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Structures and light-induced surface electron behavior of some oxo-vanadium complexes

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ABSTRACT

Four oxo-vanadium coordination complexes, $\{[V^{IV}_{0.5}V^{V}_{3}P_4O_{20}(OH)]\cdot 2(H_2en)\cdot 1.5H_2O\}_n$ (**1**), $\{[V^{IV}_{0.5}V^{V}_{4}P_4O_{22}(H_2O)]\cdot(H_2en)\}_n$ (**2**), $\{[V^{IV}_{1}V^{V}_{2}O_5(SO_4)_2(phen)_3(H_2O)_3]\cdot 6H_2O\}$ (**3**) and [VO(o-phta)(phen)(H$_2$O)] (**4**) (en = 1,2-ethanediamine, o-phta = o-phthalic group, and phen = 1,10-phenanthroline), were synthesized hydrothermally and the structures were determined through single-crystal X-ray diffraction. The surface electron behaviors and photo-electric conversion properties of the complexes were studied emphatically by SPS and UV–Vis absorption spectra. Structural analysis indicates that **1** and **2** are both oxo-vanadium phosphate polymers with V^{+4}/V^{+5} mixed valence states. Complexes **3** and **4** are vanadyl coordination supramolecules including organic ligands. There are all positive response bands within the range 300–800 nm in the SPS of the four complexes, which indicates that they all possess photo-electric conversion properties. There are three species of O → V LMCT response bands in the SPS and UV–Vis spectra of the complexes, because the coordinated oxygen atoms are from different groups. The similarities and differences of the spectra are compared and discussed.

1. Introduction

Oxo-vanadium coordination complexes are an active area of research [1]. There are many kinds of building blocks, such as $\{VO_4\}$, $\{VO_5\}$ and $\{VO_6\}$, in oxo-vanadium clusters, which may be connected to a discrete cluster, 1D chain, 2D layer or 3D framework by the mode of co-corner, co-border and co-planarity [2–5]. Moreover, vanadium ions can present different valences in complexes, such as V^{5+}, V^{4+}, V^{3+} and mixed valences. So far, many structural types of oxo-vanadium cluster complexes have been developed, e.g., Keggin structures, all of which display the complexity and diversity of vanadium chemistry [6–11]. At present, a number of 2D and 3D structures based on oxo-vanadium phosphate have been reported [12,13]. The syntheses of these coordination complexes not only enriched the structural chemistry of oxo-vanadium phosphates, but also modified the physical chemistry properties on a molecular level, so these complexes were widely applied to the fields of light, electricity, magnetism and catalysis. For example, Feng reported $[C_2N_2H_{10}]\cdot[(VO)_3(H_2O)(HPO_3)_4]\cdot H_2O$ with a 3D framework and it displayed paramagnetism in the temperature range 4–298 K [14]. Oxo-vanadium phosphate complexes can link with other metal ions forming hetero-nuclear complexes with novel structures. For example, the complexes $\{M(VO)_2(PO_4)_2\}_n$ (M = Co, Ni), possessing a 3D structure, were reported by Chamin-ade [15]. Recently, great interest has been given to oxo-vanadium coordination complexes with organic ligands because of their predominant catalysis and biological activities [16–19]. For instance, Pessoa and Correia reported a series of VO(Salen) complexes and found that they can be applied as catalysts in the oxidation of styrene and cyclohexene by H_2O_2 [20]; Xing reported the catalysis reactions by VO-tp complexes in phenol bromination [21]. In fact, some special functions of complexes are associated with their electron behaviors. Different arrangements and exchange of electrons may arouse changes of magnetism. The electron transitions between different components of complexes give rise to redox changes, which is the source of the catalysis. Electron transitions under light-inducement and separation or transfer of photo-generated charges may bring about a voltage on the surface, which is photo-electric conversion. Therefore, making sure of the surface electron behaviors of complexes has an important significance for deep research on the properties and applications of complexes. Surface photovoltage spectroscopy (SPS) is a high sensitive tool to investigate the change of surface electron behaviors by the reasons of speed, facility and without breakage (Eq. D) [22]. SPS not only relates to the electron transitions under light-inducement, but also reflects the separation and transfer of photo-generated charges, so it is significant in research on electron diversions of surfaces and interfaces. SPS has been applied in the studies of charge transfer in photo-stimulated surface interactions, dye sensitization processes, photo-catalysis, charge transitions between different phases and photo-electric conversion [23–25], but reports on

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surface electron behaviors of complexes by SPS are rare [26–28]. Our group has approached and reported the surface electron behaviors and photo-electric conversion properties of coordination complexes with nickel, manganese, iron, cobalt and copper ions [29–33], but that of oxo-vanadium complexes has not yet been reported.

In this paper, surface electron behaviors and photo-electric conversion properties of oxo-vanadium complexes were studied with SPS and UV–Vis absorption spectra. The SPS and UV–Vis absorption spectra were compared and analyzed.

2. Experimental

2.1. Materials and apparatus

All reagents in the experiment were A.R. Single crystal X-ray diffraction data were collected with a Smart 1000 APEX II diffractometer. IR spectra were recorded as KBr pellets with a JASCO FT-IR/480 spectrophotometer and UV–Vis diffuse reflectance spectra were recorded with a JASCO V-570 UV–Vis–NIR spectrophotometer. The elemental analyses were detected on PE-240C Analyzer and TLASMA-II ICP instruments. SPS were performed on a home-built surface photovoltage spectrophotometer.

2.2. Preparation of complexes

2.2.1. Preparation of $\{[V^{IV}_{0.5}V^{V}_{3}P_4O_{20}(OH)]\cdot 2(H_2en)\cdot 1.5H_2O\}_n$ (1)

NH_4VO_3 (0.35 g, 3.0 mmol) was dissolved in deionized water (10 mL) and a yellow solution was obtained. H_3PO_4 (5 mL) and ethanediamine (2 mL) were added to the solution, and the color turned green. The mixture was placed in a Teflon-lined stainless reactor and heated at 160 °C for 90 h. Blue crystals of **1** were obtained (0.33 g, 24.5%). *Anal.* Calc. for $C_8H_{48}N_8O_{45}P_8V_7$: C, 6.08; H, 3.06; N, 7.09; V, 22.56. Found: C, 6.06; H, 3.10; N, 7.06; V, 23.22%. IR (KBr/pellets) ν_{max}/cm^{-1}: 3432 (O–H); 3169 (N–H); 1631, 1532 (V=O); 1011 (P–O); 550–323 (V–O).

2.2.2. Preparation of $\{[V^{IV}_{0.5}V^{V}_{4}P_4O_{22}(H_2O)]\cdot(H_2en)\}_n$ (2)

V_2O_5 (0.09 g, 0.5 mmol) was added to deionized water (10 mL), resulting in a yellow turbid mixture. H_3PO_4 (1 mL) and ethanediamine (1.5 mL) were added to the mixture and it turned a light green color. The pH value was 3. The mixture was placed in a Teflon-lined stainless reactor and heated at 170 °C for 72 h. Blue crystals of **2** were obtained (0.08 g, 23.2%). *Anal.* Calc. for $C_4H_{24}N_4O_{46}P_8V_9$: C, 3.06; H, 1.54; N, 3.57; V, 29.19. Found: C, 3.05; H, 1.56; N, 3.58; V, 28.21%. IR (KBr/pellets) ν_{max}/cm^{-1}: 3585 (N–H); 3373 (O–H); 1620, 1534 (V=O); 1009 (P–O); 633–246 (V–O).

2.2.3. Preparation of $\{[V^{IV}_{1}V^{V}_{2}O_5(SO_4)_2(phen)_3(H_2O)_3]\cdot 6H_2O\}$ (3)

Phen (0.20 g, 1 mmol) was dissolved in ethanol (10 mL), which was added to a water solution (10 mL) containing $VOSO_4\cdot 6H_2O$ (0.14 g, 0.5 mmol). A green solution was obtained and the pH value was 4. The mixture was placed in a Teflon-lined stainless reactor and heated at 150 °C for 90 h. One month later, dark blue crystals of **3** were obtained (0.06 g, 31.9%). *Anal.* Calc. for $C_{36}H_{42}N_6O_{22}S_2V_3$: C, 38.34; H, 3.75; N, 7.45; V, 13.55. Found: C, 38.21; H, 3.77; N, 7.42; V, 13.13%. IR (KBr/pellets) ν_{max}/cm^{-1}: 3419 (O–H); 3065 (C–H); 1626 (V=O); 1585, 1519, 1428 (C⋯C); 1031, 969, 943 (S–O); 728 (V–N); 594, 392 (V–O).

2.2.4. Preparation of [VO(o-phta)(phen)] (4)

o-Phthalic acid (0.09 g, 0.5 mmol) and NaOH (0.04 g, 1.0 mmol) were dissolved in deionized water (10 mL). Under constant stirring, $VOSO_4\cdot 6H_2O$ (0.14 g, 0.5 mmol) in water (10 mL) was added to the solution and the color of the solution turned light blue. Phen (0.20 g, 1 mmol) in ethanol (5 mL) was added to the solution, and the solution turned dark green. The mixture was placed in a Teflon-lined stainless reactor and heated at 150 °C for 90 h. Brown crystals of **4** were obtained (0.18 g, 43.2%). *Anal.* Calc. for $C_{20}H_{14}N_2O_6V$: C, 55.96; H, 3.29; N, 6.53; V, 11.87. Found: C: 55.77; H, 3.31; N, 6.51; V, 12.28%. IR (KBr/pellets) ν_{max}/cm^{-1}: 3419 (O–H); 1606 (as-COO^-); 1563, 1518, 1480 (C⋯C); 1402 (s-COO^-); 1143, 1105, 1042, 975 (C–C, C–N, C–O); 475 (V–N); 408 (V–O).

2.3. Determination of crystal structures

X-ray diffraction data of the complexes were collected with a Bruker Smart APEX II diffractometer equipment with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293(2) K and empirical absorption corrections were applied. The structures were solved by the direct method and refined by the full matrix least-squares method on F^2. All the structural calculations and drawings were taken from the SHELXL-97 crystallographic software package [34,35]. Further details of X-ray structural analysis are given in Table 1. Selected bond lengths are given in Table 2 and selected bond angles are listed in Table S1 (Eq. A).

3. Results and discussion

3.1. Structural description of complexes

3.1.1. Structural description of $\{[V^{IV}_{1}V^{V}_{3}P_4O_{20}(OH)]\cdot 2(H_2en)\cdot 1.5H_2O\}_n$ (1)

The building unit of **1** is $[V^{IV}_{1}V^{V}_{3}P_4O_{20}(OH)]\cdot 2(H_2en)\cdot 1.5H_2O$ (Fig. 1). There are four crystallographic independent vanadium ions. V1–V3 are of +5 valence, with VO_5 cores, but their micro coordination environments are different. O-Atoms coordinating to V1 are from four different PO_4^{3-} groups and a terminal O-atom (=O). Three of the O-atoms coordinating to V2 and V3 are from different PO_4^{3-} groups and the others are μ-O and terminal O-atoms. V4 is of +4 valence and it is in a special position with an occupancy of 0.5 and coordinates (0.75, 0.25, 0.5). V4 is six-coordinated by O-atoms, four of which are from different PO_4^{3-} groups and the other two are from hydroxyl groups, leading to a distorted octahedral structure (Eq. B, Fig. S1). Furthermore, there are two protoned ethanediamine and 1.5 water molecules in the building unit. The vanadium ions are bridged by PO_4^{3-} groups and bridging-O (μ-O) in the crystal. There are three kinds of coordination fashions of PO_4^{3-} groups: (I) two oxygen atoms from the PO_4^{3-} groups are coordinated to vanadium ions, but the other oxygen atoms are not coordinated, such as $P1O_4^{3-}$ and $P2PO_4^{3-}$; (II) three oxygen atoms from the PO_4^{3-} groups are coordinated to vanadium ions, but the last one does not join in the coordination, such as $P3O_4^{3-}$; (III) all the oxygen atoms from PO_4^{3-} are coordinated to vanadium ions, such as $P4O_4^{3-}$ (Eq. B, Fig. S1).

The V1, V2 and V3 ions are linked by PO_4^{3-} and μ-O groups, forming a 2D layer structure in the *bc* plane (Eq. B, Fig. S2). A drawing of the polyhedron figure (VO_5 is square-pyramidal and PO_4 is tetrahedral. Eq. B, Fig. S3) shows that there are many regular quadrate holes.

Along the *a*-axis, the adjacent 2D layers are linked by V^{4+} ions that are not in the layer (Fig. 2). Thereby a 3D framework is formed. Two types of hydrogen bonds, N–H···O and O–H···O, are formed by free protonated ethanediamine and water molecules, which stabilize the structure.

3.1.2. The structural description of $\{[V^{IV}_{1}V^{V}_{4}P_4O_{22}(H_2O)]\cdot(H_2en)\}_n$ (2)

The building unit of **2** is $[V^{IV}_{1}V^{V}_{4}P_4O_{22}(H_2O)]\cdot(H_2en)$ (Fig. 3). There are five crystallographic independent vanadium ions in the building unit. V1–V4 are of +5 valence, while V5 is +4 valence. All the V^{5+} ions are five-coordinated by oxygen atoms, three of