

Synthesis, characterization and analytical study of tellurated Schiff base of bis[2-(3-nitrobenzylideneamino)-5-nitrophenyl]telluride and its complexation reactions with Mn(II), Co(II) and Ni(II) ions

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ABSTRACT

Reaction of 2-amino-5-nitrophenylmercuric chloride with 3-nitro benzaldehyde gave 2-(3-nitrobenzylideneamino)-5-nitrophenylmercuric chloride (1). Reaction of the mercurated Schiff bases 1 with tellurium tetrabromide in 2:1 mole ratio gave the tellurated Schiff bases, bis[2-(3-nitrobenzylideneamino)-5-nitrophenyl] tellurium dibromide (2). Reduction of compound 2 by hydrazine hydrate gave the corresponding telluride, bis[2-(3-nitrobenzylideneamino)-5-nitrophenyl]telluride (3). Complexation reactions of equilibrium mole ratios compound 3 with MnCl₂.4H₂O, CoCl₂.6H₂O and NiCl₂.6H₂O gave the corresponding complexes, i.e compounds 4-6, respectively. All the prepared compounds were characterized by elemental analysis, conductivity measurements and ¹H and ¹³C NMR, FT-IR and UV-visible spectroscopic data. These data suggested that the compound 3 coordinate with metal ions as tridentate ligand. The molar conductivity study indicated compounds 1-3 are neutral and behave as non-electrolytes in DMSO solvent at room temperature while compounds 4-6 behave as 1:1 electrolytes in the same conditions. The molar ratio method was used to determine metal-ligand ratio, which was found as 1:1, metal: ligand. The thermal analysis of compounds 2 and 3 were also investigated and discussed.

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1. Introduction

In recent decades, there has been a growing interest in studying the organotellurium compounds containing nitrogen and tellurium atoms. One of these compounds represent in organotellurium compounds which contain azomethine groups (CH=N) which their compounds called Schiff bases [1-3]. Several attempts to prepare tellurated Schiff bases by direct reacting of Schiff bases with tellurium tetrabromide were failed and leading to ionic products [4,5]. Singh and McWhinnie [6] prepared {4-substituted-2-(phenylimino-methyl)phenyl}tellurium tribromide by reacting {4-substituted-2-(phenylimino-methyl) phenyl}mercuric chloride with tellurium tetrabromide which in turn reduced to the corresponding ditellurides by hydrazine hydrate. Menone *et al.* [7] prepared a novel of chiral carbon compounds having an azomethine groups in *ortho*-position to tellurium atom by reaction of bis(2-formylphenyl)telluride or 2-butyl-telluro benzaldehyde with 1-phenylethylamine. Al-Rubaie *et al.* [8] reported the synthesis of a new series of tellurated Schiff bases compounds of formula Ar₂TeBr₂ (Ar: 5-R-C₆H₃N=CHC₆H₅; R: Cl, Br, CH₃O and NO₂) were prepared by reaction of tellurium tetrabromide with the corresponding arylmercuric chloride in

1:2 mole ratio. Reduction of Ar₂TeBr₂ by hydrazine hydrate gave the corresponding diaryltelluride (Ar₂Te).

In last two decades, a good number of publications devoted to polydentate acyclic tellurated Schiff bases ligands were appeared in literatures [9-13]. Recently, Kumar *et al.* [14] synthesized (Te, N and O) type of acyclic Schiff bases of type [4-MeOC₆H₄TeCH₂N=C(CH₃)C₆H₄.2OH] by reacting 2-(4-methoxyphenyltelluro)ethylamine with 2-hydroxyaceto-phenone. The X-ray diffraction study shows that this compound is a tridentate ligand which coordinates through Te, N and O sites when its reaction with Pd(II) ion.

On the other hand, diorganyl tellurides containing azomethine groups formed several complexes with mercury (II) halides [11-15]. Chauhan *et al.* [9] prepared monomeric tellurides 4-R-C₆H₄(SB)Te, where SB: 2-(4,4'-NO₂C₆H₄CH=N C₆H₃-Me); R: H, Me and OMe and reacted with mercuric halides (HgX₂; X: Cl, Br). These telluride interact coordinatively with mercury (II) halides to give 1:2 complexes of type HgX₂[4-RC₆H₄(SB)Te]₂.

Recently, Al-Rubaie *et al.* [16] describes the synthesis of a new series of organotellurium compounds containing azomethine groups. The reaction of 4-aminophenylmercuric chloride with substituted benzaldehyde gave the *p*-mercurated

Schiff bases. Reaction of *p*-mercurated Schiff bases with tellurium tetrabromide in 1:1 and 2:1 mole ratio gave the tellurated Schiff bases, ArTeBr₃ and Ar₂TeBr₂, respectively, where Ar: 4-(2-MeOC₆H₄C=N)C₆H₄, 4-(3-MeOC₆H₄C=N)C₆H₄, 4-(4-MeOC₆H₄C=N)C₆H₄, 4-(2-ClOC₆H₄C=N)C₆H₄, 4-(3-ClOC₆H₄C=N)C₆H₄ or 4-(4-ClOC₆H₄C=N)C₆H₄. Reduction of ArTeBr₃ and Ar₂TeBr₂ by hydrazine hydrate gave the corresponding ditellurides (*i.e.* Ar₂Te₂) and tellurides (*i.e.* Ar₂Te), respectively, in good yields. *Bis*[2-(2-methoxybenzylideneamino)-5-methylphenyl]tellurium dibromide was prepared by reacting tellurium tetrabromide with 2-(2-methoxybenzylideneamino)-5-methylphenylmercuric chloride in 1:2 mole ratio. The dibromide compound was reduced to *bis*[2-(2-methoxybenzylideneamino)-5-methylphenyl]telluride by hydrazine hydrate. *Bis*[2-(2-methoxybenzylideneamino)-5-methylphenyl] telluride has the ability to form complexes with K₂PtCl₄, Na₂PdCl₄, HgCl₂ and CuCl.

Al-Fregi *et al.* [17] synthesized a series of two new tellurated Schiff bases compounds containing azomethine and azo groups, [2-(2-hydroxynaphthylazo)phenyl][2-(2-methoxybenzylideneamino)-5-methylphenyl]telluriumdibromide and [2-(2-hydroxynaphthylazo)-5-nitrophenyl][2-(2-methoxybenzylideneamino)-5-methylphenyl]tellurium dibromide by reacting reaction of 2-(2-methoxybenzylideneamino)-5-methylphenyltellurium tribromide with 2-(2-hydroxynaphthylazo)phenyl mercuric chloride, and 2-(2-hydroxynaphthylazo)-5-nitrophenyl mercuric chloride, respectively, gave the corresponding unsymmetrical diaryltellurium dibromide which were reduced by sodium metabisulfite in two phases reduction system.

Al-Fregi and Shabeeb [18] synthesized of tellurated Schiff base namely 4-(4-*N*, *N*-dimethylaminobenzylideneamino) phenyltellurium tribromide by reaction of ethanoic solutions of 4-aminophenylmercuric chloride with 4-*N,N*-dimethyl aminobenzaldehyde then with tellurium tetrabromide.

In the present work, attempts will be made to prepare a new organotellurium compound containing azomethine groups (CH=N) namely *bis*[2-(3-nitrobenzylideneamino)-5-nitrophenyl]telluride. Furthermore, the ligand properties for the prepared telluride after complexation reactions and some analytical information will be explored with several metal ions such as Mn(II), Co(II) and Ni(II).

2. Experimental

2.1. Reagents and chemicals

All chemicals used in this work were supplied from the commercial sources by famous chemical companies and directly used without further purification. Bromine, carbon tetrachloride, dichloromethane, hydrazine hydrate, and mercuric acetate were supplied by British Drug House (BDH). Absolute ethanol, anhydrous calcium chloride, chloroform, copper (II) chloride, 3-nitrobenzaldehyde, tellurium 99.5%, *p*-toluenesulfonic acid were supplied from Fluka company. Argon gas 99.995% was purchased from Jordan Gases Company. Dimethyl sulfoxide was supplied from Reidal de Hien Company.

Tellurium tetrabromide which used in the present work was prepared by a literature method [19]. 3-Amino-5-nitrophenyl mercuric chloride was prepared by the literature method [20]. All the prepared compounds gave the correct melting points and infrared spectra.

2.2. Purification of solvents

All the reagents used were of analar or chemical pure grade. The solvents were obtained from commercial sources and are analytically pure solvents. Some solvents such as dioxane, ethanol and chloroform were cautiously purified and drying according to literature methods and were kept over

molecular sieve type A₄ and stored in clean dark containers [21,22].

2.3. Physical measurements

Melting or decompositions points of all solid compounds were determined by using a Gallenkamp Thermo point apparatus and are uncorrected. Elemental analysis for carbon, hydrogen and nitrogen were performed at Al Al-Bayt University, Al-Mafraq, Jordan using a Euro vector EA 3000A Elemental Analysis (Italy). Infrared spectra for the synthesis compounds were recorded as KBr disc using a FT-IR spectrophotometer SHIMADZU model 8400S (Japan) in range 4000-400 cm⁻¹ at Department of Chemistry, College of Science, University of Basra. UV-Vis spectra for the synthesized compounds were recorded at Department of Chemistry, College of Science, University of Basra by using Scan 80D (England) at range 200-800 nm using chloroform as a solvent and 1 cm³ pathway quartz cells. ¹H and ¹³C NMR spectra were recorded at Al Al-Bayt University, Jordan by using a Bruker 300 MHz (Germany). Chemical shift of all ¹H and ¹³C NMR spectra were recorded in δ (ppm) unit downfield from the internal reference tetramethylsilane (TMS), using CDCl₃ solvent. The thermogravimetric analysis (TGA) curves were recorded on a TGA Q50 V20.13 Build 39 model Universal V4.5A instruments. The instrument was pre-calibrated with (CaC₂O₄·6H₂O) as standard material. All measurements were carried out under nitrogen atmosphere, by rate (50 °C/min). The molar conductivity for some synthesized compounds were measured in 1×10⁻³-1×10⁻⁵ M solutions of dimethyl sulfoxide solvent at room temperature using a Konduktoskop model 365B using standard conductivity cell with constant equal to 0.81 cm⁻¹.

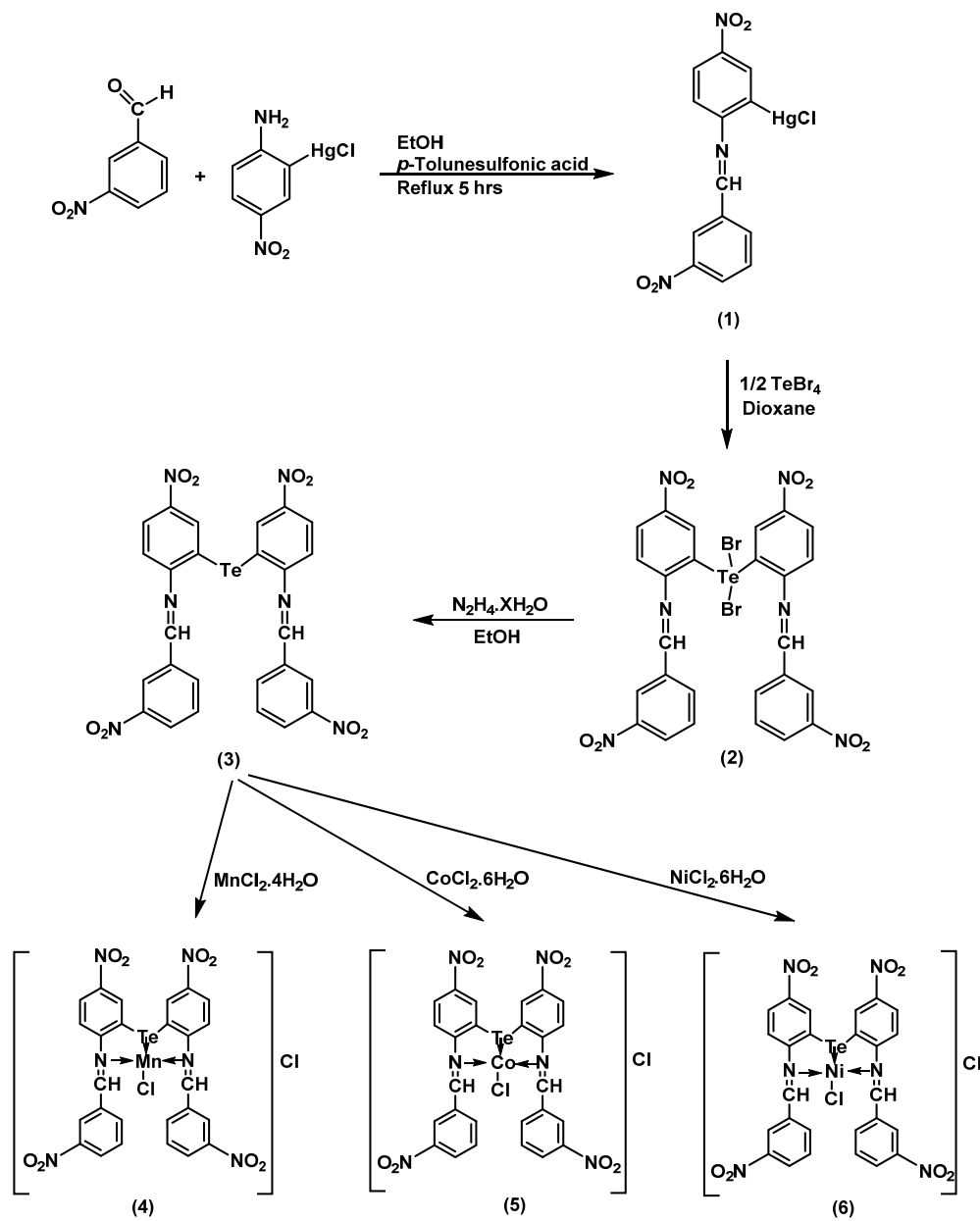
2.4. Synthesis

2.4.1. Synthesis of 2-(3-nitrobenzylideneamino)-5-nitrophenylmercuric chloride (1)

A mixture of 3-amino-5-nitrophenylmercuric chloride (5.06 g, 10.00 mmol) in 50 mL of absolute ethanol and 3-nitrobenzaldehyde (1.51 g, 10.00 mmol) in 50 mL of absolute ethanol containing 0.1 g of *p*-toluene sulfonic acid was refluxed with stirring for 5 h. After cooling, the precipitate was collected by filtration and washed several times with absolute ethanol. The solid product was twice recrystallized from a mixture of ethanol: chloroform (3:2, v:v) to give a yellowish green solid (Scheme 1). Color: Yellowish green. Yield: 91%. M.p.: 243-245 °C. FT-IR (KBr, v, cm⁻¹): 3068 (w, aromatic C-H), 2931, 2885 (w, aliphatic C-H), 1600 (s, CH=N), 1518(s, asymmetrical NO₂), 1498-1412 (s, aromatic C=C), 1265(s, C-N), 1118 (s, C-O). ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.30-8.05 (m, 7H, Ar-H), 8.06 (s, 1H, CH=N). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 164.00 (C7), 160.16 (C6), 149.28 (C10), 148.48 (C3), 135.86 (C13), 133.75 (C8), 130.95 (C12), 126.87 (C11), 125.07 (C2), 125.71 (C4), 124.83 (C9), 121.68 (C5), 118.32 (C1). Anal. calcd. for C₁₃H₈ClHgN₃O₄: C, 30.84; H, 1.59; N, 8.30. Found: C, 30.60; H, 1.51; N, 8.09 %. UV/Vis (CHCl₃, λ_{max}, nm, (ε, M⁻¹. cm⁻¹)): 213 (5250), 380 (2120). Λ_m (S.m².mol⁻¹): 29.1.

2.4.2. Synthesis of bis[2-(3-nitrobenzylideneamino)-5-nitrophenyl] tellurium dibromide (2)

A mixture of tellurium tetrabromide (0.89 g, 2.00 mmol) and 3-(3-nitrobenzylideneamino)-5-nitrophenyl mercuric chloride (2.02, 4.00 mmol) in 50 mL of dry dioxane was refluxed with stirring for 6nh under argon gas atmosphere. The resulting solution was filtered hot and cooled to room temperature. On cooling, a 2:1 complex of dioxane and mercuric halides was separated as white plates. This complex was filtered off.



Scheme 1

The filtrate solution was poured into 300 mL of distilled ice-water to obtain a brown solid immediately. The resulting precipitate was collected by filtration. Recrystallization of the product from a mixture of ethanol: chloroform (4:1, v:v) gave a yellowish brown solid (Scheme 1). Color: Yellowish brown. Yield: 77%. M.p.: 255-256 °C. FT-IR (KBr, ν , cm⁻¹): 3071 (w, aromatic C-H), 2928, 2889 (w, aliphatic C-H), 1610 (s, CH=N), 1520 (s, asymmetrical NO₂), 1500-1411 (s, aromatic C=C), 1260 (s, C-N), 1190 (s, C-O). ¹H NMR (300 MHz, CDCl₃, δ , ppm): 7.30-8.02 (m, 14H, Ar-H), 8.61 (s, 2H, CH=N). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 164.05 (C7, C7'), 160.18 (C6, C6'), 149.28 (C10, C10'), 148.50 (C3, C3'), 135.88 (C13, C13'), 133.76 (C8, C8'), 130.95 (C12, C12'), 126.89 (C11, C11'), 125.06 (C2, C2'), 125.72 (C4, C4'), 124.85 (C9, C9'), 121.70 (C5, C5'), 111.00 (C1, C1'). Anal. calcd. for C₂₆H₁₆Br₂N₆O₈Te: C, 37.72; H, 1.59; N, 10.15. Found: C, 37.49; H, 1.48; N, 10.00 %. UV/Vis (CHCl₃,

λ_{\max} , nm, (ϵ , M⁻¹.cm⁻¹): 213 (5242), 380 (2100). Λ_m (S.m².mol⁻¹): 23.2.

2.4.3. Synthesis of bis[2-(3-nitrobenzylideneamino)-5-nitrophenyl]telluride (3)

Bis[3-(3-nitrobenzylideneamino)-5-nitrophenyl]tellurium dibromide (2) (1.65, 2.00 mmol) was dissolved in 25 mL of ethanol and refluxed. A solution of hydrazine hydrate in ethanol was added drop wisely to the refluxed solution until nitrogen evolution was ceased. The resulting solution was poured into 500 mL of distilled ice-water to afford a yellow solid. The crude product was twice recrystallized from a mixture of ethanol: dichloromethane (3:2, v:v) to obtain a yellow solid (Scheme 1). Color: Yellow. Yield: 69 %. M.p.: 221-222 °C. FT-IR (KBr, ν , cm⁻¹): 3040 (w, aromatic C-H), 2955, 2930 (w, aliphatic C-H), 1600 (s, CH=N), 1520 (s, asymmetrical

NO₂), 1499-1411 (s, aromatic C=C), 1235(s, C-N), 1165 (s, C-O). ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.29-8.01 (m, 14H, Ar-H), 8.61 (s, 2H, CH=N). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 164.77 (C7, C7'), 160.00 (C6, C6'), 149.21 (C10, C10'), 148.49 (C3, C3'), 135.68 (C13, C13'), 133.70 (C8, C8'), 130.87 (C12, C12'), 126.89 (C11, C11'), 125.00 (C2, C2'), 125.67 (C4, C4'), 124.84 (C9, C9'), 121.72 (C5, C5'), 111.00 (C1, C1'). Anal. calcd. for C₂₆H₁₆N₆O₈Te: C, 46.75; H, 2.41; N, 12.58. Found: C, 46.51; H, 2.26; N, 12.12 %. UV/Vis (CHCl₃, λ_{max}, nm, (ε, M⁻¹.cm⁻¹)): 213 (5170), 380 (1995). Λ_m (S.m².mol⁻¹): 5.1.

2.4.4. General method for the synthesis of the complexes with bis[2-(3-nitrobenzylideneamino)-5-nitrophenyl]telluride

Metal salt with hydrate [MnCl₂.4H₂O] (0.39 g, 2.00 mmol); [CoCl₂.6H₂O] (0.47 g, 2.00 mmol); [NiCl₂.6H₂O] (0.47 g, 2 mmol) was dissolved in absolute ethanol (25 mL). The Schiff base, bis[3-(3-nitrobenzylideneamino)-5-nitrophenyl]telluride (2.00 mmol) in hot absolute ethanol (50 mL) was added to the metal salt solution. The mixture was then refluxed for 2 h and then cooled. The precipitate of complexes **4** or **5** or **6** was filtered off and washed with hot ethanol and dried in vacuum over anhydrous CaCl₂ (Scheme 1).

Bis[2-(3-nitrobenzylideneamino)-5-nitrophenyl]tellurid chloromanganese(II) chloride (4): Color: Yellowish green. Yield: 81 %. M.p.: 151-153 °C. FT-IR (KBr, ν, cm⁻¹): 3052 (w, aromatic C-H), 2945, 2892 (w, aliphatic C-H), 1606 (s, CH=N), 1516 (s, asymmetrical NO₂), 1497-1413 (s, aromatic C=C), 1250 (s, C-N). ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.28-8.19 (m, 14H, Ar-H), 8.40 (s, 2H, CH=N). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 164.68 (C7, C7'), 159.91 (C6, C6'), 149.20 (C10, C10'), 148.47 (C3, C3'), 135.70 (C13, C13'), 133.64 (C8, C8'), 130.85 (C12, C12'), 126.77 (C11, C11'), 125.00 (C2, C2'), 125.15 (C4, C4'), 124.81 (C9, C9'), 121.70 (C5, C5'), 111.06 (C1, C1'). Anal. calcd. for C₂₆H₁₆N₆O₈TeMnCl: C, 39.34; H, 2.03; N, 10.59. Found: C, 39.09; H, 1.88; N, 10.54 %. UV/Vis (CHCl₃, λ_{max}, nm, (ε, M⁻¹.cm⁻¹)): 260 (3010), 391 (2000). Λ_m (S.m².mol⁻¹): 32.2.

Bis[2-(3-nitrobenzylideneamino)-5-nitrophenyl]tellurid chlorocobalt (II) chloride (5): Color: Yellowish green. Yield: 85 %. M.p.: 159-161 °C. FT-IR (KBr, ν, cm⁻¹): 3054 (w, aromatic C-H), 2976, 2891 (w, aliphatic C-H), 1612 (s, CH=N), 1516 (s, asymmetrical NO₂), 1500-1416 (s, aromatic C=C), 1259 (s, C-N). ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.28-8.20 (m, 14H, Ar-H), 8.38 (s, 2H, CH=N). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 164.70 (C7, C7'), 159.93 (C6, C6'), 149.22 (C10, C10'), 148.51 (C3, C3'), 135.71 (C13, C13'), 133.68 (C8, C8'), 130.89 (C12, C12'), 126.79 (C11, C11'), 125.06 (C2, C2'), 125.20 (C4, C4'), 124.90 (C9, C9'), 121.71 (C5, C5'), 111.02 (C1, C1'). Anal. calcd. for C₂₆H₁₆N₆O₈TeCoCl: C, 39.14; H, 2.02; N, 10.53. Found: C, 39.20; H, 1.96; N, 10.48 %. UV/Vis (CHCl₃, λ_{max}, nm, (ε, M⁻¹.cm⁻¹)): 262 (4000), 397 (2500). Λ_m (S.m².mol⁻¹): 30.1.

Bis[2-(3-nitrobenzylideneamino)-5-nitrophenyl]tellurid chloronickel (II) chloride (6): Color: Yellowish green. Yield: 80%. M.p.: 147-149 °C. FT-IR (KBr, ν, cm⁻¹): 3066 (w, aromatic C-H), 2971, 2885 (w, aliphatic C-H), 1615 (s, CH=N), 1517 (s, asymmetrical NO₂), 1499-1414 (s, aromatic C=C), 1271 (s, C-N). ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.28-8.18 (m, 14H, Ar-H), 8.39 (s, 2H, CH=N). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 164.68 (C7, C7'), 159.91 (C6, C6'), 149.18 (C10, C10'), 148.50 (C3, C3'), 135.70 (C13, C13'), 133.60 (C8, C8'), 130.86 (C12, C12'), 126.77 (C11, C11'), 125.01 (C2, C2'), 125.18 (C4, C4'), 124.87 (C9, C9'), 121.70 (C5, C5'), 111.03 (C1, C1'). Anal. calcd. for C₂₆H₁₆N₆O₈TeNiCl: C, 39.15; H, 2.02; N, 10.54. Found: C, 39.10; H, 2.01; N, 10.52 %. UV/Vis (CHCl₃, λ_{max}, nm, (ε, M⁻¹.cm⁻¹)): 262 (4000), 397 (2500). Λ_m (S.m².mol⁻¹): 33.1.

3. Results and discussion

2-Amino-5-nitrophenylmercuric chloride was prepared by reacting the same moles ratio of 4-nitro aniline with mercuric

acetate followed by addition of sodium chloride [23]. 2-Amino-5-nitrophenylmercuric chloride was reacted with 1:1 mole ratio 3-nitrobenzaldehyde in absolute ethanol containing a small amount of *p*-toluene sulfonic acid (~0.1 g) to give the mercurated Schiff bases 2-(3-nitrobenzylideneamino)-5-nitrophenylmercuric chloride (**1**). The mercurated Schiff base **1** was obtained as a yellowish green solid. Reaction of mercurated Schiff base, 2-(3-nitrobenzylideneamino)-5-nitrophenylmercuric chloride, with tellurium tetrabromide in 2:1 mole ratio gave bis[2-(3-nitrobenzylideneamino)-5-nitrophenyl]tellurium dibromide (**2**) as yellowish brown solid. Reduction of compound **2** by ethanolic solution of hydrazine hydrate gave bis[2-(3-nitrobenzylideneamino)-5-nitrophenyl]telluride (**3**) as a yellow solid. Complexation reactions of 1:1 mole ratios compound **3** with MnCl₂.4H₂O, CoCl₂.6H₂O and NiCl₂.6H₂O gave the corresponding complexes, i.e compounds **4-6**, respectively, as yellowish green to yellowish brown (Scheme 1).

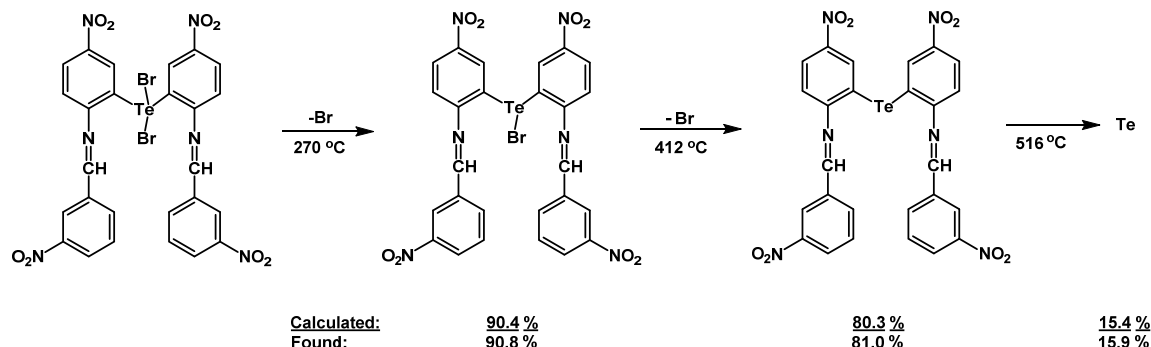
In general, the structural assignment of were based on the elemental analysis of all the prepared compounds **1-6** which are in good agreement with the calculated values and proposed structures. The molar conductivities were determined for compounds **1-3**, and all metal complexes of bis[2-(3-nitrobenzylideneamino)-5-nitrophenyl]telluride solutions (i.e. complexes **4-6**) in 1×10⁻³ M of DMSO solvent at room temperature. The molar conductance of compound **1-6** were found at 29.1, 23.2, 5.1, 32.2, 30.1 and 33.3 ohm⁻¹.cm².mol⁻¹, respectively. This indicates that these compounds behave as 1:1 electrolyte which are in agree well with previous work in DMSO solution [24-26]. This observation may be due to ionic nature of Hg-Cl of compound **1** and the ionic nature of one Te-Br bonds in compound **2** which makes this compound undergo bromine exchange [24-26] and the ionic nature of complexes **4-6** which contain chlorine counter ion. On the other hand, the molar conductance of bis[2-(3-nitrobenzylideneamino)-5-nitrophenyl]telluride (**3**) was found at 5.1 ohm⁻¹.cm².mol⁻¹ which indicate that this compound behave as non-electrolyte in nature.

The IR spectra of all new synthesized compounds **1-6** display common feature in certain region and characteristic bands in the fingerprint and other regions which are in good agreement with previous works [14,27,28]. The IR spectral data of the Schiff bases **1-3** show a strong absorption band at 1626, 1622 and 1619 cm⁻¹, respectively, can be assigned to the ν(CH=N) stretching while in the metal complexes (i.e. compounds **4-6**), the stretching band pointed at the 1596, 1594 and 1601 cm⁻¹, respectively. The ν(CH=N) stretching of compounds **4-6** shifted to lower frequencies (about ~25-18 cm⁻¹), due to the lowering of the CH=N bond order as a result of the metal-nitrogen bond formation. The IR spectra of compounds **1-6** show a weak band in the range 3031-3024 cm⁻¹ due to aromatic C-H stretching [27,28]. Two weak bands were appeared at 2995-2990 and 2930-2918 cm⁻¹ due to asymmetrical and symmetrical stretching of aliphatic C-H bands, respectively [27,28]. Two strong bands appeared in the range 1513-1493 and 1460-1422 cm⁻¹ can be attributed to asymmetrical and symmetrical stretching of aromatic (C=C), respectively, [27,28]. The bands between 1521-1516 and 1338-1320 cm⁻¹ are assigned to the asymmetrical and symmetrical stretching vibrations of the NO₂ group, respectively [3,27,28]. Furthermore, three variable bands between 889-730 cm⁻¹ range can be assigned to aromatic C-H bending [27,28]. The IR spectra of compounds **1-6** show a strong band at 1279-1271 cm⁻¹ range attributed to ν(C-N).

The ¹H NMR spectra of the new synthesized compounds **1-6** were recorded in CDCl₃ solvent. The ¹H NMR spectra of compounds **1-6** show that the signals of the aromatic protons were observed in the range δ 7.28-8.20 ppm. The ¹H NMR spectra of compounds **1-6** gave another evidences for forming azomethine group (-CH=N-) by showing a singlet signal at δ 8.59, 8.61, 8.61, 8.40, 8.38 and 8.39 ppm, respectively.

Table 1. Stability constants, decomposition degrees of complexes 4-6.

Complexes	Value A_s	Value A_m	α	K
L:Mn	0.082	0.084	0.0238	0.1723×10^8
L:Co	0.139	0.168	0.1726	0.2777×10^{10}
L:Ni	0.166	0.173	0.0404	0.5879×10^9

**Scheme 2**

The shift (about 0.2 ppm approximately) between signal of azomethine groups of compounds 4-6 (i.e. the complexes) and compound 3 (i.e. the ligand), which indicated that azomethine groups (-CH=N-) were the coordinate site of ligand and Co^{2+} , Cu^{2+} and Ni^{2+} ions. These values are in agreement with previously reported data [3,27-29].

The ^{13}C NMR spectra of compounds 1-6 were recorded using CDCl_3 . ^{13}C NMR spectra proved further evidences about characterization of synthesized compounds. ^{13}C NMR spectra of compounds 1-6 show the signal of methine carbon atoms around of δ 164 ppm which are in agreement with previous reported works, [3,27-29]. The ^{13}C NMR spectra of compounds 1-6 show a low field signal at δ 160.16, 160.18, 160.00, 159.91, 159.93 and 159.91 ppm, respectively, can be attributed to aromatic carbon atoms which attached with nitrogen atom (CH=N-C, i.e. C6) [3,27-29]. All ^{13}C NMR spectra of compounds show a low field signals at δ 149.28 and 148.48; 149.28 and 148.50; 149.21 and 148.49; 149.20 and 148.47; 149.22 and 148.51; 149.18 and 148.50 ppm, respectively, can be assigned to aromatic carbon atoms which attached with nitro groups (i.e. C10 and C3). The high chemical shifts for these carbon signals attributed to presence of high electronegativity of nitrogen atoms [3,27-29]. The ^{13}C NMR spectra of compound 2-6 show a high field signal around δ 111 ppm can be assigned to tellurated carbon atoms (Te-C) [3,27-29]. The low chemical shift, comparatively, for carbon atoms bearing tellurium atom compared with other aromatic carbon atoms may be attributed to the polarity of Te-C bond [16]. Generally, the other signals between δ 135.68-118.32 ppm can be assigned to aromatic carbon atoms.

The UV-Vis spectrum of compounds was measured at 1×10^{-4} M using chloroform as a solvent. The UV-Vis spectra of compound 1-3 showed two strong bands. The first band at 213 nm with molar extinction (ϵ) ranged $5170\text{-}5250 \text{ M}^{-1}\cdot\text{cm}^{-1}$ is attributed to $\pi \rightarrow \pi^*$ transitions of the aromatic rings [27-29]. The second band observed at 380 nm as a shoulder band (molar extinction $\epsilon = 1995\text{-}2120 \text{ M}^{-1}\cdot\text{cm}^{-1}$ range) which attributed to $\pi \rightarrow \pi^*$ transitions of azomethine groups [27-29]. On the other hand, the UV-Vis spectra of complexes 4-6 showed two strong bands, the first band located at 260, 262 and 261 nm respectively, with molar extinction (ϵ) ranged $3010\text{-}4600 \text{ M}^{-1}\cdot\text{cm}^{-1}$ while the second band observed at 391, 397 and 395 nm with molar extinction ranged $2000\text{-}2900 \text{ M}^{-1}\cdot\text{cm}^{-1}$. Each of the characteristic peak had red shift about 48 nm, respectively, for first band and about 11-17 nm for the second band can be attributed to coordinate azomethine groups with Mn^{2+} , Co^{2+} and Ni^{2+} ions. No *d-d* transitions were

observed for complexes 4-6. This may be due to their overlap with $\pi \rightarrow \pi^*$ of the -CH=N- groups.

To determine the metal-ligand ratio, it has been used the molar ratio method by preparation a series solutions for each complexes 4-6, respectively, by fix the concentrations of metals and change the ligand concentrations then measurement of their absorbencies. It was found that the ratio between metal and ligand for complexes 4-6 is 1:1 [30].

To determination of the stabilities of complexes 4-6, it was calculated the stability of these complexes as following, equation (1):



where α = Decomposition degree, C = Molar concentration stability constant complex (K) can be calculated by the Equation (2).

$$K = [\text{ML}] / [\text{M}][\text{L}] \quad (2)$$

Decomposition degree (α) can be calculated [31] according of the Equation (3).

$$\alpha = A_m - A_s / A_m \quad (3)$$

where A_s = Absorption when concentration of metal and ligand is equal (equivalent point) absorption when there are excess of ligand, A_m = concentrations applied the Equation (3) in (2) is result Equation (4), [32],

$$K = (1 - \alpha) / \alpha^2 C \quad (4)$$

From the Table 1, can be concluded that all complexes 4-6 have high stability. Also, the order of the stability for complexes 4, 5 and 6 are: $5 > 6 > 4$.

The thermogravimetric analysis (TGA) for compounds bis[2-(3-nitrobenzylideneamino)-5-nitrophenyl]tellurium dibromide (2) and bis[2-(3-nitrobenzylideneamino)-5-nitrophenyl] tellu-ride (3) were recorded. For compound 2, according to the thermogravimetric calculations, three decomposition peaks were observed on TG curve, Scheme 2, Figure 1. The first peak at 270 °C due to the eliminating of one bromide ion which attached to tellurium atom while the second peak at 412 °C due to the eliminating the second bromide ion. This data are in well agreement with the previously literatures that prove that one of halides attached to tellurium atom have ionic bond behavior while the other is

covalent bond [33,34]. The third peak at 516 °C can be attributed to the loss of organic groups, forming tellurium metal of percent weight of 15.9% compared with calculated value of 15.4%. The thermogram of compound **3** shows one decomposition peak was observed on TG curve at 495 °C can be attributed to loss all organic groups as volatile species and form tellurium metal of percent weight of 20.5% compared with calculated value of 19.2% (Scheme 3, Figure 2).

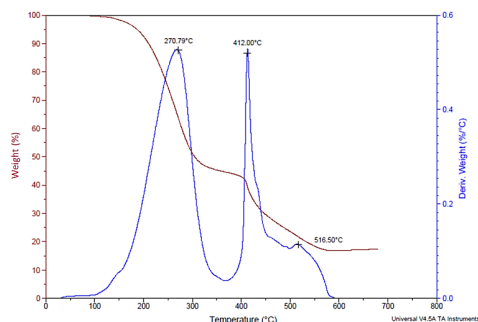


Figure 1. TG curve of compound **2**.

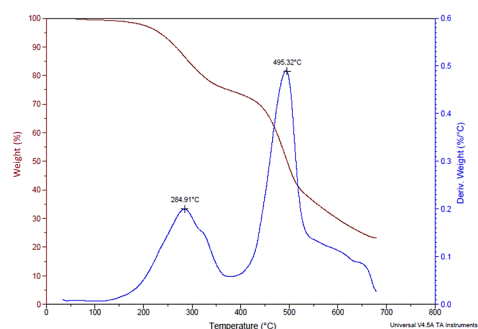
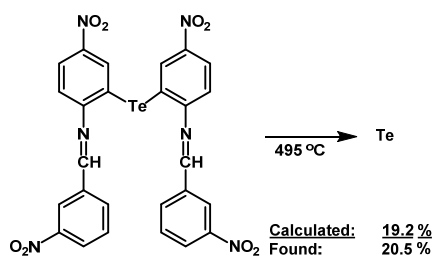


Figure 2. TG curve of compound **3**.



Scheme 3

4. Conclusions

In conclusions, new organotellurium compounds containing azomethine group based on *bis*[2-(3-nitrobenzylideneamino)-5-nitrophenyl] were prepared by convent method. The ligand properties of *bis*[2-(3-nitrobenzylideneamino)-5-nitrophenyl]telluride will be carried out with Co(II), Mn(II) and Ni(II). The spectroscopic data, physical properties, molar conductivity and molar ratio method indicated that the prepared telluride ligand behave as tridentate ligand and forming cationic complexes with metal ions. Thermal analysis data for *bis*[2-(3-nitrobenzylideneamino)-5-nitrophenyl] tellurium dibromide (**2**) indicate the bromide atoms eliminated in two steps at 270 and 412 °C due to the difference in ionic nature between them while completely decomposition occurs at 516 °C participated tellurium atom. *Bis*[2-(3-nitrobenzylideneamino)-5-nitrophenyl] telluride (**3**) shows one decomposition peak was

observed at 495 °C can be attributed to loss all organic groups as volatile species and form tellurium metal.

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