POTENTIOMETRIC AND THERMOGRAVIMETRIC STUDIES ON SOME METAL–OXINE–SULPHADRUGS TERNARY COMPLEXES

M. M. Omar

Chemistry Department, Faculty of Science, Cairo University, Egypt

Abstract

Formation constants ($\log K_{MAL}^{MA}$) of the mixed complexes of the type *M–A–L* (where *M*=Mn(II), Co(II), Ni(II), Cu(II), Ce(III), Th(IV), and UO$_2$(II); *A*=oxine and *L*=sulphamerazine or sulphadiazine) have been determined pH-metrically in 60% (*v/v*) ethanol–water mixture at 25°C and constant ionic strength (μ=0.1 M NaCl). The mode of chelation was ascertained by conductivity measurements. The stability sequence with respect to metal ions have been found to be Cu(II)>Ni(II)> Co(II)>Mn(II) and Th(IV)>UO$_2$(II)>Ce(III). CuAL ternary solid complexes have been prepared and characterized on the basis of elemental analysis and IR-spectroscopy. The thermal degradations of the prepared complexes are discussed in an attempt to assign the intermediate compounds formed.

Keywords: metal complexes, potentiometry, stability constant, thermogravimetry

Introduction

8-Hydroxyquinoline (oxine) and its derivatives have long been established as potential antifungal, antibacterial agents and pharmacological drugs [1–3], oxine also behaves as uninegative bidentate chelating ligand ON potential donor sites [3]. Stability of oxine chelates and analogous reagents have been determined pH-metrically [4–7].

Sulphanilamide (H$_2$NC$_6$H$_4$SO$_2$NH$_2$) and its N-substituted compounds are well known as sulphadrugs [8], which are in general bacteriostatic drugs [9]. The role of mixed ligand complexes in biological, environmental and analytical chemistry has been well recognized [10]. Thermal analysis have been reported for mixed ligand complexes of Cu(II), the course of thermal decomposition differs for each of the simple complexes but in all cases it finally leads to CuO formation [10–14]. Accordingly, study of mixed-ligand metal complexes containing oxine is considered as an important effort to understand their metal ion complexation in the biological systems. Although studies on the chelating properties of some sulphadrugs have been reported in literature [15–17], no work has been done on the formation constants of ternary complexes of oxine with metal ions with sulphadrugs as secondary ligands.

In the present article, the overall formation constants of ternary complexes of oxine–Cu(II), Ni(II), Co(II), Mn(II), Th(IV), UO_2(II), and Ce(III) with sulphamerazine(I) and sulphadiazine(II) as secondary ligands were determined in 60% (*v/v*) ethanol medium at 25°C and ionic strength of 0.1 M (NaCl). Also, a detailed thermal analysis of the solid complex is reported to obtain information concerning the thermal stability of CuAL complex and to suggest a general scheme for its thermal decomposition.
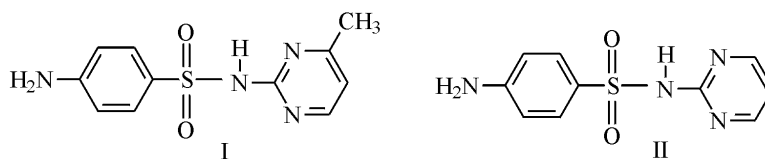
Experimental

All chemicals employed were of analar or chemically pure grade. Metal solutions were prepared and standardized by usual methods reported elsewhere [18]. Pure oxine was recrystallized several times from water and alcohol till constant melting point at 74–76°C. All the standard sulphamerazine and sulphadiazine were carefully recrystallized before use. Chemically pure sodium chloride was used to keep the ionic strength constant. Sodium hydroxide and hydrochloric acid were standarized by usual methods [18]. Three mixtures (for binary complexes) and four mixtures (for ternary complexes) were prepared and potentiometrically titrated [19] using a digital pH-meter (Orion Research model 701 A Digital Ionalizer) at 25°C in a purified nitrogen atmosphere. The pH-meter and electrode were calibrated by using standard buffer solutions. The measurements of pH values of partially aqueous solvents were carried out according to Bate [20]. The $\bar{n}_A$ (average number for protons associated with the ligands), $\bar{n}$ (average number of ligands attached per metal ion), and *pL* (free ligand exponent) values were calculated using a method of Irving and Rossotti [19]. The successive formation constants of the complexes ($\log K_1$, $\log K_2$) were calculated applying the interpolation at half $\bar{n}$ values [19].

Conductometric titrations of mixtures containing: 10 mL of 0.02 M metal ion, 10 mL of 0.02 oxine, 10 mL of 0.02 M sulphadrug and 30 mL absolute ethyl alcohol with standard CO_2-free sodium hydroxide solution (0.02 M) were performed. Conductometric curves were traced by plotting the specific conductance as a function of the equivalents of base added per mole of metal ion. The electrolytic conductances were measured using Orion conductivity meter, model 150.

The ternary solid complexes of Cu(II) with oxine and sulphadrugs were prepared by mixing hot ethanolic solution of Cu(II) acetate with the requisite amounts of ligands sufficient to form 1:1:1 (Cu(II):oxine:sulphadrug) molar ratios. The solution was refluxed for 1–2 h, left to cool, filtered and washed with ethanol. The green colored complexes were separated as fine crystals. Cu(II) ions in the complexes were estimated gravimetrically [18].

The solid complexes were subjected to elemental analysis. IR-spectra (KBr) of the ligands and complexes were recorded on a PYE Unicam SP 3-300 spectrophotometer. Thermogravimetric analysis (TG) was carried out under nitrogen atmosphere with a heating rate of 10°C min^{-1} using a Shimadzu DT-50 analyzer.

Determination of reaction order of decomposition

The reaction order of decomposition of Cu complex was calculated from its DTG plots [19]. The mass fraction of the substance present at DTG peak (C_s) can be determined from the following relation:

$$C_s = (W_s - W_f)/(W_i - W_f) \tag{1}$$

where W_s is the mass remaining at T_s (the temperature of DTG peak), and W_i and W_f are the initial and final masses of the substance. The order of the decomposition reaction (n) could then be calculated from the relation:

$$C_s = (n)^{1/1-n} \tag{2}$$

Calculation of kinetic and thermodynamic parameters

Using the Coats–Redfern equation [22], for a first order process, the activation energy E^* in J mol^{-1} could be calculated from the following equation:

$$\log\left[\frac{\log\frac{W_\infty}{W_\infty - W}}{T^2}\right] = \log\left[\frac{AR}{\phi E^*}\left(1 - \frac{2RT}{E^*}\right)\right] - \frac{E^*}{2.303RT} \tag{3}$$

where W_∞ is the mass loss at the completion of the decomposition reaction, W is the mass loss up to temperature T, R is the gas constant, A is the Arrhenius constant and ϕ is the heating rate. Since for most values of E^* and for the temperature range over which reactions generally occur the expression $\log[AR/(\phi E^*)(1-2RT/E^*)]$ is sensibly constant [22], the plot of the left-hand side of Eq. (3) vs. $1/T$ would give a straight line (Fig. 1). E^* was then calculated from the slope and A from the intercept. The activation entropy S^*, activation enthalpy H^* and the free energy of activation G^* were calculated using the following equations:

$$S^* = 2.303\left(\log\frac{Ah}{kT}\right)R \tag{4}$$

$$H^* = E^* - RT \tag{5}$$

$$G^* = H^* - TS^* \tag{6}$$

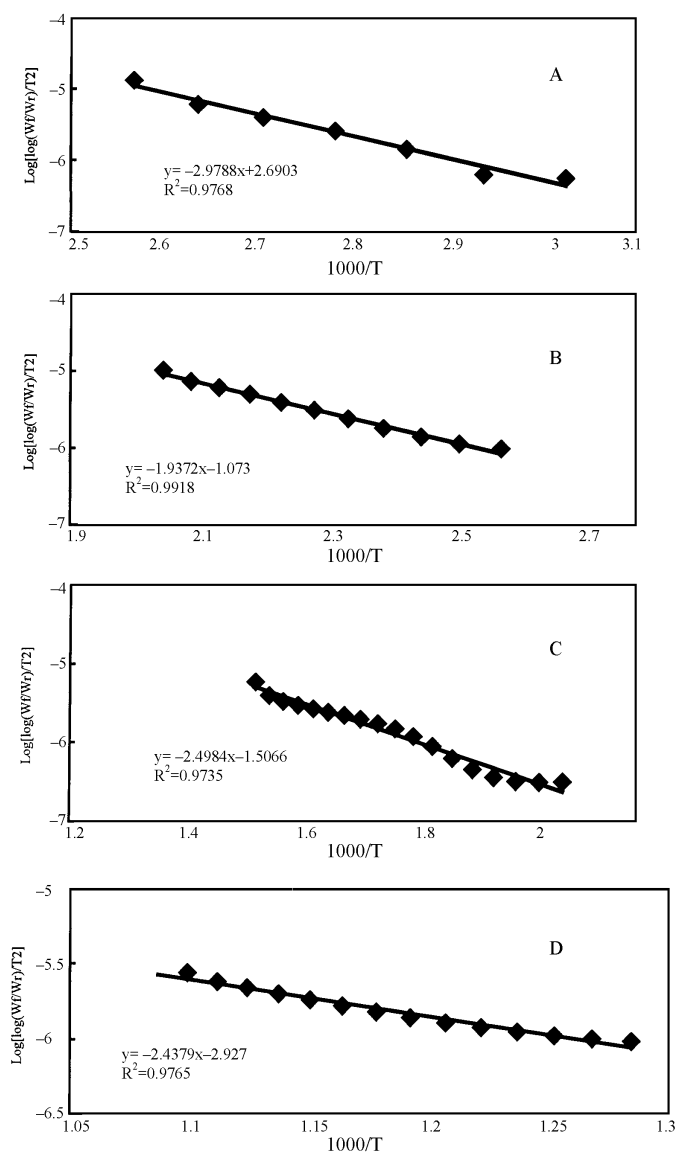where k and h are Boltzmann and Planck constants, respectively.

Fig. 1 Coats–Redfern plots of the thermal decomposition

Results and discussion

## Proton-ligand formation constant

From the titration curves of solutions of acid alone and in the presence of ligands; the proton-ligand formation number ($\bar{n}_A$) was calculated at various pH values and plotted *vs.* pH. The proton-ligand stability constants were calculated by: (a) the method of in-

terpolation at half $\bar{n}_A$ values and (b) by plotting $\log(\bar{n}_A/1-\bar{n}_A)$ and $\log[(\bar{n}_A-1)/(2-\bar{n}_A)]$ *vs.* pH for mono- and di-basic acids respectively, whereby linear curves were obtained in each case intersecting the pH axis at pK_a values. The values obtained at $\mu=0.1$ M for the investigated ligands are summarized in Table 1.

Table 1 pK_a values of ligands in 60% ethanol–water mixture

Ligand	Method (a)		Method (b)		Mean pK_a	
	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2
Oxine	3.58	10.95	3.70	11.20	3.64	11.08
Sulphamerazine	6.41	10.10	5.80	10.82	6.11	10.46
Sulphadiazine	4.90	10.30	4.50	11.20	4.70	10.75

The above data show that the primary ligand 'oxine' has two proton-ligand formation constants (pK_{NH} and pK_{OH}). These constants correspond to the following neutralization reaction:
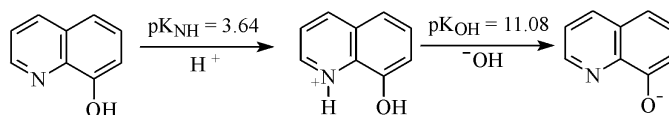
The data show also that sulphamerazine and sulphadiazine have two ionization steps. The first is assigned to the deprotonation of the protonated molecule when present in acid medium ($H_3N^+-C_6H_4-SO_2-NH-R$) and the second is due to ionization of the $-SO_2-NH-R$ group. The pyridyl nitrogen is not protonated since pH *vs.* volume of NaOH added curve overlaps the acid curve at low pH values.

However, the lowest pH value observed in the present work is 2.3 and the protonation of the pyridyl nitrogen occurs at this value. Also, the presence of ethanol as a protogenic solvent may solvate the pyridyl nitrogen and prevents its protonation.

Metal–ligand stability constants of the investigated metal ions with oxine

The pH-titration curves reveal that the metal–ligand titration curves are well separated from the ligand titration curve indicating the liberation of proton through complex formation between the ligand and the metal ions under investigation. The average number of ligand molecules attached per metal ($\bar{n}$) ion and the free ligand exponent pL were calculated at different pH's by Irving and Rossotti technique [19] using the titration curves of the three mixtures. However, $\bar{n}$ values greater than 2, have not been obtained in any case. It is, therefore, concluded that the only 1:1 and 1:2 (metal:ligand) complexes are possible to be formed in each system. The stepwise formation constants ($\log K_1$ and $\log K_2$) were computed by interpolation at half $\bar{n}$ values, the results are listed in Table 2. The order of stability constants was found to be Cu(II)>Ni(II)>Co(II)>Mn(II), in agreement with Irving and Williams order [23].

Also, the order of stability constants for Th(IV), UO₂(II) and Ce(III) was found to be Th(IV)>UO₂(II)>Ce(III). The lower stability of the other metal complexes can be ascribed to the fact that the lanthanide complexes are substantially dissociated in aqueous solutions. On the other hand, the higher stability of Th(IV) complex relative to UO₂(II) complex is due to the high positive charge on Th(IV), which makes it much more susceptible to complex formation than UO₂(II).

Table 2 Formation constants of binary complexes of oxine with the investigated metal ions

Metal ion	$\log K_1$	$\log K_2$	$\log B_2$
Cu(II)	12.03	11.90	23.93
Ni(II)	10.22	9.80	20.02
Co(II)	10.00	9.00	19.00
Mn(II)	8.00	7.17	15.17
Th(IV)	11.30	9.98	21.28
UO₂(II)	11.00	9.50	20.50
Ce(III)	9.00	7.80	15.80

Metal–ligand stability constants of the investigated metal ions with sulphadrugs

The values of the stepwise formation constants ($\log K_1$, $\log K_2$) of the investigated complexes are given in Table 3. The complexation takes place at higher pH values after deprotonation of both H_3N^+ and NH groups. The presence of metal ion may assist in the ionization of the NH group. The order of stability constants was found to be the same as in the case of metal-oxine complexes.

Table 3 Formation constants of binary complexes of sulphadrugs with the investigated metal ions

Ligand	Metal ions	$\log K_1$	$\log K_2$	$\log B_2$
Sulphamerazine	Cu(II)	4.00	3.42	7.42
	Ni(II)	3.50	2.70	6.20
	Co(II)	3.46	2.65	6.11
	Mn(II)	3.08	2.58	5.66
	Th(IV)	7.05	6.55	13.60
	UO₂(II)	5.88	5.60	11.48
	Ce(III)	4.25	3.95	8.20
Sulphadiazine	Cu(II)	7.49	3.11	10.60
	Ni(II)	5.40	3.09	8.49
	Co(II)	5.00	2.80	7.80
	Mn(II)	4.00	2.75	6.75
	Th(IV)	8.00	7.05	15.05
	UO₂(II)	6.95	5.80	12.75
	Ce(III)	5.35	4.85	10.20

Table 4 $\log K_{MA}^{M}$, $\log K_{MAL}^{MA}$, $-\Delta\log K$ values

Secondary ligand (L)	Property	Values for metal ions							
		Cu(II)	Ni(II)	Co(II)	Mn(II)	Th(II)	UO_2(II)	Ce(III)
Sulphamerazine	$\log K_{MA}^{M}$	12.03	10.22	10.00	8.00	11.30	11.00	9.00
	$\log K_{MAL}^{MA}$	7.05	6.95	5.90	5.25	8.75	8.00	6.95
	$-\Delta\log K$	4.98	3.27	4.10	2.75	2.65	3.00	2.85
Sulphadiazine	$\log K_{MA}^{M}$	12.03	10.22	10.00	8.00	11.30	11.00	9.00
	$\log K_{MAL}^{MA}$	9.05	7.70	7.50	6.00	9.00	8.05	6.25
	$-\Delta\log K$	2.98	2.62	2.50	2.00	2.30	2.95	2.75

Stability constant of ternary complexes

The necessary conditions for the study of the ternary complexes is that the 1:1 (metal: primary ligand), *MA*, complex formation should be complete at low pH and that the metal–primary ligand complex (*MA*) should be stable at higher pH where the combination of secondary ligand (*L*) with *MA* takes place; which holds well in the present study. The stability constants of the mixed complexes were determined pH-metrically using the method described by Dixit and Munshi [24]. The values of $\bar{n}$, in the plot of $\bar{n}$ *vs*. *pL*, never exceeded unity, which reveals the formation of only 1:1:1 mixed complex. The values of $\log K_{MAL}^{MA}$ were evaluated using the method of interpolation at half $\bar{n}$ value. This constant is a step constant for the reaction:

$$MA + L \leftrightarrow MAL$$

where *M* is the metal ion, *A* is the primary ligand, and *L* is the secondary ligand. The experimental values of $\log K_{MAL}^{MA}$ and $-\Delta \log K = (\log K_{MAL}^{MA} - \log K_{MAL}^{M})$ are reported in Table 4.

It is clear from Table 4 that the stability constant of the mixed ligand complexes of Cu(II) are considerably larger as compared to other metals of 3d series. Under the influence of ligand field Cu(II) ($3d^9$) will receive some extra stabilization [25] due to tetragonal distortion of octahedral symmetry in its complexes. Subject to Jahn–Teller effect, Cu(II) complexes will be further stabilized [25].

$\Delta \log K$ values are negative; this can be reasonably explained on the basis of the electrostatic repulsion between the incoming sulpha drug ion L^- and $(MA)^-$ complex, and the basicity of the ligand involved. $\Delta \log K$ may be expressed as the equilibrium constant for the reaction ($MA + ML = MAL + M$) and its value may be regarded as a measure of the coordination tendency of L towards *MA* relative to *M* (charges on the species have been omitted for the sake of simplicity).

Correlation of the properties of metal ions with the formation constants of mixed ligand complexes

The formation constants of mixed ligand complexes of bivalent 3d transition metal ions with oxine and sulphamerazine or sulphadiazine are in the order: Cu(II)>Ni(II)> Co(II)>Mn(II) in accordance with Irving and Williams order [23]. The correlation between the $\log K_{MAL}^{MA}$ and the reciprocal ionic radii (1/*R*) of the studied bivalent transition metal ions was found to be almost linear. Also, a good linear correlation has been obtained between $\log K_{MAL}^{MA}$ and the electronegativities of the metal ions under study. A good linear relationship has been obtained between $\log K_{MAL}^{MA}$ and the second ionization potential of the bivalent metal ions under study. The lower stability of Mn(II) chelates in the two sulphadrugs may be due to its larger radius (0.78).

Conductometric studies

The conductometric titration curve of the mixed ligand complexes of Cu(II) (Fig. 2), shows an initial decrease, then an inflection at *a*=2. This probably corresponds to the
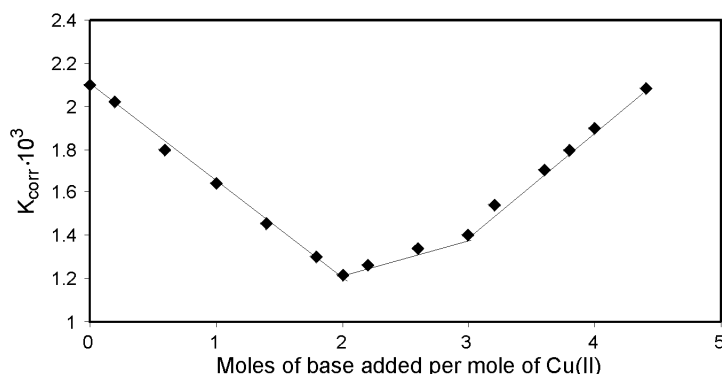
Fig. 2 Conductometric titration curve of Cu(II)–oxine–sulphadiazine system

neutralization of H^+ ions resulting from the formation of Cu(II)–oxine complex. Between $a=2$ and $a=3$, the slight increase of conductance is due to added Na^+ ions, where the formation of the ternary complex which is associated with the release of a proton from the sulphadrug. This is readily neutralized by the OH^- added. Beyond $a=3$, the conductance increases more appreciably simply due to the addition of excess NaOH.

Composition and structure of solid complexes

The results of experimental analysis and metal content estimation are in good agreement with those required by the proposed formula where 1:1:1 (*M:A:L*) solid chelates were isolated. IR-spectra of the chelates under investigation show that OH stretching vibration is still observed, but is either shifted to lower frequency or split into two bands, indicating the presence of more than one type of OH groups, namely, the phenolic OH group of oxine which was involved in chelate formation and those due to ν_{OH} of hydrated or coordinated water. A strong band is observed at ~1130 cm^{-1} indicating the presence of the oxine group in the complexes coordinating through its nitrogen and oxygen atoms as a uninegative bidentate ligand. Chelation with sulphadiazine or sulphamerazine may be achieved by a tautomeric shift of the sulphonamide hydrogen to sulphonyl oxygen [26]. This can explain the chelating ability of sulphamide when a six membered ring is formed. Two prominent bands near 1350 and 1160 cm^{-1} are to be assigned to asymmetric and symmetric vibration, respectively, of the two S–O bands in the free sulphadrugs ligands. These two bands are slightly shifted to higher frequency regions indicating that sulphadrugs coordinate to the metal ion through oxygen of SO_2 group. The presence of M–N, M–O is evident from the new bands appearing near 480, 410 cm^{-1}, respectively.
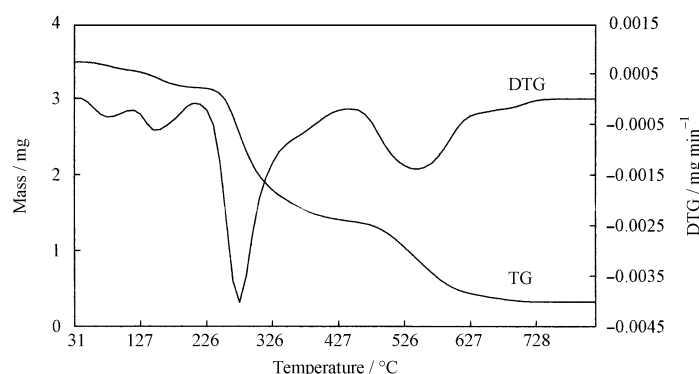
Fig. 3 TG and DTG plots
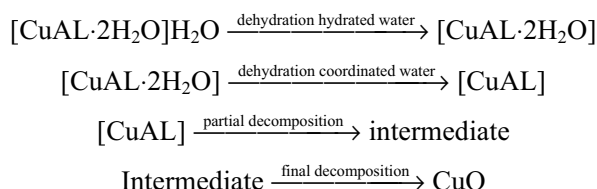
Thermogravimetric analysis

From the TG of the CuAL complex (Fig. 3), the mass loss for the investigated chelate was calculated within the temperature range at which pronounced decrease in mass was observed. The found and calculated mass losses are listed in Table 5. The mass loss within the temperature range 60–117°C is probably due to the loss of hydration water molecules. A loss of 3.32% is observed (Table 5), corresponding to the elimination of one water molecule.

The water of coordination is usually eliminated in the temperature range 150–250°C. Two molecules are coordinated to the metal ion to fulfil the coordination number six and they are expelled within the temperature range 117–215°C. Further heating results in gradual decomposition of the complex, as may be seen from the mass loss continuing until constant mass where the copper oxide residue is formed as the final product near 640°C. The TG curve shows additional inflections in the temperature range 390–640°C, such inflections may be attributed to the formation of unstable intermediate products. Accordingly, the final stage at 600–740°C includes the conversion of such intermediates to the residual oxide, CuO, with a percentage of 15.53%.

**Table 5** Thermal analysis data of CuAL complex

Molecular formula	Decomposition steps/°C	Mass loss/%	Species eliminated	Solid decomp. product/%
	60–117	3.32	H_2O	–
	117–215	6.24	$2H_2O$	–
$C_{19}H_{19}N_5O_5SCu$	215–390	47.92	$C_{10}H_9N_4OS$	–
	397–640	30.29	–	–
	600–740	–	–	CuO
	–	–	–	15.53

On the basis of the above observations, the following scheme of thermal decomposition may be proposed for the CuAL complex (*A*=oxine, *L*=sulphadiazine).

$$[CuAL \cdot 2H_2O]H_2O \xrightarrow{\text{dehydration hydrated water}} [CuAL \cdot 2H_2O]$$

$$[CuAL \cdot 2H_2O] \xrightarrow{\text{dehydration coordinated water}} [CuAL]$$

$$[CuAL] \xrightarrow{\text{partial decomposition}} \text{intermediate}$$

$$\text{Intermediate} \xrightarrow{\text{final decomposition}} CuO$$

Based on the above results (elemental analysis, IR and TG analysis), the reaction of oxine and sulphadiazine with Cu(II) ion is accompanied by the displacement of one proton from oxine molecule forming a covalent bond in addition to the coordination bond with the N-atom of quinoline moiety. On the other hand, sulphadrug coordinates to the metal ion through oxygen of SO_2 group and N of the heterocyclic nucleus.

In the light of these findings, the structure of the 1:1:1 complex can be represented as follows:
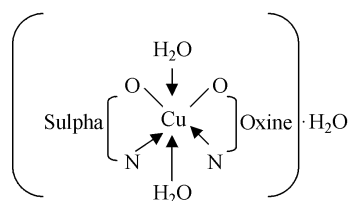
Kinetic and thermodynamic parameters

The estimated value of C_s for the thermal decomposition of the investigated complex was found in the range 0.28–0.31. This range indicates that the decomposition reactions of the complex follow first order kinetics [21]. The values of activation energies, as well as the Arrhenius constants are given in Table 6. The correlation coefficients of the Arrhenius plots of the thermal decomposition steps were found to lie in the range 0.97–0.99, which demonstrates good fitness of the linear function. The activation energy of the decomposition step of the investigated complex is found to be 37.12–57.08 kJ mol^{-1}. This low value of the activation energy expected for this broad decomposition step, which extends over 250 K, results in a very low temperature coefficient. This reaction may occur through a complex sequence of linked consecutive and/or concurrent rate process. The entropy of activation varies from –102 to –218 J K^{-1} mol^{-1} Table 6. The negative values of S^* indicate that the reactions are slow in nature, hence assisted by the wide range of decomposition temperatures.

Table 6 The kinetic and thermodynamic data of the thermal decomposition

Decomp. temp./K	$E^*/$ kJ mol^{-1}	R^2	A/s^{-1}	$S^*/$ J mol^{-1} K^{-1}	H^* kJ mol^{-1}	G^* kJ mol^{-1}	C_s
354	57.08	0.98	$3.30 \cdot 10^7$	−102.26	54.13	90.31	0.30
427	37.12	0.99	$3.70 \cdot 10^3$	−179.47	33.56	110.24	0.29
559	47.87	0.97	$1.79 \cdot 10^3$	−187.89	43.22	148.31	0.28
813	46.71	0.98	$0.66 \cdot 10^2$	−218.40	39.95	217.42	0.31

Conclusions

An attempt was made to study the structure of mixed ligand complexes of Cu(II) with oxine as a primary ligand and sulphadrugs as a secondary one. The results suggested that oxine coordinates to the metal ion through N of the quinoline moiety and O of the phenolic group and sulphadrug coordinates through N of the heterocyclic nucleus and O of the SO_2 group. The study also shows that the thermal decomposition of the complexes follows first order kinetics and the course of thermal decomposition leads finally to CuO formation.

References

 1 A. Kumar, B. P. Jaju, S. Gurtu, J. N. Sinha and K. Shanker, Indian J. Chem., 27 (1988) 93.
 2 A. S. A. Zidan, A. I. El-Said, M. S. El-Meligy, A. A. M. Aly and O. F. Mohammed, J. Therm. Anal. Cal., 62 (2000) 665.
 3 W. Johnstan and H. Freiser, J. Am. Chem. Soc., 74 (1952) 5239.
 4 B. Bipin Mohapatra and S. K. Pujari, J. Indian Chem. Soc., 59 (1982) 1183.
 5 M. M. Omar and F. A. A. El-Seify, Monatshefte für Chemie, 122 (1991) 445.
 6 R. Dixit, D. G. Marathe and N. S. Bhave, J. Indian Chem. Soc., 64 (1987) 435.
 7 S. Panda, R. Mishra, A. K. Panda and K. C. Stapathy, J. Indian Chem. Soc., 66 (1989) 472.
 8 K. K. Narang and J. K. Gupta, J. Indian Chem. Soc., 13 (1975) 705.
 9 J. G. Scholton and U. G. Stone, Anal. Chem., 21 (1952) 49.
10 A. M. Donia, T. Y. Al-Ansi and M. Q. Othman, J. Thermal Anal., 50 (1997) 857.
11 A. Turek and M. Olczak-Kobza, J. Therm. Anal. Cal., 54 (1998) 133.
12 W. Brzyska and W. Ozga, J. Therm. Anal. Cal., 61 (2000) 135.
13 M. Merdivan, F. Kripein, N. Kulcu and R. S. Aygun, J. Therm. Anal. Cal., 55 (1999) 551.
14 W. Wolodkiewicz and W. Brzyska, J. Therm. Anal. Cal., 55 (1999) 288.
15 G. N. Mukherjee and S. Basu, J. Indian Chem. Soc., 76 (1999) 288.
16 N. M. El-Guindi, A. A. Salman and C. Sharaby, Egypt. J. Pharma. Sci., 30 (1989) 23.
17 A. L. El-Ansary, W. F. El-Hawary and A. M. Atwa, Indian J. Chem., 32 (1993) 913.
18 W. Scott and H. Furman, Standard Methods of Chemical Analysis, Von Nostrand, New York 1962.
19 H. Irving and H. S. Rossotti, J. Chem. Soc., (1953) 3397; (1954) 2904.
20 R. G. Bate, M. Paabo and R. A. Robinson, J. Phys. Chem., 67 (1963) 1833.
21 H. H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.

22 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
23 H. Irving and R. J. P. Williams, Nature, 162 (1948) 746.
24 K. R. Dixit and K. N. Munshi, J. Indian Nucl. Chem., 57 (1980) 576.
25 L. E. Orgel 'An Introduction to Transition Metal Chemistry Ligand Field Theory', Methuen, London 1966.
26 N. N. Ghosh and M. M. Nadi, Indian J. Chem., 14A (1976) 778.