

Full Paper

咪唑配位的夹心型锑钨多氧酸盐 $\text{Na}_9[\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{M}(\text{C}_3\text{H}_4\text{N}_2)\}_3(\text{SbW}_9\text{O}_{33})_2\cdot x\text{H}_2\text{O}$ (M= NiII, CoII, ZnII, MnII)

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摘要 在 $\text{pH}\approx 7.5$ 的水溶液中, $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$, $\text{SbCl}_3\cdot 6\text{H}_2\text{O}$, 咪唑与 $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (或 $\text{MnSO}_4\cdot \text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$)反应得到了四种咪唑配位的夹心型锑钨多氧酸盐 $\text{Na}_9[\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{M}(\text{C}_3\text{H}_4\text{N}_2)\}_3(\text{SbW}_9\text{O}_{33})_2\cdot x\text{H}_2\text{O}$ (M=NiII, x = 32, CoII, x = 32, ZnII, x = 33, MnII, x = 34)。用X射线单晶衍射法确定了 $\text{Na}_9[\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)\}_3(\text{SbW}_9\text{O}_{33})_2\cdot 32\text{H}_2\text{O}$ 的结构, 聚阴离子 $[\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)\}_3(\text{SbW}_9\text{O}_{33})_2]^{9-}$ 具有近似 C_{3v} 对称性, 3个咪唑环垂直于中心带上六个金属离子(Na-Ni-Na-Ni-Na-Ni)所形成的平面。晶体结构中相邻的阴离子间存在着 π - π 相互作用, 相邻咪唑的二面角为 60° 。用IR, UV-vis, TG和DSC, 对这些化合物的性质进行了表征, 推测了它们的热分解过程。

关键词 杂多化合物, 晶体结构, 咪唑, 过渡金属

分类号

Imidazole Coordinated Sandwich-type Antimony Poly-oxotungstates $\text{Na}_9[\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{M}(\text{C}_3\text{H}_4\text{N}_2)\}_3(\text{SbW}_9\text{O}_{33})_2\cdot x\text{H}_2\text{O}$

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Abstract The imidazole covalently coordinated sandwich-type heteropolytungstates $\text{Na}_9[\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{M}(\text{C}_3\text{H}_4\text{N}_2)\}_3(\text{SbW}_9\text{O}_{33})_2\cdot x\text{H}_2\text{O}$ (M=Ni^{II}, x=32; M=Co^{II}, x=32; M=Zn^{II}, x=33; M=Mn^{II}, x=34) were obtained by the reaction of $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$, $\text{SbCl}_3\cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ [$\text{MnSO}_4\cdot \text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$] and imidazole at $\text{pH}\approx 7.5$. The structure of $\text{Na}_9[\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)\}_3(\text{SbW}_9\text{O}_{33})_2\cdot 32\text{H}_2\text{O}$ was determined by single crystal X-ray diffraction. Polyanion $[\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)\}_3(\text{SbW}_9\text{O}_{33})_2]^{9-}$ has approximate C_{3v} symmetry, imidazole coordinated six-nuclear cluster $[\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)\}_3]^{9+}$ is encapsulated between two $(\alpha\text{-SbW}_9\text{O}_{33})^{9-}$, the three rings of imidazole in the polyanion are perpendicular to the horizontal plane formed by six metals (Na-Ni-Na-Ni-Na-Ni) in the central belt, and π -stacking interactions exist between imidazoles of neighboring polyanions with dihedral angle of 60° . The compounds were also characterized by IR, UV-Vis spectra, TG and DSC, and the thermal decomposition mechanism of the four compounds was suggested by TG curves.

Key words polyoxometalate crystal structure imidazole transition metal

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