers with mono- [1–3], bi- or tridimensional extended [4] structures with special magnetic [5] and catalytic properties [6]. Heterometallic copper(II)–oxovanadium(IV) oxalates have been the subject of recent studies [7] with the aim of elucidating the mechanism of exchange interaction between paramagnetic centres, bridged by polyatomic ligands, a common event in polymetallic systems. Bimetallic oxalate complexes in the copper(II)–oxovanadium(IV) system have been synthesised [8] and their ability to bind small molecules has been proved. Combining polymeric oxalate complexes with an organic donor can add complexity and interest to the resulting material [9–11]. Thus, organic multidentate amine can act as structure-directing agent [12] allowing a rational design of crystalline solids through their coordinating propensities and geometry [13]. They enhance the thermal stability of the structure and can be removed by calcinations. Recently, many reports have focused on the synthesis of inorganic-organic hybrid materials in the copper–vanadium system in which organic donor 4,4'-bipyridine (bpy) can act as neutral bridging ligand leading to compounds with a pillared layer structures [14]. As a continuous work in copper(II)–oxovanadium(IV) system, we report here the synthesis of a new hetero-trinuclear complex $[\text{Cu}(\text{VO})_2(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{C}_2\text{O}_4)_3\cdot 2\text{H}_2\text{O}]$. The compound

was characterised by chemical and elemental analysis, IR and UV-Vis spectrum, molecular electrical conductivity and thermal behaviour. The thermal behaviour of the investigated complex was studied, because in the last decade, this method had been proved as a powerful tool for characterisation of different transition metal complexes e.g. [15–19], amongs them 4,4'-bipyridine and oxalato complexes too [17–19].

Experimental

Synthesis of the complex:



0.29 g (1.5 mmol) $\text{Cu}(\text{CH}_3\text{COO})_2\cdot \text{H}_2\text{O}$ dissolved in 20 mL water was mixed with 0.46 g (3 mmol) 4,4'-dipyridyl and the obtained blue solution was poured under vigorous stirring into 36 mL water solution containing 5 mmol $\text{VO}(\text{C}_2\text{O}_4)$. The obtained mixture was heated to 60°C for 8 h. After cooling to room temperature, the solid green product was separated by filtration, washed with hot water and dried over CaCl_2 . Yield 0.89 g (70%).

Elemental analysis: calc. (%) for $\text{C}_{26}\text{H}_{20}\text{N}_4\text{CuV}_2\text{O}_{16}$ (MW 809.89 g mol⁻¹): C 38.56; H 2.49; N 6.92; V 12.58; Cu 7.85. Found: C 36.52; H 2.18; N 6.15; V 12.67; Cu 8.03.

Molar conductivity in DMSO, Λ_M (Ω⁻¹ mol⁻¹ cm²)=6.24.

IR spectra: (v/cm⁻¹): 3509m, 3306m, 3156s, 3083s, 3043s, 2885w, 1703vs, 1681vs, 1657vs,

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1636vs, 1577sh, 1482s, 1452m, 1405vs, 1376m, 1269vs, 1204s, 1102m, 1069m, 993sh, 962s, 895m, 819vs, 801vs, 716m, 644w, 613sh, 551s, 491s, 433m.

UV-Vis spectra: Λ_{\max} , nm (ϵ , L mol⁻¹ cm⁻¹)=797 (1500); 680sh; 630sh.

Physical measurements

Analytical data were obtained by a Perkin Elmer model 240 C elemental analyzer for C, N, H and the metal ions were determined with GBC SENSAA apparatus. Electronic absorption spectrum of the complex was recorded on freshly prepared DMSO solution on a Lambda 12 Perkin-Elmer spectrophotometer. Electric conductivity was measured on DMSO solution with a WTW LF 340-A conductometer. IR spectrum in range 4000–400 cm⁻¹ was recorded on KBr pellet with a Perkin-Elmer 16PC FT-IR spectrometer. The thermal analyses were performed with a computer-controlled MOM derivatograph. Ceramic crucible was used and α -Al₂O₃ served as a reference material.

Results and discussion

The compound [Cu(VO)₂(C₁₀H₈N₂)₂(C₂O₄)₃·2H₂O] has been obtained from aqueous solution as microcrystalline green powder. Experiments have shown that the product depends on the initial vanadium to copper and metal to oxalate ratio. Thus, the above compound has been obtained starting from vanadium to copper ratio of 2:1 and bipyridine to oxalate of 1:1.5. 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 compound is insoluble in water and in the common polar organic solvents like C₁–C₅ alcohols, acetone, acetonitrile and chloroform, slightly soluble in dimethylformamide and dimethylsulphoxide. The low value of molar conductivity in DMSO shows that the complex behaves as a nonelectrolyte in this solvent.

Information regarding the geometry of the metal ions has been obtained from the electronic spectrum. Thus, a band centered at 797 nm and two shoulders at lower wavelengths could be noticed. Such a spectrum may be explained by the model suggested by Ballhausen and Gray [20] for oxovanadium(IV) ion having C_{4v}. The spectrum of copper(II) ion with a distorted octahedral geometry [21] might be superimposed on that of VO(IV). The shoulder at 680 nm is tentatively assigned to a ²T_{2g}→²E_g transition, characteristic for carboxylates containing CuO₄ planar chromophore units and among these, copper–copper interaction occurs.

IR spectrum

The IR spectrum of the complex shows a broad absorption band centered at 3445 cm⁻¹, which is consistent with the presence of coordinated water molecules. The characteristic bands of the coordinated oxalate group can be noticed in the IR spectrum of the complex. The strong absorption at 1670 cm⁻¹ assigned to the $\nu_{\text{as(C-O)}}$ mode and the $\nu_{\text{sym(C-O)}}$ which appears as shoulders of medium intensity at 1342 and 1376 cm⁻¹ indicates that oxalate is present as bridging tetradentate ligand. However, the patterns of the $\nu_{\text{as(OCO)}}$ (1707sh cm⁻¹ and the width of the band at 1670 cm⁻¹), $\nu_{\text{s(C-O)+}\nu_{\text{C-C}}$ (1410vs cm⁻¹) and $\nu_{\text{s(C-O)+}\delta_{\text{O-C=O}}$ (1273vs cm⁻¹) support the presence of chelating oxalate. Additional, weak peaks can be noticed at 443 and 554 cm⁻¹ which can be tentatively assigned to $\nu_{\text{M-O}}$ mode combined with chelated ring deformation and $\nu_{\text{C-C}}$, respectively [22]. Bands resulting from skeleton vibrations of the aromatic pyridyl rings in the 1400–1600 cm⁻¹ region can be noticed. Also, the spectrum of the complex displays a doublet at 821 and 799 cm⁻¹, which originates from the band at 809 cm⁻¹ in the free *dpy* spectrum. This band is assigned to the out-of-plane vibration of the hydrogen atoms and its splitting denotes the presence of the coordinated *dipy* [23].

Thermal behaviour of the complex

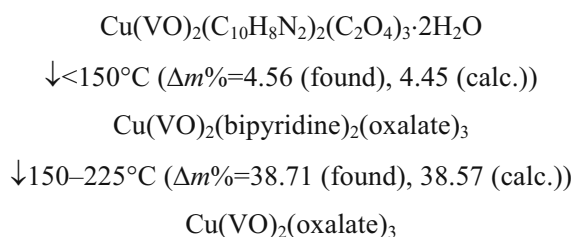
The thermoanalytical curves of the investigated complex are shown on Fig. 1.

The thermal decomposition of the investigated complex proceeds in three temperature range.

- I below 150°C
- II between 150 and 225°C
- III between 225 and 500°C

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

At higher temperature, two (150–225, 225–500°C) steps could be observed on the TG curves. According to the losses of mass in the case of the compound, the release of the bipyridyl moiety could be suggested in the first step, while the change of the oxalate to oxids take place in the second step. In this case the following decomposition scheme is suggested:



↓225–500°C ($\Delta m\%$ =24.77 (found), 24.70 (calc.))

CuO, V₂O₅

These data support the Cu(VO)₂(bipyridyl)₂(oxalate)₃·2H₂O composition of the complex.

In the second decomposition steps (225–500°C) the DTG and ΔT curves have fine structure. In the DTG curve there are two main peaks with several shoulders. The DTA curve consists from one large peak with one defined peak between 250 and 270°C and a shoulder around 280°C. The losses of masses between 250 and 270°C equal with amount of one mole CO. It is supposed that the CuO₄ planar chromophore units decompose firstly to CuCO₃ (split of the C–C bond in the oxalate ion). It is a normal case in the case of metaloxalates, that they decompose through the appropriate metal-carbonates. At higher temperature the remained vanadiumoxalate decomposes – probably – in the same way (by CO splitting) and the final products are the CuO and the V₂O₅.

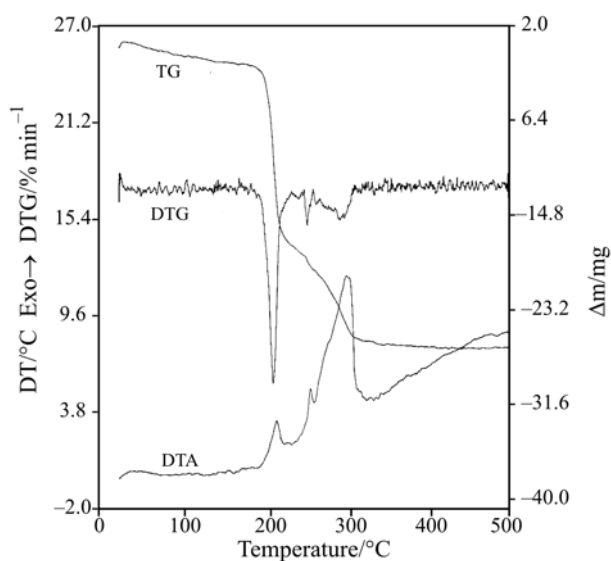


Fig. 1 The thermoanalytical curves of the investigated complex

Conclusions

The nature of the heteronuclear complex Cu(VO)₂(C₁₀H₈N₂)₂(C₂O₄)₃·2H₂O depends on the initial vanadium to copper and vanadium to oxalate ratio, as well as on the nature of the used ligands. The elemental analyses data, Vis and IR spectroscopy prove the reproducible character of the synthesis method and, at same time, the good definite nature of the obtained new compound. Based on the analytical and spectral properties, a polymeric nature is proposed, in which both oxalate and bipyridine act as bridging ligands. At least a terminal oxalate ligand

acts as a bidentate ligand, which closes a chelate ring. According to the published data [1–6, 14, 24] a polymeric structure is proposed.

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