



Synthesis and Characterization of s-Triazine Derivatives Containing Theophylline Group and Some Transition Metal Complexes

Teofilin Grubu İçeren s-Triazin Türevlerinin ve Bazı Geçiş Metal Komplekslerinin Sentezi ve Karakterizasyonu

Ahmet Caymaz[✉], Ahmed Hamdi Mirghani[✉], Saban Uysal[✉]

Department of Chemistry, Faculty of Engineering and Natural Sciences, Karabuk University, Karabuk, Türkiye.

ABSTRACT

In this paper, two novel theophylline-substituted s-triazine ligands and their trinuclear complexes were synthesized. Theophylline-7-acetic acid (I) was reacted with thionyl chloride, resulting in chlorination of the acidic moiety to afford 2-(1,3-dimethyl-2,6-dioxo-2,3-dihydro-1H-purin-7(6H)-yl)acetyl chloride (II). This compound was reacted separately with o-phenylenediamine and p-phenylenediamine in the presence of $AlCl_3$ as a catalyst in dichloromethane at $-10^\circ C$ for 24 h. As a result of these reactions, compounds III and IV were obtained. Compounds III and IV were then separately reacted with 2,4,6-tri(p-formylphenoxy)-1,3,5-triazine (TRIPOD) in ethanol, yielding the s-triazine-cored tripodal ligands ACL1 and ACL2. Tripodal transition metal complexes (ACC1-ACC8) were obtained by reacting ACL1 and ACL2 with various transition metal salts ($MCl_2 \cdot nH_2O$, $M=Mn^{2+}$, Co^{2+} , Ni^{2+} , and Cu^{2+}). The structures of all obtained ligands were elucidated by ^1H and ^{13}C NMR, FTIR, and elemental analysis methods. The structures of the complexes were characterized using FTIR, magnetic susceptibility, ICP-OES, and TGA methods.

Key Words

Theophylline, theophylline-7-acetic acid, s-triazine, metal complexes.

Öz

Bu çalışmada, iki yeni teofilin süstitüe s-triazin ligandı ve bunların trinükleer kompleksleri sentezlendi. Teofilin-7-asetik asit (I), tıyonil klorür ile reaksiyona sokularak asidik kısmın klorlanmasıyla 2-(1,3-dimetil-2,6-diokso-2,3-dihidro-1H-purin-7(6H)-il)asetil klorür (II) elde edildi. Bu bileşik, $AlCl_3$ katalizörlüğünde diklorometan içinde $-10^\circ C$ 'de 24 saat boyunca ayrı ayrı o-fenilendiamin ve p-fenilendiamin ile reaksiyona sokuldu. Bu reaksiyonlar sonucunda III ve IV bileşikleri elde edildi. Daha sonra III ve IV bileşikleri, etanol içinde ayrı ayrı 2,4,6-tri(p-formilfenoksi)-1,3,5-triazin (TRIPOD) ile reaksiyona sokularak s-triazin çekirdekli üç ayaklı ligandlar ACL1 ve ACL2 elde edildi. Tripodal geçiş metal kompleksleri (ACC1-ACC8), ACL1 ve ACL2'nin çeşitli geçiş metal tuzları ($MCl_2 \cdot nH_2O$, $M=Mn^{2+}$, Co^{2+} , Ni^{2+} ve Cu^{2+}) ile reaksiyonu sonucu elde edildi. Elde edilen tüm ligandların yapıları ^1H ve ^{13}C NMR, FTIR ve elementel analiz yöntemleriyle aydınlatıldı. Komplekslerin yapıları ise FTIR, manyetik duyarlılık, ICP-OES ve TGA yöntemleri kullanılarak karakterize edildi.

Anahtar Kelimeler

Teofilin, teofilin-7-asetik asit, s-triazin, metal kompleksleri.

Article History: Received: Aug 21, 2025; Accepted: Feb 13, 2026; Available Online: Apr 1, 2026.

DOI: <https://doi.org/10.15671/hjbc.1770103>

Correspondence to: S. Uysal, Department of Chemistry, Faculty of Engineering and Natural Sciences, Karabuk University, Karabuk, Türkiye.

E-Mail: sabanuysal@karabuk.edu.tr

INTRODUCTION

S-Triazines are heterocyclic organic compounds composed of a six-membered ring containing three carbon and three nitrogen atoms. Owing to their distinctive structural and electronic properties, *s*-triazines have attracted considerable interest in many scientific fields, including agriculture, pharmaceuticals, materials science, and environmental chemistry [1, 2]. Cyanuric acid (1,3,5-triazine-2,4,6-triol) is one of the most important representatives of this class and serves as a key precursor for numerous *s*-triazine derivatives. *s*-Triazines are widely applied in agriculture, particularly as herbicides such as atrazine and simazine, due to their effective and selective weed-control properties [3,4]. They are also used as intermediates in the synthesis of pharmaceuticals, agrochemicals, and functional materials because of their high reactivity and ease of functionalization [5]. In environmental chemistry, *s*-triazines are of concern because of their chemical stability and persistence, which can lead to accumulation in soil and water and potential ecological and health risks, especially in the case of atrazine [6,7].

Theophylline was first isolated from tea leaves by Albrecht Kossel in 1888, and its structure and first synthetic method were established by Emil Fischer in 1895. It was introduced as a weak diuretic for renal and cardiac edema in 1907 and was included in the United States Pharmacopeia in 1918 [8-11]. The clinical use of theophylline began in 1932. It is a methylxanthine derivative primarily used as a bronchodilator in the treatment of asthma, respiratory tract obstruction, and chronic obstructive pulmonary disease (COPD). Its medical use has continued due to its effectiveness and low cost [12-16]. In experimental animal models of melanoma, theophylline has been shown to reduce tumor volume and inhibit angiogenesis. It also suppresses DNA and protein synthesis in human breast cancer cells. Several studies report that theophylline inhibits cell growth and induces apoptosis in various cancer cell lines. At low concentrations (20–25 µg/mL), it induces apoptosis in human prostate, lung, and ovarian cancer cells and enhances the apoptotic effects of anticancer drugs such as cisplatin, possibly through increased cAMP levels. Additionally, increased apoptosis has been observed in chronic lymphocytic leukemia (CLL) cells [17,18].

In our previous studies, we synthesized and characterized

tripodal *s*-triazine compounds, including dopamine [19], catechol [20], keto-oxime [21], vic-dioxime [22], and salicilimine [23] in the structure and their [MSalen/Saloph] ($M = Cr^{3+}$ and Fe^{3+}) capped complexes. The pharmacological behavior of theophylline refers to its electron-rich carbonyl and heterocyclic systems, which allow theophylline to block receptors, inhibit enzymes, and chelate with metal ions [24,25]. In this study, unlike our previous studies, we synthesized two novel tripodal *s*-triazine ligands, including theophylline groups in their environment, unlike other studies in the literature. Then, we obtained Mn^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} complexes of these ligands from the reaction of these two ligands with transition metal salts ($MCl_2 \cdot nH_2O$) according to the literature. Finally, magnetic susceptibility measurements of these complexes were carried out, and their magnetic properties and thermal durabilities were investigated.

This study reports the first theophylline-substituted *s*-triazine cored ligands and their trinuclear metal complexes, while other studies focused only on either theophylline or *s*-triazine cored ligands.

MATERIALS and METHODS

In this study, the ^1H and ^{13}C NMR analyses of the synthesized ligands were conducted by using a Bruker AvanceCore NMR spectrometer (400 MHz) device. The ^1H and ^{13}C NMR spectra of the ligands were recorded in $DMSO-d_6$ solvent. The elemental analyses of the compounds (C, H, N) were performed using a LECO 932 CHNS instrument (Leco-932, St. Joseph, MI, USA). The FTIR spectra of the synthesized complex compounds were obtained using a Thermo Nicolet IS5 model FTIR instrument with an ID7 model ATR attachment. The magnetic susceptibility measurements of the complexes were carried out by using the Sherwood Scientific MX Gouy device with $Hg[Co(SCN)_4]$ as the calibrant and the Gouy method. The effective magnetic moments, μ_{eff} per metal atom were calculated based on the expression $\mu_{eff} = 2.84 \sqrt{X_M}$ B.M., where X_M is the molar susceptibility. The TGA analyses of the compounds were performed by using a HITACHI model STA7300 Thermal Analysis System device.

Cyanuric chloride (Merck), 4-hydroxybenzaldehyde (Sigma), o-phenylenediamine (Sigma), p-phenylenediamine (Sigma), salicylaldehyde (Sigma), theophylline-7-acetic acid (I) (TCI), thionyl chloride (Sigma), aluminum

chloride (Sigma), Manganese(II) chloride tetrahydrate (Sigma), Cobalt(II) chloride hexahydrate (Sigma), Nickel(II) chloride hexahydrate (Merck), Copper(II) chloride dihydrate (Merck), ethanol (Merck), methanol (Sigma), 1,4-Dioxane (Merck), N,N-dimethylformamide (Merck), acetonitrile (Sigma), dichloromethane (Sigma), chloroform (Sigma), diethyl ether (Sigma). The central molecule used in ligand synthesis, coded as TRIPOD, 2,4,6-tri(p-formylphenoxy)-1,3,5-triazine, was also synthesized and used according to literature [26].

Synthesis of 2-(1,3-dimethyl-2,6-dioxo-2,3-dihydro-1h-purin-7(6h)-yl)acetyl chloride (II)

Theophylline-7-acetic acid (I) (11.91 g, 50.00 mmol) is dissolved in 100 mL of acetonitrile. Then, an excess of 10% thionyl chloride (6.54 g, 3.99 mL, 55.00 mmol) is added, and the mixture is stirred at 85°C for 90 minutes under a reflux condenser. The solvent of the resulting mixture is completely evaporated. The solid product is washed twice with diethyl ether to remove unreacted thionyl chloride.

II: MW= 256.65 g, Color: Cream-colored solid; Yield: 8.7261 g (68%); Melting Point: $\geq 200^{\circ}\text{C}$ (Dec.); FTIR (ATR, cm^{-1}) peaks: 2854, 2960, 2997 (C-H_{aliphatic}), 3068, 3124 (C-H_{aromatic}), 1651 (C=N_{xanthine}), 1702, 1724 (C=O); ^1H NMR (400 MHz, DMSO- d_6): 8.04 (s, 1H), 5.07 (s, 2H, CH₂), 3.43 (s, 3H, CH₃), 3.20 (s, 3H, CH₃); Analytical Calculated/Found: C: 42.12/42.09, H: 3.53/3.49, Cl: 13.81/13.77, N: 21.83/21.79.

Synthesis of N-(2-aminophenyl)-2-(1,3-dimethyl-2,6-dioxo-2,3-dihydro-1h-purin-7(6h)-yl) acetamide (III)

Compound II (0.6416 g, 2.50 mmol) was dissolved in 50 mL of dichloromethane at -10°C for 1 h with stirring. Then, AlCl_3 (1.00 g) was added, and the mixture was stirred for another hour. Subsequently, this solution was slowly added dropwise over 30 minutes onto excessively diluted o-phenylenediamine (1.35 g, 12.48 mmol, and 100 mL of dichloromethane) at -10°C and stirred for 48 h. The resulting mixture was filtered through filter paper. The solid material was poured into methanol. The solid material insoluble in methanol was filtered and dried.

III: MA = 328.33 g, Color: Red solid; Yield: 0.5089 g (62%); Melting Point: $170-174^{\circ}\text{C}$; FTIR (ATR, cm^{-1}) peaks: 2845, 2915 (C-H_{aliphatic}), 3253 (C-H_{aromatic}), 1641 (C=N_{xanthine}), 3252 (N-H_{amide}), 3330 (NH₂), 1702, 1732 (C=O); ^1H NMR (400 MHz, DMSO- d_6) δ (ppm): 3.20 (s, 3H), 3.44 (s, 3H), 5.09

(s, 2H), 5.51 (s, 2H), 6.85 (m, 2H), 7.00 (m, 2H), 8.07 (s, 1H), 8.23 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm): 168.5 (1C), 155.0 (1C), 151.3 (1C), 150.0 (1C), 149.8 (1C), 148.5 (1C), 125.6 (1C), 125.4 (1C), 125.1 (1C), 119.0 (1C), 114.5 (1C), 107.5 (1C), 34.5 (1C), 30.8 (1C), 29.1 (1C); Anal. Calculated/Found: C: 54.87/54.85, H: 4.91/4.89, N: 25.60/25.58.

Synthesis of n-(4-aminophenyl)-2-(1,3-dimethyl-2,6-dioxo-2,3-dihydro-1h-purin-7(6h)-yl) acetamide (IV)

Compound II (0.6416 g, 2.50 mmol) was dissolved in 50 mL of dichloromethane at -10°C for 1 h with stirring. Then, AlCl_3 (1.00 g) was added and stirred for another hour. Subsequently, this solution was slowly added dropwise over 30 minutes onto excess dilute p-phenylenediamine (1.35 g, 12.48 mmol, and 100 mL dichloromethane) at -10°C and stirred for 48 h. The resulting mixture was filtered through filter paper at the end of the reaction. The solid material insoluble in methanol was filtered and dried.

IV: MA= 328.33 g, Color: light blue-gray solid; Yield: 0.5335 g (65%); Melting Point: $\geq 200^{\circ}\text{C}$ (dec.); FTIR (ATR, cm^{-1}) peaks: 2851, 2944 (C-H_{aliphatic}), 3027 (C-H_{aromatic}), 1634 (C=N_{xanthine}), 3225 (N-H_{amide}), 3325 (NH₂), 1699 (C=O); ^1H NMR (400 MHz, DMSO- d_6) δ (ppm): 3.21 (s, 3H), 3.45 (s, 3H), 5.09 (s, 2H), 5.51 (s, 2H), 6.70 (d, 2H), 7.00 (d, 2H), 8.00 (s, 1H), 8.09 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm): 168.4 (1C), 155.0 (1C), 151.3 (1C), 149.8 (1C), 148.5 (1C), 144.2 (1C), 128.6 (1C), 122.5 (2C), 116.7 (2C), 107.5 (1C), 34.4 (1C), 30.8 (1C), 29.1 (1C); Analyzed/Found: C: 54.87/54.84, H: 4.91/4.88, N: 25.60/25.57.

The synthesis of N,N',N''-(((1E,1'E,1''E)-(((1,3,5-triazin-2,4,6-triyl)tris(oxy))tris(benzene-4,1-diyl)) tris(methanediyl))tris(azanediyl)) tris(benzene-2,1-diyl))tris(2-(1,3-dimethyl-2,6-dioxo-2,3-dihydro-1h-purin-7(6H)-yl)acetamide) (ACL1)

Compound III (0.10 g, 0.30 mmol) is dissolved in 50 mL of ethanol. Then, TRIPOD (0.044 g, 0.10 mmol) is added, and the mixture is stirred at 85°C for 2 h under a reflux condenser. At the end of the reaction, the solvent is evaporated under vacuum. The resulting solid is recrystallized from a mixture of ethanol and petroleum ether.

ACL1: MA = 1372.32 g, Color: Red solid; Yield: 0.1043 g (76%); Melting Point: $185-188^{\circ}\text{C}$; FTIR (ATR, cm^{-1})

peaks: 2910, 2970 (C-H_{aliphatic}), 3023, 3102 (C-H_{aromatic}), 1567 (C=N_{triazine}), 1626 (C=N_{xanthine}), 1608 (C=N_{imine}), 3211 (N-H_{amide}), 1215 (C-O_{phenolic}), 1698, 1737 (C=O); ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 3.20 (s, 9H), 3.24 (s, 6H), 3.44 (s, 9H), 6.85 (dd, 6H), 7.00 (dd, 6H), 7.47 (m, 6H), 7.76 (m, 6H), 8.06 (s, 3H), 8.26 (s, 3H), 8.38 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ (ppm): 182.3 (3C), 168.5 (3C), 160.5 (3C), 155.0 (3C), 151.4 (3C), 151.1 (3C), 149.8 (3C), 148.5 (3C), 147.0 (3C), 132.3 (3C), 130.7 (6C), 129.2 (3C), 129.1 (3C), 126.0 (3C), 123.5 (3C), 119.0 (3C), 116.1 (6C), 107.5 (3C), 34.5 (3C), 30.8 (3C), 29.1 (3C); Anal. Calculated/Found: C: 60.39/60.35, H: 4.19/4.15, N: 21.43/21.39.

Synthesis of transition metal (Mn²⁺, Co²⁺, Ni²⁺, and Cu²⁺) complexes of ACL1 ligand (ACC1-ACC4)

ACL1 (0.06 g, 0.04 mmol) was dissolved in 50 mL of ethanol, and then MCl₂.nH₂O (0.12 mmol) (M= Mn²⁺, Co²⁺, Ni²⁺, and Cu²⁺) was added. The mixture was stirred at 80°C for 3 h, and after cooling to room temperature for 3 h, the pH of the solution was adjusted to 6 by adding 0.10 M NaOH solution. It was further kept in a water bath at 45°C for 1 hour. The resulting solid precipitate was filtered off and dried.

ACC1: MA= 1749.86 g, Color: Dark brown solid; μ_{eff}: 1.79 B.M.; Yield: 0.0511 g (73%); Melting Point: ≥250°C (Dec.); FTIR (ATR, cm⁻¹) peaks: 3055 broad (C-H_{aliphatic}), 3194, (C-H_{aromatic}), 1557 (C=N_{triazine}), 1647 (C=N_{xanthine}), 1609 (C=N_{imine}), 3345 (N-H_{amide}), 1694, 1737 (C=O); Calculated/ Found Analysis: C: 47.36/47.33, H: 3.28/3.25, Cl: 12.16/12.13, Mn: 9.42/9.39, N: 16.81/16.78.

ACC2: MA= 1761.84 g, Color: Black solid; μ_{eff}: 3.89 B.M.; Yield: 0.0529 g (75%); Melting Point: ≥250°C (Dec.); FTIR (ATR, cm⁻¹) peaks: 3062 broad (C-H_{aliphatic}), 3151 (C-H_{aromatic}), 1564 (C=N_{triazine}), 1645 (C=N_{xanthine}), 1609 (C=N_{imine}), 3380 broad (N-H_{amide}), 1209 (C-O_{phenolic}), 1698, 1736 (C=O); Anal. Calculated/Found: C: 47.04/47.02, H: 3.26/3.24, Cl: 12.07/12.05, Co: 10.03/10.01, N: 16.70/16.68.

ACC3: MA= 1761.12 g, Color: Light brown solid; μ_{eff}: 2.85 B.M.; Yield: 0.0507 g (72%); Melting Point: ≥250°C (Dec.); FTIR (ATR, cm⁻¹) peaks: 3062 broad (C-H_{aliphatic}), 3140 (C-H_{aromatic}), 1568 (C=N_{triazine}), 1644 (C=N_{xanthine}), 1608 (C=N_{imine}), 3305 broad (N-H_{amide}), 1212 (C-O_{phenolic}), 1695, 1737 (C=O); Anal. Calculated/Found: C: 47.06/47.02, H: 3.26/3.22, Cl: 12.08/12.04, N: 16.70/16.66, Ni: 10.00/9.96.

ACC4: MA= 1775.68 g, Color: Brown solid; μ_{eff}: 1.81 B.M.; Yield: 0.0497 g (70%); Melting Point: ≥250°C (Dec.); FTIR (ATR, cm⁻¹) peaks: 3196 broad (C-H_{aliphatic}) and (C-H_{aromatic}), 1567 (C=N_{triazine}), 1652 (C=N_{xanthine}), 1608 (C=N_{imine}), 3320 broad (N-H_{amide}), 1212 (C-O_{phenolic}), 1698, 1738, (C=O); Anal. Calculated/Found: C: 4p.67/46.65, H: 3.24/3.22, Cl: 1.98/1.96, Cu: 10.74/10.72, N: 16.56/16.54.

Synthesis of N,N',N''-(((1Z,1'Z,1''Z)-((((1,3,5-triazine-2,4,6-triyl)tris(oxo))tris(4-benzene-1-yl))tris(methanilidene))tris(azanilidene)) tris(4-benzene-1-yl))tris(2-(1,3-dimethyl-2,6-dioxo-2,3-dihydro-1H-purin-7(6H)-yl)acetamide) (ACL2)

Compound IV (0.1 g, 0.30 mmol) dissolves in 50 mL of ethanol. TRIPOD (0.044 g, 0.10 mmol) is then added, and the mixture is stirred at 85°C under reflux for 2 h. Upon completion of the reaction, the solvent is evaporated under vacuum. The resulting solid is recrystallized from an ethanol-petroleum ether mixture.

ACL2: MA= 1372.32 g, Color: Orange solid; Yield: 0.1070 g (78%); Melting Point: ≥300°C (Dec.); FTIR (ATR, cm⁻¹) peaks: 2817 (C-H_{aliphatic}), 3035 (C-H_{aromatic}), 1566 (C=N_{triazine}), 1652 (C=N_{xanthine}), 1621 (C=N_{imine}), 3360 broad (N-H_{amide}), 1202 (C-O_{phenolic}), 1698 (C=O); ¹H NMR (400 MHz, DMSO-d₆)δ (ppm): 3.18 (s, 9H), 3.25 (s, 6H), 3.46 (s, 9H), 6.70 (d, 6H), 7.00 (d, 6H), 7.45 (d, 6H), 7.75 (d, 6H), 8.00 (s, 3H), 8.10 (s, 3H), 8.45 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ (ppm): 182.3 (3C), 169.0 (3C), 155.1 (3C), 154.8 (3C), 151.4 (3C), 149.8 (3C), 148.4 (3C), 147.8 (3C), 137.2 (3C), 130.7 (6C), 122.5 (6C), 121.5 (6C), 120.5 (6C), 107.6 (3C), 34.5 (3C), 30.8 (3C), 29.1 (3C); Anal. Calculated/Found: C: 60.39/60.35, H: 4.19/4.15, N: 21.43/21.39, Cr: 13.99/13.95.

Synthesis of transition metal (Mn²⁺, Co²⁺, Ni²⁺, and Cu²⁺) complexes of ACL2 ligand (ACC5-ACC8)

ACL2 (0.06 g, 0.04 mmol) is dissolved in 50 mL of ethanol, and then MCl₂.nH₂O (0.12 mmol) (where M= Mn²⁺, Co²⁺, Ni²⁺, and Cu²⁺) is added to the solution. The mixture is stirred at 80°C for 3 h, and after cooling to room temperature over 3 h, the pH is adjusted to 6 by adding 0.1 M NaOH solution to the solution. It is then left in a water bath at 45°C for an additional hour. The resulting solid precipitate is filtered off and dried.

ACC5: Molecular weight (MW) = 1803.90 g, Color: Black solid; μ_{eff}: 5.82 B.M.; Yield: 0.0512 g (71%); Melting Point: ≥350°C (Dec.); FTIR (ATR, cm⁻¹) peaks: 2920 broad (C-H_{aliphatic}), 3031, 3193 (C-H_{aromatic}), 1595 (C=N_{triazine}),

1675 (C=N_{xanthine}), 1595 (C=N_{imine}), 3317 (N-H_{amide}), 1245 (C-O_{phenolic}), 1694 (C=O); Analyzed/Found: C: 45.90/45.94, H: 3.48/3.52, Cl: 11.75/11.79, Mn: 9.10/9.14, N: 16.27/16.31.

ACC6: MW= 1815.89 g, Color: Black solid; μ_{eff} : 3.77 B.M.; Yield: 0.0530 g (73%); Melting Point: $\geq 350^\circ\text{C}$ (Dec.); FTIR (ATR, cm^{-1}) peaks: 2972 (C-H_{aliphatic}), 3155 (C-H_{aromatic}), 1576 (C=N_{triazine}), 1652 (C=N_{xanthine}), 1598 (C=N_{imine}), 3321 (N-H_{amide}), 1216 (C-O_{phenolic}), 1737 (C=O); Analyzed/Found: C: 45.60/45.64, H: 3.46/3.50, Cl: 11.67/11.71, Co: 9.70/9.74, N: 16.16/16.20.

ACC7: MW= 1815.17 g, Color: Black solid; μ_{eff} : 2.86 B.M.; Yield: 0.0545 g (75%); Melting Point: $\geq 350^\circ\text{C}$ (Dec.); FTIR (ATR, cm^{-1}) peaks: broad (C-H_{aliphatic}), 3136, 3241, 3285 (C-H_{aromatic}), 1579 (C=N_{triazine}), 1652 (C=N_{xanthine}), 1599 (C=N_{imine}), 3339 (N-H_{amide}), 1230 (C-O_{phenolic}), 1737 (C=O); Analyzed/Found: C: 45.63/45.66, H: 3.47/3.50, Cl: 11.69/11.72, N: 16.17/16.20, Ni: 9.67/9.70.

ACC8: MW= 1829.73 g, Color: Yellow solid; μ_{eff} : 1.83 B.M.; Yield: 0.0520 g (71%); Melting Point: 350°C (Dec.); FT-IR (ATR, cm^{-1}) peaks: broad (C-H_{aliphatic}), 3190 (C-H_{aromatic}), 1579 (C=N_{triazine}), 1670 (C=N_{xanthine}), 1598 (C=N_{imine}), 3315 (N-H_{amide}), 1214 (C-O_{phenolic}), 1670, 1736 (C=O); Analyzed/Found: C: 45.26/45.29, H: 3.44/3.47, Cl: 11.60/11.63, Cu: 10.39/10.42, N: 16.05/16.08.

RESULTS and DISCUSSION

In this study, 2,4,6-trichloro-1,3,5-triazine (Cyanuric chloride) was used as the starting material. Cyanuric chloride (CC) was threefold bound to 4-hydroxybenzaldehyde in a benzene medium, according to literature, to obtain "TRIPOD" [27]. Later, theophylline-7-acetic acid (I) was chlorinated by reacting with thionyl chloride in an acetonitrile medium. Chlorinated theophylline-7-acetic acid (II) was reacted by a 1:1 reaction with o-phenylenediamine and p-phenylenediamine, respectively, in the presence of AlCl_3 catalyst in dichloromethane medium. At the end of these reactions, N-(2-aminophenyl)-2-(1,3-dimethyl-2,6-dioxo-2,3-dihydro-1H-purin-7(6H)yl)acetamide (III) and N-(4-aminophenyl)-2-(1,3-dimethyl-2,6-dioxo-2,3-dihydro-1H-purin-7(6H)-yl)acetamide (IV) were obtained. Compounds III and IV were then reacted with TRIPOD, previously synthesized according to the literature, in a 3:1 ratio in an ethyl alcohol medium, resulting in ACL1 and ACL2. Target tripodal trinuclear

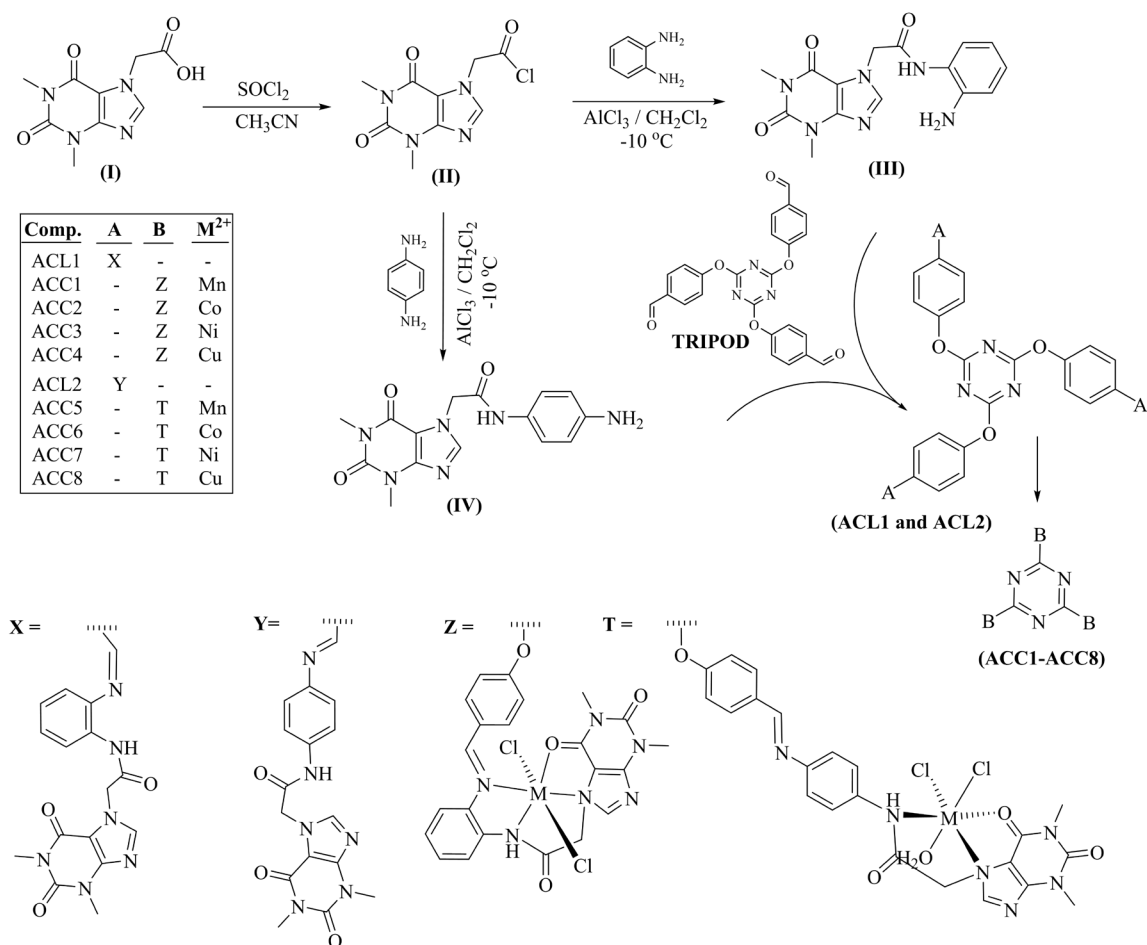
complexes were synthesized by reacting the compounds (ACL1 and ACL2) with $\text{MCl}_2 \cdot n\text{H}_2\text{O}$ (3,00 mmol) ($\text{M} = \text{Mn}^{2+}$, Co^{2+} , Ni^{2+} , and Cu^{2+}) salts in ethanol medium (Scheme 1). The structures of the obtained ligands were elucidated by ^1H NMR, FTIR, elemental analysis, and mass spectrometry methods. The structures of all obtained complexes were characterized by FTIR, magnetic susceptibility, elemental analysis, and ICP-OES methods.

Evaluation of ^1H -NMR spectra

When we obtained the ^1H NMR spectrum (Figure S1) of the theophylline-7-acetic acid compound that we purchased ready-made, we observed H_c at 8.03 ppm for 1H, H_d at 5.07 ppm for 2H, H_a at 3.43 ppm for 3H, H_b at 3.20 ppm for 3H, and a broad signal of H_e protons at 13.25 ppm for 1H. In the ^1H NMR spectrum of the compound II obtained from the reaction with thionyl chloride in an acetonitrile medium (Figure S2), the absence of the H_e proton and the observation of other signals at the same positions proved that the hydroxyl group had been replaced by a chlorine atom.

When we examined the ^1H NMR spectrum of the compound III synthesized in our study, we observed singlet signals at 3.44 ppm and 3.20 ppm corresponding to total 6 H, respectively, for signals H_a and H_b , a singlet signal at 5.09 ppm corresponding to 2H for signal H_d , a singlet signal at 5.91 ppm corresponding to 2 H for H_h , multiplet signals observed at 6.85 and 7.00 ppm corresponding to a total of 4 H for H_g and H_f , a singlet signal at 8.07 ppm corresponding to 1H for H_c , and a broad band observed at 8.23 ppm corresponding to 1H for H_e , which proved that o-phenylenediamine is bonded to the carbonyl carbon of the theophylline-7-acetic acid (Figure S3).

When we examined the ^1H NMR spectrum of the compound IV synthesized in our study, the signals observed as a singlet at 3.45 and 3.21 ppm for H_a and H_b correspond to 6 H, respectively, the signal observed as a singlet at 5.09 ppm for H_d corresponds to 2 H, the signal observed as a singlet at 5.51 ppm for H_h corresponds to 2 H, the signals observed as a doublet at 6.70 and 7.00 ppm for H_g and H_f correspond to a total of 4 H, respectively, the signal observed as a singlet at 8.09 ppm for H_c corresponds to 1 H, and the signal observed as singlet at 8.00 ppm for H_e corresponds to 1 H, proved that p-phenylenediamine is attached to the carbonyl carbon of the theophylline-7-acetic acid (Figure S4). The signals observed in the range of 107.5-150.0 ppm for



Scheme 1. Synthetic route of both ligands and their all complexes.

aromatic carbons and in the range of 151.3-168.5 ppm for carbonyl carbons are another important evidence for the successful synthesis of compound III and IV (Figure S5 and Figure S6).

In this study, the ¹H NMR spectra of ACL1 and ACL2 were examined. The disappearance of the signals at 5.09 ppm and 5.51 ppm, which correspond to compounds III and IV, was observed. Instead, new singlet signals appeared at 8.38 ppm and 8.45 ppm, corresponding to the H_h protons of the imine groups (3H each). Additionally, multiplet signals at 7.47/7.45 ppm and 7.76/7.75 ppm, corresponding to H_i and H_j protons from TRIPOD (6H each), were detected. These spectral changes provide clear evidence for the formation of the tripodal ligands. [26-31]. Additionally, the singlet at 3.20 ppm, the singlet at 5.09 ppm, the singlet at 3.44 ppm, the doublet of the doublet at 6.85 ppm, the doublet of the doublet at 7.00 ppm, the singlet at 8.06 ppm, and the singlet at 8.26 ppm are attributed to the signals H_b, H_d, H_a, H_g, H_f, H_c, and H_e for ACL1, and the singlet corresponding to 9 H at 3.20 ppm, the singlet corresponding to 9 H

at 3.46 ppm, the singlet corresponding to 6 H at 5.09 ppm, the doublet corresponding to 6 H at 6.70 ppm, the doublet corresponding to 6 H at 7.00 ppm, the singlet corresponding to 3 H at 8.00 ppm, and the singlet corresponding to 3 H at 8.10 ppm are attributed to the signals H_a, H_b, H_d, H_g, H_f, H_e, and H_c for ACL2, respectively (Figure 1 and Figure 2).

The signals observed at 119.0 ppm, 125.1 ppm, 114.5 ppm and 149.8 ppm for the C₁₂, C₁₃, C₁₄ and C₁₅ carbons in the ¹³C NMR spectrum of compound III, shifted down to 123.5 ppm, 129.1 ppm, 129.2 ppm and 152.5 ppm for the ACL1 ligand and additional signals belonging to the tripod were observed, indicating that the ACL1 ligand was successfully synthesized (Figure 3). Similarly, the signals observed at 116.7 ppm and 144.2 ppm for the C₁₂ and C₁₃ carbons in the ¹³C NMR spectrum of compound IV, respectively, shifted down to 120.5 ppm and 151.8 ppm for the ACL2 ligand, and additional signals belonging to the tripod were observed, indicating that the ACL2 ligand was successfully synthesized (Figure 4).

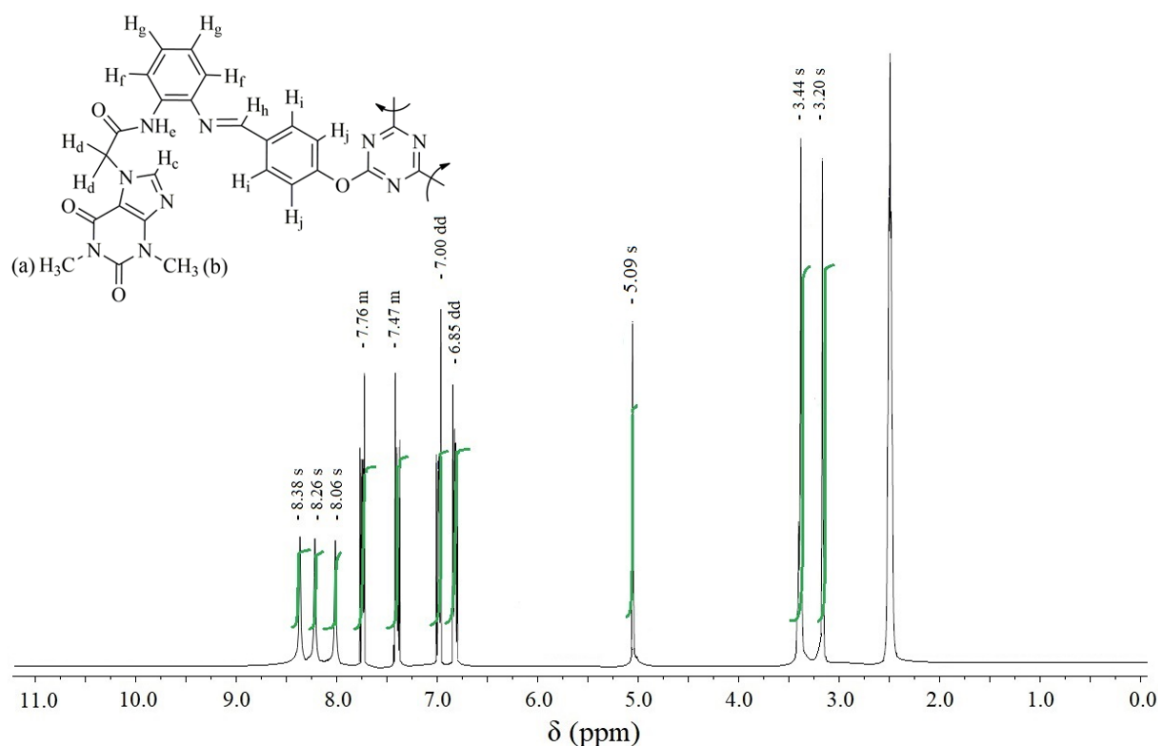


Figure 1. ^1H NMR spectrum of ACL1.

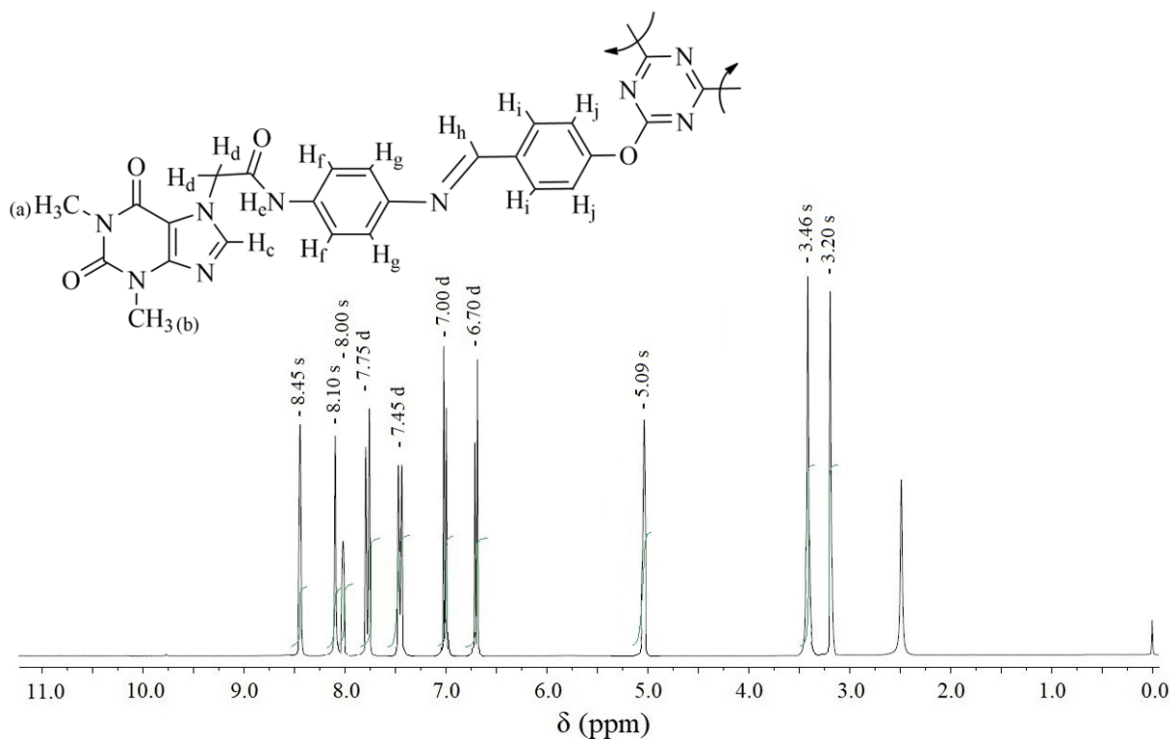


Figure 2. ^1H NMR spectrum of ACL2.

Evaluation of FTIR spectra

When we examined the FTIR spectrum of the compound II synthesized in our study, the shift of the acidic carbonyl $\text{C}=\text{O}$ band belonging to the theophylline-7-acetic acid compound (1732 cm^{-1}) to a lower frequency

(1724 cm^{-1}) is evidence that a chlorine atom is attached to the carbonyl group of the compound I (Figure S7). In the next stage, by binding o-phenylenediamine or p-phenylenediamine to this compound in a 1:1 ratio, compound III and compound IV were obtained. When

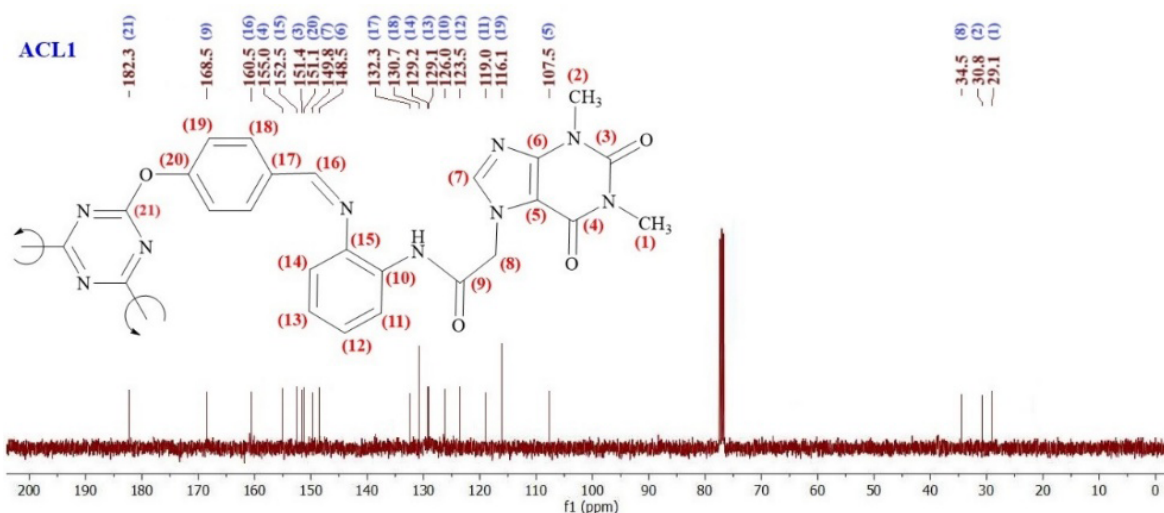


Figure 3. ^{13}C NMR spectrum of ACL1

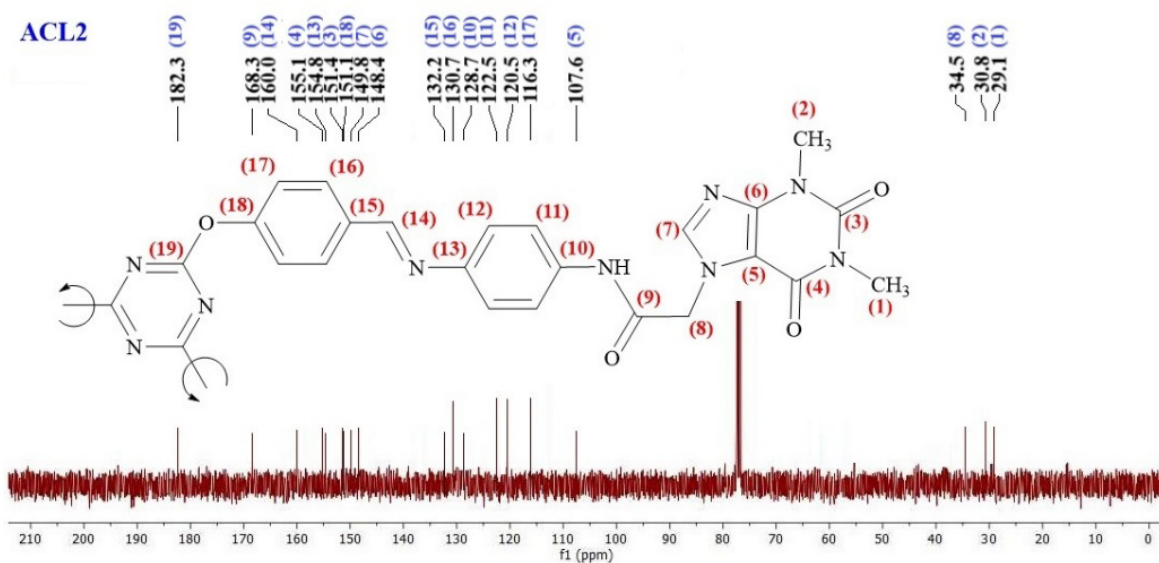


Figure 4. ^{13}C NMR spectrum of ACL2.

we examined the FTIR spectrum of the compound III, the respectively observation of the carbonyl band at 1706 cm^{-1} and 1634 cm^{-1} belonging to the xanthine rings, which is also observed at 1702 cm^{-1} in the FTIR spectrum of compound I, as well as the observation of the stretching band at 3330 cm^{-1} and 3325 cm^{-1} belonging to the amine group of o-phenylenediamine and p-phenylenediamine, respectively and the observation of the amide N-H stretching band at 3253 cm^{-1} , is strong evidence that the o-phenylenediamine or p-phenylenediamine groups are attached to the compound II from only one amino group, that is, unidirectionally (Figure S8 and Figure S9).

In the next stage, the compound III and compound IV were bound trilaterally to TRIPOD to obtain ACL1 and

ACL2, respectively. Evidence for this is the observation of the disappearance of the NH_2 stretching band observed at $3325\text{--}3330\text{ cm}^{-1}$ in our compound III and IV, replaced by the band at $1608\text{--}1621\text{ cm}^{-1}$ belonging to the azomethine ($-\text{C}=\text{N}-$) group, and also the observation of the stretching band at 1566 and 1567 cm^{-1} for the specific triazine ring of TRIPOD, indicating the successful synthesis of the compounds ACL1 and ACL2 (Figure 5 and Figure 6) [28-34].

Tripodal trinuclear complexes (ACC1-ACC8) of ACL1 and ACL2 were obtained as a result of the reaction with $\text{MCl}_2 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Mn}^{2+}$, Co^{2+} , Ni^{2+} , and Cu^{2+}) salts in a 1:3 ratio. When we examine the FTIR spectra of these complexes, the shift of the band belonging to the carbonyl group on the xanthine ring from 1698 cm^{-1} to a lower frequency

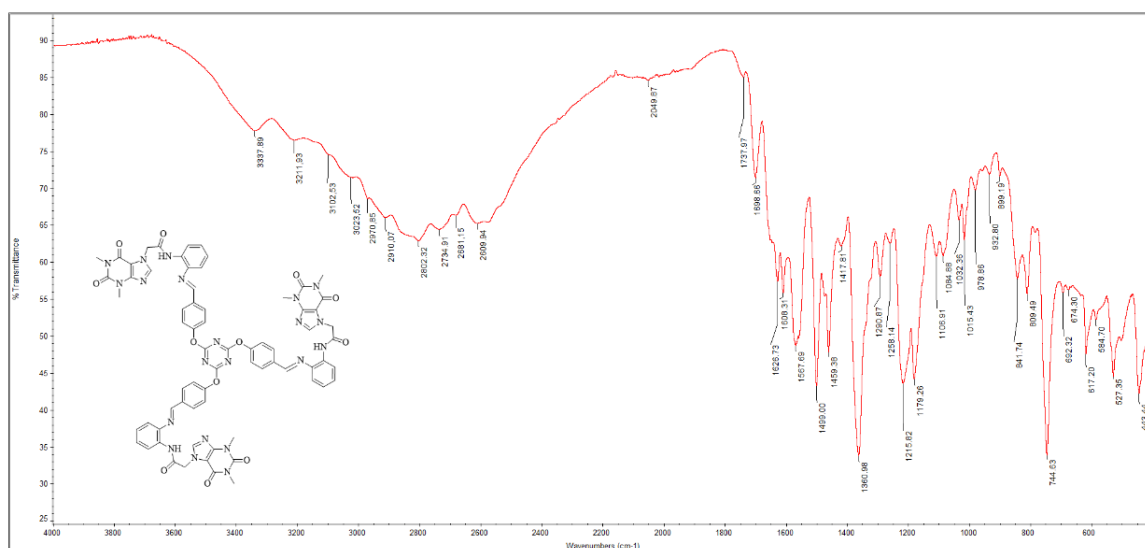


Figure 5. FTIR spectrum of the compound ACL1

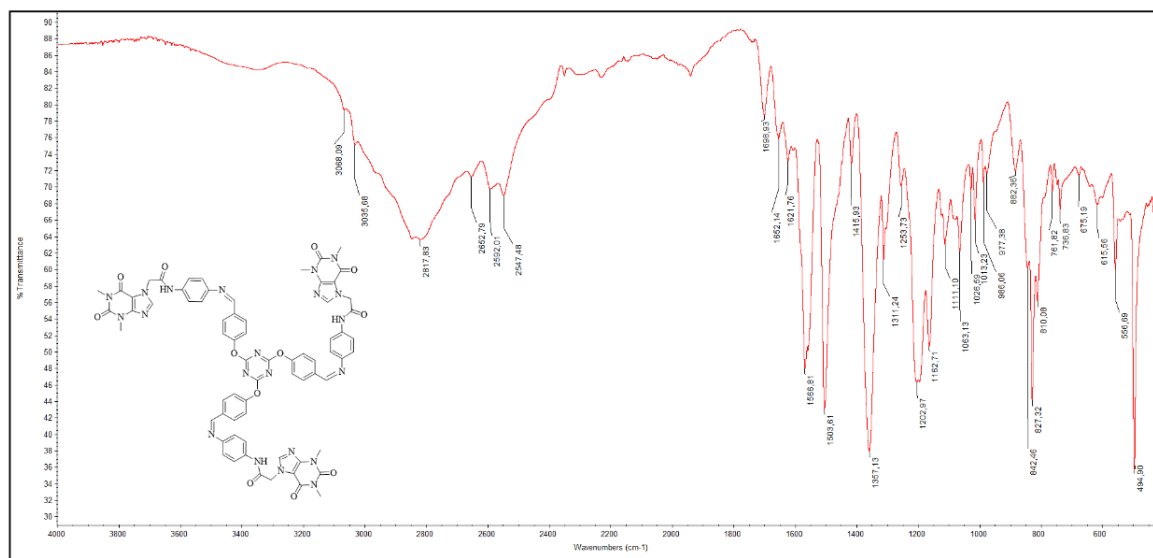


Figure 6. FTIR spectrum of the compound ACL2.

of 1695 cm^{-1} in the complexes, and the observation of the band at $1608\text{--}1609\text{ cm}^{-1}$ for the azomethine group ($\text{C}=\text{N}$) indicate the occurrence of chelation for (ACC1-ACC4). And, the observation of the NH stretching band of the amine group at 3325 cm^{-1} , which is observed as a broad band due to intramolecular H-bonds, as a sharper band in the range of $3317\text{--}3339\text{ cm}^{-1}$ in the complex structures (ACC5-ACC8), indicate coordination of this group to the metal center and thus the occurrence of chelation (Figure S10-Figure S17).

The evaluation of magnetic susceptibility results

In this study, magnetic susceptibility values of all tripodal trinuclear complexes synthesized were measured at room temperature using a Gouy balance to determine

their molecular geometries. The molar magnetic susceptibility (μ_{eff}) values of all complexes in terms of Bohr magneton (B.M.) are given in "Experimental Section".

The tripodal trinuclear complexes ACC1-ACC4 were obtained by reacting the ligand-coded ACL1 with $\text{MCl}_2 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Mn}^{2+}$, Co^{2+} , Ni^{2+} , and Cu^{2+}) salts in a 1:3 ratio. Paramagnetic measurements of Mn(II) , Co(II) , Ni(II) , and Cu(II) complexes of this ligand yielded magnetic moments of 1.79 B.M. with a $t_{2g}^5 e_g^0$ electron configuration for each Mn(II) ion, 3.89 B.M. with a $t_{2g}^5 e_g^2$ electron configuration for each Co(II) ion, 2.85 B.M. with a $t_{2g}^6 e_g^2$ electron configuration for each Ni(II) ion, and 1.81 B.M. with a $t_{2g}^6 e_g^3$ electron configuration for each

Cu(II) ion. The Mn(II) complex from these complexes was evaluated as low-spin, while Ni(II), Co(II), and Cu(II) complexes couldn't be distinguished as high or low spin due to their electron configurations [23,30,34-39]. From magnetic susceptibility measurements and ICP-OES analysis, we infer that these tripodal complexes have octahedral geometry.

Similarly, we have obtained tripodal trinuclear complexes ACC5-ACC6 by reacting the ligand-coded ACL2 with $MCl_2 \cdot nH_2O$ ($M = Mn^{2+}$, Co^{2+} , Ni^{2+} , and Cu^{2+}) salts in a 1:3 ratio. Paramagnetic measurements of Mn(II), Co(II), Ni(II), and Cu(II) complexes of this ligand yielded magnetic moments of 5.82 B.M. with a $t_{2g}^3 e_g^2$ electron configuration for each Mn(II) ion, 3.77 B.M. with a $t_{2g}^5 e_g^2$ electron configuration for each Co(II) ion, 2.86 B.M. with a $t_{2g}^6 e_g^2$ electron configuration for each Ni(II) ion, and 1.83 B.M. with a $t_{2g}^6 e_g^3$ electron configuration for each Cu(II) ion. The Mn(II) and Co(II) complexes from these complexes were evaluated as high-spin and outer orbital complexes, while Ni(II) and Cu(II) complexes couldn't be distinguished as high or low spin due to their electron configurations [23,28,30,32-39]. From magnetic susceptibility measurements and ICP-OES analysis, we infer that these tripodal complexes also have octahedral geometry [23,30,34-39].

The Evaluation of TGA Results of Some Complexes

In our study, thermogravimetric (TGA) analyses were conducted under N_2 atmosphere with a heating rate of $10^\circ C/min$ in the range of $50-800^\circ C$ to determine the thermal stabilities of some of the complexes we obtained AAC3 and AAC1.

From the thermogravimetric analysis graph of the compound AAC1, it is observed that the decomposition occurs in three steps. In the first step, with a mass loss of 8.50%, the CH_2-CO group on the theophylline moiety separates from the main body as CH_4 and CO groups. The theoretical mass loss at this step is 7.17%. In the second step, with a mass loss of 17.50%, the phenol group attached to the cyanuric chloride center separates from the complex center, separating the complex center from the molecule center. The theoretical mass loss at this step is 18.05%. In the final step, with a mass loss of 49.20%, the ligand groups attached to the nickel center leave the environment. The theoretical mass loss at this step is 49.52%. Since the heating process was terminated at $800^\circ C$, further mass losses could not be observed. FTIR and ICP-OES analysis of the remaining substances from the TGA analysis revealed that the remaining substances after decomposition were cyanuric chloride center and Mn_2O_3 . It is observed that theoretical and experimental data are in good agreement with each other [28-30,32,34,36,38-41]. TGA data of the obtained complexes show that these compounds have very high thermal stability (Figure 7).

Upon examining the thermogravimetric analysis graph of the compound AAC3, it has been observed that decomposition occurs in three stages. In the first stage, with a mass loss of 6.00%, the CH_2-CO group on the theophylline moiety separates from the main body as CH_4 and CO groups. The theoretical mass loss at this stage is 7.17%. In the second stage, with a mass loss of 20.00%, the phenol group attached to the cyanuric chloride center detaches from the molecule, separating

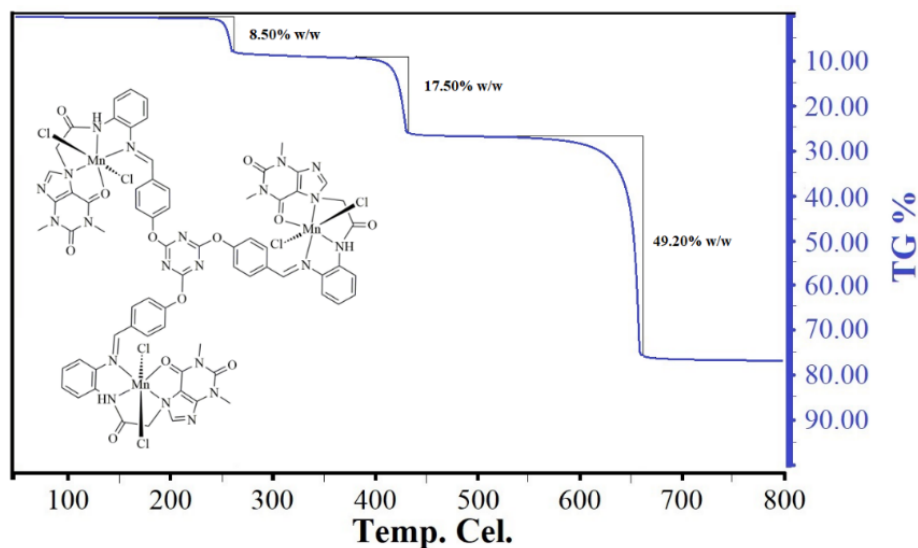


Figure 7. TGA curve of the AAC1 complex.

the complex center from the molecule center. The theoretical mass loss at this stage is 17.94%. In the final stage, with a mass loss of 50.00%, ligand groups attached to the nickel center leave the environment. The theoretical mass loss at this stage is 49.20%. Since the heating process was terminated at 800°C, further mass losses could not be observed. FT-IR and ICP-OES analyses of the remaining substances from the TGA analysis revealed that the remaining substances are cyanuric chloride center and NiO after decomposition (Figure 8). The theoretical and experimental data are in good agreement with each other [28-30,32,34,36,38-41].

CONCLUSION

In this work, two novel s-triazine-based tripodal theophylline ligands (ACL1 and ACL2) were adeptly synthesized and meticulously characterized through the application of elemental analysis, ^1H and ^{13}C NMR, FTIR spectroscopy, and thermogravimetric analysis. Eight novel transition metal (Mn^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+}) complexes (ACC1-ACC8) of these ligands were synthesized, and showed high thermal stability.

Spectroscopic and magnetic data indicated effective metal coordination through azomethine nitrogen, carbonyl oxygen, and phenoxy donor sites, leading to predominantly octahedral coordination environments around the metal ions. Magnetic susceptibility measurements revealed distinct spin states depending

on the ligand environment, particularly highlighting the contrasting inner- and outer-orbital character of the Mn(II) complexes derived from ACL1 and ACL2. Thermogravimetric analyses demonstrated that both ligands and their metal complexes exhibit high thermal stability, supporting the robustness of the s-triazine-based tripodal scaffold.

Overall, this work represents the first report of theophylline-functionalized s-triazine tripodal ligands and their trinuclear transition-metal complexes, bridging coordination chemistry with biologically relevant xanthine derivatives. The structural versatility, thermal stability, and rich magnetic behavior of these complexes suggest that such systems may serve as promising platforms for future studies in bioinorganic chemistry, catalysis, and functional materials. Further investigations focusing on their biological activity and physicochemical applications are currently underway.

Acknowledgment

We acknowledge that this study was financially supported by the Karabuk University Scientific Research Projects Coordinatorship (Project No: KBUBAP-21-YL-082).

Supporting Information

Supporting information is available on [the article's webpage](#) under Supporting File.

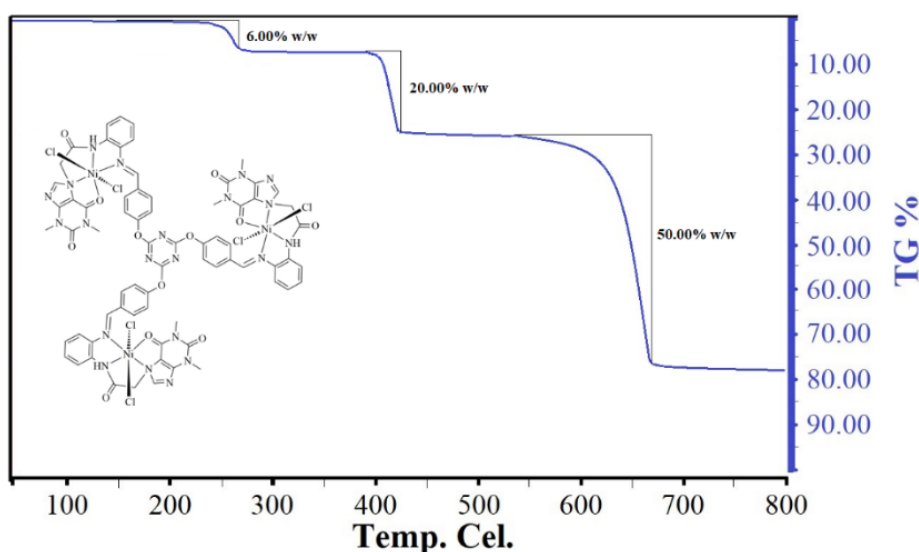


Figure 8. TGA curve of AAC3 complex.

References

1. E.M. Smolin, L. Rapoport, *S-Triazines and Derivatives*, Vol. 13, John Wiley & Sons, 2009.
2. A. Schwarzer, T. Saplinova, E. Kroke, Tri-s-triazines (s-heptazines)—From a “mystery molecule” to industrially relevant carbon nitride materials, *Coord. Chem. Rev.*, 257 (2013) 2032-2062.
3. N. Kushwaha, C. Sharma, The chemistry of triazine isomers: Structures, reactions, synthesis and applications, *Mini-Rev. Med. Chem.*, 20 (2020) 2104-2122.
4. B. Salaković, S. Kovačević, M. Karadžić Banjac, S. Podunavac-Kuzmanović, L. Jevrić, I. Pajčin, J. Grahovac, New perspective on comparative chemometric and molecular modeling of antifungal activity and herbicidal potential of alkyl and cycloalkyl s-triazine derivatives, *Processes*, 11 (2023) 358.
5. F.G. Zhang, Z. Chen, X. Tang, J.A. Ma, Triazines: Syntheses and inverse electron-demand Diels–Alder reactions, *Chem. Rev.*, 121 (2021) 14555-14593.
6. E.T. Parker, *Scope and Influence of Enhanced Triazine Degradation in US Soils*, 2017.
7. S. Klementova, L. Keltnerova, Triazine herbicides in the environment, in: *Herbicides, Physiology of Action, and Safety*, 2015, pp. 71-96.
8. T.W. Baumann, Some thoughts on the physiology of caffeine in coffee: and a glimpse of metabolite profiling, *Braz. J. Plant Physiol.*, 18 (2006) 243-251.
9. S. Budavari, M.J. O’Neil, A. Smith, P.E. Heckelman, *The Merck Index*, Vol. 11, Merck, Rahway, NJ, USA, 1989.
10. S. Scheindlin, A new look at the xanthine alkaloids, *Mol. Interv.*, 7 (2007) 236.
11. S.O. Kayaalp, *Rasyonel Tedavi Yönünden Tıbbi Farmakoloji*, 1. Cilt, Hacettepe-Taş Kitapçılık, 2000.
12. E. McFadden Jr., Methylxanthines in the treatment of asthma: The rise, the fall, and the possible rise again, *Ann. Intern. Med.*, 115 (1991) 323-324.
13. C. Persson, A. Draco, Xanthines as airway anti-inflammatory drugs, *J. Allergy Clin. Immunol.*, 81 (1988) 615-617.
14. P. Sullivan, Anti-inflammatory effect of low-dose oral theophylline in atopic asthma, *Lancet*, 343 (1994) 1512.
15. Y. Cevik, C. Kavalci, M. Daş, S. İzdeş, Severe theophylline intoxication, rhabdomyolysis, disseminated intravascular coagulopathy and death, *J. Emerg. Med. Case Rep.*, 1 (2010) 24-27.
16. M.W. Edmunds, M.S. Mayhew, *Pharmacology for the Primary Care Provider*, Elsevier Health Sciences, 2013.
17. M. Caraglia, M. Marra, G. Giuberti, A.M. D’Alessandro, S. Beninati, A. Lentini, S. Pepe, M. Boccellino, A. Abbruzzese, Theophylline-induced apoptosis is paralleled by protein kinase A-dependent tissue transglutaminase activation in cancer cells, *J. Biochem.*, 132 (2002) 45-52.
18. M. Mabed, S. Aref, M. Fouda, S. El-Sharawy, Chlorambucil plus theophylline vs chlorambucil alone as a front line therapy for B-cell chronic lymphatic leukemia, *Leuk. Lymphoma*, 45 (2004) 2029-2035.
19. Ş. Uysal, Z.E. Koç, Synthesis and characterization of dopamine substitute tripodal trinuclear complexes capped s-triazine complexes: Investigation of their thermal and magnetic properties, *J. Mol. Struct.*, 1109 (2016) 119-126.
20. Ş. Uysal, H.I. Uçan, The synthesis and characterization of 2,4,6-tris(3,4-dihydroxybenzimidino)-1,3,5-triazine and its complexes, *J. Incl. Phenom. Macrocycl. Chem.*, 65 (2009) 403-409.
21. Ş. Uysal, A. Coşkun, The novel triazine cored tripodal and trinuclear Schiff base-oxime metal complexes: Their magnetic properties and thermal decompositions, *J. Heterocycl. Chem.*, 48 (2011) 936-941.
22. Ş. Uysal, Synthesis and characterization of a new dioxime: Thermal and magnetic behavior of its complexes, *J. Coord. Chem.*, 63 (2010) 2370-2378.
23. Ş. Uysal, A.N. Kurşunlu, The synthesis and characterization of star-shaped metal complexes of triazine cored Schiff bases, *J. Inorg. Organomet. Polym. Mater.*, 21 (2011) 291-296.
24. M. Bevilacqua, V. Giuso, M. Rancan, L. Armelao, C. Graiff, W. Baratta, V. Di Marco, A. Biffis, Coordination chemistry of Ir with chelating ligands containing a xanthine-derived NHC moiety, *Eur. J. Inorg. Chem.*, (2022) e202200484.
25. A.A. El-Habeeb, M.S. Refat, Synthesis, spectroscopic and biological characterizations of metal–theophylline complexes, *Bull. Chem. Soc. Ethiop.*, 38 (2024) 725-738.
26. P. De Hoog, P. Gamez, W.L. Driessen, J. Reedijk, New polydentate ligands from triazine, *Tetrahedron Lett.*, 43 (2002) 6783-6786.
27. D.C. Tahmassebi, T. Sasaki, Synthesis of a new trialdehyde template for molecular imprinting, *J. Org. Chem.*, 59 (1994) 679-681.
28. B. İşi, Ş. Uysal, The synthesis and characterization of trinuclear Schiff base complexes, *J. Incl. Phenom. Macrocycl. Chem.*, 92 (2018) 281-299.
29. Z.E. Koç, Complexes of iron(III) and chromium(III) Schiff bases, *J. Heterocycl. Chem.*, 48 (2011) 769-775.
30. Ş. Uysal, Z.E. Koç, Synthesis and characterization of dendrimeric melamine cored complexes, *J. Hazard. Mater.*, 175 (2010) 532-539.
31. Ş. Uysal, H.I. Uçan, The synthesis and characterization of melamine based Schiff bases, *J. Incl. Phenom. Macrocycl. Chem.*, 65 (2009) 299-304.
32. I.M. Aouled, Ş. Uysal, Investigation of thermal and magnetic properties of dinuclear complexes, *J. Mol. Struct.*, 1280 (2023) 135084.
33. I.M. Aouled, Ş. Uysal, Investigation of dinuclear complexes of triazine compounds, *Synth. Commun.*, 51 (2021) 3642-3655.
34. K. Kıymaz, Ş. Uysal, Synthesis and characterization of dendrimeric s-triazine Schiff bases, *J. Mol. Struct.*, 1271 (2023) 134029.
35. M. Erdogan, K. Kıymaz, H. Tahtaci, Ş. Uysal, Synthesis and characterization of Co(II) and Ni(II) complexes, *J. Coord. Chem.*, 74 (2021) 2508-2533.
36. Ş. Uysal, M. Er, H. Tahtaci, Synthesis and characterization of thiosemicarbazone complexes, *Synth. Commun.*, 46 (2016) 1820-1832.
37. Ş. Uysal, Z.E. Koç, The synthesis and characterization of heteromultinuclear complexes, *J. Mol. Struct.*, 1165 (2018) 14-22.
38. Ş. Uysal, Z.E. Koç, Ş. Çelikkilek, H.I. Uçan, Synthesis of star-shaped macromolecular Schiff base complexes, *Synth. Commun.*, 42 (2012) 1033-1044.
39. A.A. Allothman, M.D. Albaqami, R.A. Alshgari, Synthesis and characterization of azo-dye metal complexes, *J. Mol. Struct.*, 1223 (2021) 128984.
40. Z.E. Erdem Koç, Ş. Uysal, Synthesis and characterization of dendrimeric complexes, *Helv. Chim. Acta*, 93 (2010) 910-919.
41. I.M. Aouled, Ş. Uysal, The synthesis and characterization of s-triazine bridged Schiff base complexes, *J. Mol. Struct.*, 1250 (2022) 131872.