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Order–Disorder Effects of Small Guests in Clathrates Studied by Nuclear Quadrupole Resonance and Crystallography. Part I. Carbon Tetrachloride and Related Molecules in $Ni(SCN)_2$(3-methylpyridine)$_4$

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Abstract. NQR spectroscopy and X-ray crystallography have been jointly applied to the study of the small guest molecules CH_2Cl_2, $CHCl_3$, CCl_4, CBr_2Cl_2, $C(CH_3)_2Cl_2$ etc. in the Werner host complex $Ni(SCN)_2$(3-methylpyridine)$_4$. Specific host–guest dipole–dipole interactions play an important role in order–disorder effects for guest molecules in the cavities of orthorhombic system, *Fddd*. Thus a weakly polar molecule such as CBr_2Cl_2 exhibits a disordered alternation, both the bromine and the chlorine atoms occupying the two possible sites in the C_2 cavity, whereas for the polar molecule $C(CH_3)_2Cl_2$, an ordered structure is observed. In addition, two new types of crystal structures, $C2/c$ and $P\bar{1}$, are reported here for dichloromethane and chloroform clathrates.

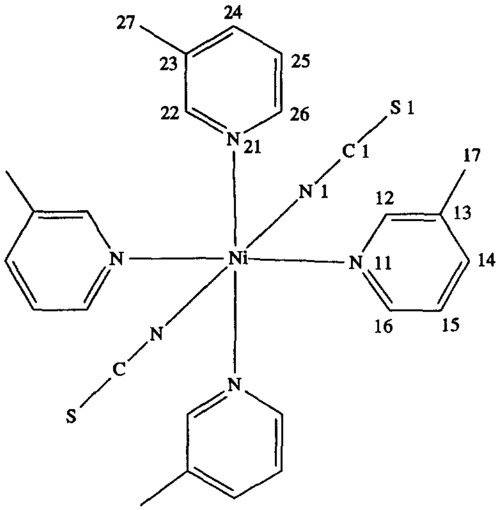
Key words. NQR, chloromethanes, structure.

Supplementary Material Available. Atomic positions and displacement parameters for the compounds **2**–**3**, **6** and **7**. Lists of structure factors, atomic positional and anisotropic displacement parameters for all atoms and other information in the printed form of the Standard Crystallographic File Structure of Brown (1985) [13] have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 82130 (9pp.).

1. Introduction

The ability of Werner complexes, $M^{(II)}X_2Y_4$, to form inclusion compounds with a wide variety of organic molecules is well known and has been reviewed recently [1], where M is a bivalent transition-metal e.g. $Ni^{(II)}$, $Co^{(II)}$, $Fe^{(II)}$, $Mn^{(II)}$ and $Cu^{(II)}$ etc.; X is an anion e.g. SCN^-, $SeCN^-$, OCN^-, Cl^-, Br^-; the ligand Y is an electrically neutral substituted pyridine or α-alkylaniline.

In the course of our previous studies of these and other inclusion compounds using ^{35}Cl Nuclear Quadrupole Resonance of chlorine-containing guest molecules [2, 3] it was postulated that broad or absent NQR signals could be ascribed to static or dynamic disorder. We report here the results of an NQR and crystallographic study of the small guest molecules CCl_4, **1**, CBr_2Cl_2, **2**, $C(CH_3)_2Cl_2$, **3**, CH_2Cl_2, **4** and **6**, $CHCl_3$, **5** and **7**, included in the same Werner complex $Ni(SCN)_2$(3-methylpyridine)$_4$ which support this hypothesis and which cast light on the factors which favour the adoption of ordered structures. The existence of two different clathrate phases for the complexes with CH_2Cl_2 and $CHCl_3$ is also reported.



Scheme 1. Atom numbering for the host molecule ($Ni(SCN)_2(3MePy)_4$) in clathrates **2**, **3**, **6** and **7**. The Ni atom is located on a C_2 axis for **2**, **3** and **6** and on an inversion center for **7**.

2. Experimental

2.1. PREPARATIONS

The host complex $Ni(SCN)_2$(3-methylpyridine)$_4$ was prepared by titrating an aqueous solution of nickel diisothiocyanate with a stoichiometric quantity of 3-methylpyridine according to Schaeffer *et al.* [4]. The clathrates were prepared by recrystallisation of the host complex from the appropriate guest solvent. Thus the compounds **1–5**, which have 1 : 1 host/guest ratios, were crystallized by using 2-methoxyethanol as cosolvent with an excess of the guest solvents. The clathrates **6**, **7**, which have 1 : 2 host/guest ratios, were obtained by slow evaporation from the saturated solutions of guest solvent. All clathrates were characterised using density measurements from the crystal structure parameters (see Table II).

2.2. NUCLEAR QUADRUPOLE RESONANCE

NQR spectra were measured on a Decca super-regenerative spectrometer, frequencies being compared to harmonics from an internal crystal-controlled oscillator. Temperatures were measured with a Hewlett Packard 2802A digital thermometer using a platinum thermocouple (precision ±0.5°C) and varied with an Artronix 5301-E temperature controller.

2.3. CRYSTALLOGRAPHIC MEASUREMENTS

The single crystals of the clathrates were obtained and mounted in capillaries filled with the mother liquor to prevent deterioration in air. Cell parameters and reflection intensities were measured on Nonius CAD4 (for compounds **1** and **2**) and

Philips PW1100 (for compounds **3**, **6** and **7**) diffractometers with graphite-monochromated MoK_α radiation. A summary of crystal data and structure refinement are given in Tables I and II, respectively, final atomic coordinates for **2**, **3**, **6** and **7** are reported in Table IV. The structures were solved by direct methods (MULTAN-87 [5]) and refined by least-squares analysis with XTAL [6]. Atomic scattering factors and anomalous dispersion terms are taken from Ref. [7].

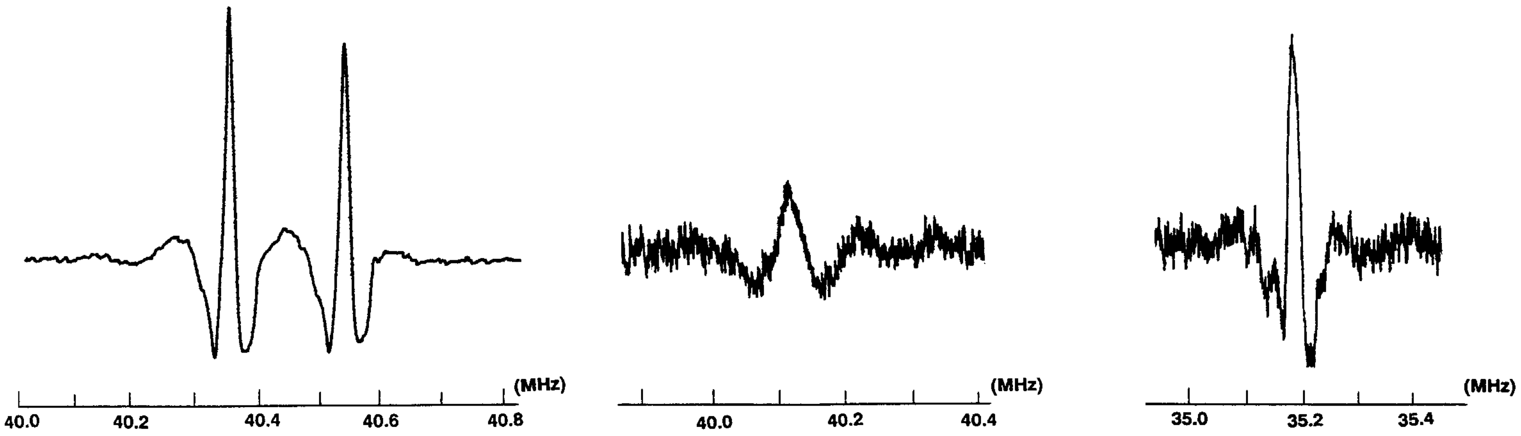
3. Results and Discussion

The ^{35}Cl NQR spectra of clathrates **1**–**3** are shown in Figure 1(a)–(c). The narrow and intense lines of **1** and **3** indicate that the orientation of the guest molecules is ordered, whereas the broad and weak signal of **2** demonstrates that the orientation of the guests is disordered. On the other hand, the absence of NQR signals for the clathrates **4** and **5** is indicative either of molecular motion or of a disordered orientation of the CH_2Cl_2 and $CHCl_3$ guests, whereas the intense resonance lines shown by these two guests in **6** and **7** demonstrate an ordered structure. The resonance frequencies of all clathrates, measured at 77 K, are shown in Table I.

As is always the case in NQR, the resonance frequencies are temperature-dependent. For all these complexes the usual negative temperature coefficients are observed, their values of around $-10\,\text{kHz}\,\text{K}^{-1}$, being similar to those for other such inclusion complexes [3]. In all cases, when the temperature is in the region of 150 K, the amplitude of molecular motion is such that the NQR signals disappear and the temperatures at which such high-amplitude motion sets in can be correlated with the sizes of the cavities [3]. For the two complexes, **4** and **5**, which did not show a signal at 77 K, measurements at 4 K were likewise unsuccessful. Possible causes for the absence or weakness of NQR signals other than molecular motion or those discussed below are considered to be negligible under the present circumstances. Thus, although paramagnetic impurities can cause broadening of NQR signals, the fact that the most likely source of such impurities, the metallic host complex, was the same for all these complexes, and that several of these complexes yield strong narrow NQR lines, makes it unlikely that such impurities are in fact present. Lattice strain and lattice deformation are also sources of line-broadening but are considered to be almost certainly negligible for these complexes which have been crystallized slowly from solution and where the host molecule is completely free to make all necessary adjustments to its position and orientation to accommodate the guest molecule.

The crystal structures of **1**–**3** and **6**, **7**, have been determined and the cell parameters are listed in Table II, together with the data for **5**, previously reported by Nassimbeni [8]. Clathrates **1**–**5**, which have 1 : 1 host/guest ratios, are isostructural (space group: *Fddd*), and the cavity containing the guest molecules is essentially the same in all five cases, whereas clathrates **6** and **7**, which have 1 : 2 host/guest ratios, crystallize respectively into monoclinic, *C*2/*c*, and triclinic, $P\bar{1}$, systems. Thus, the shapes and sizes of the cavities in these clathrates are very different from those of the orthorhombic ones.

The cavity in the orthorhombic system has C_2 symmetry in the three axis directions and contains two guest molecules in a special position (site g) related by the C_2 axis. The height of the cavity is 15.7 Å, longer than that of Dianin's clathrate



(a) CCl_4 in (**1**)

(b) CBr_2Cl_2 in (**2**)

(c) $C(CH_3)_2Cl_2$ in (**3**)

Fig. 1. ^{35}Cl NQR signals (77 K) of the guest molecules in Werner clathrates formed by $Ni(SCN)_2(3\text{-}MePy)_4$ as host.

Table I. ^{35}Cl NQR frequencies at 77 K of the clathrates formed by the host $Ni(SCN)_2(3\text{-}MePy)_4$

Compound	Guest	Host : guest ratio	Frequency (MHz)	Orientation
1	CCl_4	1 : 1	40.351	ordered
			40.541	
2	CBr_2Cl_2	1 : 1	40.106	disordered
3	$C(CH_3)_2Cl_2$	1 : 1	35.178	ordered
4	CH_2Cl_2	1 : 1	no signal	disordered
5	$CHCl_3$	1 : 1	no signal	disordered
6	CH_2Cl_2	1 : 2	35.633	ordered
			35.725	
7	$CHCl_3$	1 : 2	37.062	ordered
			37.287	
			37.887	

Table II. Crystal data for clathrates formed by the host $Ni(SCN)_2(3\text{-}MePy)_4$

	Clathrate						
	1	**2**	**3**	**4**[a]	**5**	**6**	**7**
Guest	CCl_4	CBr_2Cl_2	$C(CH_3)_2Cl_2$	CH_2Cl_2	$CHCl_3$	CH_2Cl_2	$CHCl_3$
Host : guest ratio	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1	1 : 2	1 : 2
Molecular weight	701.2	790.2	660.4	632.8	666.8	717.2	786.2
$D_c(g \cdot cm^{-3})$	1.35	1.51	1.26	1.22	1.29	1.34	1.44
$D_m(g \cdot cm^{-3})$	1.35	1.46	1.23	1.24	1.27	1.33	1.42
Space group	*Fddd*	*Fddd*	*Fddd*	*Fddd*	*Fddd*	*C2/c*	$P\bar{1}$
a(Å)	22.067(2)	22.234(2)	21.836(3)	22.013(7)	21.471	19.292(4)	9.2361(14)
b(Å)	23.650(2)	23.615(2)	24.118(2)	23.756(3)	24.351	11.2232(9)	9.669(2)
c(Å)	26.388(3)	26.423(3)	26.395(2)	26.370(3)	26.281	16.525(4)	11.7497(9)
α(°)	90	90	90	90	90	90	66.230(8)
β(°)	90	90	90	90	90	96.976(6)	71.351(6)
γ(°)	90	90	90	90	90	90	83.504(7)
V(Å^3)	13772(2)	13874(2)	13901(2)	13790(4)	13739	3551.5(12)	909.7(3)
Z[b]	16	16	16	16	16	4	1
Ref.	[3]	[c]	[c]	[c]	[8]	[c]	[c]

[a] Only cell parameters and space group have been determined.

[b] Number of host molecules in the unit cell.

[c] This work.

Table III. Summary of intensity measurement and structure refinement for clathrates formed by the host $Ni(SCN)_2(3\text{-}MePy)_4$

Compound	**2**	**3**	**6**	**7**
Guest	CBr_2Cl_2	$C(CH_3)_2Cl_2$	CH_2Cl_2	$CHCl_3$
Crystal size	0.32 × 0.32 × 0.32	0.15 × 0.25 × 0.25	0.25 × 0.35 × 0.38	0.30 × 0.32 × 0.32
F_{000}	6336	5504	1480	402
$\mu(\mathrm{Mo}K_\alpha)\,\mathrm{mm}^{-1}$	3.141	0.856	0.991	1.118
$\sin(\theta/\lambda)_{\max}(\mathrm{\AA}^{-1})$	0.55	0.55	0.55	0.58
Temperature (K)	298	298	298	298
No. measured refl.	2673	2630	2780	2901
No. observed refl.	1414	1553	1494	2325
Criterion for observed refl.	$\|F_0\| > 4\sigma(F_0)$	$\|F_0\| > 4\sigma(F_0)$	$\|F_0\| > 4\sigma(F_0)$	$\|F_0\| > 4\sigma(F_0)$
Refinement (on F)	full-matrix	full-matrix	full-matrix	full-matrix
No. parameters	200	182	186	196
Weighting scheme	$1/\sigma^2(F_0)$	$1/\sigma^2(F_0)$	$1/\sigma^2(F_0)$	$1/\sigma^2(F_0)$
Max. and average Δ/σ	1.303, 0.092	0.108, 0.011	0.181, 0.019	0.080, 0.014
Max. and min. $\Delta\rho$ ($e \cdot \mathrm{\AA}^{-3}$)	+0.93, −1.24	+1.97, −1.08	+0.60, −0.89	+0.55, −1.00
S	2.93	2.46	5.23	3.89
R, ωR (%)	6.7, 4.1	9.6, 7.1	8.5, 5.9	5.8, 4.5

Table IV. Fractional coordinates and equivalent isotropic atomic displacement parameters with e.s.d.'s in parentheses for clathrates formed by the host Ni(SCN)$_2$(3-MePy)$_4$. (U_{eq} is the average of eigenvalues of U)

Compound **2** Ni(SCN)$_2$(3-MePy)$_4$ CCl$_2$Br$_2$

	x/a	y/b	z/c	U_{eq}
Ni	7/8	0.11306(8)	3/8	0.038(1)
N(1)	0.8819(4)	0.1136(3)	0.2977(2)	0.052(6)
C(1)	0.8867(4)	0.1244(4)	0.2558(3)	0.040(7)
S(1)	0.8936(1)	0.1385(1)	0.19591(9)	0.070(2)
N(11)	0.9432(3)	0.1772(3)	0.3786(4)	0.036(6)
C(12)	0.9847(5)	0.1768(4)	0.4162(4)	0.046(8)
C(13)	1.0295(5)	0.2168(5)	0.4201(4)	0.055(9)
C(14)	1.0310(5)	0.2596(5)	0.3851(5)	0.05(1)
C(15)	0.9892(6)	0.2605(4)	0.3466(4)	0.050(9)
C(16)	0.9458(5)	0.2189(5)	0.3445(4)	0.047(8)
C(17)	1.0746(5)	0.2150(5)	0.4613(5)	0.10(1)
N(21)	0.8088(4)	0.0486(3)	0.3711(4)	0.042(6)
C(22)	0.8107(4)	0.0090(5)	0.3347(4)	0.048(8)
C(23)	0.7702(6)	−0.0346(5)	0.3305(5)	0.06(1)
C(24)	0.7249(6)	−0.0381(5)	0.3653(6)	0.08(1)
C(25)	0.7217(5)	0.0025(6)	0.4020(5)	0.07(1)
C(26)	0.7643(6)	0.0450(5)	0.4042(4)	0.055(9)
C(27)	0.7750(5)	−0.0783(5)	0.2898(5)	0.13(1)
C(01)	1/8	1/8	0.2422(6)	0.07(1)
Cl(1)	0.1714(9)	0.1665(8)	0.196(1)	0.11(1)
Cl(2)	0.0830(7)	0.1676(8)	0.2893(7)	0.14(1)
Br(1)	0.1789(4)	0.1658(4)	0.2067(5)	0.098(5)
Br(2)	0.0807(3)	0.1765(4)	0.2795(3)	0.107(4)

Compound **3** Ni(SCN)$_2$(3-MePy)$_4$ C(CH$_3$)$_2$Cl$_2$

Ni	7/8	0.11076(9)	3/8	0.0448(7)
N(1)	0.8836(5)	0.1104(4)	0.2980(3)	0.060(4)
C(1)	0.8887(5)	0.1211(5)	0.2553(4)	0.048(4)
S(1)	0.8978(2)	0.1364(2)	0.1959(1)	0.080(2)
N(11)	0.9437(4)	0.1737(3)	0.3800(4)	0.051(4)
C(12)	0.9835(6)	0.1750(5)	0.4166(5)	0.062(5)
C(13)	1.0283(6)	0.2148(6)	0.4202(5)	0.072(6)
C(14)	1.0325(6)	0.2552(5)	0.3845(6)	0.072(7)
C(15)	0.9918(6)	0.2532(5)	0.3457(6)	0.068(6)
C(16)	0.9479(6)	0.2128(5)	0.3449(5)	0.058(5)
C(17)	1.0730(8)	0.2157(7)	0.4630(8)	0.15(1)
N(21)	0.8068(4)	0.0485(4)	0.3700(4)	0.050(4)
C(22)	0.8112(5)	0.0084(5)	0.3369(5)	0.054(5)
C(23)	0.7690(6)	−0.0344(6)	0.3322(5)	0.069(6)
C(24)	0.7209(6)	−0.0355(6)	0.3642(6)	0.075(7)
C(25)	0.7167(6)	0.0053(6)	0.4000(6)	0.093(7)
C(26)	0.7610(6)	0.0472(6)	0.4024(6)	0.074(6)
C(27)	0.7766(7)	−0.0800(6)	0.2921(6)	0.110(8)
C(01)	1/8	1/8	0.0189(9)	0.12(1)
C(02)	0.1680(7)	0.0869(7)	0.0459(7)	0.134(9)
Cl	0.0820(3)	0.0827(3)	−0.0212(3)	0.211(4)

Table IV. (continued)

Compound **6** Ni(SNC)$_2$(3-MePy)$_4$ CH$_2$Cl$_2$

Ni	1/2	0.2492(2)	1/4	0.050(1)
S(1)	0.2962(1)	0.2423(4)	0.3873(2)	0.089(2)
C(1)	0.3725(5)	0.247(1)	0.3509(5)	0.057(6)
N(1)	0.4247(4)	0.251(1)	0.3267(4)	0.059(5)
N(11)	0.4427(5)	0.1184(8)	0.1793(5)	0.056(7)
C(12)	0.4740(5)	0.026(1)	0.1427(7)	0.057(7)
C(13)	0.4383(7)	−0.056(1)	0.0938(7)	0.069(9)
C(14)	0.3669(8)	−0.046(1)	0.0800(8)	0.08(1)
C(15)	0.3326(6)	0.039(1)	0.1157(9)	0.10(1)
C(16)	0.3715(7)	0.122(1)	0.1647(7)	0.081(9)
C(17)	0.4735(6)	−0.154(1)	0.0556(7)	0.11(1)
N(21)	0.9457(4)	0.1181(8)	0.6776(6)	0.058(7)
C(22)	0.9394(5)	0.1218(9)	0.5939(8)	0.055(7)
C(23)	0.9039(6)	0.042(1)	0.5430(8)	0.064(9)
C(24)	0.8711(8)	−0.051(1)	0.579(1)	0.09(1)
C(25)	0.8727(6)	−0.057(1)	0.663(1)	0.09(1)
C(26)	0.9119(6)	0.029(1)	0.7100(7)	0.073(8)
C(27)	0.9015(5)	0.049(1)	0.4557(7)	0.084(9)
C(01)	0.7056(7)	0.101(1)	0.684(1)	0.15(1)
Cl(1)	0.6302(2)	0.1587(4)	0.7102(3)	0.175(4)
Cl(2)	0.7270(2)	0.1656(5)	0.5942(3)	0.188(5)

Compound **7** Ni(SCN)$_2$(3-MePy)$_4$ (CHCl$_3$)$_2$

Ni	1/2	1/2	1/2	0.036(1)
N(1)	0.6349(5)	0.6606(4)	0.3354(4)	0.047(5)
C(1)	0.7241(5)	0.7417(5)	0.2477(5)	0.038(6)
S(1)	0.8521(2)	0.8581(2)	0.1226(1)	0.066(2)
N(11)	0.6642(4)	0.4802(4)	0.6011(4)	0.043(5)
C(12)	0.7661(5)	0.5936(5)	0.5572(5)	0.045(6)
C(13)	0.8795(6)	0.5885(7)	0.6107(6)	0.052(7)
C(14)	0.8899(7)	0.4609(8)	0.7144(7)	0.068(9)
C(15)	0.7851(7)	0.3427(7)	0.7653(6)	0.067(8)
C(16)	0.6749(6)	0.3579(6)	0.7055(5)	0.057(7)
C(17)	0.9906(6)	0.7188(7)	0.5541(6)	0.073(8)
N(21)	0.3920(4)	0.6752(4)	0.5689(4)	0.042(5)
C(22)	0.3226(6)	0.6409(6)	0.6972(5)	0.047(6)
C(23)	0.2482(6)	0.7466(7)	0.7481(5)	0.053(7)
C(24)	0.2503(6)	0.8948(6)	0.6603(6)	0.058(8)
C(25)	0.3230(6)	0.9309(6)	0.5298(6)	0.057(7)
C(26)	0.3919(6)	0.8194(6)	0.4872(5)	0.050(6)
C(27)	0.1666(7)	0.6986(7)	0.8912(6)	0.081(8)
C(101)	0.3426(7)	0.1595(7)	0.0952(6)	0.077(8)
Cl(1)	0.5159(2)	0.0694(2)	0.1166(2)	0.091(2)
Cl(2)	0.1912(2)	0.0578(3)	0.2269(2)	0.124(3)
Cl(3)	0.3497(3)	0.3416(2)	0.0794(3)	0.191(5)

(11 Å [3]), so it can contain two equivalent guest molecules of the dimensions of those considered here.

In compounds **1–3** the guest molecules have the same C_2 symmetry as the cavity, they can therefore fit into the cavity without altering its symmetry. CCl_4, however, can only be included in one way and thus gives rise to two distinct resonance signals since under C_2 symmetry the four equivalent chlorine atoms are reduced to two groups of two equivalent atoms. Compounds **2** and **3** already have C_2 symmetry; there are thus two distinct ways of inserting them in the cavity while maintaining the overall C_2 symmetry (Figure 2(a)–(b)). If one of these two forms is strongly preferred then an ordered structure will result and only one sharp NQR line will be observed. If, on the other hand, there is no strong preference for either one form or the other then a disordered structure will arise (Figure 2(c)). It is unlikely that this would give rise to just two NQR signals since, although there are just two distinct local environments, there are a multitude of environments if the nature of neighbouring sites are considered so that a whole spectrum of NQR lines is to be expected with the result that the resonance signal will be broad and weak or even undetectable. The NQR results indicate that the first situation occurs for **3** whereas the second arises for **2**. The crystallographic results for **3** confirm its ordered structure (Figure 3). The crystallographic data for **2**, which is manifestly disordered (Figure 4), were analysed as follows. A difference electron-density map, using calculated structure-factors derived from all atoms except Cl and Br, shows two peaks of equal electron-density, each located at a distance of 1.84 Å from the C(01) atom. A model of the disorder, using four atoms of fixed site occupation of 0.5

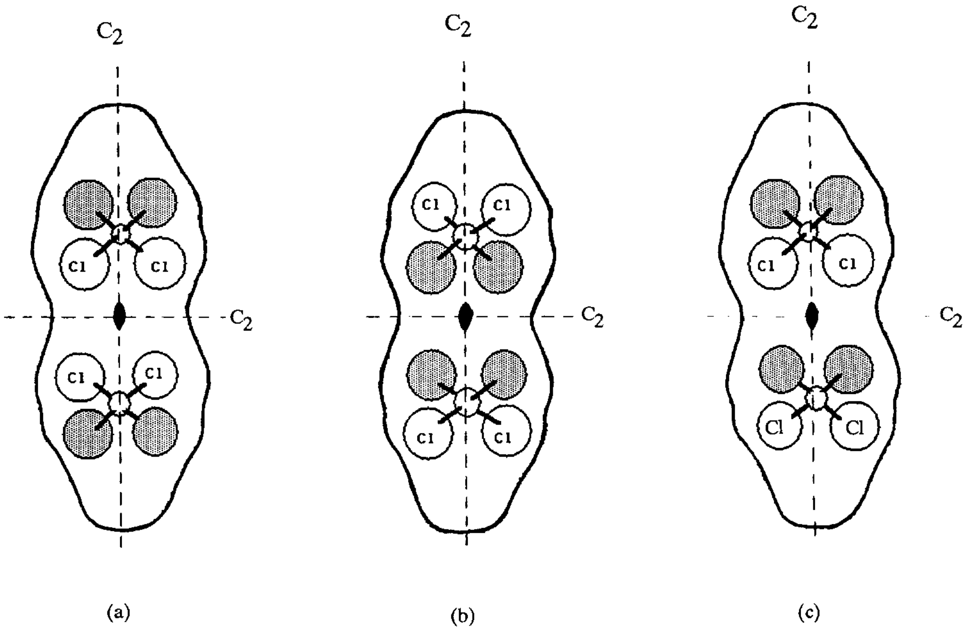


Fig. 2. Orientations of the guest molecules in a cavity having C_{2v} symmetry. (a) and (b) Ordered structures; (c) Disordered structure.

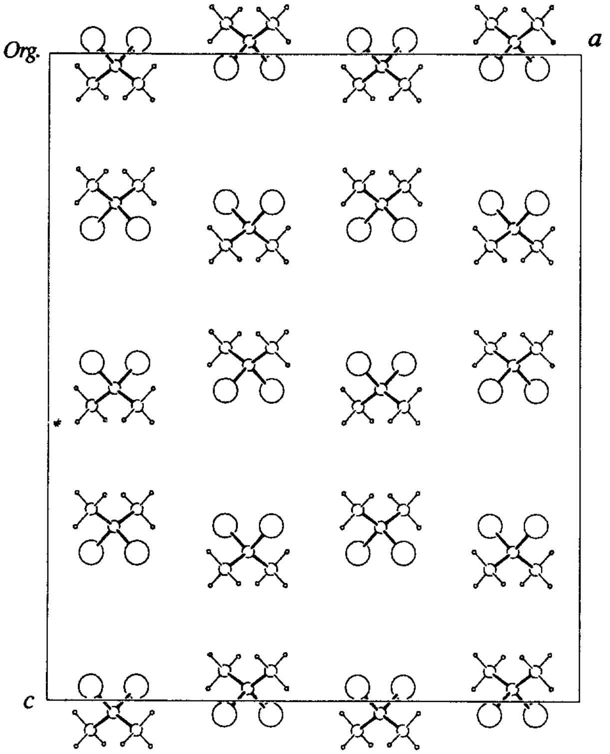


Fig. 3. Ordered guest structure of the clathrate (**3**) (projected down *b*).

consisting of one Cl and one Br initially placed on each of the two sites identified in the electron-density difference map, was refined. The refinement led to four distinct sites, arranged in pairs about their initial positions. It was not possible, on the basis of the resulting bond-lengths and atomic displacement parameters, to specify which of these sites was occupied by Cl and which by Br. Moreover, the measured density of **2** being significantly different than that calculated suggests that some vacancies (about 11% from the observed density) could occur in the crystal and contribute to the broadening and/or disappearance of the NQR signals.

Although the C—C and C—Br bond lengths are very different, the van der Waals volume of a methyl group, 23.5 Å^3, is very similar to that of a bromine atom, 26.0 Å^3 [9]; the shapes and volumes of **2** and **3** are thus very similar and probably cannot account for the difference in behaviour of these two complexes. The most likely explanation lies in the dipole moment: that of 2,2-dichloropropane, the guest molecule in **3**, is 2.27 D [10] whereas dibromodichloromethane, the guest molecule in **2**, has only the very small moment of 0.25 D [11]. Since it has C_2 symmetry, the half of the cavity is certainly polar and a polar guest will orient itself in such a way as to minimise the electrostatic energy *with respect to the host molecules.*

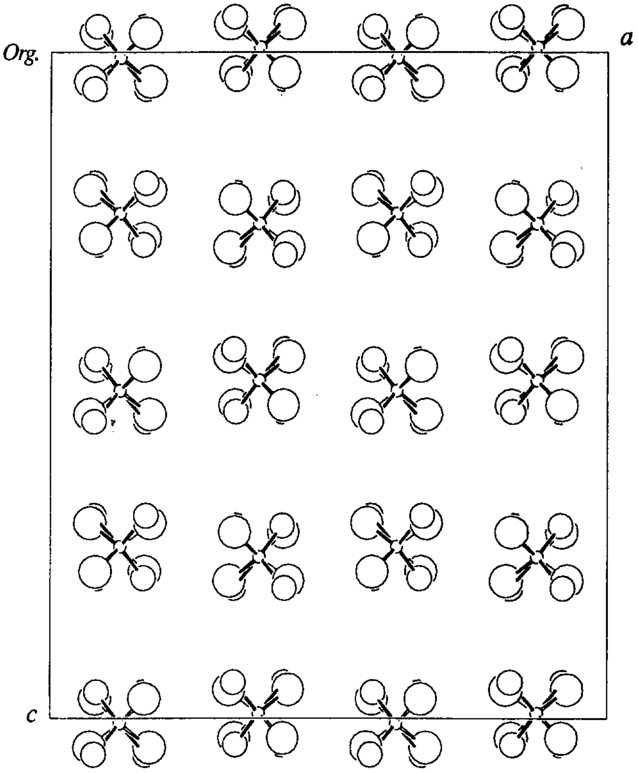


Fig. 4. Disordered guest structure of the clathrate (**2**) (projected down *b*).

In accordance with its disordered structure, [8], **5** shows no NQR signal. Although chloroform is highly polar, its C_3 symmetry is not adapted to the C_2 symmetry of the cavity and the clathrate must be either statically or dynamically disordered. Dichloromethane, however, is both polar and possesses C_2 symmetry; the absence of an NQR signal must therefore be due to rapid reorientation – rendered possible by the small size of the hydrogen atoms (6.3 Å^3, [9])-leading to interchange of the positions of the two equivalent chlorine atoms.

We have, however, obtained two new alternate forms of the complexes with dichloromethane and chloroform; $C2/c$ for dichloromethane in **6**, and $P\bar{1}$ for chloroform in **7**, which both have host/guest ratios of 1 : 2 and which respectively show two and three distinct ^{35}Cl NQR signals. Both the crystal and cavity symmetries are lower than in the orthorhombic forms and the crystal structure shows that the two chlorine atoms in dichloromethane and the three chlorine atoms in chloroform are in crystallographically distinct sites. In both cases the guest molecules are ordered and located in zig-zag channels [12] running throughout the whole crystal rather than in the closed cavities of the orthorhombic system. Figure 5 shows the structure of **6** projected along the *b*-axis whereas Figure 6 shows the ORTEP drawing of **7**.

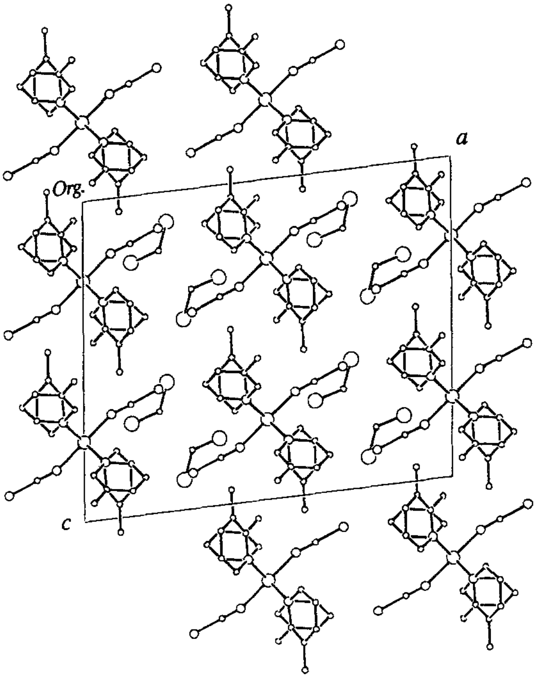


Fig. 5. Crystal structure of **6** projected down the *b* axis.

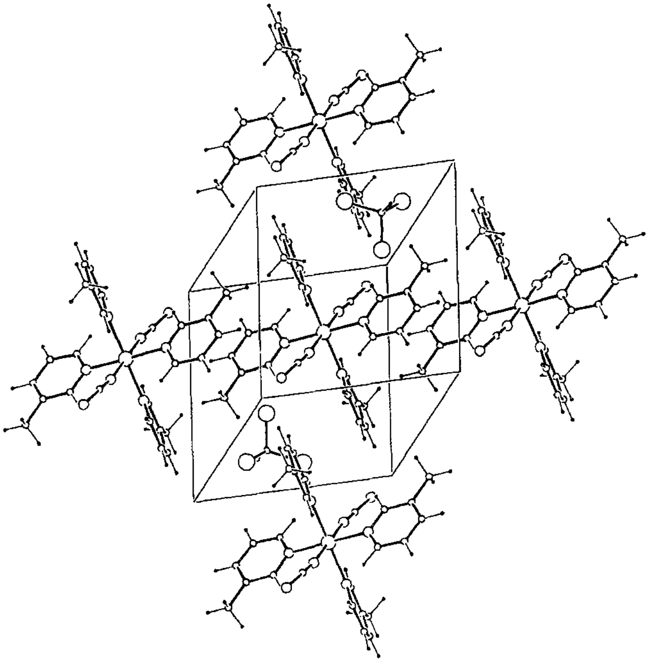


Fig. 6. ORTEP drawing of **7**.

4. Conclusion

These studies illustrate the utility of the NQR method in rapidly providing structural information which could subsequently be confirmed by crystallographic studies. These results presented here illustrate the interplay of the effects of the respective volumes, polarities and symmetries of the host cavity and the guest molecule and the ease with which these Werner complexes can adapt their crystal symmetries to the requirements of the guest molecules.

Acknowledgments

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