Thermochimica Acta, 47 (1981) 189--199
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

THERMAL DECOMPOSITION OF CHLORO COMPLEXES OF MANGANESE(II), COBALT(II), COPPER(II) AND ZINC(II) WITH TRI-*n*-OCTYLAMINE AND TRICAPRYLMETHYLAMMONIUM CHLORIDE

TAICHI SATO and TAKATO NAKAMURA

Department of Applied Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu (Japan)

(Received 10 February 1981)

ABSTRACT

The organic solutions from the extraction of divalent metals, M, of manganese, cobalt, copper and zinc from hydrochloric acid solutions with tri-*n*-octylamine (R_3N) and tricaprylmethylammonium chloride ($R_3R'NCl$) in benzene were heated in vacuo to prepare the benzene-free complexes. The resulting complexes, $(R_3NH)_2MCl_4$ and $(R_3R'N)_2MCl_4$, were examined by thermogravimetry and differential thermal analysis under an atmosphere of nitrogen. Their thermally decomposed products, such as volatile matters and residues were examined by gas chromatography, X-ray diffraction study and IR spectroscopy. As a result, it is found that the thermal decomposition of the complexes of divalent metals proceeds in the sequence

$$A_2MCl_4 \rightarrow MCl_2 + A' \rightarrow MCl_2$$

except that of the copper complex, which decomposes as

$$A_2CuCl_4 \rightarrow A_2CuCl_3 \rightarrow CuCl + A' \rightarrow Cu$$

where A denotes R_3NH or $R_3R'N$, and A' is the residue.

INTRODUCTION

Although the liquid—liquid extraction of metals with long-chain aliphatic amines has been investigated by many workers, the properties of the complexes isolated from their organic solutions have received little attention. Studies on the thermal decomposition of such complexes in order to obtain further information concerning their composition have been limited to the sulphato and nitrato complexes of uranium(VI) [1] and the chloro complexes of copper(II) [2], zirconium(IV) [3], vanadium(IV) [4] and uranium(VI) [5]. Therefore the present paper extends the work to the chloro complexes of divalent manganese, cobalt, copper and zinc with tri-*n*-octylamine (TOA, R_3N) and tricaprylmethylammonium chloride (Aliquat-336, $R_3R'NCl$).

EXPERIMENTAL

Reagents

TOA (Kao Soap Co. Ltd.), used without purification, and Aliquat-336 (General Mills), purified as described previously [6], were diluted with benzene. Aqueous solutions of divalent manganese, cobalt, copper and zinc were prepared by dissolving their chlorides ($MnCl_2 \cdot 4\,H_2O$, $CoCl_2 \cdot 6\,H_2O$, $CuCl_2 \cdot 2\,H_2O$ and $ZnCl_2$) in hydrochloric acid. All chemicals used were of analytical grade.

Preparation of the complexes $(R_3NH)_2MCl_4$ and $(R_3R'N)_2MCl_4$

On the basis of the distribution data, the chloro complexes of divalent manganese, cobalt, copper and zinc with TOA and Aliquat-336 were prepared as follows: 0.1 M TOA (or 0.1 M Aliquat-336) in benzene was shaken for 10 min with the aqueous solutions containing 200 g l^{-1} $MnCl_2$ in 8 M HCl, 200 g l^{-1} $CoCl_2$ in 8 M HCl, 200 g l^{-1} $CuCl_2$ in 6 M HCl or 100 g l^{-1} $ZnCl_2$ in 3 M HCl. The organic phases were centrifuged and shaken again with fresh aqueous solutions so that they might be saturated with divalent metals. The organic extracts so obtained contain the composition of extractant/chloride/metal in the molar ratio 2 : 4 : 1, indicating the stoichiometry to be $(R_3NH)_2MCl_4$ and $(R_3R'N)_2MCl_4$, in which M = Mn, Co, Cu and Zn, for the complexes extracted with TOA and Aliquat-336, respectively (Table 1). In this case, the concentrations of divalent metal and chloride in the organic phase were determined as described previously [7]: the metal in the organic phase was stripped with 0.1 M HCl and the metal concentration in the aqueous solution was then determined by EDTA titration [8]: the chloride concentration was established with nitrobenzene by Volhard's method. The organic phases were then heated in vacuo to prepare the benzene-free complexes.

Analysis

Thermogravimetry (TG) and differential thermal analysis (DTA) of the complexes were examined under an atmosphere of nitrogen at a heating rate

TABLE 1

Variation of the molar ratios of $[R_3N]$ or $[R_3R'N]/[Cl]/[M]$ in the metal-saturated organic solutions from solvent extraction with TOA and Aliquat-336

Metal	Molar ratio	
	$[R_3N]/[Cl]/[M]$	$[R_3R'N]/[Cl]/[M]$
Mn(II)	2.1/4.0/1.0	2.0/4.0/1.0
Co(II)	2.0/4.3/1.0	2.0/3.6/1.0
Cu(II)	1.9/3.9/1.0	2.1/4.0/1.0
Zn(II)	2.0/3.8/1.0	1.8/3.4/1.0

of 5°C min^{-1} and a flow rate of nitrogen of 50 ml min^{-1}. The residues were derived from the complex by heating to the required temperatures at a rate of 5°C min^{-1} under nitrogen atmosphere and then by cooling immediately under the same atmosphere. Infrared spectra were recorded on Japan Spectroscopic Co. Ltd. Model IRA-1 (4000—650 cm^{-1}) and IR-F (700—200 cm^{-1}) grating spectrometers. X-Ray diffraction diagrams were obtained by the procedures described previously [4]. The volatile matters generated during the DTA were collected with a 2 ml syringe at the gas outlet of the DTA apparatus and analyzed with a Shimazu Model GC-6AMPTF gas chromatograph under the following analytical conditions: carrier gas, helium at 40 ml min^{-1}; column, Porapak Q of 80/100 mesh; column temperature, 140°C; detector, FID. Each component detected was identified by gas chromatography—mass spectrometry (GC—MS). Hydrogen chloride in the volatile matter was trapped in 0.05 M silver nitrate solution in an interval of 10°C at a temperature between 200 and 350°C by passing it through the solution for 3 min, and the chloride ion concentration was determined by Volhard's method.

RESULTS AND DISCUSSION

Thermal decomposition of the complexes with TOA

The TG and DTA curves of divalent manganese, cobalt, copper and zinc complexes with TOA are shown in Fig. 1. The DTA curve of the manganese(II) complex exhibits three endotherms at 330, 370 and 630°C. In the TG curve, the weight-loss of 87% associates with the endotherms at 330 and 370°C, and a gradual loss in weight is found above 630°C. By assuming that the complex $(R_3NH)_2MnCl_4$ decomposes into manganese chloride, $MnCl_2$, at 300—400°C, its weight-loss is calculated as 86.1%, analogous to the observed value. Accordingly, it might be explained that the endotherm at 630°C and the gradual weight-loss above this temperature are ascribed to the melt of manganese chloride and the release of chloride from the resulting chloride, respectively. According to Tello et al. [9], who reported the thermal decomposition of manganese(II) complexes with primary amines, $(RNH_3)_2MnCl_4$, the decomposition takes place in two steps

$$(RNH_3)_2MnCl_4 \xrightarrow{\text{1st step}} RNH_3MnCl_3 + RNH_3Cl$$

$$RNH_3MnCl_3 \xrightarrow{\text{2nd step}} RNH_3Cl + MnCl_2$$

However, in the TG curve of the complex $(R_3NH)_2MnCl_4$ (Fig. 1) such a decomposition process is not significantly confirmed.

The DTA curve of the cobalt(II) complex exhibits endotherms at 300, 370, 385 and 420°C, which occur at the point near the change of shape in the TG curve (Fig. 1). From the TG curve, it is deduced that the residues above 400°C exist as cobaltous chloride, $CoCl_2$. For the copper(II) complex, the DTA curve gives the endotherms at 185, 300, 350 and 400°C, and the

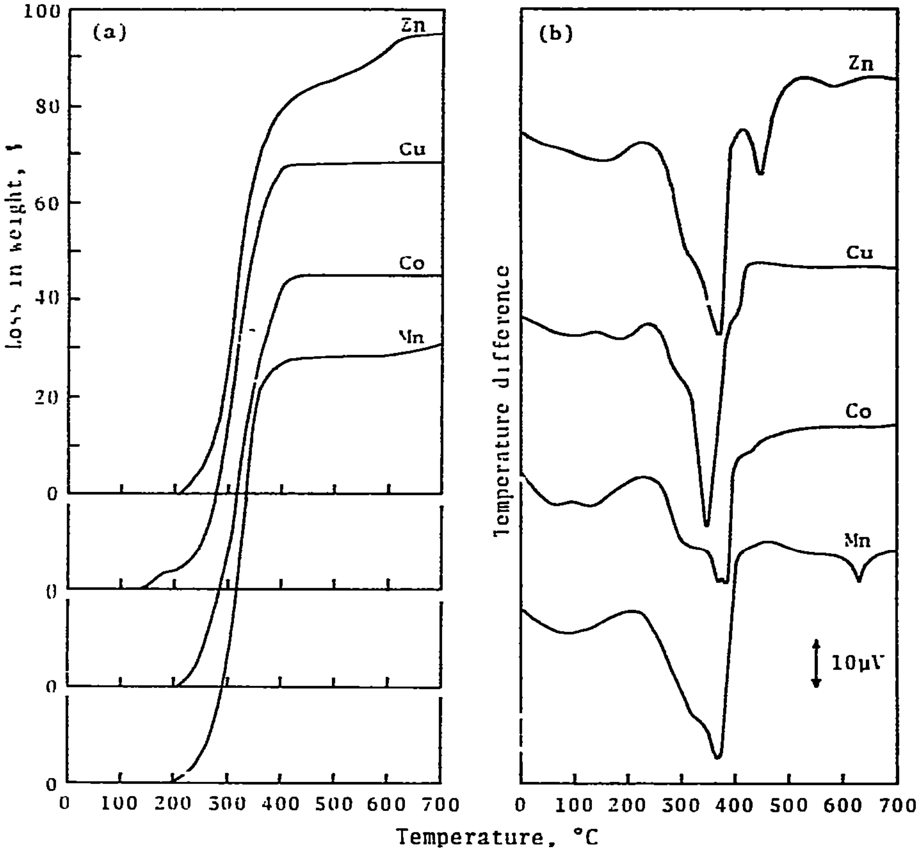

Fig. 1. TG (a) and DTA (b) curves of divalent metal complexes with TOA.

TG curve reveals the loss in weight of 4% at 140—210°C, followed by the weight-loss of 84% at 210—410°C. The weight-loss at the first stage corresponds to the release of a molecule of chlorine or hydrogen chloride. In the DTA curve of the zinc(II) complex the endotherms are observed at 320, 370, 450 and 580°C, and weight-losses of 70, 13 and 9% are obtained at 230—400, 400—500 and 500—600°C, respectively, suggesting that the thermal decomposition of its complex proceeds through three stages.

The volatile matter generated by the thermal decomposition of the metal complexes with TOA contain aliphatic compounds such as allene, ethylene, ethane, propene, propane, 1-butene, 2-butene and methyl chloride identified by GC—MS, and hydrogen chloride, trapped in silver nitrate solution. Some representative gas chromatographic data are given in Fig. 2, where the relative peak heights in the gas chromatogram for some of the components are plotted as a function of heating temperature. From this it is seen that the amounts of components detected above 250°C increase with increase in temperature, in accordance with the weight-loss in the TG curves, and their maxima correspond to the endotherms in the DTA curves. A similar trend is also observed for other organic components, except in. Fig. 2. On the other hand, it is found that hydrogen chloride evolved from the complexes is detected above 200°C (before the detection of the organic components) and its maximum amount is obtained at about 250°C for all the complexes

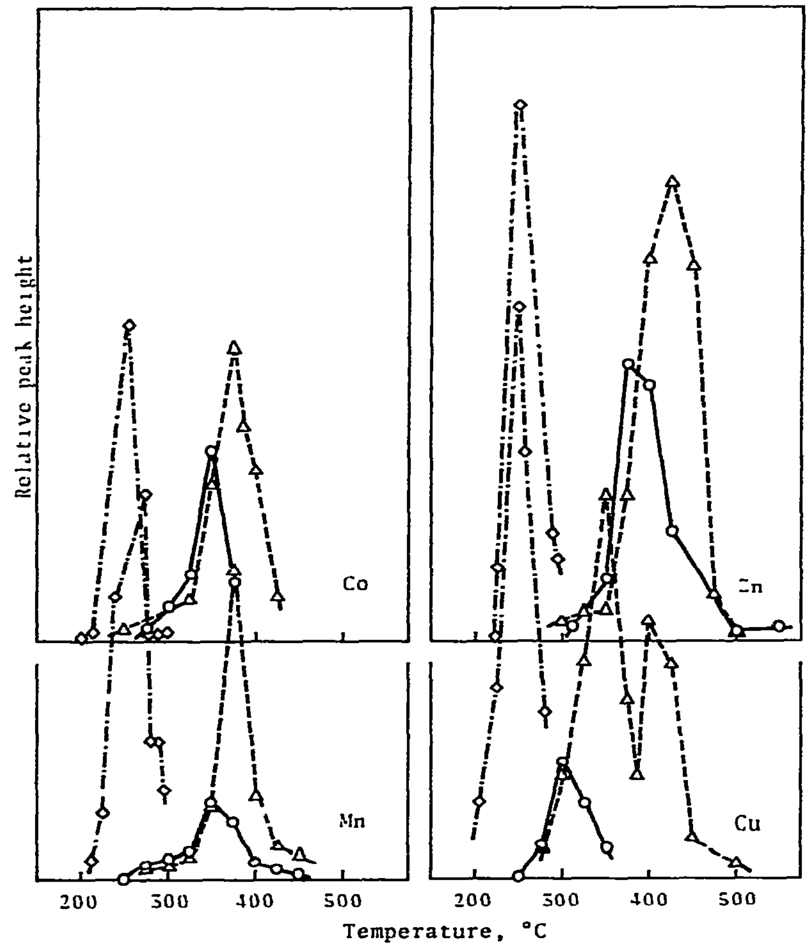

Fig. 2. Relative peak heights of C_2H_6 (- - - - - -) and CH_3Cl (————) in the gas chromatograph and the relative amount of HCl (— · — · —) determined by Volhard's method as a function of heating temperature.

studied. It is therefore inferred that the thermal decomposition is initiated by the release of hydrogen chloride, followed by the decomposition of TOA. This implies that in the DTA curves, the endotherms at 330, 300, 300 and 370°C for divalent manganese, cobalt, copper and zinc complexes, respectively, are assigned to the release of hydrogen chloride accompanied by the decomposition of TOA. Because the TG curves reveal weight-losses >5%, corresponding to the theoretical values for the thermal reactions of the complexes of divalent metals

$$(R_3NH)_2MCl_4 \rightarrow (R_3N)_2 \cdots MCl_2 + 2\ HCl$$

and in the case of the copper complex

$$(R_3NH)_2CuCl_4 \rightarrow (R_3N)_2 \cdots CuCl + 2\ HCl + (1/2)Cl_2.$$

In addition, it is considered that the endotherms at 370°C for manganese, 370 and 385°C for cobalt, 350°C for copper, and 370 and 450°C for zinc, arise from the cracking of alkyl groups.

Analytical data for the residues derived from the metal complexes with TOA by heating to the stated temperatures are indicated in Table 2. The molar ratio of the concentration of metal to that of chloride approaches 1 : 2 for manganese, cobalt and zinc and 1 : 0 for copper. It is thus postulated that all the metal complexes with TOA studied are decomposed into metal chloride, MCl_2, except the copper complex which decomposes to metallic copper. These facts are also supported by the following results: in the X-ray diffraction diagrams for the cobalt(II) complex, the formation of cobaltous chloride hydrate is found on heating above 300° C (Table 3). For the copper(II) complex, the diffraction lines assigned to cupric chloride and metallic copper are observed at 300° C, and above 350° C those of metallic copper only remain. In contrast, no diffraction lines are recognized for the complexes of manganese(II) and zinc(II), although the residues produced by heating the former complex at the stated temperatures above 400° C for 2 h exhibit the diffraction lines due to manganese chloride hydrate. In the IR spectra of the residues for the manganese(II) complex, C—H stretching bands at 2920 and 2850 cm^{-1}, CH_3 degenerate and CH_2 scissoring bands at 1470 cm^{-1}, the CH_3 symmetrical bending band at 1390 cm^{-1}, and the CH_2 rocking band at 730 cm^{-1} decrease in intensity at 300° C and disappear above 400° C, suggesting that the alkyl groups of TOA crack between 300 and 400° C. The Mn—Cl stretching band at 284 cm^{-1} fades out at 400° C, in accordance with decreasing the bands due to alkyl groups. This indicates that the conformation of the original species is held below 400° C. On heating at 300° C, a strong band arising from the N—H stretching frequency at 2640 cm^{-1} disappears, and in addition C=C stretching and/or C=N stretching vibrations appear as a broad band centered around 1600 cm^{-1}. This means that part of the TOA is thermally decomposed and an alkene and/or a C=N bearing compound is then formed. Above 400° C, a broad band is observed at 600—450 cm^{-1}, assigned to the librational vibration of H_2O and Mn—Cl vibration of manganese chloride, $MnCl_2 \cdot x\ H_2O$ [10]. A similar trend is observed for the cobalt(II) complex, but for the copper(II) and zinc(II) complexes the bands due to alkyl groups disappear at 300 and 500° C, respectively. Thus it is considered that the thermal stability of these complexes is in the order $Cu < Mn \simeq Co < Zn$. For the zinc(II) complex, the band at 275 cm^{-1} assigned to the Zn—Cl stretching vibration of the original complex

TABLE 2

Composition of residues derived from the metal complexes with TOA on heating at the stated temperatures

Temp. (°C)	Molar ratio [Cl]/[M]			
	Mn	Co	Cu	Zn
250	3.3	3.6	1.8	3.6
300	2.7	2.3	0.4	3.3
400	1.7	1.8	0	2.0
500	1.7	1.8	0	1.5

TABLE 3

X-Ray diffraction results for the residues derived from divalent metal complexes with TOA by heating to the stated temperatures

Temp. (°C)	Phase detected			
	Mn(II)	Co(II)	Cu(II)	Zn(II)
300	—[a]	$CoCl_2 \cdot 6\,H_2O$	CuCl + Cu	Am
350	—	—	Cu	—
400	Am	$CoCl_2 \cdot 6\,H_2O$	Cu	Am
500	Am	$CoCl_2 \cdot 6\,H_2O$	Cu	Am

Am denotes amorphous.

[a] Undetected.

remains up to 300°C. Above 400°C the band due to the Zn—Cl stretching vibration of zinc chloride, $ZnCl_2$ [9], appears at 500 cm^{-1}, accompanied by the weight-loss in two steps. This may be attributed to the fact that the melting point of zinc chloride formed by the thermal decomposition of the zinc complex with Aliquat-336 is in the same temperature range where the complex is thermally decomposed.

Hence the endothermic reactions in the DTA curves are assigned as given in Table 4, and accordingly it is considered that the thermal decomposition of the complexes of divalent metals with TOA proceeds as follows

$$(R_3NH)_2MCl_2 \xrightarrow{-HCl} [(R_3N)_2 \cdots MCl_2] \xrightarrow{\text{cracking}} MCl_2 + A' \xrightarrow{\text{cracking}} MCl_2$$

except the copper complex which may be expressed as

$$(R_3NH)_2CuCl_4 \xrightarrow{\text{reduction}} (R_3NH)_2CuCl_3 \xrightarrow{-HCl} [(R_3N)_2 \cdots CuCl]$$

$$\xrightarrow{\text{cracking}} CuCl + A' \xrightarrow{\text{reduction and cracking}} Cu$$

where A′ denotes the thermally decomposed product.

Thermal decomposition of the complexes with Aliquat-336

The TG and DTA curves for divalent manganese, cobalt, copper and zinc complexes with Aliquat-336 are given in Fig. 3. The endotherms appear at 250, 315 and 370°C for manganese, 250, 315, 370 and 420°C for cobalt, 215, 285, 325, 345 and 375°C for copper, and 250, 310, 360 and 425°C for zinc. In the TG curves of the complexes of manganese, cobalt and zinc, a few inflection points appear between 200 and 400°C, suggesting that some reactions occur successively in this temperature range. The metal complexes with Aliquat-336 begin to lose weight at a lower temperature than those with TOA. At 250°C the weight-losses are 3.4—8.2 and 15.3—24.0% for the complexes with TOA and Aliquat-336, respectively. It is therefore presumed that the complexes with TOA are thermally more stable than those with Aliquat-336.

TABLE 4

Probable assignment of the endothermic reactions in the DTA curves of divalent metal complexes with TOA

Temp. (°C)				Probable assignment
Mn(II)	Co(II)	Cu(II)	Zn(II)	
—[a]	—	185	—	Dechlorination
330	300	300	320	Release of HCl and cracking
370	370 385	350	370[b]	Cracking
—	420	400	450	Cracking
—	—	—	580	Cracking
630	—	—	—	Melting

[a] Undetected.

[b] This endotherm arises from cracking and melting of zinc chloride.

Some representative gas chromatographic results for the volatile matters are indicated in Fig. 4 where the relative peak heights of methyl chloride and ethane are plotted against heating temperature. Other detected hydrocarbons show a distribution similar to ethane. The volatile matters for the complexes

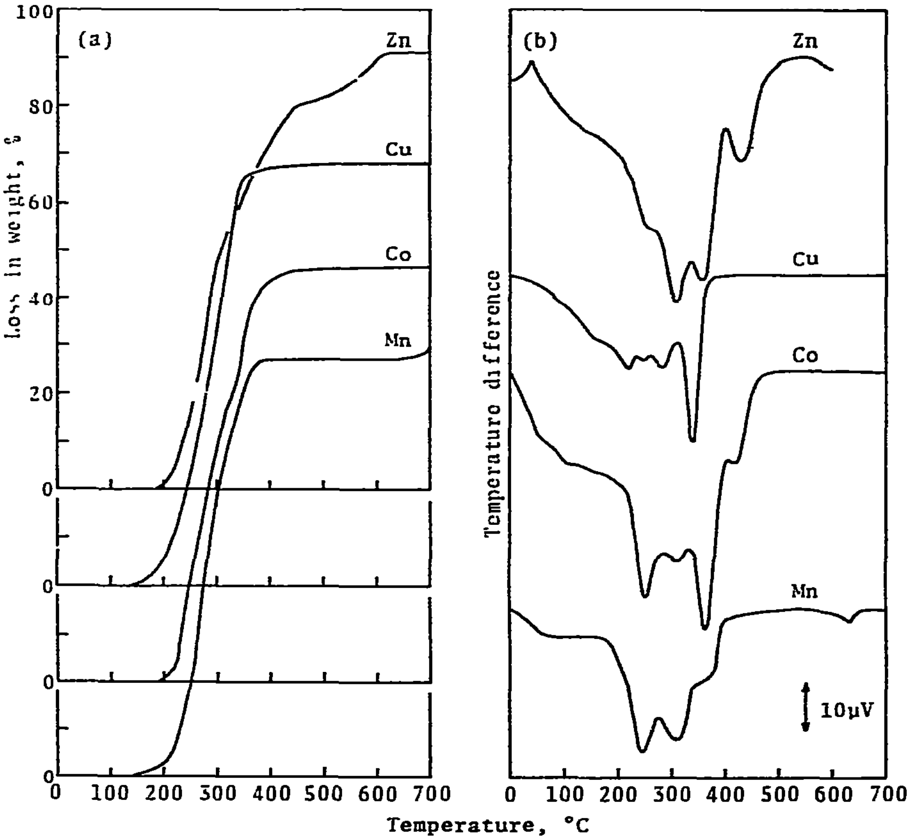

Fig. 3. TG (a) and DTA (b) curves of divalent metal complexes with Aliquat-336.

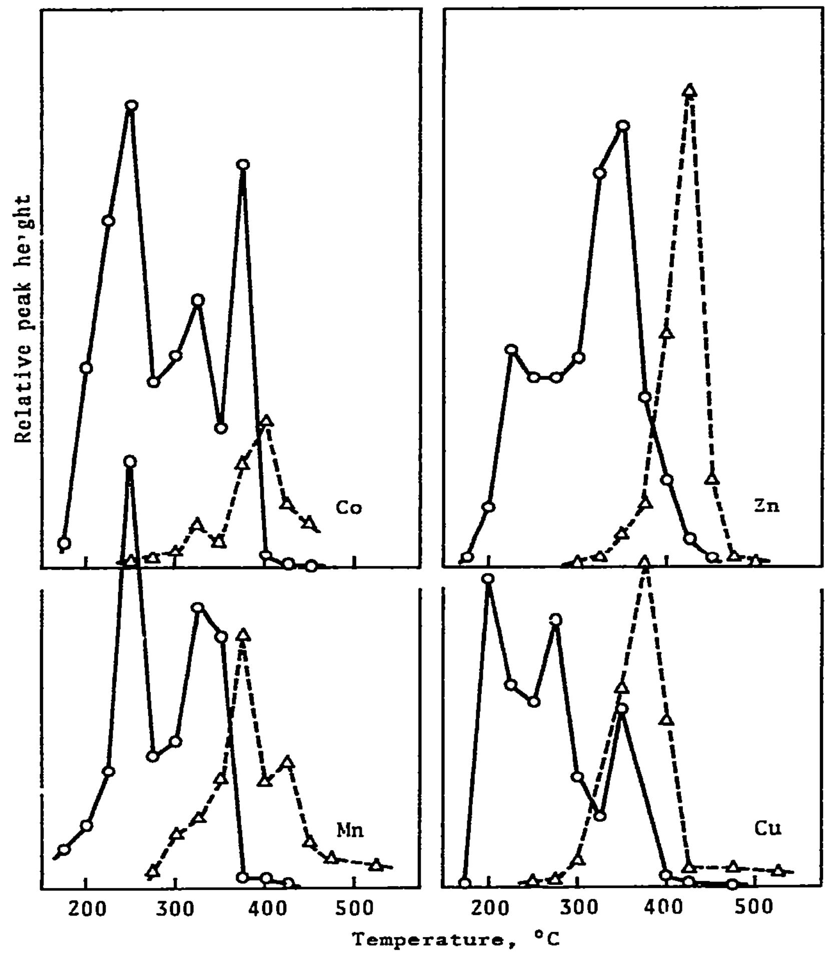

Fig. 4. Relative peak heights of C_2H_6 (- - - - - -) and CH_3Cl (————) in the gas chromatograph as a function of heating temperature.

TABLE 5

Probable assignment of the endothermic reactions in the DTA curves of divalent metal complexes with Aliquat-336

Temp. (°C)				Proable assignment
Mn(II)	Co(II)	Cu(II)	Zn(II)	
—[a]	—	218	—	Dechlorination
250	250	250	260	Release of HCl and cracking
315	315	288	310	Cracking
	370	345	355[b]	
360	420	—	425	Cracking
630	—	—	—	Melting

[a] Undetected.

[b] This endotherm arises from cracking and melting of zinc chloride.

with Aliquat-336 contain the same organic components as those for the complexes with TOA, although the former complexes contain more methyl chloride than the latter complexes. In Fig. 4 it is apparent that the distribution of methyl chloride is different from that of hydrocarbons. The maximum amount of methyl chloride is detected at 250, 250, 200 and 350° C for manganese, cobalt, copper and zinc, respectively. This component is greatly generated at the beginning of the thermal decomposition, as shown in Fig. 4, implying that the decomposition of the complexes with Aliquat-336 is initiated by the evolution of methyl chloride. The endotherms in the DTA curve correspond to the distribution of methyl chloride and hydrocarbons (Figs. 3 and 4). In the case of the manganese(II) complex, the endotherms at 250, 315 and 370° C are assigned to dechlorination due to the evolution of methyl chloride, dechlorination and/or cracking and cracking, respectively. The endothermic reactions in the DTA curves of other metal complexes are assigned as shown in Table 5. From the results obtained by chemical analysis, X-ray diffraction and IR spectroscopy, it is confirmed that after decomposition above 300° C the residues are of the same composition as described in the thermal decomposition of the manganese complex with TOA. For the complexes of manganese(II), cobalt(II) and zinc(II), metal chlorides such as $MnCl_2$, $CoCl_2$ and $ZnCl_2$ are produced, respectively, while for the copper(II) complex, metallic copper is formed via cuprous chloride.

Consequently, the following process is deduced for the thermal decomposition of divalent metal complexes with Aliquat-336

$$(R_3R'N)_2MCl_4 \xrightarrow{-CH_3Cl \text{ and cracking}} MCl_4 + A \xrightarrow{\text{cracking}} MCl_2$$

except the copper complex which may be expressed as

$$(R_3R'N)_2CuCl_4 \xrightarrow{\text{reduction}} (R_3R'N)_2CuCl_3 \xrightarrow{-CH_3Cl \text{ and cracking}}$$

$$CuCl + A' \xrightarrow{\text{reduction and cracking}} Cu$$

ACKNOWLEDGEMENTS

The authors are grateful to the National Science Foundation, provided by the Japanese Ministry of Education, Science and Culture, for support of this research through Grant-in-Aid for Scientific Research, and also thank Prof. T. Katagiri and Dr. K. Takabe of the Department of Applied Chemistry, Faculty of Engineering, Shizuoka University, for GC—MS measurements, and Messrs. S. Ishiguro, H. Okumura and M. Ishida for assistance with part of the experimental work.

REFERENCES

1 T. Sato, J. Inorg. Nucl. Chem., 26 (1964) 2229; 27 (1965) 240.
2 T. Sato and K. Adachi, J. Inorg. Nucl. Chem., 31 (1969) 1395.
3 T. Sato and H. Watanabe, Thermochim. Acta, 31 (1979) 159.

4 T. Sato, T. Nakamura and H. Watanabe, Anal. Chim. Acta, 98 (1978) 365.
5 T. Sato, Anal. Chim. Acta, 77 (1975) 344.
6 T. Sato and H. Watanabe, Anal. Chim. Acta, 49 (1970) 463.
7 e.g., T. Sato, J. Appl. Chem. Biotechnol., 22 (1972) 1233; T. Sato and M. Yamatake, Z. Anorg. Allg. Chem., 391 (1972) 174, T. Sato, M. Kawamura, T Nakamura and M. Ueda, J. Appl. Chem. Biotechnol., 29 (1979) 39.
8 H. Flaschka, Chemist-Analyst, 42 (1953) 56; J. Kinnunen and B. Wennerstrand, Chemist-Analyst, 46 (1957) 92; J. Körble and R. Pribil, Chemist-Analyst, 45 (1956) 102.
9 M.J. Tello, E.H. Bocanegra and M.A. Arrandiaga, Thermochim. Acta, 11 (1975) 96.
10 J.R. Ferraro, Low-Frequency Vibrations of Inorganic and Coordination Compounds, Plenum Press, New York, 1971, p. 140.