Thermochimica Acta, 237 (1994) 195–201
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01621-9

Photochromism and thermochromism of Sn(IV) complexes with 8-aminoquinoline and salicylidene-8-aminoquinoline

Ahmed M. Donia * and Hanaa El-Boraey

Department of Chemistry, Faculty of Science, Menoufia University, Shebin El-Kom, Egypt

(Received 22 June 1993; accepted 27 September 1993)

Abstract

Tin(IV) complexes with 8-aminoquinoline (complexes (1) and (2)) and with salicylidene-8-aminoquinoline (complex (3)) have been prepared and characterized. Complexes (1) and (3) are thermochromic, and display irreversible and reversible thermochromism, respectively. The origin of the thermochromism is discussed in terms of lattice imperfections, phase change and charge transfer (CT). The phenomena were investigated by means of DTA, TGA, X-ray diffraction, electronic spectra and solid electrical conductivity.

INTRODUCTION

Thermochromism, the reversible and irreversible change in colour of a compound as a function of temperature, is observed in many organic and inorganic compounds [1–13]. The mechanism of the thermochromic transitions depends upon the molecular or ionic crystalline structure of the compound [6]. For inorganic compounds, the transition is due to a crystalline phase change, a change in ligand geometry, or a change in the number of ligands in the coordination sphere [1, 6]. Although the thermochromic behaviour of transition metal complexes has been reported in the literature, non-transition-metal complexes have received very little attention [5, 6]. Recently, the thermochromic behaviour of some transition metal complexes with 8-aminoquinoline and its Schiff bases was studied [11, 12]. In the present work, the tin(IV) complexes of 8-aminoquinoline and salicylidene-8-aminoquinoline were prepared and characterized. The effect of precipitation on the thermochromic behaviour and the reversible thermochromism of the complexes has also been studied.

---

* Corresponding author.

TABLE 1

Analytical, spectral and thermal data of Sn(IV) complexes

Colour	Found (Calcd)/%				Λ_m/cm^2 ^{1}mol^{-1} (acetonitrile)	IR/cm^{-1}		
	C	H	Cl	Sn		$\nu(NH_2)$	ν(C=N)	[ν(C=C) + ν(C–N)] (of quinoline ring)
Compound 1								
Off-white	26.7	2.1	34.8	29.5	11.5	3220–3140 [b]	–	1620s
	(26.7)	(2.0)	(35.1)	(29.3)				
Compound 2								
Rosy	26.8	2.1	35.2	29.0	10.6	3220–3140 [b]	–	1620s
	(26.7)	(2.0)	(35.1)	(29.3)				
Compound 3								
Yellow	39.1	2.8	21.6	23.8	0.6 [a]	–	1605s	1610sh
	(39.3)	(2.7)	(21.8)	(24.2)				

[a] In nitrobenzene. [b] Split.

EXPERIMENTAL

All the reagents used were of analytical grade, obtained from Aldrich. The Schiff's base was prepared by the method reported previously [12]. Complex (1) was prepared by drop-wise addition of tin(IV) chloride (2.8 mmole) in acetone (20 cm^3) to 2.8 mmole of 8-aminoquinoline in acetone (20 cm^3). The reaction mixture was stirred in air with heating for 2 h. Complex (2) was prepared by the same method, except that the solvent was ethanol. After the solutions were concentrated, off-white and rosy precipitates were obtained for complexes (1) and (2), respectively. The two complexes had different particle sizes (quasi-shapes).

Complex (3) was prepared by the addition of stoichiometric amounts of the metal chloride in ethanol to a hot alcoholic solution mixture of 8-aminoquinoline and salicyldehyde (1 : 1 : 1) molar ratio. A yellow precipitate was obtained after stirring in air with heating for 2 h. All the precipitates were filtered, washed with the appropriate solvent several times and dried over $CaCl_2/P_4O_{10}$.

Elemental analyses were carried out at the Micro-Analytical Centre, Cairo University. Tin was estimated as SnO_2 [14]. Chlorine was estimated by Volhard's method. IR spectra were recorded using KBr discs and a Perkin-Elmer 1430 spectrophotometer. Electronic spectra were measured in nujol mulls and acetone using a Perkin-Elmer Lambda 4B sectrophotometer. The molar conductivity measurements were made in acetonitrile or nitrobenzene using a Tacussel conductimeter, type CD6N. The thermal analyses (DTA and TGA) were carried out using a Shimadzu DT-30 thermal analyser, with a heating rate of 10°C min^{-1}. X-ray powder diffrac-

ν(C–N)	ν(C–O)	ν(M–O)	ν(M–N)	ν(M–Cl)	Electronic spectra in mulls/nm		Thermal data, initial temp. of decomp./°C	
					(CT) band	Other bands	DTA	TG
1232s	–	–	425m	320s	470sh	400s, 345, 333	234	234
1322s	–	–	245m	320s	460s	320s	242	242
–	1300s	535w	430s	322s	425m	350m, 310s, 235s	280	280

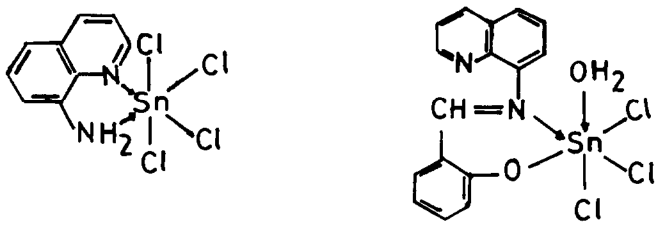
tion was measured using a Shimadzu XD-3 diffractometer with Cu Kα radiation. The solid electrical conductivity measurements were taken in air on a Keithley 175 multimeter, using a two-probe method. The applied potential was 200 V and the discs were pressed under 500 kg cm^{-3}.

RESULTS AND DISCUSSION

The complexes are stable in air at room temperature; complexes (1) and (3) change colour on heating; complexes (1) and (2) change in the dark (light sensitive). The conductivity values of the compounds in acetonitrile or nitrobenzene (Table 1) are commensurate with non-electrolyte behaviour, indicating coordination of the chloride ions [15, 16].

Vibrational spectra

The IR group frequencies of diagnostic importance are collected in Table 1. The spectra of complexes (1) and (2) show a band at approx. 1620 cm^{-1}, which is assigned to ν(C–C) + ν(C–N) of the quinoline ring [11, 17]. This band is shifted to a higher frequency in comparison with that of the free 8-aminoquinoline (1610 cm^{-1}). The ring vibrations at 980 and 380 cm^{-1} in the free ligand also shift to higher frequencies (995 and 405 cm^{-1}). These observations suggest coordination through the quinoline ring nitrogen [11, 17] (but this is not the case for complex (3), which shows no shift). The complexes show additional bands at around 3220–3140 and 1322 cm^{-1}, assigned to coordinated ν(NH_2) and ν(C–N), respectively. We therefore conclude that the ligand is bidentate, chelating through both nitrogen



(1) and (2) (3)

Scheme I

atoms. For complex (3), the C=N vibration observed at 1635 cm^{-1} in the spectrum of the free ligand is shifted to a lower frequency (1605 cm^{-1}) in the spectrum of the complex, showing coordination through the azomethine nitrogen [12, 18]. The phenolic C–O stretching of the free ligand at 1270 cm^{-1} is shifted to a higher frequency (1300 cm^{-1}) in the complex. This shift indicates bonding of the ligand through the phenolic oxygen [18, 19]. This is further supported by the disappearance of the broad ν(O–H) band at 3400 cm^{-1} in the spectrum of the complex. The complexes display a strong band at approx. 320 cm^{-1}, which is assigned to terminal ν(Sn–Cl) in hexa-coordinated structures [15]. The new bands obtained at 535 and 425 cm^{-1} may be assigned to ν(Sn–O) and ν(Sn–N), respectively [18, 19]. The above discussion, together with the elemental analyses (Table 1), suggest the structures shown in Scheme I.

Thermal investigation

All three complexes are thermally stable in air and start their decomposition at 234, 242 and 280°C, respectively as indicated on the DTA and TG curves (Fig. 1). The complexes have no unpaired electrons, and their colours are attributed to lattice defects and/or charge transfer (CT) [3, 20]. The electronic spectra of the complexes in both nujol mulls and in acetone display a CT band in the range 550–350 nm. The X-ray patterns of complexes (1) and (2) (Table 2) are typically the same. This indicates that the two complexes have the same phase. The observed slight differences in the values of the interplanar distances (*d*) or the relative intensities may be attributed to lattice imperfections (as a result of the method of preparation). These imperfections are responsible for the different colours [20] and the different decomposition mechanisms of the two complexes (Fig. 1) [21]. The off-white complex (1) changes gradually to the rosy form in the temperature range 45–180°C. The observed changes in *d* values or relative intensities of both forms (Table 2) confirm the transformation. The change in colour is irreversible, and the charge transfer (CT) band of the off-white form is deformed and shifted slightly towards a longer wavelength (Table 1) relative to that of the rosy form. The gradual colour change takes place without a

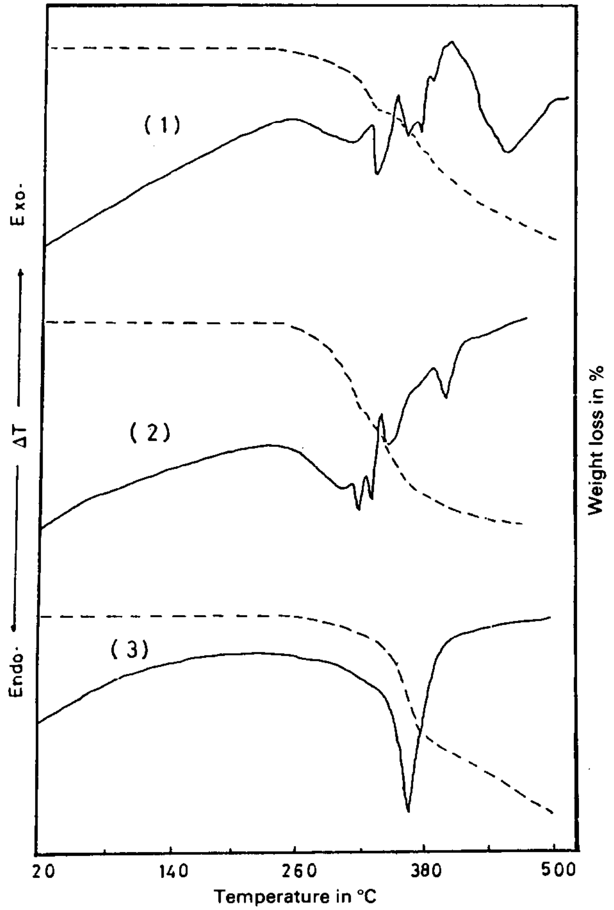


Fig. 1. DTA and TG curves of complexes (1), (2) and (3).

noticeable peak in the DTA curve (Fig. 1). It is concluded that relatively small changes in lattice imperfections can easily take place upon heating, so that a continuous thermochromism is observed. The energy required for

TABLE 2

Interplanar distances $d/\text{Å}$ and relative intensities (values in parentheses) of the diffraction lines of complex (1) before and after heating, and of complex (2)

Complex (1)		Complex (2)
Off-white form	Rosy form	
8.665 (100)	8.838 (100)	8.838 (100)
6.104 (11)	6.146 (12)	6.104 (12)
5.181 (37)	5.181 (52)	5.181 (36)
3.864 (9)	3.864 (18)	3.864 (9)
2.928 (14)	2.928 (16)	2.938 (13)

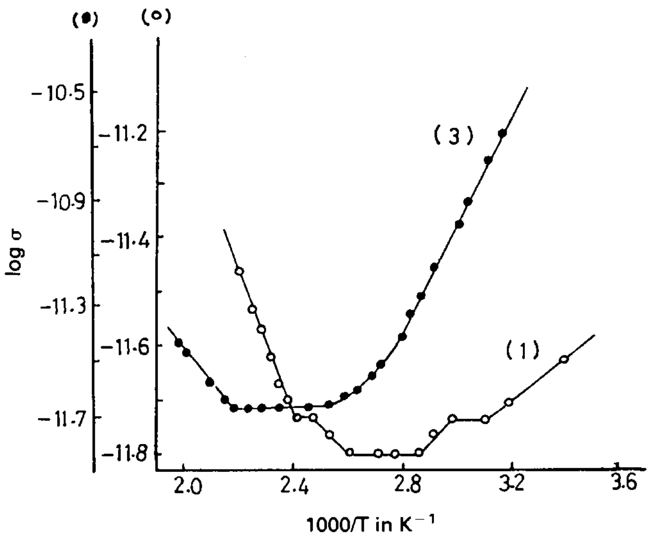


Fig. 2. Temperature dependence of the electrical conductivity of complexes (1) and (3).

these imperfection changes was detected in the temperature dependence of the electrical conductivity of complex (1) which shows clear metal-like and semi-conducting behaviours ($\Delta E = 0.32$ eV) in the two temperature ranges 25–50 and 139–180°C, respectively (Fig. 2). The observed unsteady variation of conductivity values in the temperature range 50–139°C may be attributed to changes in the lattice imperfections. Moreover, the temperature range lies within the colour change range, indicating that energy is mainly directed towards the imperfection changes rather than towards thermal agitation of the electrons. However, both complexes change colour, from off-white or a rosy colour to yellow, in the dark. The colour change is reversible, and the yellow forms change again to the corresponding off-white or rosy forms in the light. The transformation of the off-white form to the yellow is faster (overnight) than that of the rosy form (several days), whereas the back transformation in the light takes nearly the same time.

For complex (3), the colour changes from yellow to orange upon heating. The colour change is reversible in air or silicon oil and takes place continuously over a relatively wide range of temperature (120–180°C). This change in colour may be attributed to a phase change, as indicated from the temperature dependence of the electrical conductivity (Fig. 2). The complex (yellow form) shows metal-like and semi-conducting ($\Delta E = 0.23$ eV) behaviours in the temperature ranges 45–117 and 182–220°C, respectively. The temperature range within which the conductivity values remain constant (120–182°C) coincides quite closely with the colour change, indicating that the energy is consumed in the phase transition rather than in the thermal agitation of electrons. Moreover, the change in colour takes place without a noticeable peak in the DTA curve (Fig. 1). It is concluded that relatively small structural modifications take place upon heating [3, 12].

REFERENCES

1 J.H. Day, Chem. Rev., 69 (1968) 649.
2 D.R. Bloomquist and R.D. Willett, Coord. Chem. Rev., 47 (1982) 47.
3 K. Sone and Y. Fukuda, Inorganic Thermochromism, Springer-Verlag, Berlin, 1987.
4 D.R. Bloomquist and R.D. Willett, J. Am. Chem. Soc., 103 (1981) 2515.
5 S. Nakada, M. Yamada, T. Ito and M. Fujimoto, Chem. Lett., (1977) 1243.
6 Z. Halmos and W.W. Wendlandt, Thermochim. Acta, 7 (1973) 113.
7 A.M. Donia and Z.M. Ebied, Thermochim. Acta, 131 (1988) 1.
8 A.M. Donia, S.A. Amer and M.M. Ayad, Thermochim Acta, 137 (1989) 189.
9 A.M. Donia and M.A. El-Rayes, Thermochim. Acta, 147 (1989) 65.
10 A.M. Donia, H. Saloum and M.A. El-Ries, Thermochim. Acta, 159 (1990) 85.
11 A.M. Donia and H.A. El-Boraey, Transition Met. Chem., 17 (1992) 307.
12 A.M. Donia and H.A. El-Boraey, Transition Met. Chem., 18 (1993) 315.
13 A.M. Donia, Thermochim. Acta, 217 (1993) 225.
14 B.S. Saraswat, G. Sirvastava and R.C. Mehrotra, J. Organomet. Chem., 129 (1977) 135.
15 A. Arquero, P. Souza, J.A. Garcia-Vazquez and J.R. Masaguer, Transition Met. Chem., 10 (1985) 424.
16 V.V. Savant, P. Ramamurthy and C.C. Patel, J. Less-Common Met., 22 (1970) 479.
17 N. Saha and D. Mukherjee, Polyhedron, 2 (1983) 47.
18 B. Khera, A.K. Sharma and N.K. Kaushik, Polyhedron, 2 (1983) 1177.
19 A. Sexena, J.P. Tandon and A.J. Crowe, Polyhedron, 4 (1985) 1085.
20 J.D. Lee, A New Concise Inorganic Chemistry, 3rd edn., ELBS, 1977.
21 R.B. Heslop and K. Jones, Inorganic Chemistry, 1st edn., Amsterdam, 1976.