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Mono and binuclear Ag(I), Cu(II), Zn(II) and Hg(II) complexes of a new azo-azomethine as ligand: Synthesis, potentiometric, spectral and thermal studies

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ABSTRACT

New azo-azomethine dyes were prepared by reaction of p-aminobenzoic acid, o-anisidine, o-nitroaniline, and p-bromoaniline with salicylaldehyde respectively to form azo compounds and then condensation by urea to form 4-(R-arylazo 2-salicylaldene)-urea azo-azomethine derivatives (I_{a-d}). The complexes of these ligands with Ag(I), Cu(II), Zn(II) and Hg(II) metal ions were prepared. The structure of the free ligands and their complexes were characterized by using elemental analysis (C, H, N), ¹H NMR, IR and UV–Vis-spectra. The proton dissociation constants of the ligands and the stability constant of their complexes have been determined potentiometrically in 40% (v/v) alcohol–water medium as well as the stoichiometry of complexes were determined conductometrically. The data reveal that the stoichiometries for all complexes were of the complexes were assigned based on molar conductance measurements. The thermogravimetric (TG), and differential thermal analyses (DTA) were studied in nitrogen atmosphere with heating rate 10 °C/min. The kinetic and thermodynamic parameters for thermal decomposition of complexes have been calculated by graphical method using Coats–Redfern (CR) method.

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1. Introduction

Azo compounds and their metal (II)-complexes are very important molecules and have attracted much attention in both applied and academic research [1–3]. On the other hand, azo compounds are known to be involved in a number of biological reactions, such as inhibition of DNA, RNA, and protein synthesis, nitrogen fixation, and carcinogenesis [4]. The azo dyes and their metal complexes are more light stable, allow for easier control of the wavelength by selection of the appropriate substitute groups and have scarce of thermal studies [5–9]. TG and DTA have been found wide application in material characterization [10], since these methods essentially depend on measurements of the changes in physico-chemical properties as a function of increasing temperature with time [11–13]. Metal (II)-azo complexes are highly colored that enjoy widespread use as dyes and pigments in a variety of applications that include textile dyeing [14] as well as non-linear and photoelectronics [15], especially in optical information storage [16-24].

The formation and stability of binary and ternary complexes of copper(II) with 2,3-pyrazinedicarboxylic acid as a primary ligand and some biological important aliphatic, aromatic and heteroaromatic carboxylic acids as secondary ligands were determined by potentiometric technique [25]. The composition and stability of the complexes of isatin-thiosemicarbazone with Co(II), Ni(II), Cu(II), Zn(II), Pd(II), and Hg(II) have been investigated using spectrophotometric method [26,27]. The stoichiometries of Mn(II), Co(II), Ni(II), Cu(II) complexes with azo sulfonamide derivatives were determined conduct metrically [28,29]. Azo compounds were the subject of many spectral studies for purpose of identification or structure elucidation [30-33], as they are capable of forming metal chelates with transition metal ions [34,35]. The objective of this work concern synthesis and characterization of 4-(R-arylazo 2salicylaldene)-urea azo-azomethine derivatives as new dyes and their complexes.

2. Experimental

2.1. Materials and reagents

Chemicals used in this study were of pure grade and of highest purity available and used without further purification.

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Table	1

Elemental analysis	data of	the ligan	ds (I _{a-d}).

Ligand	M.wt.	m.p.	Color	Yield%	%C	%Н	%N
					Found (calc.)	Found (calc.)	Found (calc.)
Ia	312	210	Orange	85	56.8 (57.7)	3.6 (3.8)	17.2 (17.9)
Ib	298	298	Yellow	78	59.0 (60.4)	4.1 (4.7)	17.9 (18.8)
Ic	313	266	Orange	90	53.6 (53.7)	3.3 (3.5)	21.6 (22.4)
I _d	346	270	Brownish yellow	88	48.0 (48.6)	3.1 (3.2)	15.6 (16.2)

2.2. Preparation of the 4-(R-arylazo-2-salicylaldene)-urea derivatives

The azo dye is firstly prepared which in turn is refluxed with urea to form the azo-azomethine as following:

50 mmol of aniline derivatives (p-aminobenzoic acid, oanisidine, o-nitroaniline, and p-bromoaniline0 were dissolved in (1:1) of hydrochloric acid (mixture A) and then diazotized in 50 mmol of sodium nitrite is dissolved in bidistilled water (mixture B), 50 mmol of salicylaldehyde was dissolved in 10% sodium acetate (mixture C), then the usual way put the three mixtures in ice path, add the contents of mixture B to A to form diazotized compound, then the diazotized add to mixture C with continuums stirring for one half hour, then leaf the mixture after complete reaction overnight then filtrate and dry, resulting azo dyes were crystallized from appropriate solvents.



where x = (p-COOH), $(o-OCH_3)$, $(o-NO_2)$ and (p-Br).

50 mmol of azo dye is dissolved in methanol, then added to 50 mmol of urea in methanol as solvent and reflux for four hours, the azo-azomethine was obtained. The resulting precipitates were crystallized from appropriate solvent and subject to, m.p. determine and elemental analysis (Table 1).



4-(R-arylazo 2-salicylaldene)-urea azo-azomethine where R = p-COOH (I_a), o-OCH₃ (I_b), o-NO₂ (I_c) and p-Cl (I_d).

2.3. Apparatus

Schott Geratte pH meter model CG 710, fitted with a combination glass-calomel electrode, was used for pH adjustment and potentiometric measurements. The used apparatus for conduct metric work was Hanna instrument HI 9032 micro computer conductivity meter.

The IR spectra were recorded as KBr discs using Matson FT-IR spectrophotometer in the 4000–200 cm⁻¹ range. The ¹H NMR spectrum of the ligands was obtained using a varian EM 390-90 NMR spectrometer in d6 – DMSO as solvent using tetramethylsilane (TME) as an internal standard. The microanalysis for C, H and N were performed in the Microanalytical Center, Faculty of Science,

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Assignment and chemical shift (ppm) of different types of protons of ligands (I_{a-d}).
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Compound	Chemical shift (δ), ppm of protons								
	H (1) _{OH}	H(2) _{NH} 2	H(4)	H(5)	H(6)				
Ia	10.392	6.05	8.1	7.901	7.32	-			
Ib	10.37	6.04	8.13	8.03	7.24	3.96			
Ic	10.42	6.05	8.18	7.84	7.30	-			
Id	10.396	6.10	9.1	7.79	7.32	-			

Cairo University, Egypt. Thermogravimetric analysis (TGA; were obtained using TA Instruments, SDT2960) of the precursor was carried out at a heating rate of $10 \,^{\circ}$ C/min in nitrogen atmosphere.

2.4. Synthesis of solid complexes

The solid complexes of some selected metal ions were prepared by mixing 0.01 M of the metal ions solutions with a hot alcoholic solution of 0.01 M of ligands. The mixture was refluxed on a water bath for about 6 h and then allowed to cool; the solid complexes were separated and recrystallized from absolute ethanol, dried and preserved in desiccators over dried silica gel.



Fig. 1. Potentiometric titration of ligand I_a in presence of metal ions.

	Proton ionization constants Metal-ligand stability constant										
Ligand	pk_1^H	pk_2^H	Ag(I)		Cu(II)	Cu(II)		Cu(II)		Zn(II)	
			$\log \beta_1$	$\log \beta_1$	$\log \beta_1$	$\log \beta_2$	$\log \beta_1$	$\log \beta_2$	$\log \beta_1$	$\log \beta_2$	
Ia	7.2	8.4	3.6	5.6	3.5	6.6	4.6	7.1	4.4	6.8	
Ib	5.5	-	3.9	-	4.3	-	4.4	-	4.1	-	
Ic	8.2	-	4.2	-	5.2	-	5.8	-	5.6	-	
Id	7.3	-	3.2	-	3.6	-	3.9	-	3.8	-	

 Table 3

 Proton ionization constant and metal-ligand stability constant deducted from potentiometric titrations.

2.5. Solutions

0.01 M azo-azomethine solution was prepared by dissolving the calculated amount of the reagent in the requisite volume of ethanol.

0.1 M stock solution of sodium acetate was prepared by dissolving the calculated amount in the necessary volume of distilled water.

0.01 M stock solution of Ag(I), Cu(II), Zn(II) and Hg(II) metal ions was prepared by dissolving the calculated amount of each salt in a definite volume of distilled water.

1.0 M potassium nitrate was prepared by dissolving the calculated amount of KNO₃ in the appropriate volume of distilled water.

2.6. Procedures

2.6.1. Potentiometric titration

The proton dissociate of the ligands and stability constants of complexes of 4-(R-arylazo 2-salicylaldene)-urea



Fig. 2. ¹H NMR spectra of 4-(o-methoxyarylazo 2-slicyladene)-urea azoazomethine derivatives (Ib). azo-azomethine derivatives of ligands (I_{a-d}) with Ag(I), Cu(II), Zn(II) and Hg(II) metal ions were determined using potentiometric titration method where the titration of an acid, ligand and ligand–metal mixture have been titrated against 0.01 M NaOH.

(i) The acid mixture (mixture A)

The acid mixture (mixture A) used consisted of 5.0 ml 0.1 M HNO₃, 5.0 ml 1 M KNO₃ then completed to 50 ml with 40% alcoholic water (A) and titrated against 0.01 M sodium hydroxide. (ii) Ligand mixture (mixture B)

5.0 ml of 0.1 M HNO₃, 5.0 ml 0.1 M KNO₃, 25 ml of ligand $(1 \times 10^{-3} \text{ M})$ was completed to 50 ml with 40% alcoholic water and titrated against 0.01 M NaOH.

(iii) The metal-ligand mixture (mixture C) To mixture B, 5.0 ml metal ion $(1 \times 10^{-4} \text{ M})$ is added, and then titrated against 0.01 M NaOH.

2.6.2. Conductometric titration

The conductometric titration of 4-(R-arylazo 2-salicylaldene)urea azo-azomethine derivatives as ligands (I_{a-d}) with Ag(I), Cu(II), Zn(II) and Hg(II) metal ions were carried out in aqueous media



Fig. 3. ¹H NMR spectra of 4-(R-arulazo 2-slicyladene)-urea azo-azomethine derivatives (lc).

with the ligand, giving inflection point, from the titration plots, the stoichiometry of metal–ligand complexes was determined where 50 ml of metal ions $(1 \times 10^{-4} \text{ M})$ was titrated with $(1 \times 10^{-3} \text{ M})$ of the ligands.

3. Results and discussion

3.1. ¹H NMR spectra

The ¹H NMR spectra of ligands (I_{a-d}) were carried out and chemical shifts of the different signals are recorded in Table 2. It is clear from ¹H NMR spectra of these ligands that signals lying at 10.392, 10.37, 10.42 and 10.396 ppm give evidence that they are due to the OH group attached to the phenyl ring of ligands I_{a-d} , respectively. A signal appeared at 3.96 ppm which attributed to hydrogen proton of $-OCH_3$ group which confirmed the structure of I_b reagent as present in Fig. 2. A new multiple signals at range 6.37–7.713 ppm are due to the protons of the phenyl ring as shown in Fig. 3. The signals lying in range of 8.18–9.2 ppm are assigned to the proton of azomethine group of these compounds.

3.2. Potentiometric studies

The potentiometric technique has been used in many fields of chemistry [36–38]. Fig. 1 shows the titration curve

3.4. The IR-spectra

When a ligand coordinates to a metal ion M^{z+}, new modes of vibrations, are not present in the free compound may become infrared active. For a coordinated water molecules, rocking, twisting and wagging modes become possible and of course, this is in addition to the M–O and M–N bond which are due to the metal ligand bonds stretching vibrations. In general, the frequencies of these new bands not only depend on the ligand involved but are also sensitive to the nature of the metal ion, its size and charge.

The IR spectra of the ligands show a sharp strong band in the frequency range 3412–3440 cm⁻¹ which is due to v_{OH} but these bands become broadened and suffer a frequency shift when the ligand is bonded with the metal ions to give the chelate. This indicates the deprotonation of the replaceable hydrogen atom. The IR spectra of reagents (I_{a-d}) show the presence band in the frequency range 1630–1695 cm⁻¹ which is due to $\nu_{C=0}$, these bands become broadened and suffer a frequency shift when the ligand is bonded with the metal ions to give the chelate. The IR spectra of reagents (I_{a-d}) confirmed the presence of azo group due to the band in the frequency range 1475–1482 cm⁻¹. A weak band appears in the vicinity of 450 cm⁻¹ which is attributed to an M-N bond in the reagents chelates. Also, the IR spectra of the solid complexes confirmed the presence of coordinated water molecules by the broad band in the frequency range 3400–3600 cm⁻¹. The IR spectra of these compounds are compared to that of the free ligand. The data are listed in Table 4. Accordingly, the mode of the metal ions with the ligand under investigation can be represented as follow:



which used in this work is developed by Calvin and Bjerrum and the proton-reagent stability constants (k_n^H) were determined. The average number of protons associated with the reagent molecules n_A^- , the average number of molecules attached per metal ion n^- , free ligand exponent pL and the values of ionization and stability constants of ligands and their complexes were determined Table 3.

3.3. Conductometric and molar conductivities studies

The conductometric titrations were carried out for metal ions Ag(I), Cu(II), Zn(II) and Hg(II) with the ligands (I_{a-d}) . The changes in the conductance depend on the change in the number and character of the conducting species in solution.

The conductivity in nonaqueous solutions in dimethylformamide (DMF) had frequently been used in the structure studies of metal complexes within the limits of their solubility. It is clear from the conductivity data, shown in Table 3, that all the complexes (1:1) (M:L) present behave as strong electrolytes with values in range 62.9–92.7 Ω^{-1} cm² mol⁻¹. On the other hand, the conductivity of complexes (1:2) (M:L) have lower values of conductivity with non-electrolytic nature of conductivity.

(1:1) (M:L)

where R=p-COOH (I_a); o-OCH₃ (I_b); o-NO₂ (I_c) p-Br (I_d); M=Ag(I), Cu(II), Zn(II) and Hg(II) metal ions; *X* = number of water molecules coordinated to metal ion; Y=OCOCH₃, SO₄^{2–} or Cl[–] anions; *z*=overall charge on the complex; *N*=Number of crystalline water molecules; *A*=number of anion in outer sphere; *a*, *y*, *x* and *n* are stoichiometric ratio of anions and water molecules.



where R = p-COOH (I_a), o-OCH₃ (I_b), o-NO₂ (I_c), p-Br (I_d); M = Ag(I), Cu(II), Zn(II) and Hg(II) metal ions; z = overall charge on the complex; x = 2; n = 1 or 2.

Table 4
Assignment of the important bands in the IR spectra of I_{a-d} , ligands and their complexes and molar conductivity values

Complex	Ratio (M:L)	ν_{-OH}	δ_{OH}	$\nu_{-C=N}$	$\nu_{-N=N-}$	$\nu_{C=0}$	ν_{C-0}	ν_{M-0}	Chemical formula	Molecular weight	$\Lambda_{\rm M}(\Omega^{-1} {\rm cm}^2{\rm mol}^{-1})$
Ia	-	3412	1378	1573	1455	1660	1156	-	$C_{15}H_{12}N_4O_4$	312	-
$Zn^{2+}-I_a$	(1:1)	3680	1376	1576	1424	1665	1150	408	[Zn·L·4H ₂ O]CH ₃ COO·H ₂ O	525.5	67.9
Hg ²⁺ -I _a	(1:1)	3738	1375	1576	1423	1620	1155	412	[Hg·L·H ₂ O]NO ₃ ·H ₂ O	609.59	87.5
Cu ²⁺ -I _a	(1:1)	3742	1384	1527	1425	1645	1150	408	$[Cu \cdot L \cdot H_2O]SO_4 \cdot H_2O$	506.55	62.9
Ag ⁺ -I _a	(1:1)	3427	1378	1574	1427	1630	1159	404	[Ag·L·H ₂ O]NO ₃	499	87.2
Ib	-	3440	1366	1586	1482	1685	1151	-	$C_{15}H_{14}N_4O_3$	298	-
Hg ²⁺ -I _b	(1:1)	3424	1370	1585	1482	1610	1153	453	$[Hg \cdot L \cdot H_2O]SO_4 \cdot H_2O$	629.59	67.0
Ag^+-I_b	(1:2)	3424	1366	1586	1484	1650	1151	454	$[Ag \cdot L_2 \cdot H_2O]2H_2O$	783	33.0
Zn ²⁺ -I _b	(1:1)	3398	1393	1530	1478	1670	1152	439	$[Zn \cdot L \cdot H_2O]SO_4.H_2O$	494.5	73.0
Zn ²⁺ -I _b	(1:2)	3360	1394	1528	1480	1665	1152	455	$[Zn \cdot L_2 \cdot 2H_2O] 3H_2O$	629.59	25.5
Ag^+-I_b	(1:1)	3741	1375	1582	1482	1650	1162	449	$[Ag \cdot L \cdot H_2O] NO_3 \cdot H_2O$	503	82.8
Cu ²⁺ –I _b	(1:2)	3429	1394	1593	1463	1625	1151	425	$[Cu \cdot L_2 \cdot 2H_2O] 3H_2O$	843.55	13.4
Ic	-	3742	1344	1576	1480	1690	1145	-	$C_{14}H_{11}N_5O_4$	313	-
$Zn^{2+}-I_c$	(1:2)	3742	1344	1579	1479	1620	1144	449	$[Zn \cdot L_2 \cdot 2H_2O]3H_2O$	838.5	16.5
Zn ⁺² -I _c	(1:1)	3314	1346	1622	1472	1615	1150	523	$[Zn \cdot L \cdot H_2O]CH_3COO \cdot H_2O$	472.5	88.5
Id	-	3691	1380	1619	1475	1695	1143	-	$C_{14}H_{14}N_4O_2$	305.5	-
Hg ²⁺ –I _d	(1:1)	3742	1374	1617	1472	1630	1160	407	[Hg·L·H ₂ O]NO ₃ ·H ₂ O	644.49	84.7
Hg ²⁺ -I _d	(1:2)	3741	1384	1617	1471	1670	1160	421	$[Hg\cdot L_2\cdot 2H_2O]\ 3H_2O$	1044.39	19.2

3.5. Thermal analysis

Thermal methods of analysis introduce a new possibility for investigation of complexes [39]. The thermal analysis for some complexes of 4-(R-arylazo 2-salicylaldene)-urea azo-azomethine derivative with Ag(I), Cu(II) and Zn(II) metal ions were carried out in nitrogen gas atmosphere with heating rate 10 °C/min. They include such technique as thermogravimetric (TGA) and differential thermal analysis (DTA). The TGA and DTA curves give interesting information about the various unexpected phenomena observed during thermal degradation. It is important to take into account that the TGA curves reveal the variation in weight, whereas the DTA is concerned calorimetrically with weight changes which often occur with observed detection.

From TG curves, one can calculate the percentage of water molecules and metal ion in the complexes, whereas those of DTA make it possible to characterize, thermographically, the process of phase transformation in the examined system. To understand the thermal decomposition of the complexes under investigation, the mechanism of the decomposition has to be established from TG-DTA data. The kinetic and thermodynamic parameters: activation energy(E_a) and pre-exponential factor (A), enthalpy ($\Delta H^{\#}$), entropy ($\Delta S^{\#}$) and free energy ($\Delta G^{\#}$) are calculated from TG/DTA curves in the temperature range 30–1000 °C using Coats–Redfern method [40].

3.5.1. The thermal degradation of mono and binuclear Ag(I), Cu(II), and Zn(II) complexes

TG/DTA analysis for [Ag–I_a·H₂O] NO₃. H₂O complex (1:1), shows that the water molecules were expelled after raising temperature up to 216 °C with weight loss 14.11% (theoretically 13.36%) corresponding to the loss of four molecules of water. This step is accompanied by an endothermic peak in the DTA curve, the second weight loss (found 11.90%) takes place between 216 and 336 °C having endothermic peak in the DTA curve at 336 °C which is attributed to elimination of nitrate ion (theoretically 11.45%) the final step which is shown in the TG curve in the range 350–850 °C with weight loss 54.50% (theoretically 54.93%) and this corresponding to the decomposition of the organic part of the complex having exothermic peak in DTA curve at 750 °C. The metal oxide is formed at 850 °C and the activation energy of degradation process is 32.39 kJ mol⁻¹.

Thermal analysis has been carried out on $[Zn\cdot I_c \cdot 4H_2O]$ CH₃COO·H₂O complex. From TG-curves as shown in Fig. 4, the weight losses were calculated for the different overlapping steps and compared with those theoretically calculated for the suggested formula. The first weight loss at temperature up to 120 °C is

attributed to dehydration of one hygroscopic water molecule, the found weight losses is 3.25% (calc. 3.56%), having broad endothermic peak in DTA at 100 °C whereas the second step of weight loss within the range 120–220 °C is attributed to release of four water molecules coordinated with metal ion with endothermic peak, the third weight loss within the range 220–320 °C is attributed to one acetate ion with exothermic peak in DTA curve at 280 °C. The found weight losses of the complex amount to 14.75 and 13.25% compared with the calculated values (14.65 and 11.95%) for four water molecule and acetate ion, respectively. The organic part of the complex is decomposed in range 307–523 °C, the found weight loss



Fig. 4. TG/DTA analysis of 4-(R-arylazo 2-salicylaldene)-urea azo-azomethine (I_c) with Zn^{2+} ion in ratio (1:1) (M:L) in a nitrogen gas with a heating rate of 10° C/min.

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Table	5

TC_DTC/DTA data of Ag(I)	Cu(II) and	7n(II) complexes with 4	(R-arylazo 2-salicy	ore conu-(ono)	azomethine derivative
IG-DIG/DIA data OI Agii	(, Cu(II) all u)	ZII(II) COMPLEXES WITH 4	-(R-di Vidzu Z-Sdiiu)	VIaluelle)-ulea azo-	azometnine denvative.

Complex	Temperat ure range (°C)	Weight loss	%	Type of peak	Assignment
		Calc.	Found		
	30-360	13.41	13.66	Endo	Four water molecules and nitrate ion
$Ag(I)-I_{a}(1:1)$	120-220	11.54	11.90	Endo	Nitrate ion
	220-850	54.93	54.50	Exo	Organic part
	35-180	8.22	8.75	Endo	2H ₂ O
$Zn(II) - I_{c}(1:1)$	180-300	13.35	13.25	Endo	3H ₂ O
.,,	300-350	12.41	12.36	Exo	Acetate ion
	350-600	70.41	70.36	Exo	Organic part
$Zn(II)-I_{a}(1:2)$	40-150	2.57	2.30	Endo	One molecule of H_2O
() = ()	150-350	5.14	4.95	Endo	Two coordinate of water
	350-600	80.16	80.25	Exo	Organic part
	40-125	4.98	5.12	Endo	2H ₂ O
$Cu(II) - I_{h}(1:2)$	120-250	2.49	2.60	Endo	One molecule of coordinate H ₂ O
	250-600	81.60	82.43	Exo	Organic part

of organic part is 56.16% (theoretically 53.41%), and having sharp exothermic peak at 500 $^\circ$ C. The activation energy of degradation process is 46.7 kJ mol^{-1}.

The thermal decomposition of $[Zn \cdot 2I_a] 4H_2O$ complex in ratio (1:2) (M:L) has been carried out in temperature range 30–1000 °C in nitrogen atmosphere with heating rate of 10 °C/min. From TGA curve in Fig. 5, the weight losses were calculated and compared with those theoretically calculated for the suggested formula. The first weight loss at temperature up to 120 °C is attributed to elimination of four water molecules, having broad endothermic peak in DTA at 100 °C whereas the second step of weight loss within the range 120–550 °C is attributed to organic part with exothermic peak in DTA curve at 499 °C. The found weight losses of the complex



Fig. 5. TG/DTA analysis of 4-(R-arylazo 2-salicylaldene)-urea azo-azomethine (I_c) with Zn(II) (1:2) (M:L) in a nitrogen gas with a heating rate of 10 °C/min.

amount to 10.55% compared with the calculated values (10.26%) for four water molecules. The organic part of the complex is decomposed in range 120–523 °C, the found weight loss of organic part is 77.16% (cal. 77.86%), and having sharp exothermic peak at 500 °C with forming zinc oxide 11.21 (cal. 11.59%). The activation energy of thermal degradation process is 41.33 kJ mol⁻¹.

TGA/DTA analysis of the [Cu·2I_b] H₂O complex in ratio (1:2) (M:L) has been carried out with heating rate 10 °C/min. in nitrogen atmosphere. The found weight losses of the complex amount to 2.12% compared to calculated 2.62% for one water molecule having endothermic peak in DTA at 120 °C. The organic part of the complex is decomposed in range 120–423 °C, the found weight loss of organic part is 87.16% (cal. 88.14%), and exothermic peak observed at 400 °C with forming copper oxide 11.21 (cal. 11.58%). The activation energy of degradation process is 33.2 kJ mol⁻¹.

3.5.2. Coats-Redfern method

Coats-Redfern [40] simplified Van Krevelen's interpretation [41] according to the following:

$$\ln\left(-\ln \ \frac{c^{-1}}{T^2}\right) = \ln\left(\frac{ZR}{E_a\beta}\right) - \frac{E_a}{RT}$$
(1)

With $c = (w_{\infty} - w)/w_{\infty}$, where w_{∞} is the total mass loss for a particular stage, w is the mass loss of absolute temperature *T*, *Z* the frequency factor and β the heating rate.

Also, Coats-Redfern suggested an asymptotic expansion of the temperature integral, giving:

$$\ln \quad \frac{f(\alpha)}{T^2} = \ln \left(\frac{AR}{E_a\beta}\right) - \frac{E_a}{RT}$$
(2)

Plotting $\ln(-\ln c^{-1}/T^2)$ and $\ln f(\alpha)/T^2) \rightarrow 1/T$ for all the steps gives the value of activation energy E_a from the slope and Z and A from the intercept.

Tables 5 and 6 demonstrated the thermal behaviors of the complexes, the activation kinetic and thermodynamic parameters; activation energies (E_a), pre-exponential factor (A), entropy ($\Delta S^{\#}$), enthalpy ($\Delta H^{\#}$) and free energy ($\Delta G^{\#}$) were calculated from TG–DTG/DTA-curves in the temperature up to 1000 °C in nitrogen atmosphere by using the following equations:

$$\Delta S^{\#} = R \quad \ln \frac{Ah}{kT} \tag{3}$$

$$\Delta S^{\#} = R \ln \frac{Ah}{kT} \tag{4}$$

$$\Delta G^{\#} = \Delta H^{\#} - T \Delta S^{\#} \tag{5}$$

where *k* and *h* are the Boltzman and Plank constants, respectively. The correlation coefficients of the Arrhenius plots of the thermal

Table 6

The activation kinetic and thermodynamic parameters of thermal decomposition of Ag(I), Cu(II) and Zn(II) complexes with 4-(R-arylazo 2-salicylaldene)-urea azo-azomethine derivative.

Complex	Step	Т, К	Correlation coefficient, r	E _a kJ mol ⁻¹	$\Delta H^{\#}$ kJ mol ⁻¹	Pre-exponential factor, A Sec ⁻¹	- $\Delta S^{\#} kJ mol^{-1}k^{-1}$	$\Delta G^{\#}$ kJ mol-1
Ag(I)–I _a (1:1)	1	580	0.998	61.27	56.16	$2.13 imes 10^6$	129.28	7.5×10^4
	2	775	0.966	17.07	10.63	$4.02 imes 10^3$	183.91	14.3×10^4
	3	1151	0.909	42.66	33.09	$2.10 imes 10^4$	173.42	20.0×10^4
$Zn(II)-I_{a}(1:2)$	1	441	0.996	31.77	28.10	$3.50 imes 10^4$	161.21	$7.1 imes 10^4$
	2	574	0.992	22.48	17.71	$1.20 imes 10^4$	172.29	$9.9 imes10^4$
	3	766	0.99	33.07	27.24	$4.06 imes 10^4$	164.56	12.6 imes 104
$Cu(II)-I_{b}(1:2)$	1	496	0.962	28.20	24.08	$2.63 imes 10^4$	164.57	8.14×10^4
	2	556	0.956	21.17	16.55	$1.03 imes 10^4$	173.30	9.64×10^4
	3	700	0.998	34.87	29.05	$4.54 imes10^4$	162.88	$11.0 imes 10^4$
$Zn(II)-I_{c}(1:1)$	1	363	0.929	17.05	14.03	1.02×10^2	212.06	$7.7 imes 10^4$
	2	530	0.995	33.9	29.49	2.8×10^{2}	185.21	$9.8 imes 10^4$
	3	648	0.928	14.92	10.04	2.26×10^3	146.48	$9.5 imes10^4$
	4	788	0.991	48.52	41.97	$8.43 imes 10^4$	158.71	15.5×10^4

degradation stages were found to lie in range 0.928–0.998, showing a good fit with the linear function.

3.5.3. The thermal decomposition can be formulated as the following:

(a) The thermal degradation Ag(I)–I_a complex (1:1)

(1)
$$[Ag-L \cdot 2H_2O] \quad NO_3 \cdot 2H_2O \xrightarrow{3O-360} C [Ag-L]NO_3 + 4H_2O$$

- (2) $[Ag-L \cdot 2H_2O] NO_3 \xrightarrow{360-750} {}^{\circ}C[Ag-L] + NO_3^{-1}$
- (3) $[Ag-L]^{+750-950} \xrightarrow{\circ C} Ag_2O + organic part$
- (b) The thermal degradation Zn(II)–Ic complex (1:1)
 - (1) $[Zn-L \cdot 4H_2O] CH_3COO \cdot H_2O$ $\xrightarrow{35-180} {}^{\circ C}[Zn-L \cdot 3H_2O] CH_3COO + 2H_2O$
 - (2) $[Zn-L \cdot 3H_2O] CH_3COO$ $\stackrel{180-300}{\longrightarrow} \ ^{\circ C}[Zn-L \cdot 3H_2O] CH_3COO + 3H_2O$
 - $(3) \quad \left[Zn L \cdot 3H_2O \right]^{+300 350} \stackrel{\circ C}{\longrightarrow} \left[Zn L \right]^+ + CH_3COO^-$
 - (4) $[Zn-L]^+ \xrightarrow{350-600} \circ C$ organic part + ZnO
- (c) The thermal degradation Zn(II)–Ia complex (1:1)
 - (1) $[Zn-2L] 4H_2O \xrightarrow{40-150} {}^{\circ}C [Zn-2L \cdot 2H_2O] + 2H_2O$

- (2) $[Zn-2L \cdot 2H_2O]^{150-350} \xrightarrow{\circ C} [Zn-2L] + 2H_2O$
- (3) $[Zn-2L]^{350-600} \xrightarrow{\circ C} organic part + ZnO$
- (d) The thermal degradation Cu(II)–Ib complex (1: 2)
 - (1) $[Cu-2L2H_2O] H_2O \xrightarrow{40-125} {}^{\circ}C [Cu-2L \cdot H_2O] + 2H_2O$
 - (2) $[Cu-2L \cdot H_2O]^{125-250} \xrightarrow{\circ C} [Cu-2L] + H_2O$
 - (3) $[Cu-2L]^{250-500} \xrightarrow{\circ} Corganic part + CuO$

3.6. Electronic spectra

The electronic absorption spectra of the prepared solid complexes are measured in nujol mull and in DMF solution within the range 29411.46–12,500 cm⁻¹, based on the fact that the electronic absorption spectra are very diagnostic of the stereochemistry of complex. The spectra of the free ligands (I_{a-d}) in DMF indicate that the wave number ν^- (cm⁻¹) of the CT band are 21,186, 26,041, 23,547 and 25,687 cm⁻¹ for ligands (I_{a-d}), respectively whereas those taken in nujol mull are 24,752, 28,011, 27,472 and 28,818 cm⁻¹ respectively. The value ν^- (cm⁻¹) of the CT bands of all complexes displays a red or blue shift due to substituent effect compared to that of the free ligands. The spectral complexes Ag(I), Cu(II) and Zn(II) metal ions in comparison to those of the corresponding free ligands are listed in Table 7.

Table 7

Electronic spectra of Ag	g(I), Cu(II) and Zn(II) complexes with 4	4-(R-phenylazo 2	2-salicylaldene)-ure	ea azo-azomethine d	erivative in DMF	and nujol mull.
Dieeti onne opeetita or ng	5(1), ea(11) and bii(in) compreneo mien	((pricily allo	s suncynaraence) and	eu ubo ubonneennie u	ciriu a ciri e ini e ini i	and major main

Ligand/complex	Ratio (M:L)	Band Maxima in range (cm ⁻¹)	Assignment	
		DMF	Nujoll mull	
Ia	-	21,186, 24,212, 28,222	24,752, 26,224, 29,235	π-π*, n-π*, CT
$Ag(I)-I_a$	1:1	21,834, 25,232, 29,154	25,773, 27,585, 30,395	π−π*, n−π*, CT
Ib	_	20,234, 22,315, 26,040	19,978, 24,587, 28,011	π−π*, n−π*, CT
Cu(II)–I _b	1:2	21,254, 24,568, 27,454	24,154, 26,464, 29,411	$^{2}T_{2g} \rightarrow ^{2}E_{g}$
Ic	_	18,154, 21,232, 23,547	20,289, 25,221, 27,472	$\pi - \pi^*$, $n - \pi^*$, CT
Zn(II)–I _c	1:1	21,881, 22,421, 25,125	21,598, 26,986, 28,254	π−π*, n−π*, CT
	1:2	24,224, 25,212, 26,354	22,587, 25,462, 27,771	<i>π</i> − <i>π</i> *, <i>n</i> − <i>π</i> *, CT

4. Conclusions

Based on the results of potentiometry, conductometry elemental analysis, molar conductivity, spectral data and thermal analysis for the 4-(R-arylazo 2-salicylaldene)-urea azo-azomethine as new ligands and their complexes with Ag(I), Cu(II), Zn(II) and Hg(II) metal ions in ratios (1:1), (1:2) (M:L) were investigated in solution and solid form for all ligands as well as some complexes were determined in solution in ratio (2:1), (2:3) and (3:2)(M:L). The most important data draw the above investigations are that the mono basic bidentate ligand is coordinated to the metal ions through O and N as donor atoms. The proton dissociation constants of the ligands and the stability constant of their complexes have been determined. The activation kinetic and thermodynamic parameters were calculated in different stages of thermal decomposition using Coats–Redfern (CR) method.

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