

Hydrothermal Synthesis and Physical Studies of Cobalt Substituted Trilacunary Polyoxotungstates

Rajarshi Chatterjee*

*Assistant Professor, Department of Chemistry, Bidhannagar College, Saltlake, Kolkata-64
Email: rajuchacha.2009@gmail.com

Abstract

In order to enrich structural chemistry of polyoxometalates and further expand or optimize their applications, researchers have started to design and construct functionalized POMs. In this article, one pot synthesis of a new Co-substituted Keggin-type polyoxometalate (POM) was successfully executed under hydrothermal conditions. The research performed here deals with the synthesis and spectral characterization of novel POMs and the investigation of their physicochemical properties.

Keywords: polyoxometalates, hydrothermal syntheses, transition metal substituted POM.

Introduction

The last decade has seen increasingly rapid advances in the field of transition metal substituted polyoxometalates owing to their intriguing structural diversity as well as their special properties applicable to magnetism, catalysis, medicine, or materials science.[1] Variety of lacunary POMs, are mostly derived from Keggin and Wells-Dawson polyoxotungstates. Here we are working on trilacunary phosphotungstate $[PW_9O_{34}]^{9-}$ which can constitute a large class of rigid diamagnetic multidentate inorganic ligands by binding transition metal ions (d- or f-block) through oxo, hydroxo or aqua bridge groups. [2,3] Furthermore, lacunary (vacant) heteropolytungstates are known to act as all-inorganic, diamagnetic ligands for various transition metal ions. [4,5] In particular, trilacunary polyanions have a high tendency to stabilize cationic, multinuclear metal-oxo assemblies, leading to compounds with interesting and unusual electronic and magnetic behavior. They not only assist in stabilizing and bridging of metal ions, but also function as diamagnetic tungsten-oxo capping fragments to isolate and embed the magnetic clusters in the POM frameworks. Formation of POMs in aqueous solution is highly dependent on divergent variables like pH, temperature, concentration, reaction medium, and counter-ions. [6] While solution chemistry of metal oxides is generally limited due to solubility

limitations, polyoxometalates are important exceptions that form a unique class of compounds of special properties. The insoluble metal oxides are composed of close packed arrangements of oxide ions which form infinite chains, sheets or three-dimensional lattices, whereas the polyoxometalates with 2–4 Co(II) centers encapsulated by lacunary Keggin and Wells–Dawson units have been reported. However it is still a great challenge to isolate some very interesting structural architecture, which has potential applications in aforementioned areas. There are different factors for instance a subtle change in pH, buffer capacity, ionic strength, cation size and type, and presence of auxiliary ligands etc. which play an important role in isolation of target molecules. [7] This review article shows a novel aggregation of cobalt in polyoxotungstate chemistry.

2. Experimental

2.1. Materials and methods

Reagent grade chemicals were used and all syntheses and studies were carried out in distilled water. Chemicals were readily available from commercial sources (Merck, India) and were used as received without further purification

2.1.1. Preparation of the precursor ligand $\text{Na}_9[\text{PW}_9\text{O}_{34}]$ (1)

$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ is dissolved in 30ml of water and then 85% H_3PO_4 is added drop wise with stirring (0.8ml) to achieve pH at 8. Later on glacial AcOH is added drop wise with vigorous stirring to achieve the final pH of 7.5. During addition of AcOH, large quantities of white precipitate are formed. The solution is then stirred for 1hr and the precipitate is collected & dried by suction filtration. The same synthetic procedure was followed as reported by Knoth et al [8]. It is mentioned as PW_9 (1) in the rest of the article.

2.1.2. Preparation of the complex $\text{Co}^{\text{II}}\text{PW}_9$ (2)

$\text{Na}_9[\text{A}-\alpha\text{-PW}_9\text{O}_{34}] \cdot 7\text{H}_2\text{O}$ (0.320 g, 0.125 mmol) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.820 g, 3.44 mmol) were stirred in 9 mL 0.5 mol/L sodium acetate buffer (pH = 4.8) for 10 min. The resulting solution was sealed in a 25 mL Teflon-lined stainless-steel autoclave and heated at 170 °C for 5 days. After cooling down to room temperature and washing with distilled water, purple block shaped crystals were obtained with a yield of 34% (based on $\text{Na}_9[\text{A}-\alpha\text{-PW}_9\text{O}_{34}] \cdot 7\text{H}_2\text{O}$)

2.3 Physical measurements

Elemental analyses were carried out using a Perkin–Elmer 240 elemental analyzer. UV-Vis spectra were recorded on a Perkin-Elmer Lambda 19 spectrometer using Teflon-stoppered quartz cells with a path length of 1 cm. IR spectra ($400\text{--}4000\text{ cm}^{-1}$) were recorded in KBr

pellets on a Perkin-Elmer Spectrum 10.4.1 series FTIR spectrophotometer. Variable-temperature susceptibility measurements were carried out in the temperature range 2–300 K on a magnetometer equipped with a SQUID sensor (Quantum Design MPMS-XL-5). Each sample was covered with the minimum amount of liquid eicosane (40 °C) in order to prevent crystallite phase change. The data were corrected for diamagnetic contribution from eicosane and for the diamagnetic contributions of the polyanions as deduced by using the Pascal's constant tables. Isothermal magnetization measurements at low temperature (2 K and 5 K) were performed up to a field of 5 T in the same apparatus.

3.1 Vibrational Spectroscopy

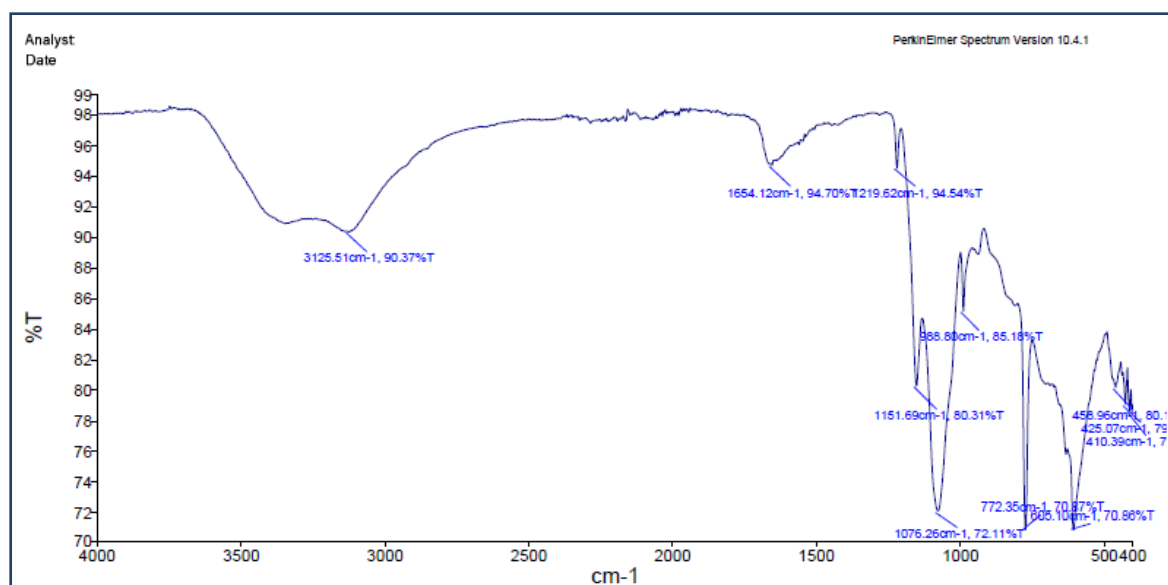


Fig-1. IR spectra of Co^{II}PW₉ complex

The IR spectra of **(1)** in **Fig-1** display the characteristic features of a typical trilaunary Keggin-type structure. That is why PW₉ shows usual five strong symmetric and asymmetric stretching frequencies at 1076 cm⁻¹ [$\nu_{as}(W=O_t)$ with terminal oxygen O_t], shoulder peak at 880 cm⁻¹ [$\nu_{as}(P-O_i)$ with internal oxygen atom which links P and W], 988 cm⁻¹ [$\nu_s(W-O_e-W)$ where O_e connects edge-sharing octahedra,], 772 cm⁻¹ [$\nu_s(W-O_c-W)$ octahedral corner sharing] and 458 cm⁻¹ [$\nu_s(W-O_{c,e}-W)$ where O_{c,e} connects corner and edge-sharing octahedra,]. Similarity of FT-IR spectra for PW₉ **(1)** and for Co^{II}PW₉ **(2)** shows that vibration bands are mainly due to the polyoxotungstates (POT) structure. When comparing the IR spectra of Co^(II)PW₉ **(2)** complex with that of the PW₉ ligand **(1)**, a shift of the asymmetric stretching vibrations $\nu_{as}(P-O_i)$, the main band of the ligand, appearing in the 1200-700 cm⁻¹ range towards higher frequencies indicates that the coordination of the transition metal ions increases the cohesion of the trilaunary structure. [9]. The tiny shift of the $\nu_{as}(W=O_t)$ stretching vibration in the spectra of Co^{II}PW₉ complex

as compared to PW_9 , can be explained by the fact that terminal O_t atoms are not involved in the coordination of lanthanide $Co(II)$ ion. On the other hand, the larger shift of the $\nu(W-O_{c,e}-W)$ stretching vibrations for the bonds from the belt and cap areas indicates the coordination of $Co(II)$ ions by O_c and O_e oxygen atoms from corner-sharing and edge-sharing octahedra. This results to a new symmetric stretching frequency band for $(Co-O-W)$ at 1151.69 cm^{-1} . Apart from these, in the range $1000-700\text{ cm}^{-1}$, the complex exhibits a new band, due to the asymmetric stretching vibrations of the bridges $\nu_s(W-O_b-W)$, proving the presence of two PW_9O_{34} units connected by bridging O_b atoms. The other new $\nu(Co-O_{c,e})$ bands, expected in the $500-300\text{ cm}^{-1}$ range, are masked by the stronger vibration band of the ligand in this area. Five strong vibration bands are indeed observed for $\nu(P-O)$, $\nu(W=O)$, and $\nu(W-O-W)$ at 1104.8 , 1060 , 957 , 889 , and 796.5 cm^{-1} . That shows a splitting of the $P-O$ stretching band (1104.8 and 1058.7 cm^{-1}), indicative of the lacunary anion and originating from the loss of an $\{W-O\}$ unit from $[PW_{12}O_{40}]^{3-}$, which is identical with that of $[Ln(PMo_{11}O_{39})_2]^{11-}$ [10]. The splitting of the characteristic $P-O$ asymmetric stretching vibration between 1100 and 1000 cm^{-1} suggests a decrease in the PO_4 group symmetry by coordination of the lanthanide ions to the ligand [11]. The lack of the $P=O$ band above 1100 cm^{-1} in the infrared spectra of the PW_9 ligand and $Sm^{III}PW_9$ polyoxometalate complexes proves that both of them have A-type structures and therefore the preservation of the A- PW_9 fragments in the $Sm^{III}PW_9$ complex is confirmed [12]. The red shifts of $\nu(W=O)$ and $\nu(W-O-W)$ can be ascribed to the influence of incorporating Co ions into the polyanion framework. In addition, a strong broad peak observed at 3125 cm^{-1} is assigned to $\nu(-OH)$ absorption along with the hydrogen bonds which proves the presence of lattice water.

3.2 Electronic spectroscopy

The UV-electronic spectra of the PW_9 complex exhibits two characteristic bands at ~ 200 and $\sim 250\text{ nm}$, assigned to $W-O_t$ and $W-O_b-W$ transitions respectively. (O_t is a terminal oxygen and O_b is a bridging oxygen) [13]. As expected, the spectra of the cobalt centers present several absorption bands in the visible light region. Thus we expect a broad band roughly at 530 nm followed by two peaks at 512 nm and 484 nm . In the complex the bands are shifted to lower frequencies by comparing with the PW_9 ligand, due to the coordination of the transition metal cations. The $Co^{II}PW_9$ complex exhibits an additional metal-to ligand charge transfer band at $\sim 538\text{ nm}$ of the $Co^{2+}-O^{2-}$ ions [14]. UV spectra of the PW_9 ligand and $Co^{II}PW_9$ complex are also very similar, evincing that the charge transfer inside the polyoxotungstate structure is not significantly affected by coordination. However, the

molar absorption coefficient ϵ of the ν_2 band, which is proportional to the number of W atoms, is almost twice greater in complexes than in the PW_9 ligand ($\epsilon \approx 1.40 \times 10^5$ vs. $0.75 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$). These values also indicate the existence of two PW_9O_{34} trilacunary units [15].

3.3 Magnetic Studies

The magnetic properties of $\text{Co}^{\text{II}}\text{PW}_9$ polyanion was investigated using polycrystalline sample dispersed in grease. As expected, the compounds exhibits a very similar temperature dependence of the magnetic susceptibility, in which, upon lowering the temperature, the χT value first declines gradually and then increases rapidly to reach a maximum and finally falls sharply until 1.8 K. Such behavior indicates that dominant ferromagnetic interactions are present in the compound, but the decrease of the χT value at high temperatures originates from spin-orbit coupling of the Co^{II} ions. Actually the room temperature χT value rises up to $48 \text{ cm}^3 \text{ K mol}^{-1}$ which is much higher than the expected value of $30 \text{ cm}^3 \text{ K mol}^{-1}$. This can be attributed to strong orbital contribution of the Co^{II} ions. To analyse the results it is necessary to take into account the contributions of the cobalt ions. Octahedral Co^{2+} ions are described by a high-spin ground electronic term 4T_1 with first-order spin-orbit coupling. This ground state is split into six anisotropic Kramer's doublets. At low temperature, only the lowest anisotropic Kramer's doublet is populated. The final decrease below 5 K is associated with magnetic anisotropy, as the Co^{II} ions are shielded by the diamagnetic POM shells, thus not allowing for intermolecular anti-ferromagnetic interactions.

4. Conclusion

A new cobalto-heteropolyoxometalate complex was synthesized by the reaction of $\text{Co}(\text{II})$ ions through one-pot synthetic approach with the trilacunary Keggin 9-tungstophosphate. The reaction stoichiometry and all the spectroscopic studies suggest that it has a sandwich-type structure. Last but not the least, it has to be noted that the synthetic strategy reported in this work can be further exploited to obtain other new POMs with larger nuclearities with other polyoxoanion fragments, by substitution of the water ligands coordinated to the cobalt atoms of the sandwich-type structure cluster.

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