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吡啶配位的夹心型杂多阴离子 $\{[\text{Na}(\text{H}_2\text{O})_2]_3[\text{Ni}(\text{C}_5\text{H}_5\text{N})]_3(\text{AsW}_9\text{O}_{33})_2\}^{9-}$ 的结构及磁学性质

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摘要 在pH≈7.0的水溶液中, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$,

NaAsO_2 , 吡啶与 $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 反应, 得到了吡啶配位的夹心型杂多钨酸盐 $\text{Na}_7[\text{Ni}(\text{H}_2\text{O})_6]\{[\text{Na}(\text{H}_2\text{O})_2]_3[\text{Ni}(\text{C}_5\text{H}_5\text{N})]_3$

$(\text{AsW}_9\text{O}_{33})_2\} \cdot 28\text{H}_2\text{O}$ 单晶, 用X射线单晶衍射法及元素分析确定了其结构, 晶体属单斜晶系, P

$\text{src}="/1.files/image012.gif">$ 空间群, 其晶胞参数为: $a = 1.3153(9)$, $b = 1.7228(12)$, $c = 2.6866(19)$ nm, α

$\text{src}="/1.files/image014.gif">$ $= 74.130(11)^\circ$, $\beta = 78.032(12)^\circ$, $\gamma = 73.179(12)^\circ$, $Z = 2$, $R_1 = 0.0604$, wR_2

$\text{src}="/1.files/image016.gif">$ $= 0.0915$ [$I > 2\sigma(I)$]. $\{[\text{Na}(\text{H}_2\text{O})_2]_3[\text{Ni}(\text{C}_5\text{H}_5\text{N})]_3(\text{AsW}_9\text{O}_{33})_2\}^{9-}$

具有 C_3

对称性, 3个吡啶配位的 $\text{Ni}(\text{C}_5\text{H}_5\text{N})^{2+}$

和3个 $\text{Na}(\text{H}_2\text{O})_2^+$ 夹在两个 $\text{AsW}_9\text{O}_{33}^{9-}$ 之间。磁性质研究表明该化合物中的Ni(II)

三核簇基团存在着铁磁耦合($J = 6.17 \text{ cm}^{-1}$).

关键词 [杂多化合物](#), [晶体结构](#), [吡啶](#), [磁性质](#)

分类号

Structure and Magnetic Properties of Pyridine Coordinated Sandwich-type Heteropolyanion

$\{[\text{Na}(\text{H}_2\text{O})_2]_3[\text{Ni}(\text{C}_5\text{H}_5\text{N})]_3(\text{AsW}_9\text{O}_{33})_2\}^{9-}$

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Abstract The pyridine coordinated sandwich-type heteropolytungstate $\text{Na}_7[\text{Ni}(\text{H}_2\text{O})_6]\{[\text{Na}(\text{H}_2\text{O})_2]_3[\text{Ni}(\text{C}_5\text{H}_5\text{N})]_3(\text{AsW}_9\text{O}_{33})_2\} \cdot 28\text{H}_2\text{O}$ was obtained by the reaction of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, NaAsO_2 and pyridine with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ at pH=7.0 and characterized by elemental analysis, IR, UV-Vis, ¹H NMR spectra and magnetic measurement. The structure of this heteropolytungstate was determined by X-ray diffraction analysis, which crystallized in triclinic system, space group P with $a=1.3153(9)$ nm, $b=1.7228(12)$ nm, $c=2.6866(19)$ nm, $\alpha=74.130(11)^\circ$, $\beta=78.032(12)^\circ$, $\gamma=73.179(12)^\circ$ and $Z=2$, $R_1=0.0604$, $wR_2=0.0915$ [$I > 2\sigma(I)$]. Polyanion $\{[\text{Na}(\text{H}_2\text{O})_2]_3[\text{Ni}(\text{C}_5\text{H}_5\text{N})]_3(\text{AsW}_9\text{O}_{33})_2\}^{9-}$ has approximately C_3 symmetry, and three pyridine coordinated $\text{Ni}(\text{C}_5\text{H}_5\text{N})^{2+}$ and three $\text{Na}(\text{H}_2\text{O})_2^+$ are encapsulated between two $\text{AsW}_9\text{O}_{33}^{9-}$. Magnetic measurements show that central Ni_3 unit in the polyanion exhibits ferromagnetic Ni—Ni exchange interactions ($J=6.17 \text{ cm}^{-1}$).

Key words [polyoxometalate](#) [crystal structure](#) [pyridine](#) [magnetic property](#)

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