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TRIS(1,10-PHENANTHROLINE)-COBALT(III) TRIPERCHLORATE DIHYDRATE CRYSTAL: CHARACTERIZATION BY XRPD, DSC AND HIRSHFELD SURFACE ANALYSIS

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ABSTRACT

The study of transition metal complexes with bidentate ligands is gaining prominence due to its potential for biological application. Therefore, studying these complexes' structure, thermal stability, and intermolecular interactions is crucial to understanding their properties and assessing their potential use in pharmaceutical drugs. From this location, the tris(1,10-phenanthroline)-cobalt(III) triperchlorate dihydrate complex was synthesized by the slow solvent evaporation technique in 20 days, with a prismatic shape and orange coloration. The structure was confirmed by the powder XRPD technique combined with refinement by the Rietveld method at room temperature, with formula $[Co(C_{12}H_8N_2)_3](ClO_4)_3{\cdot}2H_2O$, monoclinic structure, space group $C2/_C$. From the differential scanning calorimetry (DSC) analysis in the temperature range between 300 K and 750 K, we observed an exothermic peak at 625 K that indicates a total enthalpy involved in the process of 1313.07 kJ/mol, referring to the vaporization of uncoordinated water and the $(ClO4^-)_3$ molecule, indicating that the material has good thermal stability. The Hirshfeld surface analyses demonstrated that the main intermolecular interactions involve the atoms of H···H (34.5%), H···O/O···H (34.4%), H···C/C···H (15.9%), C···O/O···C (12.8%) e C···C (1.8%). Therefore, the results obtained demonstrate that the material has good thermal stability and potential for carrying out intermolecular interactions that allow new characterizations in order to investigate its possible application in biological activities.

Keywords: *Cobalt(III) complex, Hirshfeld surface analysis, biological activity.*

INTRODUCTION

Coordination complexes based on transition metal ions and nitrogenous ligands have attracted increasing interest due to their physicochemical properties, as well as their potential biological, chemical and medicinal applications [1-2]. Complexes containing cobalt ions, for example, have been the subject of recent studies regarding their pharmacokinetic, antibacterial and anti-inflammatory properties [3-4].
Among the ligands used in these complexes, 1,10-phenanthroline (phen) stands out, widely used in recent research because it presents good structural, luminescent and cytotoxic properties when complexed with metal ions [5]. Furthermore, despite having a relatively low protonation

constant in aqueous solution (log K = 4.95), it demonstrates considerable coordination capacity with transition metal cations, facilitating the formation of coordination complexes [6].
In this context, this work studies the tris(1,10-phenanthroline)-cobalt(III) triperchlorate dihydrate complex using the X-ray diffraction (XRPD) technique and refinement using the Rietveld method to confirm the obtaining of the material and obtain details of the coordination geometry, differential scanning calorimetry (DSC), in order to understand the events related to the thermal stability of the material and analysis of Hirshfeld Surfaces to visualize and quantify the intermolecular interactions present in the crystal structure. In this way, we try to verify the potential of the material to be used as a possible candidate for biological applications.

MATERIALS AND METHODS

Synthesis of the crystal tris(1,10-phenanthroline)-cobalt(III) triperchlorate dihydrate

The tris(1,10-phenanthroline)-cobalt(III) triperchlorate dihydrate complex was obtained by the slow solvent evaporation technique. Initially, a methanolic solution of 20 mL of 1,10-phenanthroline (1 mmol) was prepared and added dropwise to an aqueous solution of 5 mL of cobalt chloride hexahydrate (1 mmol). The resulting solution was stirred for 1 hour for complete homogenization, after which 10 mL of perchloric acid (0.5 mol/L) was added dropwise. The resulting final solution was stirred for 2 hours, then sealed with plastic film with small holes and placed in a growth room at room temperature, remaining for 20 days.

Powder X-ray Diffraction (XRPD) and Rietveld refinement

The powder X-ray diffraction (XRPD) technique was used to confirm the obtaining of the studied material. For this, the crystal powder was analyzed in an Empyrean diffractometer (PANalytical), CuKα radiation (λ = 1.54 Å), angular step of 0.02º, angular range 2θ of 5-45º and 2s/step. The refinement by the Rietveld method was performed using the GSAS program in order to compare the experimental data with the theoretical ones obtained from the Cambridge Crystallographic Data Centre database (CCDC code 1243980) [7].

Thermal Analysis – DSC

The material was subjected to thermal analysis using differential scanning calorimetry (DSC) in order to verify the enthalpy variation involved in the process. For this purpose, a Shimadzu DSC-60 was used, with a mass of 1,640 mg, flow rate of 100 mL/min, heating flow of 10ºC/min and temperature between 300 K and 800 K.

Hirshfeld surface analysis

The 2D printing data for Hirshfeld surfaces were obtained using the Crystal Explorer 17 software [8-9]. These surfaces aim to analyze the intermolecular interactions that exist in the complex and the percentage of empty spaces in the unit cell. For this purpose, normalized distances (dnorm) were generated in relation to a specific point on the surfaces of the internal (di) and external (de) atoms, and the van der Waals radius. In addition, to quantify the intermolecular contacts existing in the crystal lattice, 2D prints were generated as a function of di and de. Finally, to calculate the existing voids, calculations of the complex's electron density isosurfaces were used.

RESULTS AND DISCUSSION

Powder X-ray Diffraction (XRPD) and Rietveld refinement

The tris(1,10-phenanthroline)-cobalt(III) triperchlorate dihydrate complex was obtained after 20 days in prismatic form and orange coloration. Fig. 1(a) shows the X-ray diffraction of the material at ambient conditions (300 K) and the refinement used by the Rietveld method. The complex has formula $[Co(C_{12}H_8N_2)_3](ClO_4)_3{\cdot}2H_2O$, molecular mass of 933.98 g/mol, monoclinic structure, space group C2/c and four molecules per unit cell (Z = 4). The data obtained in the refinement using the Rietveld method indicated the following lattice parameters: a = 17.81(3) Å, b = 18.29(3) Å, c = 23.16(4) Å, $\alpha = \gamma = 90°$, β = 92.70(1)° e V = 7545.19(2) Å^3. The refinement quality factors were: R_{WP} = 5.34%, R_P = 4.18%, with S = 1.11. Thus, the data are in agreement with the literature [7].

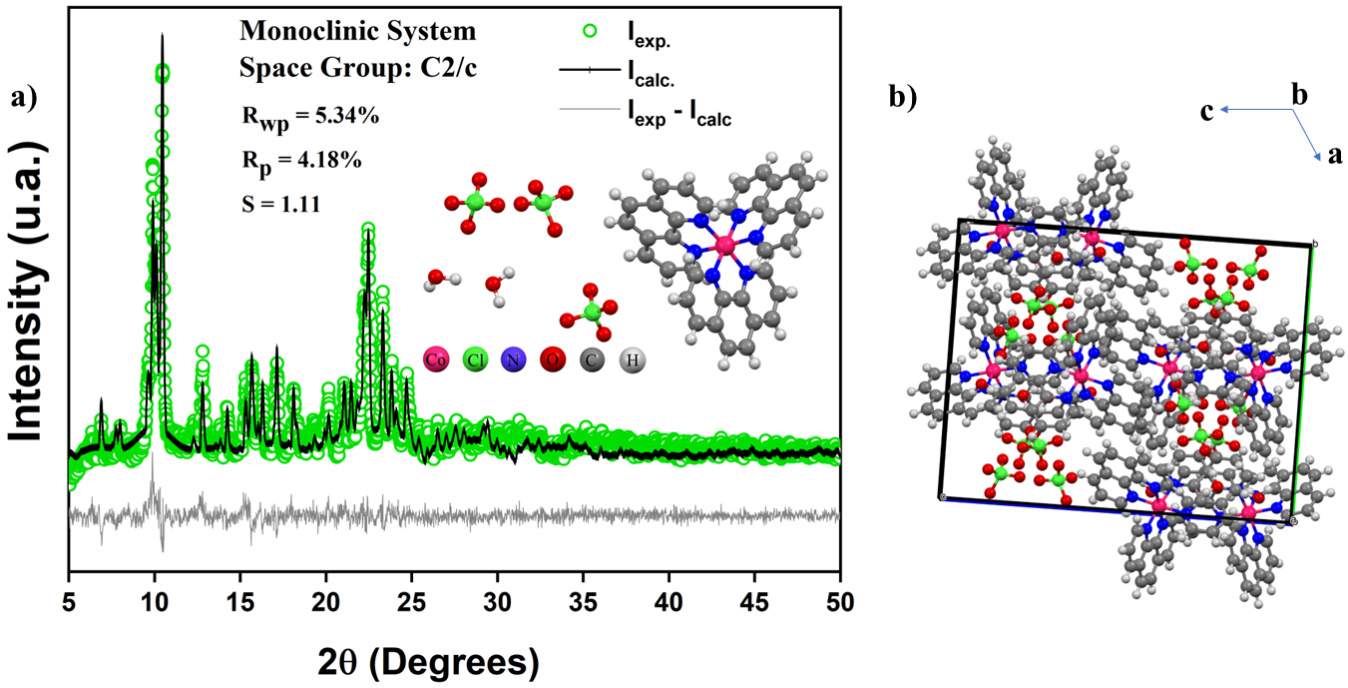

Fig. 1. (a). X-ray powder diffractogram, refinement by the Rietveld method for the tris(1,10-phenanthroline)-cobalt(III) triperchlorate dihydrate complex and molecular structure of the complex (b) unit cell.

The molecular structure of the complex is shown in Fig. 1-(a). It is possible to observe the cobalt(III) ion centralized and coordinated by six nitrogen atoms of the 1,10-phenanthroline molecules, forming a distorted octahedral geometry. The stability of the complex is achieved through interactions with three perchloric acid molecules that occur by ionic attraction and with two water molecules, by hydrogen bonding. Fig. 1-(b) shows the amount of molecules existing in each unit cell and their respective arrangements along the crystal lattice.

Thermal Analysis – DSC

The DSC curve highlighted in Fig. 2 shows the enthalpy variation involved in the temperature range between 300 K and 750 K of the tris(1,10-phenanthroline)-cobalt(III) triperchlorate dihydrate complex. According to the analysis, the total enthalpy involved in the process is 1313.07 kJ/mol. The vaporization process of uncoordinated water is approximately 40 kJ/mol [10], representing a total of 80 kJ/mol associated with the two molecules present by interaction

in the study material. The indication of only one exothermic event in the DSC curve indicates that due to the proximity to the $(ClO_4^-)_3$ molecule, both decompositions can occur together [11].

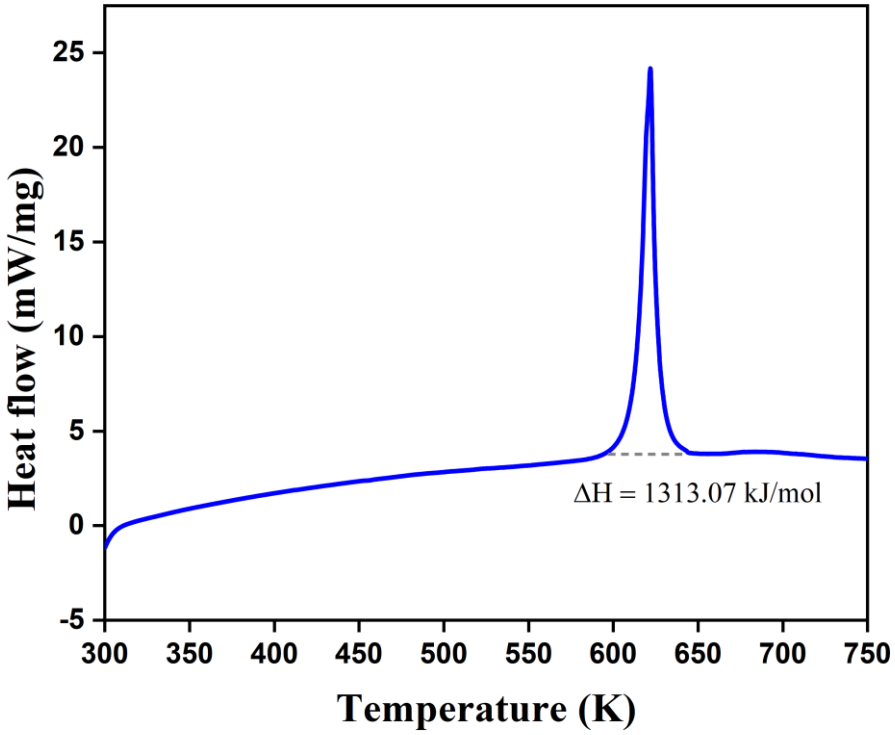

Fig. 2. DSC of the tris(1,10-phenanthroline)-cobalt(III) triperchlorate dihydrate complex.

The exothermic peak in the 600 K region is a characteristic of perchlorate decomposition, with volatilization occurring approximately with an enthalpy variation of ΔH = 400 kJ/mol for each molecule of $(ClO_4^-)_3$, resulting in approximately 1200 kJ/mol [12]. The values obtained in the analysis indicate that the studied complex has considerable thermal stability, decomposes irreversibly and has a large amount of energy involved in the decomposition process.

Intermolecular analysis by Hirshfeld surfaces

Hirshfeld surface analysis allows us to verify the intermolecular interactions that exist in the tris(1,10-phenanthroline)-cobalt(III) triperchlorate dihydrate [13] complex based on the symmetric unit Fig. 3(a). The normalized distance (d_{norma}) (Fig. 3(b)) discriminates the regions with equal or close distances (white coloring) and regions with greater or lesser distances (blue or red coloring) in relation to the van der Waals radii. The outermost atoms (d_e) Fig. 3(c) with regions of more intense colors indicate the sites most favorable to the acceptance of intermolecular interactions, while the inner ones (d_i) Fig. 3(d) with the same coloring represent the donor sites, mainly related to the atoms with greater interactions.
The places where the molecules of the complex interact with each other are indicated by colors that vary between red and yellow, called the shape index Fig. 3(e), while the smaller interactions with neighboring molecules are represented by the green color and the larger ones in blue, in the curvature Fig.(f). The stacking of neighboring molecules is represented by the patch fragments, in which the colors of greater intensity represent where these accommodations would occur. Fig.3(h) indicates the voids existing in the unit cell (opaque color) with a total volume of 952.63 A^3 (12.62% of the total) and a surface area of 2688.47 A^2 indicating that the complex has strong molecular interactions, with a high amount of energy existing in the crystal lattice.

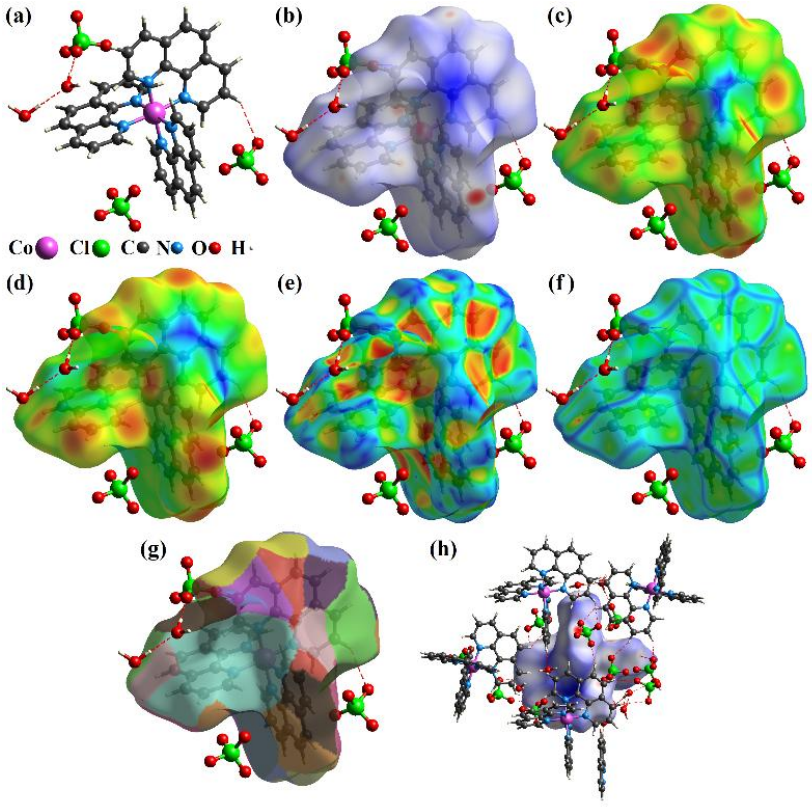

Fig. 3. Hirshfeld surface of the tris(1,10-phenanthroline)-cobalt(III) triperchlorate dihydrate complex in (a) asymmetric unit, (b) d_{norm}, (c) d_e, (d) d_i, (e) shape index, (f) curvedness, (g) fragments patch and (h) voids

The 2D fingerprint plots (Fig. 4) highlight the most significant types of interactions in the study material, being H···H (34.5%), H···O/O···H (34.4%), H···C/C···H (15.9%), C···O/O···C (12.8%) e C···C (1.8%), which represents 99.4% of the interactions occurring in the tris(1,10-phenanthroline)-cobalt(III) triperchlorate dihydrate complex.

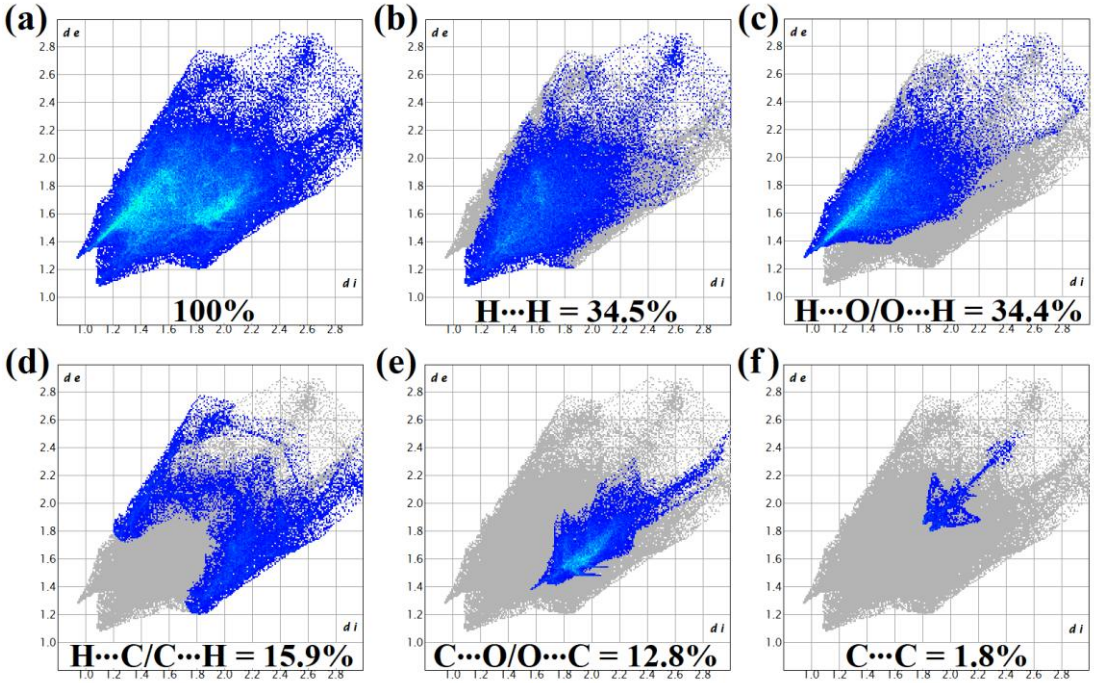

Fig. 4. 2D fingerprint plots of the tris(1,10-phenanthroline)-cobalt(III) triperchlorate dihydrate complex for the complete (a) interactions, (b) H···H, (c) H···O/O···H, (d) H···C/C···H, (e) C···O/O···C, (f) C···C.

CONCLUSIONS

The tris(1,10-phenanthroline)-cobalt(III) triperchlorate dihydrate complex was obtained after 20 days using the slow solvent evaporation technique and confirmed by XRPD analysis combined with Rietveld refinement at room temperature. The material has the formula $[Co(C_{12}H_8N_2)_3](ClO_4)_3{\cdot}2H_2O$, molecular mass of 933.98 g/mol, monoclinic structure, space group C2/c and four molecules per unit cell. Thermal analysis by differential scanning calorimetry (DSC) in the temperature range between 300 K and 750 K showed an exothermic peak at 625 K, indicating a total enthalpy involved in the process of 1313.07 kJ/mol, referring to the vaporization of uncoordinated water from the $(ClO_4^-)_3$ molecule. These values indicate that the complex has thermal stability and has a large amount of energy involved in the decomposition process. Hirshfeld surface analyses demonstrated that the main intermolecular interactions involve the atoms of H···H (34.5%), H···O/O···H (34.4%), H···C/C···H (15.9%), C···O/O···C (12.8%) and C···C (1.8%). Finally, the results obtained demonstrate that the material has good structural conformation, excellent thermal stability and potential to perform intermolecular interactions that allow new characterizations in order to investigate its possible application in biological activities.

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