Thermochimica Acta, 35 (1980) 67—72 67
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THE THERMAL BEHAVIOUR OF MONO-OXALATO-BIS-BIPYRIDINE-COBALT(III) COMPLEXES

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(Received 28 March 1979)

ABSTRACT

The thermal redox decomposition reactions were determined for $[Co(bipy)_2ox]X \cdot nH_2O$ type coordination compounds (bipy = 2,2'-bipyridine; ox = $C_2O_4^{2-}$; X = F^-, Cl^-, Br^-, I^-, ClO_4^-, BF_4^-, $HCOO^-$, H_3CCOO^-; n = 0—3). Data were obtained using thermogravimetry and DTA. In the solid phase the thermal reaction pathways were found to be essentially influenced by different anions, X, in the second coordination sphere. The reaction pathways are described and some interpretations of potential reaction mechanisms are proposed.

INTRODUCTION

Mixed ligand $[Co(N{-}N)_2ox]X$ type complexes (N—N = α-diimine ligand from π-acceptor molecules such as 2,2'-bipyridine and 1,10-phenanthroline) are known to be light-sensitive [1—3]. Some of these compounds could be used in photocatalytic systems [4]. The thermal behaviour of such mixed ligand complexes is therefore of particular interest in distinguishing between photochemical and thermal reaction pathways. Furthermore, an exact distinction between photochemical and thermal behaviour is essential because the same final products are produced by both thermolysis and photolysis experiments in solution as well as in the solid phase.

$$2[Co(N{-}N)_2\,ox]\,X \xrightarrow[kT]{h\nu} [Co(N{-}N)_2\,ox] + [Co(N{-}N)_2\,X_2] + 2\,CO_2$$

Although studies of the redox behaviour of some of these mixed ligand complexes in solution have been described [5], the thermal redox behaviour in the solid phase remains largely unknown. As far as we are aware, thermal investigations of mixed ligand complexes which fall in the described category are known for only $[Co(phen)_2ox]X$ compounds [6]. Many papers, however, deal with the thermal decomposition reactions of mixed ligand complexes of cobalt(III) with σ-donor ligands such as ammonia and ethylenediamine [7]. However, the π-acceptor ability of nitrogen ligands exerts a special influence on the thermal reactivity of this particular type of mixed ligand complex [8].

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In the framework of our thermal [6], photochemical [1,3,4] and quantum-chemical studies of diimine/oxalato mixed ligand complexes [8,9] we are interested in the thermal redox behaviour of bis-bipyridine-mono-oxalato-cobalt(III) complexes with different anions, X, in the second coordination sphere. In the present paper we report the results of DTG and DTA experiments on selected $[Co(bipy)_2ox]X$ complexes.

EXPERIMENTAL

Compounds

$[Co(bipy)_2ox]Cl$, $[Co(bipy)_2ox]ClO_4$ and $[Co(bipy)_2ox]I$ have been described by Kane-Maguire and co-workers [10]. These and the other complexes were prepared as follows. 2,2′-Bipyridine (0.0076 M) dissolved in 35 ml acetone/ethanol was added to a solution of $K_3[Co(ox)_3] \cdot 3H_2O$ (0.005 M) in 40 ml of distilled water. The mixture was heated for several minutes to 70—75°C on a steam bath. During this period the colour of the solution changed from green to red. After cooling to room temperature and filtration, the appropriate alkali salts (NaX preferred) were added in excess (0.06 M), with stirring. After the addition of 20 ml of acetone and cooling to about 5°C the mixed ligand complexes crystallized as small needles. The complexes obtained were filtered, washed with an ice-cold water/acetone mixture and dried over $CaCl_2$. All procedures were carried out in the dark. Because of the heat sensitivity of the compounds described, long heating periods were avoided.

The complexes obtained were characterized by the usual IR, UV/vis and magnetic behaviour; conductivity values which decrease in solution indicate ion-pair interactions. The analytical data obtained were in accordance with those calculated [11].

Thermal analyses

The thermal studies were performed using a Seteram microthermoanalyzer equipped with a 1700°C furnace. The samples were prepared in the usual manner. The following parameters were used: TG-sensitivity, 2 mV mg^{-1}; DTA-sensitivity, 10 μV; heating rates, 2 and 5°C min^{-1}; alumina was the reference material, quartz boats (TG), platinum crucibles (DTA) and a dynamic argon atmosphere were used.

RESULTS AND DISCUSSION

The combined DTA/DTG curves of the halides of the $[Co(bipy)_2ox]X$ complexes are presented in Fig. 1. These are characterized by the following stages. The first mass loss, which is endothermic, begins at about 350 K; three further endothermic reaction steps then follow, each connected with each other. The last step is also endothermic in the temperature region moni-

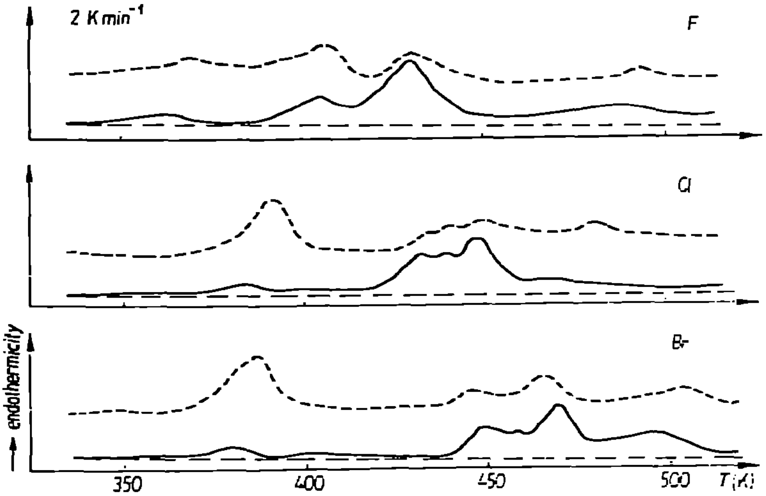

Fig. 1. Differential thermogravimetric (———) and differential thermal analysis (- - - - - -) curves for: $[Co(bipy)_2ox]F \cdot 3H_2O$ (F), $[Co(bipy)_2ox]Cl \cdot 3H_2O$ (Cl) and $[Co(bipy)_2ox]Br \cdot 3H_2O$ (Br).

tored. The thermograms of the alkanate compounds have the same shape as those of the halides.

The shapes of the DTA/DTG curves of the corresponding $[Co(bipy)_2ox]X$ perchlorate and tetrafluoroborate complexes, however, are quite different (see Fig. 2). There are no thermal reactions up to 350 K; only two combined reaction steps could be observed at about 450 K. In contrast to those of the halides and alkanates, the DTA curves of the perchlorate and tetrafluoroborate compounds show an endothermic step followed by an exothermic one. Since the separation of the DTG peaks is very poor, the mass loss estimations are not very satisfactory. However, they agree with the reaction pathway discussed below (see Fig. 3).

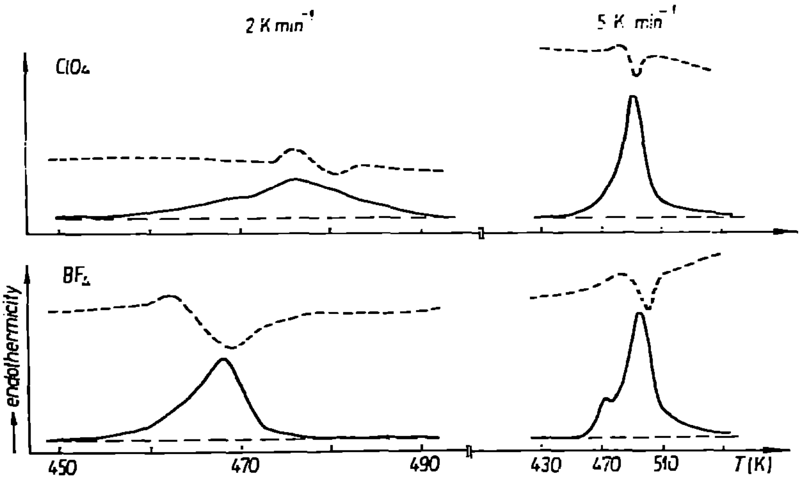

Fig. 2. Differential thermogravimetric (———) and differential thermal analysis (- - - - - -) curves for: $[Co(bipy)_2ox]ClO_4 \cdot 0.5H_2O$ (ClO_4) and $[Co(bipy)_2ox]BF_4$ (BF_4).

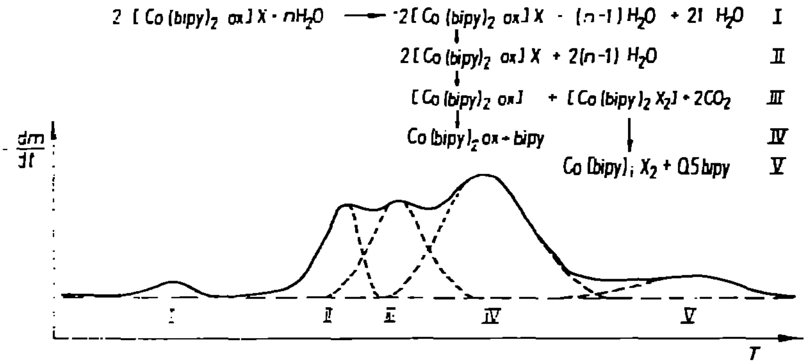

Fig. 3. Scheme of the thermal decomposition reaction pathway of [Co(bipy)$_2$ox]X compounds with respect to their general thermogravimetric behaviour.

The first step (I), the loss of a stoichiometric quantity of water, is observable between 350 and 370 K only for complexes which contain more than 1 mole of water of crystallization (the halides and alkanates). The reaction steps above 400 K are probably connected with the loss of the residual water (II). Furthermore, these steps are closely connected with the redox reaction (III) indicated by a mass loss due to the formation of CO_2. Controlled pyrolysis experiments at appropriate temperatures showed unambiguously that CO_2 and mixed ligand complexes of cobalt(II) were formed. Both could be identified by different analytical methods. The loss of CO_2 was deduced from IR studies of heated samples in KBr. The [Co(bipy)$_2$X$_2$] complexes formed could be identified by their elemental analyses, magnetic measurements, IR and UV/vis spectra, among other methods [11]. The separated cobalt(II) complexes are consistent in their behaviour with independently prepared compounds of the same composition.

The endothermic steps connected with the loss of water are as expected. Furthermore, this result agrees with thermolysis experiments carried out on the appropriate [Co(phen)$_2$ox]X complexes [6]. In contrast, the thermal redox properties of [Co(phen)$_2$ox]X complexes are somewhat different to those of the corresponding [Co(bipy)$_2$ox]X compounds. The thermal redox reactions of bis-phenanthroline-mono-oxalato-cobalt(III) complexes are exothermic for halides and alkanates, as well as for perchlorate and tetrafluoroborate. The bipyridine compounds [Co(bipy)$_2$ox]X show exothermic steps only for perchlorate and tetrafluoroborate. The endothermic redox decomposition of the halide and alkanate compounds is probably an effect due to the weak exothermic redox reactions combined with the strong endothermic splitting of bipyridine (IV), which immediately follows the redox reaction. Finally, further thermal splitting of bipyridine occurs (V). The influence of different anions (X) in the second coordination sphere on the onset temperature of the redox decomposition reactions is of particular interest. Table 1 shows some of these temperatures for different [Co(bipy)$_2$ox]X complexes, compared with those of the corresponding [Co(phen)$_2$ox]X compounds. Some redox enthalpy values obtained from DSC studies are also given in Table 1.

The onset temperature seems to be a useful measure of the thermal redox

TABLE 1

Onset temperatures (*T*) of thermo-redox reactions of $[Co(bipy)_2ox]X$ and $[Co(phen)_2ox]X$ complexes, and redox enthalpy values (ΔH) of the phenanthroline compounds

X	*T*(K)		$-\Delta H$(kJ mole^{-1})
	bipy	phen	phen
HCOO	370	383	
CH_3COO	373	388	
F	391	434	21.3
Cl	423	454	21.0
Br	431	456	13.9
ClO_4	448	487	4.2
BF_4	454	490	5.9

stability of the complexes described. The onset temperatures increase in the following series: alkanates < halides < perchlorate < tetrafluoroborate. Because of inadequate kinetic parameters an exact interpretation of this gain in the "thermostability" is difficult [12]. However, assuming that the increase in the onset temperature depends on the activation energy, the influence of different anions on the thermostability of $[Co(bipy)_2ox]X$ compounds can be explained in the following manner. For an associative mechanism the energy of the transition state will be influenced by interactions between the complex unit and the anion X. Small anions with strong ion potentials decrease the energy of activation more than bulky ions, such as perchlorate and tetrafluoroborate [13]. Correlations between the position of different anions X in the spectrochemical series and their influence on the redox enthalpy values support this interpretation. Furthermore, ion-pair interactions between the complex unit and the anion X also seem to influence the thermoreactivity of $[Co(bipy)_2ox]X$ complexes.

CONCLUSIONS

In comparison with the parent compound $K_3[Co(ox)_3]$, the α-diimine/oxalate mixed ligand complexes of $[Co(N—N)_2ox]X$ type are thermally stable up to about 360 K. This means that π-acceptor ligands of the α-diimine type are useful in quenching thermoreactions of oxalato-metallates at low temperatures. The mixed ligand complexes described therefore allow the study of photochemical reactions which are not primarily connected with thermoreactions at room temperature. Furthermore, the influence of non-coordinated anions X in the second coordination sphere on the thermoreactivity of $[Co(N—N)_2ox]X$ complexes may be used for selective quenching of thermal redox processes. It is of particular interest that π-acceptor ligands do not quench the photoreactivity of oxalato-metal units significantly [1,4,11].

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge Mr. L. Engels and Dr. G. Kühn for their cooperation in obtaining and interpreting the DTA and DTG data for this study.

REFERENCES

1 H. Hennig, K. Hempel, M. Ackermann and P. Thomas, Z. Anorg. Allg. Chem., 442 (1976) 65.
2 C.P.J. Vuik, N.A.P. Kane-Maguire and C.H. Langford, Can. J. Chem., 53 (1975) 3121.
3 H. Hennig, K. Jurdeczka and P. Thomas, Z. Chem., 16 (1976) 161.
4 H. Hennig and K. Jurdeczka, J. Signalaufzeichnungsmaterialien, 6 (1978) 193.
5 K. Ohashi, Bull. Chem. Soc. Jpn., 45 (1972) 3093.
6 H. Hennig and K. Hempel, Z. Anorg. Allg. Chem., 425 (1976) 81.
7 See, for example, L.W. Collins, W.W. Wendlandt and E.K. Gibson, Thermochim. Acta, 8 (1974) 303; N.I. Lobanov and O.S. Konovalenko, Zh. Neorg. Khim., 13 (1968) 409.
8 J. Reinhold, R. Benedix, P. Birner and H. Hennig, Inorg. Chim. Acta, 32 (1979) 209.
9 J. Reinhold, R. Benedix and H. Hennig, Z. Phys. Chem., (Leipzig), in press.
10 J.A. Bromhead, M. Dwyer and N. Kane-Maguire, Inorg. Chem., 7 (1968) 1388.
11 H. Hennig, K. Jurdeczka, J. Lerchner and R. Benedix, Z. Anorg. Allg. Chem., in press.
12 A.V. Nikolaev and V.A. Legvinenko, J. Therm. Anal., 13 (1978) 253.
13 See, for example, H.E. Le May, Thermochim. Acta, 23 (1978) 349.