Thermochimica Acta, 132 (1988) 297–300
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

THERMAL STUDIES ON COMPLEXES OF ZINC(II) AND CADMIUM(II) WITH 5,6-BENZOQUINOLINE-*N*-OXIDE

A.K. SRIVASTAVA, ANUPAMA SRIVASTAVA and P.C. JAIN
Meerut College, Meerut-250 001 (India)

(Received 8 January 1988)

In recent years, a number of complexes of 5,6-benzoquinoline [1–5] and aromatic amine-*N*-oxides [6–9] have been isolated and characterised. However, the thermal investigations of these complexes have been carried out only to a limited extent. In this paper we report the thermal decomposition characteristics, i.e. cleavage of metal–ligand bond and accompanying enthalpy change, as determined by thermogravimetry (TG), differential thermal gravimetry (DTG) and differential thermal analysis (DTA), of zinc(II) and cadmium(II) complexes of 5,6-benzoquinoline-*N*-oxide and their intermediates.

EXPERIMENTAL

5,6-Benzoquinoline was obtained from Merck and its oxide was prepared by the method described for quinoline-*N*-oxide [10]. The metal salts and other chemicals used were of BDH AnalaR grade.

The metal complexes were prepared by the following general method: an ethanolic solution of the corresponding metal salt (0.01 mole in 40 ml) was refluxed with a solution of the ligand (0.04 mole in 30 ml ethanol) on a waterbath for about 0.5 h. From the refluxate the complexes were separated either on standing or on concentrating and cooling to room temperature. The product was collected, washed with cold ethanol and finally with diethylether and dried in vacuo over P_4O_{10}.

The elemental analyses and physical measurements were made as reported earlier [11]. The differential thermal analysis and thermogravimetry units employed were similar to those described earlier [12]. All experiments were carried out in static air. Heating rates employed were $10\,^\circ C\ min^{-1}$ for DTA and $5\,^\circ C\ min^{-1}$ for TGA.

RESULTS AND DISCUSSION

The composition together with the analytical and partial IR data of Zn(II) and Cd(II) complexes of 5,6-benzoquinoline-*N*-oxide (BenzqnO) are

TABLE 1

Analytical, partial IR and thermal decomposition data of 5,6-benzoquinoline-*N*-oxide complexes of Zn(II) and Cd(II)

Compound	Metal (%)	N (%)	Anion (%)	ν(NO)	δ(NO)	ν(MO)	Decomp. temp. (°C)		Decomp. product	Wt. loss (%)	
	Found calcd.	Found calcd.	Found calcd.				Initial	Final		Found	Calcd.
BenzqnO	–	–	–	1240sh	840s	–	–	–	–	–	–
				1235s							
$ZnCl_2\cdot$4BenzqnO	7.31	6.23	7.51	1215m	835m	450m	210	290	$ZnCl_2\cdot$2BenzqnO	44.12	42.57
	7.09	6.11	7.75				310	390	$ZnCl_2$	86.95	85.15
							530	630	ZnO	92.39	91.15
$ZnBr_2\cdot$4BenzqnO	6.57	5.70	15.61	1220s	830m	445m	205	285	$ZnBr_2\cdot$2BenzqnO	40.16	38.80
	6.46	5.57	15.92				305	390	$ZnBr_2$	79.32	77.61
							540	610	ZnO	93.32	91.57
$ZnI_2\cdot$4BenzqnO	6.16	5.29	22.76	1225s	830m	440m	–	–	–	–	–
	5.91	5.09	23.11								
$Zn(NCS)_2\cdot$4BenzqnO	6.92	8.92	11.73	1225m	835m	435m	200	295	$Zn(NCS)_2\cdot$2BenzqnO	42.16	40.58
	6.76	8.74	12.07				320	390	$Zn(NCS)_2$	83.02	81.16
							545	620	ZnO	93.16	91.57
$Zn(CH_3COO)_2\cdot$4BenzqnO	6.91	5.96	–	1225s	830m	440m	190	280	$Zn(CH_3COO)_2\cdot$2BenzqnO	42.16	40.49
	6.74	5.81	–				330	395	$Zn(CH_3COO)_2$	82.36	81.16
							520	615	ZnO	93.85	91.58
$CdCl_2\cdot$4BenzqnO	11.82	5.95	7.19	1220s	835s	445s	215	295	$CdCl_2\cdot$2BenzqnO	42.10	40.49
	11.63	5.81	7.37				305	395	$CdCl_2$	83.16	80.99
							515	620	CdO	88.92	86.70
$CdBr_2\cdot$4BenzqnO	10.80	5.51	14.82	1225m	830m	440m	210	300	$CdBr_2\cdot$2BenzqnO	39.32	37.07
	10.64	5.32	15.20				360	405	$CdBr_2$	76.20	74.14
							510	625	CdO	89.16	87.83
$CdI_2\cdot$4BenzqnO	9.91	5.02	21.56	1230m	835m	445m	–	–	–	–	–
	9.77	4.88	22.16								
$Cd(NCS)_2\cdot$4BenzqnO	11.29	8.56	11.32	1235m	840m	450m	200	290	$Cd(NCS)_2\cdot$2BenzqnO	40.16	38.69
	11.11	8.33	11.50				320	390	$Cd(NCS)_2$	79.32	77.38
							520	620	CdO	88.90	87.30

reported in Table 1. The IR assignments are largely based on the assignments in benzoquinoline and quinoline-*N*-oxide [13]. The decrease in the frequency of the ν(NO) vibrations from 1235 cm^{-1} in the ligand to 1220 ± 5 cm^{-1} in the complexes is attributed to a change in the nature of the nitrogen–oxygen bond as a result of metal–oxygen coordination [6–9]. The δ(NO) bending vibration, observed at 840 cm^{-1} in BenzqnO, also shows a slight shift supporting the metal–oxygen coordination [6–9]. The bands observed in the 450–430 cm^{-1} region have been tentatively assigned to metal–oxygen stretching vibration. In the thiocyanate complexes, the ν(C–S) vibrations lie in the 860–820 cm^{-1} region and ν(C–N) in the 2080–2060 cm^{-1} region, strongly suggesting N-bonded NCS [14].

Thermal studies

The TG and DTG curves do not show the presence of water. TG analysis of the complexes shows that all the Zn(II) and Cd(II) complexes are stable up to about 200 ° C, beyond which decomposition starts and continues up to about 300 ° C. Analysis of the thermograms shows that two moles of BenzqnO are lost at this stage. It is therefore assumed that two molecules of the ligand are loosely bonded to the metal in the complexes. On further heating in the temperature range 305–405 ° C the complexes $MX_2 \cdot$ 2BenzqnO (M = Zn, Cd) lose all the remaining ligand molecules. Finally, metal oxide is obtained as residual mass at about 600 ° C. In all cases, the second decomposition reaction is indicated by the endo peak and the final decomposition to metal oxide by the exo peak in the DTG curve.

Thus, the analysis of the thermograms indicates that the decomposition process is completed in the following three steps

$$MX_2 \cdot 4\text{BenzqnO} \rightarrow MX_2 \cdot 2\text{BenzqnO} \rightarrow MX_2 \rightarrow MO$$

(M = Zn, Cd; X = Cl, Br, CH_3COO, NCS).

If the minimum TG decomposition temperature is taken as a rough criterion of thermal stability, then the order for the complexes reported herein is: Cl > Br > NCS > CH_3COO.

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