Studies in Werner Clathrates. Part 14.[1] Analysis of the Properties selected for by the Host Bis(isothiocyanato)-tetra(4-vinylpyridine)nickel(II)

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The thermal characteristics of seven crystals with $[Ni(NCS)_2(vpy)_4]$ (vpy = 4-vinylpyridine) as host were analysed by thermal gravimetric analysis (TGA) and differential thermal analysis (DTA). No preferential guest loss for the clathrates with pairs of guests was observed. The enthalpy of the 'guest release reaction' for each clathrate was obtained from the DTA experiments. Solubility studies of the host were performed in the same guest solvents in order to obtain a better understanding of the clathration process. The results show that the basis of the selection of the host for guest molecules is related to solubility.

As discussed in Part 13,[1] the clathrating ability of the host $[Ni(NCS)_2(vpy)_4]$ (vpy = 4-vinylpyridine) has been studied in an attempt to determine the characteristics that this host selects for when enclathrating different guests. A series of guests was chosen comprising cyclic hydrocarbons each having a skeleton of six carbon atoms, but where the number of double bonds varied from zero to three: cyclohexane, cyclohexene, cyclohexa-1,3-diene, cyclohexa-1,4-diene and benzene. After extensive solid-state structural analysis of the clathrates **1**–**7** (thf = tetrahydrofuran) the hosts selectivity could not be explained.

1 $[Ni(NCS)_2(vpy)_4]\cdot 1.78\ thf\cdot 0.22\ C_6H_{12}$
2 $[Ni(NCS)_2(vpy)_4]\cdot 1.76\ thf\cdot 0.24\ C_6H_{10}$
3 $[Ni(NCS)_2(vpy)_4]\cdot 0.48\ thf\cdot 0.52\ C_6H_8$-1,3
4 $[Ni(NCS)_2(vpy)_4]\cdot 0.36\ thf\cdot 1.04\ C_6H_8$-1,4
5 $[Ni(NCS)_2(vpy)_4]\cdot 0.35\ thf\cdot 1.05\ C_6H_6$
6 $[Ni(NCS)_2(vpy)_4]\cdot 3\ C_6H_6$
7 $[Ni(NCS)_2(vpy)_4]\cdot 2$ thf

In this paper thermal gravimetric (TGA) and differential thermal analysis (DTA) of the above clathrates and solubility experiments on the host have been carried out with the intention of explaining the observed host : guest ratios and guest 1 : guest 2 ratios found in the crystal structures. Quantitative thermal analyses on Werner complexes have been reported since the mid 1960s.[2,3] As the guest molecules are not covalently bound to the host they are easily removed and usually give a characteristic weight loss at relatively low temperatures. Previous work has shown the host decomposition to proceed in four, three or two steps with each step giving the appropriate weight loss of 4-vinylpyridine.[4] Clathrates which dissociate into the host and guest before thermal decomposition of the host have been classified as thermally 'unstable' as opposed to the decomposition of 'stable' clathrates where chemical destruction of the host accompanies escape of the guest (Cassellato and Casu[5]). Werner clathrates with a high host : guest ratio are usually less stable, as shown by their layer-type structures which are less stable than the zeolite-like β-phases. Exceptions to this have been found for halogenated guests where there is secondary bonding between the host and guest.[6]

Results and Discussion

Thermal Analysis.—The isothermal runs for clathrates **1**–**5** show the loss of guest to be independent of host decomposition at 25 °C (Fig. 1). The curves indicate no preferential loss of one guest over the other in the clathrate–guest mixture. This may be expected as structural analysis shows the guest sites to be indistinguishable within each structure.[1] It is not possible to relate the different rates of guest loss to the properties of the guests alone, as the type of guest sites (channel or cavity) and the host : guest ratio must also be taken into account.

In agreement with the isomorphous nature of structures **1** and **2**, their rates of loss of guest are similar. The curves level off after 180 min with no weight loss attributable to host decomposition: weight loss 19.5 and 18.8% for **1** and **2** respectively; calculated weight loss 19.8%. The curve for structure **3** levels off after 95 min at 15.4% weight loss (calc. 11.4%). The TGA and DTA of this structure reveal an unusual host decomposition which is different from the systematic host decomposition of the other structures. The curves for structures **4** and **5** show identical rates of guest loss but do not level off after 18 h at 11.0% weight loss (calc. 15.5 and 15.3% respectively) indicating further guest desorption at a very slow rate.

The different rates of desorption may be attributed to the high vapour pressure of thf (162 mmHg at 25 °C). Structures **1** and **2** have 89 and 88% thf guest respectively, **3** with a different packing to **1** and **2** contains 48%, and **4** and **5** with the same packing as **3** contain 26 and 25% respectively.

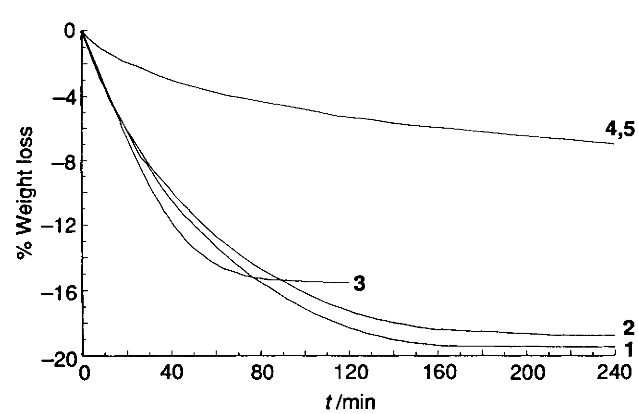

Fig. 1 Isothermal runs for clathrates 1–5

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The TGA curves (Fig. 2) show the mechanism of decomposition is as in Scheme 1 where nG = total number of guest

$$\begin{tikzcd}[\mathrm{Ni(NCS)_2(vpy)_4}]\cdot n\mathrm{G}\ (s) \arrow[d, "(1)"'] \\ [\mathrm{Ni(NCS)_2(vpy)_4}]\ (s) + n\mathrm{G}\ (g) \arrow[d, "(2)"'] \\ [\mathrm{Ni(NCS)_2(vpy)_2}]\ (s) + 2\mathrm{vpy}\ (g) \arrow[d, "(3)"'] \\ [\mathrm{Ni(NCS)_2}]\ (s) + 2\mathrm{vpy}\ (g)\end{tikzcd}$$

Scheme 1

molecules. Structure **3** deviates from the above decomposition sequence in that it has an additional step. Thus step (3) is modified as follows.

$$\begin{tikzcd}[\mathrm{Ni(NCS)_2(vpy)_2}]\ (s) + 2\mathrm{vpy}\ (g) \arrow[d, "(3a)"'] \\ [\mathrm{Ni(NCS)_2(vpy)_{0.5}}]\ (s) + 1.5\mathrm{vpy}\ (g) \arrow[d, "(3b)"'] \\ [\mathrm{Ni(NCS)_2}]\ (s) + 0.5\mathrm{vpy}\ (g)\end{tikzcd}$$

As discussed in Part 13 [1] the host molecules are isomorphous in structures **3**–**5**. The guests are in channels at the inversion centres in structure **3** and in the channels and cavities ($\bar{4}$ sites) in **4** and **5** with no host–guest interaction at the van der Waals level. This change in guest location and contents in structures **3**–**5** did not have any significance on structural analysis (host isomorphous and no change in host–guest interaction) but does show a difference in the isothermal runs (rate of guest desorption) and the TGA and DTA.

The DTA experiments were used to evaluate the enthalpy of the 'guest-release reaction' and the sample temperatures and enthalpies of each step in the above decomposition mechanism (Fig. 2). This was established by measuring the area under the endotherm in each DTA run. This area was assumed to be proportional to the enthalpy change, ΔH [equation (4)], where

$$\Delta H = Ak/m \qquad (4)$$

m = the sample mass (g), A = the area (cm^2) and k = the calibration factor (0.319 J cm^{-2}). The calibration factor was determined by relating the known enthalpy change of melting of pure naphthalene (m.p. = 80.2 °C) to the measured peak area of this enthalpy change.

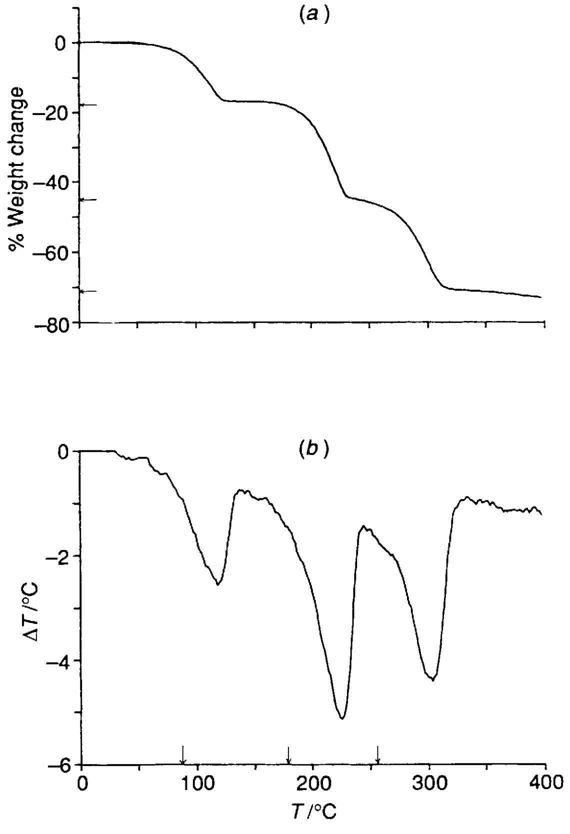

Fig. 2 The TGA (*a*) and DTA (*b*) curves for clathrate **1**

According to the previously mentioned classification all these clathrates are unstable with the guest molecules being released before host decomposition, confirming the structural result that the guests are not strongly enclosed/bonded by the host in structures **1**–**7**. The large differences in the measured enthalpies of guest release (21–55 kJ mol^{-1}, Table 1) are an unexpected result based on the crystal structure results.

The temperature of guest release (to the gaseous phase) is a function of the host–guest interactions *and* of the physical properties of the guest itself. The parameter, temperature of guest release–guest boiling point, $T - T_b$, has been used as a measurement of the relative stability of inclusion compounds.[7] In comparing structures **6** (benzene guest only, $T - T_b = 38 - 80 = -42$ °C) and **7** (thf guest only, $T - T_b = 21 - 66 = -45$ °C), according to this parameter they are of comparable stability. However solvent competition results [benzene–thf (1 : 1 v/v)] for the formation of clathrate **5** indicate the preference of benzene over thf as 3 : 1.

No correlation was found between the packing densities [1] of the structures and the temperature of guest release.[4]

The values obtained for the enthalpy associated with the

Table 1 Thermal analysis results (TGA and DTA)

Clathrate	Step	Weight loss (%) Calc.	Weight loss (%) Measured	Sample temperature*/°C	Area/cm^2	ΔH/kJ mol^{-1}
1	(1)	19.8	17.5	38	1.7	37
	(2)	48.1	45.0	137	3.9	86
	(3)	76.4	71.0	217	3.3	72
						195
2	(1)	19.8	13.0	47	1.1	26
	(2)	48.1	42.0	143	4.3	102
	(3)	76.4	68.0	217	3.9	92
						220
3	(1)	11.4	11.0	41	1.0	21
	(2)	42.7	44.0	137	4.4	92
	(3a)	66.1	67.0	223	2.4	50
	(3b)	74.0	76.5	301	0.8	17
						180
4	(1)	15.5	14.0	64	1.5	33
	(2)	45.3	44.5	140	3.9	87
	(3)	75.2	72.0	232	2.6	58
						178
5	(1)	15.3	13.0	49	2.4	52
	(2)	45.2	43.0	139	5.6	121
	(3)	75.1	69.5	232	3.9	84
						257
6	(1)	28.2	21.0	38	2.1	55
	(2)	53.6	48.0	121	3.6	94
	(3)	78.9	72.0	216	2.8	73
						222
7	(1)	19.5	16.5	21	1.6	38
	(2)	47.9	45.0	137	4.5	107
	(3)	76.4	72.0	223	4.0	95
						240

* Corrected by use of equation (5).

Table 2 Physical properties of guest molecules[9–15]

Guest	No. of π electrons	μ^a/D	V^b/Å^3	ρ^c/g cm^{-3}	M.p./°C	B.p./°C	P(vap)^d/ mmHg	M	α^e/Å^3	ΔH^f/J g^{-1} obs.	ΔH^f/J g^{-1} calc.^{g}
Cyclohexane	0	0.0	102.6	0.778	6.5	81.0	98	84.16	11.0	357 (30.05)	370
Cyclohexene	2	0.55	97.8	0.810	−104.0	83.0	89	82.15	10.7	371 (30.48)	381
Cyclohexa-1,3-diene	4	0.44	93.0	0.840	−98.0	80.5	98^h	80.13	—	—	388
Cyclohexa-1,4-diene	4	—	93.0	0.847	−49.0	87.0	68^h	80.13	10.41^i	—	395
Benzene	6	0.0	88.2	0.877	5.5	80.0	95	78.11	10.32	394 (30.78)	398
Tetrahydrofuran	0	1.63	78.4	0.889	−108.0	66.0	162	72.11	7.96^j	414 (29.85)	414

[a] Dipole moment; D $\approx 3.33 \times 10^{-12}$ Cm. [b] Theoretical volume calculated from ref. 9. [c] Density at 20 °C. [d] Vapour pressure at 25 °C; mmHg $\approx$ 133 Pa. [e] Static average electric dipole polarizability for ground state. [f] Observed enthalpy of vaporization at boiling point; values in parentheses are in kJ mol^{-1}. [g] Using Trouton's rule. [h] Calc. from ref. 12. [i] Ref. 13. [j] Ref. 14.

removal of the first two bases are always higher than those obtained for the removal of the remaining two bases, showing the two-base intermediate to be less stable than the four-base complex. The dark, yellowish brown powder remaining at the end of each thermal analysis resembled that described for [Ni(NCS)$_2$] upon thermal analysis of [Ni(NCS)$_2$(NH$_3$)$_4$] under N$_2$.[8]

Physical Properties of the Guests.—The following properties[9–15] of the guests in their pure liquid state at atmospheric pressure are listed in Table 2: number of π electrons, dipole moment, molecular volume, density, melting point, boiling point, vapour pressure, molecular weight, polarizability and enthalpies of vaporization.

The crystal structures show no significant host–guest interaction[1] and with the host and guests being essentially organic non-electrolytes one may expect selective enclathration to depend on non-specific intermolecular interactions such as dispersion forces, which should be correlated with the molar polarizability of the guests. With the exception of thf, the polarizability of the guest molecules shows a general trend of decreasing polarizability favouring enclathration. The significantly lower polarizability of thf precludes polarizability as a dominant guest property that the host selects for during enclathration.

During clathrate formation the guest molecules are separated from the liquid phase and this separation process may be likened to vaporization. With the exception of thf, the enthalpy of vaporization also shows the unexpected general trend of increasing enthalpy of vaporization favouring enclathration. The enthalpy values for thf do not fit into this trend and thus the significantly different guest ratios found in solution and in the crystal structures are unexplained.

Solubility Studies.—Fig. 3 illustrates the solubility curves obtained for [Ni(NCS)$_2$(vpy)$_4$] (weight host powder per 100 cm^3 solvent) as a function of temperature. The area below each curve represents a two-phase system which contains saturated solution and undissolved host powder. Above each curve the solution is clear with no undissolved host (single phase). The temperature range is from 24 to *ca.* 64 °C with higher temperatures resulting in host decomposition as the solutions changed from their characteristic blue to green.

Of the above guest properties, the solubility curves show the only consistent characteristic which varies in the same manner as the guest ratios found in the clathrates. As crystal formation occurred at approximately 25 °C the solubility curves are discussed in this region. For the 50% v/v mixtures the host is least soluble in thf–cyclohexane (a), with increasing solubility for the series thf–cyclohexene (b), thf–cyclohexa-1,3-diene (c), thf–cyclohexa-1,4-diene (d) and thf–benzene (e). In relation to the crystalline state it appears that as the host solubility increases for each mixture, thf is excluded.

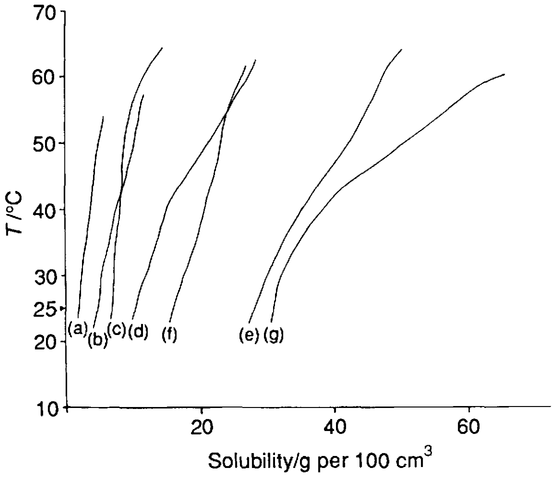

Fig. 3 Solubility curves of [Ni(NCS)$_2$(vpy)$_4$] in (a) thf–cyclohexane, (b) thf–cyclohexene, (c) thf–cyclohexa-1,3-diene, (d) thf–cyclohexa-1,4-diene, (e) thf–benzene, (f) benzene and (g) thf

Table 3 summarizes the mole ratios and volume ratios in the crystal structures and in solution at 25 °C. As solutions (a)–(e) are 50% v/v mixtures each has a molar excess of thf. The volume ratios were calculated using the experimental volume of 774.4 Å^3, as obtained from the α phase.[16]

No correlation is observed between host solubility and clathrate stability (temperature of guest release).[4]

This study provides a qualitative understanding for the observed guest ratios obtained in the clathrates **1**–**5**. That is, prior to crystallization the second solvent surrounds the host, [Ni(NCS)$_2$(vpy)$_4$], to a greater degree and is enclathrated by the host. With the volume of thf remaining constant for each solubility curve, the increased solubility can only be attributed to the second solvent. Further work in determining the enthalpy and/or free energy of solvation of the host in organic solvents

Table 3 Mole ratio (volume ratio*) in crystal structures and in solution at 25 °C

Structure or solution	
1	Host: thf : cyclohexane 1 : 1.78 : 0.22 (1 : 0.18 : 0.03)
(a)	1 : 190 : 141 (1 : 19.4 : 18.9)
2	Host: thf : cyclohexene 1 : 1.76 : 0.24 (1 : 0.16 : 0.03)
(b)	1 : 76.4 : 60.4 (1 : 7.71 : 7.60)
3	Host: thf : cyclohexa-1,3-diene 1 : 0.48 : 0.52 (1 : 0.04 : 0.06)
(c)	1 : 53.0 : 44.4 (1 : 5.34 : 5.31)
4	Host: thf : cyclohexa-1,4-diene 1 : 0.36 : 1.04 (1 : 0.03 : 0.12)
(d)	1 : 35.4 : 30.3 (1 : 3.57 : 3.63)
5	Host: thf : benzene 1 : 0.35 : 1.05 (1 : 0.03 : 0.12)
(e)	1 : 13.1 : 11.8 (1 : 1.33 : 1.35)
6	Host : benzene 1 : 3 (1 : 0.34)
(f)	1 : 41.6 (1 : 4.75)
7	Host : thf 1 : 2 (1 : 0.19)
(g)	1 : 23.6 (1 : 2.39)

* Obtained from the calculated molecular volumes in Table 2.

should be helpful in understanding selective enclathration and its potential application.

For the above experimental systems, the interpretation invokes a 'gross' selection criterion with the ratio of solvent molecules surrounding the host molecules prior to crystallization being enclathrated. However it is noted that structure **6** with only benzene as guest has the highest host:guest ratio of 1 : 3 with the host being less soluble in pure benzene than in pure thf which yielded a host:guest ratio of 1 : 2. Here the high symmetry of the guest, benzene, may be another parameter in determining its ability to co-crystallize with another molecule of high symmetry, that is to occupy similar symmetry sites in the crystal structure without disorder.

Experimental

The synthesis of the host complex $[Ni(NCS)_2(vpy)_4]$, its crystal growth and structural analysis are described in Part 13.[1]

Thermal Analysis.—All thermograms were carried out on a Stanton-Redcroft Thermal Analyser (STA 780). Crystals were cut in the presence of mother-liquor, removed, dried by patting and weighed quickly before analyses.

All isothermal runs were carried out at 25 °C and a dinitrogen flow rate of 60 $cm^3 min^{-1}$. The crystals were sufficiently large to enable each sample to have comparable dimensions. That is, each single crystal was cut to weigh 10 ± 1 mg. This is necessary in comparing rates of guest loss which may be diffusion controlled. The curves obtained are percentage weight loss *versus* time in minutes or hours.

For differential thermal analyses a heating rate of 10 °C min^{-1} and a dinitrogen flow rate of 60 $cm^3 min^{-1}$ were used with inert alumina (Al_2O_3) as the reference material. The sample container was a platinum crucible located directly on top of the thermocouple, allowing direct measurement of the furnace temperature only. The lag between furnace and sample temperature was obtained by running six standards with known melting points (373–573 K). Equation (5) is the resulting

$$\text{sample temperature} = 1.05\,(\text{furnace temperature}) - 51.45\ {}^{\circ}\text{C} \quad (5)$$

calibration with which all quoted sample temperatures were corrected.

Solubility Studies.—Solubility studies of the host in analytically pure thf, cyclohexane, cyclohexene, cyclohexa-1,3-diene, cyclohexa-1,4-diene, benzene and 50% v/v mixtures of thf with the last five solvents were performed in 100 cm^3 of solvent at 25 °C. The apparatus used was the same as for distillation with the solubility points obtained on heating and cooling about the solubility temperatures. Visual observation was used in determining the presence of undissolved host.

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