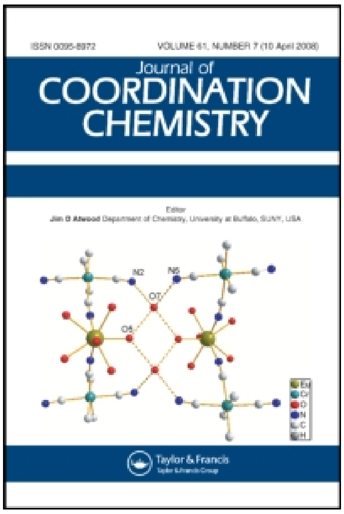

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Studies in Werner Clathrates 10[1]. Structures of Bis(Isothiocyanato)Bis(4-Methylpyridine) Bis(4-Phenylpyridine) Nickel(II) with Acetylacetone and 1-Chlorobutane

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STUDIES IN WERNER CLATHRATES 10[1]. STRUCTURES OF BIS(ISOTHIOCYANATO)BIS(4-METHYLPYRIDINE) BIS(4-PHENYLPYRIDINE) NICKEL(II) WITH ACETYLACETONE AND 1-CHLOROBUTANE

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The crystal structures of the mixed pyridine Werner clathrate $[Ni(NCS)_2(4\text{-}MePy)_2(4\text{-}PhPy)_2]$ with guest molecules acetylacetone (2,4-pentanedione) (I) and 1-chlorobutane (II) have been elucidated. The host molecule in both structures has octahedral coordination with the pairs of ligands all *trans* to each other. The channel in which the guest molecules are situated has been mapped and the guests' position located by potential energy calculations. Host-guest non-bonded energy relationships using atom-pair potentials have been examined.

Keywords: Werner clathrates, Ni(II) complexes, X-ray structures, potential energy surfaces, inclusion

INTRODUCTION

Werner clathrates were discovered by Schaeffer and Dorsey[2,3] who used these compounds as molecular filters to separate aromatic compounds from petroleum fractions. They are coordination compounds of general formula MX_2L_4 ($M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$; $X = SCN^-, NO_2^-, CNO^-$, halogen; L = substituted pyridine or 1-arylalklyamine) which entrap a wide variety of organic compounds as guest molecules. The host complex which has received the most attention is $[Ni(NCS)_2(4\text{-}MePy)_4]$, (4-MePy = 4-methylpyridine), and the clathrate structures it forms with a number of guests as well as its physico-chemical properties have been reviewed by Lipkowski.[4] We have synthesized and characterized the structures of $[Ni(NCS)_2(4\text{-}EtPy)_4]$, (4-EtPy = 4-ethylpyridine) and its clathrates with several guest molecules,[5] and have also elucidated the structures of $[Ni(NCS)_2(4\text{-}ViPy)_4]$ (4-ViPy = 4-vinylpyridine) with *o*-, *m*- and *p*-xylene.[6]

An important feature of these host molecules is the freedom of rotation of the pyridine rings about their Ni–N bonds. This may be the prime factor which allows the host molecules to adjust their shapes and form appropriate channels to accommodate the guests. We have therefore studied the clathrates formed with $[Ni(NCS)_2(4\text{-}PhPy)_4]$ (4-PhPy = 4-phenylpyridine) as host molecule,[1,7,8] because the latter has the additional rotational freedom of the phenyl groups bonded to the pyridines. Werner clathrates with chiral ligands, which are potentially useful in separating enantiomers, have also been recently studied and their structures reported.[9,10]

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We now report the structures of the mixed pyridine host complex [Ni(NCS)$_2$(4-MePy)$_2$(4-PhPy)$_2$] with guest molecules acetylacetone (2,4-pentanedione) (I) and 1-chlorobutane (II).

EXPERIMENTAL

Synthesis

The host complex of the 4-MePy derivative, [Ni(NCS)$_2$(4-MePy)$_4$] was first prepared by the method of Schaeffer *et al.*[3] Formation of the clathrate involved dissolving this host complex in the intended guest solvent, heating to approximately 60°C, and then slowly adding a four-fold excess of 4-phenylpyridine dissolved in a minimum of ethanol. Light blue prismatic crystals formed after about 1 week of slow evaporation at room temperature of the clathrate solution.

Suitable single crystals were mounted in Lindemann capillaries with mother liquor to prevent deterioration by desorption of the guest solvent.

Structure Solution

Preliminary cell dimensions and space group symmetry were determined photographically. Accurate cell parameters were then obtained by least-squares analysis of 25 reflections measured in the range $16° < \theta < 17°$ on a Nonius CAD4 diffractometer with graphite monochromated MoKα radiation ($\lambda = 0.7107$Å) at 293K. During the intensity data collection of each structure, three reference reflections were monitored after every 100 reflections to check crystal stability. Crystal data and experimental details of the data collection are listed in Tables I and II respectively. All data were corrected by a Lorentz polarization factor and also for absorption.[11]

The structures were solved by the heavy-atom method using the SHELXS-86 program,[12] and refined by full-matrix least-squares using the SHELX-76 program.[13]

Final refinement for both host structures was carried out with the Ni and S atoms treated anisotropically, and with the H atoms geometrically placed and linked with common isotropic temperature factors.

TABLE I
Crystal data for the clathrates (I), and (II).

Compound	(I)	(II)
Guest	acetylacetone	chlorobutane
H:G ratio	1 : 1	1 : 1
M_r/gmol^{-1}	771.6	764.1
D_m/gcm^{-3}	1.269	1.268
D_c/gcm^{-3}	1.28	1.26
μ(MoKα)/cm^{-1}	5.82	6.37
F(000)	1608	1592
Space Group	*C*2/*c*	*C*2/*c*
a/Å	10.541(2)	10.771(20)
b/Å	22.879(3)	23.027(9)
c/Å	16.814(2)	16.405(16)
β/°	99.8(1)	99.1(1)
U/Å^3	3995.1	4017.6
Z	4	4

TABLE II
Experimental and refinement parameters for the structures.

Compound	(I)	(II)
Crystal dimensions/mm	.22 × .22 × .25	.19 × .25 × .44
θ range scanned/°	1–25	1–25
Scan Mode	ω–2θ	ω–2θ
Ave Transmission /%	95.0	97.2
Crystal Stability /%	1.5	0.8
Scan width[a]	.64	1.34
Aperture width[b]	1.11	1.47
Vertical Aperture length/mm	4	4
Final acceptance limit	20σ at 20° min^{-1}	20σ at 20° min^{-1}
Max. recording time/s	40	40
Total no. reflections	2915	2782
Total no. observed	2086[c]	1419[c]
No. variables	132	139
R[d]	0.0862	0.0746
R_w[e]	0.0857	0.0664
Weighting scheme, w	$(\sigma^2 F)^{-1}$	$(\sigma^2 F)^{-1}$

[a] Scan width, $\Delta\omega = (y + .35 \tan\theta)°$. [b] Aperture width = $(x + 1.05 \tan\theta)$ mm. [c] $I_{rel} > 2\sigma I_{rel}$. [d] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [e] $R_w = \Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$.

Location of the guest molecules in both structures necessitated the contouring of electron density maps. For compound (I) the positions of the two oxygen atoms in the guest molecule were located unambiguously as their electron density was significantly higher than that of the carbon backbone. The difference electron density map corresponding to the C atoms, however, was diffuse and the best model, obtained by fixing bond distances as shown in Figure 1, resulted in high thermal

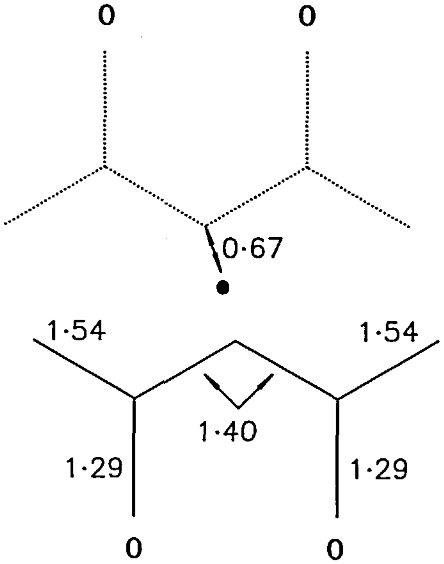

FIGURE 1 Model of the guest molecule (acetylacetone) of Compound (I), with bond distances (Å) indicated. The solid circle represents the centre of inversion at Wyckoff position *d*.

parameters (*ca* 0.15 Å^2) for all guest atoms. Two fold static disorder was invoked as the molecule is located near the centre of inversion at Wyckoff position *d*.

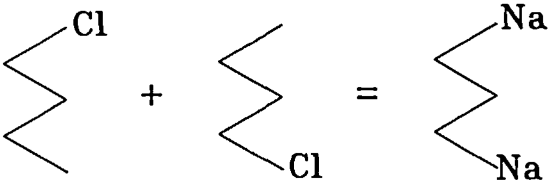

FIGURE 2 Model of the guest molecule (1-chlorobutane) of Compound (II), indicating the statistical disorder.

TABLE III
Fractional atomic coordinates (× 10^4) with e.s.d.'s in parentheses for Compound (I).

Atom	*x/a*	*y/b*	*z/c*
Ni(1)	0	1699(1)	2500
N(1)	1778(6)	1699(3)	3234(4)
C(1)	2613(7)	1701(4)	3755(5)
S(1)	3799(3)	1718(2)	4517(2)
N(11)	910(6)	1699(3)	1449(4)
C(12)	298(13)	1591(5)	724(8)
C(13)	870(12)	1580(5)	26(8)
C(14)	2155(9)	1653(4)	84(6)
C(15)	2787(10)	1758(4)	843(6)
C(16)	2147(9)	1787(4)	1487(6)
C(17)	2793(9)	1615(4)	−646(6)
N(21)	0	767(4)	2500
C(22)	1101(8)	463(4)	2536(5)
C(23)	1140(8)	−139(4)	2534(5)
C(24)	0	−466(5)	2500
C(211)	0	−1111(5)	2500
C(212)	−894(9)	−1407(4)	2857(6)
C(213)	−867(10)	−2022(5)	2864(6)
C(214)	0	−2303(7)	2500
N(31)	0	2626(4)	2500
C(32)	504(8)	2934(3)	3161(5)
C(33)	518(7)	3539(3)	3190(5)
C(34)	0	3854(5)	2500
C(311)	0	4505(6)	2500
C(312)	161(10)	4809(5)	1818(7)
C(313)	178(12)	5439(5)	1804(8)
C(314)	0	5680(8)	2500
C(1G)	2352(15)	4897(12)	5230(14)
C(2G)	3605(14)	4794(12)	4908(12)
C(3G)	4800(14)	4956(13)	5353(10)
C(4G)	5895(14)	4952(13)	4985(13)
C(5G)	7220(15)	5128(15)	5464(16)
O(1G)	3564(16)	4554(10)	4208(11)
O(2G)	5843(16)	4728(11)	4277(13)

For compound (II), the contoured electron density map revealed three peaks which could be clearly interpreted as the three methylene carbons, but the end peaks were more diffuse, with apparent bond distances of *ca* 1.6 Å. We invoked statistical disorder of the terminal C and Cl atoms. Thus the average atomic scattering factors of the terminal carbon and chlorine atoms were approximated as the atomic scattering factor of the sodium atom as shown in Figure 2. This molecule was again modelled with a site occupancy factor of $\frac{1}{2}$ as it lies close to the centre of inversion at Wyckoff position *d*.

TABLE IV

Fractional atomic coordinates ($\times 10^4$) with e.s.d.'s in parentheses for Compound (II).

Atom	*x/a*	*y/b*	*z/c*
Ni(1)	0	1793(1)	2500
N(1)	1699(7)	1787(4)	3260(4)
C(1)	2543(9)	1805(5)	3771(6)
S(1)	3773(3)	1828(2)	4490(2)
N(11)	942(7)	1787(4)	1446(4)
C(12)	395(10)	1741(6)	673(7)
C(13)	970(10)	1717(5)	−28(7)
C(14)	2266(9)	1691(5)	72(6)
C(15)	2837(10)	1760(6)	861(7)
C(16)	2179(10)	1810(5)	1502(7)
C(17)	2928(10)	1644(5)	−661(6)
N(21)	0	867(5)	2500
C(22)	1074(10)	565(5)	2558(6)
C(23)	1116(10)	−46(5)	2565(6)
C(24)	0	−378(8)	2500
C(211)	0	−1019(8)	2500
C(212)	−915(11)	−1322(5)	2835(7)
C(213)	−924(12)	−1945(6)	2839(8)
C(214)	0	−2194(9)	2500
N(31)	0	2723(5)	2500
C(32)	520(10)	3005(5)	3179(6)
C(33)	515(9)	3621(5)	3198(7)
C(34)	0	3920(7)	2500
C(311)	0	4600(9)	2500
C(312)	216(12)	4866(6)	1794(8)
C(313)	222(14)	5521(7)	1800(9)
C(314)	0	5747(10)	2500
Na(1)	2714(33)	4802(25)	4536(18)
C(2G)	3918(34)	5125(20)	5041(38)
C(3G)	5081(32)	4941(19)	4679(22)
C(4G)	6014(37)	5442(16)	4829(45)
Na(2)	7410(33)	5192(20)	4866(17)

Complex neutral atom scattering factors for all non-hydrogen atoms were taken from Cromer and Mann[14] and for hydrogen from Stewart *et al.*[15]

For both compounds, with $Z = 4$, the nickel atom and two pyridine ligands are situated on the diad at Wyckoff position *e*. The final fractional atomic coordinates are given in Tables III and IV, whilst Figure 3 gives a perspective view of the host molecule of Compound (II) with atomic nomenclature.

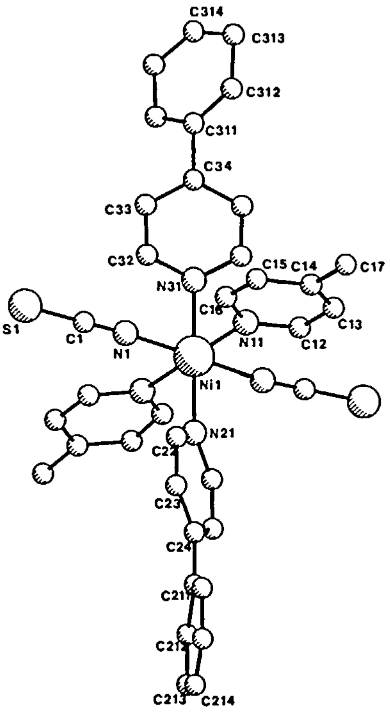

FIGURE 3 Perspective view of the host molecule of Compound (II).

RESULTS AND DISCUSSION

The host structure in both complexes has the central nickel atom in an octahedral configuration with the isothiocyanate ligands, the 4-MePy ligands and the 4-PhPy ligands in *trans* positions. The observed bond lengths and angles are within accepted limits for compounds of this type.[16]

The guest molecules in both complexes are located in undulating channels running parallel to a at $b = c = \frac{1}{2}$. The isothiocyanate and 4-MePy ligands form the roof and floor of this channel whilst the 4-PhPy ligands form the walls.

Attempts have been made to form clathrates of this host with aromatic guest molecules, aliphatic guests of the type $CH_3(CH_2)_nCl$ with $n = 2$–9, and aliphatic molecules containing potential H-bond donors. However, the cross-sectional area of the channels is too small to accommodate aromatic guests and it appears that there is a strong preference for aliphatic guest molecules which contain a skeleton of five atoms.

Figures 4 and 5 show packing diagrams of Compound (I), viewed down [100], and Compound (II), viewed down [010], respectively.

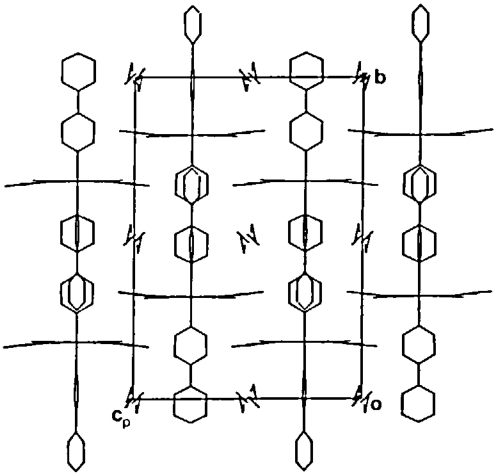

FIGURE 4 Projection of Compound (I) viewed along [100].

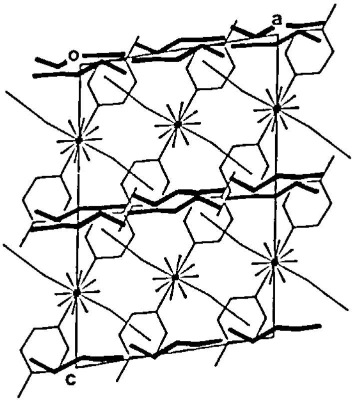

FIGURE 5 Projection of Compound (II) viewed along [010].

Energy Studies

The potential energy of the guest molecules in their crystal lattices was studied in order to determine possible dynamic conformation changes in the host molecules and to ascertain the nature and strength of the forces which retain the guest molecule in the clathrate. The program EENY[17] calculates van der Waals energy using empirical atom-pair potential curves. The equation of the atom–atom potentials is of the form:

$$U(r) = a\exp(-br)/r^d - c/r^6$$

where r is the distance (Å) between any pairs of atoms. The coefficients a, b, c and d are those given by Giglio[18] and Pavel *et al.*[19]

Attempts were first made to place the guest molecule in the channel of the clathrate. The shape of the channel was ascertained by calculating the potential energy environment of a "probe molecule". A hydrogen atom was systematically moved throughout the region of the channel. This region was sliced into 11 sections along the y-direction and at each interval two-dimensional energy maps were evaluated and contoured at the zero energy level. A model of the guest molecule, consisting of spheres representing van der Waals radii was positioned, so as to give minimal protrusion beyond the zero energy surface. The guest position was refined by energy minimization and yielded atomic positions which where essentially an intermediate between the two "half molecules" found in the crystal structure analysis. This is illustrated in Figure 6.

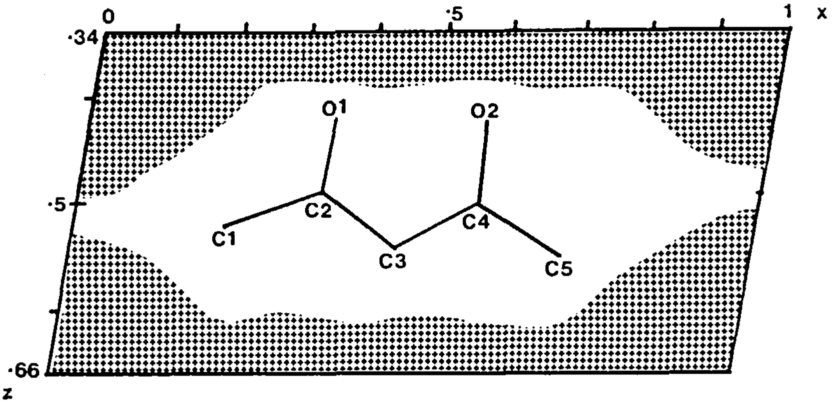

FIGURE 6 The topology of the channel of Compound (I) indicating the energy minimized position of the guest molecule, sectioned at $y = \frac{1}{2}$.

For Compound (I) in order to ascertain the forces retaining the guest molecules within the clathrate, we arbitrarily chose one of the two possible orientations of the acetylacetone as determined in the crystal structure. This molecule was then translated through the channel in steps of 1 Å and the energy calculated on the assumption that both host and guest remained rigid (Graph 1, Figure 7). This model was then refined, by allowing the guest molecule small variations in its rotational parameters and its translation in the y-direction, in order to find a local minimum in the energy profile after each 1 Å translation (Graph 2, Figure 7). Partial conformational freedom of the host molecules was then permitted by allowing all six rings and the

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