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Note

A REINVESTIGATION OF THE THERMAL DECOMPOSITION OF $Co(NH_3)_4PO_4 \cdot 2\ H_2O$

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Information on the thermal behaviour of transition metal complexes containing phosphate or polyphosphate groups as ligands is very scarce, although the interest in such complex compounds has increased in recent years due to their usefulness as simple models of biological relevance [1,2].

The thermal decomposition of $Co(NH_3)_4PO_4$ was investigated many years ago by Ocone at al. [3] using thermogravimetric techniques, but stoichiometric details and the characteristics of the decomposition residues were not reported.

Therefore, we have now reinvestigated the pyrolysis of this Co(III) complex by means of TG and DTA methods and have analyzed the product and possible intermediates by IR spectroscopy and X-ray techniques. Additionally, we have also recorded its electronic spectrum and made some comments about the reproducibility of the IR spectrum.

EXPERIMENTAL

Very pure samples of $Co(NH_3)_4PO_4 \cdot 2\ H_2O$ were obtained by one of the methods reported by Siebert [4] starting from $CoCl_2$, Na_2HPO_4 and NH_4OH solutions. They were characterized by chemical analysis and IR spectroscopy.

TG and DTA were carried out on an automatic recording Mettler thermoanalyzer (Type T2/ES), using a Pt–Pt/Rh thermoelement and working under a constant nitrogen stream at a heating rate of 6°C min^{-1}. Al_2O_3 was used as DTA standard. The sample weight varies in a range 20–25 mg.

The IR spectra were recorded on a Perkin–Elmer 580 B instrument using, alternately, the KBr pellet or Nujol-mull techniques. X-ray diffraction patterns were obtained on a Philips 1732/10 diffractometer, using CuK_α

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radiation (Ni filter). The electronic spectra of the solid samples were recorded with the reflectance attachment of a Shimadzu UV 300 instrument.

RESULTS AND DISCUSSION

Spectroscopic behaviour

It is interesting to mention that the IR spectra of $Co(NH_3)_4PO_4 \cdot 2\ H_2O$ are not always reproducible and it is often difficult to reproduce accurately the spectrum reported and discussed by Siebert [4]. Spectra in Nujol are generally not well resolved and those obtained in KBr pellets show, sometimes, important variations in the shape and positions of some bands, which are time dependent. A similar behaviour has been observed for other cobalt(III) complexes [5] and it is attributed to diffusion and interchange phenomena occurring in the KBr pellet.

We have also recorded the electronic (reflectance) spectrum of the complex. It shows two well-defined bands located at 372 and 535 nm being, therefore, similar to that of the $[Co(en)_2P_2O_7]^{3-}$ anion recently investigated [6], demonstrating that the Co(III) ion behaves in a very similar way in both complex environments.

Thermal behaviour

Typical TG and DTA diagrams are shown in Fig. 1 and the corresponding analysis is summarized in Table 1.

As can be seen, the water of hydration is lost in two steps; only 1.25 moles

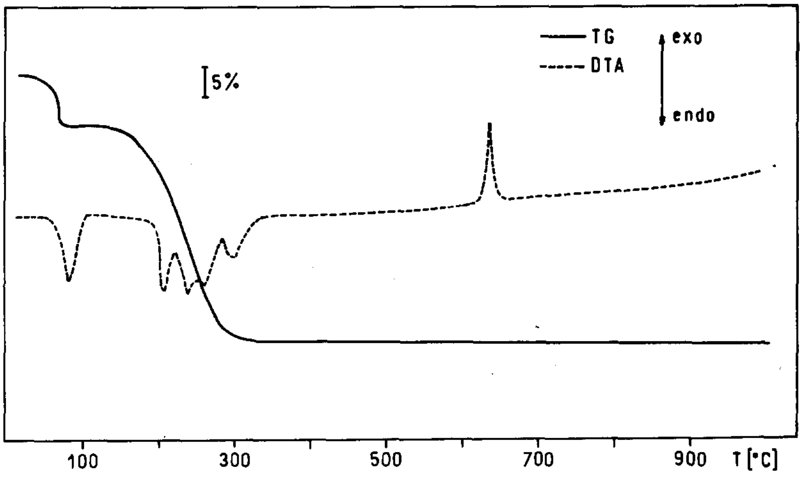

Fig. 1. Typical DTA and TG plots of $Co(NH_3)_4PO_4 \cdot 2\ H_2O$.

are released at 80°C, whereas the remainder, which are very strongly bonded, are probably removed in the first stage of the second decomposition step.

In the range 150–375°C four well-defined endothermic DTA peaks can be observed, associated with a continuous mass loss which extends up to the last mentioned temperature. These peaks clearly show the complexity of the process, which probably consists of a rapid sequence of events which conclude with the total decomposition and transformation of the original complex.

The powder patterns of the residues collected after the heating at 375°C show that the decomposition product is amorphous, but their IR spectrum clearly shows the characteristic pattern of $Co_2P_2O_7$ [7] although some bands are very broad and not well defined (this is characteristic behaviour in amorphous materials).

We have also investigated the spectra of samples heated up to 200, 250 and 300°C. The first two clearly show the presence of most of the original bands, together with very weak peaks or inflections associated with the presence of $Co_2P_2O_7$; the third only gives bands related to the diphosphate.

We could not detect bands assignable to $CoPO_4$ in any of the above mentioned cases, indicating that this phase is not produced as stable intermediate, as was previously suggested [3].

Our results point to the following decomposition scheme.

$$Co(NH_3)_4PO_4 \cdot 2\ H_2O \rightarrow Co(NH_3)_4PO_4 \cdot 0.75\ H_2O + 1.25\ H_2O \qquad (1)$$

$$6\ Co(NH_3)_4PO_4 \cdot 0.75\ H_2O \rightarrow 3\ Co_2P_2O_7 + 22\ NH_3 + N_2 + 7.5\ H_2O \qquad (2)$$

The total mass loss of eqns. (1) and (2) is 43.42%, which is in excellent agreement with the experimentally determined value of 43.3%. On the other hand, it is interesting to mention that numerous ammine complexes of Co(III) are also thermally degraded to Co(II) compounds with simultaneous N_2 liberation [8].

TABLE 1

DTA and TG data for $Co(NH_3)_4PO_4 \cdot 2\ H_2O$

T (°C)	Wt. loss (%)	Product (% theor.)	DTA signal
80	8.80	1.25 H_2O (8.72)	endo
208	34.50	see eqn. (2) (34.70)	endo
240			endo
260			endo
300			endo
610	(> 0.4%)?	crystallization	exo
375–1000	~1.5%	oxygen loss(?)	

The complex compound $[Co(NH_3)_6]PO_4$ also decomposes with the liberation of N_2 and H_2O and generates Co(II) diphosphate [8,9].

Our TG curves always show a small and continuous weight loss which extends up to the end of each of the measurements. The observed weight loss between 375 and 1000°C was approximately 1.5% and its origin cannot be easily explained. We think this mass diminution might be related to a small and continuous release of oxygen, which could generate a slight non-stoichiometric $Co_2P_2O_7$ phase. In fact, the IR spectra from samples obtained at temperatures between 375 and 1000°C do not show an appreciable change, although better definition of the bands is observed with increased temperature.

It is even more interesting to comment that the exothermic DTA peak, centred at 640°C and beginning at 610°C, is also associated with a very small break in the TG curve. This was also observed in the previous study [3]. Although the small mass diminution cannot be explained with certainty, the peak is probably related to the transformation of amorphous to crystalline $Co_2P_2O_7$. This assumption is confirmed by the fact that powder diagrams from samples obtained after this peak show some of the characteristic diffraction lines of the cobaltous diphosphate, whereas the materials heated at temperatures below 600°C are still amorphous.

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