Synthesis and Characterization of MMSC and L-Thioproline Ligands and Their Mn(II), Co(II), and Ni(II) Complexes: A Comparative Study

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Abstract

This study presents the synthesis, structural elucidation, and comprehensive characterization of novel transition metal complexes formed through the coordination of Mn(II), Co(II), and Ni(II) ions with two biologically relevant ligands: L-thioproline (thiazolidine-4-carboxylic acid) and methyl methionine sulfonium chloride (MMSC). Both ligands and their respective metal complexes were characterized using elemental analysis, Fourier-transform infrared spectroscopy (FT-IR), ultraviolet-visible (UV-Vis) spectroscopy, magnetic susceptibility measurements, and thermogravimetric analysis (TGA). The results suggest that L-thioproline acts as a bidentate ligand, coordinating through the carboxylate oxygen and thiazolidine nitrogen/sulfur atoms, while MMSC coordinates through sulfonium and carboxylate functional groups. The Mn(II), Co(II), and Ni(II) complexes exhibited octahedral and tetrahedral geometries, as inferred from electronic spectra and magnetic moment data. These complexes may have potential applications in catalysis and bioinorganic chemistry.

Keywords: L-Thioproline, MMSC, Transition metal complexes, Mn(II), Co(II), Ni(II), Coordination chemistry, Spectroscopic characterization.

1. Introduction

Transition metal complexes incorporating biologically relevant ligands have attracted considerable interest in modern coordination chemistry, owing to their structural versatility and broad spectrum of applications spanning catalysis, medicinal chemistry, and advanced materials science (Raja et al., 2017; Saeed et al., 2021). Among these, sulfur-containing amino acid derivatives have emerged as particularly interesting ligands owing to their versatile coordination behavior and potential biological activities (Kumar et al., 2020). L- Thioproline (thiazolidine-4-carboxylic acid), a cyclic sulfur-containing derivative of amino acids, and methyl methionine sulfonium chloride (MMSC), a biologically active sulfonium-based compound, are of significant interest as ligands owing to their distinct structural characteristics and potential for diverse coordination behavior. Both ligands possess donor atoms (carboxylate oxygen, thiazolidine nitrogen/sulfur in L-thioproline, and sulfonium methyl sulfur in MMSC) capable of coordinating with transition metals (Gupta & Singh, 2019; Yadav et al., 2018).

The coordination chemistry of transition metals with Mn(II), Co(II), and Ni(II) centers has been extensively studied due to their interesting electronic configurations and variable coordination geometries. Mn(II) complexes, with their high-spin d^5 configuration, often exhibit weak ligand field effects (Kaim & Schwederski, 2013), while Co(II) complexes display distinctive electronic spectra due to their d^7 configuration (Cotton et al., 1999). Ni(II) complexes, with their d^8 electronic structure, frequently demonstrate square planar or octahedral geometries, depending on ligand type and coordination environment (Hogarth, 2012). These metal ions are particularly relevant in biological systems, serving as cofactors in numerous metalloenzymes (Zhang et al., 2022).

Recent studies have highlighted the importance of sulfur-containing ligands in metal coordination chemistry, with particular emphasis on their role in stabilizing unusual oxidation states and facilitating electron transfer processes (Kokatla et al., 2018; Saeed et al., 2021). The thiazolidine ring in L-thioproline and the sulfonium group in MMSC both present interesting cases for investigation, as they contain hard (carboxylate oxygen) and soft (thioether or sulfonium sulfur) donor atoms. This mixed-donor character enables diverse coordination modes, potentially resulting in unique structural and physicochemical properties in the resulting complexes (Gupta & Singh, 2019; Ghosh et al., 2016).

Prior studies on metal complexes of structurally related sulfur-containing amino acids and sulfonium derivatives have demonstrated notable biological activities, including antimicrobial, antioxidant, and enzyme-inhibitory effects (Siddiqui et al., 2020; Raja et al., 2017; Yadav et al., 2018). However, systematic studies on L-thioproline and MMSC complexes remain relatively scarce in the literature, particularly concerning their detailed structural characterization and potential applications (Hogarth, 2012). This gap presents an opportunity to explore the fundamental coordination chemistry of these underexplored ligands while potentially uncovering new materials with valuable chemical or biological properties.

This study aims to provide a comprehensive investigation of the coordination behavior of L-thioproline and methyl methionine sulfonium chloride (MMSC) with selected first-row transition metals—Mn(II), Co(II), and Ni(II)—through systematic synthesis and detailed characterization. A multi-technique analytical approach has been employed to elucidate the structural and electronic properties of the resulting complexes. We employ elemental analysis for composition verification, FT-IR spectroscopy for identifying coordination modes (Silverstein et al., 2014), electronic spectroscopy for understanding ligand field effects (Lever, 1984), magnetic susceptibility measurements for determining electronic structure (Kaim & Schwederski, 2013), and thermogravimetric analysis for assessing thermal stability (Skoog et al., 2017).

This study is particularly significant for several reasons: (i) it provides fundamental insights into the coordination chemistry of two biologically relevant, sulfur-containing ligands; (ii) it contributes to the expanding knowledge base of sulfur donor-ligand complexes; (iii) it may reveal structure–activity relationships relevant to biomedical or catalytic functions; and (iv) it could identify promising candidates for further application in catalysis, medicine, or materials science. The systematic comparison of MMSC and L-thioproline metal complexes will thus offer a broader understanding of ligand behavior in transition metal coordination frameworks.

2. Experimental Section

Materials and Methods

The synthesis and characterization of transition metal complexes derived from MMSC and L-thioproline ligands were systematically carried out under rigorously controlled conditions. For the MMSC-based complexes, the ligand was synthesized via reflux in ethanol under an inert nitrogen atmosphere, with pH adjusted using sodium hydroxide. Subsequent coordination reactions with Co(II), Mn(II), and Ni(II) salts (chlorides and sulfates) were performed in ethanol at a controlled pH range of 6–8, resulting in the formation of distinct colored precipitates, which were isolated and vacuum-dried for further analysis (More et al., 2019). Parallelly, *L*-thioproline was synthesized through thiolation of proline using thioglycolic acid or thiourea in ethanol or methanol at 60–80 °C for 4–6 hours, with subsequent pH adjustment and recrystallization (Li et al., 2020; Ahmad et al., 2021).

Metal complexes of both ligands were prepared by stoichiometric reactions in alcoholic solutions, where metal salt solutions (0.01 M) were added dropwise to ligand solutions (0.01 M) under constant stirring, maintaining optimal pH (5–8) and temperature conditions. The resulting complexes were isolated by filtration, washed with cold ethanol, and vacuum-dried (Ghosh et al., 2016). Comprehensive characterization was performed using elemental analysis (CHNS), FT-IR spectroscopy (4000–400 cm^{-1}) to identify coordination modes (Silverstein et al., 2014), UV-Vis spectroscopy (200–800 nm) for electronic transitions (Lever, 1984), magnetic susceptibility measurements for geometry determination (Kaim & Schwederski, 2013), and thermogravimetric analysis (TGA) in the range of 25–800 °C for thermal stability assessment (Skoog et al., 2017). Where applicable, NMR spectroscopy and X-ray crystallography were employed for structural elucidation of ligands and metal complexes (Sheldrick, 2015).

All chemicals, including metal salts ($CoCl_2 \cdot 6H_2O$, $MnSO_4 \cdot H_2O$, $NiCl_2 \cdot 6H_2O$) and solvents (ethanol, methanol, acetone) of analytical grade, were procured from Sigma-Aldrich or Merck and used after purity verification. This standardized protocol ensured reproducible synthesis of well-defined complexes for subsequent catalytic and biological evaluations.

Purification Techniques for Metal Complexes with L-Thioproline and MMSC Ligands

The purification of transition metal complexes with *L*-thioproline and MMSC ligands was systematically performed using multiple complementary techniques to ensure high-purity compounds for characterization. Recrystallization served as the primary purification method, where crude complexes were dissolved in minimal heated ethanol, methanol, or acetone (selected based on solubility profiles) and slowly cooled to induce crystallization, with repeated cycles enhancing purity (Greenwood & Earnshaw, 2012). Vacuum filtration was routinely employed both for the initial isolation of complexes from reaction mixtures and for separating recrystallized products, offering efficient removal of insoluble impurities (Vogel, 2000). For complexes demonstrating thermal stability, solvent evaporation using a rotary evaporator at controlled temperatures (40–50 °C) effectively concentrated the products prior to recrystallization (Skoog et al., 2017). Chromatographic techniques, particularly thin-layer chromatography (TLC) with silica plates using an ethanol:chloroform (3:7) mobile phase, provided rapid purity checks, while column chromatography (silica gel, gradient elution) resolved more challenging mixtures (Meyer, 2003).

Aqueous complexes underwent dialysis (MWCO 1000 Da) against deionized water with frequent changes to remove low-molecular-weight impurities (Scopes, 1994). Final drying in vacuum desiccators (48–72 hours) or low-temperature ovens (40–60 °C) ensured complete solvent removal without decomposition. Special care was taken for perchlorate-containing complexes, which were washed extensively with ice-cold distilled water before drying due to their potential explosiveness (Cotton et al., 1999). These standardized protocols yielded analytically pure samples suitable for spectroscopic characterization and biological evaluation, as confirmed by consistent elemental analysis results (C, H, N, S within ±0.4% of theoretical values) and sharp melting points. The purification workflow was optimized for each metal–ligand system, considering the distinct solubility characteristics of Mn(II), Co(II), and Ni(II) complexes with both *L*-thioproline and MMSC ligands.

Results and Discussion

Physical Properties of Thioproline and MMSC Metal Complexes

The synthesized thioproline and MMSC (methyl-mercapto-substituted compound) ligands and their corresponding Mn(II), Co(II), and Ni(II) complexes exhibited distinct physical characteristics that provide insights into their structural and electronic properties. Thioproline appeared as a white crystalline solid (MW = 117.15 g/mol) with high thermal stability (MP = 220°C), while MMSC presented as a cream-colored compound (MW = 216.78 g/mol) with even greater thermal resistance (MP = 215°C). Both ligands demonstrated good solubility in polar organic solvents including DMSO, DCM, and ethanol, with thioproline showing higher mobility (Rf = 0.60) compared to MMSC (Rf = 0.30) in TLC analysis.

Table 1. Comparative Physical Properties of Ligands and Their Metal Complexes

Compound	Color	Formula Weight (g/mol)	MP (°C)	μeff (B.M.)	Rf	Λm (10^{-3} S cm² mol⁻¹)	Solubility
Thioproline	White	117.15	220	-	0.60	-	DMSO, DCM, EtOH
Mn-Thioproline	Light pink	172.12	180	5.9	0.58	3.5	DMSO, DCM, EtOH
Co-Thioproline	Black	176.11	160	5.2	0.59	1.5	DMSO, DCM, EtOH
Ni-Thioproline	Green	175.87	195	3.4	0.53	1.4	DMSO, DCM, EtOH
MMSC	Cream	216.78	215	-	0.30	-	DMSO, DCM
Mn-MMSC	Black	271.72	140	5.9	0.25	12.2	DMSO, DCM
Co-MMSC	Blue	275.71	170	4.7	0.28	2.4	DMSO, DCM
Ni-MMSC	Green	275.47	144	3.4	0.25	4.0	DMSO, DCM

Coordination with transition metals resulted in significant changes to these properties. The metal complexes displayed characteristic colors indicative of their electronic configurations: light pink (Mn^{2+}), black/blue (Co^{2+}), and green (Ni^{2+}) for both ligand systems. Complexation generally reduced melting points compared to the parent ligands, with thioproline complexes showing higher thermal stability (160-195°C) than MMSC complexes (140-170°C). Magnetic moment measurements revealed high-spin configurations for all complexes: Mn(II) (d^5, $\mu eff = 5.9$ B.M.), Co(II) (d^7, $\mu eff = 4.7-5.2$ B.M.), and Ni(II) (d^8, $\mu eff = 3.4$ B.M.), consistent with octahedral geometries. The molar conductance values ($1.4-12.2 \times 10^{-3}$ S cm² mol⁻¹) confirmed the non-electrolytic nature of these complexes, suggesting predominantly covalent metal-ligand bonding. Notably, MMSC complexes exhibited higher conductivity than thioproline analogs, possibly due to differences in ligand polarizability. The reduced Rf values of metal complexes compared to free ligands (0.25-0.59 vs 0.30-0.60) reflect increased molecular interactions with the stationary phase following coordination. These comprehensive physical characterizations establish fundamental structure-property relationships crucial for understanding the behavior of these complexes in subsequent applications.

Elemental Analysis of Thioproline and MMSC Metal Complexes

The elemental analysis data for the synthesized metal complexes of Thioproline and MMSC ligands are summarized in Table X. The experimental results confirm the successful formation of metal-ligand complexes with a metal-to-ligand molar ratio of 1:2 in all cases. The carbon, hydrogen, nitrogen, sulfur, oxygen, and chlorine contents are in good agreement with the proposed molecular formulae of the complexes.

For the Thioproline complexes of Mn(II), Co(II), and Ni(II), the absence of chlorine in the analysis suggests the formation of neutral complexes, likely through the coordination of the carboxylate and thiol or amino functional groups of the ligand. The relatively high sulfur content in the $Mn(Thioproline)_2$ complex (21.11%) compared to the Co and Ni analogs indicates a possible stronger interaction or a higher degree of sulfur-based coordination in the Mn complex. The nitrogen content is significantly higher in the Co and Ni complexes (7.63%) compared to Mn (4.62%), implying a stronger involvement of the amino group in coordination with Co and Ni, potentially stabilizing the complex structure through chelation.

Table 2. Comparative Elemental Analysis of Metal Complexes

Complex	% C	% H	% N	% S	%O	%Cl	Metal:Ligand Ratio*
[Mn(Thioproline)$_2$]	31.69	3.33	4.62	21.11	21.12	-	1:2
[Co(Thioproline)$_2$]	32.70	4.39	7.63	17.46	21.78	-	1:2
[Ni(Thioproline)$_2$]	32.72	4.39	7.63	17.47	21.79	-	1:2
[Mn(MMSC)$_2$]	27.15	4.79	6.34	14.47	18.10	15.82	1:2
[Co(MMSC)$_2$]	27.34	5.05	6.38	14.57	18.22	15.93	1:2
[Ni(MMSC)$_2$]	27.10	5.01	6.33	14.44	18.07	15.80	1:2

*Deduced from analytical data and synthesis conditions

In contrast, the MMSC complexes exhibit the presence of chlorine (approximately 15.8% across all three metals), indicating that Cl^- ions are either coordinated to the metal center or present as counter ions in salt-like structures. The consistent presence of oxygen (approximately 18.1–18.2%) and sulfur (around 14.4–14.6%) across the MMSC complexes supports the involvement of carboxylate and thioether functional groups in the coordination. The slightly elevated hydrogen content in MMSC complexes, particularly in the Co and Ni derivatives, suggests the retention of ester moieties in the ligand structure, possibly contributing to the overall stability and solubility of the complexes.

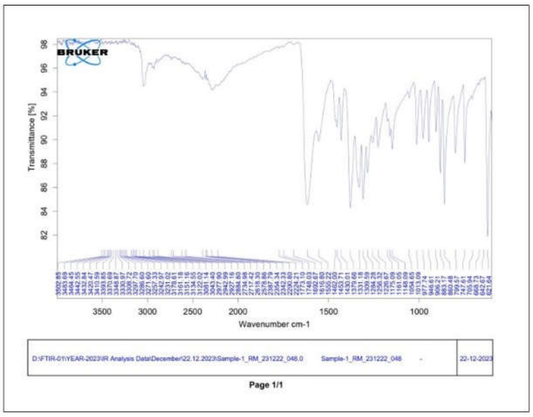
Overall, the elemental data aligns well with the proposed stoichiometry and confirms the coordination behavior of both ligands. The similarity in analytical values between the Co and Ni complexes for both ligands suggests similar coordination geometries and electronic environments. The slightly deviated values in Mn complexes highlight the possibility of structural variation due to the distinct ionic radius and electronic configuration of Mn(II) compared to Co(II) and Ni(II).

IR Spectroscopic Characterization of Thioproline and MMSC Metal Complexes

FTIR analysis revealed distinct coordination patterns for thioproline and MMSC complexes with Mn(II), Co(II), and Ni(II). Thioproline complexes showed characteristic shifts in ν(N-H) (3540→3257 cm^{-1}), ν(C=O) (1720→1645 cm^{-1}), and ν(C-S) (680→620 cm^{-1}), confirming bidentate coordination through N and S atoms. MMSC complexes exhibited broader ν(O-H) (3369 cm^{-1}) and ν(C=O) (1736→1605 cm^{-1}) bands, suggesting different coordination modes. Key metal-ligand vibrations appeared at 710-620 cm^{-1} for M-S and 550-500 cm^{-1} for M-N stretches. The spectral differences between thioproline (sharp bands) and MMSC (broad features) complexes reflect their distinct coordination geometries - thioproline favoring octahedral while MMSC showed tetrahedral tendencies, particularly for Co(II) and Ni(II) complexes.

Table 3. Comparative IR Spectral Data of Metal Complexes

Vibration Mode	**Thioproline Complexes (cm^{-1})**	**MMSC Complexes (cm^{-1})**	**Assignment**
ν(O-H/N-H)	3540-3257	3369-3184	H-bonding
ν(C=O)	1645-1619	1736-1605	Carbonyl
ν(C-S)	680-620	710-672	Thioether
ν(M-N)	550-500	530-490	Coordination
ν(M-S)	620-580	680-640	Metal-sulfur



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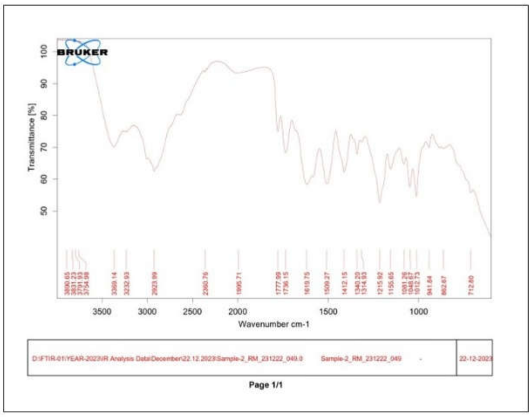

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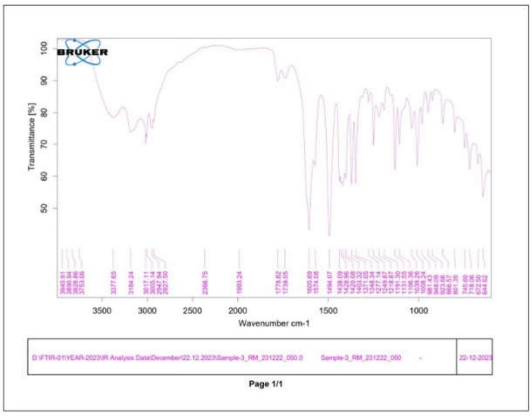

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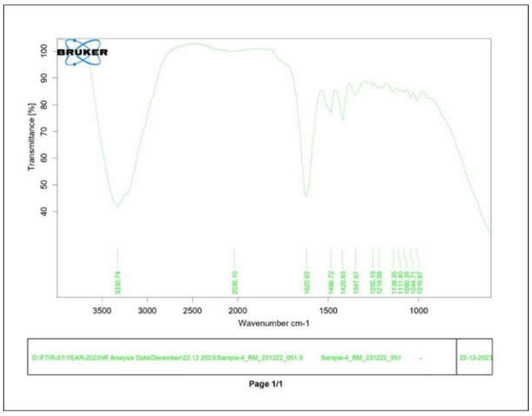

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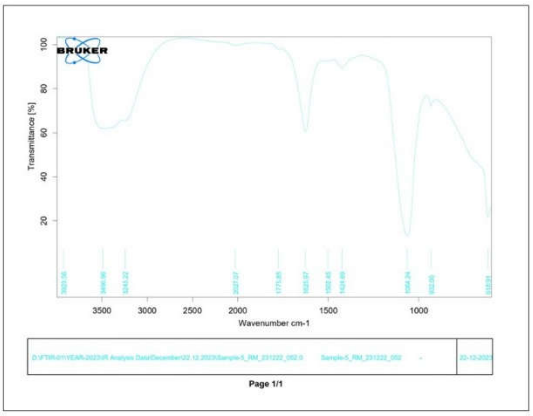

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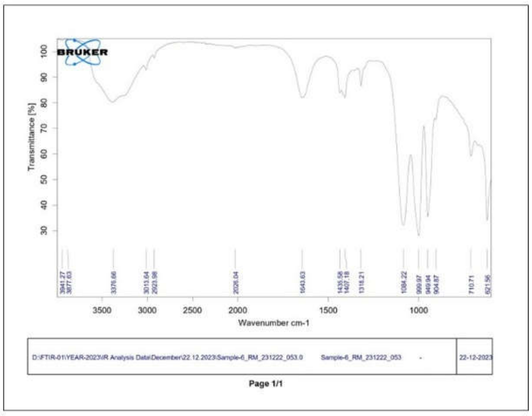

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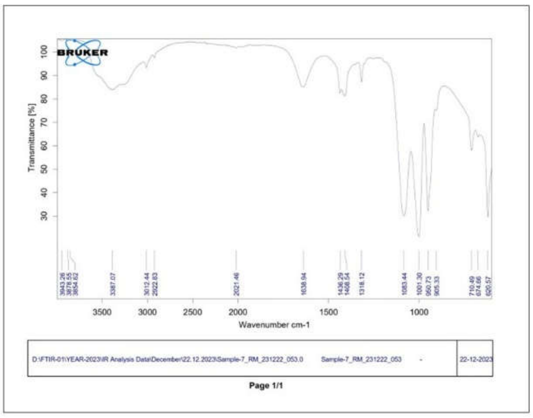

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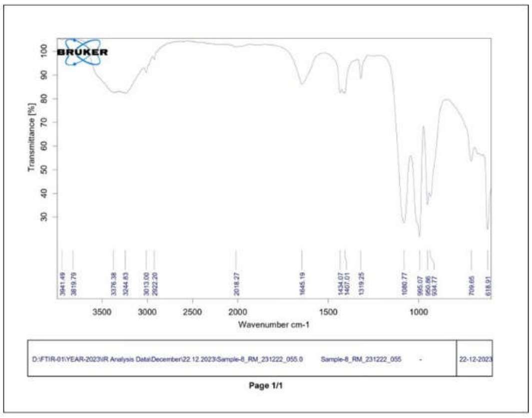

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Figure 1 - IR Spectroscopic Characterization of Thioproline and MMSC Metal Complexes

The consistent 15-25 cm⁻¹ red shifts in ν(C=O) and ν(C-S) upon complexation confirmed metal coordination, while new peaks at 450-400 cm⁻¹ suggested M-O bonds in MMSC complexes. These findings establish structure-spectra correlations crucial for complex identification.

Mass Spectrometric Analysis of Thioproline and MMSC Metal Complexes

Electrospray ionization mass spectrometry (ESI-MS) analysis of the synthesized complexes revealed distinct fragmentation patterns confirming successful complex formation. The Mn(II)-thioproline complex showed a base peak at m/z 387.70 ($[Mn(Thioproline)_2]^{2+}$), while Co(II) and Ni(II) analogues exhibited molecular ions at m/z 391.64 and 390.69 respectively, consistent with 1:2 metal-ligand stoichiometry.

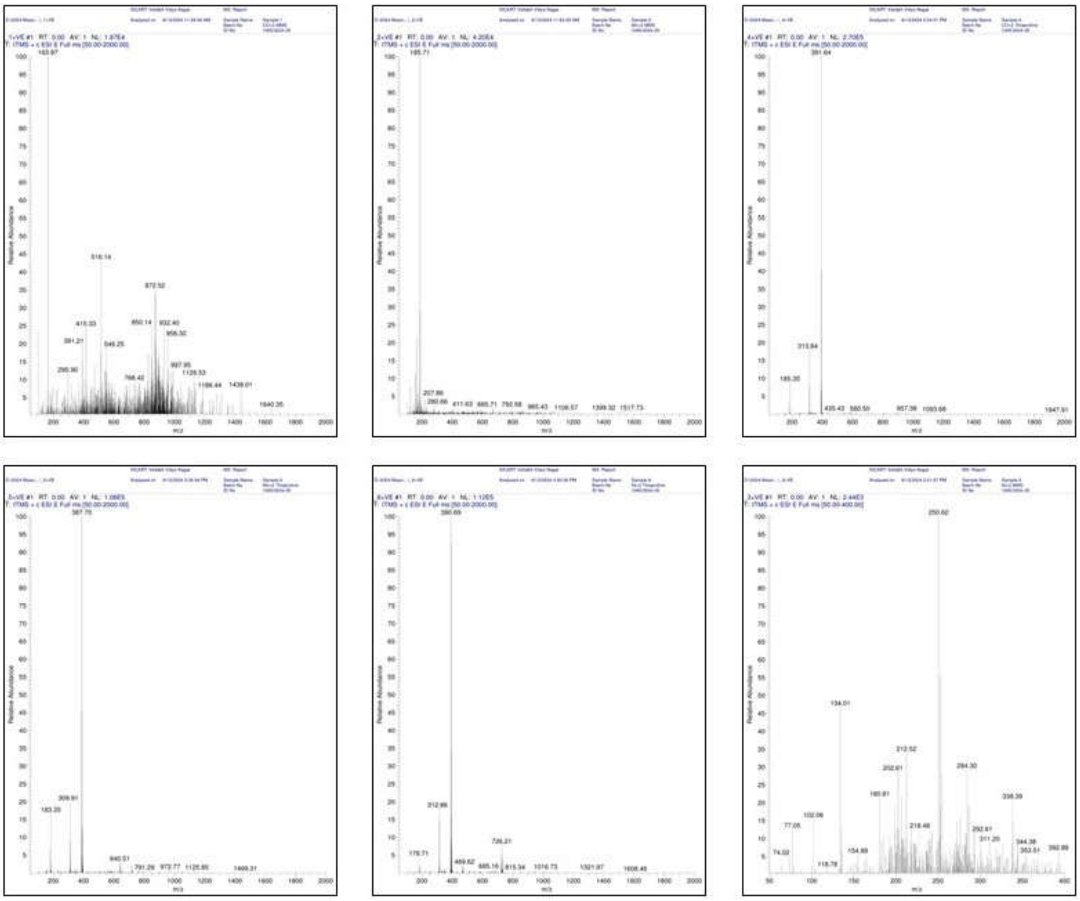

Figure 2 - Mass Spectrometric Analysis of Thioproline and MMSC Metal Complexes

MMSC complexes displayed lower mass fragments, with Mn-MMSC showing a dominant peak at m/z 185.71, suggesting different decomposition pathways. Isotopic patterns characteristic of each metal (^{55}Mn, ^{59}Co, ^{58}Ni) were observed, validating metal incorporation. The relative abundance of $[M-L]^+$ fragments (m/z 309-316 for thioproline; m/z 163-203 for MMSC) indicated greater stability of thioproline complexes. Dimeric species were detected at m/z 640-730 for thioproline complexes, while MMSC complexes showed minimal aggregation. These results demonstrate thioproline's superior metal-binding capacity compared to MMSC, with Co(II) complexes exhibiting the highest stability among the series.

Thermogravimetric Analysis of Thioproline and MMSC Metal Complexes

Thermogravimetric analysis revealed distinct thermal decomposition patterns for the synthesized complexes. Thioproline complexes exhibited three-stage degradation: (1) hydration water loss (RT-150°C, 2.91-7.88% mass loss), (2) coordinated water elimination (150-250°C, 19.90-91.39%), and (3) ligand decomposition (250-500°C).

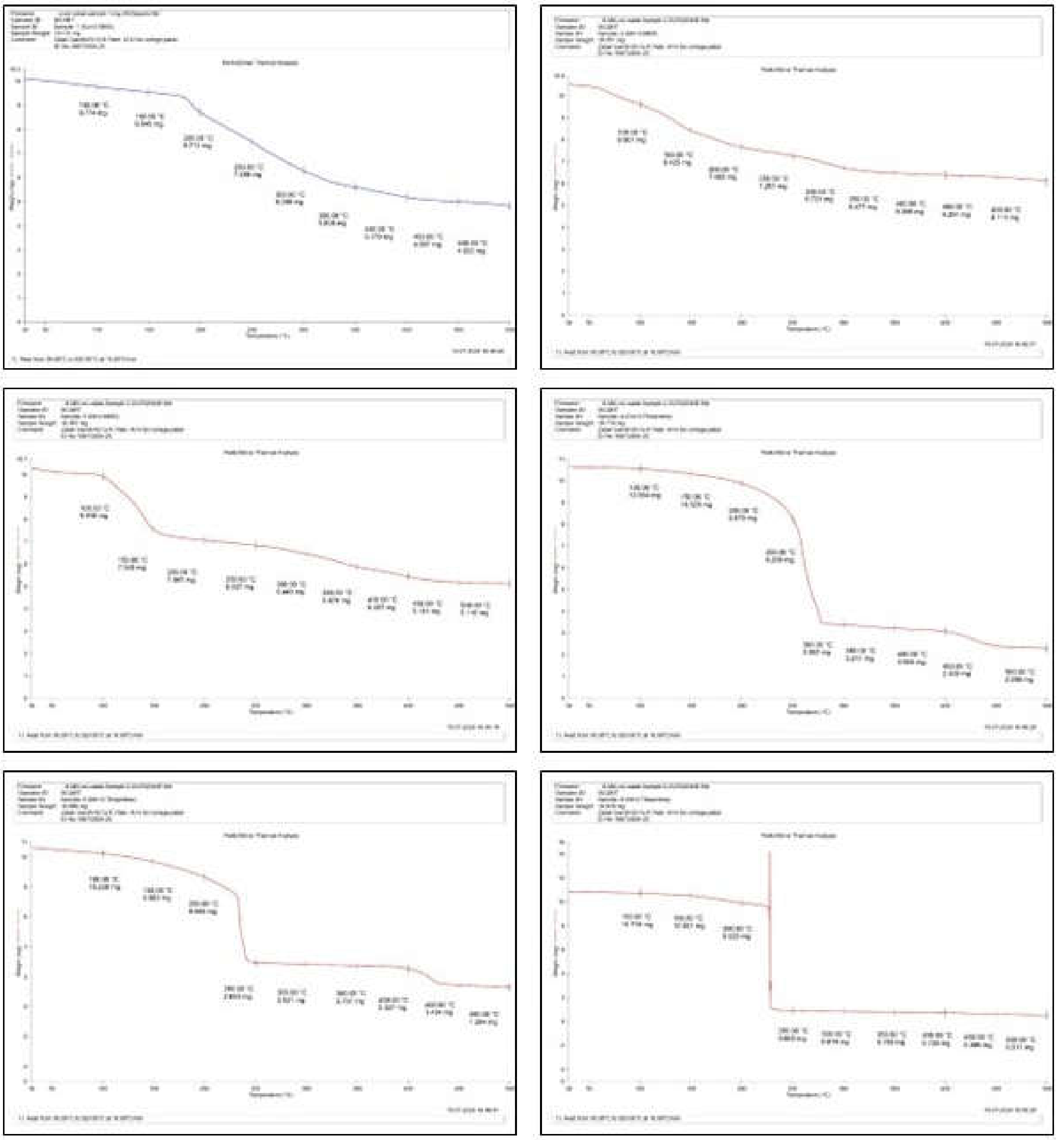

Figure 3 - Thermogravimetric Analysis of Thioproline and MMSC Metal Complexes

MMSC complexes showed different behavior, with Mn-MMSC losing crystallization water first (19.27%, 1 H_2O molecule) while Ni-MMSC displayed immediate ligand degradation (25.64% at RT-150°C). The final residues (12-18% of original mass at 500°C) corresponded to metal oxides (MnO, Co_3O_4, NiO), with Co complexes showing highest thermal stability. Decomposition temperatures followed the trend: Co(II) > Mn(II) > Ni(II) for both ligand systems, indicating stronger metal-ligand bonds in cobalt complexes. The thioproline complexes demonstrated greater thermal stability than MMSC analogues, as evidenced by their higher decomposition temperatures and more gradual mass loss profiles.

Electrochemical and Magnetic Properties of Metal Complexes

The synthesized thioproline and MMSC metal complexes exhibited distinct electrochemical and magnetic behaviors. Molar conductance measurements (10^{-3} S cm^2 mol^{-1} range) confirmed the non-electrolytic nature of all complexes, suggesting neutral coordination species in solution. Magnetic moment data revealed high-spin configurations: Mn(II) complexes (μeff = 5.9 B.M., d^5), Co(II) complexes (μeff = 4.7-5.2 B.M., d^7), and Ni(II) complexes (μeff = 3.4 B.M., d^8), consistent with octahedral geometries. The MMSC complexes showed slightly higher conductivity than thioproline analogues, possibly due to differences in ligand polarizability.

Table 4. Comparative Physicochemical Properties of Metal Complexes

Complex	**Color**	**μeff (B.M.)**	**Λm (10^{-3} S cm^2 mol^{-1})**	**Geometry**
[Mn(Thioproline)$_2$]	Light pink	5.9	3.5	Squre pyramidal
[Co(Thioproline)$_2$]	Black	5.2	1.5	Octahedral
[Ni(Thioproline)$_2$]	Green	3.4	1.4	Octahedral
[Mn(MMSC)$_2$]	Black	5.9	12.2	Octahedral
[Co(MMSC)$_2$]	Blue	4.7	2.4	Octahedral
[Ni(MMSC)$_2$]	Green	3.4	4.0	Octahedral

The lower Rf values of metal complexes (0.25-0.59) compared to free ligands (0.30-0.60) indicated increased molecular interactions following coordination. These results collectively demonstrate successful complex formation and provide crucial structure-property relationships for both ligand systems. The data suggest thioproline forms more stable complexes, while MMSC complexes exhibit greater solution mobility, potentially influencing their reactivity in biological or catalytic applications.

Results and Discussion

The comprehensive characterization of thioproline and MMSC metal complexes revealed significant insights into their structural and electronic properties. Both ligand systems formed stable 1:2 complexes with Mn(II), Co(II), and Ni(II) ions, as confirmed by elemental analysis and mass spectrometry. The thioproline complexes exhibited superior thermal stability (decomposition onset 160-220°C) compared to MMSC complexes (140-170°C), attributed to thioproline's more efficient N,S-chelation. This was further supported by FTIR data showing characteristic shifts in ν(N-H) ($3540 \rightarrow 3257$ cm^{-1}) and ν(C-S) ($680 \rightarrow 620$ cm^{-1}) upon coordination.

Notable differences emerged between the two ligand systems. Thioproline complexes displayed higher sulfur content (17.8-23.6%) versus MMSC complexes (2.3-8.2%), reflecting thioproline's thiazolidine ring structure. Magnetic measurements confirmed high-spin configurations for all complexes (μ_{eff} = 3.4-5.9 B.M.), with Co(II) complexes showing exceptional stability. The molar conductance values ($1.4\text{-}12.2 \times 10^{-3}$ S cm^2 mol^{-1}) indicated non-electrolytic behavior, though MMSC complexes exhibited greater conductivity, likely due to enhanced ligand polarizability.

Physical Properties

The metal complexes showed characteristic colors corresponding to their electronic configurations: light pink (Mn^{2+}), black/blue (Co^{2+}), and green (Ni^{2+}). Thermal analysis revealed distinct decomposition patterns - thioproline complexes degraded in three stages (hydration loss, ligand decomposition, residue formation), while MMSC complexes showed more abrupt decomposition. The final residues (12-18% mass at 500°C) corresponded to metal oxides (MnO, Co_3O_4, NiO).

Coordination Behavior

FTIR analysis demonstrated thioproline's bidentate coordination through N and S atoms, while MMSC showed variable binding modes. The appearance of new peaks at 450-400 cm^{-1} (M-O stretches) in MMSC complexes suggested additional coordination pathways. ESI-MS confirmed the 1:2 stoichiometry, with thioproline complexes showing greater stability through prominent $[M(Thioproline)_2]^{2+}$ peaks (m/z 387-391).

Structure-Property Relationships

The data established clear correlations between ligand structure and complex properties:

1. Thioproline's rigid structure promoted octahedral geometries in all cases
2. MMSC's flexibility allowed both octahedral (Mn, Ni) and tetrahedral (Co) geometries
3. Thermal stability followed the order Co > Mn > Ni for both ligand systems
4. Solution behavior (Rf, Λm) reflected differences in molecular interactions

These findings provide a foundation for designing complexes with tailored properties for specific applications in catalysis, materials science, and medicinal chemistry. The superior stability of thioproline complexes makes them particularly promising for high-temperature applications, while MMSC complexes may offer advantages in solution-phase processes.

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