SYNTHESIS AND CHARACTERIZATION OF A MULTI-IONIC POLYMERIC COMPOUND INVOLVING HEXAAMMINECOBALT(III), POTASSIUM, 4-SULFOBENZOIC, AND CHLORIDE IONS

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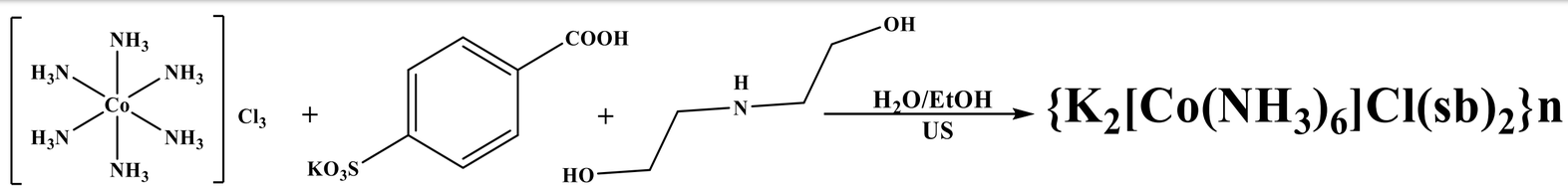
INTRODUCTION

Cobalt complexes are playing an increasing role due their therapeutic use as excellent anticancer, antiviral and antibacterial agents. Microorganisms develop resistance to existing drugs very rapidly, thus there is a need to look for new classes of drugs, especially those that show broad-spectrum properties. Hexaamminecobalt(III) chloride, $[Co(NH_3)_6]Cl_3$, shows antiviral properties against Sindbis virus, adenovirus, and also exibits activities against human immunonodeficiency virus (HIV) and the Zaire Ebola (ZEBOV) strain [1]. Recently, we reported that compounds comprising $[Co(NH_3)_6]^{3+}$ cations and various N-, N,O- and O-donor moieties showed inhibitory potential against bacterial cancer in plants [2,3].

SYNTHESIS



A new compound has been prepared from the reaction of $[Co(NH_3)_6]Cl_3$ with the potassium salt of 4-sulfobenzoic acid in the presence of diethanolamine in H_2O/EtOH.

RESULTS

STRUCTURE. The single crystal X-ray structural analysis reveals that **1** is ionic compound crystalizes in tetragonal *I*4/*m* space group. The compound comprises a potassium and $[Co^{III}(NH_3)_6]^{3+}$ cations whose charge is compensated by 2 sulfobezoic dianions and a chloride anion. The components in **1** are aditionally associated by hydrogen bonds of the type: N−H···N, N−H···O, S–O···H, C−O···H, N–H···Cl (Fig. 1).

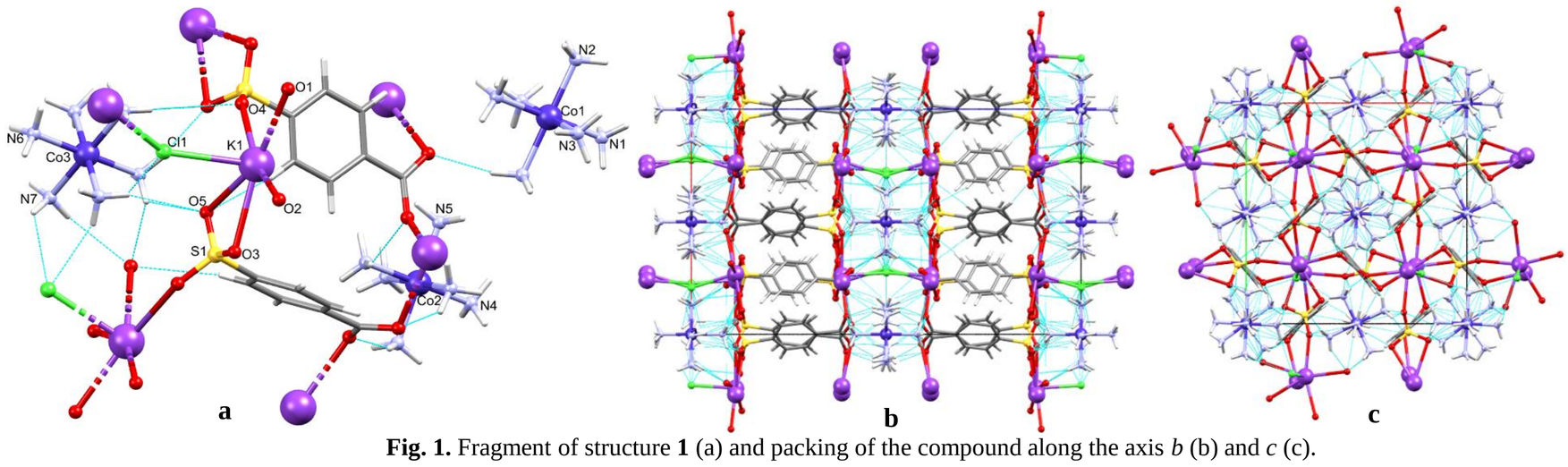


Fig. 1. Fragment of structure **1** (a) and packing of the compound along the axis *b* (b) and *c* (c).

*Crystallographic data for **1***

Formula	$C_{14}H_{26}Cl_1Co_1K_2N_6O_{10}S_2$
M_r	675,11
Singonia	Tetragonal
Space group	*I 4/m*
***a* (Å)**	14.3265(5)
***b* (Å)**	14.3265(5)
***c* (Å)**	24.7933
***α*=*β* =*γ* (grad)**	90
***V* (Å³)**	5088.8(5)

HIRSHFELD SURFACE ANALYSIS

Hirshfeld surface (HS) analysis provides the visualization of the intermolecular interactions in a crystalline environment (Figs. 2-3) and quantitatively summarizes the interactions that contribute to the overall stability to the crystal structure (Fig. 4).

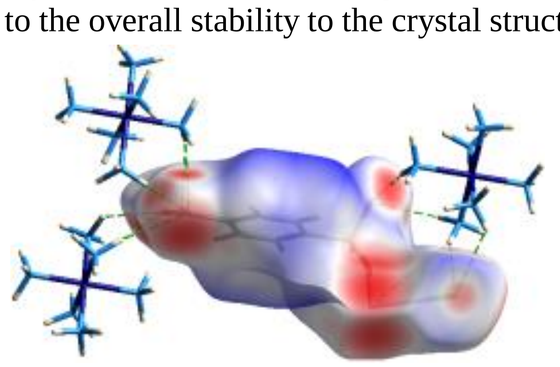


Fig. 2. Views of Hirshfeld surface mapped with d_{norm} property of Ksb^- anion highlighting close contacts (red areas) with neighbouring molecules in **1**.

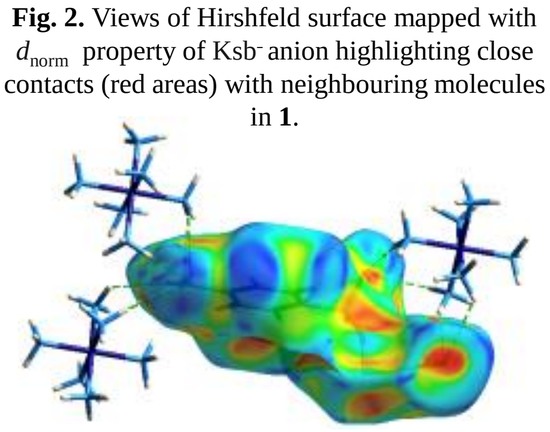
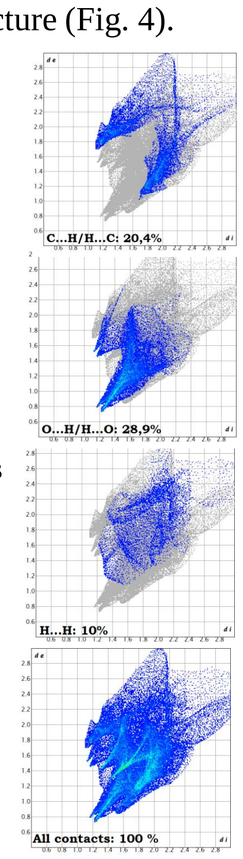


Fig. 3. The Hirshfeld surface of **1** plotted over shape-index.



The 2D fingerprint plot quantitatively revealed the contribution of close contacts in the crystal structure and Fig. 4 shows the relative contributions to the HS area for each type of intermolecular contacts in **1**. The most important contributions for crystal packing in **1** are from H···O (28,9 %) contacts.

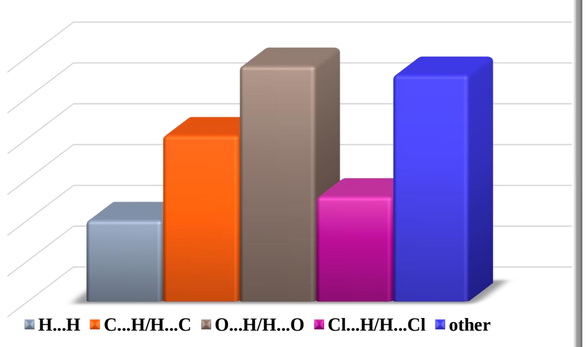
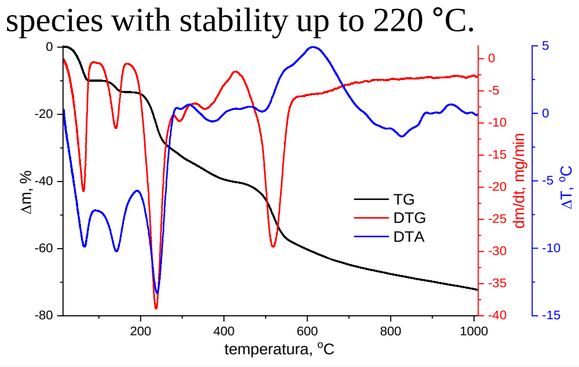


Fig. 4. 2D fingerprint plots for **1** delineated into H…H, O…H/H…O and C…H/H…C contacts.

THERMAL ANALYSIS

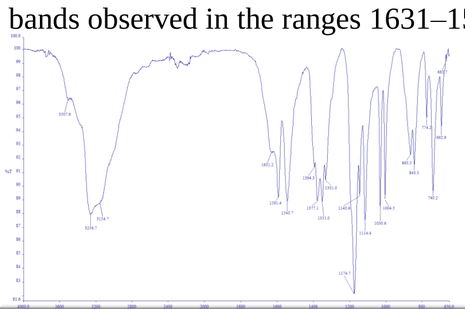
Thermal analysis for **1** reveals two clearly defined mass loss stages corresponding to desulfonation and decarboxylation of organic species with stability up to 220 °C.



The next step recorded from 220 °C to 1000 °C is characteristic for the complete decomposition of complex cations and organic anions until the formation of a metallic residue.

IR SPECTROSCOPY

The IR spectrum of **1** displays the slightly displaced stretching vibrations due to the formation for these hydrogen bonds. Asymmetric and symmetric stretching vibration of the coordinated NH_3 molecules of $[Co^{III}(NH_3)_6]^{3+}$ cation were localized in the range of 3256-3154 cm^{-1}. The strong and broad bands observed in the ranges 1631–1544 cm^{-1} correspond to carboxylic



groups of 4-sulfobenzoic acids, which overlap with δ(HNH) vibrations. The stretching vibrations (asymmetric/symmetric) of the sulfonic groups are in the range of 1394–1331 and 1174–1143 cm^{-1}.

CONCLUSIONS: A new crystalline multi-component compound **1** comprising $[Co^{III}(NH_3)_6]^{3+}$ cation and Ksb^- anions has been prepared. The compound has been characterized by elemental analysis, thermogravimetry, and IR spectroscopy. Crystal structure analysis was supported with the HS and fingerprint plots.

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1. Chang E.L., Olinger G.G. et al. J Antivir Antiretrovir. 3 (2011) 020-027.
2. Patents: MD 4725 C1 2021.06.30; MD 1459 Z din 2021.05.31.
3. Darii M., Beleaev E.S., et al., New J Chem. 46 (2022) 11404-11421.