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THE SYNTHESIS AND STUDY OF TRIS-(2,4-BIS(TRICHLOROMETHYL)) -1,3,5-TRIAZAPENTADIENATO Co(III) COMPLEX THROUGH HIRSHFELD SURFACE ANALYSIS AND EVALUATION OF ITS ANTIMICROBIAL ACTIVITY

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Abstract. In this study, the one-step synthesis of bis-(2,4-bis(trichloromethyl))-1,3,5-triazapentadienato Me(II) complexes were achieved through the reaction of trichloroacetonitrile with ammonia in the presence of metal salts (Ni, Cu, Pd, Zn). The molecular structures of the synthesized compounds were characterized via X-ray diffraction analysis. Particular attention was given to the halogenated ligand-containing complexes due to their exceptional thermal and chemical stability and solubility in organic solvents. The Zn(II) complex was evaluated in the Henry reaction and demonstrated significant catalytic activity. Moreover, the Tris-(2,4-bis(trichloromethyl))-1,3,5-triazapentadienato Co(III) complex was synthesized and its crystal structure was elucidated. Hirshfeld surface analysis revealed key intermolecular interactions, such as strong N—H···O hydrogen bonds, C—H···Cl halogen bonds and weaker C–Cl···Cl halogen interactions, which play a crucial role in crystal packing. The antimicrobial activity of the Co(III) complex was evaluated against various Gram-positive and Gram-negative bacteria, as well as yeast strains, using the agar diffusion method. The compound demonstrated the highest activity against *Staphylococcus aureus*, exceeding its effects on other tested microorganisms. These findings highlight the potential of these triazapentadienato metal complexes as promising candidates for antimicrobial applications and catalytic processes.

Keywords: *Triazapentadienato complexes, trichloromethyl ligands, Co(III) complex, Hirshfeld surface analysis, X-ray diffraction, antimicrobial activity.*

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1. Introduction

The one-step synthesis of bis-(2,4-bis(trichloromethyl))-1,3,5-triazapentadienato Me(II) complexes was carried out via the reaction of trichloroacetonitrile with ammonia in the presence of metal salts (Ni, Cu, Pd, Zn) and their molecular structures were

thoroughly investigated by using X-ray diffraction analaysis (Gurbanov *et al*., 2023; Shikhaliyev *et al*., 2012, 2013, 2014). Halogenated (CF_3, CCl_3) ligand-containing complexes are particularly interesting due to their high thermal and chemical stability, and excellent solubility in organic solvents, especially in halogenated alkanes. These properties are particularly significant for their application as catalysts. The application of the synthesized bis-(2,4-bis(trichloromethyl))-1,3,5-triazapentadienato Zn(II) complex as catalyst in the Henry reaction and its demonstrated effective catalytic activity, further confirms the validity of the aforementioned properties. In addition, we have determined that TAP complexes exhibit high antimicrobial activity (Shikhaliyev *et al*., 2013; Ahmedova *et al*., 2025).

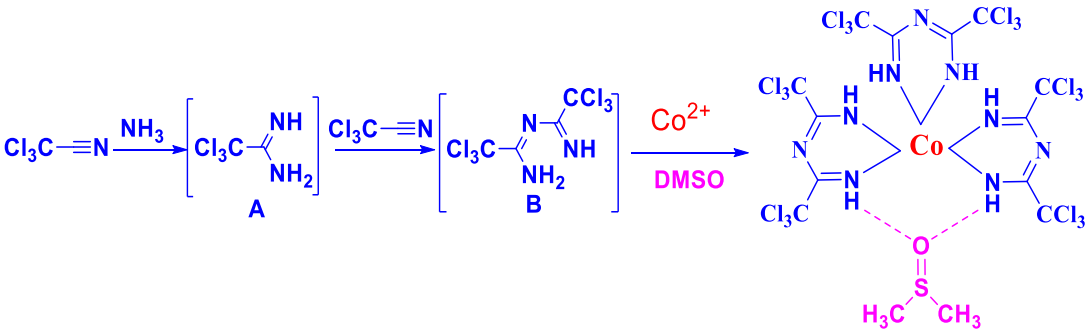
2. Materials and Methods

The reagent was prepared following a previously published method, with no significant modifications (Shikhaliyev *et al*., 2014). The Co(III) complex was synthesized under ambient conditions. To a stirred solution of ammonium hydroxide (2.5 mL, 1 M aqueous solution, 2.5 mmol) in dimethyl sulfoxide (DMSO, 20 mL), trichloroacetonitrile (1.6 mL, 11 mmol) was added dropwise at room temperature (~25 °C). After 2 minutes of stirring, an aqueous solution (1.0 mL) containing $Co(CH_3COO)_2 \cdot 4H_2O$ (1.1 mmol) was added to the reaction mixture. The resulting solution was stirred for an additional 10 minutes under ambient conditions. A light red precipitate formed during the reaction and was filtered off and dried in air. The target complex was obtained in 51% yield. Hirshfeld surface and 2D fingerprint plots were generated using CrystalExplorer software (version 21.5), based on the crystallographic information file (CIF) of the Co(III) complex. A 0.3% solution of the compound in dichloromethane was prepared for antimicrobial testing. The pathogenic test strains included Gram-positive bacteria (*Bacillus subtilis*, *Staphylococcus aureus*, *Bacillus mesentericus*), Gram-negative bacteria (*Escherichia coli*, *Acinetobacter baumannii*, *Pseudomonas aeruginosa*, *Klebsiella pneumoniae*) and yeast fungi (*Candida albicans*, *C. tropicalis*, *C. guilliermondii*). All experiments were performed in quadruplicate and the data were statistically analyzed.

3. Results and Discussion

Accordingly, the synthesis, Hirshfeld surface analysis and antimicrobial properties of the corresponding Tris-(2,4-bis(trichloromethyl))-1,3,5-triazapentadienato Co(III) complex were systematically investigated. The use of DMSO as a solvent in the synthesis of the complex revealed, through X-ray diffraction (XRD) analysis of the monocrystal, that DMSO molecules were involved in the formation of the complex (Kopylovich *et al*., 2009, 2011; Fernandes *et al*., 2011) (Scheme 1).

Although $Co(CH_3COO)_2$ was initially used in the reaction, oxidation of Co^{2+} to Co^{3+} occurred during the reaction process, indicating that the system itself possesses oxidizing properties. It was also observed that cobalt complexes derived from halogenated nitriles formed with a significant exothermic effect. This phenomenon was attributed to the activation of the cyano carbon atom by the electron-withdrawing halogen-containing group (Shikhaliyev *et al*., 2013; Kopylovich *et al*., 2012; Dias *et al*., 2011; Valente *et al*., 2021).



Scheme 1. Synthesis of the Tris-(2,4-bis(trichloromethyl))-1,3,5-triazapentadienato Co(III) complex

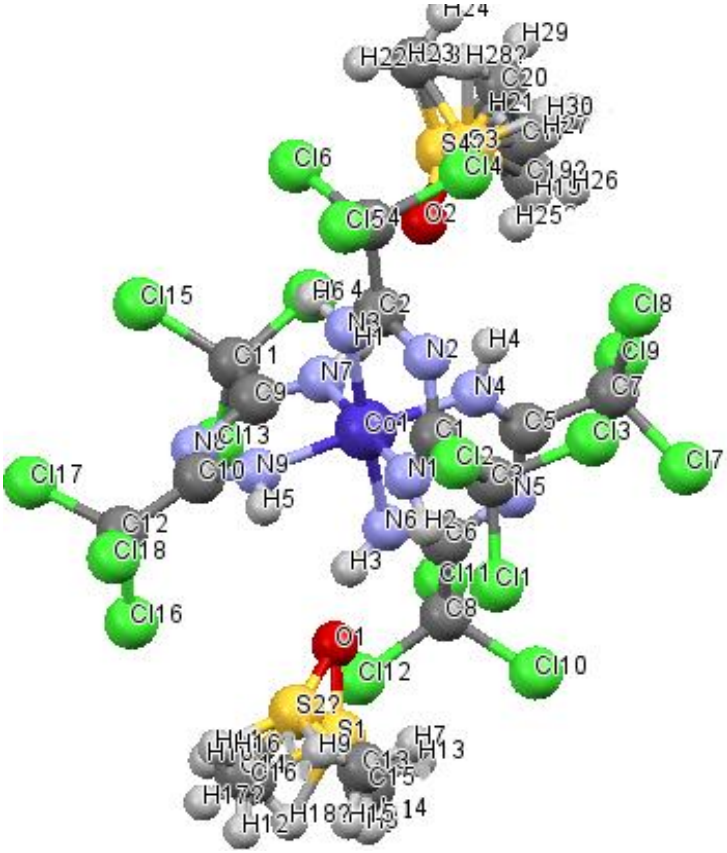


Figure 1. Molecular structure of the Tris-(2,4-bis(trichloromethyl))-1,3,5-triazapentadienato Co(III) complex

It should be noted that, as observed from the molecular structure of the complex, intermolecular halogen-halogen interactions played a key role in the formation of the crystal (Figure 2).

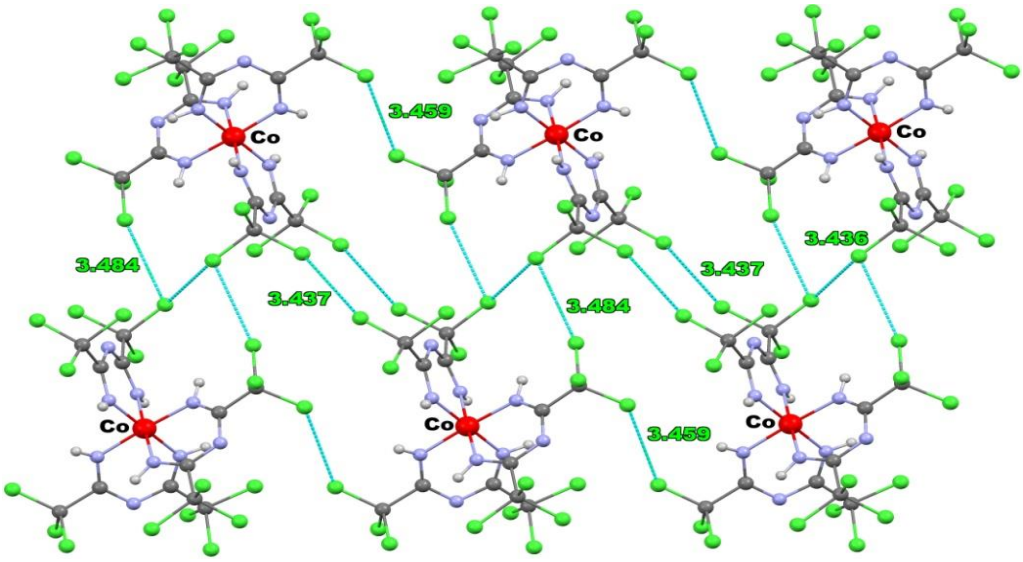


Figure 2. The intermolecular Cl···Cl distance is indicated by dashed lines. DMSO molecules are omitted for clarity

3.1. Interpretation of the structure

Intermolecular interactions and torsion angles in the Tris-(2,4-bis(trichloromethyl))-1,3,5-triazapentadienato Co(III) complex are presented in the tables below.

Table 1. Intermolecular interactions in the compound

Intermolecular interactions	Distance (A^0)	Symmetry operation
$Cl16\cdots H16$	2.477	x, y, z
$Cl5\cdots H20$	2.821	$-1+x, y, z$
$Cl10\cdots$H24	2.912	$x, -1+y, z$
$Cl9\cdots$H25	2.835	x, y, z
$H1\cdots$O2	2.352	x, y, z
$H4\cdots$O2	2.610	x, y, z
$Cl2\cdots Cl5$	3.437	$-1-x, 1-y, 1-z$
$Cl16\cdots Cl16$	3.177	$-x, -y, -z$

Table 2. Torsion angles

Atom 1	Atom 2	Atom 3	Atom 4	Torsion angle (^{0})
N3	Co1	N1	C1	-20.7(6)
N3	Co1	N1	H2	-179(4)
N4	Co1	N1	C1	68.8(5)
N9	Co1	N1	C1	-115.0(6)
N9	Co1	N1	H2	86(4)
N4	Co1	N3	H6	109(5)
N7	Co1	N3	C2	-165.5(5)

3.2. Hirshfeld surface analysis

One of the most powerful tools for obtaining additional information about intermolecular interactions in molecular crystals is Hirshfeld surface analysis. Based on the shape and size of the Hirshfeld surface, conducting qualitative analysis of the close

intermolecular interactions within the molecular crystal can be performed. For the molecule under consideration, it was determined that the electron density of the molecule in the Hirshfeld surface and surrounding molecules is equal. This surface is generated based on calculations derived from the electron density of a spherical atom. As a result, an isosurface is acquired and two distances can be determined for every point of the isosurface: d_e is the distance between the given point on the isosurface and the nearest atom outside the surface and d_i is the distance between the given point on the isosurface and the nearest atom outside the surface. Furthermore, the region significant for intermolecular interactions is identified using the distance d_{norm}.

$$d_{norm} = \frac{d_i - r_i^{vdw}}{r_i^{vdw}} + \frac{d_e - r_e^{vdw}}{r_e^{vdw}}.$$

In this context, r_e^{vdw} and r_e^{vdw} represent the Van der Waals radii of the atoms nearest to the surface, with r_e^{vdw} corresponding to the atoms inside the surface and r_i^{vdw} to those outside the surface. An intermolecular distance shorter than r^{vdw}, results in a negative value of d_{norm}, whereas a longer distance corresponds to a positive value. Accordingly, the Hirshfeld surface is color-mapped in red, white and blue: red indicates regions of short intermolecular contacts, white corresponds to contacts approximately equal to van der Waals radius (r^{vdw}) and blue represents longer contacts.

The Hirshfeld surface and fingerprint plot were generated in the *CrystalExplorer* program based on the crystallographic information file (CIF) of the compound. The d_{norm} value of the obtained compound ranges between $0{,}4616A^0$ and $1{,}3136A^0$.

The structure of this crystal includes strong N—H···O (Figure 5a) hydrogen bonds and C—H···Cl (Figure 5b) halogen bonds (Kashina *et al*., 2021; Karmakar *et al*., 2015; Sutradhar *et al*., 2020). Additionally, weak C−Cl ··· Cl halogen interactions (Figure 5c) also contribute to the formation of this structure.

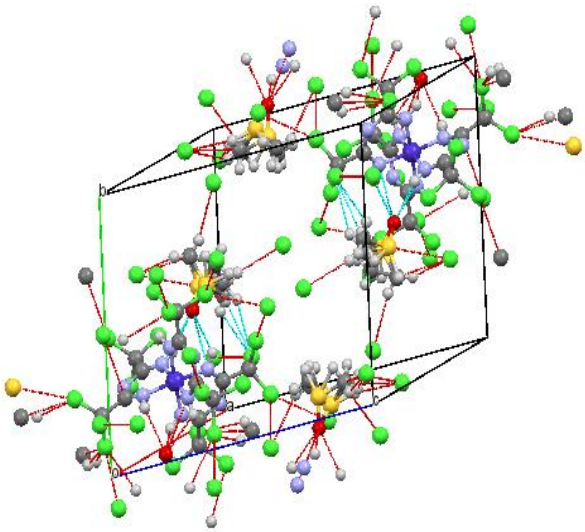


Figure 3. N—H···O hydrogen and C—H···Cl, C−Cl ··· Cl halogen interactions within the crystal lattice
Source: The figure was generated using Mercury 3.3

The dark red color on the Hirshfeld surface (Figure 5a) indicates the strength of N—H···O hydrogen bonds and C—H···Cl (Figure 5b) halogen bonds (Dasna *et al*., 2023). The light red color in Figure 5c indicates that C−Cl ··· Cl halogen bonds are weak.

Table 3. The percentage contribution of the interatomic interaction to the Hirshfeld surface in intermolecular interactions

Intermolecular interaction	Percentage Contribution
H···H	1.1
O···H/H···O	5.6
Cl···S/S···Cl	1.2
N···Cl/Cl···N	2
C···Cl/Cl···C	1.8
H···Cl/Cl···H	47.8
N···H/H···N	3.9
Cl···Cl	38.1
Cl···O/O···Cl	0.9

In the Hirshfeld surface analysis, regions with close intermolecular interactions are shown in red, regions with long-distant interactions are shown in blue and the intermediate regions are represented in white. Thus, the percentage contribution of the atomic interaction to the Hirshfeld surface characterized the magnitude of the intermolecular interaction region, rather than just their proximity. It should be noted that dark red indicates strong interactions, light red represents weak interactions and blue indicates the absence of interactions.

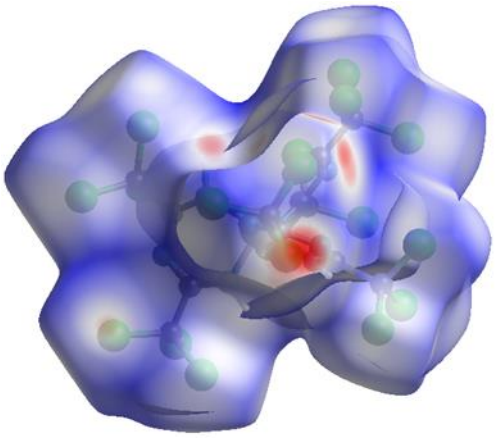


Figure 4. The three-dimensional Hirshfeld surface of the obtained compound with d_{norm} values in the range from $0{,}4616A^0$ to $1{,}3136A^0$

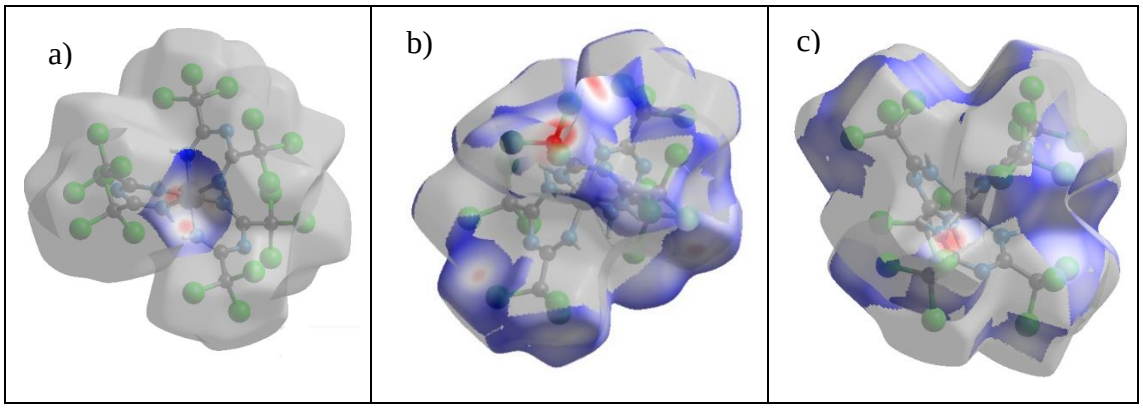


Figure 5. Hirshfeld surface: (a) H···O, (b) Cl···H, (c) Cl···Cl

The sharp peak shown in Figure 6a indicates the presence of a relatively strong H···O interaction. The presence of a peak in Figure 6b suggests the existence of H···Cl interaction. The peak shown in Figure 6c indicates the presence of a Cl···C halogen bond.

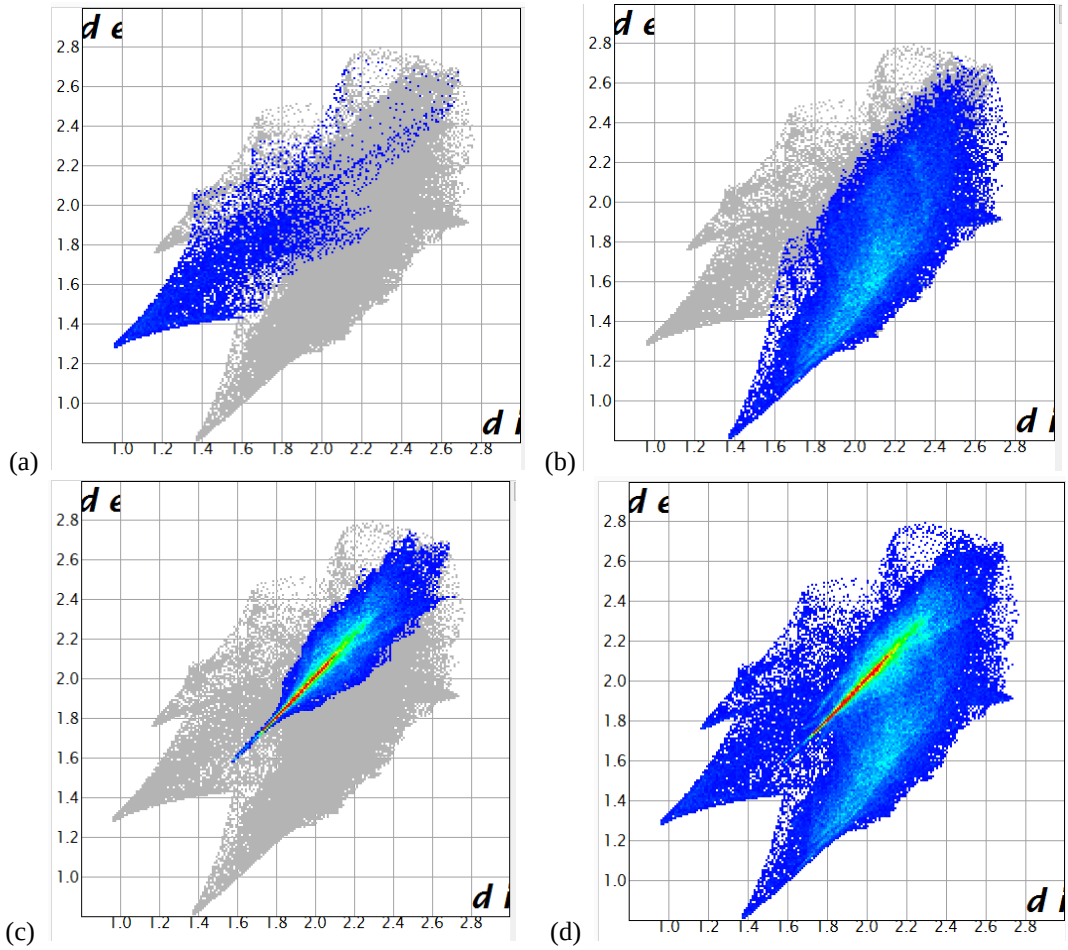


Figure 6. Fingerprint of intermolecular interactions: (a) H···O, (b) Cl···H, (c) Cl···Cl, (d) all interactions

3.3. Intermolecular interaction energies

The intermolecular interaction energy between two molecules is calculated as follows.

$$E_{tot} = k_{ele}E_{ele} + k_{pol}E_{pol} + k_{disp}E_{disp} + k_{rep}E_{rep}$$

$E_{elek} -$ represents the energy of the intermolecular electrostatic interaction, $E_{pol} -$ represents the energy of the intermolecular polar interactions, $E_{disp} -$ corresponds to the energy of the intermolecular dispersion interaction, $E_{rep} -$ indicates the energy of the exchange-repulsion and k values are the scalling factors for each energy contribution. Figure 7 illustrates the interaction energies computed using the HF/3-21G model within the Crystal Explorer software.

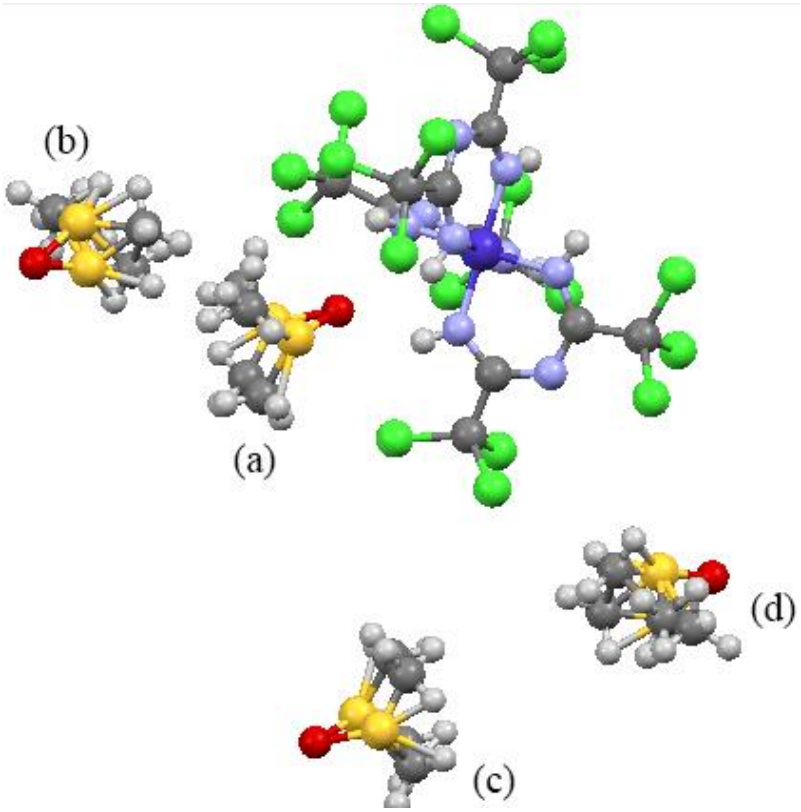


Figure 7. Interaction energies and distances (R) between the cobalt complex in the crystal and DMSO molecules in different orientations relative to the complex: (a) $-83.5\ kJ/mol$ $(5.3A^0)$; (b) $-10.1\ kJ/mol$ $(8.74A^0)$; (c)$-5.8\ kJ/mol$ $(9.25A^0)$; (d)$-17.2\ kJ/mol$ $(7.69A^0)$

The calculated interaction energies with all neighboring molecules of a selected arbitrary molecule (Figure 8, carbon atoms in black) are presented below (Table 4, Crystal Explorer, HF/3-21G model). The carbon atoms of the selected molecule are colored black, while the other molecules are colored in distinct shades. The energy values in the table correspond to the total intermolecular interaction energy between the selected molecule and the molecule of the corresponding color. As observed, the interaction energy decreases with the increasing intermolecular distance. Furthermore, the interaction energy between the selected cobalt complex and its nearest DMSO molecule is

approximately 2 times smaller than the interaction energy with its closest neighboring cobalt complex. This is a result of the H ⋯ O hydrogen bond in this crystal being weaker than the H ⋯ Cl halogen bond.

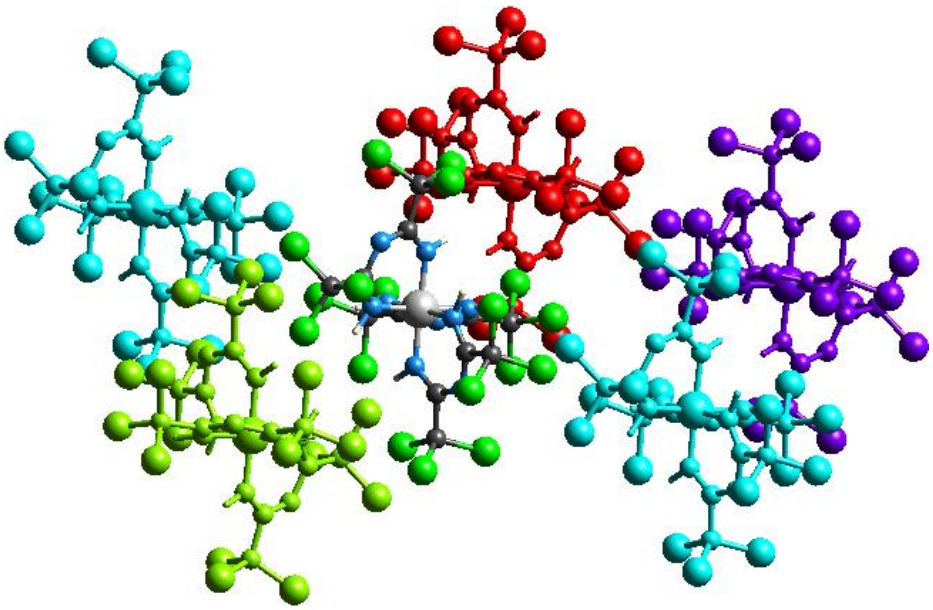


Figure 8. The molecules surrounding the selected molecule (with carbon atoms depicted in black) are represented in different colors

Table 4. Figure 8 presents the interaction energies (kJ/mol) between the surrounding colored molecules and the selected molecule, calculated using the HF/3-21G model within the Crystal Explorer software

	N	Sym.ope	R	Electron density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-x, -y, -z	9.30	HF/3-21G	-18.4	-3.2	-63.5	43.0	-43.1
	1	-x, -y, -z	10.23	HF/3-21G	-6.9	0.0	-32.3	20.1	-19.8
	2	x, y, z	10.17	HF/3-21G	-5.6	0.0	-29.9	17.6	-18.3
	1	-x. -y, -z	12.35	HF/3-21G	-1.8	0.0	-6.5	2.7	-5.4

R refers to the distance between the centers of two molecules (Å). It should be noted that the center of a molecule refers not to its center of mass, but to the average position of its atomic coordinates.

3.4. Antimicrobial activity

A correlation between molecular structure and antimicrobial activity is essential to understanding the observed biological effects. In the studied compounds, molecular geometry such as planar ligand arrangements can enhance interactions with microbial DNA through π–π stacking or intercalation, potentially disrupting replication or transcription processes (Lipinski *et al.*, 2001). Furthermore, halogen bonding interactions (e.g., Cl⋯Cl) may influence crystal packing, which in turn affects solubility, stability, and membrane permeability (Cavallo *et al.*, 2016). Efficient molecular packing can lead to improved bioavailability, while unfavorable arrangements may hinder cellular uptake. The antimicrobial properties of Tris-(2,4-bis(trichloromethyl)-1,3,5-triazapentadienato)-Co(III) complexes have been investigated against various pathogenic strains, including Gram-positive bacteria (*Bacillus mesentericus BDU-51 B. subtilis BDU-50 and*

Staphylococcus aureus BDU-23), Gram-negative bacteria (*Acinetobacter baumannii BDU-32, Escherichia coli BDU-12, Klebsiella pneumonia BDU-44 and Pseudomonas aeroginosa BDU-49*), as well as *Candida* species yeasts (*C. albicans BDU Mİ-44, C. guilliermondii BDU-217* and *C. tropicalis BDU LK-30*) using the agar diffusion method (Israilova *et al*., 2022). The fungal and bacterial cultures were obtained from the culture collection of Baku State University. A 0.3% solution of the compound in dichloromethane was used to test its effect on microbes. To compare antimicrobial activity, gentamicin, which inhibits the growth of both gram-positive and gram-negative bacteria, was used as a control. All experiments were conducted in four replicate, and the data were statistically analyzed.

All test cultures were exhibited sensitivity to the investigated substance. The sensitivity of Gram-negative bacteria to the substance was similar and the inhibitory zone of the substance against the bacteria ranged between 23-25 mm (Table 5). Among the Gram-positive bacteria, *Staphylococcus aureus* demonstrated higher sensitivity to the compound compared to bacteria of the *Bacillus genus*. Specifically, the inhibitory effect of the compound against *S. aureu*s was 1.6 and 1.4 times greater than its effect on *Bacillus mezentericus* and *Bacillus subtilis*, respectively.

The yeast strains did not show significant variation in their sensitivity to the compound; however, its inhibitory effect against *Candida albicans* was 1.2 and 1.3 times greater than that observed for *Candida guilliermondii* and *Candida tropicalis*, respectively.

It should be emphasized that the compound exhibited its highest antimicrobial activity against *Staphylococcus aureus*. The antimicrobial activity against this bacterium was 1.7-1.9 times greater than that observed against Gram-negative bacteria, 1.8-2.0 times greater than against the Gram-positive *Bacillus mesentericus* and *B. subtilis* and 2.0-2.3 times greater than the activity observed against yeast fungi (Table 5). Antimicrobial activity against *Staphylococcus aureus* was 1.3 times greater compared to the control (gentaicin). Therefore, the tris-(2,4-bis(trichloromethyl)-1,3,5-triazapentadienato)-Co(III) complexes exhibited highest antibacterial activity specifically against *Staphylococcus aureus* and may be utilized in combating this bacterium.

Table 5. Antimicrobial activity of tris-(2,4-bis(trichloromethyl)-1,3,5-triazapentadienato)-Co(III) complexes

Test Cultures		Diameter of inhibition zone (mm), M ± m	
		Co (III) complexes	Control (Gentamicin)
Gram negative bacteria	*Acinetobacter baumannii*	25.0 ± 0.8	20.0±0.4
	Escherichia coli	23.0 ± 0.8	18.0±0.5
	Klebsiella pneumoniae	23.0 ± 0.8	20.0±0.3
	Pseudomonas aeruginosa	24.0 ± 0.8	19.0±0.6
Gram positive bacteria	*Bacillus mesentericus*	21.0 ± 0.7	24.0±0.7
	Bacillus subtilis	24.0 ± 0.8	26.0±0.5
	Staphylococcus aureus	43.0 ± 1.6	32.0±0.8
Fungi	*Candida albicans*	25.0 ± 0.8	-
	Candida guilliermondii	21.0 ± 0.7	-
	Candida tropicalis	19.0 ± 0.5	-

4. Conclusion

Hirshfeld surface analysis revealed that strong N—H···O hydrogen bonds, C—H···Cl halogen bonds and weak C−Cl··· Cl halogen bonds contribute significantly to the formation of the crystal structure. Furthermore, the defining torsion angles of the molecule conformation have been calculated. The intermolecular interaction energies have also been evaluated.

Tris-(2,4-bis(trichloromethyl)-1,3,5-triazapentadienato)-Co(III) complexes possess notable antimicrobial properties, with the highest efficacy observed against *Staphylococcus aureus.* Compared to other tested microorganisms, the compound showed significantly greater inhibitory effects. These results suggest that the Tris-(2,4-bis(trichloromethyl)-1,3,5-triazapentadienato)-Co(III) complexes hold strong potential as targeted antimicrobial agents, particularly for addressing infections caused by S. aureus.

Author Contributions

Conceptualization, N.Q.S. and Kh.G.G.; software, N.E.A. and N.Q.S.; writing - original draft preparation, N.Q.S, Kh.G.G, N.E.A., G.T.; writing - review and editing, N.Q.S, N.E.A., N.R.Z., R.N.G.; isualization A.E.N., G.A.M., K.A.G.; project administration, N.Q.S., Kh.G.G., T.M.I., S.Q.A. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement

Original data supporting the findings of this study are available. These data are available upon request from the corresponding author.

Conflicts of Interest

The authors declare no conflict of interest.

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