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Tetrakis(3-cyanopyridine)diisothiocyanatonickel(II) and its clathrates with EtOH and CH_2Cl_2: structures, thermal stabilities and enthalpies of guest release †

Mairi L. Kilkenny * and Luigi R. Nassimbeni

Department of Chemistry, University of Cape Town, Rondebosch, 7701, South Africa.
E-mail: xrayluig@science.uct.ac.za

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The structures of the α-host complex, $Ni(NCS)_2(3\text{-cyanopyridine})_4$, **1**, and its clathrates with EtOH, **2**, and CH_2Cl_2, **3**, have been elucidated. The enthalpies of the guest release reaction have been determined by applying the Clausius–Clapeyron equation to the guest vapour pressure *vs.* temperature data for the thermal decomposition of the solid inclusion compounds. XRPD and thermal analysis studies show the sorption–desorption process **1**↔**3**, and the guest exchange reactions **2**↔**3**, to be fully reversible.

Introduction

Werner clathrates are formed by host molecules of general formula MX_2A_4, where M is a divalent metal ion (typically Ni^{2+}, Co^{2+}, Fe^{2+}, Cu^{2+} or Mn^{2+}), X is an anionic ligand (NCS^-, NO_3^-, Br^-, Cl^-, I^- and others), and A is a neutral pyridine derivative or arylalkylamine. The most widely used host complex to date is $Ni(NCS)_2(4\text{-methylpyridine})_4$, although complexes incorporating ethyl-,[1] vinyl-,[2] phenyl-[3] and butyl[4]-substituted pyridine ligands, as well as chiral α-substituted arylalkylamines,[5,6] have also been reported. Werner complexes are renowned for their ability to selectively enclathrate a variety of organic compounds, a property that was first applied by Schaeffer *et al.*[7] to the separation of aromatic hydrocarbon mixtures. From the many Werner-type inclusion compounds studied, four general structure types emerge:[8] (1) the true clathrate, in which the host complexes pack to form discrete cavities, as found in $Ni(NCS)_2(4\text{-methylpyridine})_2(4\text{-phenylpyridine})_2\cdot C_3H_8O_2$,[9] (2) the infinite channel structure, found in $Ni(NCS)_2(4\text{-aminopyridine})_4\cdot C_2H_5OH\cdot C_3H_6O$,[10] (3) the layer structure, found in $Ni(NCS)_2(4\text{-methylpyridine})_4\cdot 2C_{10}H_8$[11] and (4) the zeolite-type structure, consisting of an interconnected 3-D network of cages. An excellent review by Lipkowski emphasises the importance of Werner clathrates as subjects for investigating the process of host–guest molecular recognition during clathrate formation.[8] In addition, they are ideal compounds for studying the effect of external non-bonded interactions on the molecular structure of the host complex. A study of the host–host interactions as a function of guest size and shape has been made, in which the change in geometry of the host lattice upon inclusion of various guest molecules was analysed.[12] In addition, the influence of guest polarity on the process of clathrate formation has been studied.[13] The majority of Werner complexes synthesised to date have incorporated hydrocarbon-substituted pyridine ligands, with the result that only weak van der Waals interactions exist between the components in the crystal. The use of pyridine ligands with potential hydrogen bonding substituents, such as amino, cyano, hydroxy or amide groups, leads to the formation of Werner clathrates with a higher affinity for polar, rather than hydrophobic, guest molecules. We now present the structures of $Ni(NCS)_2(3\text{-cyanopyridine})_4$ and its clathrates with EtOH and CH_2Cl_2, and discuss their thermal stabilities and enthalpies of guest release.

Experimental

The host compound **1** was prepared by adding stoichiometric quantities of an aqueous solution of 3-cyanopyridine (4 ml, 0.1 M) to an ethanolic solution of nickel isothiocyanate (1 ml, 0.1 M). Blue, needle-like crystals of $Ni(NCS)_2(3\text{-cyanopyridine})_4$ appeared by slow evaporation over a period of two days (Found: C, 52.81; H, 2.73; N, 23.69; S, 10.85. $C_{26}H_{16}N_{10}NiS_2$ requires C, 52.36; H, 2.23; N, 23.54; S, 10.45%). The inclusion compounds with ethanol (**2**) and dichloromethane (**3**) were prepared in a similar way, except that the 3-cyanopyridine ligand was dissolved in ethanol and dichloromethane respectively.

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 150 K for **2** and **3**, and at 173 K for **1**. 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 SHELX-97.[14]

CCDC reference numbers 168905–168907.

See http://www.rsc.org/suppdata/dt/b1/b105299n/ for crystallographic data in CIF or other electronic format.

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

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† Werner clathrates. Part 15.[10]

Electronic supplementary information (ESI) available: XRPD traces for **1**–**3** and for the product obtained on exposure of **1** to CH_2Cl_2 vapour; graphical representation of the Clausius–Clapeyron equation for the thermal decomposition of **2** and **3**; rotatable 3-D crystal structure diagrams in CHIME format. See http://www.rsc.org/suppdata/dt/b1/b105299n/

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

	1	**2**	**3**
Molecular formula	$C_{26}H_{16}N_{10}S_2Ni$	$C_{26}H_{16}N_{10}S_2Ni{\cdot}2C_2H_6O$	$C_{26}H_{16}N_{10}S_2Ni{\cdot}2CH_2Cl_2$
Host : guest ratio	—	1 : 2	1 : 2
M	591.3	683.5	761.2
Crystal symmetry	Orthorhombic	Monoclinic	Monoclinic
Space group	$Pna2_1$	*C*2/*c*	*C*2/*c*
a/Å	20.439(4)	17.737(4)	17.813(1)
b/Å	10.413(2)	11.527(2)	11.553(1)
c/Å	12.946(3)	17.120(3)	17.112(1)
β/°	90	96.65(3)	97.67(1)
Z	4	4	4
V/Å^3	2755.3(1)	3476.8(1)	3490.0(2)
Calculated density/g cm^{-3}	1.43	1.31	1.45
μ(Mo-Kα)/mm^{-1}	0.89	0.72	1.02
F(000)	1208	1416	1544
No. reflections collected	7207	8676	6867
No. unique reflections	6333	3921	3598
R(int)	0.0202	0.0392	0.0356
Data/restraints/parameters	6333/1/353	3923/3/194	3598/4/233
Final *R* ($I > 2\sigma I$)	0.0340	0.0573	0.0550
(all data)	0.0748	0.1061	0.0737

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 conjunction with a Linkam TP92 temperature controller, at a heating rate of 20 °C min^{-1}. Images were captured and analysed using a Sony Hyper-HAD Digital video camera.

Accurate values for the enthalpies of guest release for compounds **2** and **3** were obtained by measuring the vapour pressure of the guest, resulting from the thermal decomposition of the solid clathrate, at various temperatures.[15] The powdered sample is placed in a small sample flask (volume *ca.* 2 cm^3) which is connected to a glass tube containing a transducer. The transducer produces a voltage signal that is directly proportional to the pressure at its aperture. The sample is cooled on solid CO_2, and the system evacuated to remove any surface solvent. The system is then sealed and placed in a waterbath containing a thermocouple, which monitors the temperature throughout the experiment. The temperature of the system was raised at increments of 3 °C for all experiments, allowing sufficient time after each increment for the system to reach equilibrium, and the corresponding vapour pressures were recorded. The apparatus was calibrated using liquid CCl_4, over the temperature range 25–70 °C. The enthalpy value obtained ($\Delta H_{evap} = 32.35$ kJ mol^{-1}) is in good agreement with the literature value[16] ($\Delta H_{evap} = 32.20$ kJ mol^{-1}).

Results and discussion

Crystal structures

The host compound, **1**, crystallises in the space group $Pna2_1$, with $Z = 4$. The two isothiocyanato moieties are in the *trans*-configuration, while the four 3-cyanopyridine ligands adopt the energetically favoured propeller conformation. This particular ligand arrangement is commonly observed in the structures of Werner complexes.[17] All bond lengths and angles are within the expected range for compounds of this type.[18] The host molecules pack to generate layers which run perpendicular to the [001] direction, as shown in Fig. 1. Adjacent layers are linked by weak intermolecular C–H···N≡C hydrogen bonds. Full hydrogen bonding data for compounds **1**–**3** are given in Table 2 (atom numbering schemes for **1**–**3** are provided as supplementary material).

The inclusion compounds **2** and **3** both crystallise in the space group *C*2/*c*, with $Z = 4$ and a host : guest ratio of 1 : 2. The Ni atom was located on a diad at Wyckoff position *e*. The packing of the two structures is similar, and they may be regarded as isostructural with respect to the host molecules, differing only in the positions of the guest molecules. In **2** the oxygen atom of the ethanol guest is disordered over two positions, which refined with site occupancy factors of 37% and 63%, while in **3** the entire dichloromethane molecule is disordered over two positions, which refined with site occupancy factors of 58% and 42%. The packing of **3**, as shown in Figs. 2(a) and (b), reveals the guest molecules to be located in sinusoidal channels running parallel to the [10$\bar{1}$] direction. In both **2** and **3**, weak intermolecular C–H···N≡C hydrogen bonds exist between the cyano moieties and ring hydrogen atoms of the 3-cyanopyridine ligands (host···host interactions). In **3**, weak intermolecular C≡N···H–C hydrogen bonds were identified between the cyano moieties of 3-cyanopyridine and the C–H groups of both dichloromethane fragments. In **2**, weak hydrogen bonding interactions could be identified between one of the oxygen atoms of the disordered ethanol guest, and the isothiocyanato sulfur and aromatic hydrogen atoms of a nearby host complex (host···guest interactions).

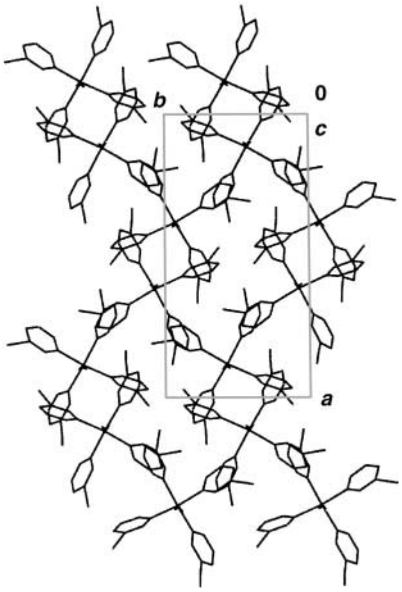

Fig. 1 The packing of **1** viewed along the [001] direction.

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

Compound	Donor···acceptor[a]	*d*(D–H)/Å	*d*(H···A)/Å	D–H···A/°	*d*(D···A)/Å
1	C7[b]···N7	0.930(4)	2.824(4)	144.0(2)	3.618(5)
	C25[c]···N8	0.930(3)	2.696(3)	152.6(2)	3.547(5)
	C3[d]···N9	0.930(4)	2.629(4)	153.9(2)	3.487(5)
	C13[e]···N10	0.930(4)	2.769(4)	139.9(2)	3.531(5)
2	C6[f]···N4	0.930(4)	2.513(4)	162.8(2)	3.412(5)
	C2[g]···N5	0.930(3)	2.472(4)	159.4(2)	3.358(5)
	C8[h]···O1B	0.930(4)	2.396(9)	160.7(3)	3.288(10)
	O1B···S1[h]	—	—	—	3.331(8)
3	C6[i]···N4	0.930(3)	2.515(3)	161.0(2)	3.408(5)
	C2[j]···N5	0.930(3)	2.471(4)	160.8(2)	3.363(5)
	C14A[k]···N4	0.970(14)	2.488(4)	147.9(7)	3.350(13)
	C14B[l]···N5	0.970(10)	2.364(4)	158.4(5)	3.285(10)

[a] A,B notation refers to atoms of a disordered system. [b] Symmetry code: $3/2 - x, 1/2 + y, 1/2 + z$. [c] Symmetry code: $2 - x, 1 - y, 1/2 + z$. [d] Symmetry code: $2 - x, 1 - y, z - 1/2$. [e] Symmetry code: $3/2 - x, y - 1/2, 1/2 + z$. [f] Symmetry code: $x, 1 - y, z - 1/2$. [g] Symmetry code: $1 - x, -y, -z$. [h] Symmetry code: $x - 1/2, 1/2 + y, z$. [i] Symmetry code: $x, 1 - y, z - 1/2$. [j] Symmetry code: $1 - x, -y, -z$. [k] Symmetry code: $1/2 - x, 1/2 - y, -z$. [l] Symmetry code: $1/2 + x, y - 1/2, z$.

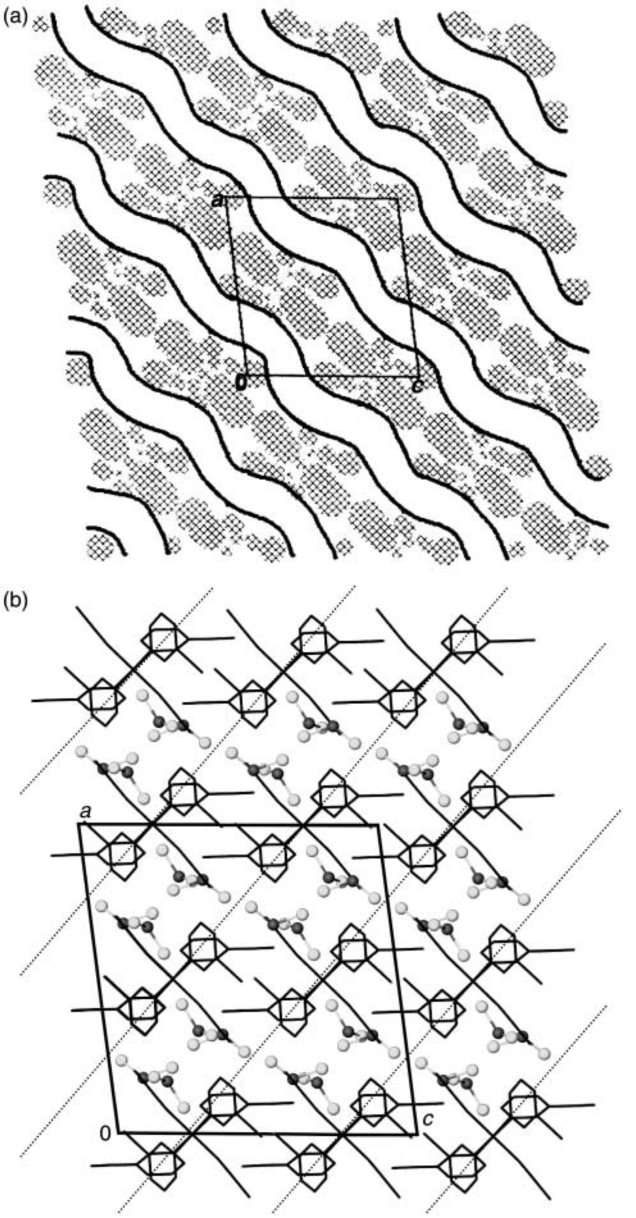

Fig. 2 (a) Space-filling representation of the host molecules in **3**, viewed along the [010] direction at $b = 0.25$, showing the sinusoidal channels. (b) Stick representation of the host molecules in **3**, viewed along the [010] direction, with the CH_2Cl_2 guests shown in ball-and-stick form.

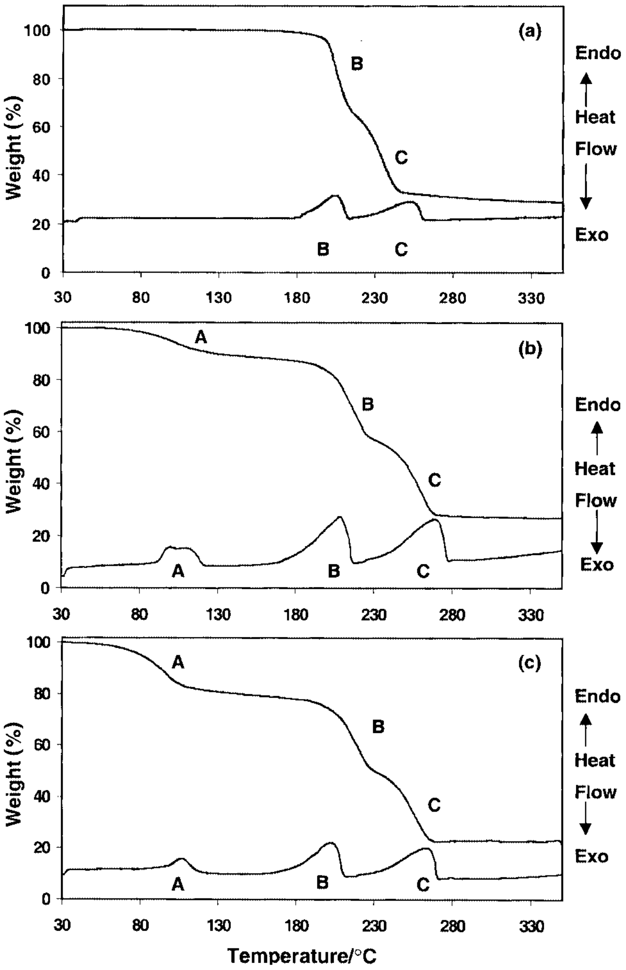

Fig. 3 Thermal analyses for compounds (a) **1**, (b) **2**, and (c) **3**.

Thermal analyses

The thermal analyses of all three compounds are shown in Figs. 3(a)–(c). The host compound **1** decomposes in two steps, shown as B and C in Fig. 3(a). Each step corresponds to the loss of two 3-cyanopyridine ligands. The DSC shows two distinct endotherms corresponding to steps B and C. The decomposition of **1** was followed by HSM. During step B the translucent blue crystals bubble and turn opaque green. Bubbling continues during step C, and the crystals turn orange-brown. The inclusion compounds **2** and **3** undergo an additional single-

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	—	—	—	—	99.8	13.5	12.7	105.9	46.8	22.3	22.0	107.3
B	179.4	35.0	34.4	205.2	179.2	30.5	30.2	209.5	179.5	27.4	27.7	203.0
C	217.8	35.0	34.4	253.8	230.5	30.5	29.9	270.4	230.2	27.4	27.7	264.7

step weight loss reaction, shown as step A in Figs. 3(b)–(c). Step A corresponds 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. The DSC traces of **2** and **3** show a broad endotherm corresponding to step A, which occurs at roughly the same temperature (T_{peak}) for both **2** and **3**. Following the guest release process, the host decomposition reactions, B and C, follow the same pattern observed for **1**. During step A the translucent purple crystals of **2** and **3** bubble and turn opaque blue. The bubbling is resumed in steps B and C, and the crystals turn green and orange-brown in turn, in accordance with the colour changes observed for **1**. The relevant TG (T_{onset}, calculated and experimental weight loss) and DSC (T_{peak}) data are given in Table 3.

Interconversion reactions

It was found that the α-host structure, **1**, could be transformed into inclusion compound **3**, by exposing single crystals of **1** to CH_2Cl_2 vapour in a sealed vessel at room temperature. The inclusion reaction **1**⟶**3** was followed by sampling the crystals, by TG, at regular intervals over a 23 hour period. The % weight loss during step A was found to increase from 0% (pure **1**) to 22.4% (pure **3**). This transformation was also observed by microscopy, with the translucent, blue single crystals of **1** gradually turning opaque purple over a 24 hour period. The analogous inclusion process, **1**⟶**2**, was unsuccessful, showing no weight gain after 5 days (we note that a possible reason for this is the difference in vapour pressure of the two liquid guests, with ethanol requiring a temperature of 63.5 °C to attain the same vapour pressure as dichloromethane at room temperature). The XRPD traces of all three compounds, as well as that of the product obtained on exposure of **1** to CH_2Cl_2 vapour, are available as ESI. In addition, XRPD shows that the product formed upon desolvation of **3**, or **2**, is the pure host **1**, indicating that the sorption process for **3** is fully reversible. Given that **2** and **3** have the same open channel structure, it should be possible to exchange one guest species for another. Single crystals of **2** were exposed to CH_2Cl_2 vapour in a sealed vessel at 4 °C. TG showed the guest exchange reaction, **2**⟶**3**, to be complete after only 30 minutes. The reverse reaction, **3**⟶**2**, however, took significantly longer to reach completion, requiring several days at 35 °C.

Determination of the enthalpies of guest release for 2 and 3

The vapour pressure *vs.* temperature data were collected in duplicate for each clathrate compound. The duplicate experiments yielded similar data in both cases. The experiments were carried out over the temperature ranges 20–62 °C for **2**, and 20–50 °C for **3**. From the Clausius–Clapeyron equation, plotting $n\ln p$ *vs.* T^{-1}, where n is the number of guest molecules present for each host molecule, yields a straight line of slope $-\Delta H°/R$ and y-intercept $\Delta S°/R$. Thus **2** yielded mean values of $\Delta H° = 76.3(1.9)$ kJ mol^{-1} and $\Delta S° = 326.8(5.2)$ J K^{-1} mol^{-1}, while **3** yielded mean values of $\Delta H° = 67.3(1.0)$ kJ mol^{-1} and $\Delta S° = 287.9(4.3)$ J K^{-1} mol^{-1} for the guest release process (Clausius–Clapeyron plots for **2** and **3** are available as ESI).

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