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Note

Thermal studies of the pyridine complexes of cobalt(II) perchlorate and cobalt(II) nitrate

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INTRODUCTION

Herlocker and Rosenthal[1] have recently studied several cobalt(II) complexes of pyridine and have surveyed the conflicting evidence for the formation of the Copy_6^{2+} ion. The result of their studies was taken to indicate that this ion is unlikely to exist either in the solid state or in solution. The spectroscopic properties of the crystalline solids, $\mathrm{Copy}_4(\mathrm{ClO}_4)_2$ and $\mathrm{Copy}_3(\mathrm{NO}_3)_2$, showed that the oxyanions were co-ordinated and that the complexes were monomeric.

Biagetti and Haendler[2] concluded that the complex $\mathrm{Copy}_3(\mathrm{NO}_3)_2$ was monomeric and contained both bidentate and monodentate nitrate groups. The results obtained by these workers also confirmed that, in solution, the nitrate complex loses pyridine to form the octahedral complex, $\mathrm{Copy}_2(\mathrm{NO}_3)_2$. In this complex, each of the nitrate groups is bidentate. Thermogravimetric studies of $\mathrm{Copy}_3(\mathrm{NO}_3)_2$ showed that a violet oil was formed above 358 K, but no further information was obtained.

In the course of some NMR studies in this laboratory, we have prepared oxyanion complexes of cobalt(II). It was considered to be of interest to isolate crystalline solids from solutions of these complexes and to carry out thermal studies on them. It was also hoped that the information obtained would supplement the information previously obtained for cobalt(II) halide complexes of pyridine[3–5].

EXPERIMENTAL

Complexes

Dinitratotripyridinecobalt(II) was prepared by the method of Herlocker and Rosenthal[1].

Hexapyridinecobalt(II) perchlorate was prepared by the addition of "Analar" pyridine to a solution of anhydrous cobalt(II) perchlorate in dry acetonitrile. The acetonitrile was dried with calcium hydride and was stored over activated molecular sieves. Cobalt was determined spectrophotometrically by atomic absorption. Percentage of cobalt: experimental, 8.6%; calculated {for $[\mathrm{Copy}_6](\mathrm{ClO}_4)_2$}, 8.04%.

Thermal measurements

A Perkin–Elmer DSC-1B differential scanning calorimeter was used, as previously described[3]. All decompositions were carried out under an atmosphere of dry nitrogen gas at a heating rate of 16 K min^{-1}.

Spectroscopy

The infrared spectrum of the perchlorate complex was obtained as a Nujol mull, using a Perkin–Elmer 457 Spectrophotometer.

RESULTS AND DISCUSSION

Dinitratotripyridine cobalt(II)

This complex decomposed over the temperature range 390–445 K, with a peak at 420 K. The decomposition was accompanied by a weight loss of 19.3% which is compatible with the following reaction (1) which requires a weight loss of 18.8%,

$$\mathrm{Copy_3(NO_3)_2\ (s) \rightarrow Copy_2(NO_3)_2\ (l) + py\ (g)} \qquad (1)$$

The product was a pink liquid which solidified to a glass on cooling. From the DSC curves, the enthalpy change for reaction (1) was found to be 58.5±0.5 kJ mol^{-1}. Further heating resulted in a complex decomposition to form charred products.

We may estimate the enthalpy change, ΔH_2, for reaction (2) in which the product is solid rather than liquid by using data for reactions of the type (3).

$$\mathrm{Copy_3(NO_3)_2\ (s) \rightarrow Copy_2(NO_3)_2\ (s) + py\ (g)} \qquad (2)$$

$$\mathrm{CoL_2X_2\ (s) \rightarrow CoL_2X_2\ (l)} \qquad (3)$$

The mean ΔH value of reaction (3) for a number of pyridine and substituted pyridine complexes of cobalt(II) halides[3–5] is 28 kJ mol^{-1}. Since $\Delta H_2 = \Delta H_1 - \Delta H_3$, then $\Delta H_2 = 30$ kJ mol^{-1}.

It is of interest to compare these enthalpy changes with those of similar reactions in which the nitrate ion is replaced by halide. For the complex $\mathrm{Copy_4I_2}$, the following reactions occur[3]

$$\mathrm{Copy_4I_2\ (s) \rightarrow Copy_2I_2\ (s) + 2py\ (g)} \qquad \Delta H = 119\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{Copy_2I_2\ (s) \rightarrow Copy_2I_2\ (l)} \qquad \Delta H = 26.4\ \mathrm{kJ\ mol^{-1}}$$

Therefore, the enthalpy change of reaction (4) is equal to 145 kJ mol^{-1}.

If the

$$\mathrm{Copy_4I_2\ (s) \rightarrow Copy_2I_2\ (l) + 2py\ (g)} \qquad (4)$$

enthalpy change per mole of pyridine removed from the cobalt complex is only approximately additive, then it is clear that the value of ΔH_1 is anomalously low by comparison. The reason for this may be that $\mathrm{Copy_2I_2}$ is tetrahedral whereas $\mathrm{Copy_2(NO_3)_2}$ is octahedral. In the course of reaction (1), a monodentate nitrate group becomes bidentate. The enthalpy change accompanying this coordination process may partially offset that which occurs on removal of the pyridine ligand. The process may also be concerted in nature.

Hexapyridinecobalt(II) perchlorate

The method of preparation of this complex differed from that of Herlocker and Rosenthai (see Experimental section). The infrared spectrum of the product possessed a peak at 427 cm^{-1}, characteristic of coordinated pyridine[6] but there was no free ligand peak at 430 cm^{-1}. This indicated that all of the pyridine molecules were coordinated.

The DSC curve of the complex is shown in Fig. 1. The low temperature peak (which is a doublet) is accompanied by a mean weight loss of 23.1% .The reaction (5) requires a weight loss of 21.6%

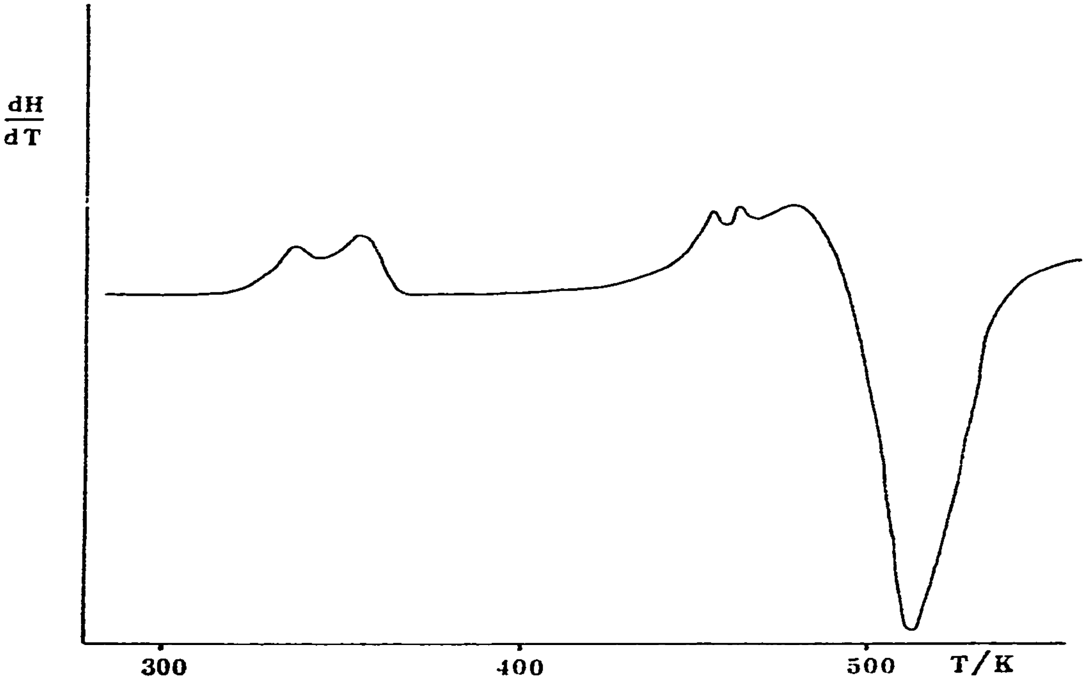

Fig. 1. DSC curve of $[\mathrm{Copy_6}](\mathrm{ClO_4})_2$ (s). Heating rate, 16 K sec^{-1}.

$$[\mathrm{Copy_6}](\mathrm{ClO_4})_2\ (\mathrm{s}) \rightarrow \mathrm{Copy_4}(\mathrm{ClO_4})_2\ (\mathrm{s}) + 2\mathrm{py}\ (\mathrm{g}) \qquad (5)$$

It is not possible to construct an equation requiring a stoichiometric loss of pyridine from a starting compound containing only cobalt(II) perchlorate and pyridine, other than that given in reaction (5). This, taken with analytical and infra-red data is taken as conclusive evidence for the formation of the $\mathrm{Copy_6^{2+}}$ ion. (This may be regarded as a limiting formulation owing to the facile loss of pyridine.)

Although the results contradict those of Herlocker and Rosenthal, it may be pointed out that the $Copy_6^{2+}$ ion has been characterised recently by Jones and Bull[7]. Drago and Cramer[8] have also characterised Mpy_6^{2+} species.

The enthalpy change for reaction (5) was found to be 121 ± 3 kJ mol^{-1}. This is similar to the enthalpy changes previously reported for many decomposition reactions of the type (6) in which both the reactant and product are octahedral species (the latter

$$Mpy_4X_2\ (s) \rightarrow Mpy_2X_2\ (s) + 2py\ (g) \qquad (6)$$

being polymeric). The solid pink product, $Copy_4(ClO_4)_2$, is formed by a similar process—that is, cleavage of Co–py and formation of Co–anion bonds. In this case, unlike the nitrate complex, the energy liberated in the latter process is insufficient to compensate for the former, endothermic, process.

At higher temperatures (Fig. 1), the complex exploded and no reliable weight losses could be obtained. This behaviour contrasts with the thermal properties of the nitrato complex. This may be interpreted by one or both of the following two explanations:

(*a*) The formation of bidentate chelating perchlorate bonds is thermodynamically unfavourable compared with the favourable formation of chelated nitrate groups.

(*b*) The process in which pyridine is oxidised by perchlorate becomes more favourable at higher temperatures than the decomposition reaction in which gaseous pyridine is removed.

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