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杂合物$(H_2en)[Mo_3O_{10}]$的水热合成与晶体结构

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摘　要:以$(NH_4)_3PMo_{12}O_{40}$,乙二胺(en),$CuCl_2\cdot 2H_2O$为原料通过水热法合成得到了标题配合物.晶体结构分析表明配合物属单斜晶系,$P2(1)/n$空间群,晶胞参数为$a=0.808\ 19(6)$ nm,$b=1.445\ 69(11)$ nm,$c=0.891\ 84(7)$ nm,$\alpha=90.00°$,$\beta=98.134\ 0(10)°$,$\gamma=90.00°$,$V=1.031\ 54(14)$ nm^3,$Z=4$,$R=0.033\ 5$,$wR=0.064\ 7$.配合物由$[Mo_3O_{10}]^{2-}$与$(H_2en)^{2+}$组成,$[Mo_3O_{10}]^{2-}$由共边和共面的MoO_6八面体连接而成,呈无限链状结构,链与链之间由$(H_2en)^{2+}$通过氢键连接成层状结构.

关键词:有机—无机杂合物;多金属氧酸盐;水热法;晶体结构

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0　引　言

近年来,有机—无机杂合物因其在光电磁,催化,吸附,超导体等领域有着广阔的应用前景而倍受关注[1-3].多金属氧酸盐是一类多核配合物,其分子结构独特,并且易于设计和组装,具有很强的接受电子的能力,是一类优秀的受体分子[4],很容易与有机分子结合形成有机—无机复合物.含N类有机配体如有机胺、氮杂环配体等,一般含有共轭体系,给电子能力强[5],是一类理想的有机—无机杂合物的构筑机团.本实验选择钼酸盐、乙二胺为配体,通过水热法合成了一个新型的有机—无机杂合物$(H_2en)[Mo_3O_{10}]$,并通过单晶X—射线衍射分析方法研究了其晶体结构.

1　实验部分

1.1　试剂

$(NH_4)_3PMo_{12}O_{40}$、乙二胺,$CuCl_2\cdot 2H_2O$均从国药集团化学试剂有限公司购得,分析纯,使用前未作进一步处理.

1.2　配合物的合成

在$(NH_4)_3PMo_{12}O_{40}$(0.03 mmol,0.055 6 g),$CuCl_2\cdot 2H_2O$ (0.09 mmol,0.013 9 g)和10 mL蒸馏水的混合物中,滴加稀释的乙二胺溶液至pH=4~5,然后将混合液转入25 mL内衬聚四氟乙烯的水热反应釜中,加热到145 ℃并恒温反应5 d后,进行程序降温(10 ℃/h)直到室温,过滤并洗涤得到淡黄色棒状晶体,产率23%.

1.3　晶体结构测定

选取尺寸为0.10 mm×0.10 mm×0.08 mm的单晶样品,在Bruker APEX面探测器衍射仪上,在298(2)K下以石墨单色化的MoK\a射线($\lambda=0.071\ 073$ nm)为衍射源,在$2.7°\leqslant\theta\leqslant 27.00°$范围内共收集了7 042个衍射数据.结构分析表明配合物属单斜晶系,$P2(1)/n$空间群,$Mr=509.94$,$a=0.808\ 19(6)$ nm,$b=1.445\ 69(11)$ nm,$c=0.891\ 84(7)$ nm,$\alpha=90.00°$,β 98.134 0(10)°,$\gamma=90.00°$,$V=1.031\ 54(14)$ nm^3,$Dc=3.284$ g·cm^{-3},$\mu=3.642$ mm^{-1},$Z=4$,F(000)=968.对数据进行吸收校正后,以可观测的独立衍射点进行结构计算.采用SMART和SAINT[6]程序进行数据的还原和晶胞参数修正,用经验法进行吸收校正,结构用直接法求解,对所有非氢原子采用全矩阵最小二乘法对F^2进行各向异性处理,用理论加氢方式找出所有氢原子,最后$R=0.033\ 5$,$wR=0.064\ 7$,$GOF=1.022$.

2　晶体结构

配合物由三钼酸根$[Mo_3O_{10}]^{2-}$与质子化的乙二胺阳离子$(H_2en)^{2+}$构成,有关的键长键角列于表1.$[Mo_3O_{10}]^{2-}$呈链状结构(如图1).由共边和共面畸变的MoO_6八面体连接而成,其中含有三桥氧、双桥氧和端基氧(与文献[7]报道的仅含有端

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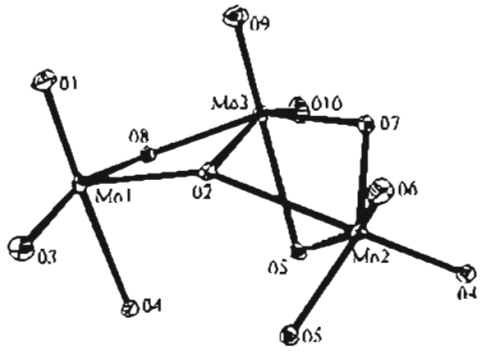
基氧和三桥氧的链状$[Mo_3O_{10}]^{2-}$有所不同)。每一个八面体包含两个较长的(0.220 4 ~ 0.241 6 nm)、两个居中的(0.185 9 ~ 0.199 7 nm)、两个较短的Mo—O(0.170 3 ~ 0.197 8 nm)键。$Mo(3)O_6$八面体与$Mo(1)O_6$八面体共用一条边Mo(3)—O(2)，与$Mo(2)O_6$通过共用一个面O(2)O(6)O(7)相连。同时，$Mo(3)O_6$八面体与$Mo(2)O_6$共用一个顶点O(4)，这样就构成了无限延伸的一维链状$[Mo_3O_{10}]^{2-}$。$(H_2en)^{2+}$位于链与链之间，并且通过氢键(N—H…O)将相邻的一维链连接起来，形成二维层状结构(如图2)，氢键用虚线表示。

表1 配合物的主要键长与键角

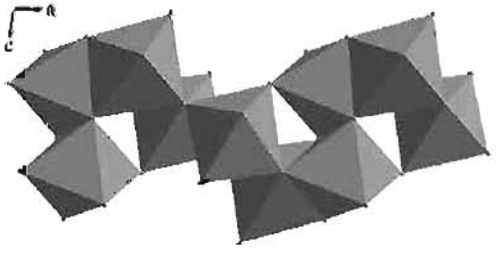
Table 1 Selected bond distances and bond angels of complex

化学键	键长/nm	化学键	键长/nm
Mo(1)－O(1)	0.170 7(3)	Mo(2)－O(7)	0.197 8(3)
Mo(1)－O(3)	0.171 6(3)	Mo(2)－O(5)^{b}	0.229 4(3)
Mo(1)－O(2)	0.186 7(3)	Mo(2)－O(2)^{b}	0.231 1(3)
Mo(1)－O(8)^{a}	0.199 7(3)	Mo(3)－O(8)	0.195 0(3)
Mo(1)－O(8)^{b}	0.220 4(3)	Mo(3)－O(9)	0.170 3(3)
Mo(1)－O(4)	0.233 8(3)	Mo(3)－O(10)	0.170 9(3)
Mo(2)－O(6)	0.171 1(3)	Mo(3)－O(7)	0.189 8(3)
Mo(2)－O(4)	0.173 2(3)	Mo(3)－O(2)^{b}	0.226 8(3)
Mo(2)－O(5)	0.185 9(3)	Mo(3)－O(5)^{b}	0.241 6(3)

注：用于产生等效原子的对称操作：a = －1 + x，y，z；b = 1 － x，－y，2 － z



a. $[MO_3O_{10}]^{2-}$的结构图



b. $[MO_3O_{10}]^{2-}$的多面体图

图1 $[Mo_3O_{10}]^{2-}$的链状结构图

Fig. 1 The chain structure of $[Mo_3O_{10}]^{2-}$

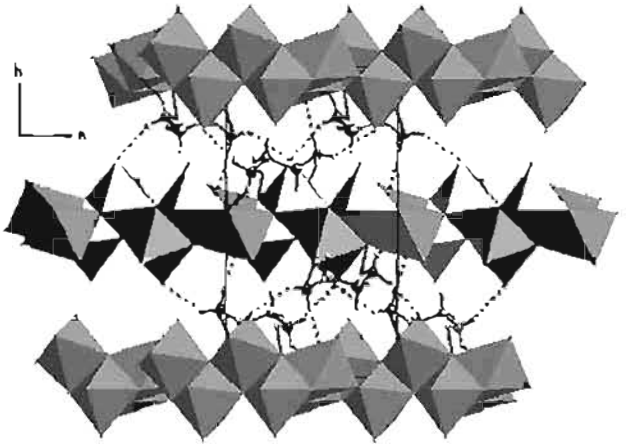


图2 配合物的层状结构图

Fig. 2 The layer structure of the title complex

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Fabrication of gold nanoparticles in HEPES buffer in the presence of surfactants

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Abstract: Gold nanoparticles with different morphologies and sizes were obtained in HEPES buffer solution in the absence and presence of surfactants (polyvinylpyrrolidone and poly(ethylene glycol)) at room temperature. These nanoparticles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and selected area electron diffraction (SAED). The kinetics of the formation of gold nanoparticles in HEPES buffer was studied by UV-visible spectrophotometer. Gold nanoparticles could be obtained easily at room temperature with continuous vigorous stirring. The surfactants play a crucial role in the size and shape controlled synthesis of gold nanoparticles.

Key words: gold nanoparticles; HEPES buffer solution; PVP; PEG

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Hydrothermal synthesis and crystal structure of an organic-inorganic hybrid $(H_2en)[Mo_3O_{10}]$

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Abstract: The title complex was hydrothermally synthesized from $(NH_4)_3PMo_{12}O_{40}$, $CuCl_2 \cdot 2H_2O$ and en (ethylenediamine). X-ray structural analyses reveal that the compound crystallizes in the monoclinic system and space group $P2(1)/n$, with $a = 8.081\,9(6)$ nm, $b = 14.456\,9(11)$ nm, $c = 8.918\,4(7)$ nm, $\alpha = 90.00°$, $\beta = 98.134\,0(10)°$, $\gamma = 90.00°$, $V = 1\,031.54(14)$ nm^3, $Z = 4$, $R = 0.033\,5$, $wR = 0.064\,7$. Its structure consists of infinite chains made up of distorted MoO_6 octahedra, which is connected by edges and faces. The chains are linked into layers by ethylenediamine cations through hydrogen bonds.

Key words: organic-inorganic hybrid; polyoxometalate; hydrothermal method; crystal structure

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