Synthesis, crystal structure and thermal study of the hybrid nickel sulfate: C₆N₂H₁₆[Ni(H₂O)₆(SO₄)₂].2H₂O

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Abstract. A new inorganic-organic hybrid open framework nickel sulfate C₆N₂H₁₆[Ni(H₂O)₆(SO₄)₂].2H₂O has been synthesized by slow evaporation in aqueous solution using trans-1,4-diaminocyclohexane as structure-directing agent. It was characterized by single-crystal X-ray diffraction, infrared spectroscopy and analyzed by TGA-DSC. The compound crystallizes in the monoclinic space group P2₁/n, with the unit cell parameters of a = 6.2586 Å, b = 12.3009 Å, c = 13.2451 Å, β= 98.047°, Z= 4. Its crystal structure consists of isolated polyhedrons [Ni(H₂O)₆]²⁺ and [SO₄]²⁻ and free water which connects through hydrogen bonds. This association results in the porous framework where the protonated organic molecule trans-1,4-diaminocyclohexane is located as a counter ion. The IR spectra shows the bands corresponding to the sulfate anion, water molecule and diprotonated trans-1,4-diaminocyclohexane. Thermal study indicates the loss of water molecules and the degradation of trans-1,4-diaminocyclohexane.

Keywords: Hybrid Ni-sulfate, Crystal structure, X-ray diffraction, Infrared Spectroscopy, Thermal analysis.

1. Introduction

During the last two decades, considerable efforts have been directed towards the synthesis of the hybrid organic-inorganic due to physical properties such as porosity, magnetism and electronic behavior that may lead to many applications in fields like: catalysis, gas absorption, non-linear optical and storage energy [1-4]. Among these, metal sulfates form an important class with known applications in optic and catalysis [5-12]. A large number of these materials are synthesized in the presence of organic amines acting as structure-directing agent and their crystal structure is governed by weak energy bonding, exhibiting the supramolecular open framework [13-15].
In the present work we report on the synthesis, crystal structure, infrared spectroscopy and the thermal properties of a new inorganic-organic nickel sulfate: \( \text{C}_6\text{N}_2\text{H}_{16}\text{[Ni(H}_2\text{O})_6\text{(SO}_4\text{)}_2\text{].2H}_2\text{O} \), with trans-1,4-diaminocyclohexane acting as structure-directing agent.

2. Experimental

2.1. Synthesis

The title compound was synthesized at 293 K by dissolving 400 mg of nickel sulfate \( \text{NiSO}_4\cdot6\text{H}_2\text{O} \) (Prolabo) in an aqueous solution (10 mL \( \text{H}_2\text{O} \), 300 mg of \( \text{H}_3\text{PO}_4 \)) of hypophosphorous acid (30-32%; sd Fine-Chem Limited). To the resulting solution, 70 mg of trans-1,4-diaminocyclohexane (Sigma-Aldrich) was added under continuous stirring. The mixture was allowed to concentrate at room temperature for one week and the investigated sample material was filtered off and washed with acetone. \( \text{C}_6\text{N}_2\text{H}_{16}\text{[Ni(H}_2\text{O})_6\text{(SO}_4\text{)}_2\text{].2H}_2\text{O} \) crystallizes as green crystals of plate shape.

2.2. Infrared spectrum

Infrared spectrum of the title compound was recorded on a VERTEX 70 FTIR Spectrometer, in the range 4000–400 cm\(^{-1}\), using the ATR technique.

2.3. Crystal structure determination

Single-crystal X-ray diffraction measurement was carried out at room temperature using an Agilent Gemini S diffractometer equipped with a CCD detector and Mo radiation source. Acquired data was processed with the CrysAlisPro software [16]. Using Olex2 [17], the structure was solved with the olex2.solve [18] structure solution program using Charge Flipping and refined with the olex2.refine [18] refinement package using Gauss-Newton minimisation. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in the model at calculated positions, refined with a rigid model with their \( \text{Uiso} \) value to 1.2\text{Ueq} of their parent atoms.

Table 1. Summary of crystal data and structure refinement.

| Property                        | Value                        |
|---------------------------------|------------------------------|
| CCDC no.                        | 1588709                      |
| Chemical formula                | \( \text{C}_6\text{N}_2\text{H}_{16}\text{[Ni(H}_2\text{O})_6\text{(SO}_4\text{)}_2\text{].2H}_2\text{O} \) |
| Formula weight                  | 511.15                       |
| Crystal system                  | Monoclinic                   |
| Space group                     | \( P \text{ 2}_1\text{/n} \)  |
| \( a \), Å                      | 6.2586(3)                    |
| \( b \), Å                       | 12.3009(5)                   |
| \( c \), Å                       | 13.2451(6)                   |
| \( \beta \), deg                 | 98.047(5)                    |
| Volume, Å\(^3\)                 | 1009.65(8)                   |
| \( Z \)                          | 4                            |
| \( \rho_{\text{calc}} \text{ g cm}^{-3} \) | 1.6812                      |
| \( F(000) \)                     | 541.6                        |
| \( \mu \text{(Mo K} \alpha \text{)}, \text{mm}^{-1} \) | 1.244                        |
| Reflns (collected / unique, (Rint)) | 4028 / 2185 / 0.0274       |
| Data / restraints / params       | 2185 / 2 / 157               |
| \( R_1 \), \text{wR}[F^2 > 2\sigma(F^2)] | 0.0343 / 0.0862             |
| Goodness-of-fit on \( F^2 \)     | 1.050                        |
| largest diff peak and hole (e Å\(^{-3} \)) | 0.71 / -0.49               |
2.4. Thermal analysis
Thermogravimetric analysis (TGA) data were recorded on an SDT-Q600 analyzer from TA instruments. The temperature varied from RT to 900 ºC at a heating rate of 10 ºC.min\(^{-1}\). Measurements were carried out on samples in open platinum crucibles under air flow.

3. Results and discussions

3.1. Spectroscopy
The infrared spectrum of C\(_6\)N\(_2\)H\(_{16}\)[Ni(H\(_2\)O)\(_6\)](SO\(_4\))\(_2\).2H\(_2\)O (Figure 1) shows bands corresponding to the vibrations of trans-1,4-diaminocyclohexane molecule, water molecule and sulfate anion. The broad band that appears at 3217.02 cm\(^{-1}\) is due to stretching vibrations of NH\(_2\) group and the band at 2923.83 cm\(^{-1}\) is assigned to C-H stretching vibration\([19]\). All these bands indicate the presence of trans-1,4-diaminocyclohexane in the structure. The bands observed at 3102.32 and 1649.41 cm\(^{-1}\) are associated to the stretching and bending vibrations of OH group\([19]\). This confirms the presence of crystal water. The large band at 1043.82 cm\(^{-1}\) is attributed to the S-O stretching vibration of SO\(_4\) group\([20]\).

![Figure 1. IR spectrum of C\(_6\)N\(_2\)H\(_{16}\)[Ni(H\(_2\)O)\(_6\)](SO\(_4\))\(_2\).2H\(_2\)O](image)

3.2. Description of the crystal structure
Single-crystal structure analysis reveals that the asymmetric unit of title compound contains fourteen crystallographically independent non-hydrogen atoms, including one nickel atom, one sulfur atom, one nitrogen atom, three carbon atoms and eight oxygen atoms. Figure 2 depicts a projection of the crystal structure of the title compound on the crystallographic plane (001). Ni atom lies on an inversion center, it is coordinated to six water molecules to form [Ni(H\(_2\)O)\(_6\)]\(^{2+}\) octahedron. The equatorial bond lengths Ni-O9 and Ni-O10 are 2.084 and 2.026 Å respectively while the axial bond length is 2.028 Å. The Average <Ni-O> bond length is 2.038 Å, these distances are very close to those found in [S-C\(_3\)H\(_4\)N\(_2\)][Ni(H\(_2\)O)\(_6\)](SO\(_4\))\(_2\) (2.0518-2.0732 Å)\([21]\). The deformation of [Ni(H\(_2\)O)\(_6\)]\(^{2+}\) octahedron can be evaluated by calculating the bond length distortions according to the equation (1)\([22-23]\).
\[
\Delta_{\text{oct}} = \frac{1}{6} \sum \left( \frac{R_i - \bar{R}}{\bar{R}} \right)^2
\]

(1)

Where \( R_i \) is the individual Ni-O bond length and \( \bar{R} \) is the average Ni-O bond length.

A value of 1.726 \times 10^{-3} indicates thus a moderate distortion of the octahedron [Ni(H₂O)₆]²⁺. The S atom, located in general position, is coordinated to four oxygen atoms forming a free [SO₄]²⁻ tetrahedron, which is not coordinated to metal atom. The S-O distances vary from 1.463 to 1.483 Å, behaving the same as in [S-C₅H₁₂N₂][Ni(H₂O)₆](SO₄)₂: (1.462-1.481 Å) [20]. The polyhedrons [Ni(H₂O)₆]²⁺ and [SO₄]²⁻ and free water molecules are linked to each other by O-H---O hydrogen bonds, to form a two dimensional anionic inorganic supramolecular open network. The charge of inorganic network is compensated by the protonated trans-1,4-diaminocyclohexane molecules [C₆N₂H₁₆]²⁺ which are held in the pores through N-H---Os interactions (Os from to sulfate anions) and giving rise to an organic-inorganic supramolecular open framework (Figure 3). This framework is comparable to crystal structure of (C₇N₂H₇)₂[Ni(H₂O)₆(SO₄)₂].4H₂O [24].

![Figure 2](image-url)
3.3. Thermal analysis

The results of the TGA-DSC analyses are plotted on the Figure 4. The TGA analysis of C₆N₂H₁₆[Ni(H₂O)₆(SO₄)₂]·2H₂O shows five steps of weight loss in a total of 70.55%. The first weight loss of 24.55%, starting at room temperature and ending at 150°C is in agreement with the removal of 6.5 water molecules per unit formula (theoretical loss, 22.9%). Two endothermic thermo-differential signals are associated with this dehydration reaction. It means that the removal of these 6.5 water molecules is done in two steps but very difficult to distinguish like shown on the TGA curve. The second weight loss of 5.039% in range of 150-200°C is attributed to the loss of 1.5 water molecules (theoretical loss, 5.329%). This second dehydration reaction is associated to an exothermic thermo-differential signal. The third weight loss of 23.69% occurred between 250-400°C correspond to the decomposition of trans-1,4-diaminocyclohexane molecule (theoretical loss, 22.705%). As one can expect the disintegration of organic content follows a discontinuous three-step process. According DSC curve this pyrolytic reaction is characterized by three exothermic signals. The weight loss of 7.062% and 9.939% in range of 400-800°C attributed to the final degradation of 2D inorganic framework, it can be due to the release of one dioxide molecule (theoretical loss, 6.7%) and one dioxide sulfur molecule (theoretical loss, 12%). This thermal decomposition is associated with two exothermic thermo-differential signals.
4. Conclusion
The 2D-hybrid nickel sulfate with trans-1,4-diamonocyclohexane molecule acting as structure-directing agent has been synthesized by slow evaporation. Its crystal structure exhibits a supramolecular layer made up by isolated entities $[\text{Ni(H}_2\text{O)}_6]^{2+}$, $[\text{SO}_4]^{2-}$, $\text{H}_2\text{O}$ and $[\text{C}_6\text{N}_2\text{H}_{16}]^{2+}$ which are held together through $\text{O-H}---\text{O}$ and $\text{N-H}---\text{O}$ hydrogen bonds. The DSC-TG analysis shows that beyond 50°C this compound decomposes. The infrared bands that appear at 3217.02, 3102.32, 2923.83 and 1043.82 cm$^{-1}$ are associated to the stretching vibrations of $\text{O-H}$, $\text{N-H}$, $\text{C-H}$ and $\text{S-O}$ bonds respectively and confirms the presence of $[\text{SO}_4]^{2-}$, $\text{H}_2\text{O}$ and $[\text{C}_6\text{N}_2\text{H}_{16}]^{2+}$ entities in crystal structure of the title compound.

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