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THERMOGRAVIMETRIC AND SPECTROSCOPIC STUDIES ON CADMIUM COMPLEXES WITH TWO SALICYLIDENE THIOPHENOL SCHIFF BASES

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Abstract

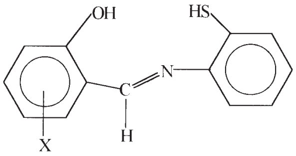
New cadmium complexes of the salicylidene-2-amino-thiophenol (I) and 3-methoxysalicylidene-2-amino-thiophenol (II) Schiff bases have been prepared and characterized by elemental analyses, IR, ^{1}H-NMR spectra, conductimetric and thermogravimetric analyses. The results suggested that the Schiff bases are bivalent anions with tridentate ONS donors derived from the phenolic oxygen, azomethine nitrogen and thiophenolic sulphur. The formulae are 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 are reported.

Keywords: cadmium complexes, salicylidene Schiff bases

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], complexing ability towards certain toxic metals [5]. Metal complexes of Schiff bases derived from substituted salicylaldehydes and various amines have been widely investigated [6–12]. 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 cadmium(II) with salicylidene-2-amino-thiophenol (I) and 3-methoxy-salicylidene-2-amino-thiophenol (II) Schiff bases.



where *X*= H (I) or 3-OCH_3 (II)

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Experimental

All chemicals used were analytical grade or of equivalent quality. The organic solvents were obtained as pure grade material from BDH or were purified by recommended methods [13].

The title Schiff bases were prepared by condensing salicylaldehyde or *o*-vanillin (3-methoxy-salicylaldehyde) with 2-amino-thiophenol and were recrystallized from dilute AcOH to constant *m.p.* (I: 128 and II: 155°C). The formulation is confirmed [14, 15] by elemental microanalysis, IR and ^{1}H-NMR spectra.

The solid complexes of Cd(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 metal contents were determined according to MacDonald's method [16] and AAS determination. 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 solvent and the spectra were measured in the 0–14 ppm range using TMS as internal standard.

The conductimetric titrations were carried out using a Jenway 4200 conductivity meter. 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^{-1} flow-rate). The mass loss was measured from the ambient temperature up to 600°C at 10°C min^{-1}.

Results and discussion

The elemental analyses (Table 1) are in good agreement with those calculated for the proposed formulae. The Cd percentage represents the average value of the Cd content determination [16] and thermal analysis (Cd oxide residue).

Table 1 Elemental analyses and molar conductivity data

Compound	Elemental analysis; found (calculated)/%					Λ/ mho cm^2 mol^{-1}
	C	H	N	S	Cd	
$C_{13}H_{11}NOS$ (I)	67.6 (68.1)	4.8 (4.8)	6.3 (6.1)	13.9 (14.0)	–	–
$C_{14}H_{13}NO_2S$ (II)	65.3 (64.9)	5.0 (5.0)	5.6 (5.4)	12.4 (12.4)	–	–
$[Cd(C_{13}H_9NOS)\cdot H_2O]$	43.8 (43.6)	3.0 (3.1)	3.8 (3.9)	8.6 (8.9)	31.2 (31.5)	2.0
$[Cd(C_{13}H_{10}NOS)_2]$	54.4 (54.9)	3.9 (3.5)	4.6 (4.9)	11.5 (11.3)	19.7 (19.8)	1.8
$[Cd({}_{14}H_{11}NO_2S)\cdot H_2O]$	43.8 (43.4)	3.6 (3.6)	3.9 (3.6)	8.1 (8.3)	29.2 (29.0)	3.0
$[Cd(C_{14}H_{12}NO_2S)_2]$	53.8 (53.5)	3.8 (3.8)	4.2 (4.5)	10.1 (10.2)	17.6 (17.9)	1.9

Conductimetric measurement

The conductimetric titration curves indicate the presence of 1:1 and 1:2 (Cd:*L*) chelates in all cases. The formation of the 1:1 and 1:2 (Cd:*L*) species may proceed as follows:

$$Cd^{2+}+H_2L\rightarrow ML+2H^+ \qquad (1:1)$$

$$Cd^{2+}+2H_2L\rightarrow M(HL)_2+2H^+ \qquad (1:2)$$

A high molar ratios may be excluded owing to steric hindrance and the geometry of the Schiff bases [17].

IR spectra

The IR spectra of the metal complexes of the Schiff base I and II were compared with that of the Schiff bases themselves in order to determine the coordination sites that may be involved in chelation; Table 2.

The OH stretching vibration; ν(OH) found as medium intense band at 3254 and 3051 cm^{-1} in the spectra of Schiff base I and II, respectively, disappear in the spectra of the 1:2 complexes indicating strong participation of the OH group in chelate formation. The presence of water of coordination in the spectra of the 1:1 complexes as broad bands in the regions 3350–3075 and 3400–3145 cm^{-1} for Cd–I and Cd–II, respectively, renders it difficult to draw a conclusion regarding the ν(OH) of the OH group of the Schiff bases in these complexes. The participation of the OH group in the 1:1 complexes is apparent from the shift in position of the δ(OH) in-plane vibration (1406 cm^{-1} in the free ligands) by 77 (Cd–I) and 88 cm^{-1} (Cd–II) and the change in the strong ν(C–O) stretching vibration in the Schiff base (1236 (I) and 1248 cm^{-1} (II)) to a moderate or weak vibration in complexes in the range 1158–1173 cm^{-1}. The participation of the OH group is further indicated by the disappearance of the OH singlet in the ^{1}H-NMR spectra of all complexes.

The presence of water in the 1:1 complexes is also confirmed by the presence of a weak band at 975 and 936 cm^{-1} for Cd–I and Cd–II, respectively, 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 (C=C vibration).

The SH stretching vibrations ν(SH) have no apparent help since they display very weak bands in both the free ligands and in the complexes. However, participation of the SH group in chelation is ascertained from the shift of ν(C–S) from 759 (I) and 758 cm^{-1} (II) to lower frequencies in the complexes (712–731 cm^{-1}). The ν(C=N) stretching vibrations, found in the free ligands at 1619 (I) and 1613 cm^{-1} (II) disappear in the spectra of all complexes indicating participation of the azomethine nitrogen strongly in coordination (M←N).

The participation of the phenolic oxygen and azomethine nitrogen is also confirmed by the appearance of new bands in the spectra of the complexes in the 541–646 and 469–553 cm^{-1} regions which may be assigned to the M–O and M–N stretching vibrations, respectively [18].

Table 2 Significant IR bands of the Schiff bases and its complexes (cm^{-1})

Compound	ν(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 I	–	1619s	1406m	1236s	759s	–	–	–
Schiff base II	–	1613w	1406m	1248s	758s	–	–	–
Cd–I (1:1)	3350–3075vb	–	1329m	1158w	712w	975w	593w	469w
Cd–I (1:2)	–	–	–	1160w	724w	–	541w	471w
Cd–II (1:1)	3400–3145vb	–	1318m	1173m	721w	936w	646w	553w
Cd–II (1:2)	–	–	–	1172m	731m	–	644w	521w

^{1}H-NMR spectra

The ^{1}H-NMR spectra of the Cd(II) complexes are compared with those of the free ligand (Table 3). The OH singlet, which appears in the free ligands at 10.9 ppm (I) and 11.19 ppm (II), disappears in all complexes, indicating the participation of the OH group in chelation through proton displacement. The SH signal, in the free ligands at 3.4 ppm (I) and 3.3 ppm (II), 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 to 3.8 ppm which indicates that the SH group may participate in coordination without proton displacement. New signals, observed at 3.4 ppm; with integration corresponding to two protons in the spectra of the 1:1 complexes, are assigned to one water molecule.

Table 3 ^{1}H-NMR data

Compound	Chemical shift (δ)/ppm	Assignment
Schiff base I [14]	10.9	(s, 1H, OH)
	6.4–7.6	(m, 9H, 8Ar H, 1 azomethine H)
	3.4	(s, 1H, SH)
	2.6	(CH_3 of solvent)
Schiff base II	11.9	(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)
	2.5	(CH_3 of solvent)
Cd–I (1:1)	6.0–8.1	(m, 8H, 1H, azomethine H and 7ArH)
	3.4	(s, 2H, 1H_2O)
	2.5	(CH_3 of solvent)
Cd–I (1:2)	6.0–8.11	(m, 16H, 14ArH and 2 azomethine H)
	3.8	(s, 2H, SH)
	2.5	(CH_3 of solvent)
Cd–II (1:1)	8.1	(s, 1H, azomethine H)
	6.0–7.9	(m, 7H, ArH)
	3.4	(s, 5H, 1H_2O and 1 OCH_3)
	2.5	(CH_3 of solvent)
Cd–II (1:2)	6.0–8.11	(m, 16H, 14ArH and 2 azomethine H)
	3.8	(s, 2H, SH)
	3.3	(s, 6H, 2 OCH_3)
	2.5	(CH_3 of solvent)

Thermogravimetric analysis

Coordinated water molecules are directly bonded to the metal ion and are usually eliminated at a higher temperature than those of hydration [19, 20]. For the 1:1 complexes under study they were eliminated within the range of 124–250°C (Table 4). The complexes decompose in one step without formation of stable intermediates. The decomposition starts within the range of 262–345 and ends between 489–600°C (oxides formation). The metal percentages of the complexes were calculated from the residual metal oxides formed in the final step and were found to be in good agreement with those obtained by the wet combustion method of MacDonald [16]. The TG and DTG plots are represented in Fig. 1. On the basis of the above observations, the following general scheme for thermal decomposition may be proposed as:

For 1:1 complexes

$$[\mathrm{CdL{\cdot}H_2O}] \xrightarrow{\mathrm{H_2O\ decoordination\ at\ 124-250\,^{\circ}C}} [\mathrm{CdL}]\ (L{=}\mathrm{I\ or\ II})$$

$$[\mathrm{CdL}] \xrightarrow{\mathrm{decomposition\ at\ 280-600\,^{\circ}C}} [\mathrm{CdO}]$$

For 1:2 complexes

$$[\mathrm{Cd(HL)_2}] \xrightarrow{\mathrm{decomposition\ at\ 262-557^{\circ}C}} [\mathrm{CdO}]$$

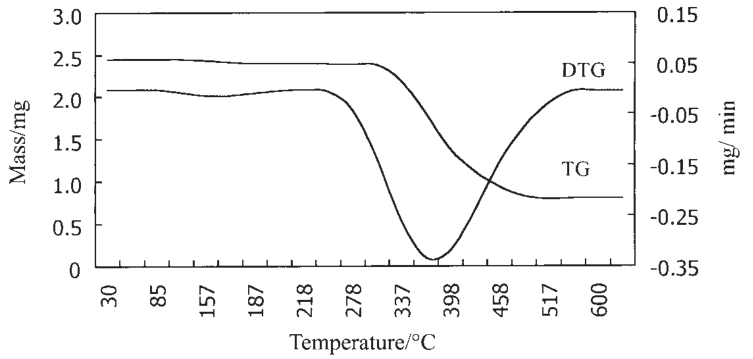


Fig. 1 TG and DTG curves of Cd–II (1:1) complex

Determination of reaction order of decomposition

The Horowitz and Metzger [20] equation $C_s=(n)^{1/(1-n)}$, where C_s is the mass fraction of the substance present at the DTG peak temperature, T_s, is given by:

$$C_s=\frac{W_s-W_f}{W_0-W_f} \qquad (1)$$

Equation (1) is used for the determination of the values of the reaction order. Here W_s stands for the mass remaining at a given temperature T_s, i.e. the DTG peak

Table 4 TG results of the Schiff bases complexes

Complex	Formulae	Dehydration stage				Decomposition stage/°C	Oxide formation (metallic residue)		
		Temperature range/°C	H_2O loss				T/°C	Cd content/%	
			calcd./%	found/%	mol			calcd.	found
Cd–I (1:1)	$[Cd(C_{13}H_9NOS)\cdot H_2O]$	150–230	4.9	4.5	1	345–600	600	31.5	31.7
Cd–I (1:2)	$[Cd(C_{13}H_{10}NOS)_2]$	–	–	–	–	332–557	557	19.8	19.6
Cd–II (1:1)	$[Cd(C_{14}H_{11}NO_2S)\cdot H_2O]$	124–250	4.5	4.4	1	280–548	548	29.0	28.7
Cd–II (1:2)	$[Cd(C_{14}H_{12}NO_2S)_2]$	–	–	–	–	262–489	489	19.1	19.0

temperature, W_o and W_f are the initial and final masses of the substance, respectively. The values of C_s for the thermal decomposition of Cd complexes are in the range 0.28–0.34 which indicates that the decomposition follows first order kinetics [21].

Integral method using the Coats–Redfern equation

For a first order process the Coats–Redfern equation [22] may be written in the form:

$$\log\left[\frac{\log\dfrac{W_f}{W_f-W}}{T^2}\right]=\log\left[\frac{AR}{\theta E^*}\left(1-\frac{2RT}{E^*}\right)\right]-\frac{E^*}{2303RT} \qquad (2)$$

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}, θ is the heating rate.

Since $1-2RT/E^*\cong 1$, a plot of the left-hand side of Eq. (2) *vs.* $1/T$ was drawn and E^* was calculated from the slope and A (Arrhenius constant) was found from the intercept. The plots are represented by Fig. 2.

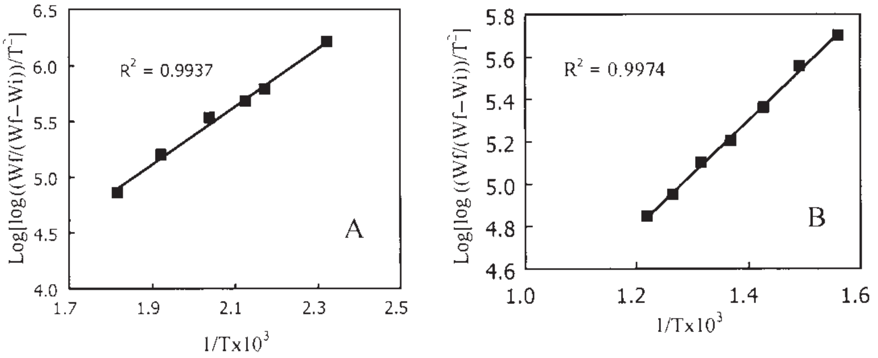


Fig. 2 Coats–Redfern plots of A – dehydration step and B – decomposition step of Cd–II (1:1) complex

The activation entropy S^*, the activation enthalpy H^* and the free energy of activation G^* were calculated using the following equations [23]:

$$S^*=2303\left(\log\frac{Ah}{kT}\right)R \qquad (3)$$

$$H^*=E^*-RT \qquad (4)$$

$$G^*=H^*-T_sS^* \qquad (5)$$

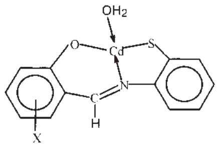
Table 5 Kinetic data of the thermal decomposition of complexes

Complex	Decomp. steps/°C	E^*/kJ mol^{-1}	A/s^{-1}	S^*/kJ mol^{-1} K^{-1}	H^*/kJ mol^{-1}	G^*/kJ mol^{-1}	C_s
Cd–I (1:1)	150–230	55.6	$4.0\cdot10^5$	–17.0	51.7	59.6	0.34
	345–600	146.4	$6.61\cdot10^9$	–7.8	140.2	146.0	0.28
Cd–I (1:2)	332–557	143.3	$2.8\cdot10^9$	–8.6	137.1	143.5	0.29
Cd–II (1:1)	124–250	47.3	$2.0\cdot10^4$	–20.0	43.4	52.8	0.33
	280–548	53.2	$1.8\cdot10^6$	–15.8	47.9	58.0	0.30
Cd–II (1:2)	262–489	102.4	$2.4\cdot10^7$	–13.3	97.0	105.6	0.31

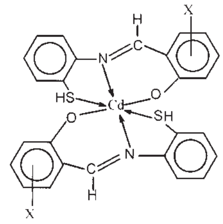
where k and h are the Boltzmann and Planck constants respectively. The calculated values of E^*, A, S^*, H^* and G^* for the dehydration and decomposition steps are given in Table 5.

Conclusions

Based on the present studies and as a general conclusion, the Schiff bases I and II behave 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. Tetrahedral and octahedral structures are suggested for the 1:1 and 1:2 complexes, respectively (Fig. 3).



1:1 (M:L)



1:2 (M:L)

Fig. 3 The proposed structures of Cd-Schiff bases complexes

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