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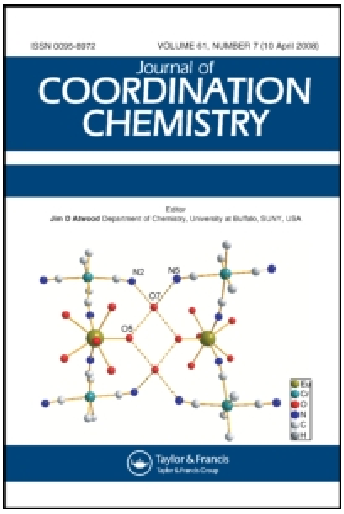

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Hydrothermal assembly of pyrite-related framework: $(NH_4)_2\{[Ni(H_2O)_3]_2[TeW_6O_{24}]\}\cdot H_2O$

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A new 3D heteropolyoxotungstate, $(NH_4)_2\{[Ni(H_2O)_3]_2[TeW_6O_{24}]\}\cdot H_2O$ (**1**), has been isolated from hydrothermal reactions and characterized by elemental analyses, IR spectra and X-ray crystallography. Single-crystal X-ray diffraction analysis reveals that compound **1** possess unusual (3,6)-connected networks constructed from Anderson-type anions $[TeW_6O_{24}]^{6-}$ and nickel cations. The compound exhibits pyrite-like topology in which $[TeW_6O_{24}]^{6-}$ anions act as 6-connecting sites and nickel cations act as 3-connecting sites. The magnetic properties of **1** are also presented.

Keywords: Tungstate; Tellurium; Hydrothermal assembly; Anderson-type polyoxoanions

1. Introduction

Heteropolyoxometalates are a unique class of inorganic metal-oxygen clusters. They are especially valuable for studies in diverse areas of current interest, which include medicine, biochemistry, catalysis and magnetism [1–5]. Development in the field of heteropolyoxometalates has largely depended on the progress made for Keggin and related species that have tetrahedral heteroatoms; progress for species with octahedral heteroatoms has been slower.

Among the wide variety of heteropolyoxometalates, the Anderson series attracts more and more attention. These heteropolyoxoanions have the general formula $[XM_6O_{24}Hx]^{n-}$ ($M = Mo$ or W, $x = 0$–6, $n = 2$–6) with an octahedral heteroatom in the center. Recently, a number of Anderson-type heteropolymolybdates were reported [6–9], however, there has been much less investigations in the literatures about heteropolytungstates with corresponding structures. We are currently interested in the Anderson-type heteropolyoxoanion, $[TeW_6O_{24}]^{6-}$, and investigating its propensity to link with metal ions for extended structures of new materials. Usually, Anderson-based compounds are synthesized in bench conditions and their structures are limited mainly one-dimensional structures. Hydrothermal synthesis of Anderson-based heteropolyoxometalates remains rarely explored. Recent elaboration has proven that hydrothermal

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reaction, which causes a reaction shifting from kinetic to thermodynamic domain compared to traditional aqueous reactions, provides a powerful tool for the synthesis of higher-dimensional oxide frameworks [10].

Inspired by our previous work [11], we have obtained a new extended structural heteropolyoxotungstate: $(NH_4)_2\{[Ni(H_2O)_3]_2[TeW_6O_{24}]\} \cdot H_2O$ (**1**), which is constructed from the A-type Anderson anion $[TeW_6O_{24}]^{6-}$ under hydrothermal conditions. The compound is a highly symmetrical three-dimensional (3D) framework with pyrite-related topology. Extended structural compounds with classical mineral structures can be found more easily in metal-organic frameworks (MOFs), such as metal-organic replicas of fluorite [12], pyrite [13], rutile [14], and quartz [15], etc. However, compound **1** represents a new example with classical mineral-related topology constructed from POMs.

2. Experimental section

2.1. *General methods*

All reagents were readily available from commercial sources and used as received without further purification. Elemental analyses (C, H and N) were performed with a Perkin-Elmer 2400 CHN Elemental Analyzer. Te, W and Ni were determined by a PLASMASPEC(I) ICP atomic emission spectrometer. IR spectra in KBr pellets were recorded in the range 400–4000 cm^{-1} with an Alpha Centaurt FT/IR Spectrophotometer. Magnetic susceptibility data were collected over the temperature range 2–300 K at a magnetic field of 10,000 Oe on a Quantum Design MPMS-5 SQUID magnetometer. TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of $10^{\circ}C\,min^{-1}$.

2.2. *Synthesis of compound 1*

Compound **1** was hydrothermally synthesized under autogenous pressure. A mixture of TeO_2 (0.0828 g), $NaWO_4 \cdot 2H_2O$ (0.9231 g), H_4NCl (0.1521 g), $NiSO_4 \cdot 7H_2O$ (0.1502 g), NaOH (0.0451 g), H_2O_2 (30%, 0.5 mL) and H_2O (6 mL) was stirred in air for 1 h after the pH was adjusted to 4.0 with HCl. The resulting suspension was sealed in a 16 mL Teflon lined stainless steel autoclave which was kept at 160°C for 4 days, then cooled to room temperature at $6^{\circ}C\,h^{-1}$. A light green block crystalline product was recovered by washing with distilled water and filtration. Any impurity was manually removed to give a yield of 76% (based upon Te). Anal Calcd for $H_{22}Ni_2W_6N_2O_{31}Te$ (**1**): H, 1.2; N, 1.5; Ni, 6.2; Te, 6.7; W, 58.2. Found: H, 1.1; N, 1.6; Ni, 6.2; Te, 6.6; W, 58.3. FT/IR (cm^{-1}) for **1**: 3435(w), 1635(w), 1421(s), 982(s), 913(m), 878(m), 668(s), 656(s).

2.3. *X-ray crystallography*

Crystal of **1** suitable for single-crystal X-ray diffraction were glued to a thin glass fiber with epoxy resin and mounted to a Siemens SMART CCD diffractometer with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation in the ω-scanning mode

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$H_{22}N_2Ni_2O_{31}TeW_6$
Formula weight ($g\,mol^{-1}$)	1892.30
T (K)	273(2)
λ (Å)	0.71073
Space group	$Pa\bar{3}$
a (Å)	14.0518(4)
V (Å^3)	2774.57(14)
Z	4
D_{Calcd} ($Mg\,m^{-3}$)	4.530
μ (mm^{-1})	27.242
$F(000)$	3336
Goodness-of-fit on F^2	0.985
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0212$, $wR_2 = 0.0402$
R indices (all data)	$R_1 = 0.0322$, $wR_2 = 0.0411$

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = \Sigma[w(F_o^2) - F_c^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **1**.

	x	*y*	*z*	*U*(eq)
Ni(1)	7995(1)	2995(1)	2005(1)	12(1)
Te(1)	5000	0	0	9(1)
W(1)	5863(1)	1922(1)	1023(1)	12(1)
N(1)	6131(4)	3869(4)	8869(4)	30(2)
O(1)	4543(3)	1225(3)	415(3)	11(1)
O(2)	6223(3)	2053(3)	−300(3)	14(1)
O(3)	5288(3)	2998(3)	1139(3)	21(1)
O(4)	6975(3)	2071(3)	1546(3)	16(1)
O(5)	8867(3)	2480(3)	942(3)	19(1)
O(1W)	5000	5000	10,000	158(10)

U(eq) is defined as one third of the trace of the orthogonalized *Uij* tensor.

at 293 K. The structures were solved by the direct method and refined by full-matrix least squares on F^2 using SHELXTL-97 software [16]. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the Fourier difference maps. Crystal parameters and details of the data collection and refinement for **1** are listed in table 1. Atomic coordinates and equivalent isotropic displacement parameters of **1** are listed in table 2. Selected bond lengths of compound **1** are listed in table 3. (CSD reference number 416157.)

3. Results and discussion

3.1. *Synthesis and structure*

The synthesis of **1** is inspired by our previous work $(NH_4)_2\{[M(H_2O)_3]_2[TeMo_6O_{24}]\} \cdot H_2O$ (M = Mn, Co, Ni, Cu and Zn) [11]. The heteropolyoxoanion $[TeW_6O_{24}]^{6-}$ has the same structure as $[TeMo_6O_{24}]^{6-}$, so replaced $[TeMo_6O_{24}]^{6-}$ with $[TeW_6O_{24}]^{6-}$ in the above compounds. Unfortunately, through a large number of experiments, only one compound instead of a series of isomorphous

Table 3. Selected bond lengths (Å) and angles (°) for **1**.

Ni(1)–O(4)	2.039(4)	Ni(1)–O(5)	2.063(4)
Te(1)–O(1)	1.928(4)	W(1)–O(1)	2.265(4)
W(1)–O(3)	1.721(4)	W(1)–O(4)	1.739(4)
W(1)–O(2)#7	1.920(4)	W(1)–O(2)	1.936(4)
W(1)–O(1)#3	2.319(4)		
O(4)–Ni(1)–O(4)#1	88.60(16)	O(4)–Ni(1)–O(5)#1	176.60(16)
O(4)–Ni(1)–O(5)	88.01(15)	O(4)#1–Ni(1)–O(5)	91.52(15)
O(5)#1–Ni(1)–O(5)	91.87(16)	O(1)#4–Te(1)–O(1)	94.18(15)
O(1)–Te(1)–O(1)#7	85.82(15)	O(1)#5–Te(1)–O(1)	180.0(3)
O(1)#3–Te(1)–O(1)#6	180.0(2)	O(3)–W(1)–O(2)#7	100.63(17)
O(3)–W(1)–O(4)	106.00(19)	O(3)–W(1)–O(2)	97.50(17)
O(4)–W(1)–O(2)#7	96.47(17)	O(2)#7–W(1)–O(2)	151.7(2)
O(4)–W(1)–O(2)	99.22(16)	O(4)–W(1)–O(1)	161.29(16)
O(3)–W(1)–O(1)	91.78(16)	O(2)–W(1)–O(1)	83.83(15)
O(2)#7–W(1)–O(1)	74.09(15)	O(4)–W(1)–O(1)#3	93.31(16)
O(3)–W(1)–O(1)#3	159.64(16)	O(2)–W(1)–O(1)#3	72.56(14)
O(2)#7–W(1)–O(1)#3	83.18(15)	Te(1)–O(1)–W(1)	103.13(16)
O(1)–W(1)–O(1)#3	69.86(18)	W(1)–O(1)–W(1)#7	91.77(13)
Te(1)–O(1)–W(1)#7	101.20(16)	W(1)–O(4)–Ni(1)	147.3(2)
W(1)#3–O(2)–W(1)	117.23(19)		

Symmetry transformations used to generate equivalent atoms: #1 $-z+1$, $x-1/2$, $-y+1/2$; #2 $y+1/2$, $-z+1/2$, $-x+1$; #3 $y+1/2$, z, $-x+1/2$; #4 $z+1/2$, $-x+1/2$, $-y$; #5 $-x+1$, $-y$, $-z$; #6 $-y+1/2$, $-z$, $x-1/2$; #7 $-z+1/2$, $x-1/2$, y.

compounds was obtained. NH_4Cl is added into the reaction system as is the counter cation in compound **1**; **1** cannot be formed without NH_4Cl.

Single-crystal X-ray structure analysis of **1** reveals a highly symmetrical structure. The polyanion $[TeW_6O_{24}]^{6-}$ in compound **1** is a typical Anderson heteropolyoxotungstate with D_{3d} symmetry, in which six WO_6 octahedra form a regular hexagon like a crown and the internal octahedral cavity is filled by a TeO_6 octahedron. The Te–O bond lengths and O–Te–O bond angles are summarized in table 3, showing only slight distortion of the TeO_6 octahedron. The WO_6 octahedron is distorted as expected for a metal atom bound to four types of different oxygen atoms: the oxygen atoms coordinated to two W atoms; the oxygen atoms coordinated to a Te atom and two W atoms; the oxygen atoms connected with a W and a transition metal center; the terminal oxygen atoms show the shortest W–O bond lengths.

Compound **1** has a 3D framework constructed from Anderson-type $[TeW_6O_{24}]^{6-}$ anions with crystallographic $\bar{\varepsilon}$m (D_{3d}) symmetry and bridging $\{Ni(H_2O)_3\}$ groups. The $[TeW_6O_{24}]^{6-}$ cluster in **1** is an A-type Anderson structure which consists of seven edge-shared octahedra, six of which are WO_6 octahedra, forming a regular hexagon around the central TeO_6 octahedron. Here each $[TeW_6O_{24}]^{6-}$ anion acts as a hexadentate ligand for six Ni(II) atoms, as shown in figure 1(a). The six Ni(II) atoms bonding to six terminal oxygen atoms of a Anderson anion are related by $\bar{\varepsilon}$ symmetry. It is noteworthy that the connectivity behavior between Anderson anions and metal ions is an unusual one compared with other Anderson-based compounds in which Anderson anions usually act as bidentate, tridentate or tetradentate ligands. Each Ni(II) cation in **1** is coordinated by three H_2O molecules and three terminal oxygen atoms from three $[TeW_6O_{24}]^{6-}$ anions, as shown in figure 1(b). The coordination geometries of Ni(II) exhibit distorted octahedra. There is a three-fold axis runing through each Ni(II) center, and three H_2O molecules and three $[TeW_6O_{24}]^{6-}$ anions linking to Ni(II) are related by the three-fold axis. The unusual connection of the alternating

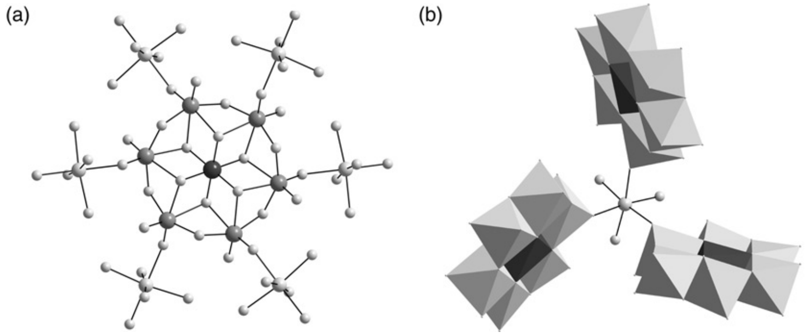


Figure 1. (a) View of the coordination of an Anderson anion $[TeW_6O_{24}]^{6-}$ to six $\{Ni(H_2O)_3\}$ groups; (b) view of the coordination of one $\{Ni(H_2O)_3\}$ group to three $[TeW_6O_{24}]^{6-}$ anions. H_2O molecules coordinated to Ni(II) have been omitted for clarity. Te-black; W-grey; Ni-big light grey atoms; O-small light grey atoms; WO_6 octahedra –light grey; TeO_6 octahedra-black.

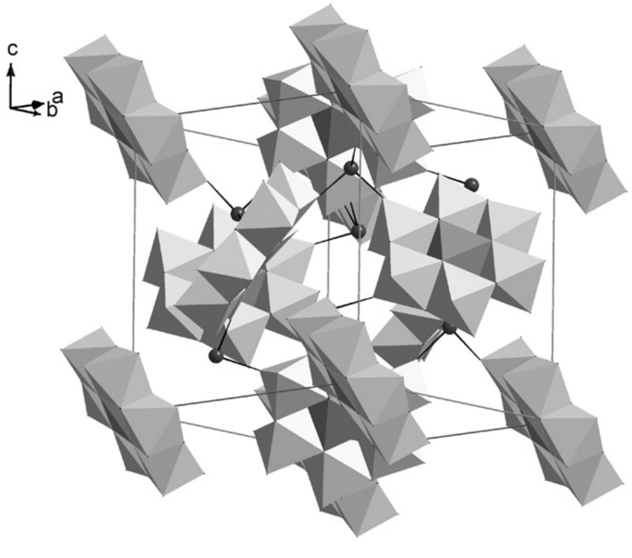
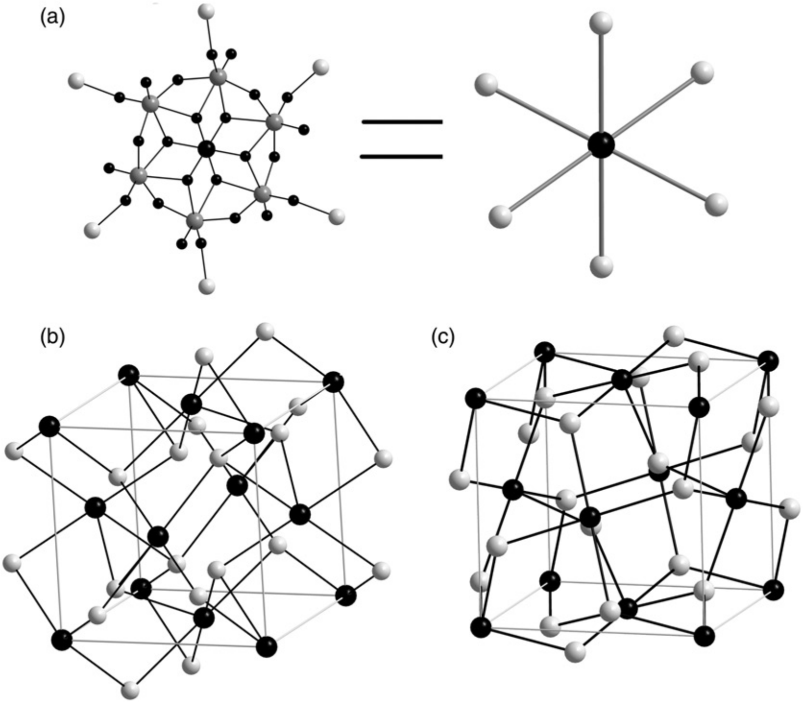


Figure 2. The 3D packing in a unit cell of compound **1**. Ni-black; WO_6 octahedra–light grey; TeO_6 octahedra-grey.

$[TeW_6O_{24}]^{6-}$ anions and $\{Ni(H_2O)_3\}^{2+}$ groups through corner-shared oxygen atoms results in a 3D (3,6)-connected network, see figure 2, which shows the 3D packing structure in a unit cell of compound **1**.

Each $[TeW_6O_{24}]^{6-}$ anion exhibits a planar structure, and six Ni(II) cations bridge the terminal oxygen atoms from above (three Ni(II) ions) and below (three Ni(II) ions) the planar structure. Therefore, $[TeW_6O_{24}]^{6-}$ anions can be considered as 6-connecting sites, and Ni(II) ions are 3-connecting sites if the H_2O molecules coordinated to them are neglected. For perspicuous representation, each 6-connecting site is simplified as a distorted octahedron through linking the Te center and Ni(II), as shown in figure 3(a). The (3,6)-connected net of compound **1** is related to the structure of the pyrite form of FeS_2; it has the same topology if the S–S bonding in pyrite is ignored.



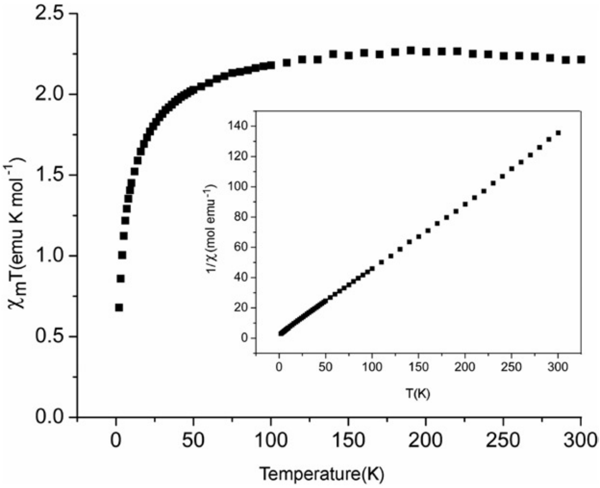
Figuer 3. (a) Simplified view of the 6-connected site as a distorted octahedron geometry in **1**; (b) the simplified structure of pyrite-related networks of **1**; (c) the structure of genuine pyrite. Terminal atoms and H_2O molecules coordinated to Ni(II) have been omitted for clarity in (b) and (c). In figure (a) and (b), Te-big black atoms; W-grey; Ni-light grey; O-small black atoms. In figure (c), Fe-black; S-light grey.

In the structure of pyrite, which has a face-centered cubic symmetry, Fe(II) ions are coordinated by six S^- ions in an octahedral geometry, and S^- ions occupy all the 3-connecting sites (figure 3c). In compound **1**, $[TeW_6O_{24}]^{6-}$ anions replace Fe(II) ions and Ni(II) cations replace S^- ions in pyrite. As one can see from the comparison in figure 3(b) and 3(c), the similarity between the structure of compound **1** and genuine pyrite is striking except for distortion in the structure of **1**. It is interesting that Anderson-type anions crystallize in such a highly symmetrical space group ($Pa\bar{\varepsilon}$: identical to pyrite), which has not been observed before. There are two ammonium cations and one H_2O molecule in a molecular unit, filling in the void space of compound **1** with hydrogen bonds between adjacent ammonium cations and H_2O molecules (N1–O4 = 2.753(6) Å).

Bond valence sum calculations [17] indicate that nickel metal centers are in the +2 oxidation state and all W and Te sites are in the +6 oxidation state; H_2O_2 is possibly responsible for the oxidation of Te (IV) to Te (VI) while stirring at room temperature.

3.2. *IR spectra*

The characteristic peaks at 650 to 1000 cm^{-1} in the infrared spectra of compound **1** are attributed to the $[TeW_6O_{24}]^{6-}$ polyoxoanion.



Figuer 4. Temperature dependence of magnetic susceptibility of compound **1** given by measurements of χ_mT *vs*. T over a temperature range of 2–300 K. The inset figures show the inverse susceptibility with a linear regression based on the Curie–Weiss law.

3.3. *Magnetic studies*

The magnetic susceptibility of 1 was investigated from 300 to 2 K, and the temperature dependence of the magnetic susceptibility data is shown in figure 4 in the form of the product χ_mT *versus* temperature (where χ_m is the magnetic susceptibility per unit of **1**). The χ_mT product at 300 K is 2.21 emu K mol^{-1}, nearly equal to the expected values for two uncorrelated Ni^{2+} centers per formula unit (2.00 emu K mol^{-1}). The χ_mT value remains almost constant from 300 to 69 K, and then decreases on further cooling, reaching a value of 0.68 emu K mol^{-1} at 2 K. The decrease in χ_mT curve observed in compound **1** at very low temperature is mostly due to single-ion zero field splitting, and possibly very weak magnetic interactions. From the structure of compound **1**, the pathways for magnetic exchange should be through the diamagnetic polyoxometalate units. Paramagnetic centers are far from each other, so the magnetic superexchange should be very weak in this case.

3.4. *TG analysis*

The thermal gravimetric (TG) curve of **1** shows a total weight loss of 9.15% (Calcd 8.56%) in the range of 100–390°C, corresponding to release of guest and coordinated water molecules as well as ammonium cations. The weight remains the same between 390 and 700°C, indicating that the framework of compound **1** can still be maintained in a wide temperature range after losing guest molecules and even coordinated water molecules. The framework starts to collapse from 700°C.

4. Conclusion

In summary, we have obtained an unprecedented 3D compound constructed from Anderson-type heteropolyanions and metal ions. It is the first Anderson-type heteropolyoxotungstate with extended structure. The successful isolation of **1** suggests that hydrothermal synthesis is an effective method to construct higher-dimensional frameworks for Anderson-based new compounds or possibily other POMs-based compounds compared with traditional aqueous reactions.

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