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Crystal structures and spectral properties of two polyoxometalate-based inorganic–organic compounds from silver–azine building blocks with bis-bidentate and tridentate ligands

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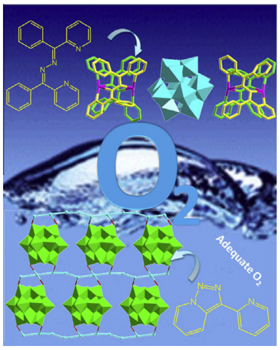
HIGHLIGHTS

- Two novel POM-based compounds have been synthesized with silver–azines.
- The compounds have been characterized by IR, UV, XRPD and elemental analysis.
- X-ray single-crystal structure analyses and discussion for the compounds.
- The two compounds exhibit fluorescent emission in solid state, respectively.

GRAPHICAL ABSTRACT



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ABSTRACT

Two polyoxometalate-based inorganic–organic hybrid compounds constructed from silver(I)-L species and saturated Keggin type polyoxoanion, $[Ag_2L^1_2]_2(SiMo_{12}O_{40})\cdot 1.5DMF\cdot 0.5CH_3OH\cdot H_2O$ **1** and $[\{Ag_4L^2_2(DMF)_5\}(SiMo_{12}O_{40})]$ **2** (L^1 = phenyl 2-pyridyl ketone azine, L^2 = 3-phenyltriazolo[1,5-*a*]pyridine), have been synthesized and structurally characterized by IR, UV, elemental analysis, XRPD and complete single crystal structure analyses, where the ligands L^1 and L^2 are bis-bidentate and tridentate azines synthesized with the same materials under different conditions. The structure of **1** exhibits a dinuclear double-helicate with $[SiMo_{12}O_{40}]^{4-}$ anions as counter ions, where all of the Ag centers coordinate to bis-bidentate chelating ligands. Compound **2** displays a two-dimensional sheet formed by the Ag–organic infinite chains and the $[SiMo_{12}O_{40}]^{4-}$ alternately arranged in a “rail-like” fashion. The luminescent properties of **1** and **2** in the solid state were investigated.

Introduction

Inorganic–organic hybrid materials have attracted a lot of attention from chemists worldwide owing to their multiformity in species and value-adding properties such as redox activity, optics, magnetism and catalysis [1–4]. The utilization of functional inorganic clusters as building blocks can likely introduce the physical and/or chemical properties to the target inorganic–organic compounds [5–7]. Polyoxometalates (POMs) are a unique class of inorganic metal–oxygen aggregates with particular interest in the fields of catalysis, surface science, and materials science because their chemical properties including redox potentials,

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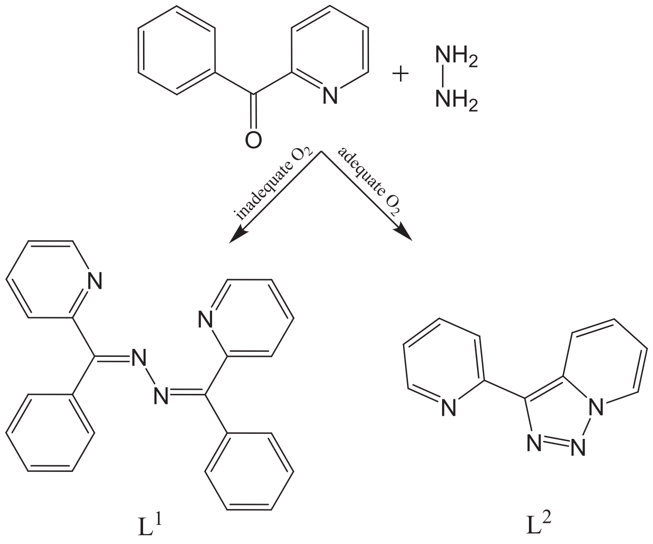
acidities, and solubility in various media, can be finely tuned by choosing the appropriate constituent elements and countercations [8–11]. One of the remarkable approaches in the construction of POM-based inorganic–organic hybrid materials is to combine the POMs with transition-metal compounds (TMCs) [12–15]. This strategy is anticipated to obtain new POM-based compounds with a variety of structural motifs and interesting properties, which should lead to new functional materials.

The organic ligands play a significant role in forming structures with different dimensionalities and fantastic topologies [16–18]. Azines taking on a well-known class of organic ligands can be divided into several species, and one type derived from the condensation of an pyridyl-based aldehyde or ketone with hydrazine can possibly obtain different polydentate azines which are widely reported in coordination chemistry [19–21]. Symmetrical diazine Schiff base ligands with two pyridylimine sites connected by amine are excellent ligands allowing us to probe systematically the effect of modifications to the ligand backbone through which we are attempting to control the precise topography, or microarchitecture, of the arrays [22–24]. In the solid state, such ligands can be locked in a twist conformation to show a double helix resulting from the constraint of the rotation around —N—N— fragments. In this kind of composite, phenyl 2-pyridyl ketone azine (L^1) (Scheme 1), which is prepared by mixing hydrazine hydrate with phenyl 2-pyridyl ketone, is selected to construct double helical compounds in which the ligand acts as a bis-bidentate chelate agent employing all four nitrogen atoms to get two five-numbered chelate rings [25,26]. Whereas there are only a few literature on the crystal engineering of POM species with Schiff base ligands [27–29], despite the Schiff base ligands are commonly used in metal–organic coordination compounds.

On the other hand, the strong oxidation process leads to the formation of 3-phenyltriazolo[1,5-*a*] pyridine (L^2) caused by oxidative cyclization of the corresponding hydrazone in the synthesis [30,31]. Curiously however, this ring system has been ignored as a ligand in coordination chemistry. There have been only a few reports of compounds with L^2 acting as a donor to metal ions and no POM-based inorganic–organic hybrid compound with this ligand was reported [21]. Continuing our studies on the construction of metal–azine species and POM-based compounds [11,32–35], in this paper we report the synthesis and characterization of two interesting polyoxometalate-based inorganic–organic hybrid compounds constructed from Ag—L species and saturated Keggin type $[SiMo_{12}O_{40}]^{4-}$ polyoxoanion, including a new POM-based hybrid compound $[Ag_2L^1_2]_2(SiMo_{12}O_{40})\cdot 1.5DMF\cdot 0.5CH_3OH\cdot H_2O$ **1** with double helical coordination cation units and a 2D crystalline array $[\{Ag_4L^2_2(DMF)_5\}(SiMo_{12}O_{40})]$ **2,** where L^1 and L^2 is phenyl 2-pyridyl ketone azine and 3-phenyltriazolo[1,5-*a*]pyridine, respectively.



Scheme 1. The syntheses of the two ligands.

Experimental

Materials and physical measurements

All the chemicals were of reagent grade quality obtained from commercial sources and used without further purification. $H_4SiMo_{12}O_{40}\cdot xH_2O$ was synthesized by the literature procedures [36]. Ligands L^1, phenyl 2-pyridyl ketone azine and L^2, 3-(2-pyridyl)-triazolo[1,5-a]pyridine were prepared by refluxing di-2-pyridylketone and hydrazine hydrate in methanol solution [21].

Elemental analyses (C, H and N) were carried out on a Perkin–Elmer 240C analytical instrument. IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4000–400 cm^{-1} region. X-ray powder diffraction patterns were recorded on a D/max-γ A rotating anode X-ray diffractometer with Cu sealed tube (λ = 1.54178 Å). The UV–vis spectra were obtained on a Shimazu UV-250 spectrometer in the range of 400–190 nm in aqueous solution, and the luminescent spectra were performed on a Hitachi F-7000 fluorescence spectrophotometer.

Preparation of the compound **1**

Ligand L^1 (0.040 g, 0.1 mmol) and $AgNO_3$ (0.051 g, 0.3 mmol) were stirred in methanol solution (5 mL) for 0.5 h. The resulting solution was slowly layered onto a solution of $H_4SiMo_{12}O_{40}\cdot xH_2O$ (0.250 g, 0.1 mmol) in DMF (4 mL). The solution was left for several days at room temperature and yellow block crystals **1** suitable for X-ray structure determination were obtained in 67% yield (based on $H_4SiMo_{12}O_{40}\cdot xH_2O$). Anal. calc. for $C_{101}H_{86.5}O_{43}N_{17.5}Ag_4Mo_{12}Si$ (%): C, 31.56; H, 2.27; N, 6.38. Found (%): C, 31.63; H, 2.23; N, 6.27. IR (KBr pellet, cm^{-1}): 3450(w), 3064(w), 1651(s), 1558(w), 1490(m), 1436(m), 1385(w), 1329(s), 1252(m), 1101(w), 987(w), 945(vs), 901(vs), 854(s), 802(vs), 789(vs), 701(w), 658(w).

Preparation of the compound **2**

$H_4SiMo_{12}O_{40}\cdot xH_2O$ (0.250 g, 0.1 mmol) was dissolved in DMF (4 mL) with $AgNO_3$ (0.068 g, 0.4 mmol) and then the solution was stirred for 0.5 h. Ligand L^2 (0.013 g, 0.1 mmol) was stirred in methanol solution (5 mL), and the resulting solution was slowly layered onto the DMF solution of $AgNO_3$ and $H_4SiMo_{12}O_{40}\cdot xH_2O$. The final solution was left for two weeks at room temperature in darkness to give X-ray quality yellow block crystals in 53% yield (based on $H_4SiMo_{12}O_{40}\cdot xH_2O$). Anal. calc. for $C_{39}H_{53}O_{45}N_{11}Ag_4Mo_{12}Si$ (%): C, 15.58; H, 1.78; N, 5.12. Found (%): C, 15.68; H, 1.64; N, 5.07. IR (KBr pellet, cm^{-1}): 2924(w), 1630(s), 1494(w), 1385(vs), 1328(m), 1255 (w), 1159(m), 1080(w), 997(w), 984(w), 954(vs), 901(vs), 851(s), 803(vs), 778(vs), 701(w).

Crystallographic studies

A suitable sample of size 0.26 mm × 0.17 mm × 0.15 mm for **1** and 0.20 mm × 0.18 mm × 0.16 mm for **2** was chosen for the crystallographic study and then mounted on a BRUKER SMART APEX CCD diffractometer with ω and φ scan mode in the range of $1.21^\circ < \theta < 25.00^\circ$ for **1** and $1.79^\circ < \theta < 25.00^\circ$ for **2**, respectively. All diffraction measurements were performed at room temperature using graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). A total of 60329 (21155 independent, R_{int} = 0.0815)