

Rapid communication

A novel 1D organic–inorganic hybrid based on alternating heteropolyanions $[\text{GeMo}_{12}\text{O}_{40}]^{4-}$ and isopolyanions $[\text{Mo}_6\text{O}_{22}]^{8-}$

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Received 14 May 2006; received in revised form 14 June 2006; accepted 18 June 2006

Available online 21 June 2006

Abstract

A novel one-dimensional (1D) coordination polymer $[\{\text{Cu}(2,2'\text{-bpy})\}_6(\text{Mo}_6\text{O}_{22})][\text{GeMo}_{12}\text{O}_{40}] \cdot \text{H}_2\text{O}$ ($2,2'\text{-bpy} = 2,2'\text{-bipyridine}$), which represents the first example of 1D organic–inorganic hybrid based on a Keggin-type heteropolyanion $[\text{GeMo}_{12}\text{O}_{40}]^{4-}$ and an unprecedented isopolyanion $[\text{Mo}_6\text{O}_{22}]^{8-}$, has been hydrothermally synthesized and characterized by single crystal X-ray diffraction. Crystal data: $\text{C}_{60}\text{H}_{50}\text{Cu}_6\text{GeMo}_{18}\text{N}_{12}\text{O}_{63}$, monoclinic, $P2_1/c$, $a = 13.9344(3)$, $b = 20.0329(3)$, $c = 17.2151(3)$ Å; $\beta = 94.0220(10)^\circ$, $V = 4793.70(15)$ Å³, $T = 293(2)$ K; $Z = 2$.

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Keywords: Polyoxometalates; Organic–inorganic hybrid; Heteropolyanion; Isopolyanion; Crystal structure

1. Introduction

Organic–inorganic hybrid compounds have attracted increasing interest in recent years due to the possibility of combining the different characteristics of the components to get unusual structures, properties or applications [1–3]. Meanwhile, polyoxometalates (POMs) are of great interest in the fields of catalysis and material science as well as in biology, medicine, molecular magnetism and nonlinear optics [4–6]. Therefore, use of the bridging capabilities of transitional metal complex fragments to connect polyoxometalate ions via covalent bonds has recently been exploited to build more and more high-dimensional organic–inorganic hybrid oxide materials [7–11]. To date, an astonishing variety of novel organic–inorganic hybrids based on the typical heteropolyanions, the vanadium/molybdenum isopolyanions or the derivatives of them have been reported [12–15]. But to the best of our knowledge, the organic–inorganic hybrid complex containing both heteropolyanions and isopolyanions in one chain has never been reported. Here we report the hydrothermal synthesis and structural characterization of the 1D chain-

like framework compound $[\{\text{Cu}(2,2'\text{-bpy})\}_6(\text{Mo}_6\text{O}_{22})] \cdot (\text{GeMo}_{12}\text{O}_{40}) \cdot \text{H}_2\text{O}$.

2. Experimental

2.1. Synthesis of $[\{\text{Cu}(2,2'\text{-bpy})\}_6(\text{Mo}_6\text{O}_{22})][\text{GeMo}_{12}\text{O}_{40}] \cdot \text{H}_2\text{O}$

All reagents were purchased commercially and used without further purification. Compound **1** was prepared from a mixture of GeO_2 (0.12 g, 1.2 mmol), $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (2.66 g, 11 mmol), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.84 g, 3.5 mmol), 2,2'-bipyridine (0.07 g, 0.45 mmol) and distilled water (20 mL) in the mole ratio 1.2:11:3.5:0.45:1100, heated in a Teflon-lined steel autoclave inside a programmable electric furnace at 180 °C for 96 h with a starting pH of 5.0, adjusted with hydrochloric acid (2 mol/L). After cooling the autoclave to room temperature for 48 h, green crystals were obtained, filtered, washed several times with distilled water and dried in air (yield: 71% based on C). $\text{C}_{60}\text{H}_{50}\text{Cu}_6\text{GeMo}_{18}\text{N}_{12}\text{O}_{63}$ (4127.89): calcd.: C 17.46, H 1.22, N 4.07; Found: C 17.38, H 1.28, N 4.02.

2.2. General methods

The elemental analyses were conducted on a Perkin-Elmer 240C element analyzer. The infrared (IR) spectrum

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was obtained from a sample powder palletized with KBr on Nicolet AVATAR 360 FTIR spectrophotometer over the range 4000–400 cm^{-1} . The thermal analysis was conducted on Exstar 6000 analyzer in the nitrogen gas atmosphere with a heating rate of 10 $^{\circ}\text{C}/\text{min}$.

2.3. Structure determination

A suitable green single crystal with dimensions $0.16 \times 0.14 \times 0.13$ mm was selected and intensity data were collected with a Rigaku RAXIS-IV image plate area detector using graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) at 293(2) K. A total of 30,636 reflections were measured in the range of $1.78^{\circ} \leq \theta \leq 25^{\circ}$ with $-14 \leq h \leq 16$, $-23 \leq k \leq 21$, $-20 \leq l \leq 19$, 8420 of which ($R_{\text{int}} = 0.0249$) were used in the refinement. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXTL-97 package [16]. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to

Table 1
Crystal data and structure refinement parameters for compound **1**

Empirical formula	$\text{C}_{60}\text{H}_{50}\text{Cu}_6\text{GeMo}_{18}\text{N}_{12}\text{O}_{63}$
Formula weight	4127.89
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	13.9344(3)
b (Å)	20.0329(3)
c (Å)	17.2151(3)
β (deg)	94.0220(10)
V (Å ³)	4793.70(15)
Z	2
D_c (mg m^{-3})	2.875
Abs. coeff. (mm^{-1})	3.984
T (K)	293(2)
No. of reflns. collected	30,636
No. of independent reflns	8420
Data/restraints/params	8420/0/853
GOF on F^2	1.196
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0406$, $\omega R_2 = 0.0855$
R indices (all data)	$R_1 = 0.0463$, $\omega R_2 = 0.0872$
Largest diff. peak and hole ($\text{e} \text{Å}^{-3}$)	1.632 and -0.966

theoretical models. The maximum and minimum peaks on the final difference Fourier map are corresponding to 1.632 and $-0.966 \text{ e} \text{Å}^{-3}$. The crystallographic data and structure determination parameters for compound **1** are summarized in Table 1. CCDC reference number 603294.

3. Results and discussion

3.1. Structure description

A single-crystal X-ray structure analysis revealed that complex **1** (Fig. 1) displays 1D infinite chains which are built from alternating heteropolyanions $[\text{GeMo}_{12}\text{O}_{40}]^{4-}$ and $[\{\text{Cu}(2,2'\text{-bpy})\}_6(\text{Mo}_6\text{O}_{22})]^{4+}$ building blocks by means of the O–Cu–O bridges.

The $[\text{GeMo}_{12}\text{O}_{40}]^{4-}$ unit in compound **1** (Fig. 2) is a typical Keggin-type [17,18] heteropolyanion in which all of the oxygen atoms except for the terminal ones are crystallographically disordered with each having two sites and the occupancy of each one is 0.5. As shown in Table 2, the GeO_4 tetrahedron and MoO_6 octahedra of the anion are a little distorted [19–21], and further attribute to the interaction between the heteropolyanions $[\text{GeMo}_{12}\text{O}_{40}]^{4-}$ and the $[\{\text{Cu}(2,2'\text{-bpy})\}_6(\text{Mo}_6\text{O}_{22})]^{4+}$ building blocks.

The most interesting aspect of the compound **1** is the $[\{\text{Cu}(2,2'\text{-bpy})\}_6(\text{Mo}_6\text{O}_{22})]^{4+}$ building block (Fig. 3), which contains an unprecedented novel isopolyanion $[\text{Mo}_6\text{O}_{22}]^{8-}$ (Fig. 4). To the best of our knowledge, the $[\text{Mo}_6\text{O}_{22}]^{8-}$ isopolyanion in compound **1** represents the first observation of a novel $\{\text{Mo}_6\}$ cluster structure in polyoxomolybdate chemistry. The $[\text{Mo}_6\text{O}_{22}]^{8-}$ isopolyanion contains six $\{\text{MoO}_6\}$ octahedra condensed by edge/corner-sharing. The structure features of the $[\text{Mo}_6\text{O}_{22}]^{8-}$ isopolyanion are very different from those of the traditional Lindqvist-type isopolyanion $[\text{Mo}_6\text{O}_{19}]^{2-}$ [4,22]. First, the coordination environment of the six Mo centers in the Lindqvist-type isopolyanion $[\text{Mo}_6\text{O}_{19}]^{2-}$ is identical and there is only one terminal oxygen atom around each Mo atom, however, in the novel isopolyanion $[\text{Mo}_6\text{O}_{22}]^{8-}$, the Mo atoms can be divided into two types according to their coordination

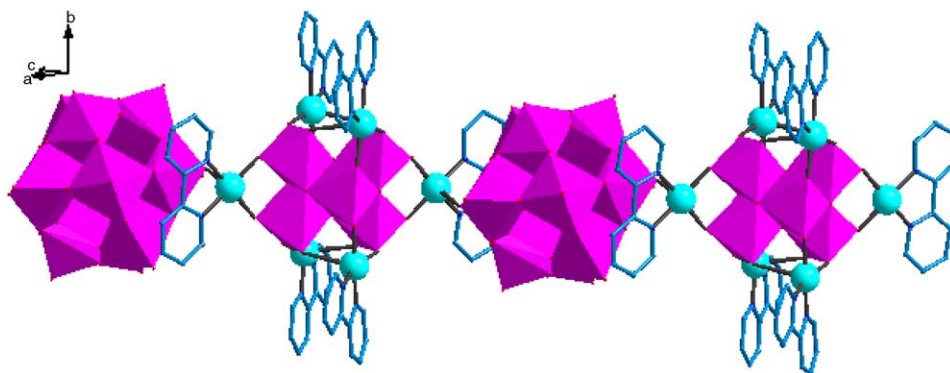


Fig. 1. The 1D chain-like framework of compound **1**. The polyhedra represent MoO_6 (purple), the balls represent copper atom (cyan), the ring represent 2,2'-bipyridine molecules (blue).

environment: (I) (Mo7, Mo8, Mo7A, Mo8A) each is coordinated to three O(t), two O(μ 3) and one O(μ 4) atom; (II) (Mo9 and Mo9A) each bonds two O(t), two O(μ 3) and two O(μ 4) atoms. Second, to sum up, in the Lindqvist-type isopolyanion $[\text{Mo}_6\text{O}_{19}]^{2-}$, there are six O(t), 12 O(μ 2) and one central O(μ 6) atom, whereas there are 16 O(t), four O(μ 3) and two O(μ 4) in the isopolyanion $[\text{Mo}_6\text{O}_{22}]^{8-}$. The Mo–O(t), Mo–O(μ 3), Mo–O(μ 4) bond distances in the isopolyanion $[\text{Mo}_6\text{O}_{22}]^{8-}$ fall in the ranges of 1.716(5)–1.775(5) Å, 1.860(5)–2.227(5) Å, 2.126(5)–2.254(5) Å, and the mean values are 1.752, 2.099 and 2.169 Å, respectively. The third difference is that the six Mo atoms in the isopolyanion $[\text{Mo}_6\text{O}_{19}]^{2-}$ display an almost regular octahedron with two different Mo...Mo distances [22], but in the isopolyanion $[\text{Mo}_6\text{O}_{22}]^{8-}$ they display a distorted octahedron with four significantly different Mo...Mo distances. The four types of Mo...Mo average distances are as follows: Mo7...Mo8, Mo7A...Mo8A, 3.542(1) Å; Mo7...Mo8A, Mo7A...Mo8, 4.145(2) Å; Mo9...Mo9A, 3.681(1) Å; Mo9...Mo7 (Mo7A, Mo8, Mo8A), 3.289 Å. It should be noted that, there are more than two terminal oxygen atoms around one Mo atom (Mo7/Mo8/Mo7A/Mo8A) in the isopolyanion $[\text{Mo}_6\text{O}_{22}]^{8-}$. The feature is significantly different from that of the other typical polyanion (such as the Keggin/Anderson-type polyanion), and result in the high coordination ability of the novel isopolyanion $[\text{Mo}_6\text{O}_{22}]^{8-}$. As in Fig. 3, one $[\text{Mo}_6\text{O}_{22}]^{8-}$ isopolyanion is decorated by six coordination

cations $[\text{Cu}(2,2'\text{-bpy})]^{2+}$. Furthermore, the two 2,2'-bipyridine molecules that coordinated to Cu(1) and Cu(2) are almost parallel exhibiting the π - π interaction (the dihedral

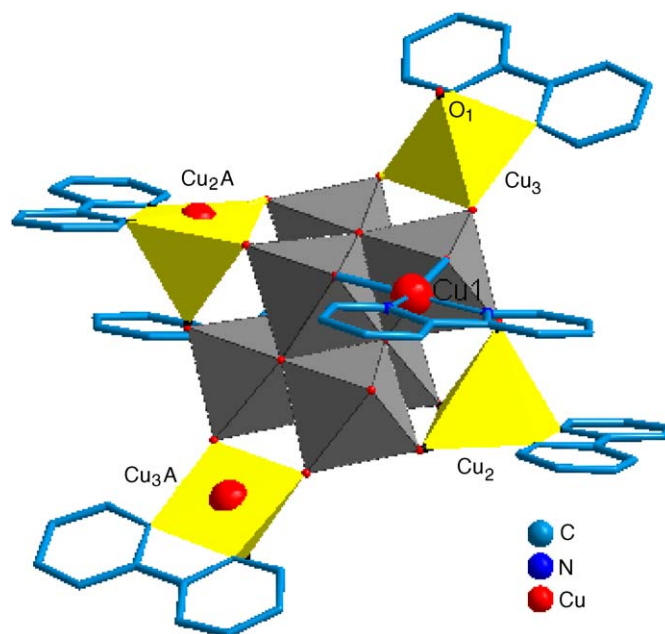


Fig. 3. Polyhedral representation of $[\{\text{Cu}(2,2'\text{-bpy})\}_6(\text{Mo}_6\text{O}_{22})]^{4+}$ building blocks; The polyhedra represent MoO_6 (gray), CuO_3N_2 (yellow), H atoms are omitted for clarity.

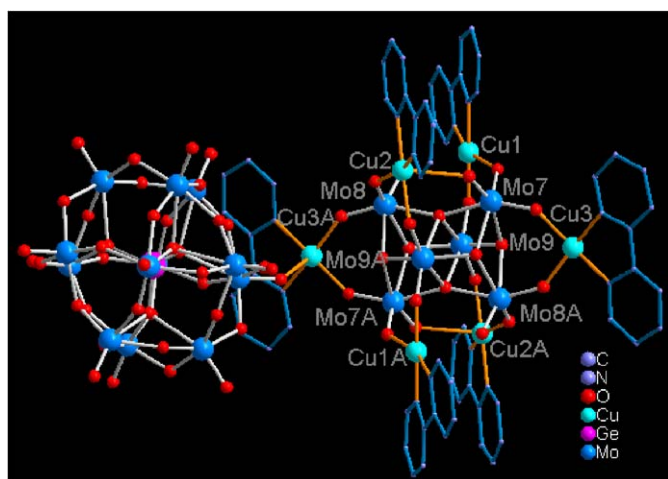


Fig. 2. Ball and stick representation of the molecular structure of compound **1**; The balls represent Mo (blue), Ge (purple), Cu (cyan), O (red), C and N (amethyst). Part of the disordered O and H atoms are omitted for clarity. (The symmetry transformation $A = -x + 1, -y + 2, -z + 1$.)

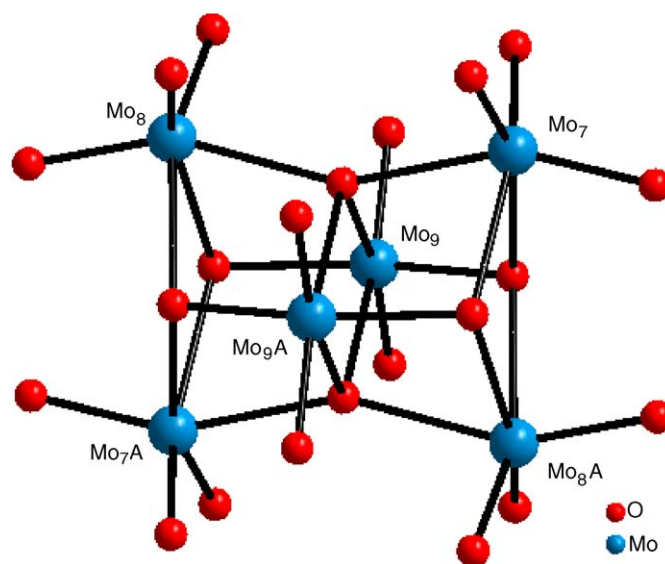


Fig. 4. Ball and stick representation of the subunit $[\text{Mo}_6\text{O}_{22}]^{8-}$. The balls represent Mo (blue), O (red).

Table 2
Selected bond lengths (Å) and angles (deg) for the heteropolyanion $[\text{GeMo}_{12}\text{O}_{40}]^{4-}$ in compound **1**

	Ge–O _a	Mo–O _a	Mo–O _{b,c}	Mo–O _t	O–Ge–O
Range	1.674–1.782	2.287(10)–2.419(8)	2.287(10)–2.419(8)	1.640(6)–1.670(5)	66.5(4)–180.0(6)
Mean	1.735	2.347	1.897	1.652	102.86

angle 2.6° and the shortest interplanar spacing 3.5 \AA) which result in the shorter Mo7...Mo8 distance, and the dihedral angle between the 2,2'-bipyridine molecules that coordinated to Cu(2) and Cu(3) is 33.3° . The other three 2,2'-bipyridine molecules that coordinated to Cu(1A), Cu(2A) and Cu(3A) are centrosymmetric to those joined to Cu(1), Cu(2) and Cu(3), respectively. Thus the six coordination cations $[\text{Cu}(2,2'\text{-bpy})]^{2+}$ display the fan-shaped distributing around the isopolyanion $[\text{Mo}_6\text{O}_{22}]^{8-}$. Interestingly, the π - π interaction also exist between the polymeric chains $\{[\text{Cu}(2,2'\text{-bpy})]_6(\text{Mo}_6\text{O}_{22})\} \cdot (\text{GeMo}_{12}\text{O}_{40})_n$, resulting in the 3D network (S9).

There are three crystallographically unique Cu atoms in the asymmetric unit (Fig. 3): (1) the square-planar coordination Cu(1), which links to two nitrogen donors from one 2,2'-bipyridine ligand and two terminal oxygen atoms of the $[\text{Mo}_6\text{O}_{22}]^{8-}$ isopolyanion with the Cu-N average distance of $1.963(7) \text{ \AA}$ and the Cu-O average distance of $1.941(5) \text{ \AA}$; (2) the square pyramidal coordination Cu(2) and Cu(3), in both of which the geometry and the bond lengths of the basal plane formed by two nitrogen atoms and two terminal oxygen atoms are similar to that of Cu(1) with the Cu-N average distance of $1.982(6) \text{ \AA}$ and the Cu-O average distance of $1.944(5) \text{ \AA}$. Additionally, another terminal oxygen atom (O24) of the $[\text{Mo}_6\text{O}_{22}]^{8-}$ isopolyanion is coordinated to Cu(2) center forming one longer axial bond with a bond length 2.422 \AA owing to the strong interaction between the two parallel 2,2'-bipyridine ligands, and the terminal oxygen atom (O1) of the heteropolyanion $[\text{GeMo}_{12}\text{O}_{40}]^{4-}$ bonds to Cu(3) atom with the Cu(3)-O1 distance of $2.370(6) \text{ \AA}$ making the coexistence of the $[\text{GeMo}_{12}\text{O}_{40}]^{4-}$ and $[\text{Mo}_6\text{O}_{22}]^{8-}$ unit in one chain. And the Mo-O distance for the oxygen atom coordinated with the Cu ion in the heteropolyanion $[\text{GeMo}_{12}\text{O}_{40}]^{4-}$ (Mo1-O1) is $1.670(5) \text{ \AA}$ and is 0.022 \AA longer than the average of the other Mo-O_t distances; in the isopolyanion $[\text{Mo}_6\text{O}_{22}]^{8-}$, the mean value of the Mo-O_t distances for the oxygen atoms coordinated with the Cu ions is 1.757 \AA and is 0.036 \AA longer than the other Mo-O_t distances.

The existence of the $[\text{Mo}_6\text{O}_{22}]^{8-}$ moiety in compound **1** may be due to the following characteristics of the organic-inorganic building block $[\{\text{Cu}(2,2'\text{-bpy})\}_6(\text{Mo}_6\text{O}_{22})]^{4+}$: (1) the coordination of the six copper coordination cations $[\text{Cu}(2,2'\text{-bpy})]^{2+}$ decrease the high negative charge of the $[\text{Mo}_6\text{O}_{22}]^{8-}$ isopolyanion; (2) the π - π interaction resulting from the fan-shaped distributing of the six 2,2'-bipyridine molecules around the isopolyanion $[\text{Mo}_6\text{O}_{22}]^{8-}$ existing at the inter and intra polymer chains stabilize the whole framework of compound **1**; (3) the structure of $\{(\text{Cu}(2)\text{N}_2)(\text{Mo}_6\text{O}_{22})(\text{Cu}(2\text{A})\text{N}_2)\}$ cluster can be considered as the substitution of two Mo centers of the well-known isopolyanion $\beta\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$ by two Cu centers (S6–7).

3.2. IR spectral characterization

In the low-wavenumber region ($\nu < 1000 \text{ cm}^{-1}$) of the IR spectrum for compound **1** (S2), the bands at 949 and 511

are attributed to $\nu_{\text{as}}(\text{Mo}-\text{O}_t)$ and $\nu_{\text{as}}(\text{Ge}-\text{O}_a)$, respectively, while the intense bands in the range of $625\text{--}873 \text{ cm}^{-1}$ ($625, 727, 782, 814, 840, 873 \text{ cm}^{-1}$) are attributed to $\nu_{\text{as}}(\text{Mo}-\text{O}-\text{Mo})$. In addition, the presence of 2,2'-bipyridine ligands in compound **1** is suggested by the occurrence of a series of vibrational bands at 1598, 1446, 1171 and 1022 cm^{-1} . In comparison with the free 2,2'-bipyridine, the resonance at 1446 cm^{-1} attributed to the $\nu_{\text{as}}(\text{C}-\text{N})$ in compound **1** has a red-shift of 9 cm^{-1} , indicating that the 2,2'-bipyridine ligands have coordinated to the Cu^{2+} ions by means of the N atoms.

3.3. Thermal analysis

The TG curve of the compound **1** showed three weight loss stages, giving a total loss of 23.42% in the range of $27\text{--}900 \text{ }^\circ\text{C}$, which approximately agrees with the calculated value of 23.14%. The weight loss (6.4%) of the first two steps ($27\text{--}488 \text{ }^\circ\text{C}$) corresponds to the release of the crystal water and two 2,2'-bipyridine molecules. In the corresponding DTA curve, the two exothermal peaks at 328 and $408 \text{ }^\circ\text{C}$ were resulted from the oxidation of organics. Another exothermal peak at $488 \text{ }^\circ\text{C}$ indicates the collapse of the polyanion framework, at which two 2,2'-bipyridine molecules have been lost. This result also reveals that the existence of the coordination cations $[\text{Cu}(2,2'\text{-bpy})]^{2+}$ plays an important role in stabilizing the whole framework.

Acknowledgement

This work was supported by National Nature Science Foundation of China, Program for New Century Excellent Talents in University of Henan Province, the Specialized Research Fund for the Doctoral Program of Higher Education, Henan Innovation Project for University Prominent Research Talents and the Natural Science Foundation of Henan Province.

Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.06.014.

The main bond distances and angles, IR spectrum, X-ray crystallographic files in CIF format for **1**.

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