Journal of Thermal Analysis, Vol. 42 (1994) 1175-1184

THERMOGRAVIMETRIC AND SPECTROSCOPIC STUDIES ON La(III) AND Ce(III) COMPLEXES WITH SOME THIO-SCHIFF BASES

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(Received November 25, 1993; in revised form January 31, 1994)

Abstract

Solid complexes of five derivatives of thio-Schiff bases with La(III) and Ce(III) ions were prepared and characterized by elemental and thermogravimetric analyses. The suggested general formula of the solid complexes is $[ML_2(H_2O)X]\cdot 2H_2O$, where M = trivalent lanthanide ion, L = Schiff base and X = Cl^- or ClO_4^-. Information about the water of hydration, the coordinated water molecules, the coordination chemistry and the thermal stability of these complexes was obtained and is discussed. Additionally, a general scheme of thermal decomposition of the lanthanide-Schiff base complexes is proposed.

Keywords: Ce(III) complexes, La(III) complexes, TG-DTA

Introduction

Schiff bases have received great attention due to their use as chemical intermediates and perfume bases in dyes and rubber accelerators and in liquid crystals for electronics. Some Schiff bases were tested for fungicidal activity and correlations were made with the chemical structure [1]. Studies on the Schiff base complexes with the lanthanides are limited as compared with those with the *d*-block elements [2–7]. However, there has recently been renewed interest in the lanthanide complexes with Schiff bases due to the simplicity of the Schiff base molecules and the important applications of both lanthanides and Schiff bases. Bullock *et al.* have prepared lanthanide-Schiff base complexes of the forms $MLCl_3\cdot nH_2O$ and $ML_2Cl_3\cdot nH_2O$, where L is a bidentate Schiff base [8]. Misra studied some lanthanide-Schiff base complexes and interpreted the covalency in the bonding in terms of the nephelauxetic ratio, the metal orbital and ligand orbital mixing coefficient [9]. The thermal behaviour of Nd(III) and Sm(III)-Schiff base complexes was studied by Goel *et al.* by means of TG, DTG and DSC techniques [6]. Liu Guofa *et al.* prepared lanthanide-Schiff base com-

0368–4466/94/ $ 4.00

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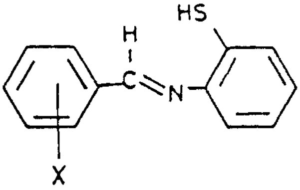
plexes of the form $[ML_2(NO_3)](NO_3)_2$ in which one nitrate group is in the inner coordination sphere of the lanthanide metal ion [7].

In the present work, TG and DTA were carried out on La(III) and Ce(III) complexes with new thio-Schiff bases in order to obtain information on the thermal stabilities of these new lanthanide complexes and to suggest a general scheme for their thermal decompositions.

Experimental

The Schiff bases were prepared by condensation of *o*-aminothiophenol with the appropriate amount of aldehyde in ethanol, according to the general method of synthesis of Schiff bases reported by Savich *et al.* [10]. The solution was refluxed for 1 h and then left to cool, and the solid product was filtered off, washed repeatedly with ethanol and then dried. The solids that separated out were purified by crystallization from dilute acetic acid until constant melting points were obtained. The purity of the prepared Schiff bases was confirmed by elemental analysis, which indicated that the azomethine group was not hydrolysed by dilute acetic acid. The results indicate a high purity of ≥ 99.5%. The ligands used in the present investigation have the structure



where $X = p\text{-Cl(L1)}, p\text{-N(CH}_3)_2\text{(L2)}, p\text{-NO}_2\text{(L3)}, p\text{-OCH}_3\text{(L4)}$ or $p\text{-CH}_3\text{(L5)}$.

The solid complexes were prepared by mixing hot saturated alcoholic solutions of 0.005 mole of La(III) perchlorate or Ce(III) chloride with the corresponding Schiff base to form 1:2 (M:L) complexes. The *pH* of the mixture was raised with a few drops of ammonia solution to *pH* 6 and the reaction mixture was refluxed for 3–4 h and then left to cool. The formation of $M(NH_3)_n$ from the lanthanides can be excluded since NH_3 molecules can not compete with the Schiff bases or H_2O molecules. The solid complexes produced were filtered off and washed repeatedly with ethanol until the filtrate became colourless. The solid complexes were kept in a vacuum desiccator and subjected to elemental analysis in the Microanalytical Centre of Cairo University (Table 1). The metal contents of these complexes were determined after wet decomposition of the complexes as previously described [11].

The thermal analysis of some lanthanide complexes was performed with an OD 102 Derivatograph (MOM, Budapest). The mass loss was measured from

Table 1 Elemental analysis of La(III) and Ce(III) complexes with thio-Schiff bases

Complex	Formula	%C	%H	%N	%S	%Cl	%M
La–L1	$[La(C_{13}H_9NSCl)_2{\cdot}H_2O{\cdot}ClO_4]2H_2O$	39.83	3.12	3.70	8.23	13.66	17.80
		(39.70)	(3.50)	(3.56)	(8.16)	(13.56)	(17.67)
La–L2	$[La(C_{15}H_{15}N_2S)_2{\cdot}H_2O{\cdot}ClO_4]2H_2O$	44.78	4.51	6.91	8.10	4.52	17.41
		(44.82)	(4.48)	(6.97)	(7.98)	(4.42)	(17.10)
La–L3	$[La(C_{13}H_9N_2O_2S)_2{\cdot}H_2O{\cdot}ClO_4]2H_2O$	38.82	3.08	7.03	7.91	4.50	17.29
		(38.66)	(2.48)	(6.94)	(7.95)	(4.40)	(17.21)
La–L4	$[La(C_{14}H_{12}NOS)_2{\cdot}H_2O{\cdot}ClO_4]2H_2O$	43.51	3.90	3.66	8.19	4.64	17.80
		(43.24)	(3.86)	(3.60)	(8.25)	(4.57)	(17.88)
La–L5	$[La(C_{14}H_{12}NS)_2{\cdot}H_2O{\cdot}ClO_4]2H_2O$	45.30	4.11	3.92	8.73	4.81	18.67
		(45.10)	(4.03)	(3.76)	(8.61)	(4.67)	(18.64)
Ce–L1	$[Ce(C_{13}H_9NSCl)_2{\cdot}H_2O{\cdot}Cl]2H_2O$	43.20	4.38	3.86	8.91	14.84	19.45
		(43.15)	(4.43)	(3.87)	(8.87)	(14.73)	(19.38)
Ce–L2	$[Ce(C_{15}H_{15}N_2S)_2{\cdot}H_2O{\cdot}Cl]2H_2O$	48.75	5.12	7.71	8.77	4.73	18.81
		(48.63)	(5.13)	(7.56)	(8.66)	(4.79)	(18.93)
Ce–L3	$[Ce(C_{13}H_9N_2O_2S)_2{\cdot}H_2O{\cdot}Cl]2H_2O$	41.89	3.26	7.67	8.59	4.81	18.79
		(41.92)	(3.22)	(7.52)	(8.62)	(4.77)	(18.83)
Ce–L4	$[Ce(C_{14}H_{12}NOS)_2{\cdot}H_2O{\cdot}Cl]2H_2O$	47.12	4.19	3.96	8.91	4.91	19.72
		(47.04)	(4.20)	(3.92)	(8.98)	(4.47)	(19.61)

Calculated values in parenthesis

Table 2 Band assignment of the IR bands of La(III) and Ce(III) complexes with some thio-Schiff bases (L1–L5)

Lanthanum complexes					Cerium complexes				Assignment
La–L1	La–L2	La–L3	La–L4	La–L5	Ce–L1	Ce–L2	Ce–L3	Ce–L4	
3413 b	3400 b	3500 b	3433 b	3400 b	3400 b	3410 b	3500 b	3450 b	ν_{OH} (water)
1650 m	1615 s	1615 w	1643 w	1630 w	1626 b	1675 w	1642 w	1637 w	$\nu_{C=N}$
(1598 s)	(1600 s)	(1600 s)	(1610 s)	(1608 m)	(1598 s)	(1600 s)	(1600 s)	(1610 s)	
1100 m	1080 s	1100 m	1030 s	1050 w	–	–	–	–	$\nu_{ClO_4^-}$
620 w	620 m	611 w	620 s	620 m	–	–	–	–	
966 m	956 m	970 m	970 s	961 m	967 s	957 b	972 m	967 m	δ_{OH} (water)
690 w	730 m	685 m	653 s	750 s	686 s	719 m	720 b	720 s	ν_{C-S}
(700 s)	(750 s)	(762 s)	(760 s)	(762 s)	(700 s)	(750 s)	(762 s)	(760 s)	
500 w	510 w	467 w	511 m	483 m	485 m	511 w	510 m	511 w	ν_{M-N}

s = strong, w = weak, m = medium, b = broad; wavenumbers of free ligands are in parenthesis

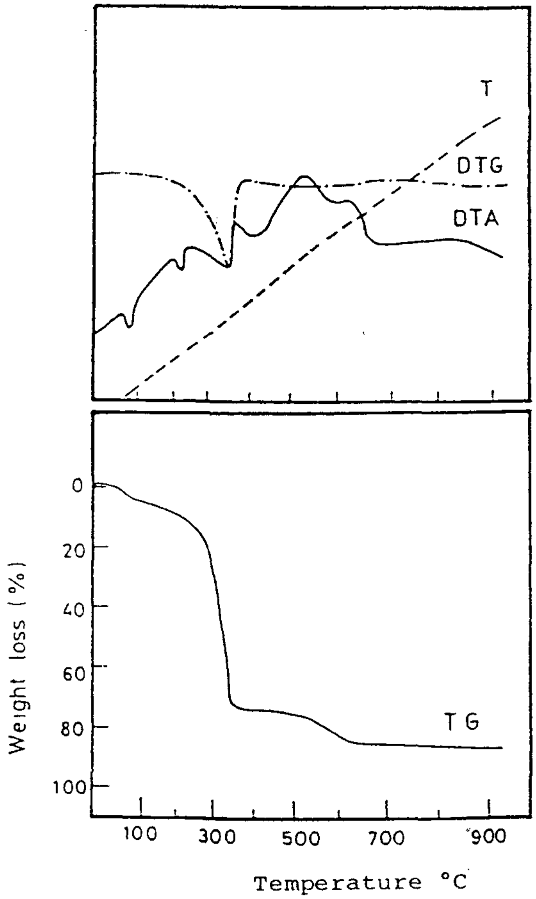


Fig. 1 TG and DTA curves of La(III) complexes with ligand L1

ambient temperature up to 950°C at a heating rate of 10 deg·min^{-1}. The TG, DTG and DTA curves are shown in Figs 1 and 2, and the thermal results are given in Table 2.

Results and discussion

Formulation of the solid complexes

The formulation of the Schiff base complexes as hydrated 1:2 species is in good agreement with the C, H, N, S, Cl and metal analyses (Table 1). The analytical results show that these complexes have the general formula $[ML_2 \cdot H_2O \cdot X]2H_2O$, where *M* = trivalent lanthanide metal ion, *L* = depro-

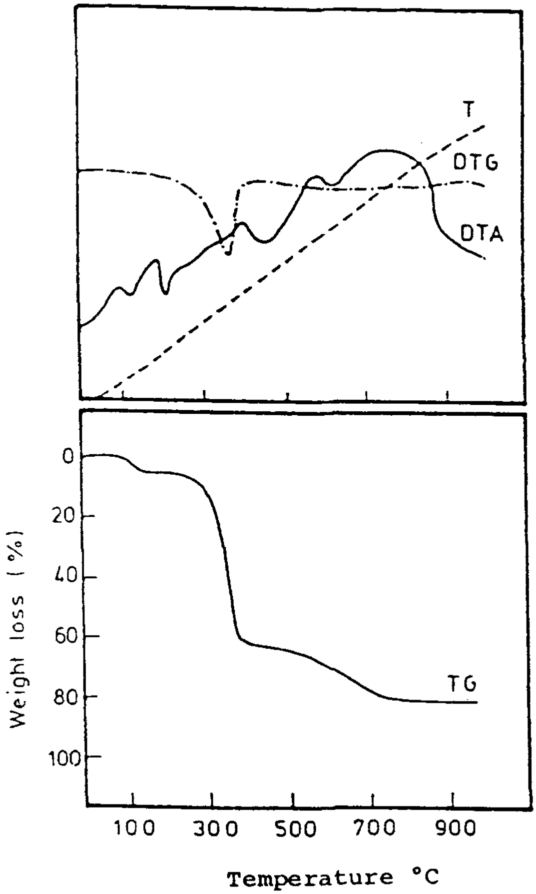


Fig. 2 TG and DTA curves of Ce(III) complexes with ligand L3

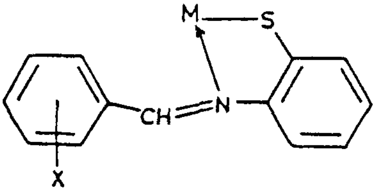
tonated Schiff base, and X = Cl^- or ClO_4^-. According to this formula, the *M* ion has a coordination number of 6, provided that the Schiff bases under investigation are bidentate ligands. The very low molar conductances (0.7–2.2 $ohm^{-1}\cdot cm^2\cdot mol^{-1}$) indicate that they behave as nonelectrolytes in solution and that the anion X is coordinated to the metal ion (Table 1).

Substituent effect

The effects of substituents on the complexation ability of the thio-Schiff bases can be deduced from the values of the stability constants of their complexes [12]. It was found that the derivatives containing electron-withdrawing groups (e.g. Cl and NO_2) have lower abilities for complexation as compared with those containing electron-donating groups (e.g. CH_3 and OCH3). This can be explained on the basis of the effects of such groups on the donation of the azomethine nitrogen of the Schiff bases. The donation property of the azomethine nitrogen atom involved in chelation is decreased by the presence of the electron-withdrawing groups and increased by the presence of the electron-donating groups [12].

IR spectra of solid complexes

In order to determine the mode of chelation of the Schiff bases under investigation, it is necessary to investigate their IR spectra and compare them with those of the free ligands (Table 2). From this comparison it was found that:



1. The broad weak S–H stretching band is not significant enough to give information about the participation of the SH group in chelation (as concluded from the NMR spectra). However, the shift in ν_{C-S} to lower frequencies ($\Delta\nu_{C-S}$ = 10–90 cm^{-1}) may be taken as an indication of the participation of the SH group in chelation.
2. Upon chelation, the C=N stretching band of the Schiff bases is shifted to higher frequencies, indicating the involvement of the N of the azomethine group in chelation with the metal ion [13].
3. The broad band at 3500–3170 cm^{-1} in the spectra of the complexes implies the presence of H_2O molecules. The band due to the bending vibration of H_2O was found at 972–813 cm^{-1}.
4. The new band at 516–467 cm^{-1}, which is assignable to the M–N stretching vibration (not present in the spectra of the free ligands), indicates the formation of a coordinate M–N bond in the complexes.
5. The two bands in the regions 1100–1010 cm^{-1} and 625–611 cm^{-1} (in the spectra of the complexes) are assigned to the vibration of ClO_4^-. This implies the presence of ClO_4^- in the solid complexes.

NMR spectra of solid complexes

The NMR spectra of the thio-Schiff bases showed two signals at 3.4 and 7.4 ppm, which are assignable to SH and azomethine H, respectively. Upon

Table 3 TG results of some Ln(III) complexes with thio-Schiff bases

Complex	Formula	Dehydration stage*			Start of decom-position	Oxide formation		
		Temperature range /°C	H_2O loss / %			Metallic residue / %		
			Calc.	Found		Temp. /°C	Calc.	Found
La–L1	$[La(C_{13}H_9NSCl)_2{\cdot}H_2O{\cdot}ClO_4]{\cdot}2H_2O$	50–100	4.56	4.67	200	640	17.67	17.80
La–L5	$[La(C_{14}H_{12}NS)_2{\cdot}H_2O{\cdot}ClO_4]{\cdot}2H_2O$	60–100	4.80	4.87	210	550	18.64	18.67
Ce–L2	$[Ce(C_{15}H_{16}S)_2{\cdot}H_2O{\cdot}Cl]{\cdot}2H_2O$	80–160	5.25	5.33	250	650	20.42	20.12
Ce–L3	$[Ce(C_{13}H_9N_2O_2S)_2{\cdot}H_2O{\cdot}Cl]{\cdot}2H_2O$	50–150	4.83	4.80	210	725	18.83	18.72
Ce–L4	$[Ce(C_{14}H_{12}NOS)_2{\cdot}H_2O{\cdot}Cl]{\cdot}2H_2O$	30–110	5.04	5.20	190	550	19.61	19.72

*2 mol of H_2O are lost in each cases

chelation, the first signal disappeared completely, indicating the participation of the SH group in chelation. Moreover, new broad signals appeared near 4 ppm in the spectra of the complexes (with integration corresponding to 4 protons) and can be assigned to $2H_2O$ molecules.

TG and DTA of solid complexes

It is not possible to distinguish between the hydration and the coordinated H_2O molecules from the IR spectral data. The TG method can here demonstrate the nature of the H_2O molecules in the complexes. The TG and DTA curves are shown in Figs 1 and 2, while Table 3 lists the losses in mass (found and calculated) of the solid complexes in relation to the temperature.

The initial mass losses within the range 50–160°C are attributed to elimination of the hydration H_2O molecules. The mass loss percentages correspond to 2 H_2O molecules. In the DTA curves, this dehydration process appeared as an endothermic peak. The coordinated water is known to be eliminated at 150–250°C [14]. This process could not be detected for the lanthanide–Schiff base complexes. It is believed that such coordinated water is eliminated at the start of decomposition at 200°C. This is further supported by the presence of another endothermic peak at 170–190°C before decomposition starts. The final stage, at 600–700°C, is the formation of the stoichiometric oxides La_2O_3 and CeO_2 as end-products. The small inflection observed at 400–500°C corresponds to the oxycarbonate intermediate $M_2O_2CO_3$ before oxide formation. The intermediate $M_2O_2CO_3$ has previously been observed in the same temperature range during the thermal decompositions of some other lanthanide complexes [15, 16].

On the basis of the above observations, the following general scheme of thermal decomposition may be proposed for the lanthanide-Schiff base complexes:

$$1.\ [ML_2\cdot X\cdot H_2O]2H_2O \xrightarrow[100\,-\,160^{\circ}C]{\text{dehydration}} [ML_2\cdot X\cdot H_2O]$$

$$2.\ [ML_2\cdot X\cdot H_2O] \xrightarrow[160\,-\,200^{\circ}C]{\text{decoordination}} \underset{\text{unstable}}{[ML_2\cdot X]}$$

$$3.\ [ML_2\cdot X] \xrightarrow[400\,-\,500^{\circ}C]{\text{partial decomposition}} \text{intermediate}$$

$$4.\ \text{Intermediate} \xrightarrow[600\,-\,700^{\circ}C]{\text{final decomposition}} \text{metal oxides}$$

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Zusammenfassung — Feststoffkomplexe von fünf Derivaten von Thioschiff'schen Basen mit La(III)- und Ce(III)-Ionen wurden hergestellt und mittels Elementaranalyse und TG charakterisiert. Die vorgeschlagene Formel der Feststoffkomplexe lautet $[ML_2(H_2O)_X]2H_2O$ mit M= dreibindiges Lanthanidenion, L= Schiff'sche Base und X= Cl^-- oder ClO_4^--Ion. Informationen über das Hydratwasser, die koordinierten Wassermoleküle, die Koordinationschemie und die thermische Stabilität dieser Komplexe wurde ermittelt und diskutiert. Außerdem wurde ein allgemeines Schema für die thermische Zersetzung der Lanthaniden-Schiff'schen Basen vorgeschlagen.