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Tetrakis(4-aminopyridine)diisothiocyanatonickel(II) and its clathrates with EtOH, Me_2CO and DMSO: structures, thermal stabilities and guest exchange †

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The structures of the Werner complex, $Ni(NCS)_2(4\text{-}NH_2\text{-}py)_4$ as the apohost, **1**, and its inclusion compounds with EtOH/Me_2CO, **2**, and DMSO, **3**, have been elucidated. The dynamics of guest exchange between the clathrates have been monitored by DSC. The inclusion compounds can be formed by exposing the host to vapour of the guest, and powder XRD shows this reaction to be fully reversible.

Introduction

Werner clathrates are formed by hosts of general formula MX_2A_4, where M is a divalent transition metal (typically Ni^{2+}, Co^{2+}, Fe^{2+} or Mn^{2+}), X is an anionic ligand such as NCS^- or a halide, and A is a pyridine or arylamine. These compounds have the ability to enclathrate a variety of aromatic compounds, and the fact that the process is selective was exploited by Schaeffer *et al.*[1] for the separation of hydrocarbon mixtures. The subject has been reviewed by Lipkowski[2] and continues to attract attention because the inclusion compounds formed yield detailed structural information which is of importance to the understanding of molecular recognition. The aristotype of these host compounds is $Ni(NCS)_2(4\text{-Me-py})_4$ which has been studied intensively. In particular, a thermokinetic study of this host with xylene isomers has revealed the mechanism of enclathration,[3] and a calorimetric and thermogravimetric study of this host with mixtures of methanol/4-methylpyridine and acetone/4-methylpyridine yielded values of the partial molar enthalpies of enclathration of individual guests.[4] The librational frequencies of *p*-dichlorobenzene in various Werner clathrates have been determined from the temperature dependence of the ^{35}Cl nuclear quadrupole resonance frequencies.[5] Recently, the influence of guest polarity[6] and host–host interactions as a function of guest size and shape has been studied.[7] The novel host bis(dibenzoylmethanato)dipyridinenickel(II) and the structures of its clathrates with various guests, have been elucidated.[8] We now present the structures of $Ni(NCS)_2(4\text{-}NH_2\text{-}py)_4$ **1** and its clathrates with EtOH/Me_2CO and DMSO, and discuss their thermal stabilities and dynamics of guest exchange.

Experimental

The host compound **1** was prepared by adding stoichiometric quantities of a methanolic solution of 4-aminopyridine (4 ml, 0.1 M) to an ethanolic solution of nickel isothiocyanate (1 ml, 0.1 M). Crystals appeared by slow evaporation over a period of seven days (Found: C, 47.99; H, 4.39; N, 25.60; S, 11.34. $Ni(NCS)_2(C_5H_6N_2)_4$ requires C, 47.95; H, 4.39; N 25.42; S, 11.64%). The inclusion compounds **2** and **3** were prepared in a similar way, except that in the preparation of **2** the 4-aminopyridine ligand was dissolved in acetone, while in that of **3** the nickel isothiocyanate was dissolved in DMSO.

Preliminary cell parameters and space groups were determined photographically, and subsequently refined by standard procedures on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-Kα radiation. The data collections were carried out at 173 K for **1** and **2**, and at 100 K for **3**. The relevant crystal and experimental data are given in Table 1. All three structures were solved by direct methods using SHELXS 97, followed by full-matrix least squares refinement on F^2 with SHELXL 97.[9]

CCDC reference number 155036–155038.

See http://www.rsc.org/suppdata/dt/b0/b010042k/ for crystallographic data in CIF or other electronic format.

Thermal analyses were performed on a Perkin-Elmer PC7 series system. All samples were air-dried and lightly crushed before analysis. They were placed in vented aluminium pans for differential scanning calorimetry (DSC) and in an open platinum pan for thermogravimetry (TG). Sample masses used varied from 2 to 5 mg, and the samples were purged by a stream of nitrogen flowing at 40 ml min^{-1}. A heating rate of 20 °C min^{-1} was employed in all cases.

X-Ray Powder Diffraction (XRPD) experiments were carried out on a Phillips PW1752/00 diffractometer using Cu-Kα radiation. The sample was ground to a fine powder and loaded into an aluminium tray. Hot-stage Microscopy (HSM) was performed on a Linkam TH600 hot-stage in conjuction with a Linkam TP92 temperature controller, at a heating rate of 20 °C min^{-1}. Images were captured by a Sony Hyper-HAD Digital video camera.

Results and discussion

The host compound, **1**, crystallises in the space group *Pccn*, with $Z = 4$. Symmetry requirements place the Ni atom at a special position, and it was located on a diad at Wyckoff position *d*. The isothiocyanato moieties are in the *trans* configuration and the 4-aminopyridine ligands adopt the propeller configuration, a common feature in the structure of Werner clathrates.[10] All bond lengths and angles are within the expected range for compounds of this type.[11] The packing of **1** as viewed along [001] is shown in Fig. 1. The host molecules are located in columns stacked in the [001] direction, and are related by centres of inversion. The molecules are stabilised by weak intermolecular N–H···N and N–H···S hydrogen bonds, represented in Fig. 1 as broken and dotted lines respectively. Of

† Werner clathrates. Part 14.[13]

Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagrams in CHIME format. See http://www.rsc.org/suppdata/dt/b0/b010042k/

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Table 1 Crystal data, experimental and refinement parameters for compounds **1**–**3**

	1	**2**	**3**
Molecular formula	$C_{22}H_{24}N_{10}NiS_2$	$C_{22}H_{24}N_{10}NiS_2{\cdot}C_2H_6O{\cdot}C_3H_6O$	$C_{22}H_{24}N_{10}NiS_2{\cdot}2C_2H_6SO$
Host : guest ratio	—	1 : 1 : 1	1 : 2
M	551.32	655.47	707.60
Crystal symmetry	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$Pccn$	$P2_12_12_1$	$P2_12_12_1$
a/Å	17.046(3)	10.529(1)	10.264(1)
b/Å	9.627(2)	15.816(1)	15.790(1)
c/Å	16.129(3)	21.700(1)	21.883(1)
Z	4	4	4
V/Å^3	2646.8(9)	3613.6(2)	3546.5(2)
μ(Mo-Kα)/mm^{-1}	0.922	0.689	0.821
No. reflections collected	12674	17030	15491
No. unique reflections	3517	7029	7790
R(int)	0.0356	0.0463	0.0251
Data/restraints/parameters	3517/0/207	7029/0/350	7790/0/403
Final R ($I > 2\sigma I$)	0.0319	0.0632	0.0551
(all data)	0.0584	0.1144	0.0629

Table 2 Hydrogen bonds for compounds **1** to **3**

Compound	Donor···acceptor[a]	d(D–H)/Å	d(H···A)/Å	D–H···A/°	d(D···A)/Å
1	N5···N3[b]	0.843	2.414	168.35	3.244
	N5···S1[c]	0.854	2.830	144.13	3.558
	N3···S1[d]	0.820	2.862	152.40	3.609
2	N10···O1	0.880	2.164	161.01	3.010
	N6···O2A	0.880	2.037	158.65	2.875
	N6···O2B	0.880	2.073	151.40	2.877
3	N10···O2A	0.880	2.068	156.90	2.899
	N10···O2B	0.880	1.913	163.74	2.769
	N6···O1A	0.880	2.077	168.64	2.945
	N6···O1B	0.880	1.985	151.67	2.791

[a] A,B notation refers to atoms of a disordered system. [b] Symmetry operation $x, \frac{3}{2} - y, \frac{1}{2} + z$. [c] Symmetry operation $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$. [d] Symmetry operation $x, \frac{1}{2} - y, z - \frac{1}{2}$.

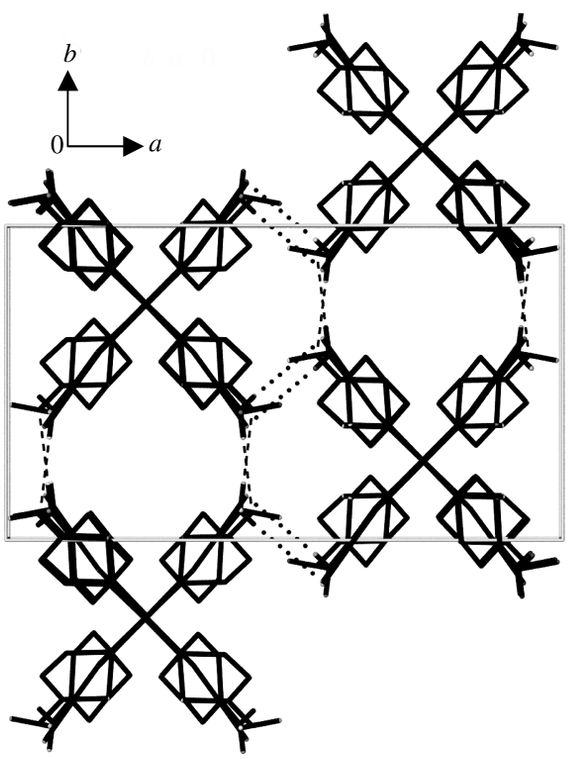

Fig. 1 The packing of **1** viewed along [001].

the two amino groups present in the asymmetric unit, one is planar and acts as a hydrogen bond donor only (N5), whereas the other is pyramidal, with the lone pair on N3 acting as a hydrogen bond acceptor. Full hydrogen bonding data for all three compounds are given in Table 2.

The inclusion compounds **2** and **3** both crystallise in the space group $P2_12_12_1$, with $Z = 4$, and the Ni atoms occupy a general position in the unit cell. The packing of **2** and **3** is similar. The two structures may be regarded as isostructural with respect to the host molecules, differing only in the positions of the guest molecules. In **2** the ethanol molecule is disordered over two sites, with a shared α-C atom, and in **3** the two independent DMSO guests are each disordered over two sites. The packing of **2,** shown in Fig. 2(a), reveals the guest molecules to be located in channels running parallel to [100]. A space-filling projection of the channels in **2**, with the guest molecules omitted, is shown in Fig. 2(b). The EtOH, Me_2CO and DMSO guests form (guest)O···H–N(host) hydrogen bonds to the amino groups of 4-aminopyridine ligands. In addition, weak (host)N–H···S(host) interactions, in the range 2.579 to 2.823 Å, could be identified in **2** and **3**. Although the aromatic rings of the host molecules appear to be stacked, this interaction must be weak, as the distance between the rings exceeds the expected value of ≈3.5 Å for π–π stacking.

The thermal analyses of all three compounds are shown in Fig. 3(a)–3(c). The host compound, **1**, decomposes in three distinct steps, as shown in Fig. 3(a). The first step, B, corresponds to the loss of two 4-aminopyridine ligands, followed by steps C and D, each corresponding to loss of one 4-aminopyridine ligand. The DSC shows two endotherms corresponding to steps B and C, but the trace for step D is complex due to ligand decomposition. This multi-step decomposition was followed by hot-stage microscopy. The first change observed in the crystals occurs in the temperature range corresponding to step B, when the translucent purple crystals bubble and turn opaque blue. The bubbling continues during step C, and the

Table 3 Thermal analysis data for compounds **1**–**3**

	1				**2**				**3**			
Step	T_{onset}/°C	Calc. %	Exp. %	T_{peak}/°C	T_{onset}/°C	Calc. %	Exp. %	T_{peak}/°C	T_{onset}/°C	Calc. %	Exp. %	T_{peak}/°C
A	—	—	—	—	58.7	15.9	17.0	107.1	131.4	22.1	22.4	198.2
B	215.2	34.2	33.0	292.3	211.5	28.7	28.0	289.6	207.2	26.6	25.9	288.6
C	289.9	17.1	17.8	320.7	288.6	14.4	14.3	316.6	270.9	13.3	12.6	319.6
D	332.6	17.1	16.7	—	327.6	14.4	13.9	—	311.6	13.3	13.3	—

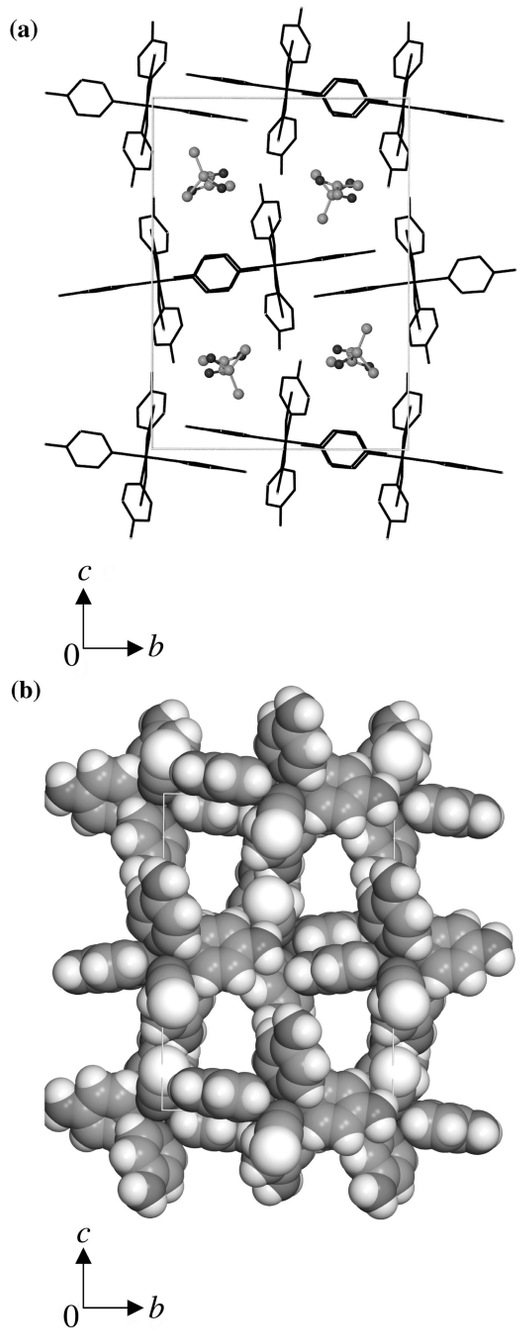

Fig. 2 (a) The packing of **2** viewed along [100], with host molecules in stick form and EtOH/Me_2CO guests in ball-and-stick form. (b) Van der Waals representation of the host molecules of **2** viewed along [100], showing the channel structure.

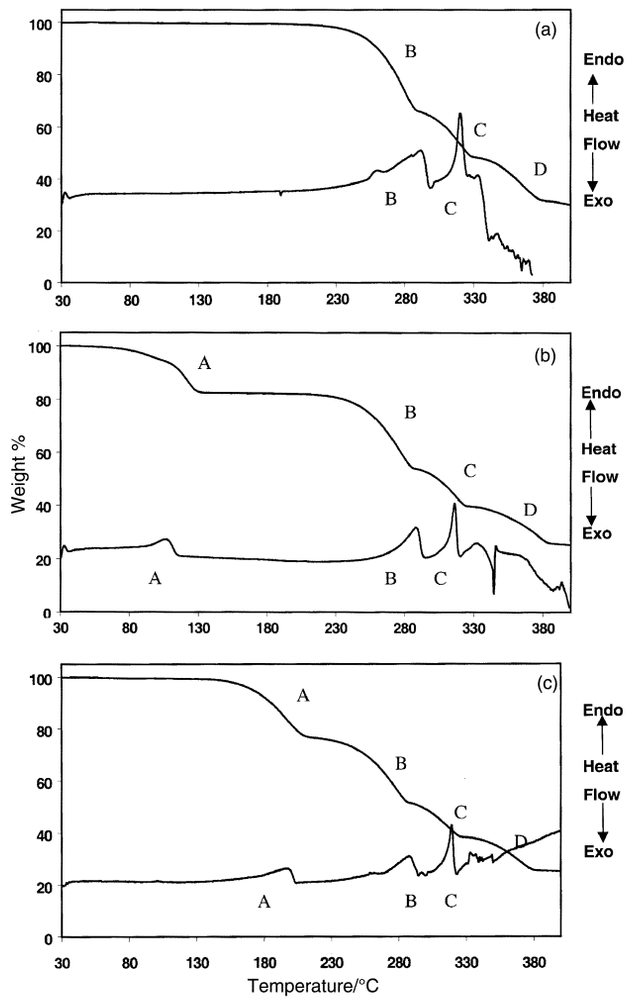

Fig. 3 TG and DSC scans of compounds (a) **1**, (b) **2**, and (c) **3**.

crystals turn green. In the early stages of step D the crystals melt to a dark black-brown liquid, confirming the ligand decomposition reaction observed in the DSC. The inclusion compounds **2** and **3** undergo an additional, single-step weight loss reaction, shown as step A in Fig. 3(b) and 3(c), corresponding to the release of the guest molecules from the host channels. The observed weight loss justifies the assignment of a host: guest ratio of 1 : 2 for both compounds (in the case of **2** the presence of two different guest molecules was also confirmed by GC). Following guest release the host decomposition reactions, B–D, follow the same pattern observed for **1**. A comparison of the thermal analysis data of **2** and **3** reveals that the more volatile EtOH/Me_2CO guests are released *ca.* 90 °C before the DMSO guests. During step A, in both **2** and **3**, the translucent purple crystals bubble and turn opaque. Thereafter, the crystals turn blue, then green, before melting to a dark liquid, as observed in the HSM of **1**. The relevant TG (T_{onset}, calculated and experimental weight loss) and DSC (T_{peak}) data are given in Table 3.

The fact that **2** and **3** have the same infinite channel structure led us to attempt a guest exchange reaction. Small single crystals of **2** were exposed to DMSO vapour in a sealed vessel at 35 °C. The crystals were sampled at regular intervals by DSC. The resulting DSC traces are shown in Fig. 4. The initial endotherm at T_{peak} = 107 °C, corresponding to the release of the EtOH/Me_2CO guests, migrates to the right until it reaches 198 °C, corresponding to the release of pure DMSO. A single,

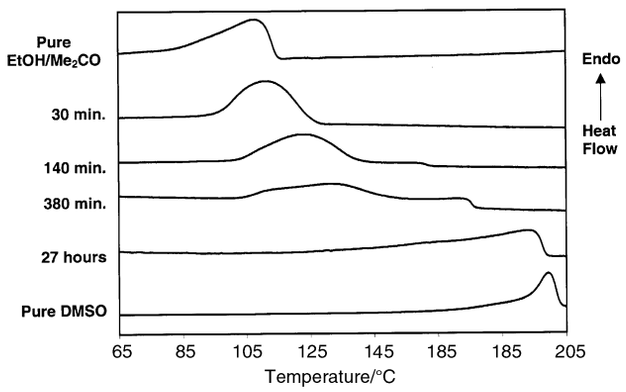

Fig. 4 Migration of desolvation endotherm as a function of time ($H{\cdot}EtOH{\cdot}Me_2CO \longrightarrow H{\cdot}2DMSO$).

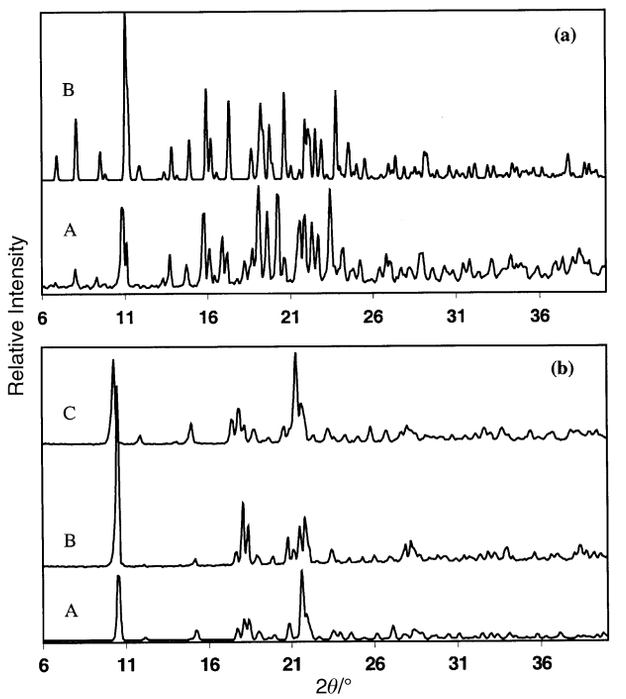

Fig. 5 (a) XRD traces of (A) **1** after exposure to DMSO vapour, and (B) the calculated pattern for **3**. (b) XRD traces of (A) the calculated pattern for **1**, (B) the experimental pattern for **1** and (C) the experimental pattern obtained by heating **2**.

moving endotherm indicates that a continuous solid solution of the mixed guests is formed in the channels of the host. This result is similar to that obtained for the Me_2CO and DMSO inclusion compounds formed by the organic host 1,4-bis(9-hydroxy-9-fluorenyl)benzene.[12]

It was found that **3** could also be generated by exposing the single crystal or powder forms of the pure host, **1**, to DMSO vapour in a sealed vessel at 35 °C. The inclusion process **1** $\longrightarrow$ **3** was confirmed by TG and XRPD, and the XRPD trace of the product is shown in Fig. 5(a). In addition, the product obtained on heating **2** or **3** at *ca.* 70 °C for 30 minutes was found to be the pure host, **1**, indicating that the inclusion process is fully reversible. The desolvation process **2/3** $\longrightarrow$ **1** was again confirmed by TG and XRPD. The XRPD trace of compound **1**, as well as that of the product obtained on heating **2**, are shown in Fig. 5(b).

Concluding remarks

The structures of two new Werner clathrate inclusion compounds, as well as that of the pure host, have been elucidated. The two inclusion compounds are found to be isostructural with respect to the host lattice, which forms an infinite channel structure. This open channel structure allows for the exchange of guest molecules without disruption of the host lattice.

Acknowledgements

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