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SOLID-STATE THERMOLYSIS OF *trans*-DIAMMINENICKEL(II) *catena*-TETRA-μ-CYANONICKELATE(II) CLATHRATES AND THEIR DEGRADATION INTERMEDIATES

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ABSTRACT

The solid state decomposition of $Ni(CN)_2(NH_3)(G)_n$ (or strictly, $Ni(NH_3)_2Ni(CN)_4 \cdot 2nG$) where G = aniline, benzene and phenol, has been monitored by infrared spectroscopy, and thermogravimetric (TG) and differential scanning calorimetric analyses. The inclusion ratio, n, which can be conveniently obtained from the thermal profiles, follows the order $C_6H_5NH_2 > C_6H_5OH > C_6H_6$. The step-wise degradation of these clathrates has been followed by TG and modelling experiments in Schlenk flasks. All the decompositional intermediates have been isolated and identified by TG, IR and microanalyses.

INTRODUCTION

For decades, dicyanonickel(II) clathrates have been one of the most intriguing aspects of nickel(II) ammine chemistry [1]. Attention has been focussed not only on the classical Hofmann-type clathrates [2–10], but also on the tetrahedral Iwamoto-type clathrates [11–15]. Because of their intrinsic insolubility and the ready liberation of the guest molecules in solution and liquid states, most of these compounds are unsuitable for spectroscopic and other solution studies. The use of elemental analyses is also severely handicapped by the hygroscopic nature of these species. Even though stoichiometric clathration, i.e. when the inclusion ratio, n is 1, can be achieved when special precautions are taken, it more often occurs that the lattice voids are only partially occupied, with $n < 1$. With the advent of numerous thermoanalytical techniques, many of these clathrates could be analysed and studied in their solid state. Surprisingly perhaps, with a few notable exceptions [16–18], the thermal properties of these clathrates have

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not so far been subjected to systematic investigations. In this report, we demonstrate that thermogravimetry can be applied to stoichiometric analysis, namely, the host/guest ratio, and that the intermediates observed in the thermogravimetric (TG) profiles can be isolated and analysed independently. The results thus obtained are of immense use in the design of novel clathrates and the realization of selective clathration of the existing inclusion compounds [19].

EXPERIMENTAL

The preparations were carried out in air but the heating experiments were performed in Schlenk flasks under a dry nitrogen atmosphere. The TG and derivative thermogravimetric (DTG) experiments were conducted on a Du Pont 9900 thermal analyser in dry nitrogen. The nitrogen flow was 75 cm^3 min^{-1} and the heating rate was 10 °C min^{-1}. The scans were conducted from 20 to 700 °C. Sample residual weight (in %[total weight]) versus temperature curves and their derivatives (DTG, %[total weight] min^{-1}) were generated by Du Pont software programs. About 10–15 mg of sample were used. Differential scanning calorimetric (DSC) experiments were carried out in a self-generating atmosphere on the same instrument and calibrated to have a cell constant of 1.19. The temperature range was from room temperature to 500 °C with the same heating rate of 10 °C min^{-1}. The corresponding modelling experiments in Schlenk flasks were performed with 0.5–1.0 g of sample. All the intermediates were isolated and independently analysed by thermogravimetry and IR spectroscopy. IR spectral analysis was carried out in Nujol mull and KBr discs on a Perkin–Elmer 1310 IR spectrophotometer. The microanalyses were done in this department. All the reagents were supplied by commercial sources and used without further purification. The aniline, benzene and phenol clathrates and the pyridine complex were prepared according to the literature [20]. The guest-free clathrate was similarly prepared but without the addition of the guest species. For comparative purposes, the benzene clathrates was also prepared with a ten-fold excess of benzene, as used in the literature. The tests on selective clathration were done on the mixture: aniline with benzene, aniline with pyridine and pyridine with benzene. A typical procedure is described below.

Concentrated NH_3 (20 cm^3) was added to an aqueous solution (20 cm^3) of $NiSO_4$ (5.0 g) to give a dark blue solution. KCN (2.5 g in 10 cm^3) was then introduced, and the resulting solution filtered. To the latter, 60% acetic acid (approx. 5 cm^3) was added until turbidity occurred. A 1 : 1 mixture (by volume) of aniline and benzene (6.0 cm^3) was immediately added and the mixture stirred and chilled at around 5 °C for 1 h. Filtration followed by washing with aqueous NH_3 (5%), ethanol and acetone gave a blue product (1.8 g) which was briefly air-dried. The fresh sample was subjected to IR, TG, DSC and microanalyses. Found: C, 34.81; H, 2.71; N, 21.33. Calculated for $C_2H_3N_3Ni \cdot 0.68[C_6H_5NH_2] \cdot (H_2O)$: C, 34.89; H, 4.66; N, 24.68%. Upon heating to 255° C, anhydrous nickel cyanide was generated. Found: C, 22.12; N, 25.67. Calculated: C, 22.20; N, 25.93%.

RESULTS AND DISCUSSION

Some of the earlier literature have misidentified the cyano pyridyl complex as a genuine clathrate. For comparative purpose, this "pyridine clathrate" and the "empty clathrate", where no guest was introduced, are included in our study. As evident from the TG profiles illustrated in Figs. 1 and 2, the decomposition of the clathrates typically proceeds in four steps: liberation of crystallization solvents, release of the trapped guest molecules, cleavage of the Ni–NH_3 bonds and, finally, reductive elimination of cyanogen which deposits nickel metal. The second and third steps occur concurrently in the pyridyl complex while in the aniline clathrate, liberation of the guest molecules takes place in two stages with the later step overlapping with the NH_3 release. By using the quantitative liberation of the cyanogen as reference, the degree of inclusion, n, in $Ni(CN)_2(NH_3)G_n$ can be reasonably estimated from the TG plots. This, together with the temperature ranges for the degradative steps and the percentages of metal residue, are listed in Table 1.

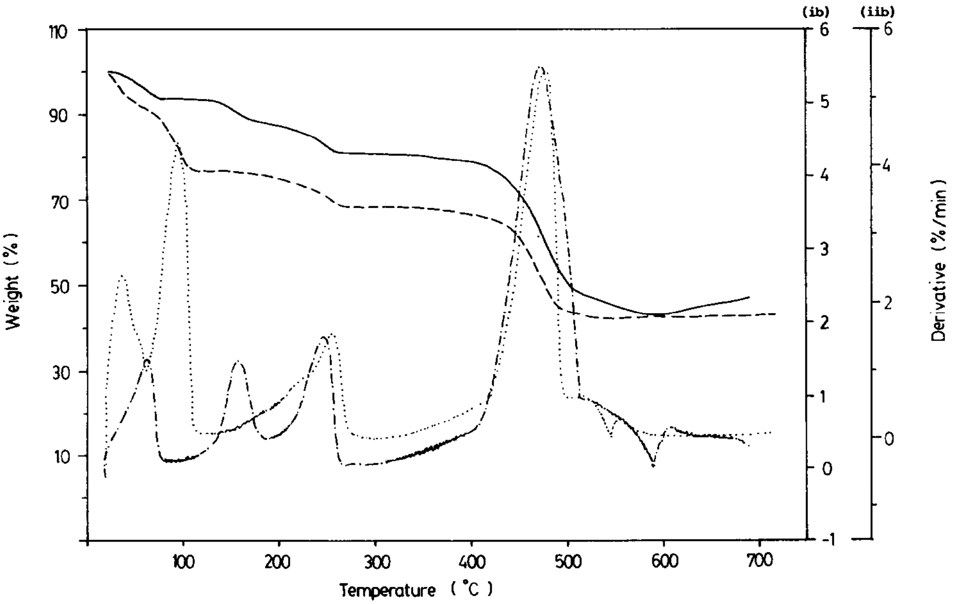

Fig. 1. Guest-free clathrate: TG (———); DTG (ib) (·—·—·). Benzene clathrate: TG (— — —); DTG (iib) (······).

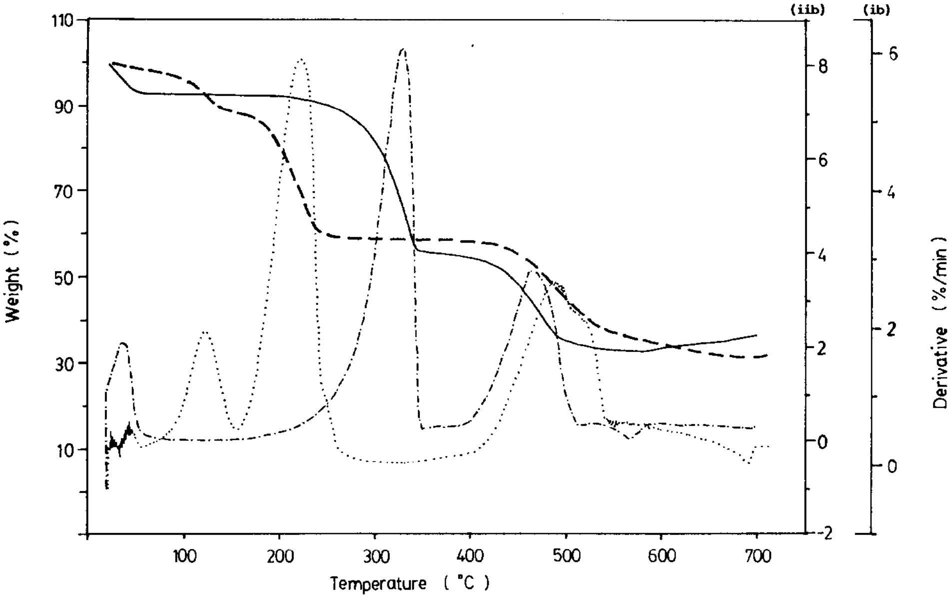

Fig. 2. Aniline clathrate: TG (— — —); DTG (ib) (· · · · · ·). Pyridine complex: TG (———); DTG (iib) (·—·—·).

Most of the clathrates studied display a high tendency to absorb water and solvent molecules. Though these adhered molecules can be released easily by mild heating, upon exposure to the atmosphere, water-recapturing proceeds readily, particularly in the case of the guest-free clathrate, which strictly should be treated as a hydrate-type clathrate, $Ni(CN)_2(NH_3) \cdot xH_2O$ [21]. Release of the guest molecule, however, is an irreversible process.

TABLE 1

Decompositional data for $Ni(CN)_2(NH_3)(G)_n(solv)$

Clathrate	Decompositional steps (°C) [a]				Degree of inclusion, *n*	Metal residue (%)
	A	B	C	D		
Aqua	24–73	122–180	180–268	345–530	–	43
Benzene	20–85	85–130	164–298	400–540	0.41	30
Aniline	23–60	80–144/ 150–256	150–256	400–540	0.68	31
Phenol	24–80	87–176	180–273	328–479	0.45	37
Pyridine [b]	20–50	180–347	180–347	390–520	0.98	36

[a] Step A: $Ni(CN)_2(NH_3)(G)_n(solv) \rightarrow Ni(CN)_2(NH_3)(G)_n + solv$
Step B: $Ni(CN)_2(NH_3)(G)_n \rightarrow Ni(CN)_2(NH_3) + nG$
Step C: $Ni(CN)_2(NH_3) \rightarrow Ni(CN)_2 + NH_3$
Step D: $Ni(CN)_2 \rightarrow Ni + (CN)_2$

[b] Steps B and C of this coordination complex are the cleavage of the Ni–py bonds.

In a similar way to the cadmium Hofmann-type clathrates, these clathrates lose their clathrating properties after they are completely depleted of the guest molecules. This is demonstrated by our unsuccessful attempts to activate the clathrate by removing the trapped solvent through heating, and then adding this decompositional intermediate to aqueous or hydrocarbon solutions containing potential guests such as aniline and phenol. The fact that these thermal intermediates can no longer trap any of the guests is incongruent with the theory that the lattice framework collapses as soon as the guests are stripped. For similar reasons, the hygroscopic nature of the clathrates is lost when the lattice collapses.

Among all the compounds under study, the pyridyl complex exhibits the highest resistivity towards thermal degradation, which provides further proof that this is a coordination complex in which the lattice breakdown involves the cleavage of the Ni–py bonds. Although the TG plots cannot differentiate the two steps in which the pyridine molecules are liberated, the DSC scan clearly shows two endothermic peaks. As expected, however, the elimination of cyanogen from $Ni(CN)_2$ is virtually independent of the preceding steps. The brownish-yellow anhydrous $Ni(CN)_2$ generated from these clathrates displays two cyanide absorptions at 2160 and 2200 cm^{-1}, in contrast to the single absorption of the clathrates at 2160 cm^{-1}. The splitting of this vibration is probably a consequence of local dissymmetry which accompanies the collapse of the three-dimensional network in the decomposition process. The Cd and other related Hofmann clathrates are reported to give Cd^{2+} (or other divalent metals) $Ni(CN)_4^{2-}$ as the decompositional residue [17]. We have, however, no evidence that species such as the two well-known cyano nickelates, $Ni(CN)_4^{2-}$ [22] and $Ni(CN)_5^{3-}$ [23] are formed. The residue at around 350 °C should be polymeric $[Ni(CN)_2]_n$ with the ligand in a bridging mode. This bridging nature of the cyano groups parallels the shifting of the CN absorption to a higher frequency in the IR spectrum.

Most of the sequential decompositional reactions are clearly defined in the TG and DTG profiles. The low-level troughs on the DTG plots which correspond to the clearly defined inflection points on the TG curve (Figs. 1 and 2) suggest that the intermediates are highly stable. Therefore, the modelling experiments were carried out in Schlenk flasks and all the intermediates were isolated at their points of inflection as defined by the TG runs. These intermediates were then subjected individually to thermal and IR analyses. For every clathrate, the TG profiles of the thermal intermediates were found to represent a portion of the plot of their respective parent clathrates. Even the pyridyl coordination complex, as indicated in Fig. 3, shares this characteristic. This additive effect of the TG plots and the spectral changes of these intermediates lend further support to the mechanism proposed. For the guest-free (or aqua) clathrate, the TG plots and IR spectra of the intermediates at 75 and 180 °C bear a striking resemblance to

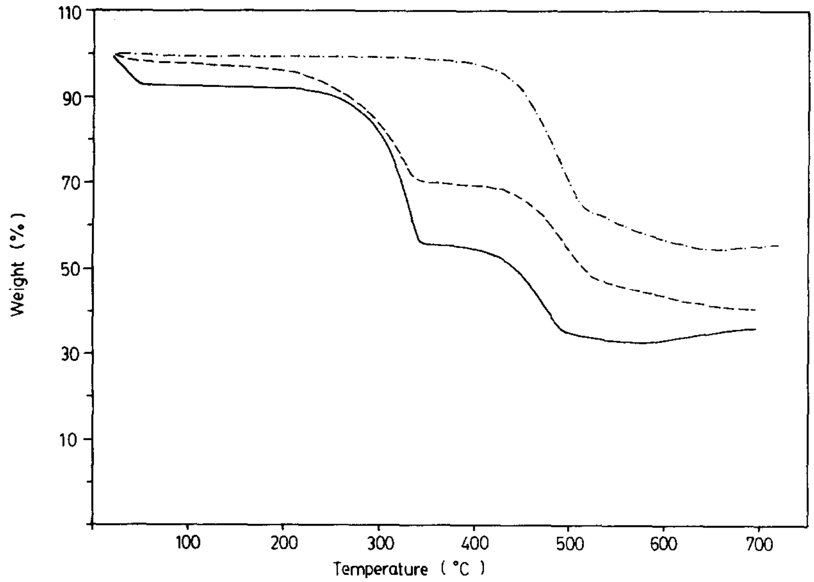

Fig. 3. TG curves of the pyridine complex (———) and the decompositional intermediates at 65 °C (— — —) and 345 °C (·—·—·).

those of the parent clathrate. The recapturing of water vapour from the atmosphere is a feature of the nickel ammine complex. The DSC examinations revealed only endothermic peaks corresponding to all the decompositional steps. The last step, which corresponds to the reductive elimination of the nickel cyanide is, however, exothermic if the thermolysis is done under a dynamic air atmosphere. This can be understood in terms of the oxidation of the metal or the cyano ligand. The enthalpic changes associated with the de-guesting process in the benzene and phenol clathrates have been discussed by Uemasu and Iwamoto [18].

As noted above, the degree of inclusion varies according to the preparative methods, and the precautions taken in the drying process. Under our experimental conditions, n rarely reaches the limiting value of one except in the case of pyridine when the guest functions as a ligand in the coordinating sphere. As such, we decided to evaluate this inclusion ratio, n, from the TG profile and in this way the ability of the clathrate to entrap different guests under similar conditions can be compared. The ease of inclusion, as indicated by n in Table 1, follows the order aniline > phenol > benzene. The earliest report on this benzene clathrate suggested its stability under atmospheric conditions [2]. This was, however, questioned by Aynsley et al. [16] who reported the liberation of the guest under vacuum. In our experience, the benzene clathrate cannot be kept at ambient temperature (25 °C) under a static or dynamic N_2 atmosphere. After prolonged storage, the IR absorptions resulting from benzene are considerably reduced. We have also realized that the inclusion ratio of the benzene clathrate tends to be higher for

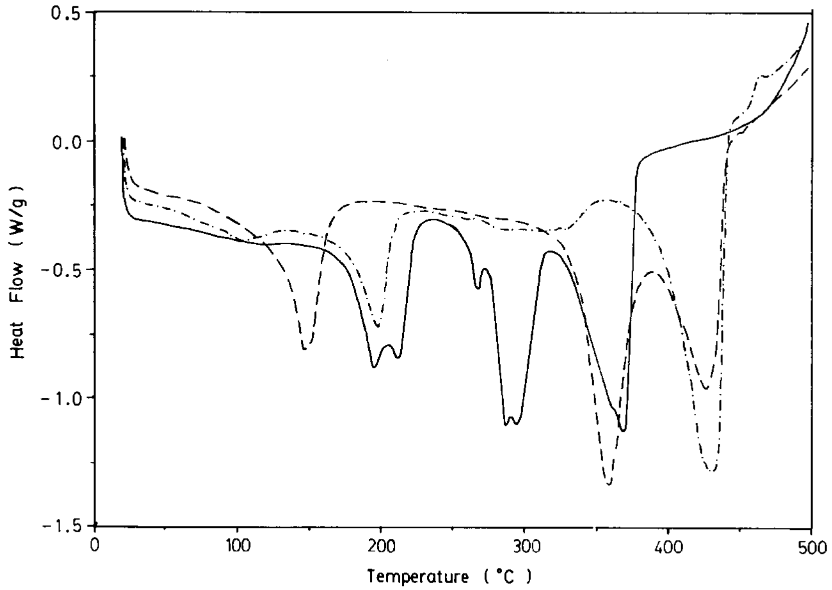

Fig. 4. DSC curves of the clathrates from aniline (———), pyridine (— — —) and aniline/pyridine mixture (· — · — ·).

preparations done at low temperature (0–10 ° C) or with a higher concentration of benzene. This poor affinity for benzene cannot be explained on steric grounds. The relatively higher stability of the aniline and phenol compounds, and their higher entrapping ratios, may in part be due to some electrostatic interactions between the host and guest. A lower dipole and polarity, and the absence of an electrophilic group, may render the benzene molecule unfavourable for such interaction.

To demonstrate a possible use of this nickel ammine complex as a selective scavenger for organic substrates, three experiments were carried out on the equimolar mixtures of pyridine and aniline, pyridine and benzene, and aniline and benzene. The latter two situations produced almost exclusively the pyridyl complex or aniline clathrate. The absence of the benzene clathrate is evident from the TG and DSC plots and the IR spectra. Only when a large excess (10-fold) of benzene is present does the clathrate show any significant trapping of the guest. The complex, however, shows no exclusive clathrating ability for aniline or pyridine. The IR spectrum of the product shows not only the usual coordinated pyridine absorptions but also those of free aniline. The DSC profile (Fig. 4) demonstrates that neither a pure pyridyl complex nor aniline clathrate is formed.

CONCLUSION

Our results demonstrate unequivocally that many thermal decompositional intermediates can be isolated and independently analysed. Through this quantitative and qualitative monitoring of the thermal degradation of the clathrates, one can have a better understanding of the composition and the guest/host relationship of many related clathrates which are difficult to evaluate by most solution and spectroscopic techniques currently used by coordination chemists.

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