

Zn-Containing Double Complex Salts Formed by Keggin Type Polyoxotungstates: Synthesis and Crystal Structure

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Abstract—Novel double complex salts, $[\text{Zn}(\text{DMF})_6]_2[\text{SiW}_{12}\text{O}_{40}] \cdot 2\text{H}_2\text{O}$ (**I**) and $[\text{Zn}(\text{H}_2\text{O})_2(\text{DMF})_4][\text{Zn}(\text{DMF})_6]_2[\text{PW}_{12}\text{O}_{40}]_2 \cdot 6\text{DMF}$ (**II**) (DMF = *N,N*-dimethylformamide), were prepared by the reaction of Zn^{2+} and heteropoly acids $\text{H}_x[\text{EW}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$ (E = P, X = 3, E = Si, X = 4) in DMF. Compounds **I** and **II** were studied by X-ray diffraction (CIF files CCDC nos. 1497570 (**I**) and 1497571 (**II**)) and IR spectroscopy.

Keywords: polyoxometalates, zinc, double complex salts, crystal structure

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INTRODUCTION

Polyoxometalates (POMs) represent an extensive class of polynuclear coordination compounds consisting of transition metal atoms in a high (most often, the highest) oxidation state and the coordination environment composed of O atoms [1–3]. These complexes are of considerable interest for both fundamental inorganic chemistry and various related areas. Particular attention is paid to the catalytic activity of POMs [4–13], the possibility of using them as components of hybrid functional materials [14–22] and so on.

The classic Keggin type polyoxo anions $[\text{XM}_{12}\text{O}_{40}]^{n-}$ (M = Mo, W) belong to the most studied structural types of POMs [1]. These compounds tend to lose one or several $\{\text{WO}\}^{4+}$ groups (with increasing solution pH) to give lacunary POMs ($[\text{PW}_{11}\text{O}_{39}]^{7-}$, $[\text{SiW}_{11}\text{O}_{39}]^{8-}$, etc.), which are, in turn, able to coordinate heterometal atoms, while functioning as polydentate ligands [23]. Also, several complexes in which heterometal ions are coordinated to non-lacunary POM via terminal oxygen atoms have also been reported. This behavior is especially typical of the most oxophilic elements [24–26]. Complexes of this type are often synthesized using donor organic solvents that can complete the coordination sphere of the heteroatom. Previously [27], we demonstrated that an attempt to prepare a Cd-containing POM complex in DMF gives only a double complex salt with the $[\text{Cd}(\text{DMF})_6]^{2+}$ cation; that is, Cd^{2+} is not coordinated to the polyoxo anion. Here we attempted the coordi-

nation of Zn^{2+} under similar conditions; this gave the complexes $[\text{Zn}(\text{DMF})_6]_2[\text{SiW}_{12}\text{O}_{40}] \cdot 2\text{H}_2\text{O}$ (**I**) and $[\text{Zn}(\text{H}_2\text{O})_2(\text{DMF})_4][\text{Zn}(\text{DMF})_6]_2[\text{PW}_{12}\text{O}_{40}]_2 \cdot 6\text{DMF}$ (**II**), which were studied by X-ray diffraction.

EXPERIMENTAL

The syntheses of **I** and **II** were performed in air. Reagent grade chemicals were received from commercial sources and used as received. The numbers of solvation water molecules for phospho- and silicotungstic acids were determined by elemental analysis (~11 and 15, respectively). Infrared spectra (KBr) were measured on a Scimitar FTS 2000 spectrometer. Powder X-ray diffraction analysis was performed on a Shimadzu XRD-7000 diffractometer at room temperature.

Synthesis of I. Dimethylformamide (3.5 mL) was added to a mixture of ZnCl_2 (43 mg, 0.32 mmol) and AgNO_3 (108 mg, 0.64 mmol). After vigorous stirring, the AgCl precipitate that formed was filtered off, and $\text{H}_4[\text{SiW}_{12}\text{O}_{40}] \cdot 15\text{H}_2\text{O}$ (500 mg, 0.16 mmol) in 3 mL of DMF was added to the resulting solution. Slow diffusion of diethyl ether vapor into the mixture gave crystals suitable for X-ray diffraction in 78% yield.

IR (4000–400 cm^{-1}): 3483 w, 2934 w, 2814 w, 1645 s, 1494 w, 1433 m, 1375 m, 1253 w, 1116 m, 1060 w, 1014 m, 968 s, 918 s, 885 m, 793 s, 681 w, 534 m, 384m.

Synthesis of II. Dimethylformamide (3.5 mL) was added to a mixture of ZnCl_2 (24 mg, 0.17 mmol) and