有机膦酸构筑的多钨氧簇稀土化合物的设计合成、结构及性质

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摘要 在常规水溶液条件下, 选择介稳态的前驱体 $K_{14}[As_2W_{19}O_{67}(H_2O)]$ 与配体羟基乙叉二膦酸(HEDP)及稀土化合物反应, 合成了一例有机膦酸构筑的多钨氧簇稀土化合物 $CsH[Pr(H_2O)_4(AsW_9O_{33})(W_2O_3)(O_3PCOHCH_3PO_3)Pr(H_2O)_7] \cdot 19H_2O(1)$, 并通过单晶X射线衍射分析、元素分析、傅里叶红外光谱分析等对其结构进行了表征. 晶体解析表明, 化合物 1 由1个S形结构框架 $\{[(AsW_9O_{33})(W_2O_3)]_2\}$, 2个有机膦酸基团 $\{O_3PCOHCH_3PO_3\}$ 和4个 Pr^{3+} 离子通过一定的方式键连形成三维框架结构. 磁学性质研究表明, 化合物 1 呈现出反铁磁性耦合作用. 荧光性质研究表明, 化合物 1 在近红外区呈现出双寿命发光, 其中 $\tau_1=4.76 \mu s(35.53\%)$, $\tau_2=9.71 \mu s(64.4\%)$.

关键词 多金属氧簇, 有机膦酸, 晶体结构, 稀土

多金属氧酸盐(POMs)由于其阴离子结构的多样性及良好的理化性质, 在光、电、磁材料及催化方面具有广阔的应用前景, 受到人们的广泛关注^[1-5]. 有机膦酸结构多样、种类繁多, 并且具有高熔点、可修饰、丰富的键合方式等特性, 在材料、医药和催化等领域具有潜在应用价值. 因此, 将多金属氧酸盐和有机膦酸结合起来, 有望构筑结构新颖、性能优良的有机-无机杂化化合物, 逐渐成为多酸化学的研究热点之一. 1994年, Pope课题组^[6]合成了首例有机膦酸构筑的多钨氧簇, 其阴离子结构为 $[(O_3PCH_2PO_3)_4-W_{12}O_{36}]^{16-}$. 在1998和1999年, Thouvenot课题组报道了几例有机膦酸构筑的多钨氧簇 $\{PW_9O_{34}(RPO)_2\}$ ($R=Et, n-Bu, t-Bu$ 烯丙基, Ph)^[7]和 $\{SiW_{10}O_{36}(RPO)_2\}$ ($R=Et, n-Bu, t-Bu, C_2H_4COOH, Ph$)^[8]. 其后许多基于缺位Keggin和Lindqvist结构的有机膦酸修饰的多钨氧簇被报道, 比如: $\{(SiW_{10}O_{36})[O=PCH_2(C_6H_4)_nCH_2P=$

$O]\}_2(n=1, 2)^{[9]}$, $\{NbW_{10}O_{38}(RP)_2\}$ ($R=Me, Et, Pr, nBu$, 己基, 庚基, 环己基, Ph , 烯丙基)^[10], $\{(R-PO)_2(\gamma XW_{10}O_{36})\}$ ($X=Si, Ge; R=$ 氮被保护的氨基烷基或氧被保护的氨基酸衍生物)^[11], $\{[(B-\alpha-PW_9O_{34})Co_3(OH)(H_2O)_2(O_3PC(O)(C_3H_6NH_3)PO_3)]_2Co\}^{[12]}$, $\{[(BPW_9O_{34})Ni_3(OH)(H_2O)_2(Ale)]_2Ni\}$ ($Ale=H_2O_3PC(C_3H_6N-H_2)(OH)PO_3H_2$)^[13], $\{AsW_9O_{33}\{P(O)R\}_2\}$ ($R=CH_2CH_2COOH, CH_2-CH_2CONHCH_2C_6H_5$)^[14]和 $\{H_4(AsW_9O_{33})_2(TM(H_2O)W_5O_{11}(N(CH_2PO_3)_3)_2(\mu_2-O)_2)\}$ ($TM=Zn, Ni, Co, Mn$)^[15,16], 已报道的该类化合物大多呈现孤立结构, 并且大多数的化合物只含有过渡金属离子或者没有含额外的金属离子. 相比较而言, 有机膦酸构筑的多钨氧簇稀土化合物则非常少见, 目前只有本课题组^[17]于2017年报道的4例同构化合物, 它们的分子式为 $K_2[Ln-(H_2O)_4(AsW_9O_{33})(W_2O_3)(O_3PCOHCH_3-PO_3)Ln(H_2O)_7] \cdot 15H_2O$ ($Ln=Ce, Nd, Sm, Eu$). 稀土元素因其特有的4f

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电子,使其具有良好的光、电、磁性质,所以将稀土元素引入到有机膦酸构筑的多钨氧簇阴离子的骨架中,不仅可以构筑结构新颖的化合物,而且可使化合物具有优良的荧光和磁学等性质.这使得我们对探索稀土离子参与构筑有机膦酸功能化的多钨氧簇产生了极大的兴趣.本文通过引入抗衡阳离子Cs⁺,运用常规水溶液法得到了1例有机膦酸构筑的多钨氧簇稀土化合物CsH[Pr(H₂O)₄(AsW₉O₃₃)(W₂O₃)(O₃PCOHCH₃-PO₃)Pr(H₂O)₇]₂·19H₂O(**1**).

1 实验

(i) 试剂和仪器. 前驱体K₁₄[As₂W₁₉O₆₇(H₂O)]根据文献[18]合成并通过红外表征,其余试剂为商业购买的分析纯试剂,使用时未经进一步纯化.红外光谱用Bruker VERTEX 70 IR型傅立叶红外光谱仪测定,记录范围为4000~450 cm⁻¹,KBr压片.热分析数据用Mettler-Toledo TGA/SDTA851^e型热重分析仪在N₂氛围中测量.C, H, N元素分析使用Perkin-Elmer 240C型元素分析仪测定.X射线粉末衍射数据使用Bruker AXS D8 Advance粉末衍射仪测定(射线源为Cu Kα射线,λ=1.54056 Å, 2θ=5°~40°).磁学性质利用美国Quantum Design MPMS3 SQUID系统测定(H=1000 Oe, T=1.8~300 K).荧光光谱使用英国EDINBURGH FLS 980型瞬态稳态荧光光谱仪测定.

(ii) 化合物**1**的合成. 将K₁₄[As₂W₁₉O₆₇(H₂O)](0.66 g, 0.125 mmol)和羟基乙叉二膦酸(HEDP, 0.11 g, 0.36 mmol)溶解于15 mL蒸馏水中,搅拌至澄清后加

入PrCl₃·6H₂O(0.107 g, 0.30 mmol),之后滴加3 mol/L KOH调节pH 1.30,将此溶液置于60℃水浴中搅拌下反应1 h,取出溶液趁热加入0.1 g CsCl.冷却至室温,过滤后滤液室温下缓慢挥发,大约2周后得到绿色针状晶体.产率: 0.205 g(37.89%,以PrCl₃·6H₂O计).元素分析(%): 理论值: C, 0.67; H, 1.28; 实验值: C, 0.67; H, 1.21. IR(v, cm⁻¹): 3419(br), 1616(s), 1168(s), 1085(m), 968(s), 868(s), 768(s), 668(s).在合成中尝试将Cs⁺离子替换为其他种类的阳离子,如K⁺, Rb⁺, TMA⁺,通过大量对比实验发现都无法获得此化合物.由此推测,抗衡阳离子的尺寸、电荷、对称性及溶解性等可能对多酸阴离子的结晶、构型、原子配位有一定影响^[19-21].

(iii) X射线晶体结构测定. 选取大小为0.23×0.18×0.15的绿色针状晶体,置于Bruker Apex-II CCD衍射仪上,采用石墨单色器的Mo Kα射线(λ=0.71073 Å)为辐射源,以ω-2θ扫描方式收集衍射数据.在296(2) K温度下,3.25°<θ<50.2°的范围内共收集30761个衍射点.晶体结构通过直接法解出,全部数据经Lp因子和经验吸收校正.全部计算工作均使用SHELXTL-97程序系统在计算机上完成.晶体数据的CCDC号为708379.

2 结果与讨论

2.1 晶体结构

X射线单晶结构分析表明,化合物**1**属于单斜晶

表1 化合物**1**的主要晶体学数据

Table 1 Crystal data and structure refinements for compound **1**

化合物 1 的主要晶体学数据		化合物 1 的主要晶体学数据	
分子式	C ₄ H ₉₁ P ₄ O ₁₂₇ As ₂ Pr ₄ W ₂₂ Cs	单胞中电子的数目	6202.0
分子量	7186.44	晶体尺寸(mm ³)	0.23×0.18×0.15
衍射实验温度(K)	296(2)	最大与最小衍射指标	-17 h 18
空间群	P2 ₁ /c		-18 k 17
晶系	单斜		-30 l 31
a(Å)	15.1101(6)	衍射角(°)	3.25~50.2
b(Å)	15.8956(7)	总衍射点数目	30761
c(Å)	26.1615(11)	等效点平均标准偏差	0.0526
β(°)	106.6120(10)	拟合优度	1.024
晶胞体积(Å ³)	6021.3(4)	对于可观测衍射点的最终残差因子	R ₁ =0.0428, wR ₂ =0.0996
单胞中分子式的数量	2	对于全部衍射点的最终残差因子	R ₁ =0.0626, wR ₂ =0.1093
衍射实验计算获得的晶胞密度(g cm ⁻³)	3.892		

系, $P2_1/c$ 空间群. 价键计算结果表明^[22], 该化合物中所有W, As, P和Pr原子的化合价依次为+6, +3, +3和+3. 该化合物包含19个结晶水分子, 1个 Cs^+ 离子, 1个 H^+ 和1个聚阴离子 $\{[\text{Pr}(\text{H}_2\text{O})_4(\text{AsW}_9\text{O}_{33})(\text{W}_2\text{O}_3)(\text{O}_3\text{-PCOHCH}_3\text{PO}_3)\text{Pr}(\text{H}_2\text{O})_7]_2\}^{2-}$. 化合物1的聚阴离子可以看作3步形成: (1) 2个 $\{\text{AsW}_9\text{O}_{33}\}$ 亚单元通过1对 $\{\text{W}_2\text{O}_{11}\}$ 片段连接形成S形结构框架 $\{[\text{AsW}_9\text{O}_{33})(\text{W}_2\text{O}_3)]_2\}$ (图1(c)); (2) 2个Pr1离子分别通过4个Pr1-O-(W)共价键与S形结构框架连接, 形成 $\{[\text{Pr}(\text{H}_2\text{O})_4(\text{AsW}_9\text{O}_{33})(\text{W}_2\text{O}_3)]_2\}$ 单元(图1(d)); (3) 2个 $\{(\text{O}_3\text{PCOHCH}_3\text{PO}_3)\text{Pr}(\text{H}_2\text{O})_7\}$ 单元分别通过4个P-O-(W)共价键与 $\{[\text{Pr}(\text{H}_2\text{O})_4(\text{AsW}_9\text{O}_{33})(\text{W}_2\text{O}_3)]_2\}$ 单元连接, 形成聚阴离子, 如图1(e)所示. 该聚阴离子通过(W)-O-Pr1-O-(W)连接形成一维链状结构, 同时通过(P)-O-Pr2-O-(P)与4个相同的阴离子相连无限延伸形成二维平面结构. 经过Pr1, Pr2离子和有机磷酸片段的协同延伸, 化合物1的三维堆积图(图1(f)).

在化合物1中, 2个晶体学独立的Pr离子都是九配位的单加冠四方反棱柱构型. 对于Pr1来说(图1(g)), 单加冠的位置被O2W占据, 四方反棱柱的2个底面分别由O5, O1W, O3W, O4W和O1, O2, O29, O40构成. Pr1离子与4个水分子和5个二重桥氧配位, 化学键键

长范围是Pr1-O(H_2O): 2.514(16)~2.550(16) Å和Pr1- μ_2 -O: 2.495(10)~2.517(10) Å. 对于Pr2来说(图1(h)), 单加冠的位置被O26占据, 2个底面分别由O5W, O6W, O8W, O11W和O28, O7W, O9W, O10W构成. Pr2离子与7个水分子配位, 化学键键长范围是Pr2-O(H_2O): 2.491(16)~2.641(19) Å, 另外2个配位点为二重桥氧原子, 对应的键长分别为Pr2-O26: 2.405(12) Å, Pr2-O28: 2.385(10) Å.

2.2 红外光谱, 热重分析及X射线粉末衍射

化合物1的红外光谱如图2(a)所示, 出现在768, 868和968 cm^{-1} 位置的特征振动峰分别归属于 $\nu(\text{W}-\text{O}_b)$, $\nu(\text{As}-\text{O}_a)$ 和 $\nu(\text{W}-\text{O}_i)$ 的伸缩振动^[23]. 1168和1085 cm^{-1} 位置的特征振动峰可归属为HEDP中P-O键的伸缩振动, 而HEDP中P-C的伸缩振动峰出现在的668 cm^{-1} 附近^[24]. 此外, 化合物1在3419 cm^{-1} 附近的宽强信号峰和1616 cm^{-1} 处的信号峰可分别归属于化合物中结晶水以及配位水的 $\nu(\text{O}-\text{H})$ 的伸缩振动和 $\delta(\text{O}-\text{H})$ 的弯曲振动^[23].

如图2(b)所示, 化合物1的热重分析在 N_2 气氛保护下, 以10 $^\circ\text{C min}^{-1}$ 的升温速率在25~800 $^\circ\text{C}$ 范围内测定, 总失重量为14.77%(理论值:14.51%). 在25~80 $^\circ\text{C}$ 之间第1步失重约10.53%(理论值: 10.28%), 对应于

图1 化合物1的结构. (a)~(e) 化合物1的组装示意图 $\{\text{WO}_6\}$: 天蓝色和红色的八面体; $\{\text{PrO}_9\}$: 金色的单加冠四方反棱柱体; Pr: 绿色; P: 紫红色; As: 深蓝色; C: 灰色; O: 红色; 为清晰可见, 略去氢原子. (f) 化合物1的三维堆积图. (g)~(h) Pr1和Pr2离子的配位环境

Figure 1 The structure of compound 1. (a)~(e) The assembly diagram of compound 1. Color code, $\{\text{WO}_6\}$, sky-blue and red octahedral; $\{\text{PrO}_9\}$, gold monocapped square antiprism; Pr, green ball; P, fuchsia ball; As, dark-blue ball; C, gray ball; O, red ball; H atoms are omitted for clarity. (f) The 3D framework of compound 1. (g)~(h) The coordination environment of Pr1 and Pr2 ions

图2 化合物1的红外曲线(a)、热重曲线(b)和粉末衍射图(c)
Figure 2 The IR spectra (a), thermogravimetric curve (b), and XRPD patterns for experiment (top) and simulation (bottom) (c) of compound 1

19个结晶水分子和22个配位水分子的失去。在380~800 °C, 第2步失重约4.24%(理论值4.23%), 对应于2个有机片段{-COHCH₃}的失去, As₂O₃分子的升华及1个结构水的失去^[16]。

如图2(c)所示, 化合物1的实测与理论X射线粉末衍射图谱吻合较好, 说明化合物1样品是纯净的。

2.3 磁学性质

在1.8~300 K温度范围内, 对化合物1进行了磁学性质的测试。如图3(a)所示, 室温时, 化合物1的摩尔磁

图3 化合物1的 $\chi_m T$ 随 T 变化的曲线(a)和 $1/\chi_m$ 随 T 变化的曲线(b)
Figure 3 $\chi_m T$ versus T curves (a) and $1/\chi_m$ versus T curves for compound 1

化率与绝对温度的乘积 $\chi_m T$ 值为 $6.42 \text{ cm}^3 \text{ K mol}^{-1}$, 与4个无相互耦合作用的Pr^{III}离子理论值 $6.40 \text{ cm}^3 \text{ K mol}^{-1}$ 非常接近(角量子数 $L=5$, 光谱支项为³H₄, 朗德因子 $g=4/5$, 自旋量子数 $S=1$)。随测试温度的下降, $\chi_m T$ 缓慢减小, 在温度低于101 K时, $\chi_m T$ 值随温度的降低而迅速减小, 在1.8 K时, 达到最小值 $0.43 \text{ cm}^3 \text{ K mol}^{-1}$ 。这可能是因Pr离子激发态电子的去布居作用引起的。此外, 如图3(b)所示, 在68~300 K温度范围内, 通过居里-外斯定律拟合化合物1的 $1/\chi_m$ 随温度的变化曲线, 结果表明居里常数 $C=7.20 \text{ cm}^3 \text{ K mol}^{-1}$, 外斯常数 $\theta=-39.02 \text{ K}$ 。结果表明, 化合物1呈现出反铁磁性耦合作用。

2.4 荧光性质

对化合物1的固态粉末室温下的近红外区荧光性质进行了研究, 结果如图4所示。化合物1在448 nm的激发波长下, 于871, 1017, 1515 nm处出现3个特征发射峰, 分别归属为¹D₂→³F₂, ¹D₂→³F₄和¹D₂→¹G₄的光

图4 化合物1的近红外发射光谱(激发波长为448 nm)(a)、近红外激发光谱(b)和近红外区荧光寿命(c)

Figure 4 The NIR emission spectrum (upon 448 nm excitation) (a), NIR excitation spectra (b), and NIR lifetime decay curve (c) of compound 1

谱跃迁^[25]. 此外, 通过监测1017 nm发射峰和448 nm激发峰, 测得化合物1的寿命曲线, 该寿命曲线遵循双指数函数 $I = A_1 \exp(t/\tau_1) + A_2 \exp(t/\tau_2)$, 其中 t 为某一时刻, I 为某时刻 t 时的荧光强度, A_1 和 A_2 为加权参数, τ_1 为短寿命, τ_2 为长寿命, 拟合得到荧光寿命 $\tau_1 = 4.76 \mu\text{s}$ (35.53%), $\tau_2 = 9.71 \mu\text{s}$ (64.47%).

3 结论

本文采用常规水溶液法, 选择HEDP作为配体, 与介稳态的前驱体 $\text{K}_{14}[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]$ 反应, 同时

引入稀土离子, pH 1.30的条件下制备了一例有机膦酸构筑的多钨氧簇稀土化合物, 并对该化合物进行了磁学性质和荧光性质的研究. 磁学性质研究表明, 化合物1呈现出反铁磁性耦合作用. 荧光性质研究表明, 化合物1呈现出双寿命发光. 后续工作将通过选择不同的前驱体, 其他种类的有机膦酸作配体, 引入稀土或过渡金属离子, 调控抗衡阳离子, 以期构筑出其他结构新颖且功能优良的化合物, 系统研究合成化合物的磁学性质和荧光性质, 并探索化合物的催化性能.

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Summary for “有机膦酸构筑的多钨氧簇稀土化合物的设计合成、结构及性质”

Synthesis, structure and properties of a Pr-containing organophosphonate-functionalized polyoxotungstate

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Polyoxometalates (POMs), a unique class of metal-oxygen clusters with an oxygen-rich surface and high negative charge, have attracted great attention due to their unique structural variety and excellent physicochemical properties. In addition, organophosphonates, as an important kind of organic ligands with wide various and rich coordination modes, have lots of potential applications in materials, medicine and catalysis. Therefore, the synthesis of organophosphonates-based POMs with novel structure and good property is of contemporary interest. Polyoxotungstates (POTs) are viewed as one of the most important and vibrant subfamilies in POM chemistry and have been increasingly used as building blocks for the construction of systems with inorganic-organic hybrid compounds. Nevertheless, compared to the abundant derivatives of polyoxomolybdates and polyoxovanadates, organophosphonate-based POTs have been rarely studied. It is commonly that most of the structures just anchor some common transition metals (Co, Ni, Cu) or even do not anchor any metal ions. In contrast, POTs incorporated with lanthanide (Ln) ions and organophosphonate ligands have been rarely explored. Up to now, only a series of Ln-containing organophosphonatebased POTs have been reported. Moreover, the Ln ions possess the 4f electrons, leading to interesting properties such as magnetic and photoluminescent properties. It appeals us to devote in investigating the interesting Ln-containing organophosphonate-functionalized POTs. Herein, a new organic-inorganic hybrid $\text{CsH}[\text{Pr}(\text{H}_2\text{O})_4(\text{AsW}_9\text{O}_{33})(\text{W}_2\text{O}_3)(\text{O}_3\text{PCOHCH}_3\text{PO}_3)\text{Pr}(\text{H}_2\text{O})_7]_2 \cdot 19\text{H}_2\text{O}$ (**1**) has been successfully synthesized by reaction of $\text{K}_{14}[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]$, HEDP and $\text{PrCl}_3 \cdot 6\text{H}_2\text{O}$ in a conventional aqueous method. This structure was structurally characterized by single-crystal X-ray diffraction, TG analysis, PXRD and IR spectrum. The results show that compound **1** exhibits a three-dimensional (3D) framework structure which is consist of the S-shaped inorganic building block $\{[(\text{AsW}_9\text{O}_{33})(\text{W}_2\text{O}_3)]_2\}$, four Pr ions and two organophosphonate groups $\{\text{O}_3\text{PCOHCH}_3\text{PO}_3\}$. Variable temperature magnetic susceptibility of the solid state **1** was also measured at 1.8–300 K with an applied field of 1 kOe. At 300 K, the $\chi_m T$ product is $6.42 \text{ cm}^3 \text{ K mol}^{-1}$, close to the value of $6.40 \text{ cm}^3 \text{ K mol}^{-1}$ expected for four uncoupled Pr^{III} ions ($L=5$, 3H_4 , $g=4/5$, $S=1$). With cooling, the $\chi_m T$ value decreases continuously down to a value of $5.16 \text{ cm}^3 \text{ K mol}^{-1}$ at 101 K. As the temperature further decreases, the $\chi_m T$ value starts to decrease rapidly and reaches a minimum of $0.43 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 1.8 K. This behavior indicates the antiferromagnetic exchange interactions and which is further confirmed by a negative Weiss constant $\theta = -39.02 \text{ K}$ derived by fitting the Curie-Weiss law to the magnetic data between 68 and 300 K. The near-infrared (NIR) emission spectra of **1** was also investigated at room temperature. Under the excitation at 448 nm, the NIR emission spectrum of **1** consists of three characteristic peaks of the Pr^{III} ions at 871 nm ($^1\text{D}_2 \rightarrow ^3\text{F}_2$), 1017 nm ($^1\text{D}_2 \rightarrow ^3\text{F}_4$) and 1515 nm ($^1\text{D}_2 \rightarrow ^1\text{G}_4$). Moreover, the NIR decay curve of **1** is fitted into a second-order exponential function with lifetimes of $\tau_1 = 4.76 \mu\text{s}$ (35.53%), $\tau_2 = 9.71 \mu\text{s}$ (64.47%). In the following work, other bridging ligand with different functional groups such as amino or carboxyl-functionalized organophosphonate will be introduced into this system to explore much more Ln-containing organophosphonate-based POTs with intriguing structures and properties.

polyoxometalate, organophosphonate, crystal structure, lanthanide ion

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