

Synthesis, Crystal Structure and Electrochemistry of Two Complexes $(YL_n)^{3+}[PW_{12}O_{40}]^{3-}$ ($L=Me_2SO, Me_2NCHO$)

HAN Qiu-xia¹, WANG Chun-zhang², MA Jian-ru², NIU Jing-yang^{2*} and WANG Jing-ping²

1. Basic Experiment Teaching Center, 2. Institute of Molecular and Crystal Engineering, School of Chemistry and Chemical Engineering, Henan University, Kaifeng 475001, P. R. China

Abstract The reaction of α -H₃[PW₁₂O₄₀] with Y(NO₃)₃ in the presence of DMF or DMSO leads to two complexes with the formulae {Y(DMSO)₇}·PW₁₂O₄₀(**1**) and {[Y(DMF)₇]₂PW₁₂O₄₀}·PW₁₂O₄₀(**2**). The crystal structures indicate that complex **1** consists of discrete [YL_n]³⁺ cations and α -Keggin heteropolyanions [PW₁₂O₄₀]³⁻, whereas, in complex **2**, donor-acceptor interaction results in a cation-anion-cation triplet. In addition, the electrochemical behavior of the two complexes indicates the usual successive reduction processes of the W atoms in the anions.

Keywords Yttrium complex; Crystal structure; Electrochemistry study; Heteropolyanion

1 Introduction

Over the past decades, polyoxometalates have been attracting extensive interest in solid-state materials chemistry because of the wide range of their topological properties and their potential application in catalysis, photochemistry, electrochromism, and magnetism^[1–8]. The evolution of polyoxometalate chemistry is dependent upon the synthesis of the new solids possessing unique structures and properties. One of the important advances in the design of new polyoxometalate complexes is the use of the coordination abilities of polyoxometalates to produce polyoxoanion-supported metal complexes^[9–11] and metal complexes bridged by polyoxoanions to give extended structures^[12–14]. To date, the two most studied polyoxometalate types are the famous Keggin^[15] and Wells-Dawson^[16] families, which can be expressed as [XM₁₂O₄₀]ⁿ⁻ and [X₂M₁₈O₆₂]ⁿ⁻ (X=P, Si; M=W, Mo), respectively. Many Keggin polyoxometalate-based molecular materials have been obtained through combinations of Keggin polyoxolates with organic π -electron donors, such as, tetrathiafulvalene(TTF), (BET)^[17–19], and bis(ethylenedithio) tetrathiafulvalene(ET)^[20–22], to form 1D and 2D structures. In the previous work, the authors have succeeded in

taking polyoxometalates as inorganic electron acceptor components in charge-transfer salts, with the aim of examining novel structures and in particular photochromic and nonlinear optical properties^[23–25]. Of late, they have focused their attention on the new salts obtained by the combination of polyoxometalates and organic-metallic cations, coordinated by magnetic ligands.

An extended polymeric structure was obtained from Sm³⁺ complexes with the Keggin ions [SiMo₁₂O₄₀]⁴⁻^[26], and subsequently, several inorganic-organic complexes with one-dimensional chain or two-dimensional layer structures were also reported^[27–31], such as, [{Ba(DMSO)₅(H₂O)₂·(SiMo₁₂O₄₀)}], [{Ba(DMSO)₃(H₂O)₃}{Ba(DMSO)₅(H₂O)}(GeMo₁₂O₄₀)]^[27], [{Ln(NMP)₆}(PMo₁₂O₄₀)]_n (Ln=La, Ce, Pr, Gd)^[28,29], and [{Pr(DMSO)₆(H₂O)}(PMo₁₂O₄₀)·CH₃CN]_n^[30]. In these complexes, the polyanions first coordinated with metal ions, as ligands, *via* their terminal oxygen atoms, and then to the adjacent metal ions belonging to different connected structural units.

Herein lies a new type of structure complex, {[Y(DMF)₇]₂PW₁₂O₄₀}·PW₁₂O₄₀, displaying a {(donor)_n-M-(anion)-M-(donor)_n} {anion} (M=Y³⁺; anion=[PW₁₂O₄₀]³⁻; donor=DMF) interaction.

*Corresponding author. E-mail: jyniu@henu.edu.cn

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2 Experimental

2.1 Materials and Instrumentations

$Y(NO_3)_3 \cdot nH_2O$ was prepared by dissolving Y_2O_3 in HNO_3 followed by drying. All the organic solvents used for the synthesis and physical measurements were of reagent grade and used without further purification. $H_3PW_{12}O_{40} \cdot nH_2O$ was prepared by the literature method and identified by IR and UV spectra^[32].

C, H, and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on a Nicolet 170 SXFT-IR spectrometer in a range of 4000—500 cm^{-1} in the KBr pellet. Thermogravimetric analyses(TG-DTA) were performed in air on a Perkin Elmer-7 instrument. Cyclic voltammetric measurements were performed on a LK98 microcomputer-based electrochemical system(Lanlike, Tianjin).

2.2 Syntheses

Single crystals of complexes **1** and **2** suitable for single crystal structure analysis were synthesized. To a solution of α - $H_3PW_{12}O_{40}$ (0.68 mmol, 1.96 g) in water(20 mL) was added $Y(NO_3)_3 \cdot nH_2O$ powder(2.0 mmol, 0.9 g) at 60 °C, with stirring. The paste was dissolved in 30 mL of an acetonitrile-water mixture(volume ratio 2:1) and 2 mL DMSO(DMF) was added slowly to it. After 30 min, the mixture was filtered and left to evaporate at room temperature. Several days later, crystals suitable for X-ray diffraction were obtained. Excess $Y(NO_3)_3$ ensured high yields of the desired product.

Elemental analysis(%) calcd. for complex **1**: C 7.19, H 1.42, N 2.88; found: C 7.19, H 1.49, and N 2.94. Anal.(%) calcd. for complex **2**: C 4.78, H 1.21; found: C 4.83, H 1.26. IR, $\tilde{\nu}/cm^{-1}$: $\nu(C=O)$ 1650(s), $\nu(C-N)$ 1490(m), $\nu(P-O)$ 1080(w), $\nu(W-O_d)$ 978(m), $\nu(W-O_b)$ 895(s), $\nu(W-O_c)$ 808(m) for complex **1**; $\nu(P-O)$ 1080(w), $\nu(W-O_d)$ 978(m), $\nu(W-O_b)$ 892(m), $\nu(W-O_c)$ 806(m) for complex **2**.

2.3 X-Ray Crystallographic Study

The crystal structures of complexes **1** and **2** were determined from single crystal X-ray diffraction data. The intensity data were collected by ϕ -oscillation

frame scans on a Rigaku RAXIS-IV image plate area detector with Mo $K\alpha$ ($\lambda=0.071073$ nm) at 293 K, with the following index ranges: $-14 \leq h \leq 14$, $0 \leq k \leq 17$, $-41 \leq l \leq 41$, $1.18^\circ \leq \theta \leq 25.0^\circ$ for complex **1** and $-27 \leq h \leq 27$, $-15 \leq k \leq 15$, $0 \leq l \leq 26$, $0.09^\circ \leq \theta \leq 25.0^\circ$ for complex **2**. The single-crystal X-ray analysis revealed that the crystal crystallized in a monoclinic system with space group $P2_1/c$, had unit cell parameters $a=1.1804(2)$ nm, $b=1.4934(3)$ nm, $c=3.4972(7)$ nm, $\beta=99.00(3)^\circ$, $M_r=3512.98$, $V=6.089(2)$ nm³, $Z=4$, $GOF=1.086$ for complex **1** and $a=2.3166(5)$ nm, $b=1.4717(3)$ nm, $c=2.2016(4)$ nm, $\beta=101.35(3)^\circ$, $M_r=6955.50$, $V=6.359(2)$ nm³, $Z=2$, $GOF=1.148$ for complex **2**, respectively. The structures were solved by Direct Methods and were refined by using full-matrix least-squares on F^2 using the Shelxtl-97 program^[33]. Thermal displacements were treated anisotropically for all the nonhydrogen atoms. The hydrogen atoms were added in idealized geometrical positions. Final R indices were [$I \geq 2\sigma(I)$]: $R_1=0.0549$, $wR_2=0.0625$, $w^{-1}=[\sigma^2(F_o^2)+(0.0751P)^2]$ [where $P=(F_o^2+2F_c^2)/3$], $(\Delta/\sigma)_{max}=0.001$ for complex **1**, and $R_1=0.0622$, $wR_2=0.1202$, $w^{-1}=[\sigma^2(F_o^2)+(0.0528P)^2+73.1241P]$ [where $P=(F_o^2+2F_c^2)/3$], $(\Delta/\sigma)_{max}=0.001$ for complex **2**. The maximum and minimum residual peaks on the final difference Fourier map were 2284 and -2774 e/nm³ for complex **1** and 1743 and -2829 e/nm³ for complex **2**.

CCDC numbers 628253 and 628254 contain the supplementary crystallographic data for complexes **1** and **2**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.com.ac.uk/data-request/cif>.

3 Results and Discussion

3.1 X-Ray Crystal Structure

Complex **1** contains one $[PW_{12}O_{40}]^3$ unit and one $[Y(DMSO)_7]^{3+}$ subunit(Fig.1). Similar to other polyoxometalate complexes derived from the Keggin anions^[26], the charge compensating cations are detached from the polyanions. The P—O bond distances ranged between 0.1514 and 0.1543 nm, average 0.1528 nm and the O—P—O bond angles ranged between 109.0° and 110.2°. Within the WO_6 octahedra, the W—O distances were grouped into three sets: W—O₁ 0.1664—0.1704 nm, average 0.1681

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