CHAPTER 4

CONCLUSIONS

Single crystals of three nickel-polyoxovanadates *i.e.* $[V_{18}O_{42}X][Ni(C_2H_8N_2)_2]_3[Ni(H_2O)_4](NH_4)_3$ where X= Cl (Ni-POV-Cl) and Br (Ni-POV-Br) and $[V_{18}O_{42}I][Ni(C_2H_8N_2)_2]_3(NH_4)_3$ (Ni-POV-I) were successfully prepared with hydrothermal technique under the same condition.

The crystal structures of Ni-POV-Cl, Ni-POV-Br and Ni-POV-I are analogous and could be successfully solved and refined in monoclinic system. The structures compose of cage-like polyoxovanadates, $[V_{18}O_{42}]$, building unit, the encapsulating anion of Cl-, Br- and I- and crystallization ammonium cations, NH_4^+ . The extended two-dimensional networks are formed by the interconnection of each $[V_{18}O_{42}X]$ cluster to four other neighboring units *via* $[Ni(en)_2O_2]^{2+}$ and $[Ni(H_2O)_4O_2]^{2+}$ bridging groups in case of Ni-POV-Cl and Ni-POV-Br while only $[Ni(en)_2O_2]^{2+}$ acted as bridging groups in case of Ni-POV-I. The structures of compounds were stabilized by moderate and weak hydrogen bond interaction which played a vital influence on the stabilization as well as strength of the structures. Most of the observed interactions were mainly the interaction between ethylenediamine, crystallization ammonium cations as well as water ligands and oxygen atoms on the $V_{18}O_{42}X$ clusters.

The influences of encapsulating halide anion were obviously noticed in case of Ni-POV-I that has the space group, size of unit cell as well as the structure difference from the other two compounds. That was maybe due to size of I^- ion that slightly

larger than the cluster void and therefore led to an enlargement of the unit cell and an alternate of the structure. However, this size effect of I^- did not affect the vanadium valencies of Ni-POV-I. The oxidation states of vanadium atoms investigated by both manganometric titration and computational chemistry. Both approaches provided the same results in all three compounds, indicating the presence of both tetravalent and pentavalent vanadium atoms in the ratio of $16V^{IV}:2V^{V}$.

The spectroscopic methods were performed to investigate the present of the component species of the cluster compounds. It was observed that FT-IR spectra confirmed the existence of the ethylenediamine molecules and ammonium cation lattice within the crystal structures. UV-vis spectra revealed the characteristic absorption of polyoxoanadate compounds. While, layered structures of compounds indicated by the powder XRD patterns. The obtained results from thermogravimetric analysis of three compounds supporting the chemical compositions that decomposed at extremely high decomposition temperatures of the ethylenediamine dications due to the structural stabilization by hydrogen bonds.