Thermochimica Acta, 241 (1994) 103–111
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(94)01717-U

Thermal, spectroscopic and magnetic studies of some rare earth 3-halolawsonemonoximates

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(Received 26 October 1993; accepted 23 January 1994)

Abstract

The metal chelates of 3-chloro-, 3-bromo- and 3-iodo-derivatives of lawsonemonoxime with La(III), Sm(III) and Dy(III) have been synthesised. The thermal, spectral and magnetic properties of these chelates have been investigated to study the effect of variation of the C_3-halo-substituent on the chelating ability of the lawsonemonoxime. The energy of activation E_a and the order of reaction n for the decomposition stages have been calculated using the Coats–Redfern relation.

INTRODUCTION

Lawsone (2-hydroxy-1,4-naphthalenedione) is well known for its powerful chelating ability. It reacts with most metal ions in the periodic table to give stable five-membered chelates. Extensive work on its chelates with transition metals, alkaline earths and also the lanthanides has been reported [1–3]. There is only one report on C_3-substituted lawsonates of lanthanides, describing the thermodynamic studies of rare earth chelates of phthiocol (3-methyl-lawsone) in solution using potentiometry [4]. Compared to lawsone and C_3-substituted lawsones, its monoxime, lawsonemonoxime, and its C_3-substituted derivatives are found to be more powerful ligands. However, much less work has been reported on rare earth chelates of lawsonemonoxime and its C_3-substituted derivatives. Only for phthiocolmonoxime have studies similar to the above-mentioned work on the rare earth chelates of phthiocol been reported [5].

There is no report on 3-halolawsonemonoximates of lanthanides. We have, therefore, decided to synthesise and study these chelates. In the present communication, we report the study of the thermal, spectral and magnetic properties of the chelates of lanthanum(III), samarium(III) and dysprosium(III) with 3-chlorolawsonemonoxime (3-chloro-2-hydroxy-1,4-naphthalene-dione-1-oxime (**I**), 3-bromolawsonemonoxime (**II**) and 3-iodo-

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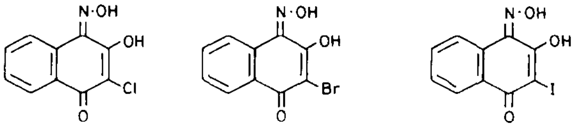
lawsonemonoxime (III), see Scheme 1). The results obtained have been compared in order to study the effect of changing the halo substituent at C_3.



(I) (II) (III)

Scheme 1. 3-Halolawsonemonoximes.

EXPERIMENTAL

Syntheses

All the chemicals used in the preparation of the ligands and metal chelates were of A.R. grade. Dichlone (2,3-dichloro-1,4-naphthalenedione) and lawsone were products of Fluka A.G. 3-Chlorolawsone was synthesised from dichlone, while 3-bromo- and 3-iodolawsone were synthesised from lawsone by known methods [6] with some modifications [7]. The 3-halolawsonemonoximates were prepared by treating the solutions of the corresponding 3-halolawsones (0.010 mol) in 2 N sodium hydroxide with an aqueous solution of hydroxylamine hydrochloride (0.015 mol) at 50–60°C for an hour. The mixture was diluted by ice-cold water and neutralised by hydrochloric acid (2 N). The chelates of La(III), Sm(III) and Dy(III) with 3-chloro-, 3-bromo- and 3-iodolawsonemonoxime were synthesised by employing procedures similar to those for the rare earth chelates reported earlier [2].

Instrumentation

The compounds were analysed microanalytically for the percentage of carbon, hydrogen and residue (as M_2O_3) using a Hosli C,H-microanalysis instrument. Lanthanides were estimated by known methods [2, 8].

Thermograms of the metal chelates were recorded on a Perkin-Elmer Delta Series, thermal analysis system TGA-7 model, with a chromelalumel thermocouple in air atmosphere. For each run, about 1–3 mg of sample was used with a heating rate of 10°C min^{-1}.

The IR spectra of the ligands and their lanthanide chelates were recorded in Nujol mulls on a Perkin-Elmer infrared spectrophotometer model 783 in the range 4000–200 cm^{-1}.

The electronic spectra of all the C_3-halolawsonemonoximes and their metal chelates were recorded in the range of 200–800 nm on a Shimadzu

UV-300 spectrophotometer using 1-cm matched quartz cells in three different solvents (chloroform, methanol and DMF) in order to study the solvent effect.

Magnetic susceptibilities were measured at room temperature by the Faraday method [9]. Diamagnetic corrections [10] for the ligands were applied and the values of the effective magnetic moments were calculated.

RESULTS AND DISCUSSION

All the metal chelates were of varying colours from yellow to orange. The elemental analyses indicated the composition of these chelates to be $[ML_3(H_2O)_2] \cdot nH_2O$ (where M is trivalent lanthanide ion, L the ligand, and $n = 0$, 1 or 5), see Table 1. The thermogravimetric analysis supported the presence of two coordinated water molecules in all the chelates. The percentage of metal calculated from the residue (as M_2O_3), obtained from elemental analyses as well as TGA, also matched with the values estimated by standard methods as well as with the calculated values for the abovementioned composition, within the experimental error.

Thermal studies

The TG and first derivative curves (Fig. 1) for all the metal chelates showed weight losses due to dehydration in the range 60–200°C, followed by decomposition.

The loss due to dehydration is attributed to that of coordinated water and also, in some cases, to lattice water. The notable accelerated weight loss for Sm(III)-3-iodolawsonemonoximate (viii) in the initial stages may be due to lattice water. This is consistent with normal behaviour for Sm(III) complexes [11].

In general, two stages are observed for decomposition for all the chelates. The decomposition temperatures were found using first derivative curves. These were found to be in the range 283–338°C. The energy of activation E_a in kJ mol^{-1} and the order of reaction n for the decomposition stages were calculated using the Coats–Redfern relation [12], see Table 2.

Except for La(III) chelates, the change in substituent at C_3 from chloro-, to bromo-, to iodo-group produced no regular effect on the decomposition temperature, E_a and n values. In fact, the bromo chelates in the present study exhibited abnormally high or low values of decomposition temperature, E_a and n. This was notable for Sm(III)-3-bromolawsonemonoximate.

Infrared studies

The IR spectra were mainly analysed for those specific frequencies which are directly involved in the chelate formation. These include the C–O

TABLE 1

Analytical data and magnetic moments of some rare earth chelates of 3-halolawsonemonoximes

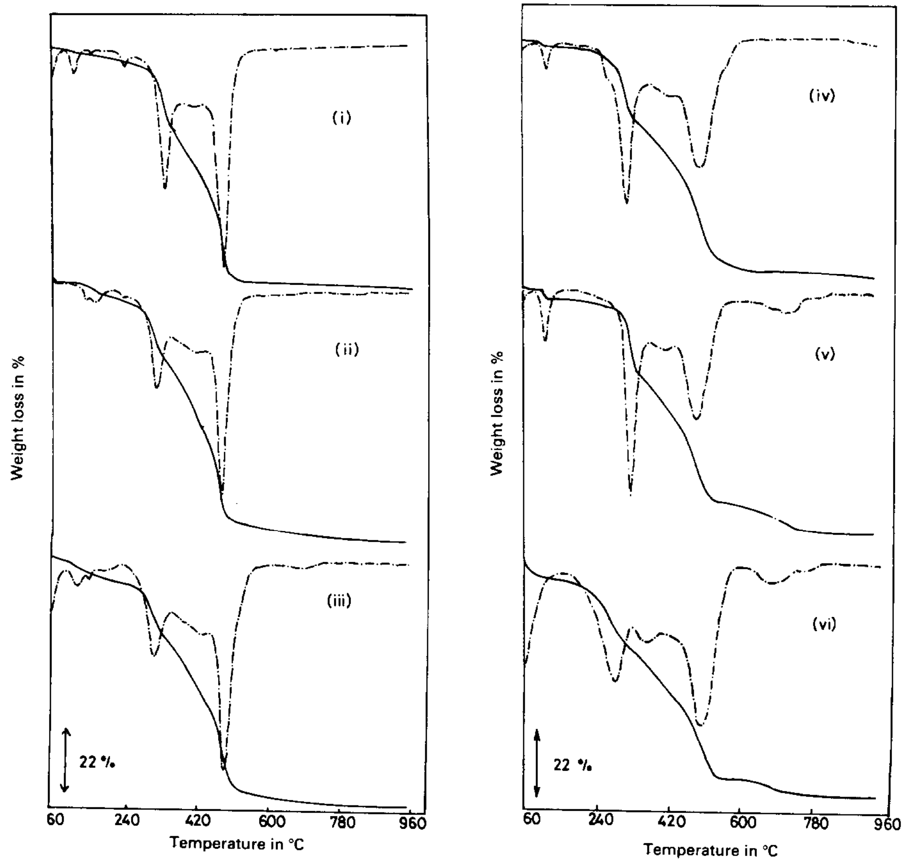
Chelate [a]	Notation	Colour	Yield/ %	Analysis/% (Calc.)			Magnetic moment μ_{eff}/BM
				Carbon	Hydrogen	Metal	
3-Chlorolawsonemonoximates							
$[LaL_3(H_2O)_2]$	(i)	Brown-orange	70	42.53 (42.75)	1.99 (2.01)	16.30 (16.49)	Diamagnetic
$[SmL_3(H_2O)_2]$	(ii)	Orange	69	41.83 (42.16)	2.15 (2.22)	17.48 (17.60)	1.20
$[DyL_3(H_2O)_2] \cdot H_2O$	(iii)	Yellow-orange	70	41.34 (41.57)	2.44 (2.54)	17.83 (18.76)	10.87
3-Bromolawsonemonoximates							
$[LaL_3(H_2O)_2]$	(iv)	Yellow-orange	75	36.26 (36.89)	1.86 (1.94)	15.28 (14.23)	Diamagnetic
$[SmL_3(H_2O)_2]$	(v)	Orange	67	36.19 (36.47)	1.80 (1.92)	13.97 (14.95)	1.19
$[DyL_3(H_2O)_2]$	(vi)	Yellow-orange	70	35.80 (36.02)	1.79 (1.90)	17.31 (16.26)	11.26
3-Iodolawsonemonoximates							
$[LaL_3(H_2O)_2]$	(vii)	Yellow-orange	68	32.10 (32.24)	1.73 (1.70)	12.29 (12.44)	Diamagnetic
$[SmL_3(H_2O)_2] \cdot 5H_2O$	(viii)	Brown-orange	69	30.44 (29.55)	2.51 (2.38)	11.82 (12.34)	1.13
$[DyL_3(H_2O)_2] \cdot H_2O$	(ix)	Brown-orange	73	30.80 (31.57)	1.52 (1.66)	14.09 (14.25)	11.31

[a] L is the ligand.

stretching frequency, the C–N stretching frequency, the M–O stretching frequency, and the M–N stretching frequency.

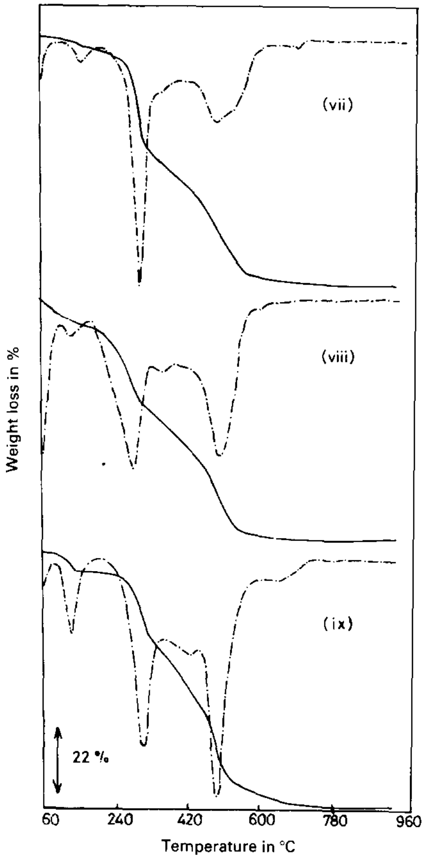
The C–O stretching frequency for the ligands is found to lie in a narrow region of 1205–1200 cm^{-1}. This frequency showed shifts to higher energies by 15–35 cm^{-1} in the chelates which indicates the strengthening of the C–O bond. The C=N stretching frequency for 3-chlorolawsonemonoxime is found at 1540 cm^{-1}, while for the other two ligands it is at 1580 cm^{-1}. This frequency was shifted to lower energies by 10–80 cm^{-1} after chelation which indicates that the C=N bond becomes weak after chelation. The M–O stretching frequencies are observed in the range 480–400 cm^{-1}, while the M–N stretching frequencies are observed in the region of 265–230 cm^{-1}.

Other IR frequencies of interest are: N–O stretching frequency at 1050–1045 cm^{-1}; O–H stretching frequency at 3600–3000 cm^{-1}; C=O stretching frequency due to the carbonyl group at the C_4 position (at $\approx$1620 cm^{-1}); and C–X stretching frequency at $\approx$680 cm^{-1}.



(a) (b)

Fig. 1(a, b).



(c)

Fig. 1. Thermograms of rare earth chelates of 3-halolawsonemonoximes. For chelate notation, see Table 1.

Of these, only the N–O frequency showed a notable shift to a higher frequency region by 5–20 cm^{-1} after chelation, which clearly indicates coordination through the oximino nitrogen [13]. The O–H stretching frequency is seen as a broad band in the ligands. On chelation, this band broadens due to an overlap with the O–H frequency of the coordinated water. Other frequencies do not show any effect of chelation and remained unaltered.

For the N–O stretching and M–O stretching frequencies, noticeable graded low-frequency shifts are observed as the substituent at C_3 is changed from chloro to bromo and then to iodo. The other frequencies, however, showed arbitrary variations on changing the halo substituent at C_3, abnormally high or low values being observed for the bromo complexes. The only exception is the regular variations in frequencies seen in lanthanum(III) chelates.

TABLE 2

Thermal analysis data for lanthanide chelates of 3-halolawsonemonoximes

Chelate [a]	Decomp. temp./°C	Temp. ranges /°C for stages of decomp.	Weight loss/%	Order of reaction n	Energy of activation E_a/kJ mol^{-1}
(i)	334	273–381	27.75	1.00	112.6
		435–570	31.80	1.00	284.5
(ii)	317	253–351	21.39	0.90	141.4
		441–559	28.33	1.00	241.6
(iii)	313	227–354	20.24	0.90	112.9
		454–583	27.75	1.00	239.7
(iv)	315	231–373	28.33	0.84	110.9
		450–613	30.07	2.20	289.7
(v)	338	278–386	28.58	2.55	290.3
		454–591	27.97	1.00	144.8
(vi)	287	167–330	21.97	1.10	072.1
		411–596	31.22	1.16	137.5
(vii)	300	214–399	45.00	1.00	058.4
		441–626	27.97	1.62	165.7
(viii)	283	180–334	30.40	0.99	069.6
		424–617	29.19	1.22	147.8
(ix)	317	221–364	26.59	1.05	117.0
		458–596	28.33	1.00	163.0

[a] For chelate notation, see Table 1.

Electronic spectra

The electronic spectra are interpreted in terms of benzenoid electron transfer (BET), quinonoid electron transfer (QET), and n → π* transitions. The spectra of the rare earth chelates in general resemble the spectra of their corresponding ligands, with certain modifications as a result of chelation.

For BET, two principal bands are observed, the first in the range 234–250 nm (except in DMF) and the second in the range 335–388 nm. The QET band is observed in the range 270–300 nm. Among the three solvents, only $CHCl_3$ showed variation in the position of this band as a result of changing the central metal ion. Two bands are detected at 412–430 and 425–460 nm, respectively, involving n → π* transitions in the spectra of all chelates recorded in CH_3OH and DMF. However, only one band is observed in $CHCl_3$ which clearly indicates the solvent effect on these bands.

The second BET band and the n → π* bands are found to be sensitive to changes in the halo substituent at C_3, to changes in the metal ion, as well as to changes in the solvent. In general, a blue shift for n → π* transitions is observed as the polarity of the solvent is increased. This clearly indicates a strong effect of the solvent on non-bonded electrons of the metal chelates.

The arbitrary trend of the variations in band positions is notable, the effect of the variation of the halo group at C_3 being abnormal in the case of the bromo substituents. Variation of the metal ion has no effect on this trend.

Magnetic properties

As expected, all La(III) chelates are diamagnetic in nature. Lower magnetic moments are observed for Sm(III) chelates as compared to the theoretical values calculated using the appropriate equations of Van Vleck and Frank [14]. This may be due to antiferromagnetic coupling between the 4f orbital of Sm(III) and the ligand orbitals, or to magnetic dilution caused by water molecules. Such anomalous magnetic behaviour has been discussed by Mulay and Bondreaux [15] and Selwood [9]. The magnetic moments of Dy(III) chelates are close to the theoretical values calculated for Dy(III) free ion.

There is a notable effect of C_3-halo substituent on the magnetic moments of the Sm(III) and Dy(III) chelates. For Sm(III) chelates, this trend follows a decreasing order from chloro to bromo to iodo C_3-halo-substituent. However, for Dy(III) chelates, the magnetic moment trend is found to be the reverse of that for Sm(III) chelates.

CONCLUSIONS

From the results obtained, we can conclude that the possibility of a much higher coordination number in lanthanide chelates of 3-halolawsonemonoximes is consistent with the previous reports [16, 17].

There is an abnormal variation in the trend as the halo substituent at C_3 in the ligands is changed, as well as in the chelates with a bromo substituent, an exception being the magnetic moments of the chelates.

ACKNOWLEDGEMENTS

The authors thank the Head, Department of Chemistry, University of Poona. One of the authors (JGK) is grateful to the Department of Atomic Energy, Bombay for the award of a K.S. Krishnan Fellowship. The authors also thank Professor S.B. Kulkarni and Dr. G.N. Natu of the Department of Chemistry, University of Poona for their encouragement.

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