SYNTHESIS, CRYSTAL STRUCTURE OF TRIS

(1,10-PHENANTHROLINE)NICKEL(II) NITRATE - 3,5-DICHLORO-2-HYDROXYBENZOIC ACID SOLVATE

A.Kh. Ruzmetov,
A.B. Ibragimov,
Institute of General and Inorganic Chemistry,

M.B. Djiemuratov,
National university of Uzbekistan

Annotation.

Mixed-ligand Ni(II) complexes based on heterocyclic N-donor ligands and halogenated hydroxybenzoic acids attract considerable interest due to their structural variability, intramolecular hydrogen bonding networks, and potential biological activities. A detailed investigation of their coordination modes, supramolecular architecture, and physicochemical properties is crucial for understanding structure-property relationships in crystal engineering. This work aims to synthesize a new mixed-ligand Ni(II) coordination compound containing 1,10-phenanthroline and 3,5-dichloro-2-hydroxybenzoic acid ligands, and to thoroughly investigate its structural, crystallographic, spectroscopic, and intermolecular interaction characteristics. The SC-XRD analysis confirmed the formation of a monometallic complex constituting a tris(1,10-phenanthroline) nickel(II) cation, a nitrate anion, and four uncoordinated 3,5-dichloro-2-hydroxybenzoic acid solvate molecules per asymmetric unit. IR spectroscopy verified the non-coordinated nature of the carboxylic acid groups and charge-balancing nitrate. UV-Vis spectra confirmed the characteristic electronic transitions of the Ni(II) d-d orbitals and ligand-to-metal charge transfer.

Key words:

Ni(II) complex, 1,10-phenanthroline, 3,5-dichloro-2-hydroxybenzoic acid, IR spectroscopy, X-ray diffraction.

Introduction.

In recent years, the field of crystal engineering and supramolecular chemistry has witnessed significant growth, driven by the design and synthesis of functional coordination compounds. Among transition metal ions, nickel(II) complexes have attracted sustained academic and industrial interest due to their rich structural diversity, fascinating magnetic and optical behaviors, and notable biochemical profiles. The structural architecture of Ni(II) complexes depends heavily on the choice of primary and auxiliary ligands, which dictate the geometry around the metal center and direct the overall supramolecular packing. A prominent strategy in constructing stable and functional materials is the utilization of mixed-ligand systems. Heterocyclic N-donor chelating ligands, such as 1,10-phenanthroline are classic and powerful building blocks in coordination chemistry. Due to their rigid, planar aromatic structure, they exhibit high coordination affinity toward transition metals and inherently promote π- π stacking interactions. These non-covalent forces play a crucial role in self-assembly processes, often leading to well-ordered molecular crystals[1].

Concurrently, substituted aromatic carboxylic acids, particularly halogenated hydroxybenzoic acids like 3,5-dichloro-2-hydroxybenzoic acid, serve as versatile components in crystal design. These molecules possess multiple functional groups capable of acting simultaneously as hydrogen bond donors and acceptors. Interestingly, in many supramolecular architectures, such aromatic acids do not directly coordinate to the metal ion. Instead, they occupy interstitial positions within the crystal lattice as solvate molecules or co-crystal formers. Through extensive O-H···O and C-H···O hydrogen bonding networks, as well as H···Cl interactions, they effectively stabilize the ionic coordination spheres, creating unique multi-component crystal systems.

Despite numerous reports on nickel complexes with salicylic acid derivatives, systematic studies exploring the co-crystallization of tris(1,10-phenanthroline)nickel(II) cations[2] with uncoordinated halogenated hydroxybenzoic acids remain limited[3]. Investigating the exact balance between coordination bonds within the inner sphere and non-covalent forces in the outer sphere is vital for predicting structure-property relationships.

Experimental.

The mixed-ligand complex of Ni(II) based on 1,10-phenanthroline and 3,5-dichloro-2-hydroxybenzoic acid (hereafter referred to as Compound 1) was synthesized by the solution method. Initially, 1.0 mmol of $Ni(NO_3)_2$ was dissolved in 10 mL of distilled water to obtain a clear solution. In a separate vessel, 3.0 mmol of 1,10-phenanthroline was dissolved in 20 mL of ethanol. concurrently, 4.0 mmol of 3,5-dichloro-2-hydroxybenzoic acid was dissolved in 25 mL of ethanol. The 1,10-phenanthroline ligand solution was then introduced into the Ni(II) solution, followed by the dropwise addition of the chloro-ligand solution, which resulted in a distinct color change of the mixture. The reaction mixture was continuously stirred using a magnetic stirrer. To ensure the initial coordination interaction and complete the complex-formation process, the system was maintained

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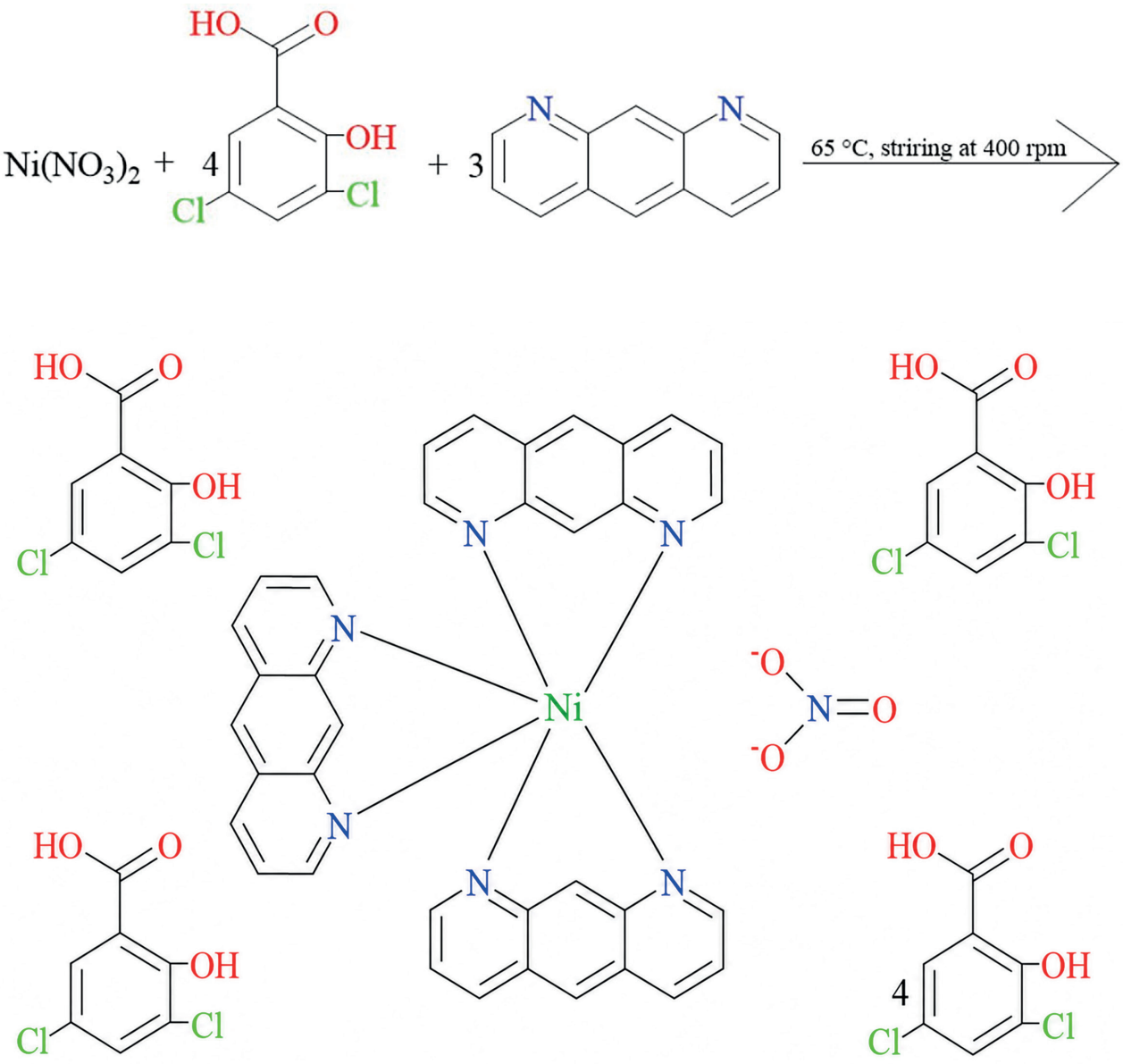
at 65°C and stirred at 400 rpm for 2 hours. After completion of the reaction, the resulting solution was transferred to an evaporation chamber and left to evaporate slowly at room temperature. Gradual evaporation of the solvent yielded single crystals of the coordination compound, which were subsequently isolated by filtration and dried.



Results and discussion.

The crystal structure of the synthesized compound was successfully determined by single-crystal X-ray diffraction. Crystallographic analysis reveals that the complex crystallizes in the triclinic crystal system under the centrosymmetric P-1 space group. This spatial arrangement indicates that the complex molecules are organized in inversion-related pairs within the crystal lattice, exhibiting a well-defined close-packed symmetry. The distinct deviation of all three unit cell angles from 90° (α=80.336(2)°,β=89.856(2)°, γ=67.787(2)°) further substantiates the triclinic nature of the crystal. The structural model was refined to a final reliability factor of 7.25%, demonstrating a high level of precision and structural fidelity. Additionally, the maximum and minimum residual electron density peaks in the final difference Fourier synthesis map are remarkably close to zero, ranging from -0.60 to 1.86 [e/Å^3]. This negligible residual density scientifically confirms the absence of any unassigned atomic positions, disorder, or systematic errors, thereby validating the accuracy of the solved crystal structure.

Table 1.
Crystal Data and Details of the Structure Determination for Compound 1

Crystal Data	
Formula	$C_{64}H_{47.5}Cl_8N_{7.5}NiO_{20.5}$
Formula Weight	1591.90
Crystal System	triclinic
Space group	P-1 (No.2)
a, b, c [Å]	13.0453(3) 15.7907(3) 18.4766(4)
alpha, beta, gamma [°]	80.336(2) 89.856(2) 67.787(2)
V [Å^3]	3465.85(14)
Z	2
D(calc) [g/cm^3]	1.456
Mu(CuKα) [/mm]	3.924
F(000)	1544
Crystal Size [mm]	0.12 x 0.14 x 0.15
Data Collection	
Temperature (K)	293
Radiation [Å]	CuKα 1.54184
Theta Min-Max [°]	2.4, 68.5
Dataset	-15: 15; -19: 18; -22: 21
Tot., Uniq. Data, R(int)	37314, 12590, 0.054
Observed Data [I > 0.0 sigma(I)]	8626
Refinement	
Nref, Npar	12590, 888
R, wR2, S	0.0725, 0.2438, 1.07
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Å^3]	-0.60, 1.86

IR spectroscopy.

The functional groups and the bonding situation of the constituent species were probed by FT-IR spectroscopy in the 4000–400 cm^{-1} region (Fig. 1). A broad, medium-intensity envelope centred at 3397 cm^{-1} is assigned to the ν(O–H) stretching of the hydrogen-bonded hydroxyl and carboxylic-acid groups of the 3,5-dichloro-2-hydroxybenzoic acid molecules, its breadth being diagnostic of extensive O–H···O hydrogen bonding [9, 10]. Weak absorptions near 3072 cm^{-1}

correspond to aromatic ν(C–H) modes of the phenanthroline and benzene rings. The strong band at 1667 cm^{-1} is attributed to the ν(C=O) stretching of a protonated carboxyl group; its position in the 1760–1660 cm^{-1} region characteristic of free –COOH (rather than the $\nu^{as}(COO^-)/\nu^{s}(COO^-)$ pair near 1550/1400 cm^{-1} expected for an ionised, metal-bound carboxylate) confirms that the acid remains neutral and uncoordinated, in full agreement with the single-crystal model[1,2].

The pair of sharp bands at 1588 and 1517 cm^{-1}, together with the intense absorption at 1426 cm^{-1}, arise from the aromatic ν(C=C)/ν(C=N) ring-stretching vibrations of the coordinated 1,10-phenanthroline skeleton[3]. The antisymmetric stretch of the ionic nitrate anion, expected near 1380 cm^{-1}, is overlapped in this study by the much stronger ligand ring modes; consistent with a non-coordinated, charge-balancing NO^{3-}. Bands in the 1330–1045 cm^{-1} interval (1332, 1281, 1221, 1185, 1145, 1045 cm^{-1}) are assigned to ν(C–O), in-plane δ(O–H) and in-plane δ(C–H) deformations. The series of strong absorptions below 900 cm^{-1} (869, 847, 795, 746, 725, 691 cm^{-1}) correspond to out-of-plane γ(C–H) bending of the phenanthroline rings and to C–Cl-related vibrations, while the low-frequency features at 559, 502, 447 and 422 cm^{-1} include ring-deformation and ν(Ni–N) skeletal modes [9, 10].

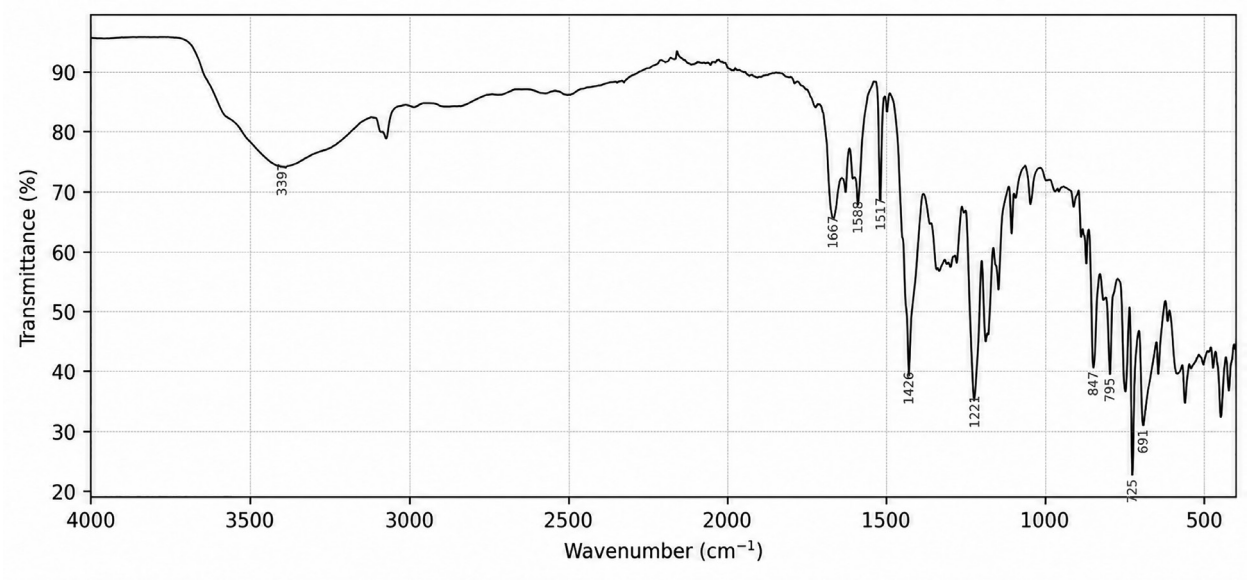


Fig. 1. FT-IR spectrum of Compound 1 in the 4000–400 cm^{-1} range.

UV–Vis spectroscopy.

The electronic absorption spectrum was recorded over the 200–1100 nm range (Fig. 2). The ultraviolet region is dominated by very intense bands below 400 nm, with maxima near 300 and 326 nm (absorbance off-scale, A > 3) and additional features at 203, 214, 243 and 275 nm. These high-intensity transitions are assigned to spin-allowed intraligand π→π* and n→π* excitations of the aromatic systems of 1,10-phenanthroline and of the 3,5-dichloro-2-hydroxybenzoic acid, with a possible contribution from ligand-to-metal charge transfer[4,5].

In the visible–near-infrared region three weak features, consistent with a d^8 Ni(II) [6]ion in a pseudo-octahedral N^6 ligand field, are resolved. A weak band at 393 nm is assigned to the $^3A_2g \rightarrow {}^3T_1g(P)$ transition, a broad low-intensity band centred at ≈723 nm to the $^3A_2g \rightarrow {}^3T_1g(F)$ transition, and the monotonic rise of absorbance towards the 1100 nm limit marks the onset of the lowest-energy $^3A_2g \rightarrow {}^3T_2g$ transition, whose maximum lies beyond the measured range. The energies and the low molar intensity of these three spin-allowed bands are fully consistent with octahedral nickel(II) and corroborate the six-coordinate N^6 geometry established by X-ray diffraction[7].

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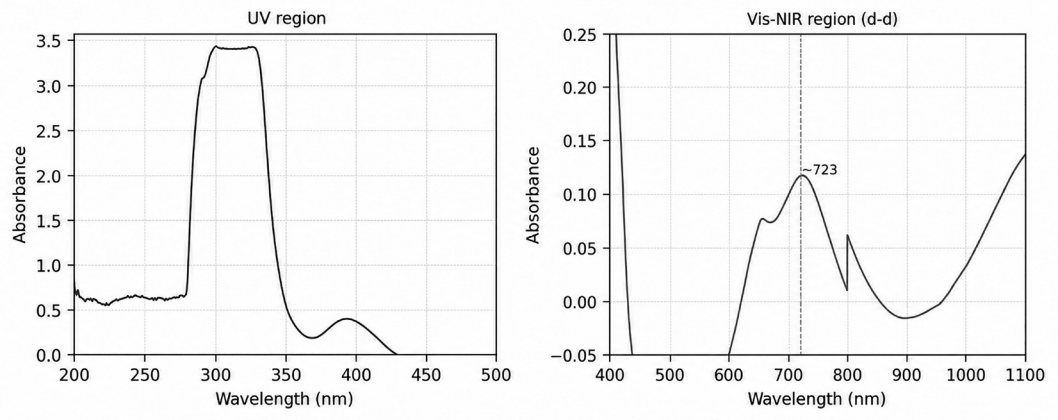

Fig. 2. UV–Vis absorption spectrum of Compound 1: UV region (left) and Vis–NIR d–d region (right).

Powder X-ray diffraction.

The bulk crystallinity and phase purity of the product were examined by powder X-ray diffraction (PXRD, CuKα) over 3–90° in 2θ (Fig. 3). The pattern displays a set of sharp reflections in the low-angle 3–15° region superimposed on a broad amorphous background centred near 22°. The positions of the principal low-angle reflections agree closely with the interplanar spacings calculated from the triclinic unit cell determined by single-crystal diffraction (Table 2), confirming that the bulk powder corresponds to the same crystalline phase as the single crystal selected for structure solution[1,2,3].

Table 2.

Comparison of observed PXRD reflections with values calculated from the single-crystal triclinic cell.

hkl	2θ (°)	2θ calc. (°)	d (Å)
0 0 1	4.86	4.86	18.18
0 1 0	6.14	6.15	14.39
0 1 1	7.15	7.12	12.36
1 0 1	9.06	9.07	9.76
0 0 2	9.76	9.73	9.06

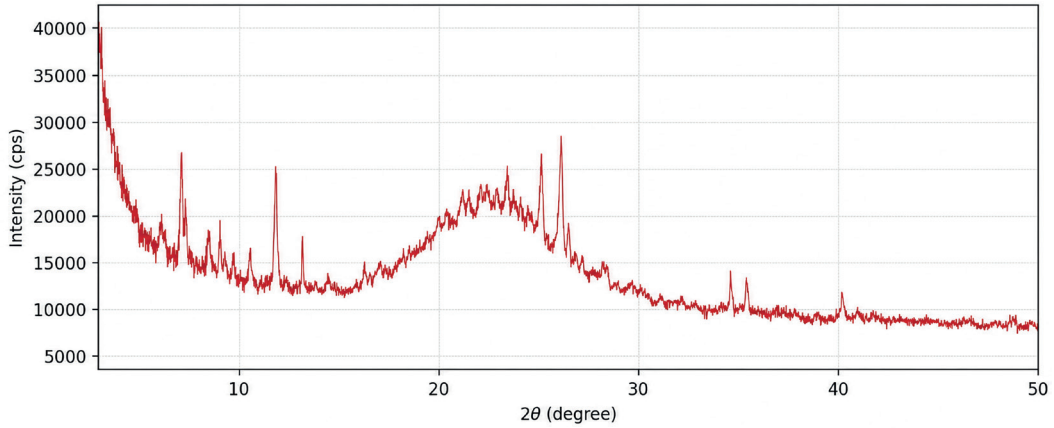

Fig. 3. Experimental PXRD pattern of Compound 1.

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X-ray fluorescence.

The elemental composition of the bulk sample was verified by energy-dispersive X-ray fluorescence (XRF; 50 kV, 6 μA, Ag source, air, 59.9 s acquisition). The spectrum (Fig. 4) shows only two element-specific emission groups above the detection threshold: the nickel K-lines (Ni Kα at ≈7.48 keV and Ni Kβ at ≈8.26 keV) and the chlorine Kα line at ≈2.62 keV. The exclusive presence of Ni and Cl, with no signals from other transition metals, confirms that nickel is the single metallic centre and that chlorine originates from the dichloro substituents of the hydroxybenzoic-acid component. This elemental fingerprint is fully consistent with the molecular formula $C_{64}H_{47.5}Cl_8N_{7.5}NiO_{20.5}$ derived from the single-crystal analysis.

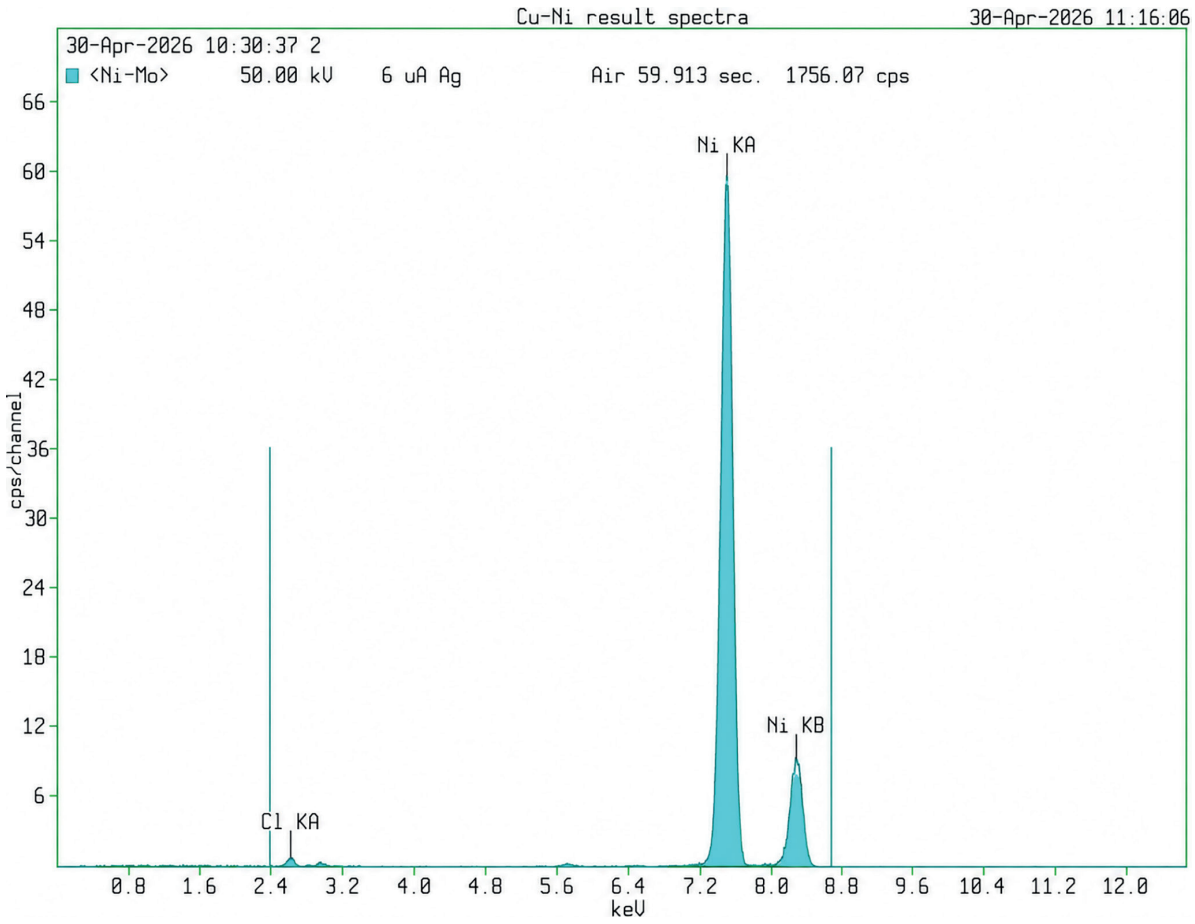

Fig. 4. Energy-dispersive XRF spectrum of Compound 1 showing Ni Kα/Kβ and Cl Kα emission lines.

Conclusion.

A new multi-component crystal built from a tris(1,10-phenanthroline)nickel(II) dication, a nitrate counter-anion and uncoordinated 3,5-dichloro-2-hydroxybenzoic acid solvate molecules was obtained and characterised. Single-crystal X-ray diffraction established a triclinic, P-1 structure with a distorted octahedral N^6 coordination sphere. The spectroscopic data form a self-consistent picture: IR spectroscopy demonstrates the protonated, non-coordinated state of the carboxylic-acid groups and the ionic character of the nitrate; the UV-Vis d-d manifold (≈393, 723 nm) confirms octahedral Ni(II). PXRD verifies that the bulk material matches the single-crystal phase; and XRF independently confirms Ni and Cl as the only detectable heavy elements[4,5]. Together these results substantiate the balance between inner-sphere coordination bonds and outer-sphere O–H···O hydrogen bonding and π–π interactions that stabilises this supramolecular assembly[6,7].

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