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Co-crystallization of Keggin type polyoxometalates $[HL]_3[PW_{12}O_{40}]$ and $[Ln(DMF)_8][PW_{12}O_{40}]$ (Ln = La, Dy, Yb) (**L** = *N*-(2-hydroxyphenyl)-3-methoxy-salicylideneamine): Syntheses, structures and magnetic properties

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ABSTRACT

Four new Keggin type polyoxometalate clusters $[HL]_3[PW_{12}O_{40}]\cdot 5MeOH$ (**1**) and $[Ln(DMF)_8][PW_{12}O_{40}]$ {Ln = La (**2**), Dy (**3**), Yb (**4**)} (**L** = *N*-(2-hydroxyphenyl)-3-methoxy-salicylideneamine) have been synthesized. Co-crystallization of complex **1** with each of the three complexes **2–4** takes place when the Schiff base ligand is treated with hydrated phosphotungstic acid, $H_3[PW_{12}O_{40}]\cdot xH_2O$, hydrated lanthanide nitrate, $Ln(NO_3)_3\cdot 6H_2O$ in the presence of $Ni(NO_3)_2\cdot 6H_2O$. The Schiff base ligand is protonated in complex **1** and thus it is neutralizing the charge of the polyoxotungstate anion, $[PW_{12}O_{40}]^{3-}$. A dimethylformamide (DMF) coordinated trivalent lanthanide ion balances the negative charge of the polyoxoanion in **2–4**. All complexes are characterized by several standard analytical techniques. Solid state molecular structures of **1–4** were confirmed by single crystal X-ray diffraction analyses. The magnetic properties of complexes **3** and **4** confirm the presence of monomeric Dy(III) and Yb(III) complexes with a thermal depopulation of the highest energy Stark levels as the temperature is decreased.

1. Introduction

Presently, polyoxometalates (POMs) have gained tremendous attention in the field of inorganic chemistry, supramolecular chemistry and materials science because of their exceptional structural diversities, physical and chemical properties [1–3]. POM exhibits an oxygen-enriched surface with high negative charges on it. They find several important applications in areas of catalysis, magnetism, nanotechnology and biomedicine [4–7]. Recent research interests revolve around the framing and synthesis of inorganic–organic hybrid POM-based materials. The rational design and synthesis of such POM-based inorganic–organic materials have been achieved using organic cations, discrete metal–organic complexes and metal–organic frameworks (MOF) [8–10]. Various organic ligands containing O, N donor atoms are extensively used as organic synthons for the construction of POM-based supramolecular architectures [11]. For instance, cyclophosphazene cations $[(RNH)_6P_3N_3H_n]^{n+}$ (R = isopropyl, isobutyl and benzyl; n = 1 and 2) containing polyoxometalates have been explored for biphasic oxidation process [12]. A metal–organic subunit $[Ag_4(ptz)_4]$ has been successfully employed for the synthesis of a two dimensional layer structure [13]. A number of metal–organic frameworks containing polyoxometalates anions and their properties and applications have been documented in the literature [14–18]. These frameworks possess various structural topologies and exhibit interesting properties. Several synthetic strategies have been employed to synthesize inorganic–organic hybrid materials utilizing transition metal ions and classic polyoxometalate anions such as Keggin, Anderson and Dawson-Wells type anions. Recently, synthesis of lanthanide ions containing polyoxometalates is a very active research area because of their interesting magnetic and luminescent properties of the lanthanide ions [6,19]. Furthermore, lanthanide ions can adopt higher coordination sites, thus resulting in novel structural types. A large number of lanthanide containing POMs have been reported [20–23]. Recently, our research group is engaged in the synthesis of discrete and framework structures based on POM building blocks and lanthanide ions. In this context, we report here one polyoxotungstate $[(HL)_3][PW_{12}O_{40}]\cdot 5MeOH$ (**1**)

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(**L** = *N*-(2-hydroxyphenyl)-3-methoxy-salicylideneamine) containing organic cations $[HL]^+$ and three trivalent lanthanide ion containing polyoxotungstate with the general formula $[Ln(DMF)_8][PW_{12}O_{40}]$ (Ln = La (**2**), Dy (**3**) and Yb (**4**); DMF = dimethylformamide). These compounds have been synthesized from phosphotungstic acid, $H_3[PW_{12}O_{40}]\cdot xH_2O$ and hydrated lanthanide nitrate in the presence of a Schiff-base ligand (**L**). Scheme 1 shows the structure of the Schiff-base ligand (**L**) and its protonated form $[HL]^+$.

Herein we describe the synthesis, characterization, solid-state structures and magnetic properties of complexes **1**–**4**.

2. Experimental

2.1. Materials

All chemicals and solvents used for the synthesis were of analytical grade. O-vanillin, 2-amino phenol, $H_3[PW_{12}O_{40}]\cdot xH_2O$ and $Ni(NO_3)_2\cdot 6H_2O$ were commercially available and used as received without further purification. The Schiff base ligand *N*-(2-hydroxyphenyl)-3-methoxy-salicylideneamine (**L**) was prepared by condensation of o-vanillin and 2-amino phenol according to the literature procedure [24]. $Ln(NO_3)_3\cdot 6H_2O$ was prepared from Ln_2O_3 and nitric acid.

2.2. Synthesis of *1*–*4*

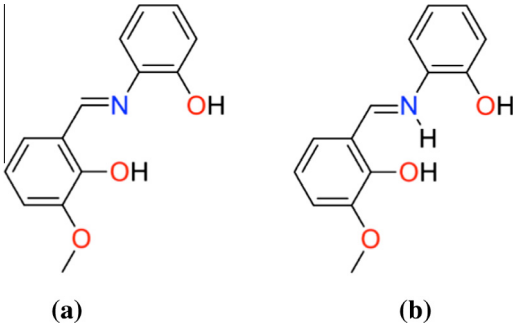
A methanolic solution (5 mL) containing the Schiff base ligand **L** (24 mg, 0.10 mmol), $Ln(NO_3)_3\cdot 6H_2O$ (0.05 mmol) and $Ni(NO_3)_2\cdot 6H_2O$ (29 mg, 0.10 mmol) was refluxed for 1 h. The resulting solution was carefully layered with a DMF (5 mL) solution of $H_3[PW_{12}O_{40}]\cdot xH_2O$ (50 mg). Colourless crystals of complexes **2**–**4** appeared within two days. Yellow crystals of complex **1** were co-crystallized with each of **2**–**4** after seven days. They were mechanically separated and used for further characterizations and X-ray diffraction analyses.

1: $La(NO_3)_3\cdot 6H_2O$ (21 mg, 0.05 mmol) was used: yield: 10 mg, 15% (co-crystallized with 2); IR (KBr pellets) cm^{-1}: 3448 (br), 2929 (w), 1653 (s), 1498 (w), 1437 (w), 1382 (w), 1257 (w), 1114 (w), 1080 (m), 979 (s), 896 (m), 810 (s), 683 (w), 597 (w), 520 (w). *Anal.* Calcd. for $C_{47}H_{62}N_3O_{54}PW_{12}$ (%): C, 14.97; H, 1.66; N, 1.11; Found: C, 14.85; H, 1.58; N, 1.09.

2: $La(NO_3)_3\cdot 6H_2O$ (21 mg, 0.05 mmol) was used: yield 20 mg, 8%. IR (KBr pellets) cm^{-1}: 2932 (w), 2368 (w), 1653 (s), 1497(w), 1437 (w), 1381 (w), 1250 (w), 1114 (w), 1082 (m), 980 (s), 890 (m), 812 (s), 676 (w), 594 (w), 523 (w). *Anal.* Calcd. for $C_{24}H_{56}LaN_8O_{48}PW_{12}$ (%): C, 8.01; H, 1.57; N, 3.11; Found: C, 7.95; H, 1.59; N, 3.07.

3: $Dy(NO_3)_3\cdot 6H_2O$ (23 mg, 0.05 mmol) was used. Yield: 18 mg, 29%. IR (KBr pellets) cm^{-1}: 2926 (w), 1651 (w), 1496 (w), 1437 (w), 1383 (m), 1257 (w), 1111 (w), 1081 (s), 975 (s), 894 (m), 810 (s), 681 (w), 596 (w), 520 (w). *Anal.* Calcd. for $C_{24}H_{56}DyN_8O_{48}PW_{12}$ (%): C, 7.95; H, 1.56; N, 3.09; Found: C, 7.80; H, 1.44; N, 2.97.

4: $Yb(NO_3)_3\cdot 6H_2O$ (22 mg, 0.05 mmol) was used. Yield: 15 mg, 23%. IR (KBr pellets) cm^{-1}: 2923 (w), 1656 (s), 1495 (w), 1434 (w), 1384 (m), 1251 (w), 1112 (w), 1079 (s), 979 (s), 896 (m), 811 (s), 685 (w), 592 (w), 523 (w). *Anal.* Calcd. for $C_{24}H_{56}YbN_8O_{48}PW_{12}$ (%): C, 7.93; H, 1.55; N, 3.08; Found: C, 7.86; H, 1.52; N, 3.01.



Scheme 1. (a) Structure of the Schiff-base ligand (**L**) and (b) its protonated form $[HL]^+$.

2.3. Physical measurements

CHN analyses were performed on a VARIO MICRO cube analyser by Elemental analyser system GMBH. IR spectra in KBr (4500–500 cm^{-1}) were recorded using a Perkin–Elmer RXI FT-IR spectrometer. EDX analyses were performed by Hitachi S3400N instrument. Variable temperature susceptibility measurements of **3**–**4** were carried out in the temperature range 2–300 K with an applied magnetic field of 0.1 T on ground polycrystalline samples (with masses of 13.32 and 16.68 mg for **3** and **4**, respectively) with a SQUID magnetometer (Quantum Design MPMS-XL-5). The susceptibilities of the samples were corrected for the sample holder contribution, previously measured under the same conditions, and for the diamagnetic contribution of the constituent atoms as deduced using Pascal's constant tables [25].

2.4. X-ray crystallography

The data of **1** was collected on a Stoe IPDS 2T diffractometer using Mo Kα radiation with graphite monochromator (λ = 0.71073 Å) at T = 100(2) K and the data of **2**–**4** were collected on an Oxford Diffraction XCalibur Eos instrument equipped with Mo Kα or Cu Kα radiation at ambient temperature. Data collection and reduction were performed with the Oxford diffraction Crysalis system. The structures were solved by direct methods (SIR92) [26] and refined on F^2 by full-matrix least-squares methods using SHELXL-2013 [27,28]. Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w(Fo^2 - Fc^2)^2]$ ($w = 1/[\sigma^2(Fo^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(Fo^2,0) + 2Fc^2)/3$ with $\sigma^2(Fo^2)$ from counting statistics. The function R_1 and wR_2 were $(\sigma||Fo| - |Fc||)/\sigma|Fo|$ and $[\sigma w(Fo^2 - Fc^2)^2/\sigma(wFo^4)]^{1/2}$, respectively.

3. Results and discussions

3.1. Synthesis

The Schiff base ligand (**L**) was prepared by the condensation reaction of 2-aminophenol with o-vanillin following the literature procedure [24]. The reactivity of hydrated phosphotungstic acid, $H_3[PW_{12}O_{40}]\cdot xH_2O$ towards trivalent lanthanide cations (La^{3+}, Dy^{3+} and Yb^{3+}) in presence of the Schiff base ligand (**L**) and Ni $(NO_3)_2\cdot 6H_2O$ has been investigated. The reaction leads to the formation of two different polyoxometalates. One of them contains a protonated Schiff base ligand: $[(HL)_3][PW_{12}O_{40}]\cdot 5MeOH$ (**1**) and the other one shows the inclusion of lanthanide cations in it: $[Ln(DMF)_8][PW_{12}O_{40}]$; Ln = La (**2**), Dy (**3**) and Yb (**4**). Scheme 2 shows the possible synthetic pathways of compounds **1**–**4**. The role of Ni $(NO_3)_2\cdot 6H_2O$ is not obvious. However, the synthesis was not possible without it under the same reaction condition. Earlier, we reported a tetranuclear NI(II) complex with Ni_4O_4 cubane core using the same ligand in methanol in the presence of a base. However, such possibility can be excluded here as the reaction is