Synthesis and Spectroscopic Characterization of Two New Dawson Sandwich Complexes: $\text{Na}_{18}[(\text{NaOH})_2(\text{VO})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2] \cdot 40\text{H}_2\text{O}$ and $\text{Na}_{18}[(\text{NaOH})_2(\text{VO})_2(\text{As}_2\text{W}_{15}\text{O}_{56})_2] \cdot 27\text{H}_2\text{O}$

MOHAMMAD HAKIMI*, MOHAMMAD REZA MOHAMMADI, AND SALMA BEHBOUPOUR

Chemistry Department, Payame Noor University, 19395-4697 Tehran, IRAN

hakimi@pnu.ac.ir

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Abstract: Reaction of the three vacant complex of $\alpha\text{-}[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ and $\alpha\text{-}[\text{As}_2\text{W}_{15}\text{O}_{56}]^{12-}$ with divalent cation of VO^{2+} in 1:1 mole ratio yields a previously unknown sandwich-type Wells-Dawson complex; $\text{Na}_{18}[(\text{NaOH})_2(\text{VO})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2] \cdot 40\text{H}_2\text{O}$ (represented as $\text{Na}_2(\text{VO})_2\text{P}_4\text{W}_{30}$) and $\text{Na}_{18}[(\text{NaOH})_2(\text{VO})_2(\text{As}_2\text{W}_{15}\text{O}_{56})_2] \cdot 27\text{H}_2\text{O}$ (represented as $\text{Na}_2(\text{VO})_2\text{As}_4\text{W}_{30}$). These complexes contain anions in which two divalent VO^{2+} cations with two Na^+ ions are symmetrically sandwiched between two $\alpha\text{-}[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ or $\alpha\text{-}[\text{As}_2\text{W}_{15}\text{O}_{56}]^{12-}$ groups leading to a "lacunary" sandwich complex. The anion complexes are isolated as sodium salts and characterized by elemental analysis, TGA, IR, ^{31}P NMR and UV-Vis spectroscopy.

Keywords: Synthesis, Polyoxometalate, VO^{2+} , Wells-Dawson structure.

Introduction

Polyoxometalates (POMs) form a distinctive class of inorganic metal-oxygen cluster compounds which is unique in its topological and electronic versatility and useful in fields as diverse as catalysis, analysis, biochemistry, medicine and material Science [1]. The class of POMs has been known for almost 200 years since the first structural details were revealed. Up to now, POMs chemistry continues to be a considerable focus in the ongoing research because large numbers of the novel structures of POMs and their properties [2]. Many of the fundamental properties of POMs that impact their applications, including elemental composition, solubility, redox potential(s), charge density, size, and shape, can be systematically altered to a considerable degree [3]. Within the class of polyoxoanions, those species based on trivalent Wells-Dawson fragments are particularly attractive. The first Wells-Dawson derivatives, $[\text{M}_4(\text{OH})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2]^{16-}$ ($\text{M} = \text{Co}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}$) [4] was reported by Finke et al. in 1983. Several years later, Bi et al. described the first arsenic(V) analogues of the Wells-Dawson type, $[\text{M}_4(\text{OH})_2(\text{As}_2\text{W}_{15}\text{O}_{56})_2]^{16-}$ ($\text{M} = \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$,

Cu^{2+} , Zn^{2+} , Cd^{2+}) [5]. These two families of complexes can be considered as "saturated", as they have in their structure the maximum number of d metal centers that can be "sandwiched" by the trivacant Wells–Dawson polyoxoanion $[\text{X}_2\text{W}_{15}\text{O}_{56}]^{12-}$ ($\text{X} = \text{As}$ or P).

The first example of a "unsaturated" sandwich-type species with less than four transition metals was described by Hill et al. [6]. The diiron(III)-substituted polyanion $[(\text{NaOH})_2\text{Fe}_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2]^{16-}$ is based on two Wells–Dawson fragments $[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ that sandwich a tetranuclear metal cluster, $[\text{Fe}_2\text{O}_{14}(\text{NaOH})_2]$, in which the two equivalent interior positions are occupied by Fe^{III} centers, and the two equivalent exterior positions are occupied by sodium ions in the solid state.

In this paper the reactions of $\alpha\text{-}[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ and $\alpha\text{-}[\text{As}_2\text{W}_{15}\text{O}_{56}]^{12-}$ with divalent VO^{2+} cation which lead to "unsaturated" sandwich-type complexes of the formula $\text{Na}_{18}[(\text{NaOH})_2(\text{VO})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2].40\text{H}_2\text{O}$ and $\text{Na}_{18}[(\text{NaOH})_2(\text{VO})_2(\text{As}_2\text{W}_{15}\text{O}_{56})_2].27\text{H}_2\text{O}$ are reported.

Experimental

Materials and methods

All reagents were commercially obtained and used without further purification. $\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ [7], $\alpha\text{-}[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ [4], $\alpha\text{-}[\text{As}_2\text{W}_{18}\text{O}_{62}]^{6-}$ [8] and $\alpha\text{-}[\text{As}_2\text{W}_{15}\text{O}_{56}]^{12-}$ [5] were prepared by the literature methods, and their purity was checked by infrared spectroscopy. V, Na, P, As and W analyses were performed by ICP-OES Simultaneous model VISTA-PRO. Infrared spectra (2% sample in KBr) were recorded on a FT-IR 8400 Shimadzu. ^1H NMR spectra were recorded on a FT-NMR model Bruker Brx 500 AVANCE using 85% H_3PO_4 as an external reference. The water contents of the complexes have been determined by Thermo Gravimetric Analysis (TGA) using TGA-50 Shimadzu apparatus. The electronic spectra were recorded on a Shimadzu UV-Vis Spectrophotometer.

Synthesis of $\text{Na}_{18}[(\text{NaOH})_2(\text{VO})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2].40\text{H}_2\text{O}$

VOSO_4 (0.25 g, 1.0 mmol) was dissolved in 60 mL of a 4 M NaCl solution with stirring. $\text{Na}_{12}\text{P}_2\text{W}_{15}\text{O}_{56}$ (4.0 g, 1.0 mmol) was then added and dissolved by heating and stirring. Any insoluble material was removed by hot filtration. The clear solution was cooled overnight at 5°C . The dark crystalline solid that formed was collected and dried at room temperature. The yield was 2.60 g of a dark crystalline solid (59.22%).

FT-IR (KBr disc, cm^{-1}): 1087 s (ν_{as} P-Oa), 1010 sh (ν_{as} P-Oa), 1041 m (ν_{as} P-O), 935 s (ν_{as} W-Od), 825 s (ν_{as} W-Ob-W), 723 s (ν_{as} W-Oc-W).

^31P NMR (500 MHz, D_2O): δ -15.0 (s, P(2)) ppm; δ 72.6 (b, P(1)) ppm.

Elemental Analysis: $\text{Na}_{18}[(\text{NaOH})_2(\text{VO})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2].40\text{H}_2\text{O}$ (8770.94 $\text{g}\cdot\text{mol}^{-1}$); Na 4.68 (Calcd. 5.51); P 1.27 (1.41); V 1.22 (1.16); W 63.31 (62.90).

Electronic Spectrum (H_2O , λ_{max} nm)/ ϵ ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 466/2750 ($\text{O}\rightarrow\text{V}$), 634/943.75 (d-d).

Synthesis of $\text{Na}_{18}[(\text{NaOH})_2(\text{VO})_2(\text{As}_2\text{W}_{15}\text{O}_{56})_2].27\text{H}_2\text{O}$

VOSO_4 (0.25 g, 1.0 mmol) was dissolved in 40 mL of a 3 M NaCl solution with stirring. $\text{Na}_{12}\text{As}_2\text{W}_{15}\text{O}_{56}$ (4.46 g, 1.0 mmol) was then added and dissolved by heating and stirring. Any insoluble material was removed by hot filtration. The clear solution was cooled overnight at 5°C . The dark crystalline solid that formed was collected and dried at room temperature. The yield was 2.42 g of a dark crystalline solid (55.49%).

FT-IR (KBr disc, cm^{-1}): 948 s (ν_{as} W-Od), 871 m (ν_{as} W-Ob-W), 817 m (ν_{as} W-Ob-W), 709 s (ν_{as} W-Oc-W).

Elemental Analysis: $\text{Na}_{18}[(\text{NaOH})_2(\text{VO})_2(\text{As}_2\text{W}_{15}\text{O}_{56})_2].27\text{H}_2\text{O}$ (8712.59 $\text{g}\cdot\text{mol}^{-1}$); Na 5.58 (Calcd. 5.54); As 3.3 (3.44); V 1.86 (1.17); W 63.1 (63.32).

Electronic Spectrum (H_2O , λ_{max} nm)/ ϵ ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 476/2350 ($\text{O}\rightarrow\text{V}$), 635/835 (d-d).

Result and Discussion

The molecular formula has been determined by elemental analysis and TGA. The elemental analysis for Na, P, W and V establishes the empirical formula as $[\text{Na}_{10}\text{P}_2\text{W}_{15}(\text{VO})\text{O}_{56}]_x$. The TG curve of the title compound shows weight loss processes in the range of 25–200°C, giving a total loss of 8.141% of its initial weight, which corresponds to the release of 40 hydration water molecules.

IR Characterization

The IR spectra of $\text{Na}_2(\text{VO})_2\text{P}_4\text{W}_{30}$ is shown in Figure 1. Except the W-O or W-O-W bands which appear at low wave numbers ($<1000\text{ cm}^{-1}$), IR spectra of phosphorus centered polyoxotungstates are characterized by well separated P-O stretching vibrations which are observed between 1200 and 1000 cm^{-1} .

The vibration modes of the unperturbed PW_9 moiety are nearly invariant, at 1087 cm^{-1} (strong) and 1010 cm^{-1} (low). For the perturbed subunit PW_6 , the number of IR absorption bands and their position depend on the interaction of the addenda atoms with the free oxygen (O_{ter}) of the phosphate group. Hence, the high-wave number band of P_2W_{15} at 1130 cm^{-1} , which can be ascribed to $\nu(\text{P-O}_{\text{ter}})$, moves to lower frequency in the sandwich complexes where the P-O bond has lost its double-bond character; it corresponds to the medium-intensity band which appears between the PW_9 bands, at 1041 cm^{-1} [9].

The $\nu_{\text{as}}(\text{W=O})$ vibration band is broader in the complexes spectra than the corresponding band in the ligand spectra because of its superposition with the stretching vibration $\nu_{\text{as}}(\text{V=O})$ [10].

Figure 1. IR spectrum of $\text{Na}_2(\text{VO})_2\text{P}_4\text{W}_{30}$ and $\text{Na}_2(\text{VO})_2\text{As}_4\text{W}_{30}$.

³¹P NMR Characterization

The ³¹P NMR spectrum of a sandwich complex may present either four or two resonances depending on the symmetry of the framework; in symmetrical complexes (C_{2h} symmetry) the two P₂W₁₅ moieties are equivalent and two bands at most can be observed.

As it is usual for such paramagnetic sandwich complexes, two markedly different types of ³¹P resonances are observed (Figure 2): the P(2) atoms in the {PW₉} subunits, far from the paramagnetic centers, give relatively narrow line at -15.0 ppm, while the P(1) atoms, close to the TM sheet, give broad and deshielded signal (72.6 ppm) [11].

Figure 2. ³¹P NMR spectrum of Na₂(VO)₂P₄W₃₀.

Electronic Spectrum

The visible electronic spectrum of the complex (Figure 3) show a relative stronger absorption at 466 nm and a band with a shoulder at 634 nm. The strong absorptions correspond to the V^{IV} charge transfer transitions [12]. The band for V^{IV} ion d-d transitions is observed at 634 nm [13].

Figure 3. UV-Vis spectrum of Na₂(VO)₂P₄W₃₀.

The molecular formula has been determined by elemental analysis and TGA. The elemental analysis for Na, As, W and V establishes the empirical formula as $[\text{Na}_{10}\text{As}_2\text{W}_{15}(\text{VO})\text{O}_{56}]_x$. The TG curve of the title compound shows weight loss processes in the range of 25-200°C, giving a total loss of 5.652% of its initial weight, which corresponds to the release of 27 hydration water molecules.

Figure 4. UV-Vis spectrum of $\text{Na}_2(\text{VO})_2\text{As}_4\text{W}_{30}$.

IR Characterization

As expected, the IR spectra of the sandwich-type complex is very similar to that of the trivacant lacunary $\alpha\text{-}[\text{As}_2\text{W}_{15}\text{O}_{56}]^{12-}$, except for the splitting of the asymmetry stretching vibration of $\text{W}-\text{Oc}-\text{W}$ (Oc is the edge sharing oxygen) (Figure. 1). This is attributed to the presence of the divalent cations (directly bound to the terminal oxygen of an edge shared pair of WO_6) [14]. Also all of the characteristic vibrational frequencies decrease compared with those of $[\text{As}_2\text{W}_{18}\text{O}_{62}]^{6-}$, which is attributed to the increase of the negative charges of the anions [5]. The $\nu_{\text{as}}(\text{W}=\text{Od})$ vibration band is broader in the complexes spectra than the corresponding band in the ligand spectra because of its superposition with the stretching vibration $\nu_{\text{as}}(\text{V}=\text{O})$ [10].

Electronic Spectrum

The visible electronic spectra of the complex (Figure 4) show a relative stronger absorption at 476 nm and a band with a shoulder at 635 nm. The strong absorptions correspond to the V^{IV} charge transfer transitions [12]. The band for V^{IV} ion d-d transitions is observed at 635 nm [13].

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