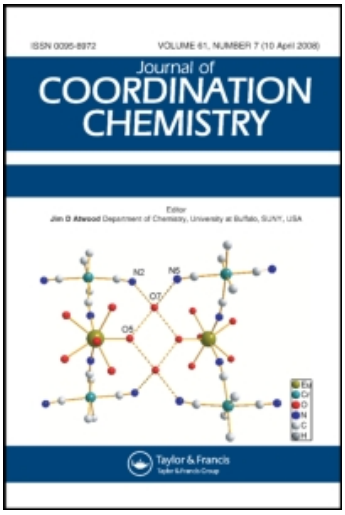

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Heteropolymolybdate-amino acid complexes: synthesis, characterization and biological activity

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HETEROPOLYMOLYBDATE–AMINO ACID COMPLEXES: SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITY

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Three Keggin-type polyoxometalates functionalized by amino acids, $(C_5H_{13}N_2O_2)_2(H_3O)PMo_{12}O_{40}\cdot 8H_2O$ **1**, $(C_5H_{14}N_2O_2)_2SiMo_{12}O_{40}\cdot 12H_2O$ **2** and $(C_5H_{14}N_2O_2)_2GeMo_{12}O_{40}\cdot 12H_2O$ **3**, were synthesized and characterized by elemental analysis, IR and ^1H NMR spectra and single-crystal X-ray diffraction. The X-ray crystallographic study showed that the structures of the three compounds involved N–H···O and O–H···O hydrogen bonds among the protonated ornithine cations, water molecules and the heteropolyanion cluster, and thus represent a model interaction between polyoxometalates and proteins. These complexes display inhibitory actions to the human cancer cells Hela and PC-3 m *in vitro*.

Keywords: Polyoxometalates; Hydrogen bond; Ornithine; Antitumor activity

INTRODUCTION

Owing to their great potential antitumor and antiviral activities, polyoxometalate complexes (POMs) have become attractive to both inorganic chemists and biochemists [1,2]. During the last 20 years it has been established that the size, shape and charge density of many polyoxoanions relate to their biological activities [3]. However, POMs show masked toxicity, making further trials as drugs unacceptable. The notable example HPA-23 succeeded in inhibiting the human immunodeficiency virus (HIV) *in vitro* but failed in clinical trials [4]. One of the solutions to the toxicity problem is to modify the POMs by different organic ligands or enzymes. Cocrystallization with small organic molecules such as amino acids to modify the surface of these polyoxometalate clusters may offer a rational way to not only fine-tune the properties of these compounds but also bring about novel synergistic effects [5].

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Amino acids are the basic units of biological molecules and their interactions with POMs are of great importance to enable a better understanding of the antitumor or antiviral activity mechanism. To date, there are only a few papers about POMs interacting with amino acids involving structural characterization [6–12]; none have infinite structures. During the course of our attempts to synthesize new polyoxometalate-based drugs [13–17], we have obtained three novel Keggin-heteropolyoxomolybdates functionalized by amino acid. This paper describes the synthesis and characterization of compounds **1**, **2** and **3**, formed by interaction between heteropoly complexes with the Keggin structure and the simple protonated amino acid ornithine (Orn). To our knowledge, **2** and **3** are the first hydrogen-bonded heteropolyoxometalate-based compounds having three-dimensional infinite supramolecular networks with amino acids as cement. MTT experiments on the resulting complexes show activities against Hela and PC-3m human tumor cell lines. The syntheses of these new POM derivatives not only enriched the family of POMs but also may provide more favorable models for medical study.

EXPERIMENTAL

General Considerations

The compounds $H_nXMo_{12}O_{40} \cdot nH_2O$, (X = P, $n = 3$; X = Si, Ge, $n = 4$) were prepared according to the published procedure and identified by comparison of the IR spectra with those previously reported [18]. Other reagents used were of analytical grade and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 C H N instrument. P, Mo, Ge and Si were determined by a Leaman inductively coupled plasma (ICP) spectrometer. The IR spectra of compounds were recorded in the range 4000–400 cm^{-1} on an Alpha Centauri FT/IR spectrophotometer as KBr pellets. The ^1H NMR spectra were obtained with a Bruker Am-500 spectrometer operating at 500 MHz using D_2O as the solvent.

Preparation of Compounds

Ornithine (0.3 g) was dissolved in 0.5 M aqueous HCl (30 cm^3) with vigorous stirring at room temperature, and a solution of 2.5 g of $H_3PMo_{12}O_{40} \cdot nH_2O$ in 20 cm^3 distilled water was then added dropwise. The resulting mixture was stirred for 3 h as a yellow precipitate formed. The precipitate was collected on a medium-porosity filter with suction. Recrystallization at 80°C from water gives, after several days at 4°C (refrigerator), yellow crystals of compound **1** (1.98 g, yield 79.2% based on $H_3PMo_{12}O_{40} \cdot nH_2O$). Anal. Calcd. for $(C_5H_{13}N_2O_2)_2(H_3O)PMo_{12}O_{40} \cdot 8H_2O$ (%): C, 5.3; H, 2.0; N, 2.5; P, 1.4; Mo, 51.1. Found: C, 5.4; H, 1.9; N, 2.6; P, 1.3; Mo, 51.6.

The following polyoxometalate salts were obtained by the same procedure as described above: $(C_5H_{14}N_2O_2)_2SiMo_{12}O_{40} \cdot 12H_2O$ **2** (2.14 g, yield 85.6% based on $H_4SiMo_{12}O_{40} \cdot nH_2O$). Anal. Calcd. for $(C_5H_{14}N_2O_2)_2SiMo_{12}O_{40} \cdot 12H_2O$ (%): C, 5.3; H, 2.2; N, 2.5; Si, 1.2; Mo, 50.8%. Found: C, 5.2; H, 1.8; N, 2.6; Si, 1.3; Mo, 50.6; $(C_5H_{14}N_2O_2)_2GeMo_{12}O_{40} \cdot 12H_2O$ **3** (1.85 g, yield 74% based on $H_4GeMo_{12}O_{40} \cdot nH_2O$): Anal. Calcd. for $(C_5H_{14}N_2O_2)_2GeMo_{12}O_{40} \cdot 12H_2O$ (%): C, 5.2; H, 2.0; N, 2.4; Ge, 3.1; Mo, 49.8%. Found: C, 5.3; H, 1.9; N, 2.5; Ge, 3.2; Mo, 49.5.

X-ray Crystallography

The selected yellow single crystal of **1**, **2** or **3** was mounted on a glass fibre and placed on a Siemens P4 diffractometer at 293°C using an ω-scan technique. An empirical absorption correction was applied. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXL crystallographic software package [19,20]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in ideal positions. A summary of the crystallographic data and structural determination for **1**–**3** is provided in Table I.

Material deposited at the Cambridge Crystallographic Data Centre, numbers CCDC 182119, 182388 and 182389 contain the detailed crystallographic data.

Antitumor Activity Test

The antitumor activity of polyoxometalates on two human cancer cell lines was tested by the MTT experiment described below.

MTT, thiazolyl blue, is a dye which can accept a hydrogen atom. Surviving tumor cells reduce the yellow MTT to an insoluble blue formazan, but dead tumor cells do not possess this capability. The formazan product is dissolved in DMSO, determined colorimetrically with a Microplate Reader (490 nm), and the cell survival rate examined.

Subcultured Hela cells and PC-3m cells were suspended in 0.25% trypsin. The cell suspension (ca. 1×10^5–10^6 cells cm^{-3}) was added to the 96-well plate at 0.11 cm^3 per well and incubated at 37°C in a 5% CO_2 incubator for 24 h. Then different 0.1-cm^3 samples containing polyoxometalates were added. After 72 h, 0.2 cm^3 of MTT solution (5 mg cm^{-3} in 0.01 m phosphate buffer saline (PBS)) was added. The mixture was further incubated for 4 h. The supernatant was removed and 1.50 cm^3 of DMSO added. The mixture was shaken for 10 min at room temperature. Colorimetric analysis was performed with a Microplate Reader (490 nm). The cell survival rate was examined

TABLE I Crystal data and structure refinements for compounds **1**, **2** and **3**

	1	**2**	**3**
Empirical formula	$C_{10}H_{45}PMo_{12}N_4O_{53}$	$C_{10}H_{48}SiMo_{12}N_4O_{54}$	$C_{10}H_{48}GeMo_{12}N_4O_{54}$
Formula weight	2251.25	2267.37	2311.87
T (K)	293(2)	293(2)	293(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*P*2(1)2(1)2(1)	*C*222(1)	*C*222(1)
a (Å)	14.590(5)	15.519(4)	15.604(3)
b (Å)	18.654(4)	21.224(4)	21.321(4)
c (Å)	18.690(4)	16.180(4)	16.239(3)
β (°)	90	90	90
V (Å^3)	5087(2)	5329(2)	5402.7(19)
Z	4	4	4
Density (calculated) (mg m^{-3})	2.923	2.827	2.843
Absorption coefficient (mm^{-1})	3.015	2.874	3.358
θ range for data collection (°)	1.54 to 25.03	1.63 to 25.03	1.62 to 27.52
Reflections collected	6298	6157	11058
Independent reflections	6298 ($R_{int} = 0.0210$)	6157 ($R_{int} = 0.0297$)	11058 ($R_{int} = 0.0516$)
Max. and min. transmission	0.4451 and 0.2642	0.6120 and 0.4476	0.6120 and 0.4476
Data/restraints/parameters	5856/0/725	4701/0/369	6113/0/367
Goodness-of-fit on F^2	0.990	1.025	1.059
R_1 [$I > 2\sigma(I)$]	0.0310	0.0363	0.0544
*wR*2	0.0732	0.0908	0.1378

and the effective cell 50% lethal concentrations (IC_{50}) were calculated by a statistical method.

The samples containing POMs were treated by the following method: the POMs were dissolved in PBS, then autoclaved and diluted by a RPMI 1640 medium with water to final concentrations of 100 $\mu g\,cm^{-3}$, 10 $\mu g\,cm^{-3}$, 1 $\mu g\,cm^{-3}$, respectively.

RESULTS AND DISCUSSION

Crystal Structures of Compounds 1, 2 and 3

The structures of **1**–**3** are all built on heteropolyoxoanionic clusters, protonated Orn cations and solvent water molecules.

Compound **1** contains discrete clusters $PMo_{12}O_{40}^{3-}$, $(HOrn)^{+}$ and water molecules interspersed in the lattice. A fully labeled plot of the anion and the cations is given in Fig. 1a. The bond lengths and bond angles observed for the $PMo_{12}O_{40}^{3-}$ unit indicate that its geometry is quite similar to those found in previously reported dodecamolybdophosphoric acid salts [21–23]. It is a Keggin structure in which the central P atom is surrounded by a tetrahedron whose oxygen vertices are each linked to one of the four Mo_3O_{13} groups. Each Mo_3O_{13} consists of three MoO_6 octahedra linked in a triangular arrangement by sharing edges, and the four Mo_3O_{13} units are linked together by sharing corners. The P–O bond lengths are in the range 1.524(6)–1.540(6) Å. The Mo–O (terminal) and the Mo–O (bridge) bond lengths are in the range 1.652(7)–1.685(8) and 1.800(7)–2.472(6) Å, respectively. The Mo–O–Mo bond angles vary between 71.0(2) and 171.7(3)°. Crystal packing of **1** along the *c* axis is given in Fig. 1b.

Short N–H···O and O–H···O contacts were found among the oxygen atoms of the polyanions, the protonated ornithine cations and the water molecules. Interatomic distances and angles involving hydrogen-bonded atoms are listed in Table II. It is interesting to observe that there are a number of short inter-species contacts in this structure; a representative one is: O(26)···O(37), 2.880 Å. Along the [001] direction, the polyanions form a zigzag chain through O(26)–O(37), alternately, Fig. 2.

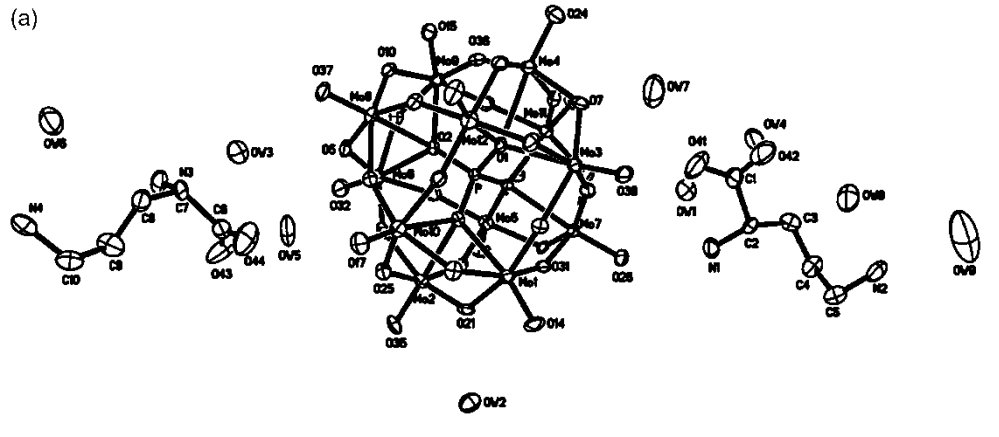

FIGURE 1 (a) View of the coordination environments of the anion and the cations of **1**, showing the atom labeling scheme and 50% thermal ellipsoids. The hydrogen atoms are omitted for clarity. (b) View of the crystal packing of **1** along the [001] direction. The dashed lines show the short contacts.

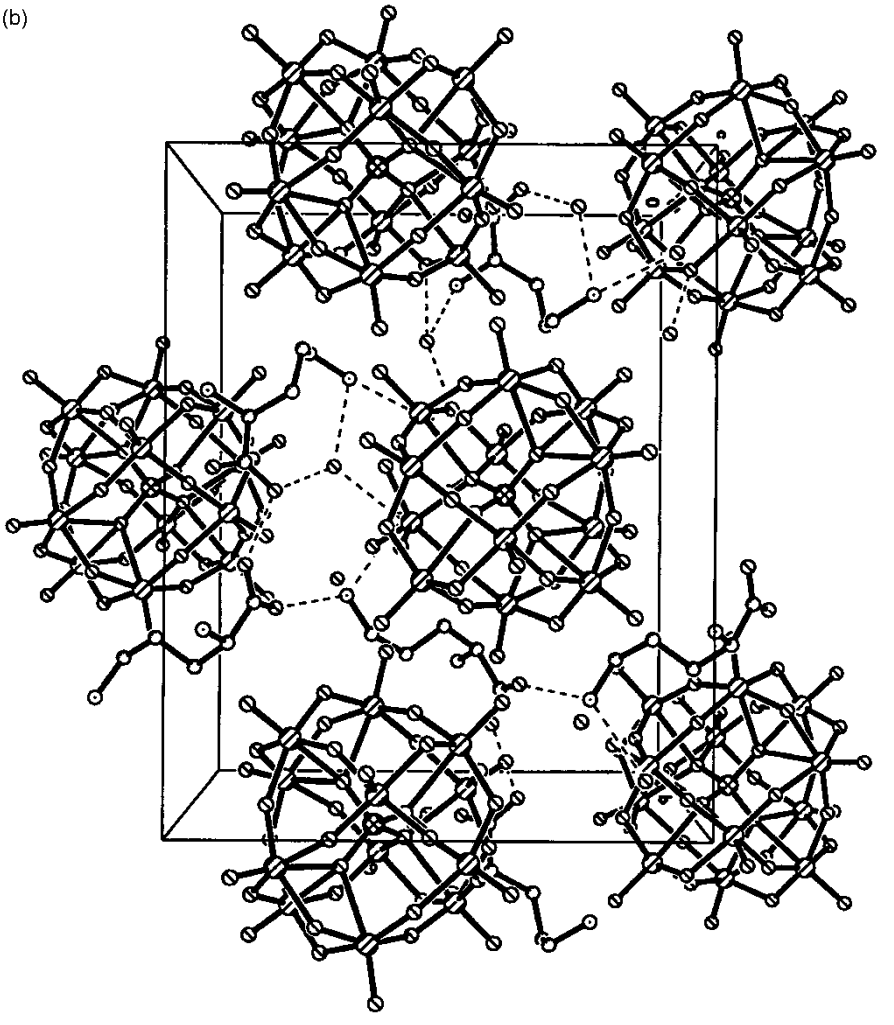

FIGURE 1 Continued.

Compounds **2** and **3** are isostructural, so only structure **2** is discussed. The water molecule and the $(H_2Orn)^{2+}$ interact with the $SiMo_{12}O_{40}^{4-}$ anion via hydrogen bonding as shown in Fig. 3. Obviously, compound **2** varies from **1** in crystal data and structures. In **1**, the organic units interact with polyanions without order, as shown in Fig. 1b. However, in **2** the polyanions, $(H_2Orn)^{2+}$ cations and water molecules join in order as shown in Fig. 4a.

The structure of the protonated Orn in **2** is different from those of other zwitterionic amino acids, which typically exhibit C–O (carboxylate) distances of $\sim$1.25 Å. The C–O (carboxylate) distances in **2** are as follows: C(l)–O(21) 1.217(10), C(l)–O(22) 1.303(12) Å. The magnitude and inequality (within experimental error) of these two C–O distances thus clearly indicate that the carboxylate group is protonated. The C–N distances, 1.479(11) Å for C(2)–N(1), 1.471(13) Å for C(5)–N(2), are slightly longer than a standard bond (1.442 Å) but similar to those of protonated compounds [24].

TABLE II Interatomic distance (Å) and angles (°) in crystals of **1**, **2** and **3**

D–H···A	D(D···A)(Å)	∠(DHA)°
Compound **1**		
N1–H1A···O28	2.856	112.65
N1–H1B···OW2	2.797	173.38
N1–H1C···OW1	2.918	141.64
N2–H2A···OW2	2.965	177.71
N2–H2B···OW3	2.992	141.64
N2–H2C···OW8	2.745	174.21
N2–H2B···OW9	2.812	176.35
N3–H3B···OW1	2.776	171.23
N3–H3A···OW3	2.836	170.25
N4–H4A···O17	2.988	123.67
N4–H4B···O44	1.799	150.98
N4–H4C···OW4	3.004	159.78
N4–H4A···OW6	2.904	143.17
Compound **2**		
N1–H1B···OW1	2.880	170.96
N1–H1C···OW2	2.861	165.29
N1–H1C···OW3	2.959	142.12
N2–H2A···O19	2.900	115.50
N2–H2B···O21	2.819	135.74
N2–H2C···OW5	2.835	150.72
O22–H22···OW4	2.630	166.78
Compound **3**		
N1–H1A···O22	2.663	147.45
N1–H1B···OW3	2.957	139.95
N1–H1C···OW4	2.862	175.71
N1–H1A···OW1	2.938	178.32
N2–H2A···OW2	2.821	165.20
N2–H2B···O19	2.919	103.19
N2–H2C···O22	2.838	145.15

The most unusual structural feature of compound **2** is that the cationic $(H_2Orn)^{2+}$ groups and the water molecules are joined together via hydrogen-bond interactions between a N–H···O [N(2AD)···O(21E), N(2AG)···O(21L), 2.819 Å], N–H···O(W1) [N(1AD)···O(W1), N(1AL)···O(W1) 2.880 Å] along the *a*-axes forming a two-dimensional grid-like network, as shown in Fig. 4b. The polyoxoanions are encapsulated inside as "guest" clusters and well surrounded by these "host" box-like units. Weak interactions arise between the oxygen atoms from different polyoxoanions in the different layers, and the polyoxoanions in one 2-D layer are linked to $(H_2Orn)^{2+}$ cations and water molecules in the other 2-D layer through hydrogen-bond interactions. Therefore, the 2-D supramolecular layers can further extend into a 3-D supramolecular network.

IR Spectra

The IR spectra of all the compounds have four characteristic Mo–Od (Od, terminal oxygen), Mo–Ob, c–Mo (Ob,c, bridging oxygen), and X–Oa (Oa, central oxygen atom) asymmetric stretching vibrational peaks, suggesting that the polyoxometalate moiety of the title complexes still retain the basic Keggin structure (see Table III). However, perturbed by organic groups, the stretching vibrational bands $\nu_{as(Mo–Ob–Mo)}$

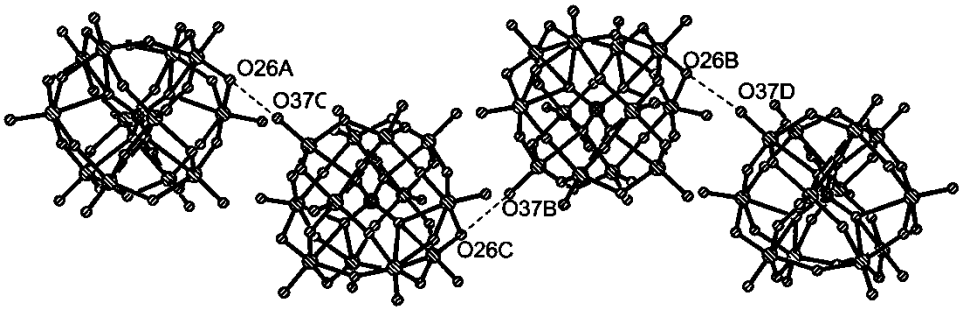

FIGURE 2 Along the [001] direction, the polyanions of compound **1** form a zigzag chain through O(26)–O(37) alternately.

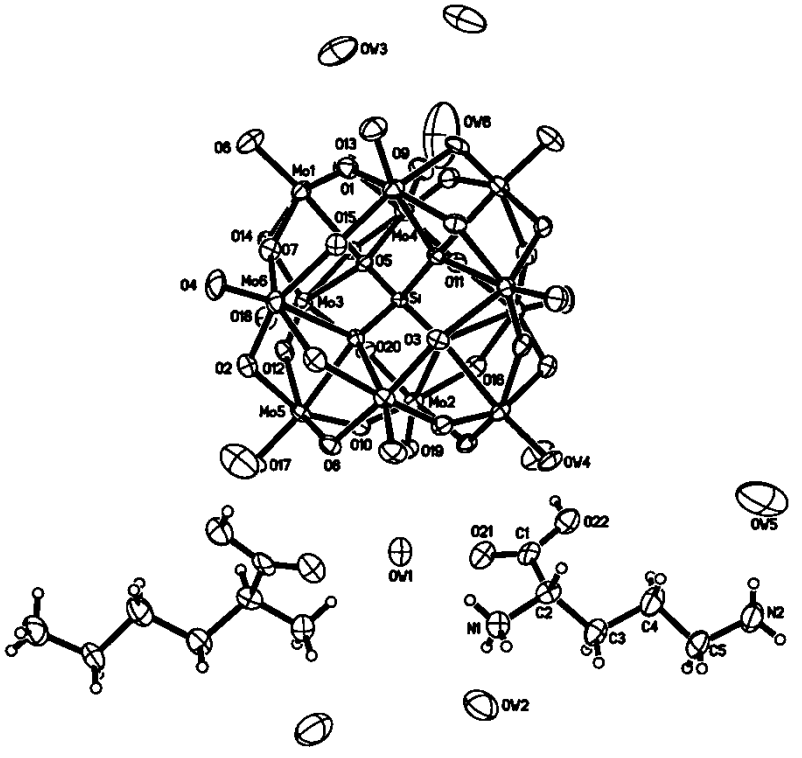

FIGURE 3 View of the coordination environments of the anion and the cations of **2**, showing the atom labeling scheme and 50% thermal ellipsoids.

and $\nu_{as(Mo–Od)}$ are shifted to higher frequency compared to those of the starting anions. Obviously, the increase of $\nu_{as(Mo–Ob–Mo)}$ and $\nu_{as(Mo–Od)}$ is due to additional negative charge on the polyanions through the link with the Orn cations [25].

Vibrational bands in the range 1200–3430 cm^{-1} are similar to those of neutral organic molecules, partly shifted, indicating the existence of the organic molecules in the compounds. These changes are related to the charges of protonated organic molecules.

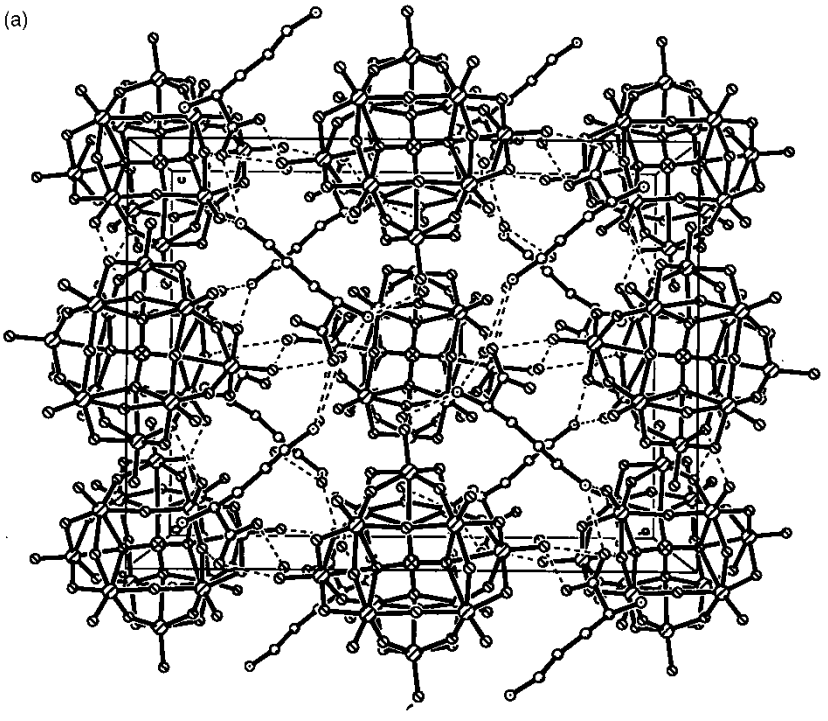

FIGURE 4 (a) View of the crystal packing of **1** along the [100] direction. The dashed lines show the short contacts. (b) Ball and stick representation of the grid-like cavity based on $(H_2Orn)^{2+}$ cations and water molecules encircling POM anions shown in polyhedral representation along the *a* axis. The hydrogen atoms are omitted for clarity.

The IR spectra indicate that polyoxometalate anions and organic substrates have interactions in the solid state.

^{1}H NMR Spectra

Complexes **1**, **2** and **3** in D_2O show similar signals, four-lines with relative intensity 2:2:2:1 corresponding to the three $-CH_2-$ units and one $-CH=$ unit in Orn cations, respectively.

Antitumor Activity

The data summarized in Table IV show that the title complexes display inhibitory action to human cancer cells Hela and PC-3m.

Table IV shows that: (1) the title complexes display inhibitory actions to Hela and PC-3m tumor cells and the inhibitory activity strengthens as the concentration of the compounds increases; (2) the degree of inhibition varies for the different compounds. The inhibitory action of the three compounds to tumor cells is in the order $(C_5H_{14}N_2O_2)_2GeMo_{12}O_{40}\cdot 12H_2O > (C_5H_{13}N_2O_2)_2(H_3O)PMo_{12}O_{40}\cdot 8H_2O > (C_5H_{14}N_2O_2)_2SiMo_{12}O_{40}\cdot 12H_2O$, similar to the order of oxidation–reduction half-wave potentials. (3) Comparing to other derivatized POMs with organometallic or amino acid components, the title compounds show better inhibitory activities [26–

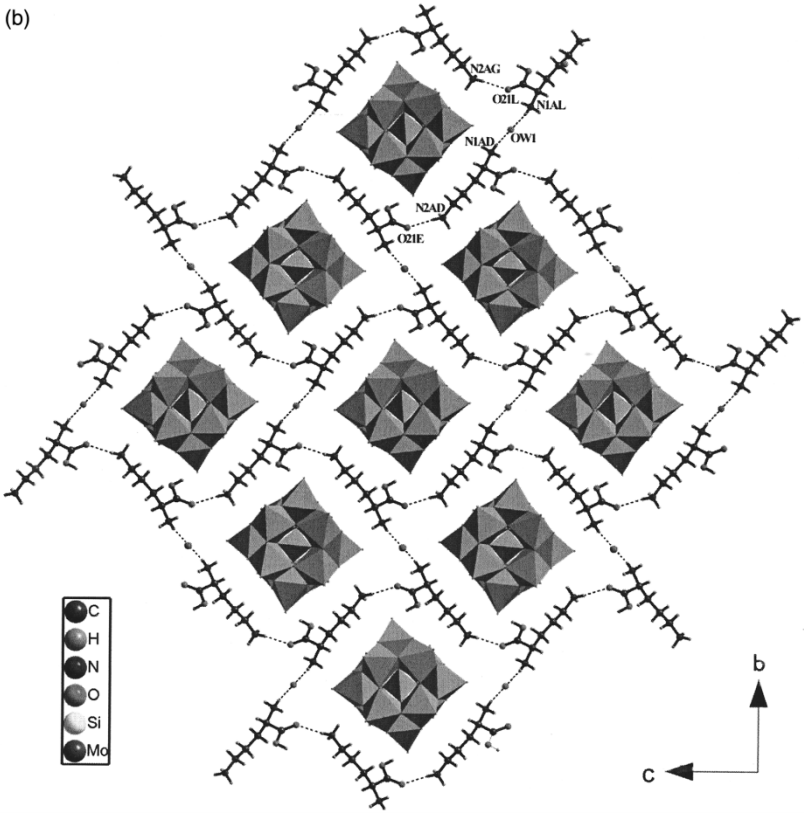

FIGURE 4 Continued.

TABLE III IR data (cm^{-1}) of compounds **1**, **2** and **3**.

Compound	$\nu_{as(M-Od)}$	$\nu_{as(X-Oa)}$	$\nu_{as(M-Ob-M)}$	$\nu_{as(M-Oc-M)}$	$\nu_{as(C=O)}$	$\nu_{as(N-H)}$
$H_3PMo_{12}O_{40}$	975, 963	1067	870	810, 785		
$C_{10}H_{45}PMo_{12}N_4O_{53}$	961	1063	878	779	1720	3436
$H_4SiMo_{12}O_{40}$	957	904	855	770		
$C_{10}H_{48}SiMo_{12}N_4O_{54}$	961	907	850	780	1724	3436
$H_4GeMo_{12}O_{40}$	951	870	790	760		
$C_{10}H_{48}GeMo_{12}N_4O_{54}$	961	880	783	770	1726	3430

28]. Yamase proposed that the mechanism for the antitumor effect of POMs revolves around a single-electron reduction–oxidation cycle in isopolymolybdates [29]. According to this hypothesis, the inhibitory activity on tumor cells of POMs is relevant to the oxidation–reduction ability. The stronger the oxidation ability, the higher is the inhibitory effect on tumor cells. The polarographic half-wave potential $E_{1/2}$ values of the three heteropolyanions is $GeMo_{12}O_{40}^{4-} > PMo_{12}O_{40}^{3-} > SiMo_{12}O_{40}^{4-}$. The sequence of antitumor activities of the complexes is consistent with the order of oxidation ability of the polyanions, so our results strengthen this hypothesis.

TABLE IV Inhibitory effects of **1**, **2** and **3** on two human tumor cell lines in vitro[a]

Anion	*Dose* ($\mu g\,cm^{-3}$)	*PC-3m*		*Hela*		*Ref*
		Inhibitory effect (%)	IC_{50}[b] (μM)	*Inhibitory effect* (%)	IC_{50}[b] (μM)	
$C_{10}H_{45}N_4PMo_{12}O_{53}$	100	80.17	20.58	82.48	17.81	
	10	32.14		30.23		
	1	0		10.05		
$C_{10}H_{48}N_4SiMo_{12}O_{54}$	100	59.89	79.87	68.25	41.88	
	10	9.08		18.07		
	1	0		0		
$C_{10}H_{48}N_4GeMo_{12}O_{54}$	100	93.15	12.67	95.09	12.51	
	10	39.27		35.44		
	1	3.78		6.53		
$(CpTi)_2SiW_{10}$			–		26.4	[26]
$(CpTi)GeW_{11}O_{39}^{5-}$ (K)			–		54.5	[27]
$(HAla)_8(H_3O)_{10}[PMo_{12}O_{40}]_6 \cdot 22H_2O$			12.3		16.2	[28]

[a]For the potassium salts dissolved in water. [b]The 50% inhibitory concentration (IC_{50}) is defined as the concentration which suppresses tumor cells by 50%.

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