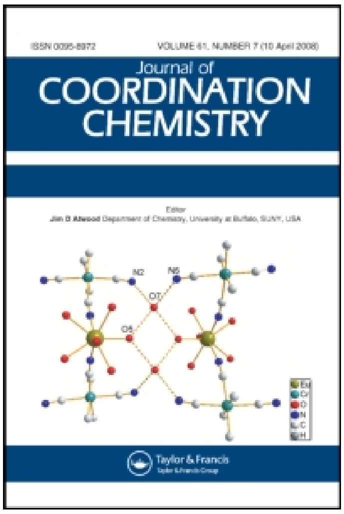

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Synthesis, Properties and Crystal Structure of A New 12-Molybdogermanic Salt of Lanthanum Coordinated to N -Methyl-2-Pyrrolidone

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SYNTHESIS, PROPERTIES AND CRYSTAL STRUCTURE OF A NEW 12-MOLYBDOGERMANIC SALT OF LANTHANUM COORDINATED TO *N*-METHYL-2-PYRROLIDONE

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A new compound $[La(NMP)_4(H_2O)_4][HGeMo_{12}O_{40}]\cdot 2NMP\cdot 3H_2O$ (NMP = *N*-methyl-2-pyrrolidone), **1**, was synthesized and characterized. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 17.3428(4)$, $b = 18.3258(5)$, $c = 23.0387(7)$ Å, $\beta = 107.088(1)^\circ$, $V = 6998.9(3)$ Å^3 and $Z = 4$. The structure was characterized crystallographically with final $R1 = 0.0589$, $wR2 = 0.1596$. The crystal structure contains $[GeMo_{12}O_{40}]^{4-}$ anions combining with $[La(NMP)_4(H_2O)_4]^{3+}$ cations through hydrogen bonds. The La^{3+} ion exhibits eight-coordination with four water molecules and four carbonyl oxygen atoms of the organic ligands. Hydrogen bonds are formed between $[GeMo_{12}O_{40}]^{4-}$ anions and coordinated water molecules, coordinating to water molecules. The anti-tumor activity of **1** was estimated against Hela and P_c-3m cancer cells.

Keywords: 12-Molybdogermanate; Rare earth; Crystal structure; Anti-tumor agent

INTRODUCTION

Polyoxometalates are molecular blocks of metal oxide formed by MoO_6 and WO_6 and the like octahedra sharing corners or edges. In recent years, more and more interest has focused on these inorganic anions due to their unique structures, electronic properties and potential applications in fields such as catalysis, biology, medicine and material science [1–6]. One of the major challenges in current polyoxometalate chemistry is the rational design and synthesis of novel compounds [7–12]. In this report we note the use of α-Keggin-type polyoxometalates, rare-earth complexes and organic groups to synthesize a new compound $[La(NMP)_4(H_2O)_4][HGeMo_{12}O_{40}]\cdot 2NMP\cdot 3H_2O$ (NMP = *N*-methyl-2-pyrrolidone), **1**. The synthetic strategy relates to biological and medicinal aspects. First, Ge and Mo were chosen as Ge has been extensively used in medicine and Mo is one of the requisite trace elements for the growth of animals and vegetation [13]. Furthermore, the rare-earth elements have many extraordinary

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physical and chemical properties due to their electronic configuration [14]. Although the rare-earth elements are not necessary elements for life, they can promote or poison substance metabolism and enzymic activities [15]. Most important of all, there are many reports of compounds based on Keggin polyoxometalate units possessing anti-tumor and anti-virus activities, especially those containing of polyoxometalates and rare-earth elements [10–21]. However, among these reports, most of the polyoxometalates are unsaturated and saturated polyoxometalates combining with rare-earth complexes are rare. As part of an investigation of interactions between saturated polyoxometalates and organic coordination complexes of rare-earth cations and their biological activity, we report the crystal structure and anti-tumor activity of compound **1**.

EXPERIMENTAL

Materials

$H_4GeMo_{12}O_{40} \cdot nH_2O$ was prepared according to the literature [22]. La_2O_3 was dissolved in 12 M HCl and then concentrated to give $LaCl_3$. Other reagents purchased were of reagent grade and used without further purification.

Physical Measurements

TG-DTA behaviour was measured on a Perkin-Elmer-7 thermal analysis system at a heating rate of $10^{\circ}C\,min^{-1}$. IR spectra (2% sample, KBr pellets) were recorded on an Alpha Centauri FTIR spectrophotometer ($400–2000\,cm^{-1}$). The ESR spectrum of Compound **1** was measured on a JES-FE3AX (Japan) instrument. Cyclic voltammograms were obtained on a CHI 660 Electrochemical work station. The working electrode was glassy carbon; a silver–silver chloride was used as the reference electrode and platinum gauze as the counter electrode.

Preparation of Compound 1

$H_4GeMo_{12}O_{40} \cdot nH_2O$ (2 g) was dissolved in 10 mL of distilled water. $LaCl_3$ (0.4067 g) was added and dissolved with stirring during 0.5 h, then the yellow solution was heated until dry. NMP (1 mL) was added dropwise into the yellow mixture with constant stirring. Subsequently, the mixture was dissolved in a mixed solution of approximate equal amounts of water and acetonitrile. The solution was filtered and then set aside to evaporate at room temperature. After a period of time, green–yellow crystals of Compound **1** separated out (yield 63.5% based on Ge). *Anal.* Cald. for $[La(NMP)_4(H_2O)_4][HGeMo_{12}O_{40}] \cdot 2NMP \cdot 3H_2O$ (%): Ge, 2.66; La, 5.10; Mo, 42.3, Found: Ge, 2.56; La, 5.07; Mo, 42.6.

X-ray Crystallography

Crystal data: $C_{30}H_{69}GeLaMo_{12}N_6O_{53}$, $M = 2724.69$, monoclinic, space group $P2_1/c$, $a = 17.3428(4)$, $b = 18.3258(5)$, $c = 23.0387(7)\,Å$, $\beta = 107.088(1)^{\circ}$, $V = 6998.9(3)\,Å^3$, $Z = 4$, $D_c = 2.586\,Mg/m^3$. A suitable single crystal with dimensions $0.310 \times 0.236 \times 0.208$ mm was sealed inside a glass capillary during the X-ray investigation.

TABLE I Summary of crystallographic data for **1**

Formula	$C_{30}H_{69}LaMo_{12}N_6O_{53}$
Formula weight	2724.69
Crystal size	$0.310 \times 0.236 \times 0.208\,mm^3$
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 17.3428(4)$, $b = 18.3258(5)$, $c = 23.0387(7)$ Å, $\beta = 107.088(1)^\circ$
Volume	$V = 6998.9(3)$ Å^3
Z	4
Density	$D_c = 2.586\,Mg/m^3$
Absorption coefficient	$3.201\,mm^{-1}$
$F(000)$	5232
θ Range	$1.23 < \theta < 27.48^\circ$
Limited indices	$-22 \leq h \leq 22$, $-22 \leq k \leq 23$, $-29 \leq l \leq 29$
Reflections collected	27595
Independent reflections	15603 ($R_{int} = 0.0283$)
Maximum and minimum transmission	1.000 and 0.587
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	15603/0/895
Goodness-of-fit on F^2	1.209
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0589$, $wR2 = 0.1596$
R indices (all data)	$R1 = 0.0721$, $wR2 = 0.1733$
Largest diff. peak and hole	2.900 and -2.158 e Å^{-3}

Determination of cell constants and data collection were carried out on a Rigaku R-Axis IP diffractometer using an $\omega - 2\theta$ scan mode in the range $1.23 < \theta < 27.48^\circ$, $-22 \leq h \leq 22$, $-22 \leq k \leq 23$, $-29 \leq l \leq 29$ with graphite-monochromated MoKα radiation (0.71073 Å) at 293(2) K. A total of 27595 (15603 independent, $R_{int} = 0.0283$) reflections were measured. The intensities were corrected for Lorentz and polarization effects and empirical absorption. The structure was solved by direct method and refined by full-matrix least-squares of F^2 using the SHELXL97. All nonhydrogen atoms were refined using anisotropic thermal parameters. Structure solution and refinement based on 15603 reflections with $I > 2\sigma(I)$ and on 895 parameters gave $R1(wR2) = 0.0721$ (0.1733), where $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}\}$. Crystal data, details of the intensity measurements, and data processing parameters are summarized in Table I and final atomic coordinates for the non-hydrogen atoms are given in Table II.

Anti-tumor Activity Tests

The anti-tumor activity of the title Compound **1** against two human cancer cells was tested by the MTT method described below. Subcultured Hela and Pc-3m cells suspension (6×10^5 cells/mL) was added to a plate with 96 wells (10 µL per well), to which 100 µL of the Compound **1** solution with different concentrations was then added (mass concentrations were calculated by dissolving a certain amount of this compound in PBS and diluted by RPMI 1640 medium to final concentrations 100, 50, 25, 12.5, 6.25, 3.17 µg/mL respectively). After incubation at 37°C in 5% CO_2 for 72 h, 10 µL of a MTT solution (5 mg/mL in 0.01 mol/L PBS) was added to the wells, mixed and allowed to incubate for 4 h. The supernatant was removed and DMSO

TABLE II Atomic coordinated ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the complex U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x/a	y/b	z/c	U_{eq}
Mo(1)	2029(1)	2591(1)	2159(1)	27(1)
Mo(2)	4245(1)	5153(1)	3202(1)	22(1)
Mo(3)	664(1)	3678(1)	1216(1)	27(1)
Mo(4)	2249(1)	5532(1)	3464(1)	24(1)
Mo(5)	3737(1)	3415(1)	3367(1)	24(1)
Mo(6)	4345(1)	3903(1)	2173(1)	24(1)
Mo(7)	1601(1)	3797(1)	3341(1)	25(1)
Mo(8)	3157(1)	5309(1)	1095(1)	24(1)
Mo(9)	1240(1)	5624(1)	1052(1)	25(1)
Mo(10)	2743(1)	6387(1)	2144(1)	23(1)
Mo(11)	2451(1)	3370(1)	971(1)	26(1)
Mo(12)	551(1)	5059(1)	2383(1)	25(1)
Ge	2415(1)	4484(1)	2216(1)	18(1)
O(1)	1863(4)	4663(4)	2714(3)	22(1)
O(2)	3404(4)	4298(3)	2620(3)	22(1)
O(3)	2397(4)	5240(4)	1763(3)	23(1)
O(4)	2009(4)	3735(4)	1773(3)	21(1)
O(5)	5178(5)	3713(4)	1952(3)	32(2)
O(6)	1849(5)	1733(4)	2345(4)	41(2)
O(7)	2311(5)	6196(4)	3981(3)	34(2)
O(8)	2736(5)	2908(4)	434(4)	37(2)
O(9)	3304(4)	6187(4)	1492(3)	24(1)
O(10)	468(5)	6089(4)	591(4)	34(2)
O(11)	4919(4)	5628(4)	3741(3)	31(2)
O(12)	2632(4)	4315(4)	830(3)	26(1)
O(13)	−445(4)	5239(5)	2258(4)	35(2)
O(14)	2344(4)	2462(4)	1475(3)	29(2)
O(15)	−250(4)	3534(5)	736(4)	38(2)
O(16)	4470(4)	3295(4)	2822(3)	26(1)
O(17)	3739(4)	5837(4)	2655(3)	24(1)
O(18)	1354(4)	3355(4)	676(3)	30(2)
O(19)	915(4)	4666(4)	935(3)	29(2)
O(20)	1032(4)	5658(4)	3024(3)	28(2)
O(21)	2007(4)	5643(4)	653(3)	28(2)
O(22)	1973(4)	4724(4)	3841(3)	28(2)
O(23)	897(5)	2778(4)	1602(4)	32(2)
O(24)	1455(5)	3308(4)	3918(4)	33(2)
O(25)	3282(4)	5286(4)	3542(3)	24(1)
O(26)	2322(4)	6154(4)	2757(3)	26(1)
O(27)	442(4)	4181(4)	1829(3)	28(2)
O(28)	4852(4)	4712(4)	2770(3)	25(1)
O(29)	4148(5)	2752(4)	3871(3)	34(2)
O(30)	2997(4)	2800(4)	2693(3)	28(2)
O(31)	2827(4)	3656(4)	3549(3)	27(2)
O(32)	1561(4)	3122(4)	2751(3)	28(2)
O(33)	1796(4)	6509(4)	1534(3)	26(1)
O(34)	4369(4)	4205(4)	3691(3)	24(1)
O(35)	791(4)	5559(4)	1787(3)	27(2)
O(36)	3932(4)	4793(4)	1633(3)	27(2)
O(37)	3540(4)	3420(4)	1617(3)	27(2)
O(38)	3553(5)	5456(4)	518(3)	34(2)
O(39)	632(4)	4238(4)	3004(3)	30(2)
O(40)	3068(4)	7256(4)	2300(3)	30(2)
La	2110(1)	9576(1)	1491(1)	30(1)
OW1	858(7)	9427(8)	595(6)	79(4)
OW2	1870(5)	10226(4)	2413(4)	42(2)
OW3	3084(7)	8828(5)	2339(5)	63(3)

(*continued*)

TABLE II Continued

	x/*a*	*y*/*b*	*z*/*c*	U_{eq}
OW4	1487(8)	10862(6)	1135(6)	74(4)
O(41)	1227(8)	8881(6)	1910(6)	78(4)
N(1)	659(10)	7800(9)	1976(11)	97(6)
C(11)	1029(9)	8376(8)	2172(8)	56(4)
C(12)	1296(17)	8402(15)	2920(12)	108(9)
C(13)	1155(19)	7677(18)	3069(15)	131(12)
C(14)	492(13)	7324(9)	2438(11)	82(6)
C(15)	343(11)	7680(15)	1353(12)	108(9)
O(42)	2555(7)	9777(6)	605(5)	59(3)
N(2)	3555(6)	10047(6)	173(4)	37(2)
C(21)	2941(9)	10228(8)	375(6)	47(3)
C(22)	2742(9)	11026(7)	269(6)	48(3)
C(23)	3440(10)	11330(8)	80(6)	50(3)
C(24)	3874(9)	10659(7)	−91(6)	46(3)
C(25)	3863(9)	9320(8)	155(6)	50(3)
O(43)	3216(5)	10430(5)	1877(4)	40(2)
N(3)	4154(5)	11287(5)	2351(4)	29(2)
C(31)	3719(7)	10703(6)	2348(5)	34(2)
C(32)	3901(8)	10388(7)	2974(6)	42(3)
C(33)	4401(7)	11000(7)	3389(6)	41(3)
C(34)	4726(7)	11463(7)	2939(6)	38(3)
C(35)	4145(8)	11723(6)	1815(6)	40(3)
O(44)	2327(6)	8362(5)	1145(4)	51(2)
N(4)	2441(13)	7646(12)	366(9)	39(4)
C(41)	2776(17)	7985(14)	889(11)	36(5)
C(42)	3766(11)	7837(10)	1141(8)	67(4)
C(43)	3823(17)	7425(16)	581(13)	49(6)
C(44)	3011(10)	7252(9)	138(7)	58(4)
C(45)	1644(12)	7700(11)	95(9)	73(5)
N(4′)	3089(13)	7711(12)	699(10)	43(5)
C(41′)	2395(18)	7977(14)	719(12)	39(5)
C(42′)	1644(12)	7700(11)	95(9)	73(5)
C(43′)	2160(20)	7280(20)	−177(18)	77(10)
C(44′)	3011(10)	7252(9)	138(7)	58(4)
C(45′)	3766(11)	7837(10)	1141(8)	67(4)
N(5)	2074(6)	11018(5)	4098(4)	32(2)
O(45)	3042(5)	10201(5)	4043(4)	44(2)
C(51)	2339(7)	10344(6)	4125(5)	31(2)
C(52)	1777(7)	9790(6)	4237(5)	35(2)
C(53)	1142(8)	10283(8)	4409(6)	44(3)
C(54)	1250(7)	11052(7)	4170(6)	42(3)
C(55)	2480(9)	11667(7)	3952(7)	46(3)
N(6)	4300(6)	8055(5)	4142(4)	35(2)
O(46)	3342(5)	8914(5)	3935(5)	50(2)
C(61)	4046(7)	8710(6)	4181(6)	35(2)
C(62)	4699(9)	9210(8)	4529(7)	50(3)
C(63)	5426(10)	8711(10)	4787(10)	78(6)
C(64)	5187(8)	7975(8)	4444(6)	47(3)
C(65)	3857(10)	7467(7)	3796(7)	53(4)
OW5	680(10)	9832(9)	−611(7)	100(5)
OW6	72(12)	6397(11)	3676(9)	121(6)
OW7	716(15)	11868(14)	157(11)	166(9)

(100 μL) added. The resulting mixture was shaken for 10 min at room temperature and then determined colorimetrically with a microplate reader (490 nm) to examine the cell survival rate and the effective concentration (EC_{50} is defined as the concentration at which 50% protection is obtained) was calculated by a statistical method.

RESULTS AND DISCUSSION

Structure of Compound 1

Figure 1 shows the structure and labeling scheme for Compound **1**, while Fig. 2 shows hydrogen bonding interactions between the 12-molybdogermanic anions and $[La(NMP)_4(H_2O)_4]^{3+}$ cations. Selected bondlengths and angles are listed in Table III. One NMP ligand is disordered (each population parameter 0.5). Disorder in the counteractions and water molecules is also common in polyoxometalate crystal structures [23]. Bondlengths and angles observed for the $GeMo_{12}O_{40}{}^{4-}$ unit indicate that the geometry is quite similar to that of the Keggin structure. In the polyoxoanion, the central Ge atom is surrounded by a tetrahedron whose oxygen (O_a) vertices are each linked to one of the four Mo_3O_{10} groups. Each Mo_3O_{10} fragment consists of three MoO_6 octahedra linked in a triangular arrangement by sharing edges (O_c), and the four Mo_3O_{10} groups are linked together by sharing corners (O_b). There is a terminal oxygen atom (O_d) in every MoO_6 octahedron. Ge–O_a bondlengths are in the normal range of 1.728–1.732 Å and Mo=O_d bond-lengths are 1.667–1.702 Å. The Mo–$O_{b,c}$ bonds in each MoO_6 unit vary from 1.798 to 2.068 Å. O–Ge–O bond angles are in the range 108.8–110.4°.

It is interesting to compare bond lengths and angles of Compound **1** with those of other 12-molybdogermanates [24,25] and data are listed in Table IV. The heteropoly anion in $[C_{10}H_{10}N]_4GeMo_{12}O_{40}$, **3** is obviously distorted owing to interaction with organic groups. In $[C(NH_2)_3]_4GeMo_{12}O_{40}$, **2**, $GeMo_{12}O_{40}^{4-}$ combines with the organic group via hydrogen-bonding interactions and the GeO_4 unit has a regular tetrahedron

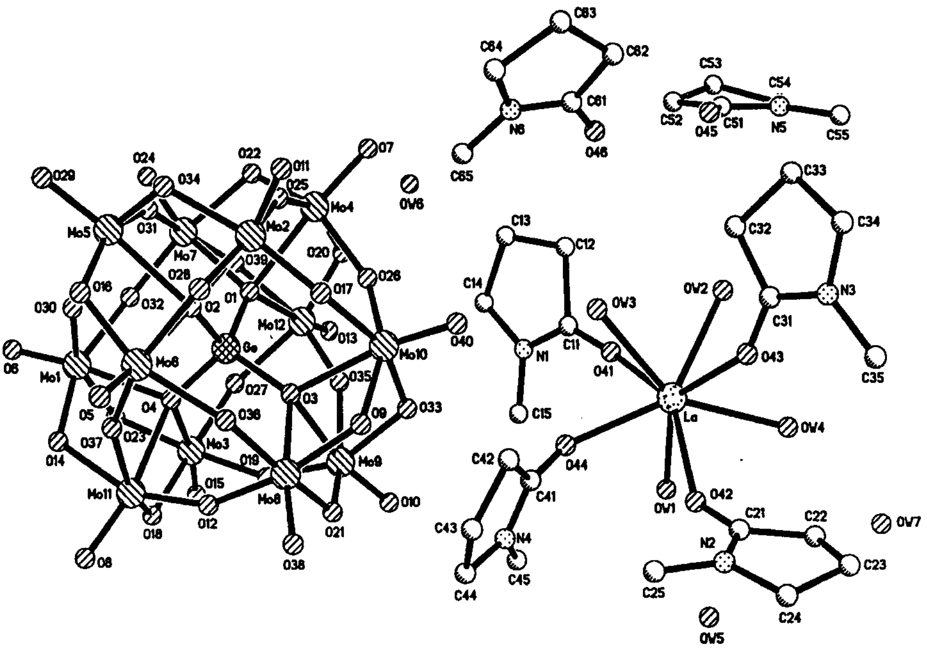

FIGURE 1 Structure and labeling scheme for compound **1**.

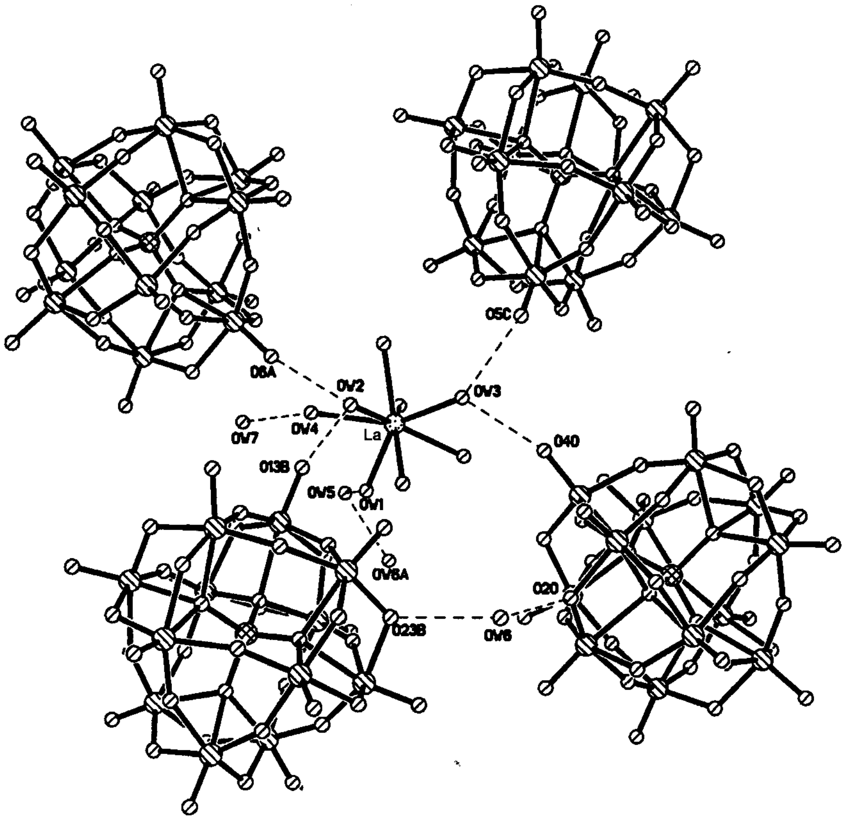

FIGURE 2 A portion of the structure of compound **1**. Hydrogen bonds between the $[GeMo_{12}O_{40}]^{4-}$ anions and $[La(NMP)_4(H_2O)_4]^{3+}$ cations as well as water molecules are indicated (for clarity, some organic groups are omitted).

structure, although the MoO_6 octahedra are highly distorted. From this we conclude that the organic groups have different effects on the heteropoly anions. In **1**, the GeO_4 unit is almost regular (the average O–Ge–O band angle is 109.3°, the average Ge–O band length is 1.729 Å, the four Ge–O band lengths are nearly equal) while the MoO_6 moieties exhibit distorted octahedral geometries similar to those of **2**. That is to say, although $[La(NMP)_4(H_2O)_4]^{3+}$ affects the MoO_6 octahedra a lot, the GeO_4 group is barely changed.

The La^{3+} ion lies in a dodecahedral environment and is coordinated to eight oxygen atoms. Four are from C=O groups of *N*-methyl-2-pyrrolidone, and the remaining four from coordinated water molecules.

The connecting links between the $[GeMo_{12}O_{40}]^{4-}$ anions are hydrogen bonds affected by the $[La(NMP)_4(H_2O)_4]^{3+}$ cations. H atoms were not definitely located, but a hydrogen-bond system can be proposed.

Among the four coordinated water molecules, only two exhibited a weak action of the hydrogen bond to the terminal oxygen atoms of two $[GeMo_{12}O_{40}]^{4-}$ anions [OW (2)$\cdots$O (6A), OW (2)$\cdots$O (13B); OW (3)$\cdots$O (40), OW (3)$\cdots$O (5C)] respectively. And the other two combined with two nomadic water molecules via hydrogen bonds [OW (5)$\cdots$OW (1); OW (4)$\cdots$OW (7)] respectively. Simultaneously, there

TABLE III Selected bondlengths (Å) and angles (degrees) for **1**

Mo(1)–O(6)	1.682(8)	Mo(8)–O(38)	1.687(8)
Mo(1)–O(30)	1.807(7)	Mo(8)–O(36)	1.805(7)
Mo(1)–O(14)	1.829(7)	Mo(8)–O(9)	1.832(7)
Mo(1)–O(32)	2.028(7)	Mo(8)–O(12)	2.046(7)
Mo(1)–O(23)	2.034(8)	Mo(8)–O(21)	2.048(7)
Mo(1)–O(4)	2.273(7)	Mo(8)–O(3)	2.305(7)
Mo(2)–O(11)	1.678(7)	Mo(9)–O(10)	1.675(7)
Mo(2)–O(17)	1.810(7)	Mo(9)–O(21)	1.825(7)
Mo(2)–O(28)	1.835(7)	Mo(9)–O(19)	1.840(8)
Mo(2)–O(34)	2.048(7)	Mo(9)–O(33)	2.041(7)
Mo(2)–O(25)	2.057(7)	Mo(9)–O(35)	2.065(7)
Mo(2)–O(2)	2.287(7)	Mo(9)–O(3)	2.297(7)
Mo(3)–O(15)	1.667(8)	Mo(10)–O(40)	1.693(7)
Mo(3)–O(27)	1.820(7)	Mo(10)–O(26)	1.823(7)
Mo(3)–O(23)	1.861(8)	Mo(10)–O(33)	1.834(7)
Mo(3)–O(19)	2.013(8)	Mo(10)–O(17)	2.048(7)
Mo(3)–O(18)	2.052(8)	Mo(10)–O(9)	2.049(7)
Mo(3)–O(4)	2.310(6)	Mo(10)–O(3)	2.289(7)
Mo(4)–O(7)	1.684(7)	Mo(11)–O(8)	1.689(7)
Mo(4)–O(25)	1.804(7)	Mo(11)–O(12)	1.807(7)
Mo(4)–O(22)	1.851(7)	Mo(11)–O(18)	1.822(7)
Mo(4)–O(26)	2.020(7)	Mo(11)–O(37)	2.035(7)
Mo(4)–O(20)	2.068(7)	Mo(11)–O(14)	2.067(8)
Mo(4)–O(1)	2.299(7)	Mo(11)–O(4)	2.297(7)
Mo(5)–O(29)	1.687(7)	Mo(12)–O(13)	1.697(7)
Mo(5)–O(31)	1.803(7)	Mo(12)–O(35)	1.798(7)
Mo(5)–O(34)	1.830(7)	Mo(12)–O(20)	1.834(7)
Mo(5)–O(30)	2.039(7)	Mo(12)–O(27)	2.027(7)
Mo(5)–O(16)	2.045(7)	Mo(12)–O(39)	2.052(7)
Mo(5)–O(2)	2.309(7)	Mo(12)–O(1)	2.295(7)
Mo(6)–O(5)	1.702(7)	Ge–O(2)	1.728(7)
Mo(6)–O(37)	1.822(7)	Ge–O(3)	1.728(7)
Mo(6)–O(16)	1.827(7)	Ge–O(1)	1.729(7)
Mo(6)–O(28)	2.038(7)	Ge–O(4)	1.732(6)
Mo(6)–O(36)	2.047(7)	La–O(41)	2.401(10)
Mo(6)–O(2)	2.288(7)	La–O(42)	2.415(9)
Mo(7)–O(24)	1.683(7)	La–O(44)	2.431(9)
Mo(7)–O(39)	1.821(8)	La–O(43)	2.432(8)
Mo(7)–O(32)	1.823(7)	La–OW(1)	2.533(12)
Mo(7)–O(22)	2.048(7)	La–OW(3)	2.571(9)
Mo(7)–O(31)	2.052(7)	La–OW(2)	2.573(9)
Mo(7)–O(1)	2.279(6)	La–OW(4)	2.621(11)
O(42)–C(21)	1.273(16)	O(44)–C(41$'$)	1.24(3)
O(43)–C(31)	1.277(14)	O(44)–C(41)	1.30(3)
O(2)–Ge–O(3)	108.8(3)	O(2)–Ge–O(4)	109.2(3)
O(2)–Ge–O(1)	109.6(3)	O(3)–Ge–O(4)	110.4(3)
O(3)–Ge–O(1)	109.5(3)	O(1)–Ge–O(4)	109.5(3)

TABLE IV Composition of bond distances (Å) and angles for **1**, **2** and **3**

	1	**2**	**3**
Mo–O$_{a}$	2.279–2.310	2.266–2.313	2.316–2.424
Mo–O$_{b,c}$	1.798–2.068	1.794–2.089	1.785–2.09
Mo=O$_{d}$	1.667–1.702	1.663–1.709	1.638–1.668
Ge–O$_{a}$	1.728–1.732	1.729–1.745	1.678–1.810
O–Ge–O	108.8–110.4	108.8–110.0	104.8–113.7

were hydrogen-bonding interactions between the rest nomadic water molecule and two bridge oxygen atoms of two $[GeMo_{12}O_{40}]^{4-}$ anions [OW (6) ··· O (20), OW (6) ··· O (23B)]. Besides, one of the nomadic water molecules combined to the nomadic water molecule of other unit via hydrogen bonds too which made the units consisting of four $[GeMo_{12}O_{40}]^{4-}$ anions and one $[La(NMP)_4(H_2O)_4]^{3+}$ cation connect each other.

IR Spectra

In contrast to the IR spectrum [26] of $H_4GeMo_{12}O_{40}$, the $Mo{=}O_d$ vibration of **1** is red-shifted from 950 to 948 cm^{-1}. However, $Mo–O_b$, $Ge–O_a$, and $Mo–O_c$ bands are blue-shifted. The results indicate the $Mo–O_b$, $Ge–O_a$ and $Mo–O_c$ bonds are strengthened in **1** while $Mo{=}O_d$ is weakened a little. With NMP coordinated to lanthanum, the, C=O band is red-shifted from 1670 to 1638 cm^{-1} while the C–N band is blue-shifted from 1506 to 1511.96 cm^{-1}. This indicates that NMP coordinates to La^{3+} so that the electron density of the O atom is reduced. The C=O bond is weakened and the C–N bond strengthened as a result.

Thermal Stability and Other Characteristic Data

In general, one may use the temperature of the exothermic peak of DTA curves as an indication of the thermal stability of heteropoly complexes [18]. Thermal analysis curves of **1** show three weight losses. The first, between 69 and 150°C gives an endothermic peak at 110°C, and corresponds to the loss of the NMP and two H_2O molecules. The second occurs between 240 and 375°C with an exothermic peak at 255°C. In this step, the compound loses two NMP and three water molecules. The third step between 398 and 520°C proceeds slowly with an exothermic peak at 423°C and the compound loses NMP and two water molecules. There is an exothermic peak at 538°C at which the heteropoly anion decomposes.

The compound turns dark green when exposed to visible light and shows a paramagnetic signal at 77 K with $\Delta HPP = 25\,G$ and $g = 1.946$, ascribed to Mo^{5+}.

Cyclic voltammetry of **1** (dark green in a buffer solution of 0.5 M H_2SO_4 and 0.1 M Na_2SO_4) gives three pairs of redox peaks ($C = 1 \times 10^{-3}$ mol/L, scan rate: 50 mv/s, current: 50 mA, range: −0.1–0.7 V). Three reversible redox waves E_{pc} (0.302, 0.220, 0.016 V), E_{pa} (0.344, 0.242, 0.152 V) with $E_{1/2}$ values of 0.323, 0.219, 0.0156 V were obtained. Voltammetric behaviour of **1** in solution is similar to that of $H_4GeMo_{12}O_{40}$, which shows that there is not a very strong interaction between $GeMo_{12}O_{40}{}^{4-}$ and the cation in **1**.

Anti-tumor Activity

The anti-tumor activity of Compound **1** was determined by the MTT method and data are listed in Table V. From the data, it can be seen that **1** shows high anti-tumor activity; the EC_{50} value is 11.7 μg mL^{-1} for the human cervix uterus cancer cells strain (Hela) and is 16.9 μg mL^{-1} for the human prostate cancer cells strain (Pc-3m).

TABLE V Cell test data for **1**

Dose/ (μg mL^{-1})	*Hela inhibitory effect* (%)	(*Pc-3 m*) EC_{50}/(μg mL^{-1})
100	96(92)	11.7(16.9)
50	93(85)	
25	77(66)	
12.5	58(41)	
6.25	26(29)	
3.17	14(6.9)	

The 50% inhibitory concentration (EC_{50}) is defined as the concentration which suppress tumor cells by 50%.

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