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Structure, Stability, and Decomposition of Nickel Cyanide-Ammonia Clathrates

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REVIEW

Structure, Stability, and Decomposition of Nickel Cyanide-Ammonia Clathrates

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Summary

The nickel cyanide-ammonia complex forms clathrate compounds with aniline, benzene, pyridine, pyrrole, and thiophene. The structure is tetragonal and the unit cell contains atoms corresponding to twice the formula when benzene is enclosed in nickel complex. Each benzene molecule is comparatively remote from nickel atoms. It is contained in a cavity where it makes contacts at van der Waals distances with other benzene molecules and with atoms of cyanide and ammonia groups. It is not linked by chemical bonds to the nickel complex. The clathrated molecules in this system are easily evolved when the compound is ground or heated to high temperatures. These clathrates are not particularly stable systems. The stability and decomposition of nickel cyanide-ammonia clathrates are described.

Clathrate compound formation is based on molecular size rather than on chemical similarity. It can be used practically in the separation of chemically similar but physically different molecules (*1*).

One example of clathrate compounds is that formed between nickel cyanide–ammonia complex and one molecule of aniline, benzene, pyridine, pyrrole, and thiophene. This clathration can be used to separate furan and phenol from other molecules of similar size as they do not form clathrates with nickel cyanide–ammonia at room temperature or at a temperature from 0°C to 25°C (*2*).

The nickel cyanide–ammonia employed as a host in the preparation of these clathrates can be prepared from nickel sulphate, potassium

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cyanide, and ammonium hydroxide (*3*). The reaction temperature is not critical but the completion of the reaction is favored at low temperatures of the order of 10–25°C. The lower temperature will undoubtedly improve in yield, and chilling to 0°C or below will be still better for higher yield. It has been suggested (*4*) that by limiting the quantity of ammonia to an amount just sufficient to effect solution of nickel cyanide, the yield of benzene clathrate can be improved.

The preparation of benzene clathrate, $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$, and other clathrates of this group has been described earlier (*5–10*). The structure of benzene clathrate has a tetragonal unit cell, $a = 7.24$ Å, $c = 8.28$ Å, which contains atoms corresponding to twice this formula (*11*). Half of the nickel atoms have four cyanide carbon atoms attached by square bonds. The metal-to-carbon distance indicates some double bonding between these atoms. The other nickel atoms are linked to four nitrogen atoms of CN groups in the form of a square, and to two ammonia groups which complete an approximately regular octahedran of nitrogen atoms. The distance nickel-to-nitrogen corresponds to single bonds. Layers of this structure are arranged parallel to each other and between them are benzene molecules with their planes at right angles to that of the layers (Fig. 1). Each benzene molecule is comparatively remote from nickel atoms. It is contained in a cavity where it makes contacts at van der Waals distances with other benzene molecules and with atoms of cyanide and ammonia groups. It is not linked by chemical bonds to the nickel complex.

The clathrate compounds of nickel cyanide–ammonia are not particularly stable systems. Clathrated benzene in the benzene clathrate

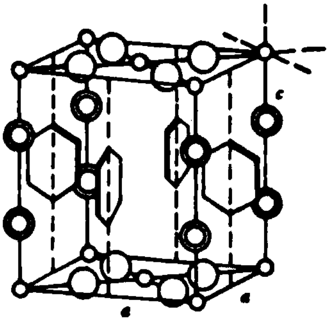

FIG. 1. The tetragonal unit cell of the clathrate compound, $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$. o, Ni; ○, CN; ◎, NH_3; benzene indicated by hexagonal plates. Courtesy University Press, Cambridge, England.

is very firmly retained, there being no detectable vapor pressure at room temperature. However, some of it may be easily removed by repeated washing with ether and it is evolved when the compound is ground or heated to sufficiently high temperatures. Crystals of thiophene clathrate also decompose fairly readily but have been examined and within 1% have the same *c* spacing as the benzene clathrate (*11*).

It is now well known that the nature of a clathrate compound is such that one cannot dissolve it as such. One expects to decompose it on solution. In this case, the nickel cyanide complex must break down to something smaller and the benzene will no longer be associated with it. The melting point also cannot be found since decomposition occurs before melting. In the absence of any strong attachment of the enclosed molecules to their surroundings it should thus be possible to set them free by mechanical breaking of the cage. Dacey et al. (*12*) gave a confusing statement that the benzene clathrate from which the benzene was removed by evacuation at room temperature was capable of sorbing benzene and molecules similar or smaller than benezene.

A number of observations have been reported from time to time that bear on the stability of the clathrates of benzene and other molecules with nickel cyanide–ammonia. The neutron irradiation of benezene clathrate showed that very little is lost by radiation damage (*13*).

Mandelcorn (*14*) has pointed out that the thermal decomposition of a clathrate into its free host and guest constituents at temperatures below its melting point could involve one or more of the following processes: (a) sublimation of the host, (b) change of clathrate structure to the nonclathrate form of the clathrate, (c) diffusion of the guest molecules through the lattice structure of the clathrate, and (d) surface desorption of the guest molecules from the surface of the solid clathrate. In the benzene clathrate, the presence of molecules between the layers contributes to the stability. This is apparent from the very close packing of the structure as a whole. Aynsley et al. (*15*) found that the benzene could be removed in vacuo, without removal of ammonia, slowly at room temperature and rapidly, 50% in 1–3 hr, at 40–60°C. Up to at least 80% removal of benzene, the decomposition was of zero order, varying in rate from sample to sample. This suggests that the rate determining step, approximate activation energy 11 kcal/mole, is escape from the surface and that migration within the lattice is comparatively easy. The X-ray powder photographs of the benzene clathrate at various stages of decomposition up to 90% removal of benzene indicate progressive changes in the unit cell dimensions and not a complete breakdown of the lattice (*15,16*). Aynsley and co-workers (*15*) also mentioned that their dehydrated monohydrate reabsorbs water from the atmosphere, but that the product resulting from removal of benzene from the benzene clathrate showed no tendency to absorb water, although Rayner and Powell (*17*) have shown that water can be absorbed while benzene is removed.

When an undecomposed crystal of the benzene clathrate had given a Weissenberg photograph, zero layer, on rotation about [100], and was then photographed again after exposure to the air for a few weeks, the original diffraction pattern had superposed on it a number of diffuse spots that coincided with the positions of diffraction spots that would be given by a single crystal of the hydrate rotating about its axis (*17*). The a, b, c of the nickel cyanide–ammonia hydrate coincide with a, a', c of the tetragonal benzene clathrate. From this it is evident that the decomposition that occurs in the presence of water vapor takes place by the escape of benzene and the displacement and puckering of layers into positions corresponding to the hydrate structure. This is presumed to be a different mode of decomposition of the compound from that reported by Aynsley and others (*15*).

Jones and Fay (*18*) recovered benzene by subjecting the hydrocarbon stock to the action of nickel cyanide–ammonia to form the solid clathrate compound with the benzene. They separated the clathrate from the stock and treated the clathrate compound with steam in the presence of ammonia to decompose it into benzene and nickel cyanide–ammonia. They used various methods of decomposition of benzene clathrate. The above-mentioned process using steam in the presence of ammonia has been found to be particularly applicable in a commercial process, particularly a process in which the recovered host is to be recycled. Dry distillation of the clathrate compound involves prolonged heating at 200–300°C, and this leads to poor heat transfer, hold-up, and evaporation losses, with low yields. Cold concentrated ammonium hydroxide slowly dissolves the complex but frees only approximately half its benzene and thus is not feasible. On the other hand, when the clathrate is treated with boiling dilute ammonium hydroxide or with steam in the presence of ammonia, desirably at a temperature of 95–120°C, preferably 100–110°C, the benzene clathrate is rapidly disintegrated and the benzene steam disstills out. Ray and Smith (*4*) also showed that the benezene clathrate decomposes at a temperature in the range of 125–200°C at ordinary pressure.

Some interesting results on benzene clathrate have been described by Kondo and Kubo (*19*). When the benzene clathrate was kept in a closed vessel, no changes had taken place in its color or in its weight even after six weeks. But, when it was left to stand and allowed to make contact with fresh air, the pale blue violet color turned into pale blue, the color change being accompanied by a gradual decrease in the weight. When the sample was left to stand in air at room temperature for two months or when it was heated at about 60°C in an air bath for two weeks, the weight decrease attained a constant value of 33%. Therefore, some component of the crystal must be capable of escaping during a long time of exposure to the air, although it has been stated (*11*) that benzene in clathrate was firmly retained. The conceivable cause of the weight decrease would be one of the following: (a) the loss of adsorbed water, (b) the escape of ammonia, and (c) the detachment of benzene. The first possibility was ruled out as drying with caustic potash had no effect on the weight. If ammonia escaped, the weight decreases ought to amount to 0.8%, whereas the observed decrease was no less than 33.3%, which was close to and a little smaller than the theoretical value of 37.9% for the complete removal of benzene. It is probable that the benzene clathrate owes its stability to the slow rate of diffusion of benzene through crystals rather than its vanishingly small vapor pressure.

Drago et al. (*20*) observed that when benzene is removed from the clathrate by vacuum, the peak at 1167 cm^{-1} disappears along with other peaks due to benzene. Kondo and Kubo (*19*) also stated that the four benzene absorptions at 702, 1031, 1406, and 1479 cm^{-1} almost disappeared when the sample was heated at about 60°C for two weeks. Pyridine clathrate showed no change in infrared spectra, even when it was exposed to air and heated in the same manner as in the case of the benzene clathrate. Bhatnagar (*21*) has shown that many of the bands due to the enclosed molecules disappeared or became less intense during the processes of grinding, heating, and evacuation. The benzene was found to escape in vacuo but only very slowly. The removal was not complete even after two months and fifteen days, though the infrared spectrum of the sample showed pronounced reduction in benzene intensities. Also, a sample of benzene clathrate from which the benzene had been removed by evacuation was exposed to a benzene vapor atmosphere. No reabsorption of benzene was found. This was due to the fact that the crystal lattice had collapsed after liberation of benzene and could not reshape itself. The benzene clathrate was also heated on a low Bunsen burner flame in a glass test tube for a short time. A brown to yellow-brown color developed and droplets of liquid benzene were observed on the sides of the test tube. The infrared spectrum of this heated sample was different from the original clathrate.

It is assumed that during heating, grinding, and evacuation the continued association between the cage and the trapped component is broken and the supply of energy from outside helps in pushing apart the system of atoms in the cage so as to provide holes large enough for the escape of the enclosed molecules.

Since this reaction of nickel cyanide–ammonia with benzene is selective to benzene and the clathrate is decomposable by heat to yield substantially pure benzene, benzene can be recovered in good yield and in an exceptionally high state of purity from difficultly separable benzene-containing streams (*4*). For example, benzene can be recovered from cracked hydrocarbon streams containing olefins and diolefins or from natural gasoline fractions that either form azeotropes with benzene or boil so close to benzene that effective separation by fractional distillation is not possible. The benzene obtained by Jones and Fay (*18*) had a refractive index n_D^{25} 1.4978. The reagent grade benzene has a refractive index of 1.4968 and pure benzene a refractive index of 1.4979. It is thus evident that the benzene recovered from the clathrate formation is extremely pure. Evans et al. (*22*) also used this effective method of purifying benzene by clathrate compound and the benzene they prepared was 99.992% pure. This undoubtedly is due to the high specificity of nickel cyanide–ammonia for benzene. The results, from the standpoint of purity, are difficult to approach by extractive distillation or solvent extraction techniques.

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