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THERMAL STUDIES ON ALUMINIUM(III) 2-SUBSTITUTED-8-HYDROXYQUINOLATES

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The thermal behaviour of some aluminium(III)-2-substituted-8-hydroxyquinolates has been studied by thermogravimetry. Derivatives of 8-hydroxyquinolines used as ligands were 2-methyl-, 2,5-dimethyl-, 2-methyl-5-chloro-, 2,3,4-trimethyl- and 2,3-dimethyl-8-hydroxyquinolines. All the aluminium(III) chelates studied in the present investigations were found to be thermally less stable than unsubstituted chelate, aluminium(III)-8-hydroxyquinolate. The thermal characteristics and stability of the tris-chelates were found to be different from those of bis-chelates. Complete decomposition of the chelates was accomplished in two or three stages. The intermediate compounds corresponding to a horizontal portion of the thermograms were analysed and studied using IR and mass spectral techniques.

INTRODUCTION

In the past 25 years, a number of investigators have reported the nonreactivity of 2-methyl-8-hydroxyquinoline with aluminium ion in aqueous solutions and have utilized it for the separation and determination of this element in the presence of others [1-10]. Research investigations by Khwaja *et al.* [12] and Cardwell [11] have shown, that with the exception of 2-phenyl-8-hydroxyquinoline, other 2-substituted-8-hydroxyquinolines react with aluminium(III) in aqueous solution forming bis- or tris-chelates. As indicated by IR, mass spectral and X-rays crystallographic studies [12, 24, 25], bis-chelates appear to be oxo-bridged complexes containing two penta-coordinated aluminium atoms linked through Al—O—Al bond.

In the present investigations, aluminium complexes with some 2-substituted-8-hydroxyquinolines were prepared and characterised. The ligands used were 2-methyl-, 2,5-dimethyl-, 2-methyl-5-chloro-, 2,3-dimethyl- and 2,3,4-trimethyl-8-hydroxyquinolines. Thermal studies were carried out using thermogravimetric techniques. The compounds corresponding to a horizontal portion of the thermograms (later referred to as the 'intermediates') were analysed and studied using spectroscopic techniques. This paper reports the details of these investigations and the results achieved.

EXPERIMENTAL

Preparation of the Ligands and Metal Complexes. All the ligands used in this study were prepared in the laboratory by known standard methods [4,13-16]. The method reported by Khwaja *et al.* [12] was used for the preparation and isolation of aluminium complexes of these ligands from aqueous solutions. The appropriate ligand solution in dilute acetic acid was added to an aluminium(III) solution (at 65–70°) and

the pH was adjusted by dropwise addition of ammonium acetate–ammonium hydroxide solution. The precipitated complex was collected on a sintered-glass crucible, washed several times with (1:1) ethanol in order to remove traces of any coprecipitated ligand, and was dried either in an oven at 110°–120° or in a desiccator over anhydrous calcium chloride.

Thermal Studies. Thermogravimetric analyses were carried out in an open crucible under atmospheric pressure on a Stanton TR-OI type automatic recording thermobalance at a heating rate of 4°/min. The crucible employed was calibrated by running a blank on empty crucible and recording the appropriate change in weight due to buoyancy.

IR Spectra. KBr discs were prepared by thoroughly mixing approximately 2 mg of samples with 0.2 g dry KBr. The resulting mixture was placed in a 13-mm die assembly and evacuated, prior to applying for 2–3 min a pressure of 11.8 kg at room temperature. All spectra were recorded on a Perkin–Elmer 337 grating spectrometer in the range 4000–400 cm^{-1} . Polystyrene film (0.07 mm thick) was used for calibration purposes.

Mass Spectra. The mass spectra were obtained on a Hitachi–Perkin–Elmer RMU-6D spectrometer.

Elemental Analysis. Micronalytical determinations of carbon, hydrogen and nitrogen were carried out by the C.S.I.R.O. Microanalytical Service, Melbourne University, Australia. Aluminium content was determined volumetrically with a standard EDTA solution [23], after digesting the sample with nitric acid (concd) and sulphuric acid (concd) until the solution decolourized. Elemental analyses of original complexes were not done as these have already been reported by Cardwell [11] and Khwaja *et al.* [12].

RESULTS AND DISCUSSION

In agreement with earlier investigations [17] on

the thermal stability of the metal chelates of 8-hydroxyquinoline and 2-methyl-8-hydroxyquinoline, the aluminium complexes studied in the present investigation were found to be thermally less stable than aluminium(III)-8-hydroxyquinolate (anhydrous $\text{Al}(\text{C}_9\text{H}_6\text{NO})_3$ stable up to 375° [18]. The lesser stability of the 2-substituted complexes could be attributed to the larger size of the ligand molecule. It could also be possibly due to some steric strain caused by the 2-methyl group, thus influencing the thermal stability of the complexes to some extent. On comparing the thermograms of the tris-chelates $\text{Al}(\text{C}_{10}\text{H}_8\text{NO})_3$, $\text{Al}(\text{C}_{11}\text{H}_{10}\text{NO})_3$ and $\text{Al}(\text{C}_{10}\text{H}_7\text{NO}-\text{Cl})_3 \cdot \text{H}_2\text{O}$ with those of bis-chelates $\text{Al}_2(\text{C}_{11}\text{H}_{10}\text{NO})_4\text{O}$ and $\text{Al}_2(\text{C}_{12}\text{H}_{12}\text{NO})_4\text{O}$ it was observed that the former were slightly more stable thermally than the latter. Complete decomposition of the chelates was accomplished in two or three stages.

Tris-Chelates $\text{Al}(\text{C}_{10}\text{H}_8\text{NO})_3$, $\text{Al}(\text{C}_{11}\text{H}_{10}\text{NO})_3$
and $\text{Al}(\text{C}_{10}\text{H}_7\text{NOCl})_3 \cdot \text{H}_2\text{O}$

(a) *Aluminium(III) 2-methyl-8-hydroxy quinolate*, $\text{Al}(\text{C}_{10}\text{H}_8\text{NO})_3$. Earlier investigations [19] showed that the complex was stable up to 150° . Decomposition took place in three stages at $150-250^\circ$, $265-400^\circ$ and $415-650^\circ$. No further loss in weight occurred above 650° as indicated by the constant weight level in the thermogram corresponding to Al_2O_3 . A considerable decrease in rate of weight loss was observed in the temperature range $250-265^\circ$ and $400-415^\circ$. The loss in weight in these temperature ranges was found to be very small. The brownish yellow intermediate compound formed at 250° appeared to be $\text{Al}_2(\text{C}_{10}\text{H}_8\text{NO})_4\text{O}$, its IR absorption spectrum showing a new intense broad absorption band at 1017 cm^{-1} (assigned to Al-O-Al antisymmetric mode) which was found to be absent in the IR absorption spectrum of the original complex $\text{Al}(\text{C}_{10}\text{H}_8\text{NO})_3$. The sample of intermediate compound collected at 400° was not of uniform colour and consisted mainly of decomposition products, little being shown by its IR absorption spectrum [19].

In the present investigations, thermal studies were carried out on aluminium(III) 2-methyl-8-hydroxyquinolate under dry nitrogen, to examine whether or not the formation of the intermediate compound $\text{Al}_2(\text{C}_{10}\text{H}_8\text{NO})_4\text{O}$ at 250° was due to oxygen in the air. The IR absorption spectrum of the resulting brownish yellow compound was found to be similar to the IR absorption spectrum of the compound obtained in air, suggesting that air was not involved in the formation of the intermediate compound.

Mass spectral studies were carried out on samples of the brownish yellow intermediate compound collected in air at 250° . The partial mass spectrum is illustrated in Table 1. No mass peak resulting from the molecular ion $\text{Al}_2(\text{C}_{10}\text{H}_8\text{NO})_4\text{O}^+$ was observed. However, mass peaks corresponding to the fragment ions $\text{Al}_2(\text{C}_{10}\text{H}_8\text{NO})_3\text{O}^+$, $\text{Al}_2(\text{C}_{10}\text{H}_8\text{NO})_2\text{O}^+$, $\text{Al}(\text{C}_{10}\text{H}_8\text{NO})_2\text{O}^+$, $\text{Al}(\text{C}_{10}\text{H}_8\text{NO})\text{O}^+$ and $\text{Al}(\text{C}_{10}\text{H}_8\text{NO})_2^+$ appeared at m/e values 544, 386, 359, 201 and 343 respectively.

(b) *Aluminium(III) 2,5-dimethyl-8-hydroxyquinolate*, $\text{Al}(\text{C}_{11}\text{H}_{10}\text{NO})_3$. The complex was found

Table 1. Mass Spectrum of Intermediate Compound $[\text{Al}_2(\text{C}_{10}\text{H}_8\text{NO})_4\text{O}]$

m/e	Abundance (%)	m/e	Abundance (%)
545	14.5	342	61.0
544	33.0	341	6.0
529	1.5	328	6.5
528	1.9	327	26.0
501	1.5	326	10.0
387	1.9	202	15.0
386	6.4	201	6.4
381	2.3	167	6.5
362	3.2	160	20.0
361	1.5	159	100.0
360	5.0	149	14.5
359	2.4	131	67.7
345	2.6	103	11.6
344	21.0	89	6.7
343	100.0		

Only % abundance >1 are reported.
 m/e values smaller than 89 are not given.

to be thermally stable, showing a constant weight level up to 200° (Fig. 1A). Decomposition was observed to take place in two stages. In the first stage at temperature $200-350^\circ$ the rate of decomposition was rather fast, the loss in weight was 30.6% which was approximately one-third of the total loss in weight and corresponded to the loss of one ligand molecule from the tris-chelate. The second stage of decomposition occurred in the temperature range $370-650^\circ$ in which the rate of decomposition was more rapid as compared to the first stage. The loss in weight was found to be 59.2%. No further loss in weight occurred above 650° as indicated by the constant weight level in the thermogram, corresponding to Al_2O_3 (total loss in weight observed=89.8%; for $\text{Al}(\text{C}_{11}\text{H}_{10}\text{NO})_3 \rightarrow \text{Al}_2\text{O}_3$ calculated loss in weight=90.5%).

A considerable decrease in the rate of weight loss was observed in the temperature range $350-370^\circ$. The loss in weight in this temperature range was found to be extremely small. Samples of the residue were collected by heating the complex (in the thermobalance) steadily up to 350° , where the temperature was held constant ($\pm 5^\circ$) for 2-3 hr, till almost constant weight was shown by the recorder. The resulting orange product, which was of uniform appearance was cooled in a desiccator over anhydrous calcium chloride. The elemental analyses indicated that the product has a metal-ligand ratio of 1:2. (Found: C 66.6, H 5.2, N 6.9, Al 7.4%. Calcd C 68.0, H 5.4, N 7.2, Al 6.9%). The formation of the intermediate compound was found to be independent of the presence of oxygen in the air as indicated by thermogravimetric analyses carried out on the

complex in a stream of dry nitrogen.

The IR absorption spectrum of the intermediate compound showed absorption bands at 1270 and 1095 cm^{-1} which have been regarded as characteristics of metal complexes of 8-hydroxyquinoline and 2-methyl-substituted-8-hydroxyquinolines [12,20,21]. The spectrum also showed an intense and broad absorption band at 1025 cm^{-1} assigned to the Al—O—Al antisymmetric mode [21,22] which was found to be absent in the IR absorption spectrum of $\text{Al}(\text{C}_{11}\text{H}_{10}\text{NO})_3$.

Mass spectral studies were carried out only on the samples of the intermediate compound collected in the air. The partial mass spectrum is given in Table 2. Whereas the mass spectrum of the original complex, $\text{Al}(\text{C}_{11}\text{H}_{10}\text{NO})_3$ showed no mass peak at m/e greater than 543 corresponding to molecular ion $\text{Al}(\text{C}_{11}\text{H}_{10}\text{NO})_3^+$ [12], the mass spectrum of the intermediate compound showed a mass peak at m/e 758 resulting from the molecular ion $\text{Al}_2(\text{C}_{11}\text{H}_{10}\text{NO})_4 \cdot \text{O}^+$. The fragmentation process appeared to start with the elimination of $(\text{C}_{11}\text{H}_{10}\text{NO})$ followed by the elimination of $\text{Al}(\text{C}_{11}\text{H}_{10}\text{NO})\text{O}$ as indicated by the mass peaks, in the spectrum, at m/e 586 and 371 corresponding to the molecular ions $\text{Al}_2(\text{C}_{11}\text{H}_{10}\text{NO})_3 \cdot \text{O}^+$ and $\text{Al}(\text{C}_{11}\text{H}_{10}\text{NO})_2^+$ respectively. Further fragmentation of the ion $\text{Al}(\text{C}_{11}\text{H}_{10}\text{NO})_2^+$ could occur by more than one processes with the elimination of smaller fragments such as H_2O , CH_3 , N , CH , AlN and CCH_3 . The fragmentation of the resulting ion $(\text{C}_{11}\text{H}_{10}\text{NO})^+$ at m/e 172 also seems to occur with the elimination of similar small fragments. The mass spectrum did not show any metastable peak.

All of the above evidence shows that the intermediate compound formed during the thermal decomposition of aluminium(III) 2,5-dimethyl-8-hydroxyquinolate could be formulated as $\text{Al}_2(\text{C}_{11}\text{H}_{10}\text{NO})_4\text{O}$ containing an Al—O—Al bond as indicated by the IR spectral studies. Mass spectral studies on the gaseous products of thermal decomposition of aluminium(III) 2,5-dimethyl-8-hydroxyquinolate, which would have given some explanation for the formation of the intermediate compound, could not be carried out because of the difficulties encountered in collecting a gaseous sample for such study.

(c) *Aluminium(III) 2-methyl-5-chloro-8-hydroxyquinolate* $\text{Al}(\text{C}_{10}\text{H}_7\text{NOCl})_3 \cdot \text{H}_2\text{O}$. The complex was found to be thermally stable up to 100° (Fig. 1B). The complete decomposition appeared to occur in three stages. In the first stage, between 100–220°, loss in weight was slow and was thought to be mainly due to loss of water of crystallization along with some decomposition of the complex. However, above 220° decomposition occurred at a comparatively faster rate which continued up to 420, the loss in weight at this stage being 44.5%. The third stage of decomposition of the complex occurred in the range 450–650° with a uniform and slightly faster rate, the loss in weight being 47.9%. No further loss in weight was observed beyond 650° as indicated by a constant weight level in the thermogram corresponding to Al_2O_3 (total loss in weight observed=92.4%; for $\text{Al}(\text{C}_{10}\text{H}_7\text{NOCl})_3 \cdot \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3$ calculated loss in weight=91.8%).

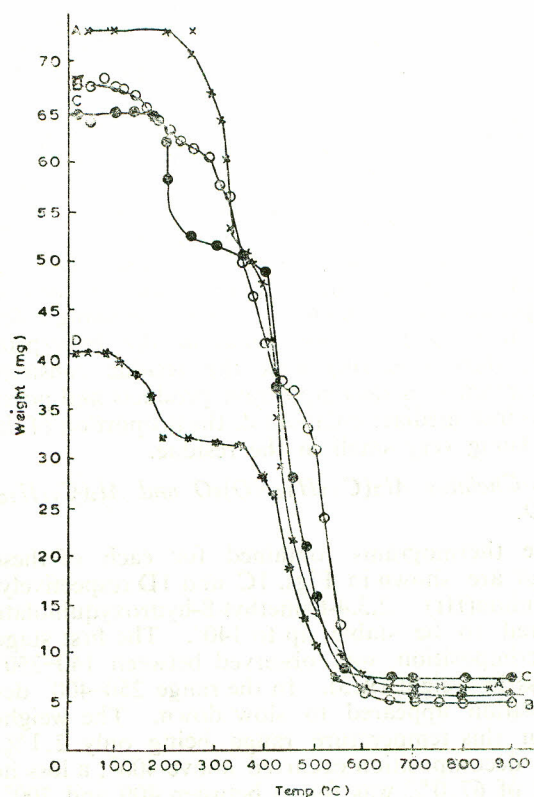


Fig. 1. Thermograms for tris-chelates (A) $\text{Al}(\text{C}_{11}\text{H}_{10}\text{NO})_3$ and (B) $\text{Al}(\text{C}_{10}\text{H}_7\text{NOCl})_3 \cdot \text{H}_2\text{O}$. Bis-chelates (C) $\text{Al}_2(\text{C}_{12}\text{H}_{12}\text{NO})_4\text{O}$ and (D) $\text{Al}_2(\text{C}_{11}\text{H}_{10}\text{NO})_4$.

Table 2. Mass Spectrum of Intermediate Compound [$\text{Al}_2(\text{C}_{11}\text{H}_{10}\text{NO})_4\text{O}$]

m/e	Abundance (%)	m/e	Abundance (%)	m/e	Abundance (%)
759	2.6	354	3.1	156	1.0
758	7.0	353	2.9	145	4.0
588	1.4	352	1.9	144	26.2
587	4.5	218	4.8	143	4.4
586	12.1	217	2.6	142	1.4
413	2.9	216	5.5	141	1.2
391	5.0	175	2.9	131	1.7
390	15.5	174	17.2	130	2.0
373	1.8	173	100.0	128	3.3
372	17.2	172	91.3	127	1.1
371	65.5	171	2.9	103	1.8
370	38.0	159	1.6	90	1.6
369	2.9	158	2.0		
355	8.6	157	1.0		

Only % abundance ≥ 1 are reported.
 m/e values smaller than 90 are not given.

A considerable decrease in the rate of weight loss was observed in the range 420–450°. The loss in weight in this temperature range was found to be extremely small. Samples of the residue in this temperature range were collected by the same procedure as described for the intermediate compound formed during the thermal decomposition of aluminium (III) 2,5-dimethyl-8-hydroxyquinolate. Elemental analyses of the resulting brownish black residue were carried out but the analytical data did not correspond to a definite stoichiometric ratio between the metal and the ligand. The IR absorption spectrum was found to be poor showing a few weak intensity absorption bands in the fingerprint region, thus indicating that the residue consisted predominantly of decomposition products and possibly an intermediate compound, the proportion of the latter being very small in the residue.

Bis-Chelates $Al_2(C_{12}H_{12}NO)_4O$ and $Al_2(C_{11}H_{10}NO)_4O$.

The thermograms obtained for each of these chelates are shown in Figs. 1C and 1D respectively. Aluminium(III) 2,3,4-trimethyl-8-hydroxyquinolate appeared to be stable up to 140°. The first stage of decomposition was observed between 140–250° (% loss in weight 19.3). In the range 250–400° decomposition appeared to slow down. The weight loss in this temperature range being only 2.1%. Rapid decomposition occurred above 400°; a loss in weight of 67.0% was found between 400 and 700°. The decomposition of the chelate was completed around 700° and no further loss in weight was observed above this temperature (total loss in weight observed=88.4%; for $Al_2(C_{12}H_{12}NO)_4O \rightarrow Al_2O_3$. Calculated loss in weight=87.6%). The residue in the range 250–400° appeared to consist of decomposed chelate. The IR absorption spectrum of the residue was found to be similar to that of aluminium (III) 2,3,4-trimethyl-8-hydroxyquinolate. Elemental analyses carried out on the residue showed a decrease in the % content of carbon, hydrogen and nitrogen, thus indicating loss of some organic matter from the chelate on its thermal decomposition. However, the analytical data did not appear to correspond to a definite stoichiometric ratio between the metal and the ligand.

Aluminium(III) 2,3-dimethyl-8-hydroxyquinolate (Fig. 1D) showed thermal behaviour similar to that observed in aluminium(III) 2,3,4-trimethyl-8-hydroxyquinolate. The complex was found to be stable up to 80°. The first stage of decomposition of the chelate was observed between 80–200° (% loss in weight = 19.9). Between 200–350° decomposition appeared to slow down, the loss in weight being 3.7%. Further decomposition occurred above 350° and the loss in weight between 350–700° was found to be 62.5%. No further loss in weight was observed above 700°, the residue at this stage being the oxide Al_2O_3 (total loss in weight observed = 86.1%; for $Al_2(C_{11}H_{10}NO)_4O \rightarrow Al_2O_3$, calculated loss in weight = 86.6%).

CONCLUSION

Thermal studies carried out on aluminium (III)

2-substituted-8-hydroxyquinolates gave evidence which throws further light on the structure of these complexes. Methyl-substituted chelates were found to be less stable than the unsubstituted chelate which could be attributed to the larger size of the ligand molecule or the stability could also be due to some steric strain caused by the 2-methyl group. The present investigations also indicated that the stability and thermal characteristics of the tris-chelates were different from those of the bis-chelates. The former were capable of forming intermediate compounds during the thermal decomposition, apparently with the loss of a ligand molecule. On the other hand, thermal decomposition of the bis-chelates appeared to slow down after the initial break up of the molecule but no evidence regarding the formation of a stable intermediate compound was obtained. If ligands 2-methyl- and 2,5-dimethyl-8-hydroxyquinolines are to be used for the gravimetric estimation of aluminium in aqueous solutions then the resulting precipitate of the metal ions with the ligand should not be dried above 140° as the decomposition of the precipitate would start.

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