An NQR and Calorimetric Study of a Phase Transition in *tetrakis*(α-Phenylethylamine)-*bis*(isothiocyanato)nickel(II)/*ortho*-Dichlorobenzene Clathrate *

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The ^{35}Cl NQR spectrum of *ortho*-dichlorobenzene as a guest molecule in *tetrakis*(α-phenylethylamine)-*bis*(isothiocyanato)nickel(II), has been studied in the temperature range of 77 K to 250 K. At 77 K the clathrate has two resonances of equal intensity at 35.840 and 36.080 MHz, to be compared with those of pure *ortho*-dichlorobenzene, where there are three lines at 35.580, 35.775 and 35.824 MHz. At 230 K there occurs an irreversible phase change which results in the expulsion of the *ortho*-dichlorobenzene from the host crystal, and the NQR signals thereafter correspond to the three lines of the unclathrated guest molecule. These events were also followed and confirmed by a calorimetric study in the range 210–300 K. The phase change is thought to be due to a transformation of the host molecule, where the thiocyanato groups are in the *trans* configuration in the clathrate, to the *cis* configuration, which is known not to form a clathrate.

Key words: Order-disorder effects, Phase transition, Potential energy, Host-guest interaction

Introduction

The formation of inclusion complexes by the Werner complexes of the type $Ni(NCS)_2$(α-arylalkylamine)$_4$ with aromatic compounds as guest molecules has recently been reviewed [1]. In contrast to the well-known complexes of $Ni(NCS)_2$(4-methylpyridine)$_4$ [2] these complexes have flexible structures which often given rise to molecular disorder, rendering difficult the determination of their crystal structure. As a consequence the physio-chemical behaviour of only a few such complexes has been studied so far [3, 4].

Nuclear Quadrupole Resonance (NQR) has previously proved to be a powerful tool for the study of inclusion complexes [5] and we report here an NQR and calorimetric study of the clathrate formed by the complex $Ni(NCS)_2$(α-phenylethylamine)$_4$ with o-dichlorobenzene (ODCB) as a guest molecule.

Experimental

Preparations

The clathrate was prepared according to the method reported in the literature [6], by titrating an aqueous solution of nickel thiocyanate with stoichiometric quantities of fresh racemic α-phenylethylamine in the presence of ODCB at room temperature. The unclathrated complex was prepared in a similar manner in the absence of ODCB. The precipitated complex was briefly sucked dry and immediately subjected to the NQR or calorimetric study. The instability of the clathrate prevented satisfactory microanalysis, but from the calorimetric study we obtained an approximate composition of 1:1.

The initial ratio of host complex to guest molecule plays an important rôle in the formation of an ordered clathrate, which was only formed when the initial host:guest ratio was kept below 1:3; an excess of ODCB always gave rise to a failure to produce the ordered clathrate.

Nuclear Quadrupole Resonance

NQR spectra were measured on a Decca super-regenerative spectrometer, frequencies being compared to harmonics from an internal crystal-con-

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trolled oscillator. Temperatures were measured with a Hewlett-Packard 2802 digital thermometer (precision ±0.5 °C) and varied between 77 K and room temperature with an Artronix 5301-E temperature controller.

Calorimetry

The calorimetric measurements were performed from 210 to 300 K in a Setaram BT 2.15 calorimeter. The samples (600±5 mg) were introduced into the calorimeter at room temperature, cooled under dry helium at a rate of 0.5 °C/minute to 200 K, held for 30 minutes at this temperature and then heated at a rate of 0.3 °C/minute to the final temperature of 300 K.

Results and Discussion

^{35}*Cl NQR*

The clathrate exhibits two ^{35}Cl resonances of equal intensity at 77 K (Fig. 1 a), situated respectively at 35.840 and 36.080 MHz. Thus either there are two distinct sites in which the ODCB molecule retains its two-fold symmetry or there is just one site in which the two-fold symmetry of free ODCB is lost. Occam's razor favours the latter hypothesis.

The temperature-dependence of the ^{35}Cl resonance frequencies is shown in Figure 2. As usual, the NQR frequencies show a negative temperature-dependence, [7], up to 230 K when they rapidly and irreversibly disappear. On cooling the sample to 77 K a new set of ^{35}Cl resonance frequencies at 35.580, 35.775 and 35.824 MHz are observed (Fig. 1b), which can be identified with those of free non-clathrated ODCB [8] (Figure 1 c).

The clathrate is in fact unstable even at 77 K, although several months are required for the transition to go to completion. It is interesting to note, however, that whereas at room temperature about one week is required for the transition to occur, at 230 K the change is over in less than an hour.

Calorimetry

Figures 3 a–d show the calorimetric curves of the host complex and of the clathrate with increasing temperature. Whereas no signals occurred for the pure host (Fig. 3 a) three endothermic signals, marked **2**, **3**, and **4** in the Figure, were observed for a 1:1 mixture of the pure host and ODCB at 249 K, 261 K and

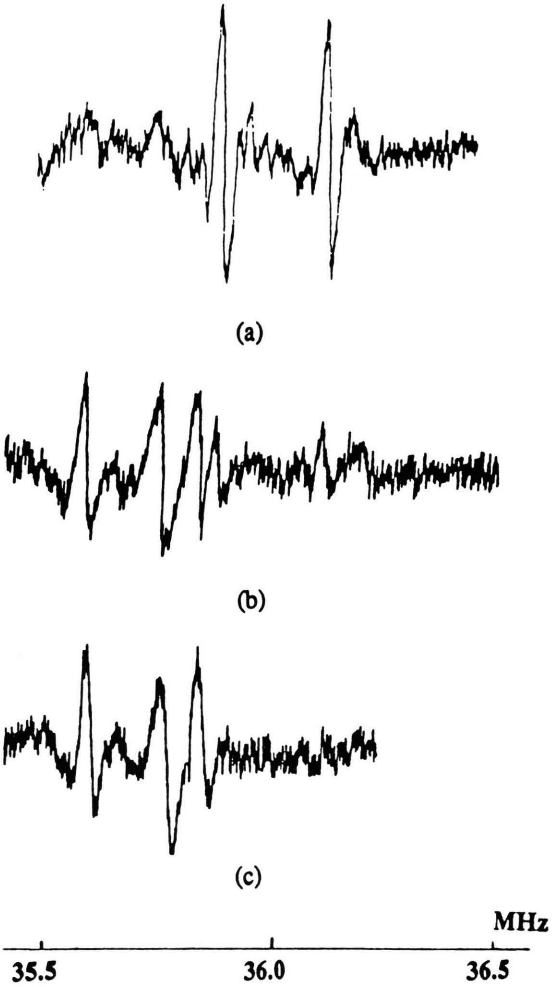

Fig. 1. ^{35}Cl NQR spectra at 77 K of ODCB: (a) in the clathrate, (b) after partial conversion and (c) after complete conversion to the unclathrated form.

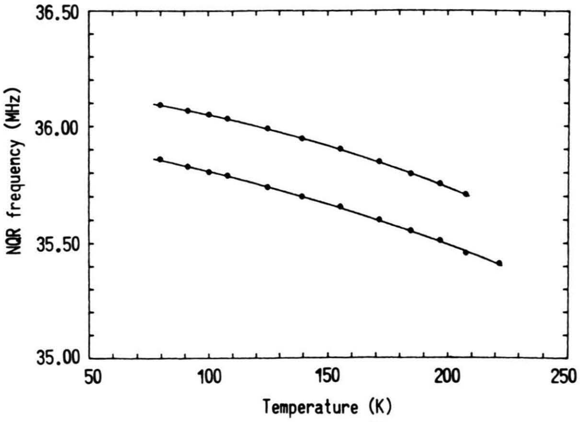

Fig. 2. Temperature dependence of the ^{35}Cl NQR frequencies of ODCB included in $Ni(NCS)_2(\alpha\text{-phenylethylamine})_4$.

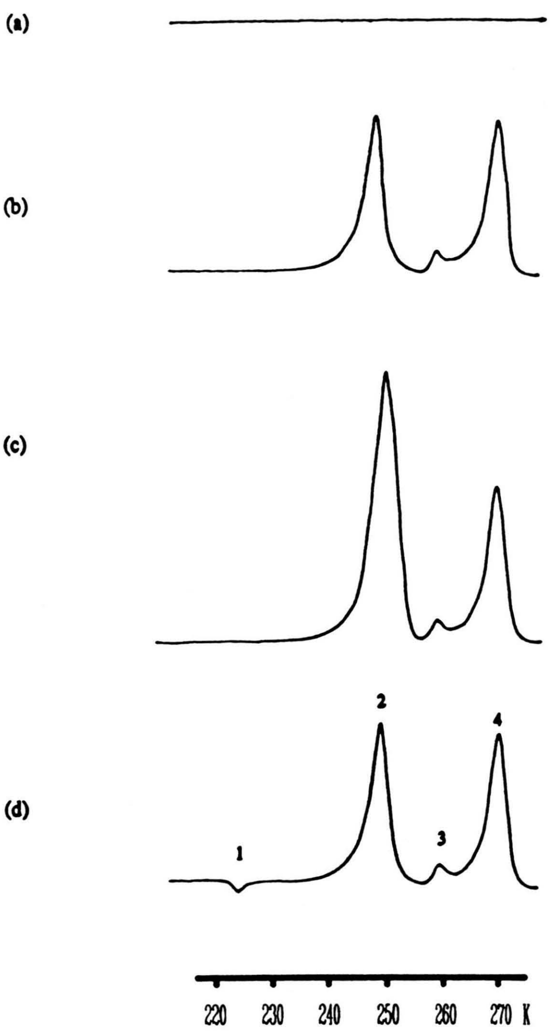

Fig. 3. Calorimetric curves, determined for increasing temperature of (a) the host complex, (b) a 1:1 mixture of the host complex and ODCB, (c) a 1:2 mixture of the host complex and ODCB, (d) the clathrate formed between the host complex and ODCB.

270 K (Figure 3b). In Fig. 3c is shown the curve for a mixture of the host with two moles of ODCB; the same three signals are observed but that at 249 K has doubled in size. Finally Fig. 3d shows the curve for the clathrate. In addition to the above three signals an exothermic signal, **1**, is observed at 225 K, in the region of temperature at which the NQR resonances irreversibly disappears. We thus attribute this exothermic signal to the phase change of the clathrate.

The three endothermic signals at 249 K, 261 K and 270 K thus arise from a physical, non-clathrated, mixture of the host molecule and ODCB. Pure ODCB melts at 256 K, the transition at 249 K is almost certainly to be ascribed to the lowered melting point of ODCB. We are unable to provide a satisfactory explanation of the two other transitions, other than saying that they must be due to (presumably) non-clathrating interactions between the pure host and guest molecules.

Nassimbeni et al. [3, 4] have reported two molecular forms for the octahedral host complex $Ni(NCS)_2$-(α-phenylethylamine)$_4$. One form, in which the thiocyanate groups are in the *trans* configuration, forms clathrates with a variety of guest molecules, while the other, where the thiocyanate groups are in the *cis* position, appears to be incapable of forming a clathrate. Nassimbeni reports a calculation of an energy difference between the *trans* and the *cis* configuration of about 10 kJ mol^{-1} and a barrier to the conversion of the *trans* configuration to the *cis* configuration of between 80 and 147 kJ mol^{-1}, depending on the path taken for the interconversion. We therefore ascribe the irreversible transition at 230 K to a change in configuration of the host complex and the expulsion of ODCB from the lattice. The similarity of the calorimetric curves of the 1:1 unclathrated mixture of the host complex and ODCB (Fig. 3b) and the clathrate above the transition temperature (Fig. 3b), both with respect to the positions of the calorimetric signals and their intensities, is the basis of our assignment of a 1:1 host:guest ratio to the clathrate.

Acknowledgements

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