

A sandwich-type tungstoantimonate containing trinuclear nickel ions modified with aminopyrazine ligand

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ABSTRACT

A new organic–inorganic hybrid tungstoantimonate, $\text{Na}_4[\text{Ni}_2(\text{apy})(\text{H}_2\text{O})_{10}]_{1/2}[(\text{Ni}(\text{Hapy}))_3(\text{Na}(\text{H}_2\text{O})_2)_3(\text{SbW}_9\text{O}_{33})_2] \cdot 23\text{H}_2\text{O}$ (1) (apy = aminopyrazine), has been synthesized and fully characterized. Single crystal X-ray diffraction analysis indicates that the polyanion $[(\text{Ni}(\text{Hapy}))_3(\text{Na}(\text{H}_2\text{O})_2)_3(\text{SbW}_9\text{O}_{33})_2]^{6-}$ displays a sandwich-type dimeric structure in which the Ni^{2+} ions in the central belt are modified by aminopyrazine ligands. The contrast experiment analyses show that the existence of organic amine ligand is a key role to the formation of the stable Hervé-type tungstoantimonate containing trinuclear nickel(II) ions, which crystallized with dinuclear nickel complex constructed from an aminopyrazine bridging two $[\text{Ni}(\text{H}_2\text{O})_5]^{2+}$ ions as part of counterions. The variable-temperature magnetic measurements of 1 exhibit the weak antiferromagnetic exchange interactions among $\text{Ni}(\text{II})$ clusters in 1.

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Polyoxometalates (POMs), a fascinating class of metal–oxygen cluster compounds, have attracted extensive attention for many years due to their wide structural variety and diverse range of applications in catalysis, materials science, bioinorganic, analytical and medicinal chemistry [1]. In the development of POM chemistry, lacunary polyoxoanions play an important role because they can serve as the nucleophilic inorganic multidentate ligands to coordinate to electrophiles of transition metal or rare earth cations, to constitute a great quantity of novel transition metal substituted POMs (TMSPs) [2]. Within the class of TMSPs, the sandwich-type polyoxoanions, accommodating lots of paramagnetic transition-metal cations between the two lacunary polyoxoanions, are an important subclass. Since the first sandwich-type polyoxoanion $[\text{Co}_4(\text{H}_2\text{O})(\text{B}-\alpha\text{-PW}_9\text{O}_{34})_2]^{10-}$ was discovered by Weakly et al. in 1973 [3], numerous sandwich-type polyoxoanions including Weakley-, Hervé-, Krebs-, and Knoth-type sandwich structures have been reported [4–7]. The class of Hervé-type sandwich POMs is based on two lone pair-containing α -Keggin fragments with general formula $[(\text{M}(\text{H}_2\text{O}))_3(\text{XW}_9\text{O}_{33})_2]^{n-}$ ($\text{X} = \text{As}^{\text{III}}, \text{Sb}^{\text{III}}, \text{Bi}^{\text{III}}, \text{Se}^{\text{IV}}$ or Te^{IV}), generally formed in weakly alkaline or neutral aqueous solution. The first member of this class $[(\text{Cu}_3(\text{H}_2\text{O})_2(\alpha\text{-AsW}_9\text{O}_{33})_2]^{12-}$ was reported by Hervé et al. in 1982 [8]. Since then a number of isostructural derivatives have been characterized: $[(\text{M}_3(\text{H}_2\text{O})_x)(\text{XW}_9\text{O}_{33})_2]^{n-}$ ($n = 12, \text{X} = \text{As}^{\text{III}}, \text{Sb}^{\text{III}}, \text{M} = \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}; n = 10, \text{X} = \text{Se}^{\text{IV}}, \text{Te}^{\text{IV}}, \text{M} = \text{Cu}^{2+}$) and $[(\text{VO})_3(\alpha\text{-XW}_9\text{O}_{33})_2]^{n-}$ ($n = 12, \text{X} = \text{As}^{\text{III}}, \text{Sb}^{\text{III}}, \text{Bi}^{\text{III}}; n = 11, \text{X} = \text{As}^{\text{III}}$) [6b,8–19]. Chemically, the polyoxoanionic structures can be modified

with proper organic ligands to substitute coordinated water molecules attached to the magnetic transition metal clusters of sandwich-type heteropolyanions. Such modification may be an effective route to tune their physical and chemical properties [20]. In 2005, our group first reported an example of pyridine modified sandwich-type heteropolytungstate $\{[\text{Na}(\text{H}_2\text{O})_2]_3[\text{Ni}(\text{C}_5\text{H}_5\text{N})]_3(\text{AsW}_9\text{O}_{33})_2\}^{9-}$ [21]. After that, we successfully synthesized the imidazole coordinated sandwich-type heteropolytungstates $\text{Na}_9\{[\text{Na}(\text{H}_2\text{O})_2]_3[\text{M}(\text{C}_3\text{H}_4\text{N}_2)]_3(\text{SbW}_9\text{O}_{33})_2\} \cdot x\text{H}_2\text{O}$ ($\text{M} = \text{Ni}^{\text{II}}, x = 32; \text{M} = \text{Co}^{\text{II}}, x = 32; \text{M} = \text{Zn}^{\text{II}}, x = 33; \text{M} = \text{Mn}^{\text{II}}, x = 34$) [22]. In 2008, Xu et al. reported two isostructural 1D chains based on sandwich-type $\{[\text{Na}(\text{H}_2\text{O})_2]_3[\text{Cu}_3(\text{im})_2(\text{H}_2\text{O})](\text{XW}_9\text{O}_{33})_2\}^{9-}$ ($\text{X} = \text{Sb}, \text{Bi}$) anions linked by $[\text{Cu}(\text{im})_4]^{2+}$ cations [23]. The same year, Niu et al. reported the 1D zigzag chain $[\text{Na}_3(\text{H}_2\text{O})_6\text{Mn}_3(\mu\text{-OAc})_2(\text{B}-\alpha\text{-SbW}_9\text{O}_{33})_2]^{11-}$ based on sandwich-type tungstoantimonate building blocks and carboxylate bridging ligands [24]. In 2010, Peng et al. reported an imidazole coordinated sandwich-type heteropolytungstate $\{[\text{Na}(\text{H}_2\text{O})][\text{Mn}(\text{C}_3\text{H}_4\text{N}_2)]_3(\text{SbW}_9\text{O}_{33})_2\}^{11-}$ [25]. In 2011, Wang et al. reported two methylimidazole modified Hervé-sandwich-type polytungstoantimonates $\text{Na}_9\{[\text{Na}(\text{H}_2\text{O})_2]_3[\text{M}(\text{C}_4\text{H}_6\text{N}_2)]_3(\text{SbW}_9\text{O}_{33})_2\} \cdot 28\text{H}_2\text{O}$ ($\text{M} = \text{Co}, \text{Mn}$) [26]. Though more sandwich-type POMs modified with different organic ligands are expected, the reported amount and the kinds are very limited due to the presence of a coordinate competition between water and nonaqueous ligands in aqueous medium, which results in the difficulty in obtaining the sandwich-type POMs modified with organic ligands. Pyrazine should be an ideal available ligand because it is a hexacyclic aromatic compound with relatively small volume and has two potential N coordination sites and a stronger coordination ability to metal ions.

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However, until now there have been no reports related to the sandwich-type POMs modified with pyrazine ligand except a “dumbbell” complex in which a pyrazine coordinates at two positions, linking two heteropoly units through coordination to metal ions that have been substituted into the heteropoly structures $[\text{SiW}_{11}\text{O}_{39}\text{Co}^{3+}(\text{pyrazine})\text{Co}^{2+}\text{SiW}_{11}\text{O}_{39}]^{11-}$, reported by Landis et al. as early as 1977 [27]. In contrast to pyrazine ligand, aminopyrazine should have a stronger coordination ability to metal ions because it has an electron-donating group. Considering the abovementioned, we devoted ourselves to synthesize new types of organic ligand modified Hervé-type sandwich POMs. Here we reported a new sandwich-type tungstoantimonate containing trinuclear nickel ions modified with aminopyrazine, $\text{Na}_4[\text{Ni}_2(\text{apy})(\text{H}_2\text{O})_{10}]_{1/2}[(\text{Ni}(\text{Hapy}))_3(\text{Na}(\text{H}_2\text{O})_2)_3(\text{SbW}_9\text{O}_{33})_2] \cdot 23\text{H}_2\text{O}$ (1).

The title compound was synthesized by treating a suspension of $\text{Na}_9[\text{SbW}_9\text{O}_{33}] \cdot 19.5\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and aminopyrazine at 80°C in $\text{pH} = 7.5$ [28]. The contrast experiment analyses show that we hardly isolate the water molecule coordinated analogue of 1 without organic ligands. The successful synthesis of 1 and other Hervé-sandwich-type polyanions containing trinuclear nickel ions modified with organic ligands [21,22], such as imidazole and pyridine, indicates that the existence of organic ligands is favorable to the formation of the sandwich-type trinuclear nickel compounds. This result is in agreement with the report of the instability of nickel complexes with $[\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ derivative, which can lead to a mixture of compounds in solution [13]. Tight control of the pH is essential for the synthesis of 1 and the pH value should be adjusted at 7.5. The main reasons are as follows: Firstly, the starting $[\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$ fragment is reasonably stable in aqueous solution at a pH of around 7.5, and exposure to an acidic medium ($\text{pH} < 5.5$) results in the following transformation $[\alpha\text{-SbW}_9\text{O}_{33}]^{9-} \rightarrow [\beta\text{-SbW}_9\text{O}_{33}]^{9-}$. Secondly, N-donor ligands are easily protonated under acidic medium, and then greatly reduce their coordination ability to metal ions.

Single crystal X-ray diffraction analysis [29] reveals that compound 1 consists of a sandwich-type $[(\text{Ni}(\text{Hapy}))_3(\text{Na}(\text{H}_2\text{O})_2)_3(\text{SbW}_9\text{O}_{33})_2]^{6-}$ polyanion, one half of $[\text{Ni}_2(\text{apy})(\text{H}_2\text{O})_{10}]^{4+}$ isolated cation, four sodium ions and twenty-three lattice water molecules (Fig. 1a). The fragment of dinuclear nickel complex constructs from an aminopyrazine ligand bridging two $[\text{Ni}(\text{H}_2\text{O})_5]^{2+}$ ions by two N atoms from the hexacyclic aromatic compound. The structure of the sandwich-type polyoxoanion

$[(\text{Ni}(\text{Hapy}))_3(\text{Na}(\text{H}_2\text{O})_2)_3(\text{SbW}_9\text{O}_{33})_2]^{6-}$ is closely related to the previously reported pyridine modified sandwich-type heteropolytungstate $\{[\text{Na}(\text{H}_2\text{O})_2]_3[\text{Ni}(\text{C}_5\text{H}_5\text{N})]_3(\text{AsW}_9\text{O}_{33})_2\}^{9-}$ [21]. It can be described as two trivacant Keggin-type $[\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$ subunits encapsulating a hexagonal $\{\text{Ni}_3\text{Na}_3\}$ core through exposed 12 bridging oxygen atoms from the lacunae of two $[\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$ subunits. In the hexagonal $\{\text{Ni}_3\text{Na}_3\}$ core (Fig. 1b), three Na^+ ions alternately linked three Ni^{2+} ions to form a six-membered ring with the interior angle sum of 719.96° , suggesting that the six atoms lie in the same plane. The central Sb–O distances of polyoxoanion vary from 1.94(2) to 1.99(2) Å, and the W–O distances can be divided into three different groups: $\text{W}-\text{O}_\text{c}$ (central), 2.204(2) to 2.354(2) Å, oxygen atoms connecting three W atoms and a Sb heteroatom; $\text{W}-\text{O}_\text{b}$ (bridge), 1.834(2)–2.057(2) Å, oxygen atoms connecting two W atoms; and $\text{W}-\text{O}_\text{t}$ (terminal), 1.651(2)–1.837(3) Å, oxygen atoms bonded to W and the central metal cluster. There are four crystallographically independent nickel(II) ions in compound 1. For Ni(1), Ni(2) and Ni(3) ions in the central belt, each nickel ion in a square-pyramidal geometry is coordinated by four terminal oxygen atoms from two different $[\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$ subunits with Ni–O bond lengths of 1.91(2)–2.04(2) Å and a nitrogen atom from the aminopyrazine molecule with Ni–N bond lengths of 1.970(10) to 2.047(10) Å. While for Ni(4) ion in $[\text{Ni}_2(\text{apy})(\text{H}_2\text{O})_{10}]^{4+}$ cation, it shows an octahedral geometry defined by one nitrogen atom from one aminopyrazine molecule and five water molecules (the average Ni–O distances and the Ni–N distance are 2.08(2) Å and 2.09(2) Å). Interestingly, these discrete sandwich polyoxoanions stack with each other to form a 1D chain by the π – π stacking interactions between adjacent pyrazine rings with the mean interplanar separation of 3.846 Å (Fig. 2). The 3D supramolecular framework of 1 is shown in Fig. S1.

The IR spectra of 1 display the characteristic vibration patterns derived from the Keggin framework in the region of $937\text{--}726\text{ cm}^{-1}$ (Fig. S2). Three characteristic vibration bands attributed to $\nu(\text{W}-\text{O}_\text{d})$, $\nu(\text{W}-\text{O}_\text{b})$, and $\nu(\text{W}-\text{O}_\text{c})$ appear at 937, 876 and 726 cm^{-1} , respectively. UV spectra of compound 1 in $\text{pH} = 7.5$ aqueous solution exhibit four characteristic bands (Fig. S3). The more intense band corresponding to the $\text{p}_\pi(\text{O}_\text{d}) \rightarrow \text{d}_{\pi^*}(\text{W})$ transitions appears at 195.2 nm and the broader band around 279.8 nm is assigned to a $\text{p}_\pi(\text{O}_\text{b,c}) \rightarrow \text{d}_{\pi^*}(\text{W})$ charge transfer transition, which are consistent with the literature values (193.6 and 271.7 nm) [16,30]. Transitions at 225.4 and 317.4 nm are assigned to intra-ligand charge transfer $\pi \rightarrow \pi^*$ and $\text{n} \rightarrow \pi^*$, respectively [31].

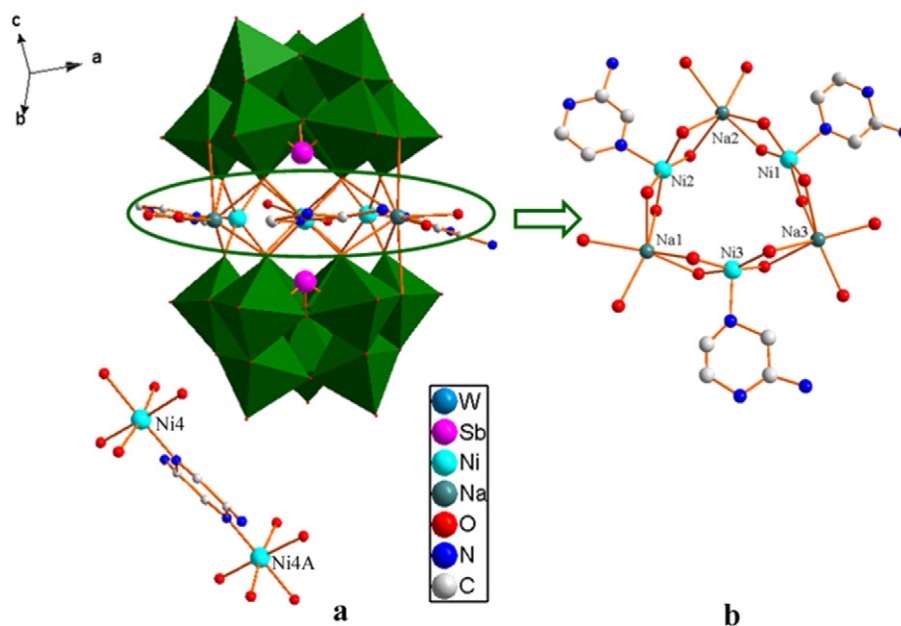


Fig. 1. (a) Ball-and-stick/polyhedral representation of the molecular unit of 1. Lattice water molecules and hydrogen atoms attached to carbon and nitrogen atoms are omitted for clarity. The atoms with the suffix A are generated by the symmetry operation: A: 1-x,2-y,-z, (b) ball-and-stick representation of hexagonal $\{\text{Ni}_3\text{Na}_3\}$ ring in 1.

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