Thermochimica Acta, 47 (1981) 359—362
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

Note

THERMAL BEHAVIOUR OF TETRAKIS-AMINE COMPLEXES OF COBALT(II) AND NICKEL(II) DICHLOROACETATES

N. KUMAR and ASHOK KUMAR GANDOTRA

Department of Chemistry, University of Jammu, Jammu 180 001 (India)

(Received 5 March 1981)

Transition metal carboxylates form addition complexes of different stoichiometries, viz. 1 : 1, 1 : 2 and 1 : 4, with various heterocyclic nitrogenous ligands under different or similar experimental conditions [1—8]. The 1 : 2 and 1 : 4 complexes are mononuclear and octahedral in which the carboxylate group is bidentate and monodentate, respectively, while the 1 : 1 complexes are dimeric and octahedral containing bridging carboxylate groups.

Complexes of Co(II) and Ni(II) haloacetates do not yield 1 : 1 dimeric complexes but instead yield monomeric octahedral complexes of 1 : 2 or 1 : 4 stoichiometries which show the usual magnetic properties [1]. The present investigation deals with a study of the thermal behaviour of 1 : 4 complexes of Co(II) and Ni(II) dichloroacetates through TGA technique attempting to obtain their 1 : 1 complexes, generally inaccessible through the usual preparative procedures, to see whether they also belong to a *syn—syn* carboxylate bridged structure and show antiferromagnetism like so many 1 : 1 adducts of Cu(II) carboxylates.

EXPERIMENTAL

Tetrakis-amine complexes of Co(II) and Ni(II) dichloroacetates with 3-methylpyridine, 4-methylpyridine and isoquinoline were prepared as

TABLE 1

Thermogravimetric data for the prepared complexes

Adduct	Charge (mg)	Initial decomp. temp. (°C)	Wt. loss (mg) to get 1 : 2 adducts		Oxide residue expected	
			Found	Reqd.	Found	Reqd.
$Co(O_2CCHCl_2)_2(3\text{-}MePy)_4$	329.2	82	88.3	89.0	39.1	38.4
$Co(O_2CCHCl_2)_2(4\text{-}MePy)_4$	341.0	100	91.8	92.5	39.5	39.8
$Co(O_2CCHCl_2)_2(IQ)_4$	459.4	110		142.8	43.1	44.3
$Ni(O_2CCHCl_2)_2(3\text{-}MePy)_4$	376.4	80	102.3	101.8	39.5	40.1
$Ni(O_2CCHCl_2)_2(4\text{-}MePy)_4$	276.2	79	73.8	74.7	29.7	30.0

reported earlier [9]. Thermogravimetric analysis was carried out on a Stanton thermobalance Model TR-1. Thermograms were obtained on 300—500 mg samples at a heating rate of 4°C min^{-1}. The complexes prepared along with their thermogravimetric data are presented in Table 1.

RESULTS AND DISCUSSION

Tetrakis cobalt complexes are red in colour while nickel complexes are blue. All these complexes are soluble in common organic solvents. Their elemental analysis, conductance, molecular weight, magnetic and spectral studies [9] show them to be mononuclear octahedral molecules of formula $M(O_2CCHCl_2)_2L_4$, containing monodentate carboxylate groups. The results of thermogravimetric analysis (Table 1) indicate that the isoquinoline complex does not show any range of thermal decomposition to metal oxide, while 3- and 4-methylpyridine complexes decompose through the formation of bis-amine complexes of 1 : 2 stoichiometry either to metal dichloroacetates and then to metal oxide or directly to metal oxide. The thermogravimetric results also indicate that the base molecules are lost at lower temperatures indicating that M—N bonds are weaker as compared to M—O bonds, in agreement with other studies [10]. Their probable mode of decomposition is deduced from their TGA curves which show that the complexes do not undergo any weight loss below 79°C. On further heating, the decomposition of $Co(O_2CCHCl_2)_2(3\text{-MePy})_4$, $Ni(O_2CCHCl_2)_2(3\text{-MePy})_4$, and $Ni(O_2CCHCl_2)_2(4\text{-MePy})_4$ begins at around 80°C while the decomposition of $Co(O_2CCHCl_2)_2(4\text{-MePy})_4$ and $Co(O_2CCHCl_2)_2(IQ)_4$ starts at 100°C and 110°C, respectively. On the basis of their initial decomposition tempera-

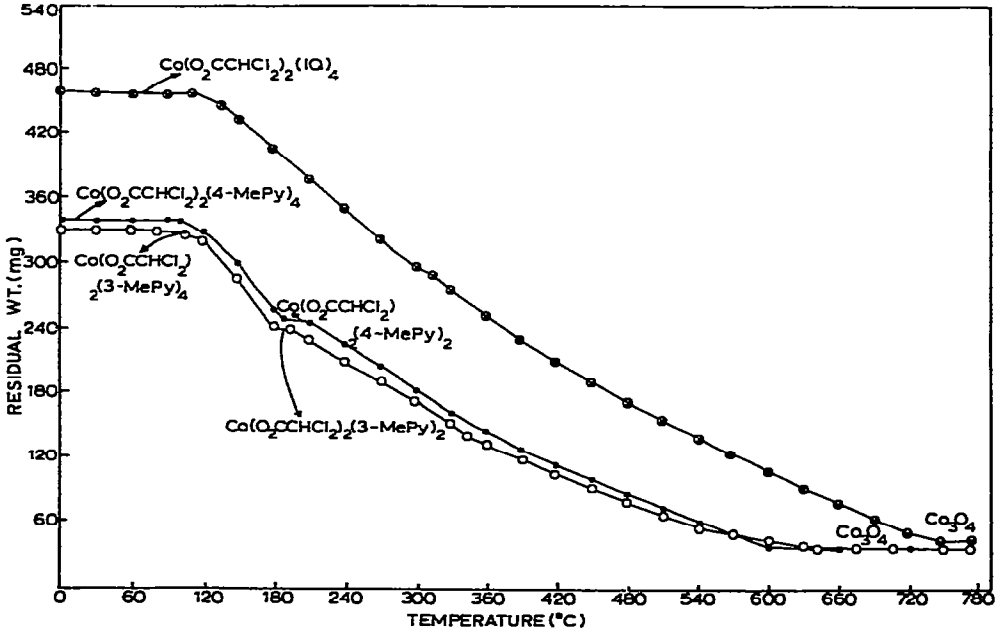

Fig. 1. TG curves of tetrakis-amine complexes of cobalt(II) dichloroacetates.

tures their thermal stability follows the order $Co(O_2CCHCl_2)_2(IQ)_4 > Co(O_2CCHCl_2)_2(4\text{-MePy})_4 > Co(O_2CCHCl_2)_2(3\text{-MePy})_4 > Ni(O_2CCHCl_2)_2(3\text{-MePy})_4 > Ni(O_2CCHCl_2)_2(4\text{-MePy})_4$.

The TGA curve of $Co(O_2CCHCl_2)_2(3\text{-MePy})_4$ (Fig. 1) shows that the complex starts to lose weight at 82°C, giving a break at 180°C in the thermolysis curve. The weight loss required for two molecules of 3-MePy is 89.0 mg which corresponds very well with the experimental value (88.3 mg), indicating the formation of a bis-amine adduct of 1 : 2 stoichiometry. However, the resulting 1 : 2 adduct does not appear to be thermally stable as decomposition continues up to 640°C.

For $Co(O_2CCHCl_2)_2(4\text{-MePy})_4$ a break at 200°C is observed in the thermolysis curve (Fig. 1) and the total loss in weight at 220°C is 91.8 mg, which corresponds well to the required weight loss of 92.5 mg for two 4-MePy molecules. However, the $Co(O_2CCHCl_2)_2(4\text{-MePy})_2$ formed does not appear to be stable and decomposes on further heating forming Co_3O_4 at 600°C.

The mode of decomposition of the isoquinoline adduct of Co(II) dichloroacetate is rather indefinite. It starts to lose weight at 110°C and continues decomposing, without having any break in its thermolysis curve pertaining to the formation of any stable intermediate, to give Co_3O_4 at 740°C as a final product of decomposition.

In the case of $Ni(O_2CCHCl_2)_2(3\text{-MePy})_4$, the complex loses two molecules of the ligand up to 180°C, as indicated by the weight loss data. Beyond this temperature no break is observed in the thermolysis curve (Fig. 2) and at 640°C it gives NiO as the final product of decomposition.

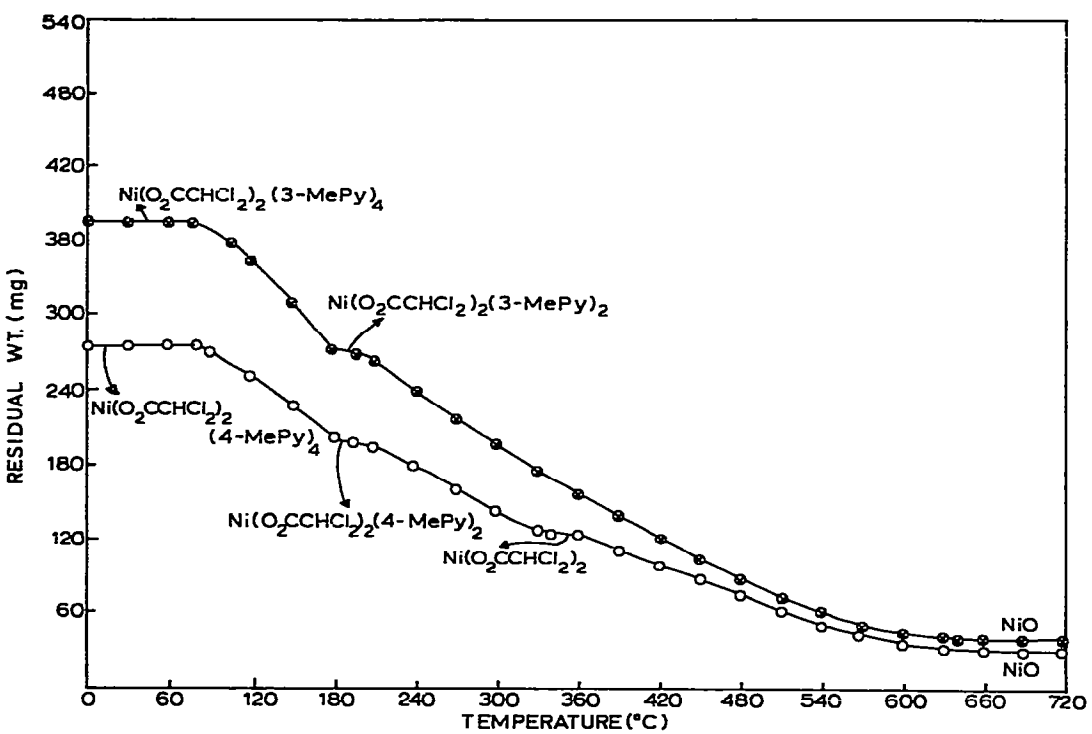

Fig. 2. TG curves of tetrakis-amine complexes of nickel(II) dichloroacetates.

The complex $Ni(O_2CCHCl_2)_2(4\text{-}MePy)_4$ shows two breaks (Fig. 2) at 180°C and 340°C which correspond to the successive loss of two molecules of 4-MePy corresponding to the formation of $Ni(O_2CCHCl_2)_2(4\text{-}MePy)_2$ and $Ni(O_2CCHCl_2)_2$, respectively. Both the intermediates are unstable and decomposition continues with rise in temperature.

For a complete sequential decomposition of the L_4 complex via the L_2 complex three breaks are expected in the thermolysis curve corresponding to the loss of the first pair of ligands, the second pair of ligands, and finally the decomposition of the metal dichloroacetates. This sequence was observed only in the 4-MePy complex of Ni(II) dichloroacetate. In all these adducts there is no evidence for the thermal stability of any of the intermediates observed, as no zero weight loss horizontal levels have been observed during their decomposition, indicating that their decomposition proceeds according to the following scheme without involving the desired 1 : 1 adducts as their intermediates, which we hoped to isolate.

$$M(O_2CCHCl_2)_2L_4 \rightarrow M(O_2CCHCl_2)_2L_2 + 2\,L \quad \text{(i)}$$

$$M(O_2CCHCl_2)_2L_2 \rightarrow M(O_2CCHCl_2)_2 + 2\,L \quad \text{(ii)}$$

$$M(O_2CCHCl_2)_2 \rightarrow \text{Residue } (Co_3O_4 \text{ or NiO}) + \text{volatile products}$$

$$M(O_2CCHCl_2)_2L_4 \rightarrow \text{Residue } (Co_3O_4 \text{ or NiO}) + \text{volatile products}$$

REFERENCES

1 A.B.P. Lever and D. Ogden, J. Chem. Soc. A, (1967) 2041.
2 J. Catterick and P. Thornton, J. Chem. Soc., Dalton Trans., (1975) 233.
3 T.A. Stephenson, S.M. Morehouse, A.R. Powell, J.P. Heffer and G. Wilkinson, J. Chem. Soc., (1965) 3632.
4 S.F.A. Kettle and A.J.P. Pioli, J. Chem. Soc. A, (1966) 1243.
5 N. Kumar and A.K. Gandotra, J. Inorg. Nucl. Chem., 42 (1980) 1247.
6 N. Kumar and A.K. Gandotra, Trans. Metall. Chem., in press.
7 J. Catterick and P.Thornton, Adv. Inorg. Chem. Radiochem., 20 (1977) 291.
8 M. Kato, H.B. Jonassen and J.C. Fanning, Chem. Rev., 64 (1964) 99.
9 N. Kumar and A.K. Gandotra, J. Indian Chem. Soc., 57 (1980) 647.
10 K.K. Sharma, Ph.D. Thesis, Panjab University, Chandigarh, 1971.