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RESEARCH ARTICLE

Spectrophotometric Studies on Binary and Ternary complexes of Some Metal Ions with Alizarin Red S and Cysteine.

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Binary complexes of Fe(III), Cu(II), Pd(II), Co(II) and Ni(II) with alizarin red S, and Cu(II), Co (II) and Ni(II) with alizarin red S (ARS) and cysteine (Cys.) amino acid (ternary complexes) have been investigated in solution using spectrophotometric method. The composition of the complexes was determined to be 1:1 and/or 1:2 (M: L) for binary complexes, and 1:1:1 or/and 1:1:2 (ternary complexes), the optimum conditions favouring the formation of the coloured complexes were studied extensively; the stability constants of the complexes were calculated. Adherence to Beer's law was observed for the μgmL^{-1} concentration range from (2.49- 52.84 μgmL^{-1}). Moreover, the solid complexes have been characterized by elemental analyses, electronic spectra, thermal method (TGA and DTA), FT-IR and X-ray powder diffraction. The antimicrobial activities of the ligands and their complexes have been studied by screening the compounds against *Aspergillus niger*, *Alternaria alternata* for antifungal and *Escherichia coli* (-ve) and *Bacillus cereus* (+ve) for antibacterial and results have been compared with the standard drug,

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Introduction

Metal coordination complexes have been extensively used in clinical applications as enzyme inhibitors [1], antibacterial [2, 3], antiviral [4–6] and as anti-cancerous [7–9]. Different kinds of metals have been employed in these complexes including platinum, gold, vanadium, iron, molybdenum, cobalt, tin, gallium, copper and many others [8]. Metal complexes of adenine (A) have been shown to possess anticancer activity [9–13]. In living systems, almost all the biochemical processes are known to proceed mostly in the solution phase where several metal ions are present in trace quantities. Most of the physiological activities regarding nucleic acid interactions are promoted by metal ions through the formation of ternary (mixed-ligand) complexes [14–20]. Whenever a metal ion exists in solution together with two or more different ligands, the formation of various simple as well as ternary (mixed-ligand) complexes are always possible, depending on the pH of the system. The actual complex-formation depends on the affinity of the metal ion towards the various ligands present, and the relative concentrations thereof. In the present study, the stability constants of mixed complexes from Alizarin Red S and amino acid with the investigated metal ions were determined using Spectrophotometric method.

Alizarin Red is used in a biochemical assay to determine, quantitatively by [colorimetry](#), the presence of calcific deposition by cells of an estrogenic lineage. As such it is an early stage marker (days 10–16 of in vitro culture) of matrix mineralization, a crucial step towards the formation of calcified extracellular matrix

associated with true bone Alizarin's abilities as a biological stain were first noted in 1567, when it was observed that when fed to animals, it stained their teeth and bones red. The chemical is now commonly used in medical studies involving calcium. Free (ionic) calcium forms precipitates with alizarin, and tissue block containing calcium stain red immediately when immersed in alizarin. Thus, both pure calcium and calcium in bones and other tissues can be stained. The process of staining calcium with alizarin works best when conducted in basic solution [21]. In clinical practice, it is used to stain [synovial fluid](#) to assess for basic [calcium phosphate](#) crystals [22]. Alizarin has also been used in studies involving bone growth, osteoporosis, and bone marrow, calcium deposits in the vascular system, cellular signaling, gene expression, tissue engineering, and mesenchymal stem cells.^[10] In geology, it is used as a stain to indicate the [calcium carbonate](#) minerals, [calcite](#) and [aragonite](#) [23].

2. Experimental

2.1. Apparatus

All The pH measurements were carried out on VWR scientific model 2000 digital analyzer accurate total 0.01 pH unit. The absorption spectra of solutions were measured at room temperature with a Perkin-Elmer Lambda 3B recording spectrophotometer, using 1-cm matched quartz cells in the wavelength range 200-800 nm. The C, H, N elemental analyses were done at the microchemical analysis Unit, Assiut University .FT-IR spectra (400- 4000 cm^{-1}) were recorded as KBr discs using a Shimadzu IR 479 spectrophotometer. Thermogravimetric analysis of TGA was recorded on Shimadzu analyser 50 in a dynamic nitrogen atmosphere (100 ml/min) at a heating rate 10°C/min at Assiut University. X-ray diffraction data were collected at room temperature ($\sim 25^\circ$) on a Philips 1710 diffractometer at Assiut University. The patterns were run with cut target and Ni filter ($\lambda = 1.5418 \text{ \AA}$) at 40 KV and 30 mA in the range of $2\theta = 40-60, 4-80$ with scanning speed of 3.6 deg min^{-1} .

2.2. Reagents and Materials

The solutions of Fe(III), Cu(II), Pd(II), Co (II) and Ni (II) ions (Merck and BDH) were prepared and titrated complexometrically by EDTA [24]. Were obtained by dissolving the accurate weight of metal salt in the appropriate volume of bi-distilled water. More dilute solutions used for spectral measurements were obtained by accurate dilution.

Stock standard solution of ($1 \times 10^{-3} \text{ M}$) of Alizarin red s (ARS) and cysteine ligands or was prepared by dissolving accurate weights of pure Ligands in bidistilled water and diluted with the same solvent to 10 mL volumetric flask (at 25°C). ARS working solutions were prepared daily by sequential dilution of the stock standard solution using bidistilled water.

Sodium hydroxide (Merck) was prepared in bidistilled water as fresh solution. The universal buffer solution were prepared as recommended [25], and used to control the hydrogen ion concentration and ionic strength.

2.3 Preparation of solid complexes:

The solid complexes were prepared by mixing equimolecular amounts of the ligand and metal salt in alcohol. The mixture was then stirred for about two hours. The solid complexes were isolated by addition of ether and then filtered immediately. Recrystallization of the solid complexes from ethanol/ether, to ensure the isolation of pure compounds was carried out. The solid complexes were then filtered off, washed and dried over P_2O_5 .

3-Results and Discussion:

3.1-Determination of the Stoichiometry of Binary complexes

The stoichiometry of the complexes was studied by applying the molar ratio [26] and continuous variation [27] methods are shown in figs. (1-4). the results proved the 1:1 or/and 1:2 (M: L) complexes were formed. The formation constants of these complexes were calculated from the molar ratio and continuous variation methods and are listed in Table (1). From Table (1) the stabilities of the complexes at (1:1) molar ratio method increase in the order Fe(III) > Cu(II) > Pd(II) > Co(II) > Ni(II). This is in agreement with general order of the stability of the complexes of these metal ions which is established before by Grinberg and Yatsimiki [28] and by Irving and Williams [29].

Table (1).Data of molar ratio method for Fe(III) -ARS complex at 25°C.

No	[Fe(III)]x10 ⁻⁴ M	[L]x10 ⁻⁴ M	[L]\[M]	Absorbance $\lambda_{\max}=562$
1	1	0.1	0.1	0.0504
2	1	0.2	0.2	0.2196
3	1	0.3	0.3	0.269
4	1	0.4	0.4	0.385
5	1	0.5	0.5	0.4493
6	1	0.6	0.6	0.5379
7	1	0.7	0.7	0.6293
8	1	0.8	0.8	0.6891
9	1	0.9	0.9	0.7676
10	1	1	1	0.8205
11	1	1.2	1.2	0.8983
12	1	1.3	1.3	0.9188
13	1	1.4	1.4	0.9902
14	1	1.5	1.5	1.1175
15	1	1.6	1.6	1.265
16	1	2	2	1.3173

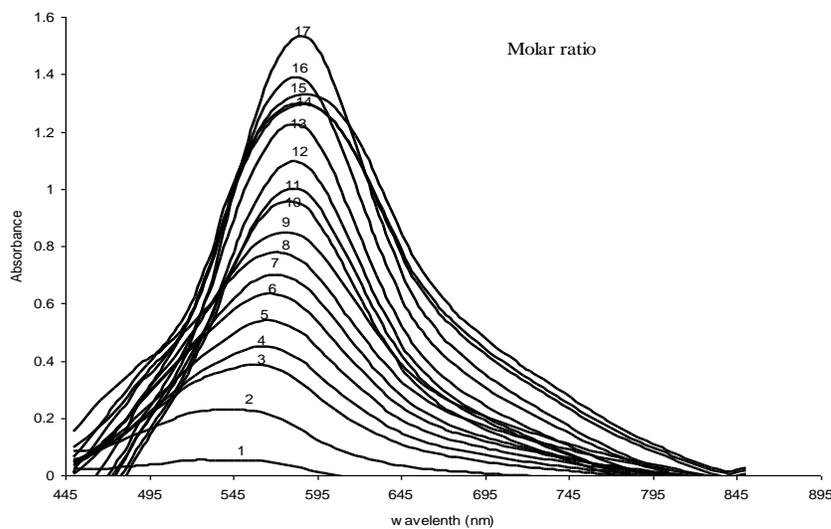
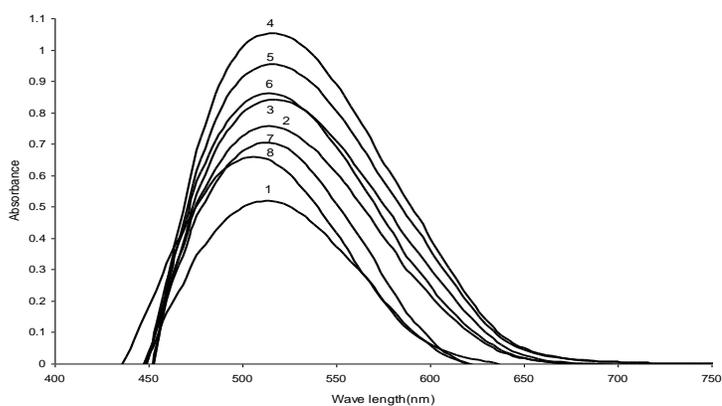
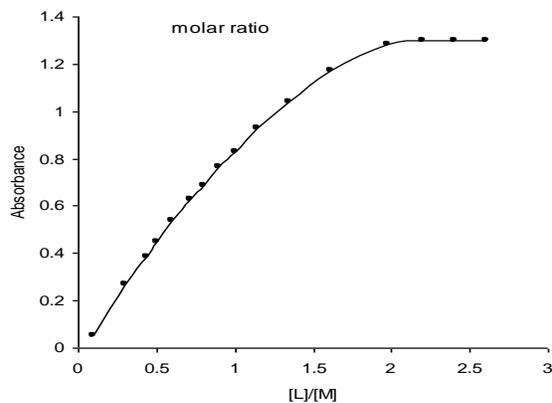


Fig.1. Absorption spectra of molar ratio for 1×10^{-4} M Fe(III)-ARS Complex at 25°C and $\lambda_{\max} = 562$ nm.

Table (4).Data of continuous variation method for Cu(II)-ARS complex at25°C.

No	[Cu (II)]x10 ⁻³ M	[L]x10 ⁻³ M	Mole fraction	Absorbance $\lambda_{\max}= 522$
1	0.7	0.2	0.22	0.5180
2	0.6	0.3	0.33	0.7565
3	0.5	0.4	0.44	0.8407
4	0.45	0.45	0.5	1.0260
5	0.4	0.5	0.55	0.9530
6	0.3	0.6	0.66	0.9101
7	0.2	0.7	0.77	0.8530
8	0.1	0.8	0.88	0.6490

Fig.2. Absorption spectra of continuous variation for 1×10^{-3} M Cu(II)- ARSComplex at 25°C and $\lambda_{\max} = 522$ nmFig.3. Absorbance molar ratio relationship for 1×10^{-4} M Fe(III)-ARS Complex at 25°C and $\lambda_{\max} = 562$ nm.

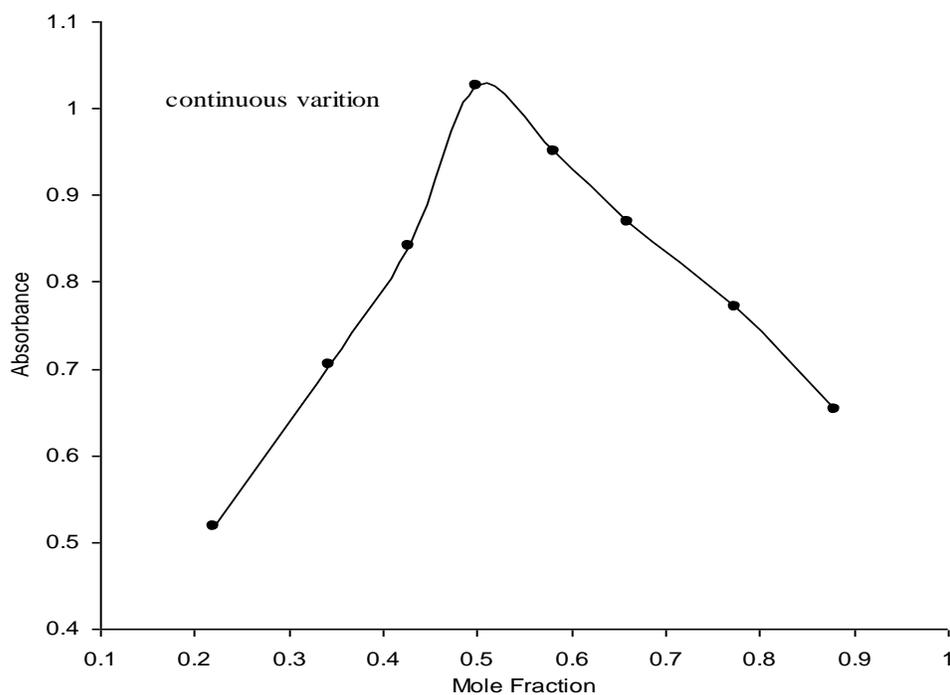


Fig.4. Absorbance mole fraction relationship for 1×10^{-3} M Cu(II)-ARS Complex at 25°C and $\lambda_{max} = 562$ nm.

Table(1):-Formation constant and free energy changes ΔG^* in (K.Cal./Mole), at 25°C of Pd(II),Cu(II),Fe(II) ,Ni(II) and Co(II) Alizarin red s chalets.

Metal ion	Method	Ratio	(formation constant) K _f	Stability constant log k _f	ΔG^*
Pd(II)	M.R.	1:1	1.06×10^5	5.02	2.969
	M.R.	1:2	7.6×10^7	7.8	4.613
	C.V.	1:1	1.4×10^4	4.1	2.425
Cu(II)	M.R.	1:1	1.3×10^5	5.1	3.016
	C.V.	1:1	2.5×10^4	4.4	2.602
Fe(III)	M.R.	1:1	4.5×10^5	5.6	3.312
	M.R.	1:2	1.4×10^{10}	10.1	5.974
	C.V.	1:1	5.3×10^4	4.7	2.780
Co(II)	M.R.	1:1	1.4×10^4	4.15	2.454
	M.R.	1:2	2.95×10^8	8.46	5.013
	C.V.	1:2	2.2×10^7	7.3	4.318
Ni(II)	M.R.	1:1	1.2×10^4	4.1	2.425
	M.R.	1:2	9.0×10^7	7.9	4.673
	C.V.	1:2	1.2×10^9	9.08	5.371

3.2-Determination of the stoichiometry of the ternary complexes:

The continuous variation method was used to establish the composition of the ternary Cu(II), Co(II) and Ni(II)-(ARS .Cys.) complexes. The molar fractions of two of the components were varied continuously, keeping their total concentration constant in presence of a large excess of the third component. Under these conditions, the ternary system was modified to a pseudo-binary system [30]. For determination the stoichiometry of M(II)-cysteine in presence of ARS as mixed ligands. A series of solutions containing different ratios of M(II):Cys., were prepared (in presence of excess of ARS), keeping the total concentration of both M(II) ion and Cysteine constant. The ratio of M(II):(Cys.), was determined from the relationship between absorbance (at the λ_{\max} of each complex) and mole fraction of cysteine. Moreover, the ratio of M(II): ARS was determined as described above in the presence of excess (Cys.)

The stoichiometry of the M(II):(Cys.) in presence of ARS was also determined by applying the molar ratio method. A series of solutions was prepared with constant concentration of M(II) ion and variable concentrations of Cys. in the presence of excess ARS. The ratio M(II):Cys. in the complex was determined from the relationship between absorbance (at the λ_{\max} of each complex) and Cys.:M(II) ratio. The ratio of M(II):ARS was also determined by molar ratio method in the presence of excess (Cys.). The results proved the 1:1:1, or/and 1:1:2 (M:ARS:Cys.) ternary complexes were formed for Cu(II), Co(II) and Ni(II). The formation of binary and ternary complexes with ARS is shown in Fig.(5).

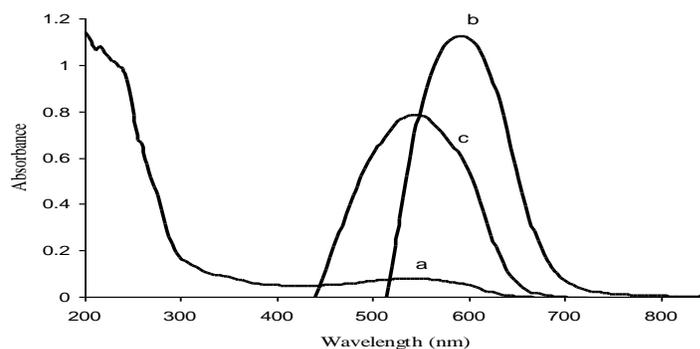


Fig.5. Absorption spectra of 5×10^{-5} M of ARS, Co(II) binary and ternary complexes (a): ARS ligand, (b): Co(II)-ARS binary complex and (c): Co(II)-(ARS.Cys.) Ternary complex.

3.3- Calibration Curve.

In order to use the complexes of the metal ions Fe(III), Cu(II), Pd(II), Co(II), Ni(II), with alizarin red s for microdetermination of metal ions in concentration range from 2.49 - 52.84 ($\mu\text{g ml}^{-1}$). Absorbance of the obtained mixture is measured at the corresponding λ_{\max} of the formed chelate. A graph of absorbance versus the concentration ($\mu\text{g ml}^{-1}$) of the tested metal ion is shown in Fig.6. The limits of the metal concentration ions are listed in Table (2).

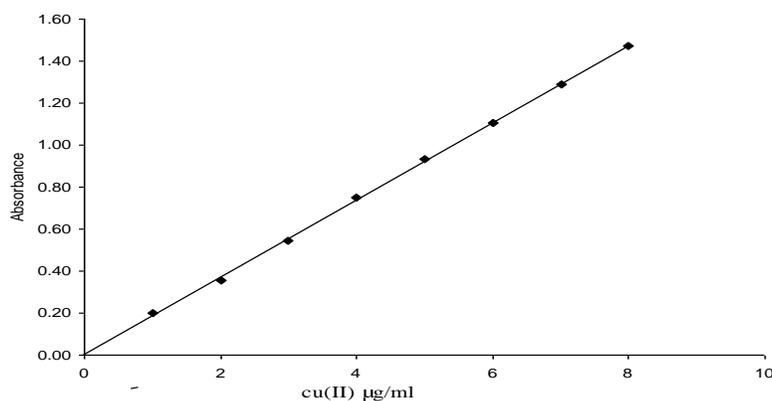


Fig.6. plot of absorbance versus different concentrations of Cu(II) ion (μgml^{-1})

Table (2): Validity of Beer's Law of Alizarine Red S chalets.

Metal ion	$\mu\text{g ml}^{-1}$	Slop	$\lambda_{\text{max}}(\text{nm})$	$\epsilon_{\text{max}} \times 10^3$ ($\text{L mol}^{-1} \text{cm}^{-1}$)	Intercept	Correlation Coefficient r	Regression equation
Fe(III)	2.8-28	0.03	574	1.701	-0.04	0.9996	$Y = 0.030X - 0.037$
Cu(II)	4.07-25.2	0.05	506	2.988	0.08	0.9992	$Y = 0.047X + 0.083$
Pd(II)	33.92-52.84	0.04	406	4.160	-1.31	0.9993	$Y = 0.039X - 1.313$
Ni(II)	3.38-14.43	0.06	582	3.555	0.15	0.9995	$Y = 0.061X + 0.155$
Co(II)	2.49- 16.85	0.07	598	4.300	0.13	0.9998	$Y = 0.072X + 0.126$

3.3. Characterization of isolated solid complexes

3.3.1. Microchemical Analysis

Microanalysis of carbon, hydrogen and nitrogen of the binary and ternary complexes were carried on Microanalysis Unit, Assuit University are listed in table (3).

3.3.2. Conductance Measurements

The observed molar conductances ($\Lambda\text{M} = 1.76 - 5.84 \text{ ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$) all the complexes in 10^{-4} molar solution in DMF, are given in table (3), which suggest the non-electrolytic nature of these complexes [31]. Such a non-zero molar conductance value for each of the complex in the present study is most probably due to the strong donor capacity of DMF, which may lead to the displacement of anionic ligand and change of electrolyte.

3.3.3. Infrared Spectra of Solid Binary Complexes of Alizarin Red s:

The FT-IR spectra of investigated solid complexes are shown in Fig. (7). It's observed the influenced bands are shifts to lower and higher frequencies by complexation. The IR spectra shows that the band at 1636 cm^{-1} in the spectrum of the ligand due to the stretching vibration of C=O carbonyl group is shifts to lower and higher frequencies by complexation from $1618 - 1647 \text{ cm}^{-1}$ for Cu(II), Pd(II), Ni(II) and Co(II) ions, but not influence for Fe(III) ion. The band at 3447 cm^{-1} in the free ligand which corresponding to $\nu(\text{OH})$ group is shifts to lower and higher frequencies in the spectra of the complexes from $3417 - 3467 \text{ cm}^{-1}$ due to coordination with metal ions. One new band appears for the all chalets at $531 - 559 \text{ cm}^{-1}$ region corresponding to stretching [M-O] metal-oxygen bond.

3.3.4. Infrared Spectra of Ternary Complexes of Alizarin red s and Cysteine:

The FT-IR Spectra of investigated ternary complexes of Fe(III), Cu(II), Pd(II), Co(II) and Ni(II) It's observed the influenced bands are shifted to lower and higher frequencies by complexation. The i.r. spectra shows that the

band at 1636 cm^{-1} in the spectrum of ARS due to the stretching vibration of C=O group is not influenced by coordination in case of Fe(III) and Cu(II) metal ions complexes and shifted to lower frequencies in case of Pd(II), Ni(II) and Co(II) metal ions from $1617\text{-}1623\text{ cm}^{-1}$. The band at 3447 cm^{-1} in the free ligand (ARS) which corresponding to $\nu(\text{OH})$ group is shifted to lower frequencies in the spectra of the complexes due to coordination with metal ions from 3419 cm^{-1} - 3435 cm^{-1} . The band at 1387 assigned to vibrations of the carboxylic group ($\nu_{\text{sym}}\text{COO}^-$) in the free ligand of cysteine is shifted to lower and higher frequencies by complexation from 1349 cm^{-1} - 1398 cm^{-1} , suggesting that this group is also involved in coordination to the metal ion. The band at 1488 cm^{-1} in the free ligand of cysteine which corresponding to δNH_3^+ group is not influenced, indicating not coordination to the metal ion. Two new bands appears for the all chalets one at $598\text{-}637\text{ cm}^{-1}$ region corresponding to stretching [M—O] metal-oxygen bond and the other at region from $566\text{-}613$ corresponding to stretching [M—S] metal-sulfur bond. The relative IR bands of alizarin red s, binary and their metal ternary complexes are listed in table (4).

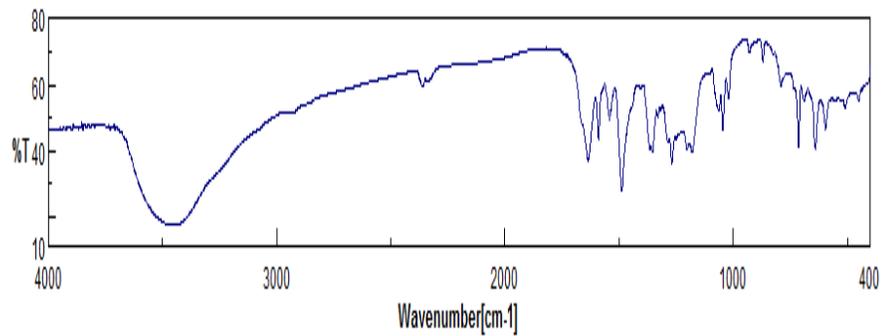
No	Compound	Colour	M.Wt.	Decomp. Temp. °C	Coord. no.	Λ_M $\text{ohm}^{-1}\text{cm}^2$ mol^{-1}	Calc. (Found) (%)			
							C	H	S	N
1	Alizarin Red S (ARS) $\text{C}_{14}\text{H}_7\text{NaO}_7\text{S}+\text{H}_2\text{O}$	Red	360.26	270	-----	-----	46.66 (46.2)	2.5 (2.66)	8.66 (8.72)	-----
2	[Fe(ARS) $\text{Cl}_3(\text{H}_2\text{O})$]. $5\text{H}_2\text{O}$	Black	612.73	>360	6	2.56	27.41 (27.49)	3.10 (3.15)	5.22 (5.19)	-----
3	[Cu (ARS) $(\text{NO}_3)_2(\text{H}_2\text{O})_2$]. $2\text{H}_2\text{O}$	Brownish-black	601.26	>360	6	2.23	27.94 (27.91)	2.49 (2.37)	5.32 (5.21)	-----
4	[Pd (ARS) $\text{Cl}_2 (\text{H}_2\text{O})_2$]. $3\text{H}_2\text{O}$	Black	609.54	>360	6	3.03	27.56 (27.51)	2.78 (2.83)	5.25 (5.11)	----
5	[Ni(ARS) $\text{Cl}_2 (\text{H}_2\text{O})_2$]. $2\text{H}_2\text{O}$	Purple	543.26	>360	6	3.96	30.92 (30.87)	2.76 (2.61)	5.89 (5.79)	----
6	[Co(ARS) $\text{Cl}_2 (\text{H}_2\text{O})_2$]. H_2O	Brown	562.99	>360	6	3.13	31.92 (31.89)	2.47 (2.38)	6.08 (6.2)	-----
7	[Fe (ARS) (Cys) Cl_2]. $3\text{H}_2\text{O}$	Black	608.76	>360	6	3.15	33.51 (33.67)	3.28 (3.20)	10.51 (10.46)	2.29 (2.21)
8	[Cu (ARS).(Cys) $(\text{NO}_3)_2$]. $2\text{H}_2\text{O}$	Brown	642.76	>360	6	1.76	31.73 (31.94)	3.11 (3.17)	9.95 (9.91)	2.17 (2.12)
9	[Pd (ARS)(Cys) Cl_2]. $4\text{H}_2\text{O}$	Purple	712.54	>360	6	1.83	28.63 (28.51)	3.08 (3.13)	8.98 (8.91)	1.96 (1.92)
10	[Ni(ARS)(Cys) Cl_2]. $4\text{H}_2\text{O}$	Reddish – brown	628.76	>360	6	2.31	32.44 (32.68)	3.49 (3.45)	10.17 (10.39)	2.22 (2.14)
11	[Co(ARS).(Cys) Cl_2]. $2\text{H}_2\text{O}$	Black	629.67	>360	6	5.84	32.39 (32.56)	3.49 (3.41)	10.16 (10.25)	22.22 (2.19)

Table (3): Physical Characteristics and Microanalytical data of Alizarin, binary and mixed- ligand complexes.

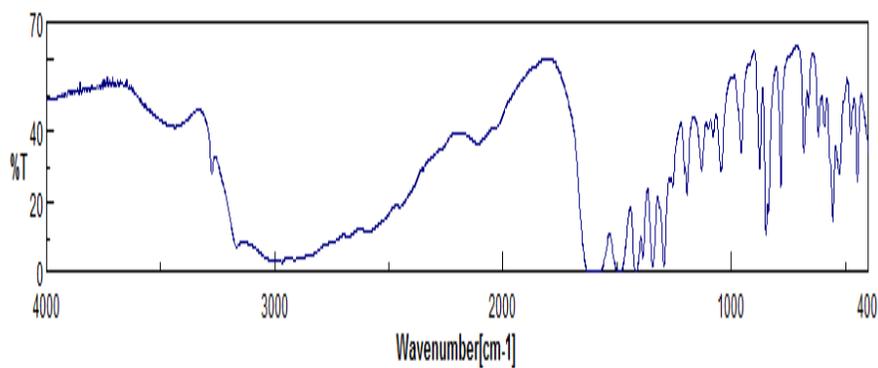
Table (4): Relative IR bands of Alizarin red S, Cysteine, Binary and their Ternary metal complexes.

Compound	νOH cm^{-1}	$\nu\text{C=O}$ cm^{-1}	νSHcm^{-1}	$\nu_{\text{asym}}\text{COO}^-$ cm^{-1}	δNH_3^+ cm^{-1}	$\nu_{\text{sym}}\text{COO}^-$ cm^{-1}	M←O	M←S	$\nu(\text{C-S})$
Alizarin red S (ARS) $\text{C}_{14}\text{H}_7\text{NaO}_7\text{S} + \text{H}_2\text{O}$	3447	1636	-----	-----	-----	-----	-----	-----	-----
Cysteine (Cys.) $\text{C}_3\text{H}_7\text{O}_2\text{NS}$	-----	-----	2589	1587	1488	1387	-----	-----	661
[Fe(ARS) $\text{Cl}_3(\text{H}_2\text{O})$]. $5\text{H}_2\text{O}$	3420	1636	-----	-----	-----	-----	605	-----	-----
[Cu (ARS) $(\text{NO}_3)_2(\text{H}_2\text{O})_2$]. $2\text{H}_2\text{O}$	3417	1618	-----	-----	-----	-----	611	-----	-----
[Pd (ARS) $\text{Cl}_2 (\text{H}_2\text{O})_2$]. $3\text{H}_2\text{O}$	3467	1647	-----	-----	-----	-----	598	-----	-----
[Ni(ARS) $\text{Cl}_2 (\text{H}_2\text{O})_2$]. $2\text{H}_2\text{O}$	3433	1622	-----	-----	-----	-----	614	-----	-----
[Co(ARS) $\text{Cl}_2 (\text{H}_2\text{O})_2$]. H_2O	3400	1634	-----	-----	-----	-----	637	-----	-----
[Fe (ARS) (Cys) Cl_2]. $3\text{H}_2\text{O}$	3435	1636	-----	-----	1501	1349	468	566	641
[Cu (ARS).(Cys) $(\text{NO}_3)_2$]. $2\text{H}_2\text{O}$	3434 3417	1636 1618	-----	-----	1460	1357	472	602	643
[Pd (ARS)(Cys) Cl_2]. $4\text{H}_2\text{O}$	3419	1618	-----	-----	1490	1398	471	598	637
[Ni(ARS)(Cys) Cl_2]. $4\text{H}_2\text{O}$	3434	1617	-----	-----	1492s	1349	471	613	636
[Co(ARS).(Cys) Cl_2]. $2\text{H}_2\text{O}$	3432	1623	-----	-----	1480	1349	467	609	639

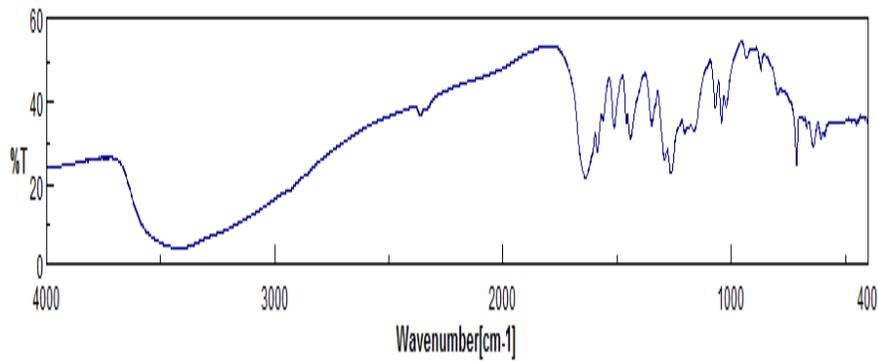
a



b



c



d

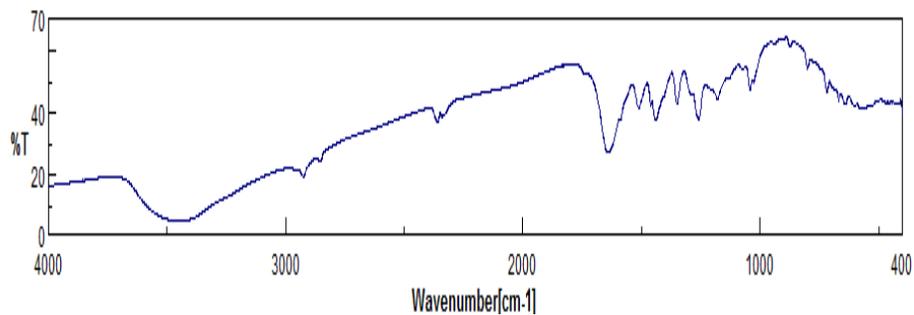


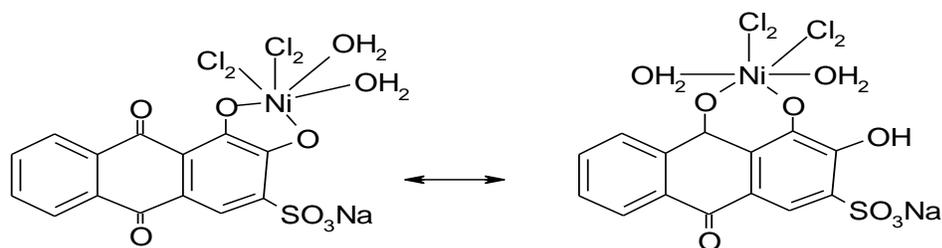
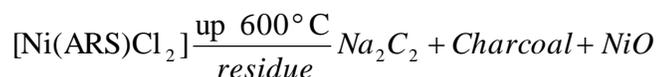
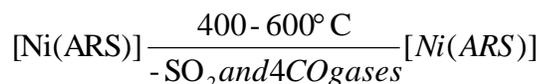
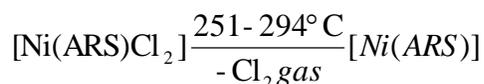
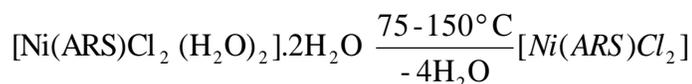
Fig.7. Infrared spectra of the ARS, Cysteine, binary and their ternary metal complexes. (a): ARS, (b): Cys., (c): Fe(III)-ARS binary, (d): Fe(III)-(ARS.Cys.) ternary complex.

3.3.5. Thermal Analysis of Binary and Ternary Complexes.

The TG curve of representative compound, $[\text{Ni}(\text{ARS})\text{Cl}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ binary complex, were recorded in the temperature range from ambient to 751°C at heating rate $10^\circ\text{C}/\text{min}$.

$[\text{Ni}(\text{ARS})\text{Cl}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ compound shows that the complex decompose completely with weight losses on three steps and finally give the NiO, sodium carbide (Na_2C_2) and charcoal as a stable product. The first step amounted to ($\sim 14\%$) at the temperature range between ($75-150^\circ\text{C}$), this can be reveal to corresponding to removal of two coordinated water molecules and two crystalline water molecules. The second step amounted to ($\sim 13.25\%$) can be attributed to liberation of Chlorine gas at temperature range between ($251-294^\circ\text{C}$). The third step amounted to ($\sim 33.65\%$) at temperature range between ($400-600^\circ\text{C}$) which can be attributed to the removal of SO_2 and four molecules of CO gases. Beyond 612°C , the residue attains a constant composition corresponding to the NiO, sodium carbide (Na_2C_2) and charcoal as stable product ($\sim 40.18\%$).

The suggested decomposition steps of Ni(II)-ARS binary complex are shown in following mechanism:



Structure of Ni- ARS binary complex

The thermogravimetric analysis of representative compound, $[\text{Co}(\text{ARS}).(\text{Cys})\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ ternary complex, were recorded in the temperature range from ambient to 747°C at heating rate $10^\circ\text{C}/\text{min}$.

The compound $[\text{Co}(\text{ARS}).(\text{Cys})\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ shows that the complex decompose completely with weight losses on three steps and finally give the CoO, sodium carbide (Na_2C_2) and charcoal as a stable product. The first step amounted to ($\sim 6.5\%$) at the temperature range between ($26-120^\circ\text{C}$), this can be reveal to corresponding to removal of two crystalline water molecules. The second step amounted to ($\sim 13.31\%$) can be attributed to liberation of chlorine gas from coordination sphere at temperature range between ($205-294^\circ\text{C}$). The third step amounted to ($\sim 25.27\%$) at temperature range between ($340-600^\circ\text{C}$) which can be attributed to the removal of SO_2 and four

molecules of CO gases. Beyond 600°C, the residue attains a constant composition corresponding to the CoO, sodium carbide (Na₂C₂) and charcoal as stable product (~ 45.18. %).

The DTA of binary and ternary complexes shows the endothermic-exothermic bands in all complexes.

The proposed decomposition steps of Co(II) ternary complex are shown in following mechanism:

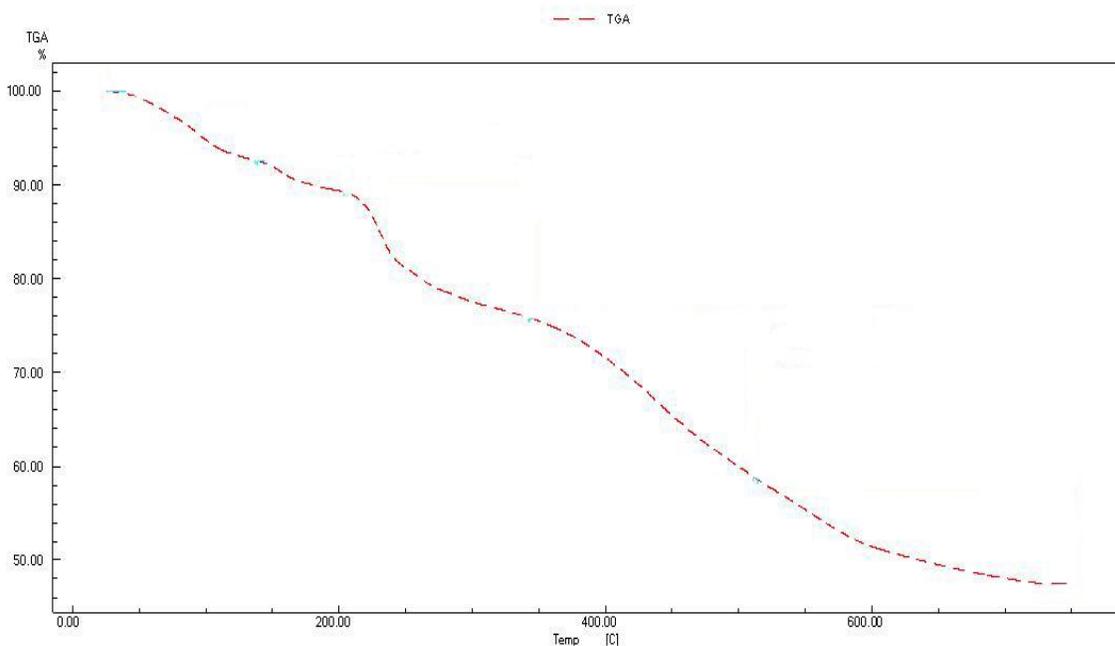
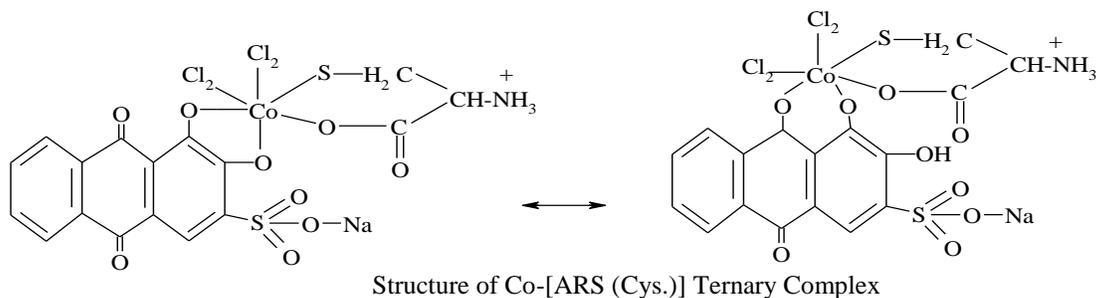
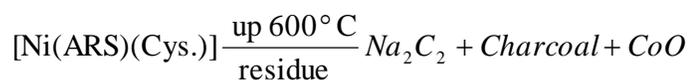
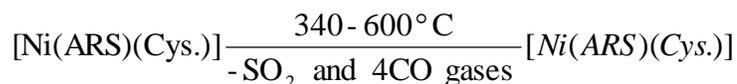
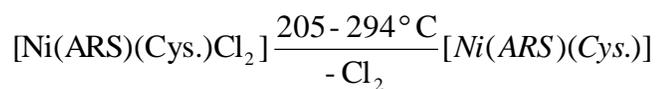
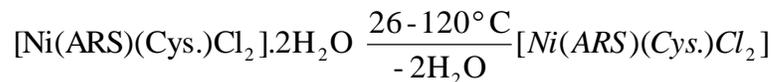


Fig.(8):-Thermogravimetric analysis curve of Co(II)-ternary complex

3.3.6. X-Ray Powder Diffraction:

The X-ray diffraction pattern is shown in Fig.(9) recorded for Fe(III) and Cu(II) with ARS binary Complexes, and Cu(II) and pd(II) with (ARS, cysteine) ternary complexes. X-ray diffraction pattern indicated that Fe(III), Cu(II) with ARS binary Complexes and Cu(II) with (ARS, cysteine) ternary complex are crystalline-amorphous structures. X-ray diffraction pattern indicated that pd(II) with (ARS, cysteine) ternary complex is crystalline structure.

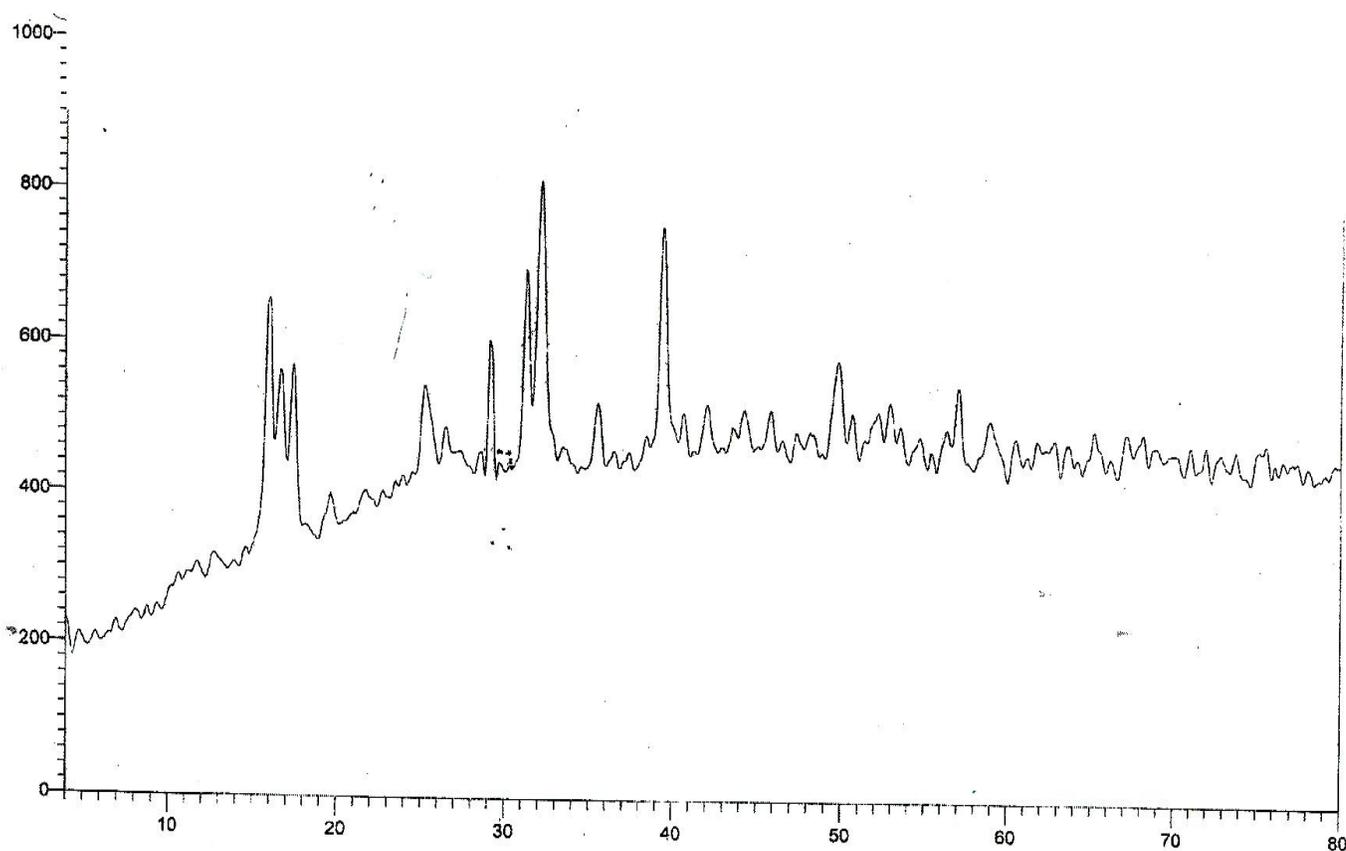


Fig.9. X-ray powder diffraction for Pd(II) - (ARS.Cys.) ternary complex.

3.4. Antimicrobial Activity:

The results of antifungal and antibacterial activity of ARS (L_1) and cysteine (L_2) and their Co(II) and Ni(II) binary and ternary complexes. The organism selected for the studies were *Aspergillus niger*, *Alternaria alternata* for antifungal and *Escherichia coli* (-ve) and *Bacillus cereus* (+ve) for antibacterial. The antibacterial activity was evaluated by inhibition zone technique. The results of antibacterial screening of ARS and Cysteine and their Co(II) and Ni(II) binary and ternary complexes at concentration of all samples is 2%. The results of antifungal and antibacterial activity of the ligands ARS and Cysteine and Co(II) and Ni(II) binary and ternary complexes are compared with the conventional fungicide clotrimazole as antifungal standards and chloroamphenicol as antibacterial standard. The antifungal antibacterial screening data in Table 5, reveal The Co(II), Ni(II) binary complexes and

Co(II) ternary complex are more fungi toxic than the parent ligands, except Ni(II) – (ARS.Cys.) ternary complex showed no significant with fungi and *Escherichia coli* (-ve). The toxicity increased with increasing concentrations. Cu(II), Ni(II) and Co(II) metal ion complexes.

Table5: Fungicidal, Antibacterial screening data for ligands (L₁and L₂) and their Cu(II), Ni(II) and Co(II) metal ion complexes. Where L₁ = Alizarin Red S L₂=Cysteine Concentration of all samples is 2%. Control =clotrimazole as antifungal standard.

Fungicidal , Antibacterial	Type of Fungicidal and Antibacterial	Ligands (L ₁ , L ₂)	Binary complexes		Ternary Complexes	
			Co(II)-L ₁	Ni(II)-L ₁	Co(II)-(L ₁ .L ₂)	Ni(II)- (L ₁ .L ₂)
Fungicidal	<i>Aspergillusniger</i>	0	35 +++	35 +++	12 +	-Ve
	<i>Alternariaalternata</i>	0	35 +++	30 +++	15 +	-Ve
Antibacterial	<i>Escherichia coli(-ve)</i>	0	20 +++	20 ++	15 +	-Ve
	<i>Bacillus cereus(+ve)</i>	0	20 ++	20 ++	20 ++	16 ++

= chloroamphenicol as antibacterial standard.

Conclusion:

A simple, rapid and sensitive spectrophotometric method has been developed for determination of investigated metal ions based on chelating reaction with alizarin red sulphonate reagent in aqueous solution. New ternary complexes with alizarin red sulphonate and cysteine in aqueous solution and solid state were studied in this work.

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