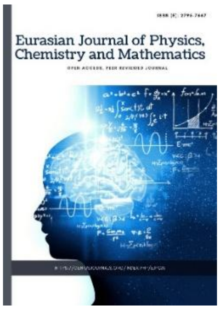


Synthesis, Structural and Spectroscopic Characterization of $[MnCl_4](L^1{\cdot}H)_2$ Complex Derived from Manganese(II) Chloride and Novocaine Hydrochloride

F.Q.Matmurodova[1]
Urgench State University named after Abu Rayhan Beruni
220100, 14 Hamid Alimjan Street Urgench, Khorezm Region, Uzbekistan[1,2] , Teacher at Urgench State University[1]
matmuradovaf.@mail.ru

A.K.Masharipova[2]
Urgench State University named after Abu Rayhan Beruni
220100, 14 Hamid Alimjan Street Urgench, Khorezm Region, Uzbekistan[1,2] , Urgench State University assistant[2]

D.S.Xaitboyev[3]
Head of the Educational Process Organization Department
Tashkent Medical Academy, Urgench Branch
28 Al-Khwarizmi Street, Urgench city, Khorezm region, Uzbekistan[3]

ABSTRACT

This study reports the synthesis and characterization of a manganese(II) complex with protonated novocaine. The complex was prepared by reacting $MnCl_2$ (0.005 mol) and novocaine hydrochloride (0.01 mol) in aqueous solution under magnetic stirring at 800 rpm for 1.5 hours, followed by slow evaporation for 21 days, yielding crystalline $[MnCl_4](L^1{\cdot}H)_2$. X-ray diffraction revealed a monoclinic system (I2/a) with Mn^{2+} coordinated by four chloride ions in a distorted tetrahedral geometry. IR spectroscopy confirmed N–H, C–H, C=O, and Mn–Cl vibrational modes, while UV-Vis analysis showed d–d transitions (λ_max = 508 nm) and ligand-centered π→π*, n→π* absorptions. SEM-EDS mapping validated elemental composition and coordination effects on ligand microstructure. Thermal analysis showed two main decomposition stages between 183–215 °C and 245–424 °C, with mass loss indicating improved thermal stability. XRD patterns and diffractograms confirmed the individuality of the complex compared to the free ligand. The reproducible spectroscopic, crystallographic, and morphological results suggest the complex's potential for further studies in coordination chemistry and material science.

Keywords: Manganese(II) complex, Novocaine hydrochloride, X-ray crystallography, Infrared spectroscopy, UV-Vis spectroscopy, Thermal analysis, Coordination geometry, Microstructural analysis, SEM-EDS characterization, Ligand coordination effects

1. Introduction.

One of the modern directions in the field of coordination chemistry is the study of complexes formed by transition metals with biologically active compounds. In particular, organic molecules containing nitrogen and oxygen atoms can form stable structures as coordination complexes with metal ions. Procaine hydrochloride (commonly known as novocaine), which possesses local anesthetic properties, is of special interest due to its ester and amine functional groups, enabling it to act as a donor ligand. Such compounds effectively coordinate with transition metals, giving rise to diverse coordination complexes with unique physicochemical, structural, and spectral characteristics.

Manganese(II), which exhibits variable oxidation states, is of particular interest because of its vital role in biological systems such as antioxidant enzymes, oxidoreductases, and coenzymes. The Mn(II) ion often forms tetrahedral coordination geometries and readily interacts with chloride ions, resulting in stable complexes with intriguing spectroscopic properties. Especially, the formation of complexes involving Mn(II) ions, chloride anions, and protonated ligands significantly influences the structural stability of the resulting compound.

In recent years, Mn(II) complexes have gained attention not only from a theoretical perspective but also for their practical significance. Comprehensive studies of their X-ray crystallographic structures, electronic spectra, hydrogen bonding systems, microstructures, and thermal properties have opened new possibilities for the synthesis of functional materials. In particular, Mn(II) complexes involving protonated organic ligands are of great importance for understanding molecular-level interactions, spatial arrangement in the crystal lattice, and prediction of compound properties.

In this study, a novel Mn(II) complex with the formula $MnCl_4^{2-}$ was synthesized using manganese(II) chloride and procaine hydrochloride. Its crystal structure and physicochemical properties were investigated through various spectroscopic, diffractometric, and thermal analytical methods. X-ray structural analysis was used to determine the lattice parameters and to evaluate the nature of metal-ligand bonding. UV-Vis and IR spectra provided insights into electronic transitions and vibrational modes of the functional groups. SEM-EDS microanalysis confirmed the elemental composition of the complex and revealed the metal-ligand microstructural relationships. Thermal analysis allowed evaluation of the thermal stability and decomposition behavior of the complex. The findings of this research provide a scientific basis for a deeper understanding of the structural organization of Mn(II) complexes, ligand-ligand interactions, and phase arrangements in the crystalline state.

2. Experimental

2.1. Complex Synthesis

A solution of M(II) chloride (0.005 mol) was prepared in water. Novocaine hydrochloride (2.725 g, 0.01 mol) was dissolved in 20 mL of water. Both solutions were transferred into a heat-resistant beaker and stirred using a glass rod. The resulting clear solution was placed on a magnetic stirrer and stirred at 800 rpm for one and a half hours.

After stirring, the solution was removed from the magnetic stirrer and placed under a fume hood. The mouth of the container was loosely covered to allow slow evaporation of the solvent. After 21 days, crystals formed in the solution. The obtained crystals were separated, washed with ethanol, and dried in a vacuum desiccator.

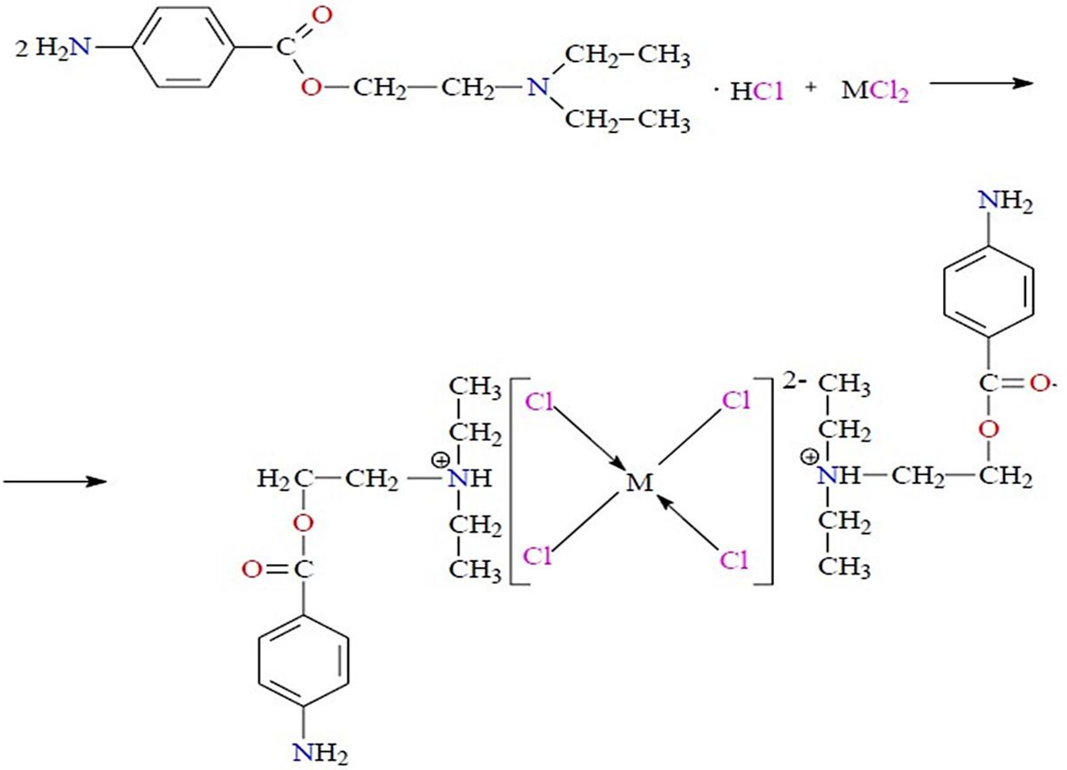


Figure 1. The complex compound with the composition $[MnCl_4](L^1{\cdot}H)_2$ synthesized from $MnCl_2$ and novocaine hydrochloride.

2.2. Characterization techniques.

Elemental analysis of C, H, N, S, and O in the $[MnCl_4](L^1{\cdot}H)_2$ complex was carried out using a FlashSmart (Thermo Fisher Scientific) analyzer. The instrument operates based on a modified Dumas combustion method, where the amounts of gases released during combustion are determined chromatographically. For the analysis of C, H, N, and S, 3–3.5 mg of the sample was sealed in aluminum foil capsules along with 4–5 mg of vanadium(V) oxide and combusted at 960 °C. Oxygen analysis was performed using 2.8–3.2 mg of sample in silver foil capsules at 1050 °C. All processes were conducted under oxygen (100 mL/min) and helium (140 mL/min) gas flows. The complex showed good solubility in water and ethanol, poor solubility in chloroform, and limited solubility in acetone.

3.Results and discussion

X-ray Structural Analysis. Single-crystal X-ray diffraction data for the $[MnCl_4](L^1{\cdot}H)_2$ complex were collected using a diffractometer with Cu Kα radiation (λ = 1.54184 Å). The crystal structure was solved and refined using the SHELX program implemented in OLEX2. The complex crystallizes in the monoclinic system, space group I2/a, with unit cell parameters a = 14.6608(3) Å, b = 14.8998(3) Å, c = 15.6942(4) Å, and β = 103.801(2)°. Full crystallographic refinement details are presented in Table 1.

Table 1. Crystal Data Table

Empirical formula	$C_{13}H_{21}Cl_2Mn_{0.5}N_2O_2$
Formula weight	335.69
Temperature/K	293(2)
Crystal system	Monoclinic
Space group	I2/a
a/Å	14.6608(3)
b/Å	14.8998(3)

c/Å	15.6942(4)
α/°	90
β/°	103.801(2)
γ/°	90
Volume/Å^3	3329.31(13)
Z	8
ρ_{calc}g/cm^3	1.339
μ/mm^{-1}	6.468
F(000)	1404.0
Crystal size/mm^3	0.18 × 0.15 × 0.14
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.298 to 142.816
Index ranges	$-17 \le h \le 16$, $-18 \le k \le 14$, $-19 \le l \le 19$
Reflections collected	8838
Independent reflections	3212 [R_{int} = 0.0275, R_{sigma} = 0.0333]
Data/restraints/parameters	3212/0/181
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0444, wR_2 = 0.1107
Final R indexes [all data]	R_1 = 0.0592, wR_2 = 0.1190
Largest diff. peak/hole / e Å^{-3}	0.39/-0.26

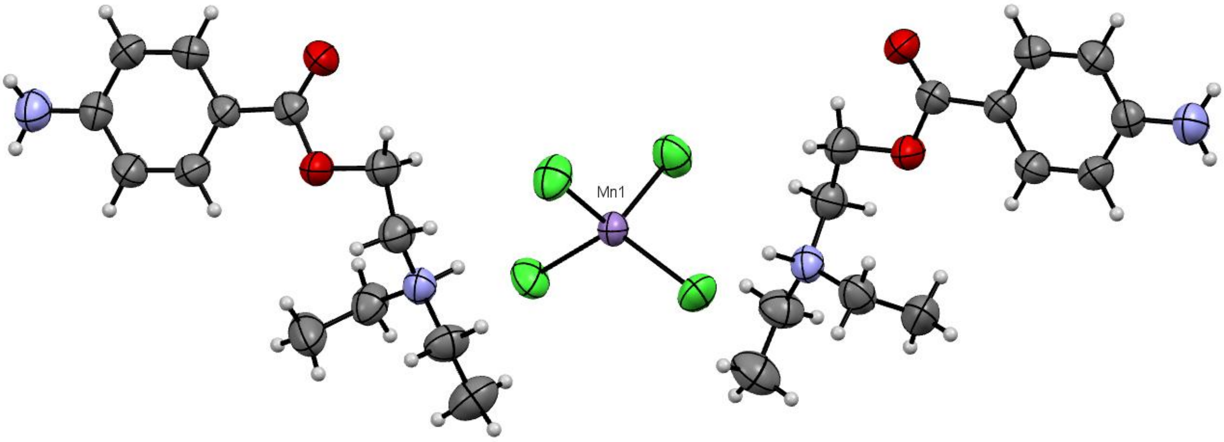


Figure 2. The bonding sequence of atoms in the $[MnCl_4](L^{1}\cdot H)_2$ complex.

The coordination compound with the composition $[MnCl_4](L^{1}\cdot H)_2$ was obtained from the reaction of manganese(II) chloride and novocaine hydrochloride. The main crystallographic data and structure refinement indicators are summarized in Table 1.

In the complex, the manganese ion is located at the center and is coordinated by four chloride ions. In this arrangement, the inner coordination sphere is formed by the $[MnCl_4]^{2-}$ anion, around which two positively charged protonated novocaine molecules are electrostatically associated (Figure 3).

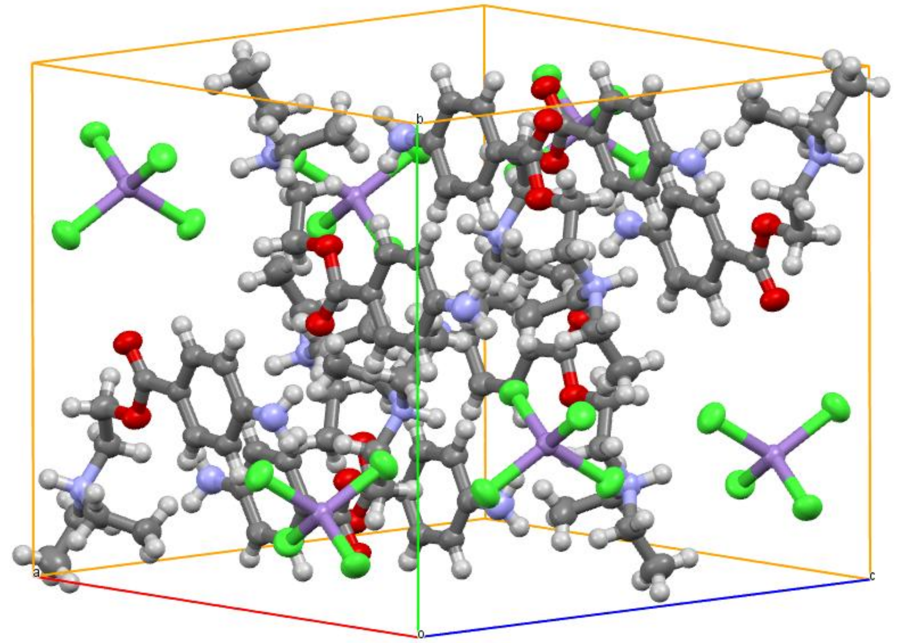


Figure 3. Crystal packing of the $[MnCl_4](L^1{\cdot}H)_2$ coordination compound.

UV-Vis Spectroscopic Analysis of the $[MnCl_4](L^1{\cdot}H)_2$ Complex

According to the UV-Vis spectroscopic analysis, an absorption band at λmax = 508 nm in the visible region corresponds to a d–d electronic transition of the Mn^{2+} ion, specifically a $^4T_1 \rightarrow {}^6A_1$ transition. This confirms that the Mn^{2+} ion is at the center of the coordination complex and is coordinated in a tetrahedral geometry. In addition, a band observed at λmax = 340 nm is attributed to $\pi \rightarrow \pi^*$ transitions in the aromatic ring of the ligand, while the band at λmax = 260 nm corresponds to $n \rightarrow \pi^*$ transitions of the carbonyl group (Figure 4).

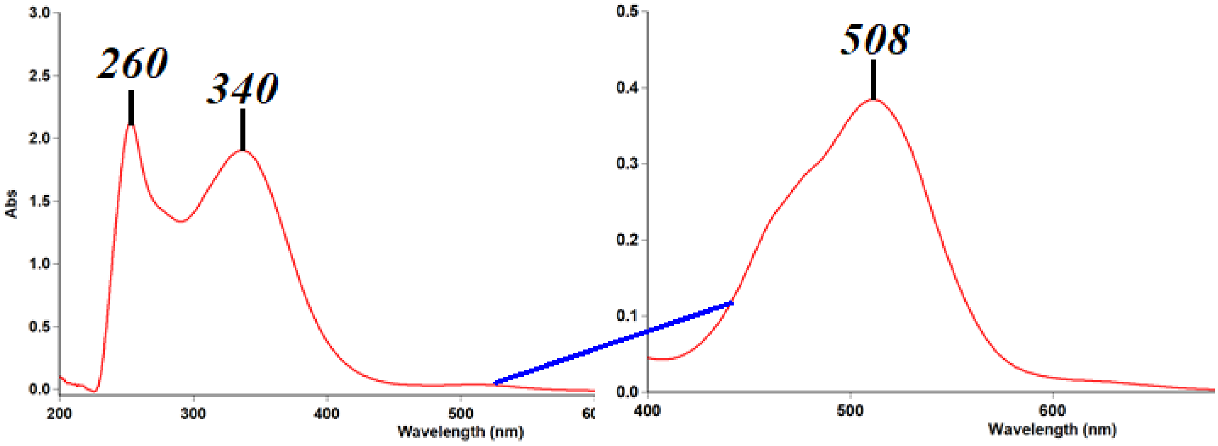


Figure 4. UV-Vis spectroscopic analysis of the $[MnCl_4](L^1{\cdot}H)_2$ complex.

IR Spectroscopic Analysis of the $[MnCl_4](L^1{\cdot}H)_2$ Complex

The IR spectroscopic analysis of the complex was recorded in the range of 400–4000 cm^{-1} (Figure 5). Absorption bands observed at 3193 cm^{-1} and 3107 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of the amine group in the ligand, respectively. The bands at 3082 cm^{-1} and 3055 cm^{-1} are assigned to the asymmetric and symmetric C–H stretching vibrations of the aromatic ring. At 1631 cm^{-1} and 1597 cm^{-1}, the asymmetric and symmetric stretching vibrations of the carbonyl group were observed. Vibrations of the ester C–O–C bond were detected at 1372 cm^{-1} and 1330 cm^{-1}. A characteristic band at 570 cm^{-1} corresponds to the Mn–Cl stretching vibrations, indicating the presence of the central $[MnCl_4]^{2-}$ ion coordinated with protonated novocaine ($L^1 \cdot H^+$) in the complex structure.

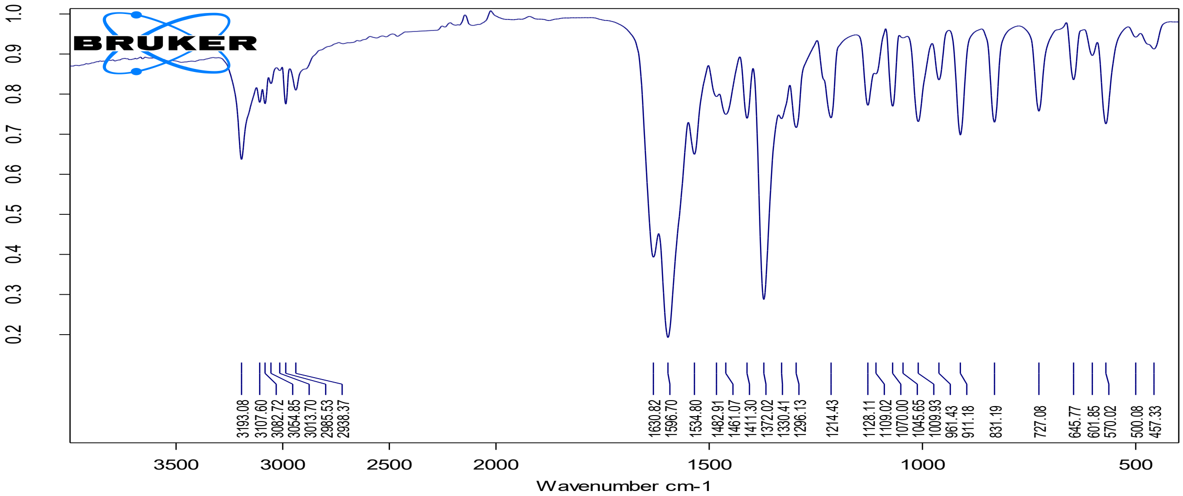
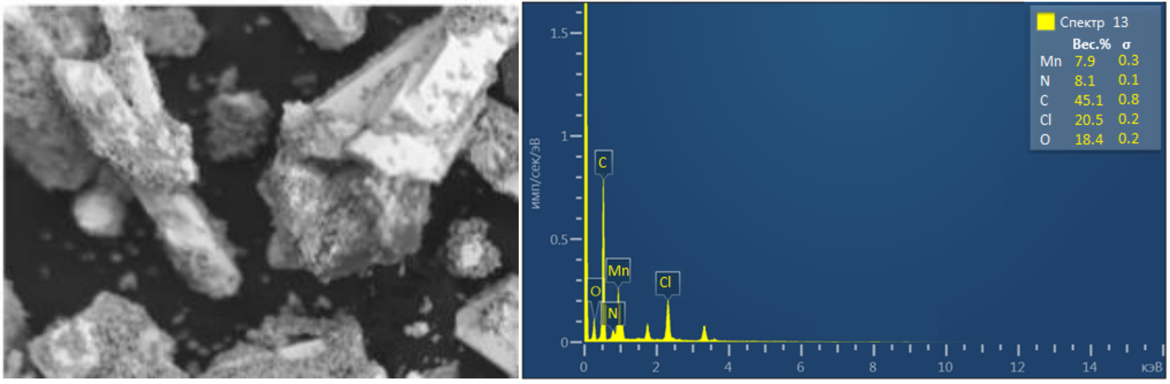


Figure 5. IR spectroscopic analysis of the $[MnCl_4](L^{1\cdot}H)_2$ complex.

SEM-EDS Analysis of the $[MnCl_4](L^{1\cdot}H)_2$ Complex

Determination of the elemental composition in substances using a scanning electron microscope (SEM) is widely applied in solving specific scientific and technological problems due to its high information content and the reliability of the results obtained.



	Вес.%	σ
Mn	7.9	0.3
N	8.1	0.1
C	45.1	0.8
Cl	20.5	0.2
O	18.4	0.2

Figure 6. Microstructure and EDS results of the $[MnCl_4](L^{1\cdot}H)_2$ complex

The amounts of carbon, oxygen, and metal elements in the resulting complex compounds were determined using the SEM-EDS method. Based on the obtained data, it can be concluded that the coordination of metal ions with the ligands leads to changes in the microstructure of the ligands. In particular, the appearance of multiple metal peaks is observed, which is confirmed by the EDS analysis (Figure 6).

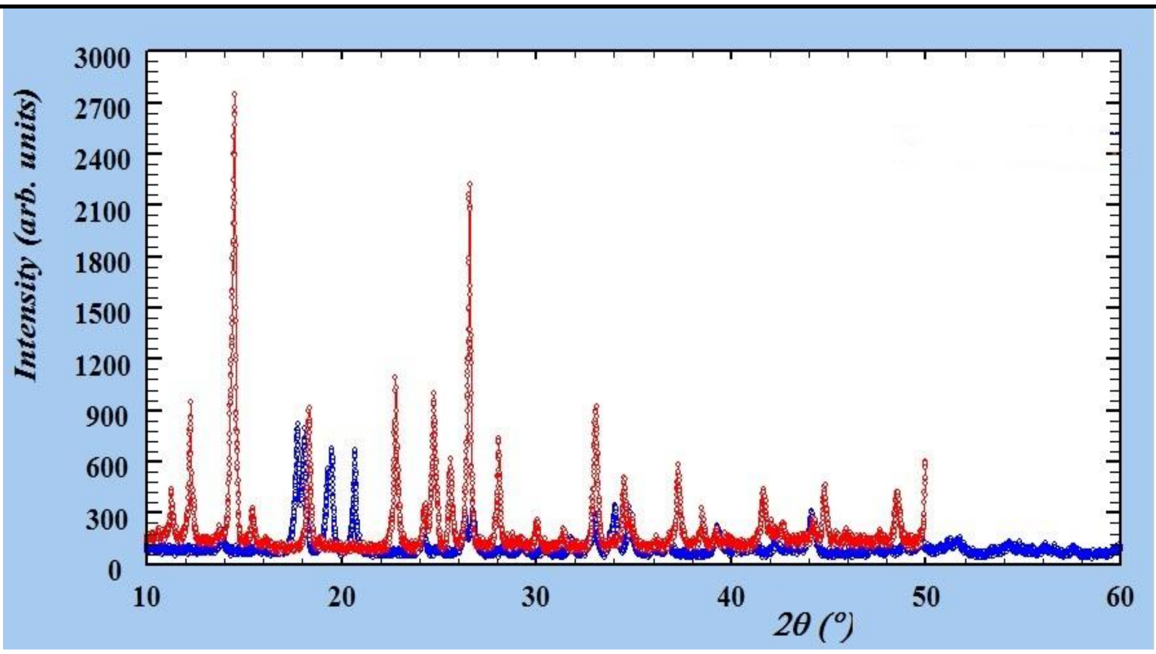


Figure 7. X-ray diffractogram of the $[MnCl_4](L^1{\cdot}H)_2$ complex (red) and the ligand (blue)

XRD Analysis of the $MnCl_{42}$ Complex

The X-ray diffractometric (XRD) analysis of the $MnCl_{42}$ complex revealed clear differences between the diffractograms of the free ligand and the resulting metal–ligand complex. The analysis results obtained from diffractogram calculations confirmed the individuality of the synthesized coordination compound. Based on the X-ray phase analysis data, it can be concluded that the obtained complexes possess a distinct crystal lattice, and the calculated values from the diffractograms once again verify the individual nature of the synthesized complex compounds.

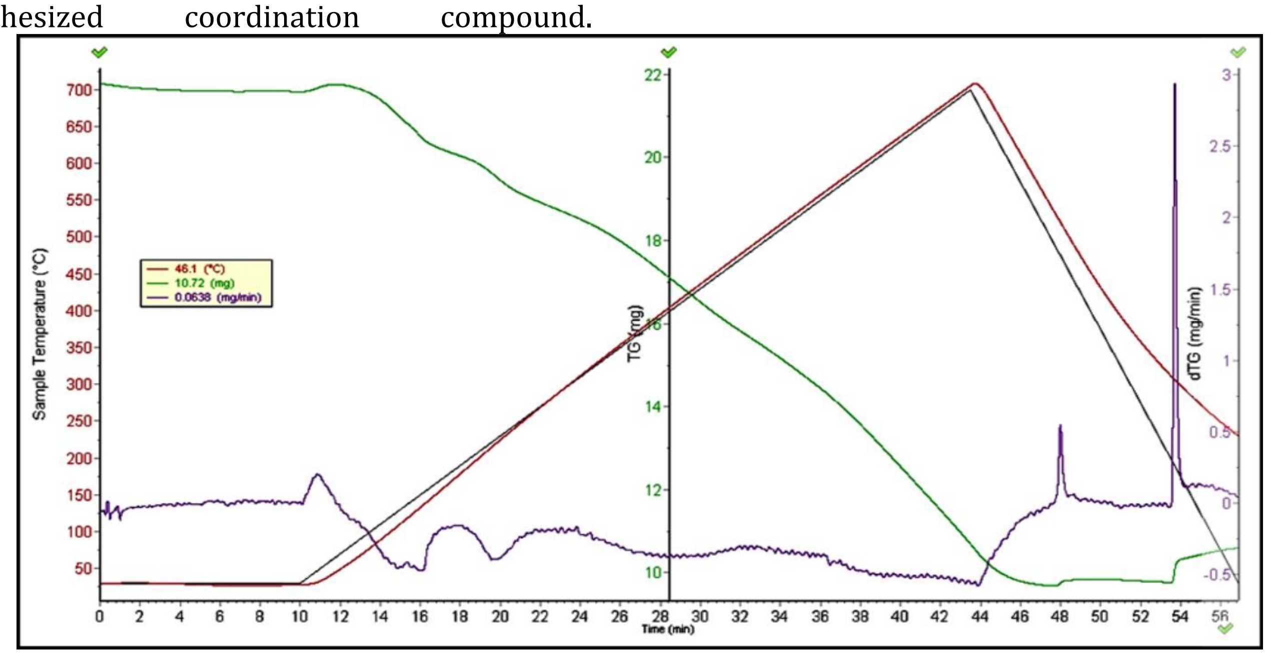


Figure 8. Thermal analysis of the $[MnCl_4](L^1H)_2$ complex

Thermal Analysis of the $MnCl_{42}$ Complex

The thermogravimetric profile (derivatogram) of the $MnCl_{42}$ complex consists of four distinct curves. Analysis of the differential thermogravimetric (DTG) curve shows that two main decomposition steps occur within specific temperature ranges. The first endothermic event is observed between 183–215 °C, and the second between 245–424 °C. The compound demonstrates relatively high thermal stability, as a gradual mass loss continues up to 473 °C.

The first decomposition stage is marked by a significant mass loss, accounting for 40.3% of the total mass. According to the analysis, after 473 °C, an additional mass loss of 49.9% occurs, after which the mass remains constant, indicating the formation of a stable residue.

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