Hydrothermal Synthesis and Structural Characterization of an Inorganic–Organic Hybrid Sandwich-type Germanotungstate

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A novel inorganic–organic hybrid germanotungstate $(H_2en)_5[\{Ni(Hen)\}_2Ni_2(GeW_9O_{34})_2]\cdot 8H_2O$ (**1**) has been hydrothermally synthesized and characterized by elemental analyses, IR, ESR spectra, TG-DTA, and X-ray diffraction. The title compound consists of a tetra-Ni^{II}-substituted sandwich-type anion $[\{Ni(Hen)\}_2Ni_2(GeW_9O_{34})_2]^{10-}$, where two monoprotonated en (en = ethylenediamine) ligands have replaced the two external water molecules of the well-known rhombohedral Ni_4O_{16} core.

The design and synthesis of new inorganic–organic hybrid materials is of current interest owing to their intriguing variety of architectures and topologies, potential applications in fields such as catalytically active, electric, absorption, optical, biochemical and magnetic materials.[1] To date, great efforts have been made to use polyoxometalates (POMs) composed of transition metals (W, Mo, V, Nb, and Ta) as important molecular building blocks to construct inorganic–organic hybrid materials.[2] Meanwhile the organic ligands are generally selected as structural directors. In recent years, sandwich-type POMs have developed as one of the most important subclass in POM chemistry.[3a] Since the first sandwich-type $[Co_4(H_2O)_2(\alpha\text{-B-PW}_9O_{34})]^{10-}$ was synthesized in 1973,[3b] an enormous number of sandwich-type POMs, containing a certain number of paramagnetic transition-metal cations sandwiched by two usual lacunary fragments have been reported.[3c] Probably the best known examples are the tetrametal-substituted sandwich-type polyoxotungstates of the Keggin type $[M_4(H_2O)_2(\alpha\text{-B-XW}_9O_{34})_2]^{n-}$ ($M = Mn^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}$, etc., X = P, As, Si, Ge, Sb, Se, and Te).[3b,4] Although many tetrametal-substituted sandwich-type POMs have been reported, POMs with organic ligand coordinated central metal atoms have rarely been observed previously.[5]

In the vast amount of published work, most sandwich-type POMs were made by conventional solution syntheses at atmospheric pressure and relatively low temperature (<100 °C).[3b,6] Recently, our laboratory tried to synthesize unexpected structures based on sandwich-type POMs by hydrothermal methods, which are inaccessible or not easily obtained under conventional solution syntheses. In this paper, we report the hydrothermal synthesis and crystal structure of a new sandwich-type germanotungstate $(H_2en)_5[\{Ni(Hen)\}_2Ni_2(GeW_9O_{34})_2]\cdot 8H_2O$ (**1**).

Compound **1** was prepared through a hydrothermal method.[7] The single crystal X-ray diffraction structure analysis indicates compound **1** consists of five isolated $(H_2en)^{2+}$ cations, a tetra-Ni^{II}-substituted sandwich-type anion $[\{Ni(Hen)\}_2Ni_2(GeW_9O_{34})_2]^{10-}$ and eight water molecules.[8] As depicted by Figure 1, the polyoxoanion consists of two trilacunary $[\alpha\text{-B-GeW}_9O_{34}]^{12-}$ Keggin moieties linked to each other via a rhomboid $Ni_4O_{14}(Hen)_2$ fragment (Figure 2) leading to a sandwich-type structure. The dimeric polyoxoanion $[\{Ni(Hen)\}_2Ni_2(GeW_9O_{34})_2]^{10-}$ is similar to the previously reported $[M_4(H_2O)_2(GeW_9O_{34})_2]^{12-}$ ($M = Mn^{2+}, Cu^{2+}, Zn^{2+}$, and Cd^{2+}),[4b] but there was an obvious difference compared to classical examples only containing inorganic sandwich-type tetrametal-substituted POMs: The two coordination-water molecules on the two external nickel centers have been substituted by nitrogen atoms of monoprotonated en cations, forming a rare inorganic–organic hybrid compound.

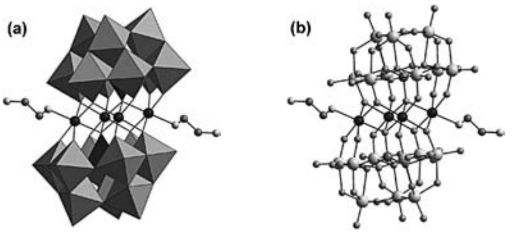

Figure 1. (a) Polyhedral/ball-and-stick and (b) ball-and-stick drawings of $[\{Ni(Hen)\}_2Ni_2(GeW_9O_{34})_2]^{10-}$.

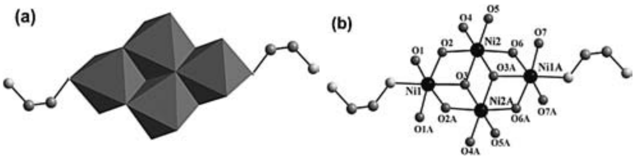

Figure 2. (a) Polyhedral/ball-and-stick and (b) ball-and-stick drawings of the central $Ni_4O_{14}(Hen)_2$ fragment of compound **1**.

The trilacunary polyanion $[\alpha\text{-B-GeW}_9O_{34}]^{10-}$ in compound **1** is derived from a saturated Keggin unit $[\alpha\text{-GeW}_{12}O_{40}]^{4-}$ by removal of one edge-sharing $\{W_3O_{13}\}$ triad, and it acts as a bulky multidentate ligand to link to four Ni^{2+} ions. The nine WO_6 octahedra in $[\alpha\text{-B-GeW}_9O_{34}]^{10-}$ moiety have essentially similar distorted octahedral environments defined by one terminal oxygen atom with short W–O bond length ranging from 1.698(11) to 1.754(11) Å, four doubly bridging oxygen atoms with intermediate W–μ–O bond lengths in the range of 1.852(10)–2.075(10) Å, and one μ_4-oxygen, also bonded to Ge, with long W–μ_4–O distances (2.273(9)–2.364(9) Å). The Ge–O bond distances in the GeO_4 polyhedra vary from 1.735(9) to 1.782(10) Å, and the O–Ge–O bond angles vary from 105.7(5) to 113.0(4)°, indicating that the GeO_4 tetrahedra are slightly distorted, which could be attributed to the effect of rhombohedral $Ni_4O_{14}(Hen)_2$.

It is noteworthy that the central cluster $Ni_4O_{14}(Hen)_2$ (Figure 2) is a rare inorganic–organic hybrid unit, four Ni^{2+} can be divided into two groups according to the positions at which they are located. The first group includes the two internal Ni^{2+} (Ni2 and Ni2A ions), the Ni2 ion is defined by six O atoms

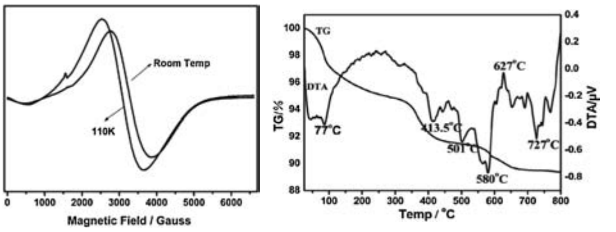

Figure 3. (a) ESR spectra of compound **1** at 110 K and room temperature. (b) TG/DTA curve of compound **1**.

(O2, O4, O5, and O6 from four WO_6 groups, O3 and O3A from two GeO_4 groups, respectively), forming a distorted octahedron with O3 and O5 atoms occupying the axial positions. The second group includes the two external Ni^{2+} (Ni1 and Ni1A ions). Ni1 ion is defined by a N atom from one monoprotonated en ligand and five O atoms (O1, O1A, O2, O2A, and O3 atoms also from two $[\alpha\text{-B-GeW}_9O_{34}]^{10-}$ moieties), forming a distorted octahedron configuration with N and O3 atoms occupying the axial position. The two external distorted octahedra ($Ni(1)NO_5$ and $Ni(1A)NO_5$) are further attached to the two internal distorted octahedra ($Ni(2)O_6$ and $Ni(2A)O_6$) by edge-sharing. The Ni1–O distances are in the range of 2.042(10) to 2.123(11) Å with an average of 2.083 Å, and the Ni2–O distances 2.019(10)–2.095(10) Å with an average of 2.065 Å, which are slightly shorter than the average Ni1–O distances, the Ni–N distances are 2.118(13) Å, whereas the corresponding O–Ni–O angles of the $Ni_4O_{14}(Hen)_2$ fragment vary from 81.5(4) to 173.5(4)°. The bond valence sum (BVS)[9] calculations of all the nickel atoms in compound **1** (1.942, 1.980 for Ni(1), Ni(1A) and Ni(2), Ni(2A) respectively) indicates these Ni atoms exhibit +2 valence. Additionally, according to the reaction environment, two pendent en ligands on $Ni_4O_{14}(Hen)_2$ group should be monoprotonated and five isolated en should be biprotonated.[5a] Therefore, the molecular formula of **1** is described as $(H_2en)_5[\{Ni(Hen)\}_2Ni_2(GeW_9O_{34})_2]\cdot 8H_2O$.

As shown in Figure 3a, the X-band polycrystalline-powder ESR spectra recorded at low temperature (110 K) and room temperature on a crystalline sample of compound **1** display signals with $g = 2.20$ and $g = 2.11$, respectively, indicating the existence of Ni^{II} with high-spin state,[10] the coordination number of this type Ni^{II} is 4 or 6, associated with the result of crystal structure analysis, the Ni atoms of compound **1** attribute to the latter distinctly.

The TG curve of **1** shows four steps of weight loss (Figure 3b), giving a total loss of 10.61% (calcd 10.77%) in the range of 25–800 °C. The first weight loss of 2.64% in 25–96 °C is ascribed to the loss of eight water molecules (calcd 2.69%), and one strong endothermal peak at 77 °C is observed in the corresponding DTA curve. The second weight loss of 2.39% from 96 to 275 °C is assigned to the release of the two isolated $(H_2en)^{2+}$ cations (calcd 2.32%). The third weight loss of 3.55% from 275 to 514 °C is attributed to the release of the other three isolated $(H_2en)^{2+}$ cations (calcd 3.48%), and two strong endothermal peaks at 413.5 and 501 °C are observed in the corresponding DTA curve. The fourth weight loss of 2.03% in the range of 518–800 °C is ascribed to the removal of two monoprotonated en ligands (calcd 2.28%), and there is a strong endothermal peak at 580 °C in the corresponding DTA curve. It should be noted that the strong exothermal peak at 627 °C in the DTA curve indicates the title polyoxoanion beginning to decompose, and the strong endothermal peak at 727 °C may be ascribed to the phase transition of the residue.

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7 Synthesis of compound **1**: $Na_2WO_4\cdot 2H_2O$ (3.3 g), GeO_2 (0.32 g), NaOH (0.3 g), $NiCl_2\cdot 3H_2O$ (0.29 g), en (2 mL), and distilled water (20 mL) were mixed, adjusted to pH 7.0 by HCl (1 mol/L) and stirred for 3 h. The mixture was then transferred to a Teflon-lined autoclave and heated for 8 days at 180 °C. After the mixture was slowly cooled to room temperature, dark-green block crystals were obtained (21% yield based on W). Elemental analysis Calcd (%) for $C_{14}H_{84}Ge_2N_{14}Ni_4O_{76}W_{18}$: C, 3.14; H, 1.58; N, 3.66%. Found: C, 3.09; H, 1.32; N, 3.71%. IR: 468(s), 515(s), 715(s), 769(s), 867(s), 932(s), and 1401 cm^{-1}(s) (see Figure S1[11]).

8 Crystallographic data for **1**: $C_{14}H_{84}Ge_2N_{14}Ni_4O_{76}W_{18}$, $M_r = 5354.26$, monoclinic, $P2_1/n$, $a = 16.8006(13)$ Å, $b = 12.4110(10)$ Å, $c = 21.5163(17)$ Å, $\beta = 110.6240(10)°$, $V = 4198.9(6)$ Å^3, $Z = 2$, $D_{calcd} = 4.237\ g/cm^3$, $F(000) = 4768$, $T = 293(2)$ K, 20827 reflections measured, 7251 independent ($R_{int} = 0.1109$), $R_1 = 0.0508$ ($I > 2\sigma(I)$), $wR_2 = 0.1324$ (all data), CCDC number: 694614.

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