of the Claisen rearrangement. The Childs NMR method[9] is not applicable to this particular Lewis acid, because of overlap of the resonances for the aromatic and for the H-3 proton.

We list in the table the sequence of Lewis acidities toward crotonaldehyde as obtained by the present MO method for ca 20 Lewis acids. A first check is its applicability to other α,β-unsaturated carbonyls as Lewis bases. The generality of the method appears to be borne out by the correlation shown in Figure 2, in which the lowering of the π^* level for methyl acrylate is seen to be linearly related to that for crotonaldehyde as the probe substance.

Conclusion

We have provided a method, simple to implement, giving direct access to a quantitative determination of the strength of a Lewis acid. It may usefully complement the array of existing experimental methods for estimating these Lewis acidities, such as Gutmann acceptor numbers,[26] the IR determination of Lappert,[24] or the astute NMR method by Childs[9] that was the springboard for our study.

(26) Gutmann, V. *Coordination Chemistry in Non-Aqueous Solutions*; Springer-Verlag: New York, 1968.

The Application of Nuclear Quadrupole Resonance to the Study of Clathrates. 35Cl NQR and Crystallography of Clathrated CCl4

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Abstract: The 35Cl nuclear quadrupole resonance (NQR) spectra of CCl_4 in more than 20 clathrates have been measured in the range 4-200 K. The crystal structures of CCl_4/Dianin's compound (1), CCl_4/Fe(AcAc)$_3$ (3), CCl_4/Ni(SCN)$_2$(3-MePy)$_4$ (4), and CCl_4/Ni(exan)$_2$(4,4'-dm-2,2'-bpy) (19) clathrates are also reported. Site symmetry and site multiplicity of the guest molecule in clathrates were determined by NQR spectroscopy and by X-ray crystallography. The degree of host–guest interaction was estimated from the NQR frequency shifts. The libration frequencies of the guest molecules in trigonal cavities were determined from NQR frequencies by Bayer–Kushida theory analysis.

Introduction

Clathrates, or more generally *inclusion compounds*, possess two essential components: the first, *the host molecule*, forms a solid lattice characterized by lacunae in which can be included the second component, *the guest molecule*. The intermolecular interactions between these two components are usually very weak compared to a normal chemical bond.

Various physical methods[1] have been used in the study of clathrates and inclusion compounds. Previously, we have briefly reported[2] the applications of the nuclear quadrupole resonance to the study of small guest molecules in different clathrate systems.

Since the electronic field gradient tensor at a nucleus in a molecule depends strongly upon the molecular structure, the nuclear quadrupole interaction offers a sensitive probe which may be used to study inclusion compounds and to obtain information on the following points: (1) site symmetry, (2) site multiplicity, (3) host–guest interaction, (4) guest molecule mobility, (5) molecular disorder, (6) the existence of different clathrate phases, and (7) phase transitions.

Some of the information given by NQR spectra can be confirmed by X-ray structure analysis. Thus, these two physical methods are complementary in studies of clathrates and inclusion compounds.

Although Dianin's compound, Ni(SCN)$_2$(3-MePy)$_4$, and Fe(AcAc)$_3$ complexes are well-known to form clathrates with a great variety of substances and the structures of the chloroform clathrates were previously described,[3-5] their CCl_4 clathrates have never been studied by physical methods, and the crystal structures were unknown. CCl_4 is, however, in our experience, a very appropriate probe molecule in this context since its high symmetry avoids disorder of the guest molecule in the cavities and its high chlorine content increases the inherent sensitivity of the 35Cl NQR method. We have therefore used this guest molecule as a probe for studying different clathrate systems by NQR and X-ray structure analysis.

Experimental Section

Preparations. All host compounds, except ferric acetylacetonate which was a commercially available product, were prepared according to literature methods and characterized by their mass spectra (Finnigan 4023, energy of the ionizing beam, 70 eV) and their 1H NMR spectra (Varian XL100) or by elemental analyses. The clathrates were prepared by recrystallization of the appropriate hosts from CCl_4 as solvent and characterized by using either elemental analyses, thermogravimetric analysis, or, for complexes with known crystal structure, density mea-

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(1) *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 3, Physical Properties and Applications.
(2) Pang, L.; Lucken, E. A. C. *J. Incl. Phenom.* **1987**, *5*, 245.
(3) Flippen, J. L.; Karle, J.; Karle, I. L. *J. Am. Chem. Soc.* **1970**, *92*, 3749.
(4) Nassimbeni, L. R.; Papanicolaou, S.; Moore, M. H. *J. Incl. Phenom.* **1986**, *4*, 31.
(5) Steinbach, J. F.; Burns, J. H. *J. Am. Chem. Soc.* **1958**, *80*, 1839.

surements. It should be noted, however, that most of the complexes lose CCl_4 very easily and thus cannot be properly dried. In these cases the analyses can only be approximate. Freshly prepared samples for NQR spectroscopy were briefly suckered dry and immediately sealed in glass vials.

4-(p-Hydroxyphenyl)-2,2,4-trimethylchroman (1)—Dianin's compound—was prepared according to Baker et al.:[6] mp 156.5-157 °C; M (Ms) 268; $\tau(CDCl_3)$ 9.06, 8.63, and 8.30 (3 H, s, CH_3), 7.68 (2 H, AB, CH_2), 5.40 (1 H, s, OH), 2.7-3.3 (8 H, complex, aromatic). A clathrate with a 6:1 host/guest ratio was formed with CCl_4 (Found: Cl, 8.25. $6(C_{18}H_{20}O_2)\cdot CCl_4$ requires Cl 8.04): mp 160-162 °C.

4-(p-Hydroxyphenyl)-2,2,4-trimethylthiachroman (22) was prepared according to MacNicol:[7] mp 106-107 °C; M (MS) 284; $\tau(CDCl_3)$ 8.88, 8.56, and 8.20 (3 H, s, CH_3), 7.70 (2 H, AB, CH_2), 5.18 (1 H, s, OH), 2.7-3.34 (8 H, complex, aromatic). A clathrate with a 6:1 host/guest ratio was formed with CCl_4 (Found: Cl, 7.86. $6(C_{18}H_{20}OS)\cdot CCl_4$ requires Cl 7.63): mp 118-120 °C.

4-(p-Mercaptophenyl)-2,2,4-trimethylchroman (23) was prepared according to Hardy and MacNicol et al.:[8] mp 136-137 °C; M (MS) 284; $\tau(CDCl_3)$ 9.06, 8.66, and 8.33 (3 H, s, CH_3), 7.80 (2 H, AB, CH_2), 2.7-3.3 (8 H, complex, aromatic). A clathrate with a 3:1 host/guest ratio was formed with CCl_4 (Found: Cl, 14.15. $3(C_{18}H_{20}OS)\cdot CCl_4$ requires Cl 14.09): mp 78-80 °C.

Hexakis(phenylthio)benzene (HPTB) (2) was prepared according to MacNicol et al.:[9] mp 178-179 °C; M(MS) 726; $\tau(CDCl_3)$ 2.7-3.2 (30 H, complex, aromatic). A clathrate with a 1:2 host/guest ratio was formed with CCl_4 (Found: loss of CCl_4 at 58-86 °C, 24.5. $C_{42}H_{30}$-$S_6\cdot 2CCl_4$ requires CCl_4 29.7): mp 179-180 °C.

Werner complexes MX_2Y_4 (4-16, 24) were prepared according to Schaeffer et al.:[10] (M = Ni, Co, Fe, Mn; X = SCN, SeCN; Y = 3-MePy, 4-EtPy, 4-ViPy; 3-MePy = 3-methylpyridine, 4-EtPy = 4-ethylpyridine, 4-ViPy = 4-vinylpyridine).

$Ni(SCN)_2(3-MePy)_4$ (4) formed a 1:1 host/guest clathrate with CCl_4 in the orthorhombic system Fddd (Found: density, 1.34 g/cm³. C_{26}-$H_{28}N_6NiS_2\cdot CCl_4$ requires 1.35 g/cm³).

$Ni(SCN)_2(4-EtPy)_4$ formed a 2:1 host/guest clathrate (8) with CCl_4 in the tetragonal system $I4_1/c$ with 2-methoxyethanol as a cosolvent (Found: density, 1.27 g/cm³. $2(C_{30}H_{36}N_6NiS_2)\cdot CCl_4$ requires 1.28 g/cm³).

$Ni(SCN)_2(4-EtPy)_4$ formed a 1:2 host/guest clathrate (9) with CCl_4 in the monoclinic system $P2_1/c$ (Found: loss of CCl_4 at 25 °C/6 h, 34.2. $C_{30}H_{36}N_6NiS_2\cdot 2CCl_4$ requires CCl_4 33.8.

$Ni(SeCN)_2(4-EtPy)_4$ formed a 1:2 host/guest clathrate (13) with CCl_4 (Found: loss of CCl_4 at 25 °C/6 h, 32.3. $C_{30}H_{36}N_6NiSe_2\cdot 2CCl_4$ requires CCl_4 28.2).

$Ni(SCN)_2(4-ViPy)_4$ formed a 1:2 host/guest clathrate (24) with CCl_4 in monoclinic system $C2/c$ (found: density, 1.41 g/cm³. $C_{30}H_{28}N_6Ni$-$S_2\cdot 2CCl_4$ requires 1.44 g/cm³).

Nickel ethyl xanthate-amine complexes $Ni(exan)_2Y$ (17-21) were prepared according to Krüger and Winter[11] (Y = 4,4'-bpy, 2,2'-bpy, 1,10-phen, 4,4'-dm-2,2'-bpy, and 2,2'-dpa; exan = ethyl xanthate, 4,4'-bpy = 4,4'-bipyridyl, 2,2'-bpy = 2,2'-bipyridyl, 1,10-phen = 1,10-phenanthroline, 4,4'-dm-2,2'-bpy = 4,4'-dimethyl-2,2'-bipyridyl, 2,2'-dpa = 2,2'-dipyridylamine).

$Ni(exan)_2(4,4'-bpy)$ (17) formed a 1:1 host/guest clathrate with CCl_4 as yellow needles (found: C, 33.52; H, 2.95; N, 4.61; Cl, 23.16. C_{16}-$H_{18}N_2NiO_2S_4\cdot CCl_4$ requires C, 33.41; H, 2.97; N, 4.58; Cl, 23.21): mp 146 °C dec.

$Ni(exan)_2(o-phen)$ (18) formed a 1:1 host/guest clathrate with CCl_4 as olive-green needles (Found: Cl, 22.36. $C_{18}H_{18}N_2NiO_2S_4\cdot CCl_4$ requires Cl, 22.3): mp > 250 °C, lost CCl_4 at 120 °C.

$Ni(exan)_2(4,4'-dm-2,2'-bpy)$ (19) formed a 1:2 host/guest clathrate with CCl_4 as olive-green needles (Found: Cl, 37.31. $C_{18}H_{22}N_2NiO_2$-$S_4\cdot 2CCl_4$ requires Cl, 35.73): mp 148 °C dec.

$Ni(exan)_2(2,2'-dpa)$ (20) formed a 1:2 host/guest clathrate with CCl_4 as green plates (Found: Cl, 43.27. $C_{16}H_{19}N_3NiO_2S_4\cdot 2CCl_4$ requires Cl, 36.37): mp 92-95 °C dec.

$Ni(exan)_2(2,2'-bpy)$ (21) formed a 1:1 host/guest clathrate with CCl_4 as brown needles (Found: Cl, 21.50. $C_{16}H_{18}N_2NiO_2S_4\cdot CCl_4$ requires Cl, 23.21): mp 125-127 °C dec.

Nuclear Quadrupole Resonance. The NQR spectra from 77 to 200 K were measured on a Decca superregenerative spectrometer, frequencies being compared to harmonics from an internal crystal-controlled oscillator. Temperatures were measured with a Hewlett-Packard 2802A digital thermometer by using a platinum thermocouple (precision ±0.5 °C) and varied with an Artronix 5301-E temperature controller.

The NQR spectra from 4 to 77 K were measured on a pulse spectrometer which consists of Bruker 323s oscillator, MATEC 5100 amplifier, MATEC 625 phase detector, LeCROY 9400 signal-averager, and a Hewlett-Packard 9816 minicomputer. Low temperatures were obtained and measured with an Oxford CF200 continuous flow system which is equipped with a cryostat (CF200), gas shielded helium transfer line (CFS300), gas flow pump (CF2), flow control (VC30), and a digital temperature controller by using a Au + 0.02% Fe thermocouple (precision ±0.1 °C).

Crystallographic Measurements. The single crystals of the corresponding clathrates were obtained by recrystallization from CCl_4 and were mounted in capillaries. The clathrates 3, 4, and 19 are unstable, so their sample capillaries must be filled with the mother liquor to prevent deterioration in air. Cell parameters and reflection intensities were measured on a Philips PW1100 (for compounds 1 and 19) and a Nonius CAD4 (for 3 and 4) diffractometers with graphite monochromated Mo $K\alpha$ radiation. A summary of crystal data, intensity measurements, and structure refinement is given in Table II, and selected geometrical parameters are reported in Tables VII and VIII. The structures were solved by direct methods (MULTAN-84[13]) and refined by least-squares analysis with the XTAL[14] program. Atomic scattering factor and anomalous dispersion terms are taken from ref 15. All coordinates of the hydrogen atoms have been calculated. Chart 1 shows the atom numbering for compounds 1, 3, 4, and 19.

Results and Discussion

Molecular Site Symmetry. The ^{35}Cl nuclei ($I = 3/2$) gives only one resonance line in NQR. Thus the isolated CCl_4 molecule, where all four chlorine atoms are equivalent, would show only one resonance. In the crystalline phase, however, if all the chlorine atoms of CCl_4 were in crystallographically nonequivalent positions one would obtain four NQR lines. However, some crystal symmetry elements may bring certain chlorine atoms into equivalent positions, so the number of NQR lines is less than 4, and the signal intensities are then proportional to the number of these equivalent atoms. Thus, one can examine the site symmetry of the guest molecule from the number and the intensity ratio of NQR signals.

Figure 1 shows the NQR spectra of CCl_4 in the three different clathrates at 77 K. The four signals of the same intensity of $CCl_4/Ni(exan)_2(4,4'-bpy)$ clathrate (17) indicate that the guest molecule is in a nonsymmetric site, i.e., the four chlorine atoms are situated respectively in four different crystallographic environments. In both the two next spectra, the guest molecule shows two signals: two signals of the same intensity for CCl_4/Ni-$(SCN)_2(3-MePy)_4$ clathrate (4), but two signals with a 3:1 intensity ratio for $CCl_4/Fe(AcAc)_3$ clathrate (3); it is clear that in this case the four chlorine atoms of the guest molecule are distributed in two nonequivalent groups. In the case of Ni-$(SCN)_2(3-MePy)_4$, there are two equivalent atoms in each group, so the guest molecule must be present at a 2-fold symmetric site, whereas in $Fe(AcAc)_3$, the ratio of the chlorine atoms is 3:1 because of the presence of a 3-fold symmetry axis, thus, one chlorine atom lies along the symmetry axis and the remaining three chlorine atoms are related by the 3-fold symmetry operation in the equatorial positions.

The ^{35}Cl NQR frequencies of CCl_4 as a guest molecule in various clathrates are shown in Table I. From the number and the intensity ratios of the signals, we can draw the following conclusions: (1) the guest molecule is in a 3-fold symmetric site in Dianin's compound (1), HPTB (2), and $Fe(AcAc)_3$ (3) clathrates; (2) the guest molecule is in the 2-fold symmetric site

(6) Baker, W.; Floyd, A. J.; McOmie, J. F. W.; Pope, G.; Weaving, A. S.; Wild, J. H. J. Chem. Soc. 1956, 2010.

(7) MacNicol, D. D. J. Chem. Soc., Chem. Commun. 1969, 836.

(8) Hardy, A. D. U.; MacNicol, D. D.; McKendrich, J. J.; Wilson, D. R. Tetrahedron Lett. 1975, 52, 4711.

(9) MacNicol, D. D.; Mallinson, P. R.; Murphy, A.; Sym, G. J. Tetrahedron Lett. 1982, 23, 4131.

(10) Schaeffer, W. D.; Dorsey, W. S.; Skinner, D. A.; Christian, C. G. J. Am. Chem. Soc. 1957, 79, 5870.

(11) Krüger, A. G.; Winter, G. Aust. J. Chem. 1971, 24, 161.

(12) Busing, W. R.; Levy, H. A. Acta Crystallogr. 1964, 17, 142.

(13) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. A System of Computer Programs for the Automatic Solution of Crystal Structure from X-ray Diffraction Data; Universities of York, England, and Louvain-la-Neuve, Belgium, 1984.

(14) XTAL2.4 User's Manual; Hall, S. R., Stewart, J. M., Eds.; Universities of Western Australia and Maryland, 1988.

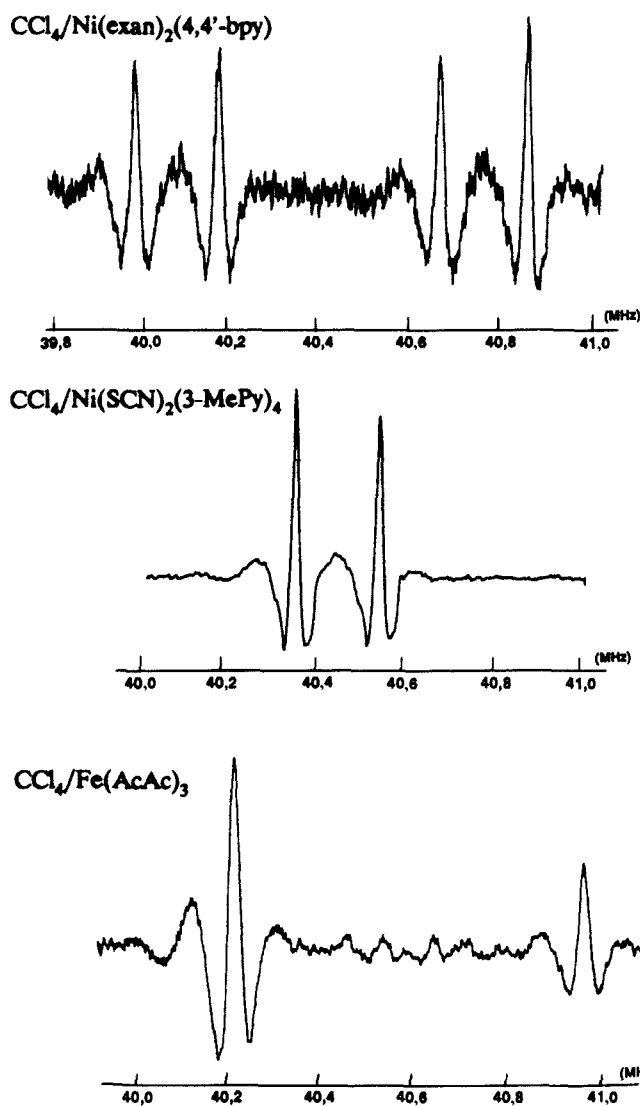(15) International Tables for X-ray Crystallography; Kynoch Press: Birmingham, 1974; Vol. IV.

CCl₄/Ni(exan)₂(4,4'-bpy)

CCl₄/Ni(SCN)₂(3-MePy)₄

CCl₄/Fe(AcAc)₃

Figure 1. ³⁵Cl NQR spectra of the CCl₄ guest molecule at 77 K in three different clathrates.
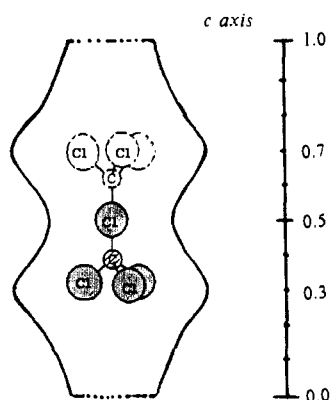
Figure 2. CCl₄ molecule in trigonal cavity of Dianin's compound.

in clathrates of M(SCN)₂(3-MePy)₄ (**4–7**) (M = Ni, Co, Fe, Mn) or in Ni(SCN)₂(4-ViPy)₄ clathrate (**24**); (3) the guest molecule is present at a nonsymmetric site in clathrates of MX₂(4-EtPy)₄ (**9–16**) (M = Ni, Co, Fe, Mn; X = SCN, SeCN) and NiX₂Y (**17–21**) (X = ethyl xanthate, Y = dinitrogen amine) because the spectra consist of four or more resonance lines.

The crystal structure analyses confirm some of these results. The CCl₄/Dianin's compound clathrate (**1**) was found in a hexagonal crystal system with the space group R3̄. The structure is similar to its chloroform analogue.³ The 3-fold symmetric cavity formed by six host molecules, parallel to the c axis, has a centrosymmetric hourglass shaped form, and the guest molecule is
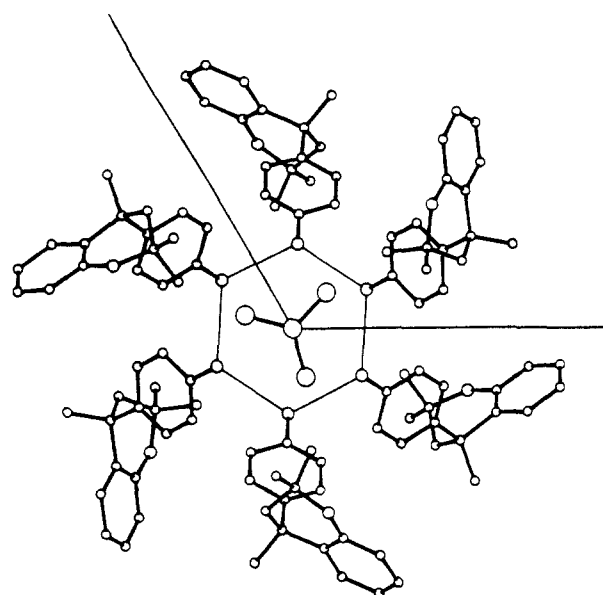

Figure 3. Projection of CCl₄/Dianin's compound (**1**) clathrate down c. The Dianin's compound molecules are linked by hydrogen bonds with O···O distances = 2.869 (11) and 2.820 (4) Å for 293 and 140 K, respectively.

T=140K

T=298K
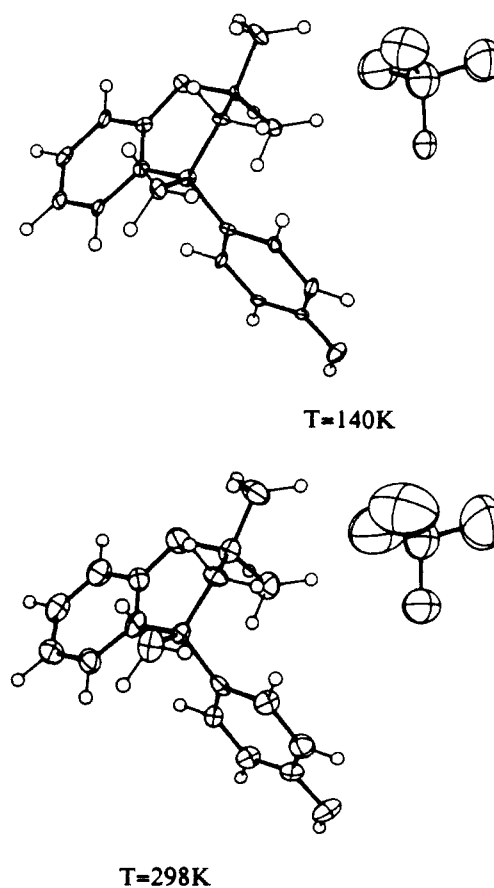
Figure 4. ORTEP drawings of Dianin's compound host molecule and CCl₄ guest in the clathrate.

situated on the trigonal axis, the axial chlorine atom is exactly at the center of inversion, and three equatorial chlorine atoms are present in one-half of the cavity at z ≃ 0.3 or z ≃ 0.7 (see Figure 2). The another half of the cavity is empty because the cavity volume is not big enough to permit a second CCl₄ guest molecule to enter, thus the host-guest ratio is kept to 6:1. Figure 3 shows the structure of the clathrate projected along the c axis. We report also the results obtained at 140 K. Figure 4 shows ORTEP drawings

Chart I. Molecular Formulas and Atomic Numbering for **1, 3, 4,** and **9**

(1) X=O, Y=O

(22) X=S, Y=O

(23) X=O, Y=S

(3) C_3 axis

(4) C_2 axis

(19)
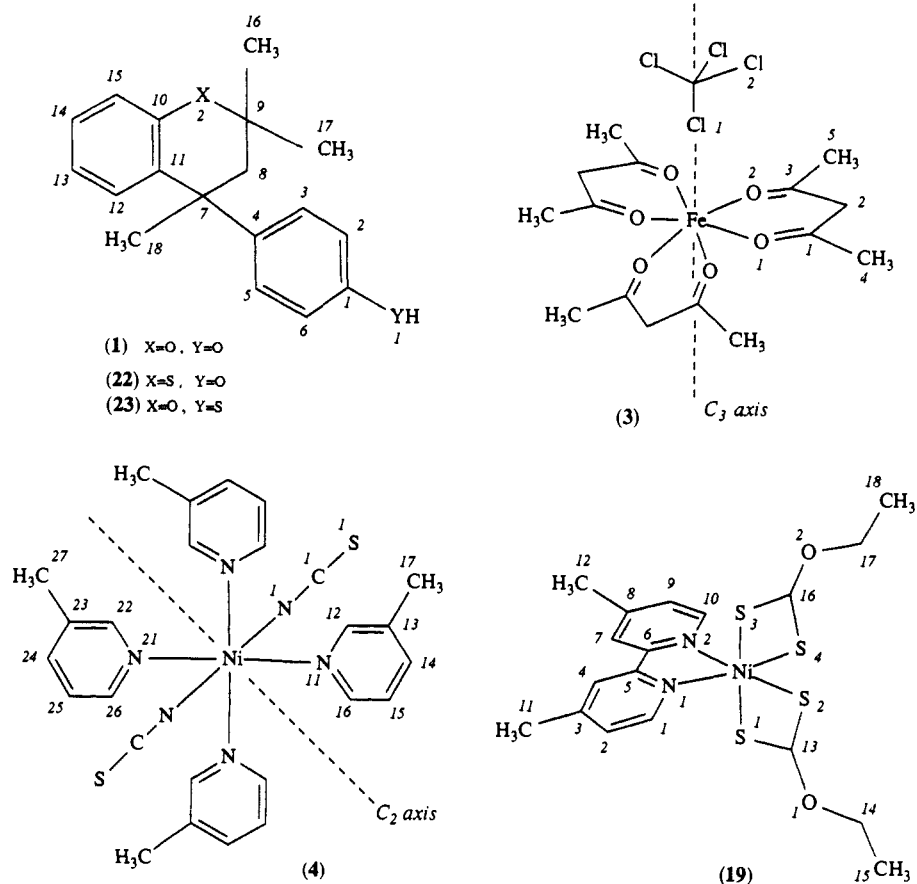
of CCl₄/Dianin's compound (**1**) at two temperatures.

The CCl₄/HPTB clathrate (**2**) crystallizes also in the space group *R*3̄ reported by MacNicol et al.[16] The slightly longer trigonally symmetric cavity, formed by HPTB host in a manner analogous to that found in Dianin's compound, can be occupied by two CCl₄ guest molecules. The guest molecules are likewise situated on the trigonal axis in ordered positions with the axial chlorine atom pointing to the center of inversion.

The CCl₄/Fe(AcAc)₃ clathrate (**3**) was also found in the hexagonal crystal system but in the noncentrosymmetric space group *R*3. The iron atom is on a 3-fold axis, and the three acetylacetonate rings are in a propeller-shaped configuration twisted by 61.1° from the coplanar arrangement. One such molecule forms the bottom of the cavity, and the molecules at *z* = 1/3 and *z* = 2/3 form the edge and the top of the cavities (see Figure 5). The trigonal cavity has an egg-shaped form without centrosymmetry, the ordered guest molecule is situated on the trigonal axis with the axial atom pointing to the narrowest end of the cavity, the axial chlorine atom is approximatively at *z* ≃ 0.23, and the equatorial atoms are at *z* ≃ 0.36. Figure 6 shows the structure of the clathrate projected along the *c* axis.

The crystal structure of CCl₄/Ni(SCN)₂(3-MePy)₄ (**4**) is analogous to that of the CHCl₃/Ni(SCN)₂(3-MePy)₄ clathrate mentioned by Nassimbeni.[21] The guest molecules are located on a 2-fold symmetric site (see Figure 7), so the two pairs of the two equivalent chlorine atoms are in different environments. The main difference from the CHCl₃ clathrate lies in the fact that the guest molecules are ordered in the molecular sites because CCl₄, unlike CHCl₃, has the same 2-fold symmetry elements as the cavity.

Fractional atomic coordinates of clathrates **1, 3,** and **4** are reported in Tables III–V (supplementary material), and Table VII shows their bond lengths.

The CCl₄/Ni(SCN)₂(4-ViPy)₄ clathrate (**24**) also possesses the 2-fold symmetric cavities in the space group *C2/c* reported by Nassimbeni et al.[20] As for its NQR spectrum, we have observed two weak and broad signals at 77 K; it is clear that the cavities are slightly bigger than those formed by the Ni(SCN)₂(3-MePy)₄ complex, so that the movements of the guest molecules are of higher amplitude, which broadens the signal and decreases its intensity.

The crystal structure of CCl₄/Ni(SCN)₂(4-EtPy)₄ (**9**) has also been reported by Nassimbeni et al.[17] The clathrate (space group
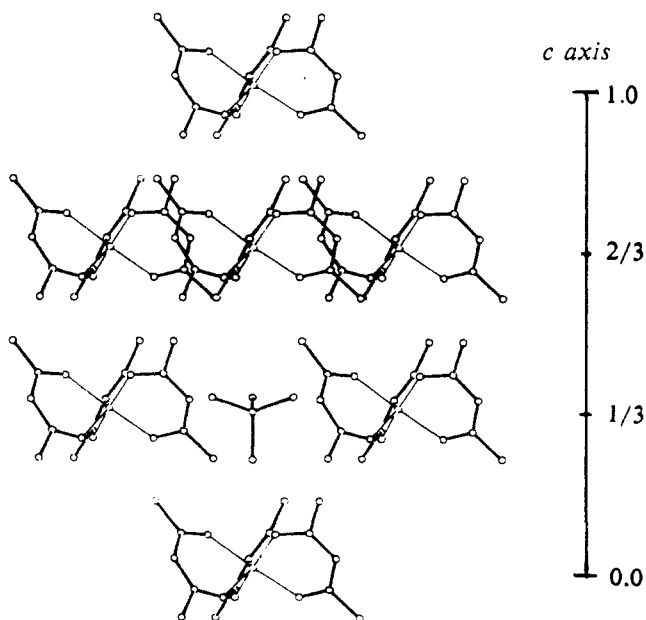

c axis

1.0

2/3

1/3

0.0

Figure 5. Molecular packing of CCl₄/Fe(AcAc)₃ (**3**) clathrate along the *c* axis in crystal.

(16) MacNicol, D. D.; Hardy, A. D. U.; Wilson, D. R. *J. Chem. Soc., Perkin Trans. II* **1979**, 1011.

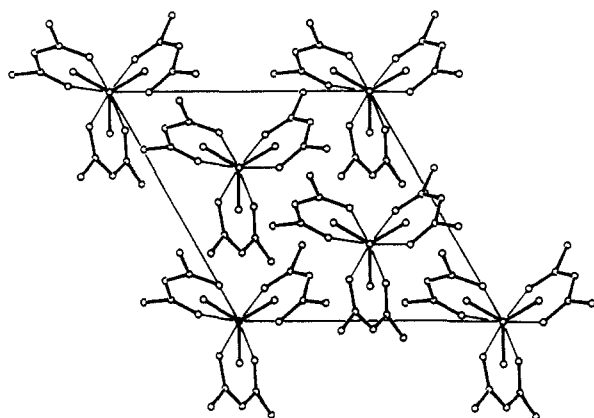**Figure 6.** Projection of $CCl_4/Fe(AcAc)_3$ (3) clathrate down c.

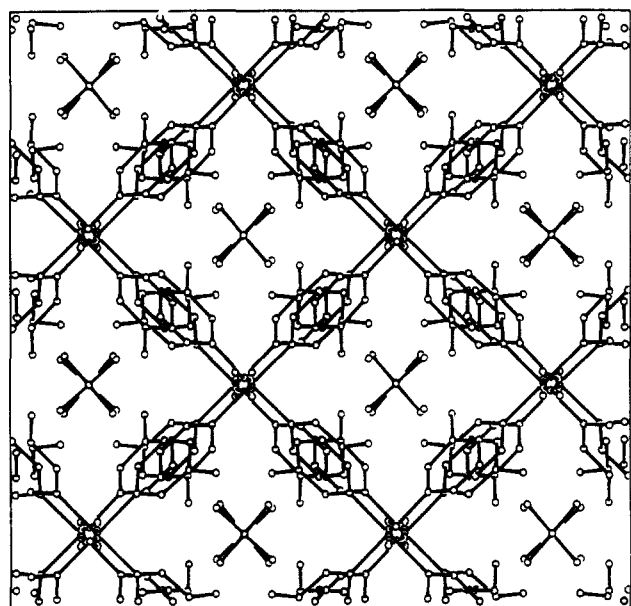**Figure 7.** Projection of $CCl_4/Ni(SCN)_2(3\text{-MePy})_4$ (4) clathrate down c.

Figure 8. Projection of $CCl_4/Ni(exan)_2(4,4'\text{-dm-2,2'-bpy})$ (19) clathrate down b.
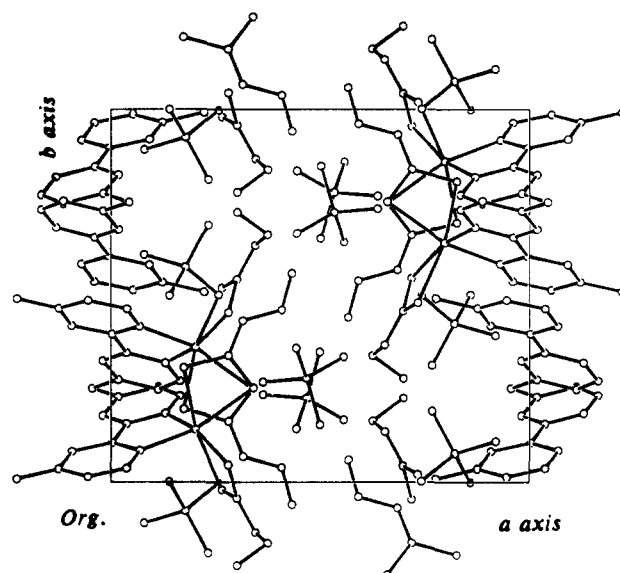
Figure 9. Projection of $CCl_4/Ni(exan)_2(4,4'\text{-dm-2,2'-bpy})$ (19) clathrate down c.

$P2_1/c$) possesses zigzag channels in which two equivalent non-symmetric guest molecules are related by a center of inversion. This result is in accord with the fact that the clathrate gives four distinct NQR signals of the same intensity.

Molecular Site Multiplicity. Guest molecules showing more distinct resonance lines than nuclei present in the isolated molecule must be in multiple molecular sites.

In Table I three clathrates (19–21) show more than four NQR lines at 77 K, which indicates that the clathrates have two non-symmetric molecular sites; the guest molecules are thus in two different environments, and each molecule has four nonequivalent chlorine atoms. The possibility of the presence of two crystal phases for these clathrates may be excluded: first, no distinct color and forms of two mixed crystal phases were found in the preparation of the clathrates; second, the intensity of all signals is always the same so that the amount of the two different molecules is equal, and it is more resonable to make the hypothesis of the presence of two molecular sites rather than to suppose being faced with two molecular crystal phases. Finally, when two crystal phases coexist in a system, one of them is usually metastable and slowly is transformed to the other more stable phase. We have observed no such change in the NQR spectra.

We have confirmed the existence of the two molecular sites in $CCl_4/Ni(exan)_2(4,4'\text{-dm-2,2'-bpy})$ clathrate (19) by crystallog-

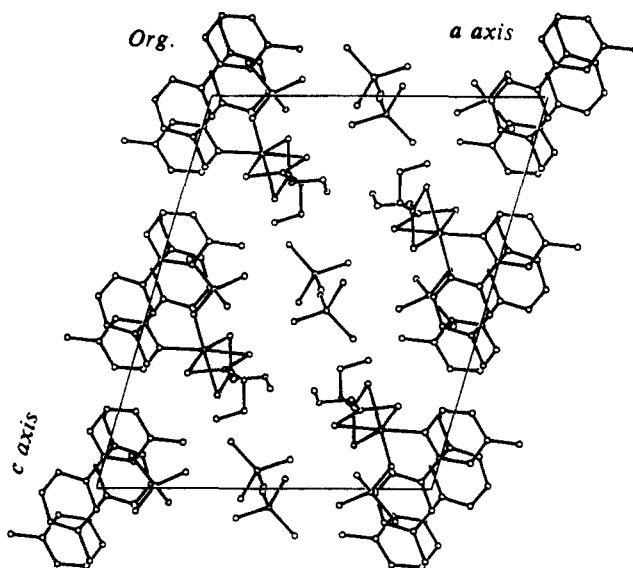raphy. The clathrate was found in a monoclinic crystal system with the space group $P2_1/c$ (see Table II).

The two independent guest molecules (G1 and G2) of the clathrate (19) are involved in three distinct channels, each of them being parallel to a crystallographic axis. G2 is implicated in two channels, one is parallel to the b axis (Figure 8) at $x = {}^1/_2$, $z = 0$ (and ${}^1/_2$), the molecules being related by a center of inversion; the second is parallel to the c axis (Figure 9) at $x \simeq {}^1/_2$, $y = {}^1/_4$ (and ${}^3/_4$), and the molecules within the channel are related by the glide plane perpendicular to the b axis. The third channel (Figure 10) is parallel to the a axis (at $y = 0$, $z = 0$ and $y = {}^1/_2$, $z = {}^1/_2$) and contains the molecules G1 related by a center of inversion. The fractional atomic coordinates and bond lengths for this clathrate are reported in Tables VI (supplementary material) and VIII.

Degree of Host–Guest Interaction. In spite of the perturbation brought about by lattice effects, the degree of host–guest interaction can be straightforwardly estimated from the NQR frequency shifts. When CCl_4 is in its pure state, i.e., the pure solid, the electric field-gradient tensor at the nuclei is affected by a molecular lattice effect generated by the neighboring CCl_4 molecules, and the intermolecular interactions are on the order of van der Waals forces.[22] When the guest molecules are introduced into a host lattice, the electric field tensor is affected by

(17) Moore, M. H.; Nassimbeni, L. R.; Niven, M. L. *J. Chem. Soc., Dalton Trans.* **1987**, 2125.
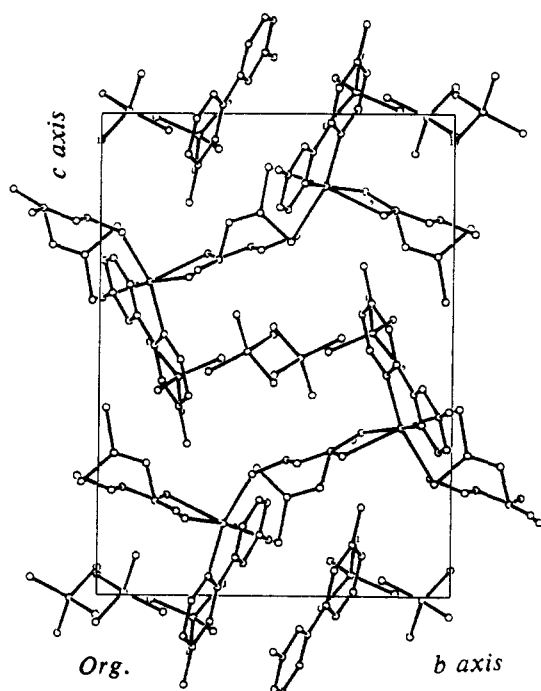
35Cl NQR and Crystallography of Clathrated CCl4

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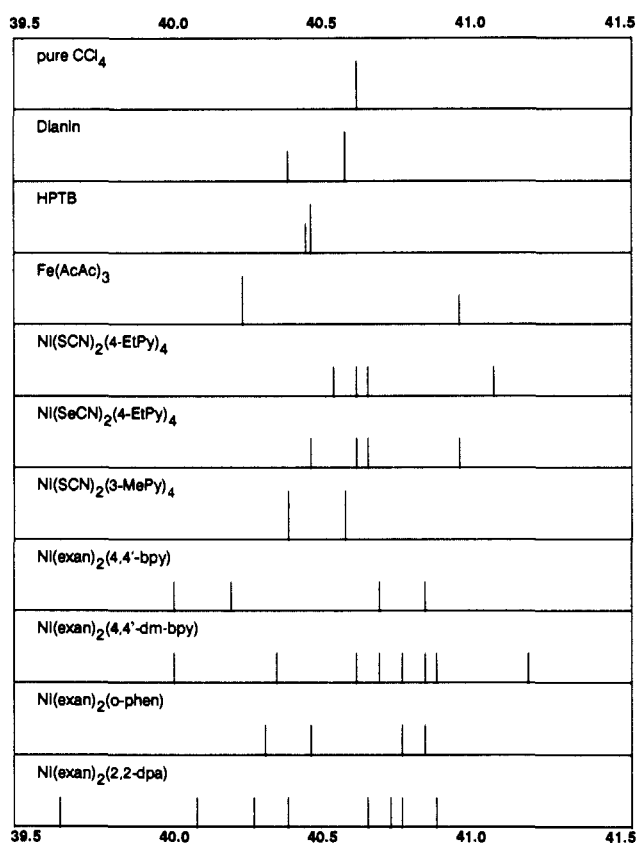Figure 10. Projection of $CCl_4/Ni(exan)_2(4,4'$-dm-2,2'-bpy) (19) clathrate down *a*.

Figure 11. ^{35}Cl NQR frequencies at 77 K of the CCl_4 guest molecule in various clathrates.

the host lattice. If we choose the NQR frequency of the pure guest molecule as a reference and if the NQR frequency shifts of the clathrates from this are not too much, then we may be sure that the host lattice effect perturbation and host–guest interactions are all on the same level as those of the pure molecule.

Figure 11 shows the NQR frequencies shifts at 77 K of the guest molecule in various clathrates. Although the guest molecule is
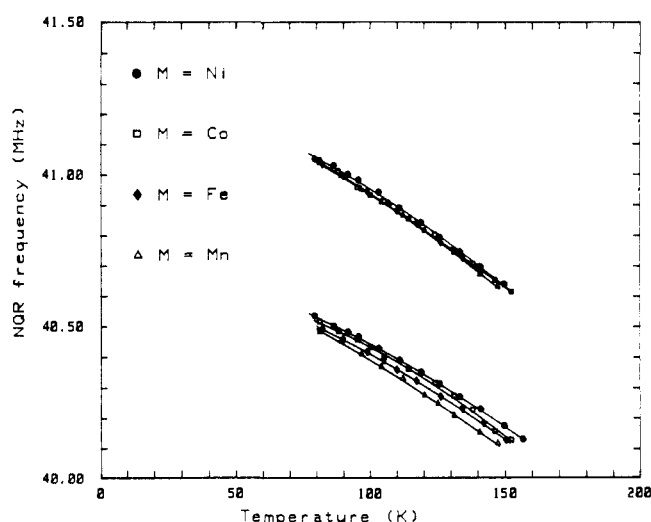

Figure 12. Temperature dependence of two of the ^{35}Cl NQR frequencies of the CCl_4 in $M(SCN)_2(4\text{-EtPy})_4$ clathrates (γ phase). The temperature dependence of the other two lines is similar, but they have been omitted for the sake of clarity.

placed in the different molecular environments of the host structures, the NQR frequencies shift only a small amount from one clathrate to another. The shifts of average frequency are not more than 0.5% of the average frequency of the guest in its pure state (40.6 MHz), although the frequency spread for a given clathrate may be as high as 1.3 MHz, 3.3% of the average frequency. Such relatively small shifts are indicative of weak intermolecular van der Waals forces.

Existence of Different Clathrate Phases. Since the crystal lattice effect affects the electric field-gradient tensor at the nuclei, we can distinguish one clathrate phase from another directly by its different resonance lines. Furthermore, as the temperature dependence of the NQR frequencies of guest molecules depends upon the cavity properties (form, size, environment, etc.), one can also distinguish different clathrate phases by the temperature dependence of their resonance frequencies.

Moore et al.[17] showed that the $CCl_4/Ni(SCN)_2(4\text{-EtPy})_4$ clathrate can crystallize in two different crystal phases: one is tetragonal, $I4_1/a$, the β phase, in which the guest molecules are located at a $\bar{4}$ (8e) site; another is monoclinic, $P2_1/c$, the γ phase, in which the guest molecules are situated at a nonsymmetric site. The tetragonal phase did not show any NQR resonance lines, probably due to effects of the disorder which was mentioned by Moore et al.;[17] on the other hand, the monoclinic phase gave four distinct signals, in agreement with the crystal structure. We can confirm that the cobalt, iron, and manganese analogues form the same monoclinic phase as the nickel complex does, because these clathrates show analogous resonance lines whose temperature dependence is very similar (see Figure 12).

The situation is different for the $CCl_4/M(SCN)_2(3\text{-MePy})_4$ clathrates (4–7). We conclude that these clathrates crystallize in the orthorhombic system *Fddd*, for M = Ni and M = Co, since these two analogous clathrates have the same temperature dependence of the NQR frequency, whereas the iron analogue has a different temperature dependence (see Figure 13). In the case of the manganese analogue, although its signals were too weak to allow the temperature dependence to be determined, its NQR frequencies are very similar to that of iron clathrate. Thus, the iron and manganese clathrates exist in a crystal phase different from the nickel and cobalt ones.

Molecular Mobility. When guest molecules are trapped in clathrate cavities, they generally will have some degree of mobility and can thus carry out a variety of molecular movements: translation, vibration, rotation, and libration. The amplitudes of the movements depend upon the ratio of the volume of the guest to the volume of the cavity—the size factor—and on the various energy barriers to molecular reorientation—the form factor. For

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Table I. [35]Cl NQR Frequencies (with Intensity Ratio in Parentheses) of CCl_4 in Various Clathrates

	resonance frequency (MHz)			
clathrate	4 K	77 K	space group	ref
(1) CCl_4/Dianin's compound	40.613 (1) 40.947 (3)	40.351 (1) 40.544 (3)	$R\bar{3}$	this work
(2) CCl_4/HPTB	40.921 (3) 41.174 (1)	40.442 (1) 40.453 (3)	$R\bar{3}$	16
(3) CCl_4/Fc(AcAc)$_3$	40.524 (3) 41.137 (1)	40.211 (3) 40.947 (1)	$R3$	this work
(4) CCl_4/Ni(SCN)$_2$(3-MePy)$_4$	40.720 (1), 41.128 (1)	40.351 (1), 40.541 (1)	$Fddd$	this work
(5) CCl_4/Co(SCN)$_2$(3-MePy)$_4$	40.728 (1), 41.126 (1)	40.337 (1), 40.522 (1)	$Fddd$	a
(6) CCl_4/Fe(SCN)$_2$(3-MePy)$_4$		40.408 (1), 40.645 (1)	unknown	
(7) CCl_4/Mn(SCN)$_2$(3-MePy)$_4$		40.406 (1), 40.561 (1)	unknown	
(8) CCl_4/Ni(SCN)$_2$(4-EtPy)$_4$		no signal	$I4_1/c$	17
(9) CCl_4/Ni(SCN)$_2$(4-EtPy)$_4$		40.533 (1), 40.599 (1) 40.650 (1), 41.051 (1)	$P2_1/c$	17
(10) CCl_4/Co(SCN)$_2$(4-EtPy)$_4$		40.514 (1), 40.582 (1) 40.653 (1), 41.046 (1)	$P2_1/c$	a
(11) CCl_4/Fe(SCN)$_2$(4-EtPy)$_4$		40.490 (1), 40.578 (1) 40.643 (1), 41.033 (1)	$P2_1/c$	a
(12) CCl_4/Mn(SCN)$_2$(4-EtPy)$_4$		40.482 (1), 40.560 (1) 40.655 (1), 41.038 (1)	$P2_1/c$	a
(13) CCl_4/Ni(ScCN)$_2$(4-EtPy)$_4$		40.430 (1), 40.615 (1) 40.652 (1), 40.937 (1)	unknown	
(14) CCl_4/Co(ScCN)$_2$(4-EtPy)$_4$		40.357 (1), 40.513 (1) 40.599 (1), 40.862 (1)	unknown	
(15) CCl_4/Fc(ScCN)$_2$(4-EtPy)$_4$		40.438 (1), 40.561 (1) 40.686 (1), 40.960 (1)	unknwon	
(16) CCl_4/Mn(ScCN)$_2$(4-EtPy)$_4$		40.421 (1), 40.553 (1) 40.673 (1), 40.961 (1)	unknown	
(17) CCl_4/Ni(cxan)$_2$(4,4'-bpy)	40.634 (1), 40.759 (1) 41.194 (1), 41.069 (1)	39.965 (1), 40.170 (1) 40.660 (1), 40.851 (1)	unknown	
(18) CCl_4/Ni(cxan)$_2$(o-phen)	40.723 (1), 40.826 (1) 40.912 (1), 41.100 (1)	40.298 (1), 40.431 (1) 40.755 (1), 40.815 (1)	unknown	
(19) CCl_4/Ni(cxan)$_2$(4,4'-dm-2,2'-bpy)		39.969 (1), 40.327 (1) 40.613 (1), 40.757 (1) 40.657 (1), 40.818 (1) 40.857 (1), 41.183 (1)	$P2_1/c$	this work
(20) CCl_4/Ni(exan)$_2$(2,2'-dpa)		39.561 (1), 40.061 (1) 40.260 (1), 40.352 (1) 40.627 (1), 40.708 (1) 40.763 (1), 40.890 (1)	unknown	
(21) CCl_4/Ni(exan)$_2$(2,2'-bpy)		40.3–40.8[b]	unknown	
(22) CCl_4/Dianin II		40.330 (1)	$R\bar{3}$	18
(23) CCl_4/Dianin III		no signal	$R\bar{3}$	19
(24) CCl_4/Ni(SCN)$_2$(4-ViPy)$_4$		40.163 (1), 40.719 (1)	$C2/c$	20

[a] The space group has not been determined by crystallographic method, but the close similarity between the NQR results for these compounds and those of the analogous nickel complex are strong evidence that the complexes are isomorphous.   [b] Eight very close resonances.

a given guest molecule in a cavity of given type, the form factor is nearly constant, so one can examine the influence of the cavity volume on the molecular movements.

Molecular motion affects nuclear quadrupole resonance frequencies in so far as such motion affects the orientation of the quadrupole coupling tensor and thus gives rise to motional averaging. Translational motion has thus no effect on quadrupole resonance frequencies. In the limit of rapid and random reorientation the average value of the field-gradient tensor is of course zero, but long before this occurs the quadrupole relaxation time will have become too short for lines to be observable. Thus the fact that the NQR signal of a guest molecule is observable at all is an indication that fits fairly closely into the molecular cavity. For moderate vibration amplitudes the effect of motional averaging is to decrease somewhat the effective value of the field gradient, and, since the vibration amplitude increases with temperature, pure quadrupole resonance frequencies are inversely proportional to temperature. Even in pure solids, however, an increase in temperature will usually eventually produce a fade-out of NQR signals as the increasing amplitude of molecular motion shortens the relaxation time and broadens the line to an extent that the signals are no longer detectable.

The Bayer–Kushida theory of the temperature dependence of NQR frequencies[23] allows one to evaluate quantitatively the vi-

bration and libration frequencies according to the following equation:

$$\nu_Q(T) = \nu_0\left\{1 - \frac{3h}{8\pi^2}\sum\frac{\sin \alpha_i}{f_iI_i}\left(\frac{1}{2} + \frac{1}{\exp(hf_i/kT) - 1}\right)\right\} \quad (1)$$

where ν_0 = NQR frequency at 0 K, α_i = the angle between the bond axis and vibration or libration axis, I = the molecular moment of inertia about the vibration or libration axis, $f_i = f_i^0(1 - g_iT)$, f_i^0 = the vibration or libration frequency at 0 K, and g_i = a semiempirical factor which includes the temperature dependence and anharmonicity of vibration or libration frequency.

Most of the intramolecular vibration frequencies of CCl_4 are

(18) MacNicol, D. D.; Mills, H. H.; Wilson, F. B. *J. Chem. Soc., Chem. Commun.* **1969**, 1332.

(19) Hardy, A. D. U.; Mckendrick, J. J.; MacNicol, D. D.; Wilson, D. R. *J. Chem. Soc., Perkin Trans. II* **1979**, 729.

(20) Nassimbeni, L. R.; Niven, M. L.; Suckling, A. P. *Inorg. Chim. Acta* **1989**, *159*, 209.

(21) Nassimbeni, L. R.; Papanicolaou, S.; Moore, M. H. *J. Incl. Phenom.* **1986**, *4*, 31.

(22) Das, T. P.; Hahn, E. L. Nuclear Quadrupole Resonance Spectroscopy. In *Solid State Physics*; Academic Press: 1958; p 165.

(23) Kushida, T. *J. Sci. Hiroshima Univ., Ser. A* **1955**, *19*, 327.

Table II. Summary of Crystal Data, Intensity Measurement, and Structure Refinement

	clathrate				
	1	**1′**	**3**	**4**	**19**
	CCl₄/Dianin's compound	CCl₄/Dianin's compound	CCl₄/Fe(AcAc)₃	CCl₄/Ni(SCN)₂(3-MePy)₄	CCl₄/Ni(exan)₂(4,4′-dm-2,2′-bpy)
formula (asym unit)	$C_{18}H_{20}O_2(CCl_4)_{1/6}$	$C_{18}H_{20}O_2(CCl_4)_{1/6}$	$(C_{15}H_{21}O_6FeCCl_4)_{1/3}$	$(C_{26}H_{28}N_6NiS_2CCl_4)_{1/2}$	$Ni(S_2C_3H_5O)_2(C_{12}H_{12}N_2)(CCl_4)_2$
temp	293	140	293	293	293
mol wt	293.8	293.8	169.0	350.6	793.0
crystal system	hexagonal	hexagonal	hexagonal	orthorhombic	monoclinic
space group	$R\bar{3}^a$	$R\bar{3}^a$	$R\bar{3}^a$	Fddd	$P2_1/c$
crystal size (mm)	0.15 × 0.25 × 0.27	0.15 × 0.25 × 0.27	0.25 × 0.3 × 0.65	0.30 × 0.37 × 0.55	0.15 × 0.35 × 0.40
a (Å)	27.147 (3)	26.912 (7)	10.3534 (6)	22.067 (2)	14.756 (3)
b (Å)				23.650 (2)	12.765 (2)
c (Å)	10.939 (2)	10.901 (3)	18.0013 (13)	26.388 (3)	18.360 (4)
β (deg)					105.92 (1)
V (Å³)	6982 (2)	6837 (3)	1671.1 (2)	13772 (2)	3326 (1)
Z	18	18	9	32	4
host guest ratio	6:1	6:1	1:1	1:1	1:2
D_m (g cm⁻³)	1.26		1.49	1.34	1.58
D_c (g cm⁻³)	1.26	1.29	1.51	1.35	1.58
F_{000}	2814	2814	777	5760	1600
μ (mm⁻¹)	0.187	0.191	1.186	1.021	1.499
(sin θ/λ)$_{max}$ (Å⁻¹)	0.58	0.58	0.71	0.55	0.59
no. of measd reflns	2583	2546	907	2606	3450
no. of obsd reflns	1275	1475	833	1733	2018
criterion for obsd reflns	$\|F_o\| > 4\sigma(F_o)$ and $\|F_o\| > 8$	$\|F_o\| > 4\sigma(F_o)$ and $\|F_o\| > 8$	$\|F_o\| > 4\sigma(F_o)$	$\|F_o\| > 4\sigma(F_o)$	$\|F_o\| > 4\sigma(F_o)$
no. of parameters	195	195	81	182	334
refinement (on F)	full-matrix	full-matrix	full-matrix	full-matrix	full-matrix
weighting scheme	$\omega = 1/\sigma^2(F_o)$	$\omega = 1/\sigma^2(F_o)$	$\omega = 1/\sigma^2(F_o)$	$\omega = 1/\sigma^2(F_o)$	$\omega = 1/\sigma^2(F_o)$
max. and av Δ/σ	0.037, 0.002	0.0005, 0.0001	0.053, 0.009	0.065, 0.017	0.838, 0.086
max. and min Δρ (eÅ⁻³)	0.76, −0.96	0.65, −0.77	0.46, −0.39	0.83, −0.81	0.97, −0.88
S	2.33	2.22	3.22	2.26	2.25
R, R_w (%)	8.0, 3.8	7.2, 4.0	4.9, 4.6	6.6, 5.1	6.4, 3.6

[a] Hexagonal axes.

Table VII. Bond Distances (Å) for Clathrates **1**, **3**, and **4**

	1 (298 K)	**1′** (140 K)	**3** (298 K)		**4** (298 K)	
O(1)–C1	1.405 (7)	1.398 (6)	Fe–O(1)	2.012 (5)	Ni–N(1)	2.050 (6)
O(2)–C9	1.466 (10)	1.472 (8)	Fe–O(2)	1.989 (4)	Ni–N(11)	2.138 (5)
O(2)–C(10)	1.375 (9)	1.379 (7)	O(1)–C(1)	1.276 (8)	Ni–N(21)	2.134 (6)
C(1)–C(2)	1.378 (10)	1.404 (8)	O(2)–C(3)	1.259 (8)	N(1)–C(1)	1.153 (9)
C(1)–C(6)	1.369 (12)	1.371 (10)	C(1)–C(2)	1.377 (9)	C(1)–S(1)	1.611 (7)
C(2)–C(3)	1.385 (9)	1.393 (7)	C(1)–C(4)	1.511 (11)	N(11)–C(12)	1.343 (9)
C(3)–C(4)	1.397 (11)	1.392 (9)	C(2)–C(3)	1.394 (11)	N(11)–C(16)	1.332 (10)
C(4)–C(5)	1.396 (9)	1.408 (8)	C(3)–C(5)	1.510 (9)	C(12)–C(13)	1.377 (11)
C(4)–C(7)	1.535 (8)	1.536 (7)			C(13)–C(14)	1.383 (12)
C(5)–C(6)	1.384 (8)	1.394 (7)			C(13)–C(17)	1.504 (15)
C(7)–C(8)	1.566 (9)	1.563 (8)			C(14)–C(15)	1.374 (12)
C(7)–C(11)	1.542 (11)	1.543 (10)			C(15)–C(16)	1.380 (11)
C(7)–C(18)	1.552 (7)	1.558 (6)			N(21)–C(22)	1.319 (10)
C(8)–C(9)	1.518 (8)	1.531 (6)			N(21)–C(26)	1.343 (10)
C(9)–C(16)	1.528 (7)	1.528 (6)			C(22)–C(23)	1.381 (11)
C(9)–C(17)	1.528 (9)	1.522 (8)			C(23)–C(24)	1.377 (12)
C(10)–C(11)	1.395 (9)	1.400 (7)			C(23)–C(27)	1.481 (13)
C(10)–C(15)	1.414 (12)	1.411 (10)			C(24)–C(25)	1.387 (13)
C(11)–C(12)	1.395 (10)	1.400 (9)			C(25)–C(26)	1.384 (12)
C(12)–C(13)	1.391 (12)	1.402 (10)				
C(13)–C(14)	1.396 (10)	1.397 (8)				
C(14)–C(15)	1.376 (11)	1.382 (9)				
			For the Guest Molecule			
C(G1)–Cl(G11)	1.72 (2) 1.77^a	1.66 (2) 1.68^a	C(G1)–Cl(G11)	1.784 (11)	C(G1)–Cl(G11)	1.719 (8)
C(G1)–Cl(G12)	1.685 (9) 1.73^a	1.725 (7) 1.74^a	C(G1)–Cl(G12)	1.730 (4)	C(G1)–Cl(G12)	1.717 (8)

[a] Values obtained for riding motion correction due to Busing and Levy.[12]

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Table VIII. Bond Distances (Å) for Clathrate **19**

Ni–S(1)	2.448 (4)	Ni–S(2)	2.454 (3)
Ni–S(3)	2.456 (3)	Ni–S(4)	2.442 (4)
Ni–N(1)	2.073 (9)	Ni–N(2)	2.068 (8)
S(1)–C(13)	1.685 (12)	S(2)–C(13)	1.669 (13)
S(3)–C(16)	1.696 (13)	S(4)–C(16)	1.682 (13)
O(1)–C(13)	1.340 (14)	O(1)–C(14)	1.43 (2)
O(2)–C(16)	1.334 (14)	O(2)–C(17)	1.46 (2)
N(1)–C(1)	1.35 (2)	N(1)–C(5)	1.339 (14)
N(2)–C(6)	1.36 (2)	N(2)–C(10)	1.33 (2)
C(1)–C(2)	1.38 (2)	C(2)–C(3)	1.39 (2)
C(3)–C(4)	1.39 (2)	C(3)–C(11)	1.47 (2)
C(4)–C(5)	1.40 (2)	C(5)–C(6)	1.48 (2)
C(6)–C(7)	1.40 (2)	C(7)–C(8)	1.37 (2)
C(8)–C(9)	1.40 (2)	C(8)–C(12)	1.51 (2)
C(9)–C(10)	1.38 (2)	C(14)–C(15)	1.50 (2)
C(17)–C(18)	1.34 (2)		

For the Guest Molecules

C(G1)–Cl(G11)	1.76 (2)	C(G2)–Cl(G21)	1.733 (11)
C(G1)–Cl(G12)	1.73 (2)	C(G2)–Cl(G22)	1.685 (14)
C(G1)–Cl(G13)	1.722 (14)	C(G2)–Cl(G23)	1.77 (2)
C(G1)–Cl(G14)	1.746 (13)	C(G2)–Cl(G24)	1.731 (14)

Figure 14. Temperature dependence of ^{35}Cl NQR frequencies of the CCl_4 in trigonal clathrates.

Figure 13. Temperature dependence of ^{35}Cl NQR frequencies of the CCl_4 in $M(SCN)_2(3\text{-MePy})_4$ clathrates.

Table IX. Main Displacement Parameters ($Å^2 \times 10^3$) and Root Mean Square Libration (RMSL) and Translation (RMST) Amplitude of Guest Molecules

	U_{11}	U_{22}	U_{33}	RMSL (deg)	RMST (Å)
Dianin's compound (140 K)					
Cl(axial)	46	46	54	7.41	0.1938
Cl(equatorial)	41	65	43	3.53	0.1529
Dianin's compound (293 K)					
Cl(axial)	107	107	65	12.27	0.2539
Cl(equatorial)	87	159	104	7.61	0.2012
Fe(AcAc)$_3$ (293 K)					
Cl(axial)	90	90	45	10.75	0.2103
Cl(equatorial)	53	119	82	6.96	0.2152

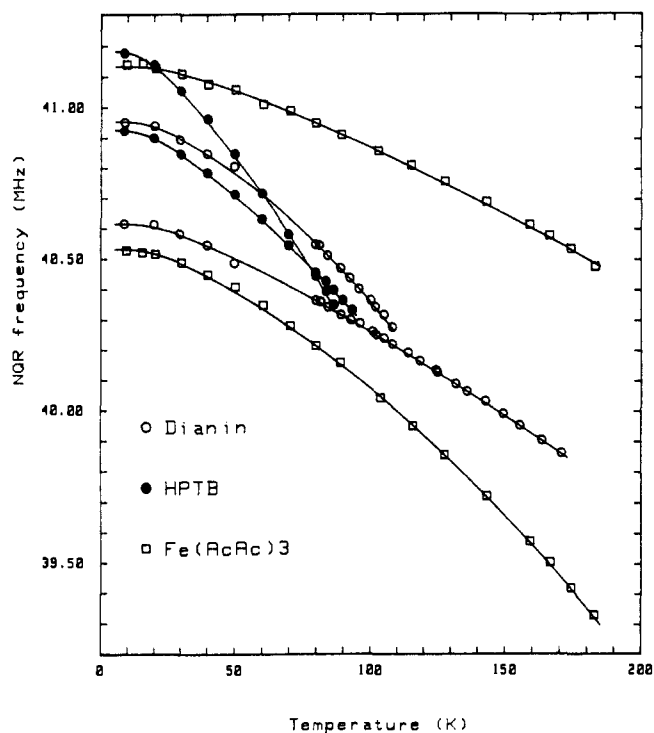too high (>650 cm^{-1}) to have any effect on the temperature dependence so only the librational movements need be considered.

For a ^{35}Cl nucleus in an organochlorine molecule, where the principal field-gradient axis lies along the C–Cl bond, libration about the bond axis has no effect on the field gradient, while libration about an axis perpendicular to the bond decreases the field gradient by an amount proportional to the square of the librational amplitude. We choose the CCl_4 guest molecule in the 3-fold symmetric cavities as an example; in this case there are only two librational modes; one is the axial libration about the 3-fold symmetry axis, and another is a pair of degenerate modes perpendicular to the first, the equatorial modes. The temperature dependence of the NQR frequency of the axial chlorine atom is affected only by the equatorial librations and is therefore expected to be less than that of the remaining three chlorine atoms, whose field gradients are affected by both libration modes.

A nonlinear regression program in the HP98820A Statistical Library supplied by the Hewlett-Packard Company was used in order to fit the temperature dependence of the NQR frequencies to the Bayer–Kushida equation. The initial values for ν_0, f^0, and g were chosen as below:

$$\nu_0 = \text{the NQR frequencies at 4 K}$$

$$f^0 < 100 \text{ cm}^{-1}$$

$$g = 0.01 - 0.001 \text{ K}^{-1}$$

The iterative fitting procedure was terminated when the fractional changes in all the parameters f and g produced by a cycle of iteration was less than 10^{-4}. The librational frequencies of CCl_4 in three trigonally symmetric hosts have been thus determined. The fitting to the equation was shown in Figure 14, and the results are in Table X.
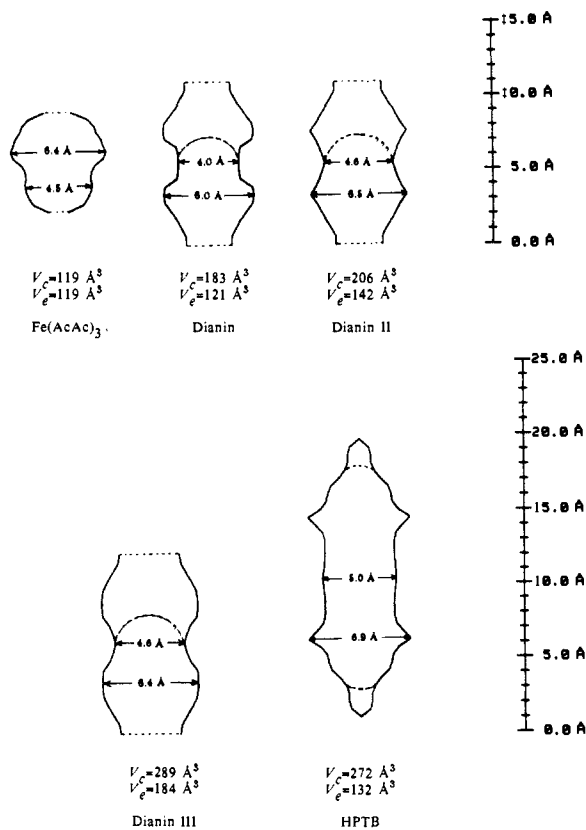
The low librational frequencies and the high values of the parameter, g, for the axial mode is evidence of the ease of rotation about the 3-fold axis in all three clathrates. For the CCl_4 adduct with Dianin's compound and with $Fe(AcAc)_3$ we have attempted to confirm these results by analyzing the crystal-structure data to yield mean-square amplitudes of libration and translation.[24] These values are shown in Table IX. They confirm that in each case the rotational amplitude about the symmetry axis is about twice that of the doubly degenerate mode. Likewise, studies of the heat capacity of the adduct with Dianin's compound[25] have been interpreted as indicating the gradual excitation of hindered rotational modes of CCl_4 from 60 up to 100 K.

(24) Cruickshank, D. W. J. *Acta Crystallogr.* **1956**, *9*, 747. Shomaker, V.; Trueblood, K. N. *Acta Crystallogr.* **1968**, *B24*, 63. Data were analyzed by using the program THermal Motion Analysis (THMA), due to K. N. Trueblood.

(25) White, M. A.; Zakrewski, M. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1990**, *8*, 215.

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Table X. Libration Frequencies of CCl_4 in the 3-Fold Symmetric Cavities

	axial		equatorial	
host	f^0 (cm^{-1})	g (10^3) (K^{-1})	f^0 (cm^{-1})	g (10^3) (K^{-1})
Fe(AcAc)₃	37.7	1.3	53.8	0.6
Dianin's compound	39.4	2.4	49.2	0.4
HPTB	28.6	1.9	38.2	1.1

V_c = 119 Å³
V_e = 119 Å³

V_c = 183 Å³
V_e = 121 Å³

V_c = 206 Å³
V_e = 142 Å³

Fe(AcAc)₃

Dianin

Dianin II

V_c = 289 Å³
V_e = 184 Å³

V_c = 272 Å³
V_e = 132 Å³

Dianin III

HPTB

V_c = cavity volume. V_e = effective cavity volume.

Figure 15. Shapes and sizes of the trigonally symmetric cavities in various clathrates.

The significant factor which influences the libration is the volume ratio of the guest to cavities, i.e., the size factor. There is always a limited region in cavities which is accessible to guest molecules, the effective volume, so the volume ratio is represented as follows:

$$P_k = \frac{\text{volume of guest molecule}}{\text{effective volume of cavity}}$$

where P_k is called the packing intensity of the guest molecule in the cavity.

We have calculated the cavity volumes for various trigonally symmetric clathrates by using the program Organic Packing Energy Calculations and Volume Analysis—OPEC—due to Gavezzotti.[26] The cavities are schematically shown in Figure 15. Except for the clathrate 3, the clathrates 1, 2, 22, and 23 all possess a centrosymmetric cavity. The height and the cross-sectional contours of the cavity vary from one to another.

The cavity volumes determined by OPEC include a number of tubes and protuberances which are completely inaccessible to a CCl_4 molecule and which thus should not be included in an estimate of the effective cavity volume. To correct for this the program was slightly modified to yield more appropriate effective volumes by using a sphere of radius 1.77 Å, the van der Waals

(26) Gavezzotti, A. *J. Am. Chem. Soc.* **1983**, *105*, 5220.

Table XI. Slope of the NQR Frequencies, Fade-Out-Temperature (FOT), and Packing Intensity P_k of CCl_4 in Various 3-fold Symmetric Clathrates

	axial		equatorial		
host	$(\partial\nu/\partial T)$ (10³) (MHz K^{-1})	FOT (K)	$(\partial\nu/\partial T)$ (10³) (MHz K^{-1})	FOT (K)	P_k
Fe(AcAc)₃	-3.9	182	-7.3	182	0.72
Dianin's compound	-5.2	171	-10.4	108	0.71
HPTB	-10.2	87	-16.9	93	0.65
Dianin II	-6.8	112			0.61
Dianin III					0.47
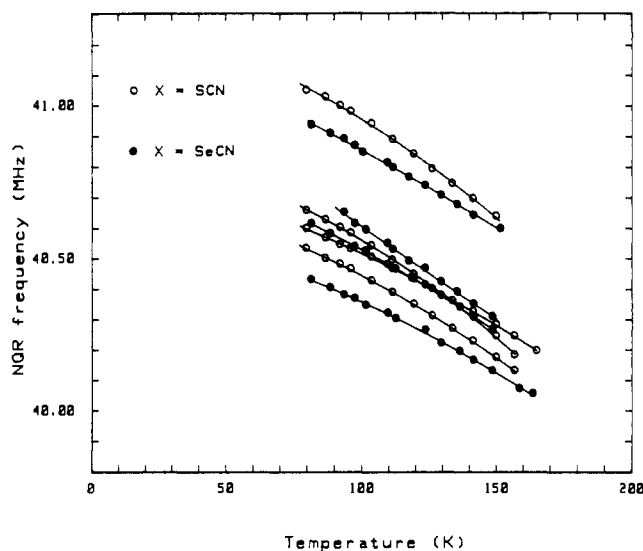
Figure 16. Temperature dependence of ^{35}Cl NQR frequencies of the CCl_4 in $NiX_2(4\text{-EtPy})_4$ clathrates.

radius of chlorine, as a probe, i.e., parts of the cavity inaccessible to such a sphere were neglected. Assuming that an ordered carbon tetrachloride molecule occupies 86 Å³, we have in this way calculated P_k for all these clathrates; the results are given in Table XI.

For the Fe(AcAc)₃ clathrate, the guest molecules fit more tightly in the cavities because of a 0.72 packing intensity, so the NQR frequencies have the smallest absolute temperature coefficients and the signals persist to a higher temperature (see Figure 14). As the packing intensity decreases the guest molecules become more mobile, the NQR temperature coefficients increase, and signals fade out at lower temperatures. Thus the HPTB clathrate has a 0.65 packing intensity, the absolute temperature coefficients are nearly twice of that of the Fe(AcAc)₃ clathrate, and the signals have disappeared at 87 and 93 K. For the sulfur analogue II (22) of Dianin's compound, where the cavities are presumably slightly bigger than that of the parent compound, the resonance from "equatorial" chlorines has already disappeared at 77 K for a packing intensity of 0.61. Furthermore, the analogue III (23) of Dianin's compound has cavities too big to observe either the equatorial resonance or the axial resonance at 77 K.

Although the librational frequencies of guest molecules in cavities other than trigonally symmetric ones cannot be straightforwardly determined, the temperature dependence of NQR frequencies gives information about guest mobility.

For high-temperature region (e.g., $T > hf/k = 1.43f$), the Bayer-Kushida equation has the following simplified form:[27]

$$\nu_Q = \nu_0\{1 + bT + c/T\} \tag{2}$$

$$b = -(3k/8\pi^2)\Sigma(1/I_i f_i^2) = -(3k/8\pi^2)M\langle(1/I f^2)\rangle$$

$$c = -(h^2/32\pi^2 k)\Sigma(1/I) = -(h^2/32\pi^2 k)M\langle(1/I)\rangle$$

(27) Lucken. E. A. C. *Nuclear Quadrupole Coupling Constants*; Academic Press: London, 1969; p 153.
(28) Brown, I. D. *Acta Crystallogr.* **1985**, *A41*, 399.

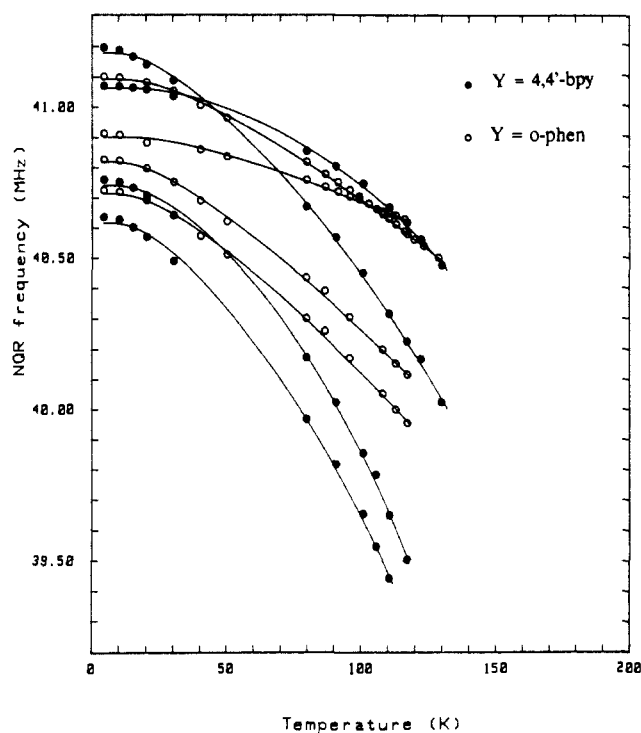**Figure 17.** Temperature dependence of ^{35}Cl NQR frequencies of the CCl_4 in $Ni(exan)_2Y$ clathrates.

Differentiation of eq 2 gives

$$(\partial v / \partial T) = v_0\{b - c/T^2\}$$

It is clear that the temperature coefficient of the resonance frequency is inversely proportional to the average of the square of librational frequencies.

The following, more qualitative, remarks may also be made on the basic of the NQR data: (i) Figure 12 shows the temperature dependence of NQR frequencies of two of the four resonance lines for $CCl_4/M(SCN)_2(4\text{-EtPy})_4$ clathrates. The absolute temperature coefficients increase in the order of Ni < Co < Fe < Mn,

which implies that the cavities are successively bigger on going from nickel to manganese. This would be expected from the fact that the ionic radii of these cations increase in the same order. (ii) Figure 16 compares the results for CCl_4 in the nickel selenocyanate and in the nickel thiocyanate. Here, the change from thiocyanate to selenocyanate produces a decrease in mobility since it can be seen that the guest molecules have smaller absolute temperature coefficients in the selenocyanate clathrate. (iii) The guest mobility for the $CCl_4/M(SCN)_2(3\text{-MePy})_4$ clathrates (4–6) can also be evaluated in Figure 13. The nickel and the cobalt analogues have comparable temperature coefficients, but the iron analogue, which probably crystallizes in another crystal phase, has the smaller temperature coefficients, so that the guest mobility has decreased. The slight difference in temperature coefficient between the nickel and cobalt complexes at high temperatures is no doubt due to the greater ionic radius of the cobalt cation. (iv) Another example is shown in Figure 17 for CCl_4 in two $Ni(exan)_2Y$ clathrates. The guest mobility is greater when Y = o-phenanthroline than when Y = 4,4'-bpy.

Conclusion

The crystallographic structure determinations which we report here confirm that NQR provides reliable structural information at relatively little cost in time or equipment. Furthermore, the temperature dependence of the resonance frequencies furnish unique information concerning the mobility of the guest molecules which is confirmed by the estimates of the volumes of the cavities derived from the structural data. NQR is, however, particularly susceptible to molecular disorder, and it has usually not been possible to observe NQR spectra when the symmetries of the guest molecule and of the cavity are mismatched.