

Anderson Type Polyoxometalates Containing Vitamin B₁

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Abstract

The novel vitamin B₁-substituted polyoxomolybdates (C₁₂H₁₇N₄OS)₃[Co(III)Mo₆O₂₄H₆]·7H₂O (**1**) and (C₁₂H₁₇N₄OS)₄[Ni(II)Mo₆O₂₄H₆]·7H₂O (**2**) have been synthesized using (NH₄)₃[Co(III)Mo₆O₂₄H₆]·7H₂O and (NH₄)₄[Ni(II)Mo₆O₂₄H₆]·7H₂O respectively as a precursor for the in situ formation of the counter ion vitamin B₁ (C₁₂H₁₇N₄OS)⁺. These compounds have been thoroughly characterized in the solid state FT-IR spectroscopy, powder X-ray diffraction (PXRD), TGA and elemental analysis.

Keywords: Cobalt, Molybdenum, Nickel, Polyoxometalate, Thiamine Hydrochloride, Vitamin B₁

1. Introduction

Polyoxometalates (POMs) are a broad class of anionic clusters composed of high oxidation state metal ions linked by oxygen atoms in a variety of structures that can be divided into two main categories: isopolyanion and heteropolyanion. An isopolyanion consists of a single element bridged by oxygen atoms. A heteropolyanion incorporates functional heteroatoms (e.g., rare earths, transition metals and noble metals) to make the design of advanced functional materials more accessible and rational. Depending on their size, charge and composition, POM frameworks exhibit numerous different properties, opening up potential applications in diverse research areas, including catalysis, materials science, biological chemistry, photophysical, energy and medicine [1-15].

Within the POM family, transition metal substituted polyoxometalates are the largest group and the activities of these compounds are also widely studied in biological studies. For example, Golubeva and Ostroushko emphasised those containing vitamin B₁ in their POM studies with their groups [16-17]. In addition the interesting biological properties of Anderson-type POMs and their use in medicine have attracted the attention of scientists. Mahvash et al., reported the synthesis and characterization of Anderson type POMs and investigated their effects against breast cancer [18]. In the study of Ramezani-Aliakbari and co-workers, the effects of newly synthesised Anderson type POMs against breast

cancer were investigated [19-20]. Considering these data, it is important to investigate the interaction between POMs and drugs. Therefore in this study, vitamin B₁ (thiamine hydrochloride) was chosen as a model drug and two new Anderson type POMs (C₁₂H₁₇N₄OS)₃[Co(III)Mo₆O₂₄H₆]·7H₂O (**1**) and (C₁₂H₁₇N₄OS)₄[Ni(II)Mo₆O₂₄H₆]·7H₂O (**2**) were synthesized and characterized. The limited number of studies on species containing vitamin B₁ in Anderson type POMs enhances the significance of this study.

2. Materials and Methods

All chemicals used were obtained from Aldrich and used without any purification. (NH₄)₃[Co(III)Mo₆O₂₄H₆]·7H₂O and (NH₄)₄[Ni(II)Mo₆O₂₄H₆]·7H₂O were synthesized as described in a previous report [21]. C, H, N and S elemental analyses were obtained on a LECO-932 CHNS elemental analyser. Ni, Mo and Co were determined by ICP-MS Agilent Technology 7700. The FT-IR spectra were measured by a Perkin Elmer LR 64912 C spectrometer in the range 400-4000 cm⁻¹ with KBr pellet. Thermal gravimetric analysis (TGA) was recorded on a Hitachi Exstar TG/DTA 7300 in flowing N₂ with a heating rate of 50.0 mL min⁻¹ 10 °C/min at 25 and 1000 °C. PXRD spectra was recorded on a PANalytical X-Pert3 Powder.

2.1. Synthesis of Compounds

2.1.1. $(C_{12}H_{17}N_4OS)_3[Co(III)Mo_6O_{24}H_6] \cdot 7H_2O$ (1)

The solutions required for the reaction were prepared separately. **Solution 1:** $(NH_4)_3[Co(III)Mo_6O_{24}H_6] \cdot 7H_2O$ was (200 mg, 0.16 mmol) was dissolved in 10 mL H_2O under stirring. **Solution 2:** Thiamine hydrochloride (excess) was dissolved in 5 mL H_2O . Afterwards the two solutions were mixed and stirred. The resulting mixture was kept at 80 °C for 24 hours and filtered. The brown product was washed with ethanol and water and dried at 60 °C. Yield: 485 mg, 25%. FT-IR data (cm^{-1}): 441 (s), 507 (m), 524 (s), 570 (m), 641 (m), 660 (m), 691 (m), 722 (m), 794 (m), 871 (m), 897 (m), 953 (m), 1046 (m), 1072 (m), 1108 (m), 1169 (m), 1186(s), 1224 (m), 1381 (m), 1421 (m), 1434(m), 1480 (m), 1530 (m), 1616 (m), 1656 (m), 1732 (m), 3044 (m), 3419 (m), 3490 (m). Anal. Calcd. (%) for $C_{36}H_{71}N_{12}S_3CoMo_6O_{34}$ (1946.77 g/mol): C, 22.21; H, 3.68; N, 8.63; S, 4.94; Mo, 29.57; Co, 3.03. Found (%): C, 20.84; H, 3.00; N, 7.54; S, 5.24; Mo, 30.75; Co, 3.22. TGA (loss of 7 H_2O): calcd. 6.48%. found 6.55%; (loss of 3 $(C_{12}H_{17}N_4OS)^+$): calcd. 40.89%, found 40.95%.

2.1.2. $(C_{12}H_{17}N_4OS)_4[Ni(II)Mo_6O_{24}H_6] \cdot 7H_2O$ (2)

The solutions required for the reaction were prepared separately. **Solution 1:** $(NH_4)_4[Ni(II)Mo_6O_{24}H_6] \cdot 7H_2O$ was (200 mg, 0.15 mmol) was dissolved in 10 mL H_2O under stirring. **Solution 2:** Thiamine hydrochloride (excess) was dissolved in 5 mL H_2O . Afterwards the two

solutions were mixed and stirred. The resulting mixture was kept at 80 °C for 24 hours and filtered. The green product was washed with ethanol and water and dried at 60 °C. Yield: 485 mg, 25%. FT-IR data (cm^{-1}): 469 (s), 507 (m), 522 (s), 568 (m), 641 (m), 663 (m), 705 (m), 750 (m), 786 (m), 873 (m), 895 (m), 989 (m), 1024 (m), 1044 (m), 1075 (m), 1088 (m), 1112 (m), 1169 (m), 1184 (m), 1224 (m), 1281 (m), 1482 (m), 1526 (m), 1657 (m), 1732 (m), 2074 (m), 3035 (m), 3428 (m), 3503 (m). Anal. Calcd. (%) for $C_{48}H_{88}N_{16}S_4NiMo_6O_{35}$ (2211.89 g/mol): C, 26.06; H, 4.01; N, 10.13; S, 5.80; Mo, 26.02; Ni, 2.65. Found (%): C, 25.93; H, 3.75; N, 9.82; S, 5.02; Mo, 26.27; Co, 2.37. TGA (loss of 7 H_2O): calcd. 5.70%. found 5.59%; (loss of 4 $(C_{12}H_{17}N_4OS)^+$): calcd. 47.98%, found 47.93%.

3. Results and Discussion

Compounds **1** and **2** were synthesized by reacting of $(NH_4)_3[Co(III)Mo_6O_{24}H_6] \cdot 7H_2O$ and $(NH_4)_4[Ni(II)Mo_6O_{24}H_6] \cdot 7H_2O$ with thiamine hydrochloride in an aqueous medium (Figure 1). The experimentally obtained spectroscopic data (ICP-MS, TGA and FT-IR) and elemental analyses results (Table 1) support the formulations of **1** and **2** as $(C_{12}H_{17}N_4OS)_3[Co(III)Mo_6O_{24}H_6] \cdot 7H_2O$ (**1**) and $(C_{12}H_{17}N_4OS)_4[Ni(II)Mo_6O_{24}H_6] \cdot 7H_2O$ (**2**).

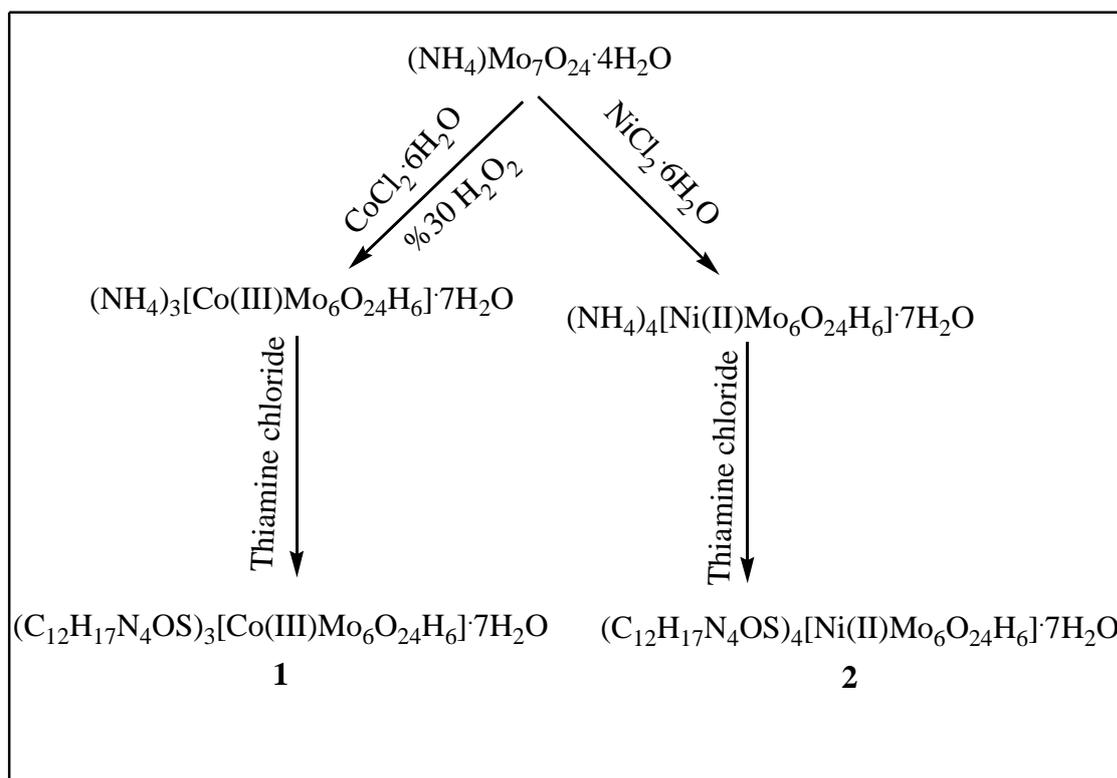


Figure 1. Synthesis of 1-2

Table 1. Elemental and ICP-MS values of **1** and **2**

Compounds	M.W.	Elemental and ICP-MS						
		C	H	N	S	Mo	Co	Ni
		C/E	C/E	C/E	C/E	C/E	C/E	C/E
1	1946.77	22.01/20.84	3.68/3.00	8.63/7.54	4.94/5.24	29.57/30.75	3.03/3.22	-
2	2211.89	26.06/25.93	4.01/3.75	10.13/9.82	5.80/5.02	26.02/26.27	-	2.65/2.37

M.W.: Molecular Weight, C: Calculated, E: Experimental

In the FT-IR spectrum of POMs, the region between 1000 and 400 cm^{-1} is characterised as the fingerprint region. The vibrations in this region can be attributed to the M=O and M-O-M (M = Co, Ni, Mo) stretching vibrations of the Anderson type POM cluster [22-24]. The characteristic bands of $\nu(\text{M}=\text{O})$ (M= Co, Ni, Mo) vibrations are observed at 952 and 989 cm^{-1} for **1** and **2** respectively (Figure 2 and 3). The peaks in the region from 469 to 953 cm^{-1} correspond to the antisymmetric and symmetric deformation vibrations of the M-O-M (M= Co, Ni, Mo). The FT-IR spectrum also shows stretching vibrations related to vitamin B₁ [17]. The selected bands of vitamin B₁ are at 3490 (OH); 3419 (N-H in NH₂); 3044 (C-H in CH₃); 1656 (NH in NH₂); 1616, 1530, 1480; 1434 (CH in CH₂-CH₂); 1046 (C-O) cm^{-1} for **1**, 3503 (OH); 3428 (N-H in NH₂); 3035 (C-H in CH₃); 1657 (NH in NH₂); 1526, 1482 (CH in CH₂-CH₂); 1044 (C-O) cm^{-1} for **2**. The broad bands at 3400-3500 cm^{-1} are due to $\nu(\text{O-H})$ stretching vibrations.

TGA results of **1** (Figure 4) exhibits that 6.55% weight loss between 65-233 °C can be assigned to approximately seven water molecules in the crystal lattice. The 40.95% weight loss between between 234-820 °C, is assigned to the removal of three thiamine cations. The TGA data for **2** (Figure 4) shows the two weight-loss steps between 25 °C and 1000 °C too. The 5.59% weight loss of **2** is due to the loss of lattice water in the temperature range of 49-169 °C. The 47.93% weight loss between 170-813 °C is assigned to the removal of four thiamine cations. The cluster is stable up to 1000 °C.

PXRD diagrams are given in Figure 5. The products were found to be amorphous because they precipitated in the form of powder rather than crystalline structure.

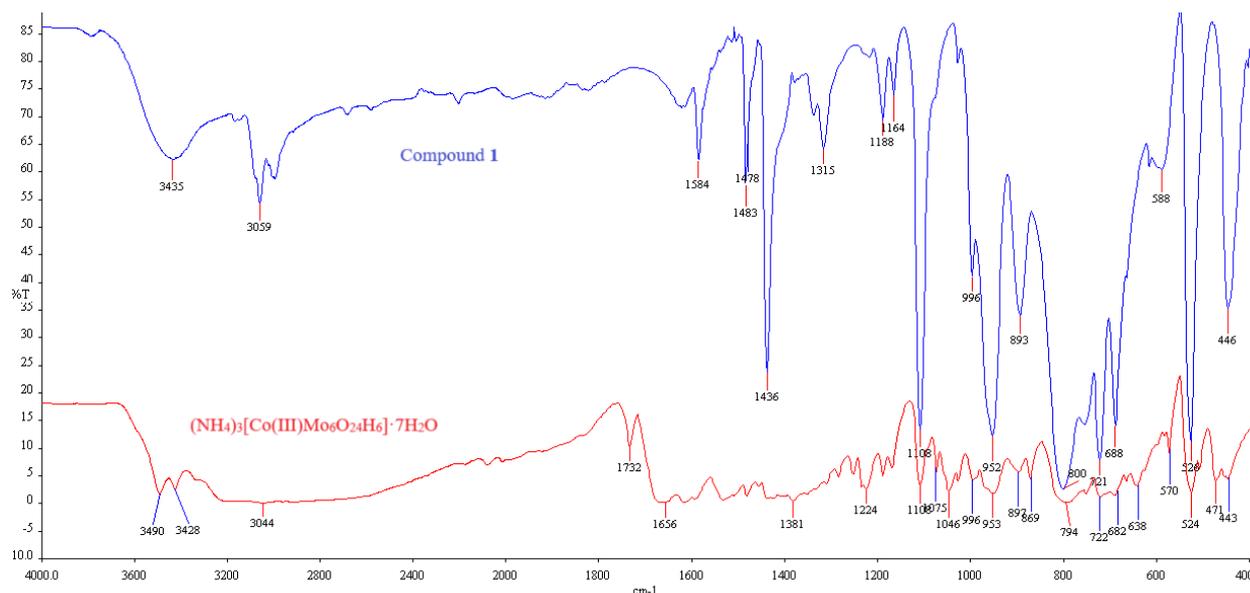


Figure 2. FT-IR spectrum of **1** and $(\text{NH}_4)_3[\text{Co(III)Mo}_6\text{O}_{24}\text{H}_6] \cdot 7\text{H}_2\text{O}$

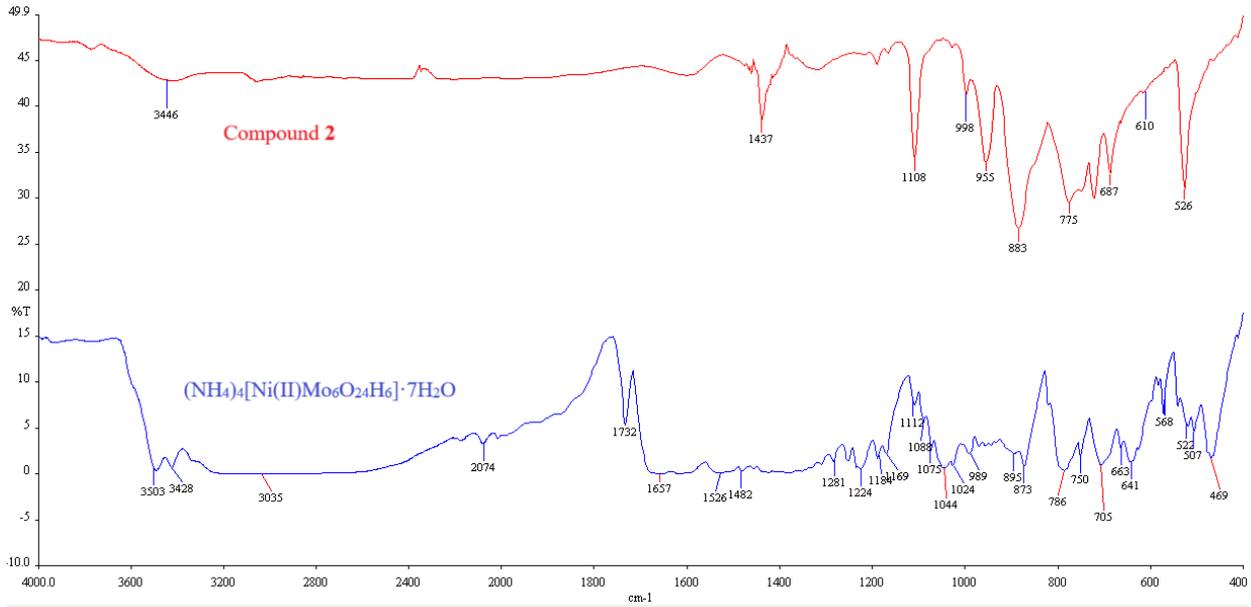


Figure 3. FT-IR spectrum of 2 and $(\text{NH}_4)_4[\text{Ni}(\text{II})\text{Mo}_6\text{O}_{24}\text{H}_6] \cdot 7\text{H}_2\text{O}$

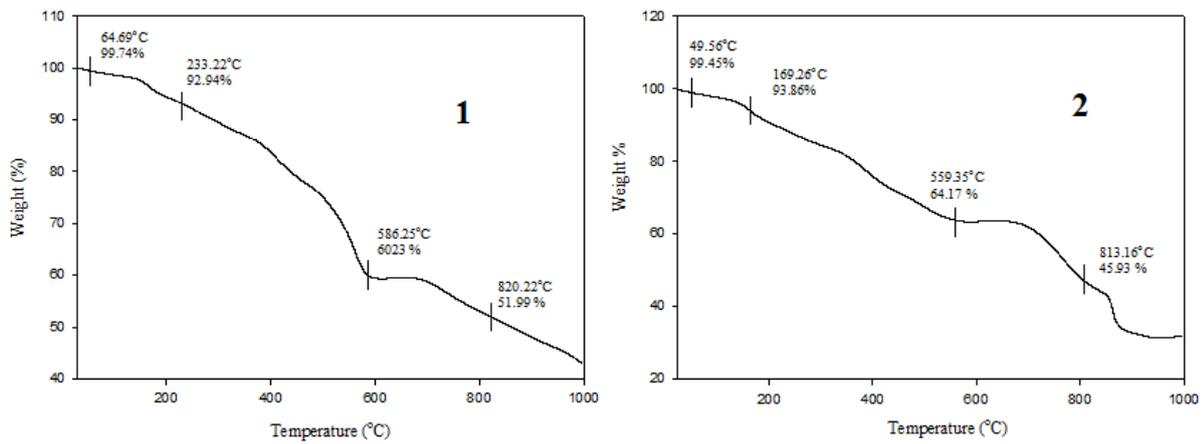


Figure 4. TGA spectrum of 1 and 2

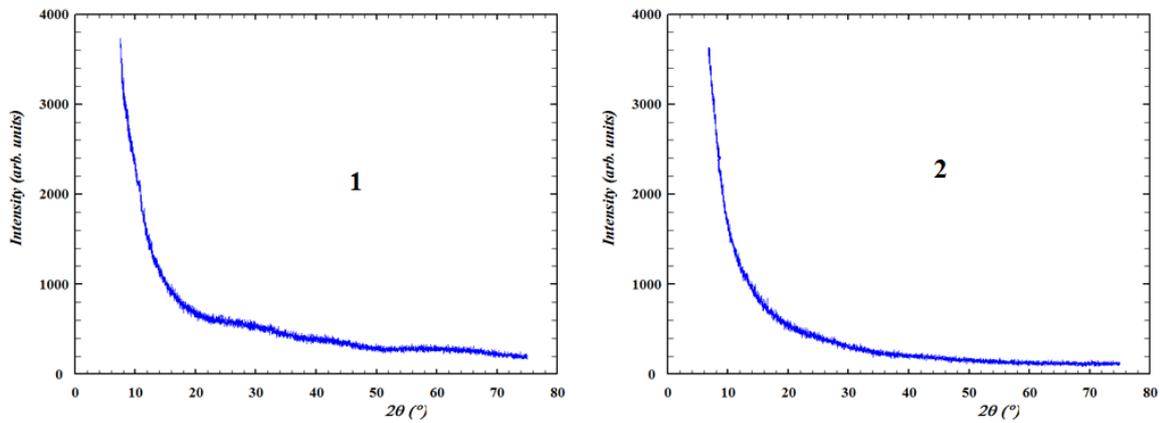


Figure 5. PXRD spectrum of 1 and 2

4. Conclusion

In conclusion, the synthesis and characterisation of Anderson-type POMs ((C₁₂H₁₇N₄OS)₃[Co(III)Mo₆O₂₄H₆]·7H₂O (1) and (C₁₂H₁₇N₄OS)₄[Ni(II)Mo₆O₂₄H₆]·7H₂O (2)) containing a biologically active moiety (vitamin B₁) were achieved in this study. Due to the limited number of studies in the literature with POM compounds containing vitamin B₁, this study may open new perspectives for the preparation of new Anderson-type POM archetypes.

Ethics

There are no ethical issues after the publication of this manuscript.

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