Thermochimica Acta, 154 (1989) 299–304
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION AND MASS SPECTRAL STUDIES OF COBALT(III) COMPLEXES WITH HEXADENTATE DIOXIME SCHIFF BASES

M. MOHAPATRA, V. CHAKRAVORTTY and K.C. DASH *

Department of Chemistry, Utkal University, Vani Vihar, Bhubaneswar 751004 (India)

(Received 23 March 1989)

ABSTRACT

The hexadentate dioxime Schiff base ligands *N,N′,N″,N‴*-triethylenetetramine bis(isonitrosoethyl methyl ketone imine) (H_2L') and *N,N′,N″,N‴*-triethylenetetramine bis(isonitrosopropiophenone imine) (H_2L'') react with CoX_2 ($X \equiv$ Br, I, NO_3) to form cobalt(III) complexes of the type $[Co(HL)]X_2$ ($H_2L \equiv H_2L'$, H_2L''). The mass spectra of the ligand (H_2L') and its complexes show fragmentation patterns for the ligand only. Thermal decomposition studies (TG, DTG and DTA) for all the complexes up to 1000 °C indicate that, in most cases, with increasing temperature the compounds decompose in a stepwise manner, finally forming Co_3O_4 as the stable end product.

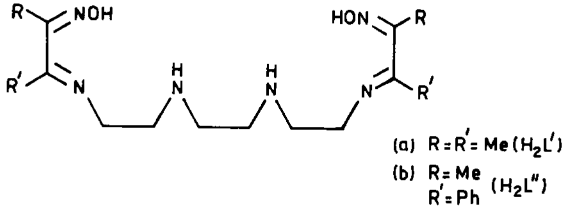
INTRODUCTION

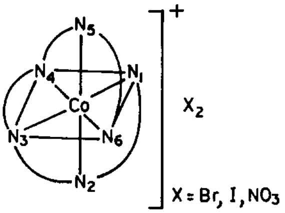
As a part of our work on cobaloximes [1–3] and complexes involving dioxime-based Schiff base ligands, we reported recently [4] on the cobalt complexes of two hexadentate ligands, N,N′,N″,N‴-triethylenetetramine bis(isonitrosoethyl methylketone imine) (H_2L') and *N,N′,N″,N‴*-triethylenetetramine bis(isonitrosopropiophenone imine) (H_2L''), synthesized by the condensation of triethylenetetramine with isonitrosoethyl methyl ketone (diacetylmonoxime) and isonitrosopropiophenone, respectively. The cobalt(III) complexes formed are of the type $[Co(HL)]X_2$ ($H_2L \equiv H_2L'$, H_2L''; $X \equiv$ Br, I, NO_3), and have been characterized by magnetic susceptibility and electronic, IR and NMR (^1H and ^{13}C) spectral measurements, as well as by cyclic voltammetry. The present work is concerned with the mass spectra of the ligand H_2L' and its complexes, and the thermal decomposition of the cobalt(III) complexes of the two hexadentate ligands H_2L' and

---

* Author to whom correspondence should be addressed.

H_2L''. The structures of the ligands and the cobalt complexes are shown below.





EXPERIMENTAL

The ligands and their cobalt(III) complexes were synthesized and characterized as reported previously [4].

Mass spectra of the compounds were obtained as reported previously [5].

Thermal measurements were made using a Shimadzu DT-30 apparatus, recording T, TG, DTG and DTA data simultaneously in static air. The rate of heating was maintained at 10 °C min^{-1}.

RESULTS AND DISCUSSION

The synthesis of these complexes and their detailed characterization have been reported previously [4]. The IR spectral data reported earlier and the thermogravimetric data reported in the present work (Figs. 1 and 2) clearly show the absence of any H_2O molecules, either coordinated or present as water of crystallization. The position and intensity of the IR bands and the ^1H and ^{13}C resonance signals clearly establish the hexadentate mode of ligation. The IR bands also fail to provide any evidence for coordination of Br, I or NO_3 to the Co(III) centre.

Mass spectra

The mass spectra of the uncomplexed ligand H_2L' and its complexes were examined. However, these complexes do not ionize under identical condi-

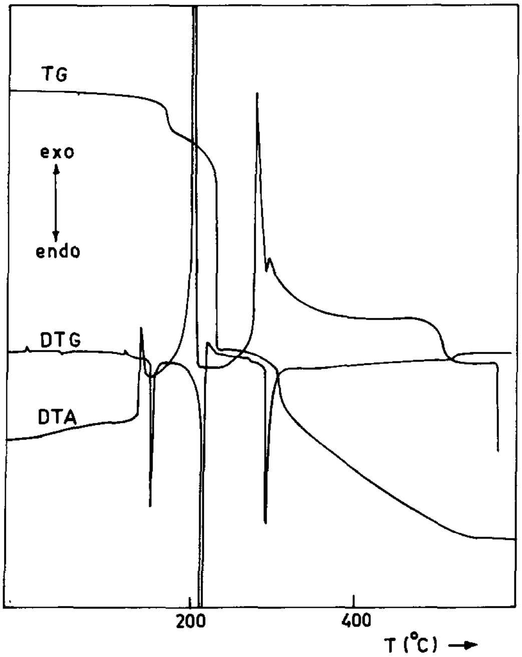


Fig. 1. Thermogravimetric curve for [Co(HL″)](NO$_3$)$_2$.

tions in the mass spectrometer, and no metallated fragmentation patterns were observed. Each time, fragmentation products of the ligand only were obtained, which were identical. The main peaks in the fragmentation pat-

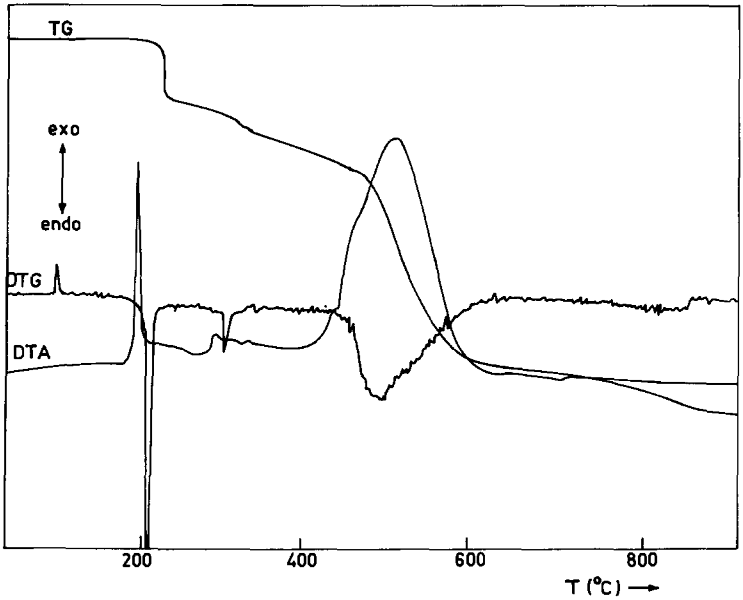
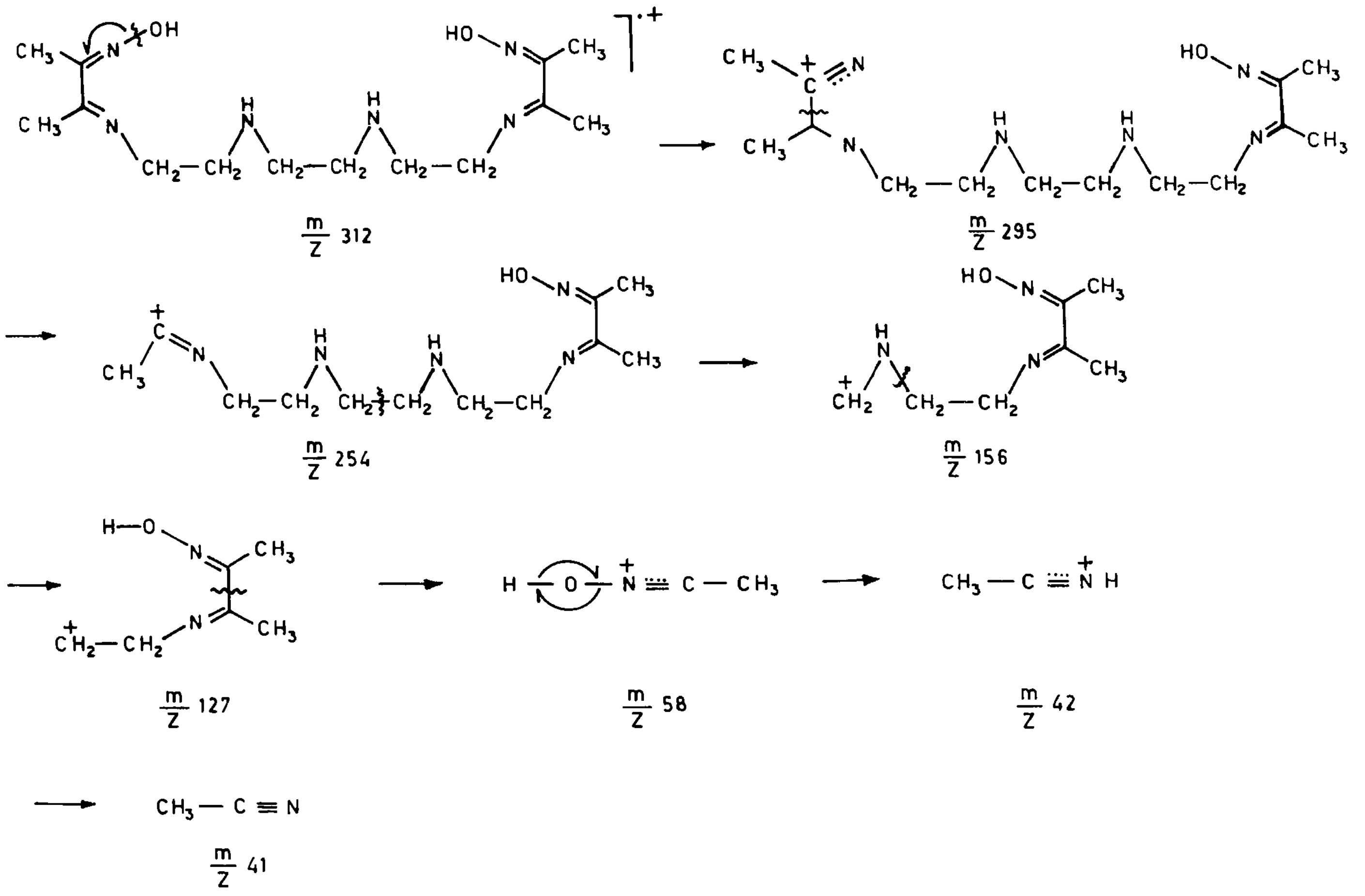


Fig. 2. Thermogravimetric curve for [Co(HL″)]I$_2$.



Scheme 1. Fragmentation pattern for the hexadentate ligand H_2L'.

terms of the ligand H_2L' are shown in Scheme 1. There were some additional peaks in the mass spectra but it was rather difficult to make an unambiguous assignment of these peaks, owing to the complex structure of the ligand, and also to the fact that the fragmentation products underwent simultaneous recombination. The molecular ion peak of the ligand appears at m/z 295, 254, 156, 127, 58, 42 and 41. The most abundant species has m/z 42 with a relative intensity of 80, corresponding to the protonated form of acetonitrile, $CH_3\text{-}C\equiv\overset{+}{N}H$.

Thermal decomposition studies

Thermal decomposition studies (TG, DTG and DTA) of the $[Co(HL)]X_2$ complexes were carried out in the temperature range 40–1000 °C. The

TABLE 1

Thermal decomposition data for some cobalt(III) complexes with hexadentate ligands

Compound	Temperature range (°C)	Weight loss (%)		Species formed	DTA peak
		Obs.	Calc.		
$[Co(HL')]Br_2$	210	30.5	29.4	$Co(HL')_{0.5}Br_2$	Exo
	210–445	38.8	36.8	$Co(HL')_{0.375}Br_2$	
	445–500	58.0	58.7	$CoBr_2$	Exo
	500–640	82.4	84.8	$\frac{1}{3}Co_3O_4$	
$[Co(HL')]I_2$	228	23.0	25.0	$Co(HL')_{0.5}I_2$	Exo
	228–410	31.0	31.2	$Co(HL')_{0.375}I_2$	
	410–615	89.3	87.1	$\frac{1}{3}Co_3O_4$	
$[Co(HL')](NO_3)_2$	200	31.0	31.4	$Co(HL')_{0.5}(NO_3)_2$	Exo
	200–250	38.8	39.4	$Co(HL')_{0.375}(NO_3)_2$	Exo
	250–360	49.5	47.3	$Co(HL')_{0.25}(NO_3)_2$	Exo
	360–570	85.4	83.7	$\frac{1}{3}Co_3O_4$	
$[Co(HL'')]Br_2$	215	22.7	24.9	$Co(HL'')_{0.625}Br_2$	Exo
	215–300	31.2	33.4	$Co(HL'')_{0.5}Br_2$	
	300–550	49.0	50.0	$Co(HL'')_{0.25}Br_2$	
	550–680	82.2	83.9	$\frac{1}{3}Co_3O_4$	Exo
$[Co(HL'')]I_2$	220	19.2	21.8	$Co(HL'')_{0.625}I_2$	Exo
	220–470	41.1	43.5	$Co(HL'')_{0.25}I_2$	
	470–645	87.0	89.3	$\frac{1}{3}Co_3O_4$	Exo
$[Co(HL'')](NO_3)_2$	160	8.08	8.78	$Co(HL'')_{0.875}(NO_3)_2$	Exo
	160–225	18.4	17.6	$Co(HL'')_{0.75}(NO_3)_2$	Exo
	235–310	61.0	61.5	$Co(HL'')_{0.25}(NO_3)_2$	Exo
	310–540	86.3	85.7	$\frac{1}{3}Co_3O_4$	

H_2L' = *N,N′,N″,N‴*-triethylenetetramine bis(isonitrosoethyl methyl ketone imine).
H_2L'' = *N,N′,N″,N‴*-triethylenetetramine bis(isonitrosopropiophenone imine).

relevant data are collected in Table 1. All the Co(III) complexes are quite stable at room temperature and remain so up to 200 ° C, after which the ligand begins to decompose slowly and the complexes lose ligands in discrete steps. In all cases, Co_3O_4 is formed as the stable end product. In general, the nitrato complexes exhibit very prominent DTG and DTA peaks and seem to be thermogravimetrically relatively less stable compared to the bromo and iodo complexes. If the initial decomposition temperature is taken as a rough criterion for the thermal stability of these complexes, the following relative order of stability can be proposed.

$$\begin{aligned}&[\mathrm{Co(HL')}]\mathrm{I_2} \approx [\mathrm{Co(HL'')}]\mathrm{I_2} > [\mathrm{Co(HL')}]\mathrm{Br_2} \approx [\mathrm{Co(HL'')}]\mathrm{Br_2}\\ &\qquad > [\mathrm{Co(HL')}](\mathrm{NO_3})_2 > [\mathrm{Co(HL'')}](\mathrm{NO_3})_2\end{aligned}$$

ACKNOWLEDGEMENTS

M.M. is grateful to the U.G.C., New Delhi, for the award of a Senior Research Fellowship.

REFERENCES

1 J.K. Das and K.C. Dash, Polyhedron, 4 (1985) 1109.
2 J.K. Das and K.C. Dash, Transition Met. Chem., 10 (1985) 422.
3 J.K. Das and K.C. Dash, Synth. React. Inorg. Metal-Org. Chem., 15 (1985) 839.
4 M. Mohapatra, V. Chakravortty and K.C. Dash, Polyhedron, in press.
5 J.K. Das, V. Chakravortty and K.C. Dash, Thermochim. Acta, 97 (1986) 303.