The Structure of Some Aquated Dicyanoammine-nickel(II) Clathrates

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RECEIVED AUGUST 5, 1957

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On the basis of an X-ray investigation and a reported value for the magnetic moment, a structure was proposed for the dicyanoammine-nickel(II) clathrate of benzene which contained a paramagnetic, square planar, nickel(II) atom. Since planar nickel(II) atoms are usually diamagnetic, it is possible that the benzene, instead of being trapped in the crystal lattice, is interacting with the planar, nickel(II) atom to produce a paramagnetic tetragonal atom. The magnetic data have been redetermined and the infrared spectra examined to provide additional structural information. The spectra indicate that water is present in these clathrates. The absorption frequencies of benzene and pyrrole attributed to in-plane vibrations are identical in both the clathrate and the pure liquid but those attributed to out-of-plane vibrations are different. A structure containing trapped benzene is proposed which is compatible with the X-ray work and is also compatible with the magnetic moment of 2.1 Bohr magnetons obtained in this study.

Introduction

The preparation of the dicyanoammine-nickel(II) clathrate of benzene was first reported by Hoffman and Kusper.1 Subsequently, clathrates of this type containing pyrrole, furane, thiophene, pyridine, phenol and aniline were prepared.2 A single crystal X-ray investigation was undertaken on the benzene compound3 and the large distance between the carbon atoms of benzene and the atoms of the caging material was interpreted to mean that the organic molecules are not bonded but are simply trapped in the crystal lattice. A structure based on the X-ray findings and a magnetic moment4 of 2.32 Bohr magnetons, was proposed containing nickel atoms in two different modes of combination, one with an octahedral arrangement of the ligands and the other with a planar arrangement. Since the magnetic data were interpreted to indicate that all the nickel atoms are paramagnetic, an attempt was made to rationalize a planar, paramagnetic nickel atom, but the arguments presented are not convincing. The proposed interpretation does not preclude the possibility of weak interaction between an edge of the benzene molecule and the z-axis of the planar nickel atom producing a structure containing only paramagnetic nickel atoms. Infrared and magnetic investigations of some of these clathrates, especially those containing organic molecules which are good elec-
The presence of appreciable interaction between benzene and nickel is best indicated by the fact that the magnetic moment was found to be independent of the amount of benzene present.

Experimental

The clathrates were prepared by methods previously described. In order to examine the caging material without anything included, Ni(CN)₂[NH₃]₂H₂O was prepared by adding potassium cyanide to an ammoniacal solution of nickel sulfate, filtering off the potassium sulfate and allowing the hydrated dicyanoammine-nickel(II) to crystallize out over a period of a few days. The formulas for the caging material and the clathrates calculated from the results of elemental analyses are reported in Table II.

The infrared spectra of the clathrates were obtained on Nujol mulls, using a Perkin-Elmer Model 21 infrared spectrometer with sodium chloride optics. The magnetic moments were measured with a modified Curie magnetic balance. Since these compounds are reportedly non-stoichiometric, the molecular weights corresponding to the stoichiometric formula determined by analysis were employed in the calculation of the magnetic moments. The cyanide and water content of a dried sample was determined, the latter by a Karl Fischer determination. The Karl Fischer reagent is capable of analyzing both coordinated and uncoordinated water.

Results and Discussion

(A) Infrared Spectra. The results of the infrared investigations are summarized in Table I.

Table I

<table>
<thead>
<tr>
<th>Compound</th>
<th>Clathrate</th>
<th>Liquid</th>
<th>Clathrate</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(CN)₂[NH₃]₂H₂O</td>
<td>3623</td>
<td>wk, m</td>
<td>1928</td>
<td>wk, s</td>
</tr>
<tr>
<td></td>
<td>1953</td>
<td>m</td>
<td>1973</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3440</td>
<td>m</td>
<td>3412</td>
<td>m</td>
</tr>
</tbody>
</table>

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The principal absorption peaks in the dicyanoammine nickel(II) caging material can be assigned as

- $3623 \text{ cm}^{-1}$ to O-H stretch (water).\(^{(11)}\)
- $3366, 3250$ and $2900 \text{ cm}^{-1}$ to N-H stretch;\(^{(12)}\)
- $1598 \text{ cm}^{-1}$ to antisymmetric NH$_2$ deformation;\(^{(13)}\)
- $1250 \text{ cm}^{-1}$ to symmetric NH$_2$ deformation;\(^{(13)}\)
- $720 \text{ cm}^{-1}$ to an NH$_2$ rocking mode;\(^{(13)}\)
- $2161 \text{ cm}^{-1}$ to C==N stretch.\(^{(13)}\)

Similar absorptions occur in all the clathrates.

The spectra of the trapped molecules are listed in Table I together with the spectra of the pure liquids. Absorptions for the trapped molecules and pure liquid attributed to in-plane vibrations\(^{(13)}\) in both benzene (1480, 1170 and 1040 cm.$^{-1}$) and in pyrrole\(^{(14)}\) are similar, within experimental error. Detectable changes in the spectrum appear to be associated with out-of-plane bending vibrations of these molecules (1962, 1818 and 682 cm.$^{-1}$ in benzene, and 735 cm.$^{-1}$ in pyrrole).

In all of the clathrates an intense peak is observed in the 1161 to 1192 cm.$^{-1}$ region. Peaks of this intensity are not present in the spectra of the caging material or the organic molecules. In view of the large intensity of these new peaks, it does not seem likely that they are Raman lines which have become infrared active. When benzene is removed from the clathrate, by vacuum, the peak at 1167 cm.$^{-1}$ disappears along with the other peaks due to benzene.

**TABLE II**

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>1</th>
<th>1b</th>
<th>2</th>
<th>3b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles of trapped molecules/g. formula wt. of Ni(CN)$_2$NH$_2$/H$_2$O</td>
<td>(\frac{1}{3})C$_6$H$_6$</td>
<td>(\frac{1}{3})C$_6$H$_6$</td>
<td>(\frac{1}{3})C$_6$H$_6$</td>
<td>(\frac{1}{3})C$_6$H$_6$</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>172.8</td>
<td>137.7</td>
<td>159.8</td>
<td>137.8</td>
</tr>
<tr>
<td>Magnetic moment (Bohr magnetons)</td>
<td>Theor. Ni</td>
<td>34.75</td>
<td>Same</td>
<td>Same</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>34.75</td>
<td>30.96</td>
<td>30.88</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>3.89</td>
<td>2.88</td>
<td>3.54</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>24.31</td>
<td>30.50</td>
<td>26.28</td>
</tr>
<tr>
<td>Anal. results, %</td>
<td>Found Ni</td>
<td>34.5</td>
<td>43.6</td>
<td>33.3</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>35.29</td>
<td>20.87</td>
<td>30.25</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>3.66</td>
<td>2.42</td>
<td>3.26</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>22.90</td>
<td>29.22</td>
<td>25.89</td>
</tr>
</tbody>
</table>

The addition, as coordinated water, of approximately one-third of a mole of water\(^{(19)}\) per gram

(13) K. S. Pitzer and D. W. Scott, THIS JOURNAL, 86, 165 (1943).
(15) The reproducibility of these measurements by a single investigator is very good, the per cent. difference in the results being less than two. However, the values vary (by as much as 0.2 B.M.) when the results of different investigators are compared.
(16) Since NH$_2$ could be lost by this treatment, water content is best determined for 1b and 3b by the Karl Fischer method.
(18) The amount of water found in these clathrates is not stoichiometric but approximates this value.
atom of nickel would produce a structure in which four out of six nickel atoms would be octahedral (thus paramagnetic) and the remainder planar (diamagnetic). The calculated theoretical moment for the hydrated sample \( (\text{i.e.}) \ Ni(CN)_{3} \cdot (\text{NH}_{3})^{+} \cdot H_{2}O \times C_{2}H_{6} \) is 2.2 B.M. and for the anhydrous sample, 1.9 B.M.\(^{20}\)

The accuracy of our measurements does not permit us to make a decision concerning the coordination of water. The precision of our measurements would enable us to decide if we could examine an anhydrous sample. This was not possible, for attempts to dehydrate the hydrated material resulted in a loss of ammonia as well as water. This observation indicates the water may be coordinated.

Though the magnetic data do not distinguish between coordinated and free water, it is conclusively established that contrary to the information presently in the literature\(^{3,4}\) these clathrates contain diamagnetic nickel atoms. The structure is represented as a hybrid of those represented in Fig. 1. Structure B has no effect upon the magnetic properties and is proposed to explain the short nickel to carbon distance found by the X-ray studies.\(^{4}\) The bond arises from the overlap of a filled "d-orbital" of the nickel atom and an empty "p-orbital" of the carbon atom. Many structures similar to B representing different numbers of cyanide groups participating in this \(d_{x^{2}}-p_{\pi}\) interaction are possible. The water has not been indicated in this figure, but if it is coordinated, there are probably two molecules on one out of every three or four planar nickel atoms.

**Acknowledgments.**—The authors wishes to acknowledge with thanks the Karl Fischer determination of water carried out by Mr. F. M. Wachi.

Thanks also are due to Mr. James Brader for measuring the infrared spectra on the many samples of clathrates which were prepared.

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**Structures of Halogen Substituted Boranes**

**BY RILEY SCHAEFFER, J. N. SHOOLEY, AND ROBERT JONES**

**RECEIVED DECEMBER 11, 1957**

The nuclear magnetic resonance spectra of several halogen substituted boranes have been observed and used to establish conclusively the structures. Both a monooiodide and a monobromide of pentaborane-9 have been shown to be apex substituted. A monooiodide and a monobromide of decaborane have been shown to be substituted at the B-2 positions. A second monooiodide of decaborane could not be conclusively assigned a structure but is most probably substituted at the B-1 position.

Relatively few substitution products of the higher boranes have been described and the structure of only one of them \((B_{8}H_{12})\) has been established.\(^{3}\) The method of preparation of \(B_{8}H_{12}\) and its structure both suggest that it is formed by electrophilic attack of the \(I^{-}\) species at a region of high electron density in the electron deficient decaborane molecule.\(^{4}\) Other boranes, particularly the two pentaboranes, would be expected to undergo similar reactions to form products with structures in accord with the above mechanism. Thus, both pentaboranes should form monohalides by substitution in the apex position. Since five new monohalides of the boranes were available to us, we desired a method of structural determination which would not only be completely reliable but would also be relatively rapid. Nuclear magnetic resonance spectroscopy seemed to be ideally suited for such work.

**Experimental**

The five new substituted boranes available to us were: \(B_{8}H_{3}Br\) (m.p. 32-34°), \(B_{8}H_{3}I\) (m.p. 53°), \(B_{8}H_{3}Br\) (m.p. 103°), \(B_{8}H_{3}Br\) (m.p. 118°) and \(B_{8}H_{3}I\) (m.p. 72°). Approximately 20% solutions of each of the compounds in pure, dry carbon disulfide were prepared in 6 mm. Pyrex tubes and sealed. A solution of \(B_{8}H_{3}I\) also was prepared using material previously studied by X-ray diffraction techniques.\(^{3}\) The tubes were stored at 80° whenever they were not being used for spectral observations.

Both proton and \(^{11}B\) nuclear magnetic resonance spectra were obtained using a Varian Associates model No. V-4300 B high resolution spectrometer. Proton spectra were obtained both in the usual manner at 30 Mc./sec. and also using a double tuned circuit resonant at both 50.0013 and 9.6257 Mc./sec. The effect of the latter method is to interrupt the spin orientations of the \(^{11}B\) nuclei frequently enough so that the \(^{11}H\) nuclei see only the average value of zero and the multiplet structure collapses.\(^{4}\) All spectra are shown with field strength increasing toward the right.

**Results**

Figure 1 compares the proton resonance spectrum of \(B_{8}H_{3}Br\) and \(B_{8}H_{3}I\) with that of \(B_{8}H_{3}\).