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Investigations on new transition metal chelates of the 3-methoxy-salicylidene-2-aminothiophenol Schiff base

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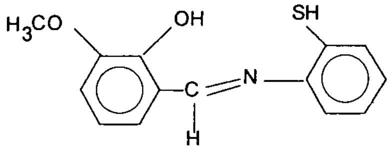
Abstract

New Co (II), Cu (II) and Zn (II) complexes of a Schiff base have been prepared and characterized by elemental analyses, IR, and ^{1}H-NMR spectroscopy, thermogravimetric analysis, conductometric and magnetic measurements. The results suggested that the Schiff base is a bivalent anion with tridentate ONS donors derived from the phenolic oxygen, azomethine nitrogen and thiophenolic sulfur. The formulae were found to be [$ML\cdot H_2O$] and [ML_2] for the 1 : 1 and 1 : 2 non-electrolytic complexes, respectively. The thermal decomposition of the complexes follows first order kinetics and the thermodynamic parameters of the decomposition were calculated. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Methoxysalicylidene-2-aminothiophenol; Transition metal complexes; Spectral and thermogravimetric studies

1. Introduction

A large number of Schiff bases and their complexes have been studied because of their interesting and important properties, e.g., their ability to reversibly bind oxygen [1], catalytic activity in hydrogenation of olefins [2] and transfer of an amino group [3], photochromic properties [4] and complexing ability towards certain toxic metals [5]. Metal complexes of Schiff bases derived from substituted salicylaldehydes and various amines have been widely investigated [6–13]. However, little attention has been given to Schiff bases, which include the ONS donor system. The aim of this work is to prepare and investigate the structure of the chelates of 3-methoxysalicylidene-2-aminothiophenol Schiff base I with cobalt (II), copper (II) and zinc (II) ions.



H_2L

2. Experimental

2.1. Chemicals

All the chemicals used were analytical grade or of equivalent quality. The organic solvents were obtained

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as pure grade material from BDH or were purified by recommended methods [14].

2.2. Preparation of the Schiff base

The title Schiff base H_2L was prepared by condensing o-vanillin (3-methoxy -salicylaldehyde) with 2-aminothiophenol and was recrystallized from dilute AcOH to constant m.p. (155°C). The proposed formulation was confirmed [14] by elemental microanalysis and its IR and 1H-NMR spectra.

2.3. Complexes and measurements

The pH-potentiometric titrations are carried out in an alcohol–water mixture (70% v/v) to ensure the complete solubility of the Schiff bases, at 25°C and ionic strength $\mu = 0.1$ (achieved by the addition of appropriate amounts of 1 M sodium chloride solution) using Jenway 3010 pH meter. The ionization constants of the investigated Schiff base 1 and the formation constants of its metal chelates were determined using the technique of Sarin and Munshi [14] and also Irving and Rossotti [15] where four methods are used in the calculation. These are interpolation at half *n* values(A), correction term(B), successive approximation(C) and mid term(D).

The solid complexes of cobalt (II), copper (II) and zinc (II) with the title Schiff bases were prepared by mixing hot saturated EtOH solutions of the metal acetates (5.0 mmol) with the necessary amount of Schiff base sufficient to form 1 : 1 or 1 : 2 (M : L) complexes. The solution was made 85% v/v ethanol water by the addition of ethanol and water in the dilution of the volume to 250 ml. The pH was adjusted to 5.0–6.0 using alcoholic ammonium hydroxide (few drops of conc. NH_4OH in ethanol) and the solution then refluxed for 2 h, evaporated under vacuum to 100 ml and cooled overnight to separate the solid complex which was filtered and washed several times with ethanol until the filtrate became colorless. The isolated complex was re-crystallized from DMF/ethanol mixture by dissolving it in the least amount of DMF, filtered while hot and diluted by ethanol to 100 ml and left overnight. The solid complex once separated was then filtered and washed first by ethanol then by diethyl ether and dried in a vacuum dessicator and subjected to elemental microanalysis.

The metal contents were determined by MacDonald's method [16,17]. The IR spectra were measured using a 1430 Perkin Elmer IR spectrometer. The ^{1}H-NMR spectra were recorded on a Varian Gemini 200 (200 MHz) spectrometer. d^6-DMSO was used as the solvent and the spectra were measured in the 0–14 ppm range using TMS as the internal standard.

The conductometric titrations were carried out using a Jenway 4200 conductivity meter. The experimental procedure involved the titration of 50 cm^3 of EtOH solution containing 0.5 mM of the Schiff base against a standard solution of the metal (10 mM) using a 5 cm^3 microburette, with continuous magnetic stirring. The conductivity values were corrected for the effect of dilution during the titration by multiplying the observed value by the ratio $V + v/V$, where V is the original volume of titrand (50 cm^3) and v is the volume of titrant. The corrected conductivity values were plotted versus the molar ratio (L : M) (Schiff base : -Metal). The resulting curves were composed of straight lines intersecting at the molar ratio of the formed chelates. However, the conductivities of the isolated complexes were measured in DMF. Magnetic measurements were carried out at 25°C using a Sherwood scientific magnetic susceptibility balance.

The thermal analyses of the complexes were carried out using a Shimadzu Thermogravimetric Analyzer with A-50H detector in nitrogen atmosphere (30.0 cm^3/min flow rate). The weight loss% was measured from the ambient temperature up to 800°C at 10°C/min.

3. Results and discussion

The elemental analyses (Table 1) are in good agreement with those required by the proposed formulae. The metal contents given are the average values of the metal content determination [18] and those calculated from thermal analysis (metal oxide residue). All the new complexes are coloured.

3.1. Potentiometric data

The ionization constants (pK_a) of the Schiff base H_2L are found to be 8.4 and 10.5 assigned to the OH and SH groups, respectively [19]. The formation constants of the metal complexes are evaluated (Table 2). It is clear from Table 2 that the Schiff base 1 has a

Table 1
Elemental analysis, molar conductivities and magnetic moments of Schiff base I complexes

Compound	Colour	Yield	%Found (Calc.)					Λ (S cm^2 mol^{-1})	μ_{eff} (B.M.)
$C_{14}H_{13}NO_2S$	Faint yellow	98.7	65.3 (64.9)	5.0 (5.0)	5.6 (5.4)	12.4 (12.4)	–	–	–
$[Co(C_{14}H_{11}NO_2S).H_2O]H_2O$	Dark brown	87.4	50.3 (50.3)	3.9 (3.90)	4.2 (4.2)	9.5 (9.6)	17.6 (17.7)	1.8	4.5
$[Co(C_{14}H_{12}NO_2S)_2]$	Dark brown	77.3	58.2 (58.4)	4.1 (4.2)	4.8 (4.9)	11.2 (11.1)	10.2 (10.3)	1.8	4.2
$[Cu(C_{14}H_{11}NO_2S).H_2O]$	Dark brown	90.2	49.4 (49.6)	3.9 (3.8)	4.1 (4.1)	9.5 (9.4)	18.7 (18.7)	3.8	1.9
$[Cu((C_{14}H_{12}NO_2S)_2]$	Dark green	81.4	57.8 (57.9)	4.1 (4.1)	4.9 (4.8)	11.1 (11.0)	11.0 (11.0)	2.2	1.85
$[Zn(C_{14}H_{11}NO_2S).H_2O]$	Yellow	87.5	49.5 (49.3)	3.8 (3.8)	4.2 (4.1)	9.3 (9.3)	19.2 (19.2)	1.9	diam.
$[Zn(C_{14}H_{12}NO_2S)_2]$ H_2O	Yellow	74.6	55.9 (56.0)	4.3 (4.3)	4.6 (4.7)	10.6 (10.7)	11.1 (10.9)	1.2	diam.

Table 2
Formation constants of Schiff base 1 complexes.[a]

Metal ion	log β_1				$-\Delta G_1$ KJ mole^{-1}	log β_2					$-\Delta G_2$ (KJ mole^{-1})
	A	*B*	*C*	mean		*A*	*B*	*C*	*D*	mean	
Co(II)	13.8	13.7	13.7	13.7(0.05)	78.3	26.1	26.0	25.0	25.9	25.8(0.4)	146.7
Cu(II)	15.2	15.2	15.1	15.1(0.05)	63.5	26.8	26.5	26.4	26.3	26.5(0.2)	151.1
Zn(II)	14.3	14.3	14.3	14.3(0.01)	81.3	25.4	24.7	24.9	24.2	24.8(0.4)	141.3

[a] log β_1 = log K_1 and log β_2 = log K_1 K_2 standard deviation is given in parenthesis; A: interpolation at *n* values method; B: correction term method; C: Successive approximation method; D: mid point method.

high affinity for chelation with the metal ions under study. The stability is in the order: Cu > Co > Zn. The high free energy change values (ΔG) indicate that the complex formation reactions are spontaneous ones.

3.2. Conductometric titration

The conductometric titration curves gave straight lines, intersecting at molar ratios 1 and 2 in all cases, indicating the formation of 1 : 1 or 1 : 2 (M : L) chelates. The formation of these species may proceed as follows:

$$M + H_2L \rightarrow ML + 2H^+ \quad (1:1)$$

$$M + 2H_2L \rightarrow M(HL)_2 + 2H^+ \quad (1:2)$$

However, a high molar ratio may be excluded, due to steric hindrance in accommodating three Schiff base molecules around a metal ion and the geometry of the Schiff base itself.

Electrical conductivities of the complexes in DMF (0.001 M) lie in the 1.2–3.80 S cm^{-2} mol^{-1} range, indicating that they are non-electrolytes. For the 1 : 1 complexes, the chelation is brought about by proton displacement from the phenolic OH and thiophenolic SH groups so as to satisfy the divalency of the metal ions. On the other hand, the 1 : 2 complexes may be formed through proton displacement of the two phenolic OH groups only and the two SH groups may form two coordinate bonds with the metal without proton displacement. This may be attributed to the fact that the phenolic proton is more readily displaced than the thiophenolic proton due to the difference in electronegativity between oxygen (3.5) and sulfur (2.5). This conclusion is supported by the appearance of the SH signal in the ^{1}H-NMR of the 1 : 2 Zn-complex at 3.8 ppm, being deshielded due to the participation in coordination.

3.3. IR spectra

The IR spectra of the Schiff base H_2L metal complexes are compared with that of the Schiff base itself in order to determine the coordination sites that may be involved in chelation. There are some guide peaks, in the spectrum of the ligand, which enable one to achieve this goal. These peaks change either in their positions and/or their intensities upon chelation. They are listed in Table 3.

The OH stretching vibration; ν(OH) found as a medium band at 3250 cm^{-1} disappears in the spectra of the Co (1 : 2) and Cu (1 : 2) complexes indicating

Table 3
Significant IR bands of the Schiff base 1 and its complexes (cm^{-1})

Compound	$\nu_{(OH)}$ (H_2O)	ν(C=N)	δ(OH) inplane	ν(C–O) str.	ν(C–S) str.	γ(OH) (H_2O)	ν(M–O) str.	ν(M–N) str.
Schiff Base	-	1613w	1406m	1248s	758s	–	–	–
Co(1 : 1)	3250vb	1703w	1313m	1176m	701ms	937w	665w	550m
Co(1 : 2)	-	-	–	1176m	724s	–	574w	461w
Cu(1 : 1)	3215b	1601s	1310m	1177m	717s	895w	665w	553w
Cu(1 : 2)	-	-	–	1174m	730m	–	630w	483w
Zn(1 : 1)	3224b	1700w	1313w	1176m	722m	936w	646w	560w
Zn(1 : 2)	3222b	-	–	1174w	722m	935w	645w	506w

strong participation of the OH group in chelate formation. The presence of water of hydration or coordination in the spectra of Co (1 : 1), Cu (1 : 1) and Zn (1 : 1 and 1 : 2) complexes as broad bands at 3215–3250 cm^{-1}, renders it difficult to draw a conclusion regarding the ν(OH) of the OH group of the Schiff base H_2L. The participation of the OH group is apparent from the shift in position of the δ(OH) in-plane vibration (1406 cm^{-1} in the free ligand) by 93–96 cm^{-1} and the change in the strong ν(C–O) stretching vibration in the Schiff base (1248 cm^{-1}) to a moderate or weak vibration in the complexes (1174–1176 cm^{-1}). For Zn (1 : 1 and 1 : 2) complexes, the participation of the OH group is further indicated by the disappearance of the OH singlet in their ^{1}H-NMR spectra.

The presence of water in the above mentioned complexes is confirmed by the presence of a weak band in the 895-937 cm^{-1} range which may be attributed to the bending vibration of the water molecules γ(OH). The other bending vibration; _δ(OH), is usually found at 1600 cm^{-1} which usually interferes with the skeleton vibration of the benzene ring (CC vibration).

The SH stretching vibrations ν(SH) have no apparent help since they display very weak bands in both the free ligand and in the complexes. However, participation of the SH group in chelation is ascertained from the shift of ν(C-S) from 759 cm^{-1} in the ligand to lower frequencies in the complexes (701–730 cm^{-1}). The ν(C=N) stretching vibration, found in the free ligand at 1619 cm^{-1}, disappears in the spectra of the 1 : 2 complexes and is shifted either to higher or lower wave numbers in 1 : 1 complexes indicating participation of the azomethine nitrogen in coordination ($M \leftarrow N$).

Participation of the phenolic oxygen and azomethine nitrogen is also confirmed by the appearance of new bands in the complexes in the 574–665 and 461–560 cm^{-1} regions which may be assigned to the M–O and M–N stretching vibrations, respectively.

3.4. ^{1}H-NMR spectra

The ^{1}H-NMR spectra of the diamagnetic Zn (1 : 1 and 1 : 2) complexes were compared with those of the free ligand (Table 4) The OH singlet which appears at 11.19 ppm in the free ligand disappears in the two complexes, indicating the participation of the OH group in chelation through proton displacement.

The SH signal which appears, in the free ligands at 3.3 ppm, completely disappears in the 1 : 1 complex indicating that the SH proton is removed by chelation. However, this signal is deshielded in the 1 : 2 complex at 3.8 ppm which indicates that the SH group may participate in coordination without proton displacement.

New signals, observed at 3.4 and 3.6 ppm; with integration corresponding to two protons in the spectra of 1 : 1 and 1 : 2 complexes, are assigned to one water molecule.

3.5. Magnetic measurements

The high spin octahedral cobalt (II) complexes have magnetic moment $\mu_{eff.}$ in the 4.3–5.2 B.M. range [20] which are higher than the spin only value (3.87) due to the high orbital contribution to the magnetic moment. Cobalt (II) (1 : 2) complex has $\mu_{eff.} = 4.52$ B.M., which assumes a high spin octahedral geometry. On the other hand tetrahedral cobalt (II) complexes with an 4A2 ground state are reported to have magnetic moments in the 4.00–5.00 B.M. range, which are higher than the anticipated ‘spin only’ value (3.87) B.M. for tetrahedral cobalt (II) species This is attributed to the mixing of the excited Triplet State with the ground state. The magnetic moment of Cobalt (II) (1 : 1) complex was found to be 4.17 B.M. which is in agreement with the reported values for high spin tetrahedral cobalt (II) complexes [21,22].

Octahedral copper (II) species have magnetic moments in the 1.7–2.1 B.M. range [20] with no orbital contribution (spin-only moment = 1.73). This however is not always the case and higher magnetic moments are expected due to Jahn–Teller distortion of the octahedral symmetry effect. The copper (II) (1 : 2) complex has $\mu_{eff.}$ of 1.85 B.M. assuming a distorted octahedral structure [23]. Square planar tetra-coordinated copper (II) species have been reported to have magnetic moment in the range of 1.73–1.87 B.M. due to dsp^2 structure whereas the tetrahedral (sp^3) or planar (sp^2d) are reported to have magnetic moments in the range 2.0–2.2 B.M. [23]. The $\mu_{eff.}$ of the copper (II) (1 : 1) complex is 2.08 B.M. which assumes tetrahedral geometry for this complex. Zinc (II) complexes (d^{10}) are diamagnetic.

Table 4
^{1}H-NMR data

Compound	Chemical shift (δ) ppm	Assignment
Schiff base (I)	11.19	(s, 1H, phenolic OH)
	8.1	(s, 1H, azomethine H)
	6.9–8.0	(m, 7H, 7ArH)
	3.8	(s, 3H, OCH_3)
	3.3	(s, 1H, SH)
Zn-I (1 : 1)	8.7	(s, 1H, azomethine H)
	6.5–7.5	(m, 7H, ArH)
	3.4	(s, 5H, 1H_2O & 1 OCH_3)
Zn-I (1 : 2)	6.4–8.11	(m, 16H, 14ArH & 2 azomethine H)
	3.8	(s, 2H, SH)
	3.6	(s, 2H, 1 H_2O)
	3.3	(s, 6H, 2 OCH_3)

3.6. Thermogravimetric analysis

The thermograms are represented by Fig. 1. Water of hydration is associated with complex formation and is found outside the coordination sphere formed around the central metal ion. The dehydration for this type of water normally takes place in the 50–140°C range. The dehydration step in Co (1 : 1) and Zn (1 : 2) complexes occurs in the 50–120°C range (Table 5). The weight losses correspond to loss of one water molecule in each case. By contrast coordinated water molecules directly bonded to the metal ion are usually eliminated at higher temperature i.e., in the 150–250°C range [24–26]. This is found to be the case for Co (1 : 1), Cu (1 : 1) and Zn (1 : 1) complexes in which the dehydration takes place in the 150–250°C range.

The Schiff base I complexes decompose in two steps via the formation of unstable intermediates. The decomposition starts at 195–285°C and ends at 490–750°C (oxides formation). The metal percentages of the complexes are calculated from the residual metal oxide % formed in the final step and are in good agreement with data obtained by the wet combustion method of MacDonald [18].

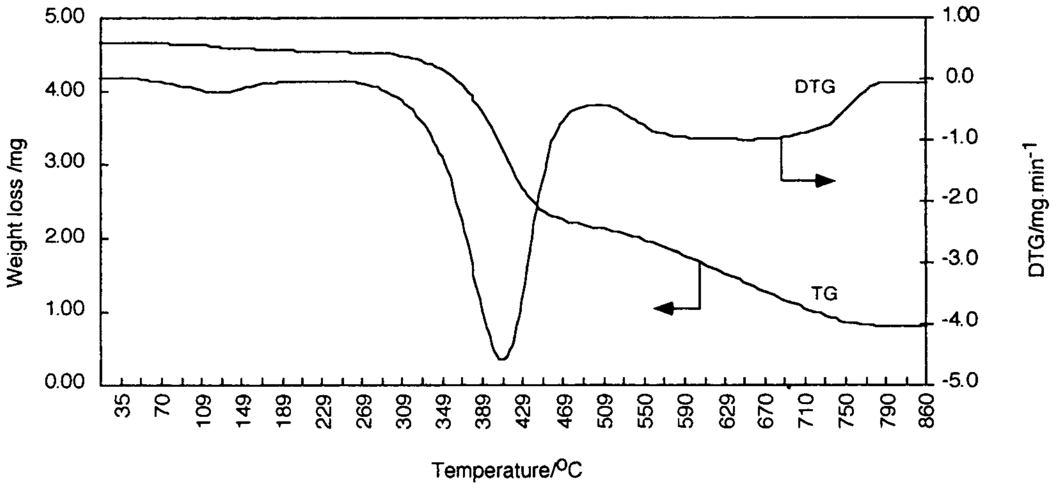


Fig. 1. TG and DTG-plots of the Co(1 : 1) complex.

Table 5
Thermoanalytical data

Complex	Dehydration stage			Decomposition stage	Metallic residue
	Temp. range (°C)	Loss of H_2O %found (Calc.)	No. of H_2O (mol.)	°C	%Found (calc.)
$[CoL.H_2O]H_2O$	50–110	10.1	2	195–240	17.7
	150–195	(10.2)		250–600	(17.7)
$[Co(HL)_2]$	–	–	–	230–500	10.1
				675–750	(10.3)
$[CuL.H_2O]$	180–240	5.4		1	18.7
		(5.3)			(18.7)
$[Cu(HL)_2]$	–	–	–	285–434	11.1
				650–720	(11.0)
$[Zn L.H_2O]$	200–250	5.2	1	250–341	19.2
		(5.3)		375–575	(19.2)
$[Zn(HL)_2]H_2O$	50–120	2.9		200–350	11.3
		(3.0)	1	400–575	(10.9)

On the basis of the above observations, the following general scheme for thermal decomposition may be proposed for the Schiff base 1 metal complexes.

For 1 : 1 complexes,

$$[ML{\cdot}H_2O]H_2O \xrightarrow[50-120^\circ C]{\text{dehydration}} [ML{\cdot}H_2O]$$

$$(\text{for Co}(1:1)\text{only})$$

$$[ML{\cdot}H_2O] \xrightarrow[50-250^\circ C]{H_2O\ \text{dehydration}} [ML]$$

$$[ML] \xrightarrow[50-250^\circ C]{\text{partial decomposition}} \text{intermediate (unstable)}$$

$$\text{Intermediate} \xrightarrow[300-600\text{degC}]{\text{final decomposition}} \text{metal oxides}$$

For 1 : 2 complexes,

$$[ML_2]H_2O \xrightarrow[50-120\text{degC}]{\text{dehydration}} [ML_2] \quad (\text{for Zn}(1:2)\text{only})$$

$$[ML_2]H_2O \xrightarrow[50-120^\circ C]{\text{dehydration}} \text{intermediate (unstable)}$$

$$\text{Intermediate} \xrightarrow[650-750^\circ C]{\text{final decomposition}} \text{metal oxide}$$

3.7. *Determination of reaction order of decomposition*

The Horowitz and Metzger [27] equation $C_s = (n)^{1/1-n}$, where C_s is the weight fraction of the substance present at the DTG peak temperature T_s, is given by

$$C_s = \frac{(W_s - W_f)}{(W_o - W_f)} \tag{1}$$

and was used for the determination of the values of the reaction order. Here W_s stands for the weight remaining at a given temperature T_s, i.e., the DTG peak temperature, W_o and W_f are the initial and final weights of the substance, respectively. The values of C_s for the thermal decomposition of the complexes are in the range 0.29–0.37 which indicates that the decomposition follows first order kinetics [27].

3.8. *Integral method using the Coats–Redfern equation*

For a first order process the Coats–Redfern equation [28,29] may be written in the form:

$$\log\left[\frac{\ln(W_f/(W_f - W))}{T^2}\right] = \log\left[\frac{AR}{qE^*}\left(1 - \frac{2RT}{E^*}\right)\right] - \frac{E^*}{2.303RT} \tag{2}$$

where W_f is the mass loss at the completion of the reaction, W is the mass loss upto temperature T, ($W_r = W_f - W$), R is the gas constant, E^* is the activation energy in J mol^{-1}, and θ is the heating rate. Since $1 - 2RT/E^* \cong 1$, a plot of the left hand side of Eq. (2) against $1/T$ was drawn and E^* was calculated from the

Table 6
Kinetic data of the thermal decomposition of the complexes

Complex	Decomp. steps (°C)	E^* (kJ mol^{-1})	A (s^{-1})	ΔS^* JK mol^{-1}	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	Cs
$[CoL.H_2O]H_2O$	50–195	28.6	4.2×10^{8}	-9.9	25.4	29.9	0.32
	195–240	313.6	1.3×10^{27}	55.4	309.3	280.7	0.31
	250–600	95.7	4.6×10^{12}	−1.1	90.4	91.1	0.29
$[Co(HL)_2]$	230–500	230.0	3.4×10^{8}	−10.1	196.7	237.1	0.34
	675–750	325.7	7.8×10^{16}	8.6	267.5	207.4	0.31
$[CuL.H_2O]$	180–240	75.7	3.5×10^{7}	−12.6	71.6	77.8	0.28
	274–360	50.0	8.5×10^{5}	−16.48	44.1	53.7	0.36
	416–490	304.0	1.9×10^{21}	18.6	297.9	284.3	0.35
$[Cu(HL)_2]$	285–434	252.2	4.3×10^{22}	22.0	247.3	234.4	0.32
	650–720	246.6	2.5×10^{18}	12.1	240.8	232.5	0.33
$[Zn\ L.H_2O]$	200–250	82.4	2.4×10^{17}	10.1	78.232	73.2	0.29
	250–341	245.3	4.7×10^{25}	29.0	240.492	223.9	0.37
	375–575	143.7	1.7×10^{16}	7.1	138.0	133.2	0.31
$[Zn(HL)_2]H_2O$	50–120	237.0	8.0×10^{32}	46.0	233.4	213.0	0.32
	200–350	281.7	1.68×10^{30}	39.4	276.7	253.2	0.35
	400–575	153.8	6.3×10^{15}	6.0	147.5	143.0	0.31

slope and then A (Arrhenius constant) was found from the intercept.

The activation entropy ΔS^*, the activation enthalpy ΔH^* and the free energy of activation ΔG^* were calculated using the following equations:

$$\Delta S^* = 2.303\left(\log\frac{Ah}{kT}\right)R \tag{3}$$

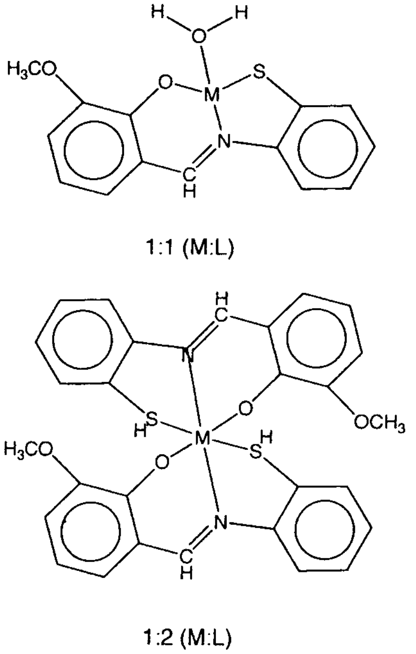
$$\Delta H^* = E^* - RT \tag{4}$$

$$\Delta G^* = H^* - TS^* \tag{5}$$

where k and h are the Boltzman and Planck constants, respectively. The calculated values of E^*, A, ΔS^*, ΔH^* and ΔG^* for the decomposition steps are given in Table 6.

4. Conclusions

As a general conclusion, the 3-methoxysalicylidene-2-aminothiophenol Schiff base behaves as a dibasic ligand in 1 : 1 complexes and as a monobasic ligand in 1 : 2 complexes with tridentate ONS donors derived from the phenolic oxygen, the azomethine nitrogen and thiophenolic sulfur. On the basis of this conclusion, tetrahedral and octahedral structures are suggested for the 1 : 1 and 1 : 2 complexes, respectively (Fig. 2).



1:1 (M:L)

1:2 (M:L)

Fig. 2. The proposed structures of the metal complexes.

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