Table III lists some exploratory experiments made with *cis*-rich diaqua perchlorate solution prepared from acid hydrolysis of carbonato-bis-ethylenediamine-cobalt(III) perchlorate. The carbonato perchlorate was prepared with an additional step of purification (precipitation of dichloro perchlorate). In addition it was a much more stable, less hygroscopic, and better defined compound than the diaqua nitrates. The perchlorate is also free from contamination of silver compounds as well as nitrate ions. Direct comparison with other data may not be justified except possibly for experiments 16 and 17 because of the difference in ionic strength. The agreement with other experiments made with different preparations (within the limitation of ionic strength difference) is quite good. The much larger difference in experiment 17 is probably due to uncertainty in hydroxide concentration.

The average of the seven rate constants of dihydroxo ion isomerization at hydroxide concentration of 0.01 M or greater is 0.155 (hr.)$^{-1}$ (probable error ± 0.0019, average residual ± 0.016) at 35.03°. Bjerrum and Rasmussen[2] estimated from one experiment (three points) the isomerization rate constant, $(k_c + k_t)$, to be 0.0274 (hr.)$^{-1}$ in a solution 0.5 M in sodium nitrate and 0.5 M in sodium hydroxide at 25°. If the difference between nitrate and perchlorate media is small and if both constants are correct, the reaction would have a very large temperature coefficient, corresponding to $E_{\text{exp}} = 31.5$ kcal.mole^{-1} and $\Delta S^* = +21.4$ e.u.; though the activation energy seems a little high, the entropy of activation is clearly of the proper sign and magnitude. It is interesting to note that our rate in acid solution is lower than theirs and our rate in alkaline solution seemed to be much larger than that to which theirs would extrapolate. It should also be pointed out that in their experiments, the rate in acid solution was measured with *trans* salt and the rate in alkaline solution was measured with *cis* salt. Since they prepared the two salts by two different methods, there was the possibility that the two preparations might have been contaminated in different ways.

Experimentally the criterion of purity (constancy of absorption spectra upon repeated recrystallization) used by Bjerrum and Rasmussen was not sufficient for kinetic studies. The rigorous test of starting material for absence of impurities which catalyze reactions by non-zero order mechanism is the independence of rate on the initial concentration of the starting material. We believe that the syntheses and purifications described above have resulted in relatively catalyst-free compounds.

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URBANA, ILLINOIS

[CONTRIBUTION FROM THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

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

BY RUSSELL S. DRAGO, JOON T. KWON AND RONALD D. ARCHER

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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 nickel 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 Kuspert.[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 compound[3,4] 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 moment[4,5] 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-

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[1] K. A. Hoffman and F. Kuspert, *Z. anorg. Chem.*, **15**, 204 (1897).

[2] K. A. Hoffman and H. Arnold, *Ber.*, **39**, 339 (1906); K. A. Hoffman and F. Hoechtlen, *ibid.*, **36**, 1149 (1903).

[3] H. M. Powell and J. H. Rayner, *Nature*, **163**, 566 (1949).

[4] J. H. Rayner and H. M. Powell, *J. Chem. Soc.*, 319 (1952).

[5] D. Craig, Thesis, University of Sydney, 1942.

TABLE I[a-c]

INFRARED SPECTRA OF SOME CLATHRATE COMPOUNDS

$Ni(CN)_2NH_3xH_2O$	C_6H_6 in clathrate	C_6H_6 (liq.)	C_6H_6 [10] (solid)	Aniline in clathrate	Aniline (liq.)
3623wk, m	1998wk, s	1962m	1973	3440m, m	3412m, m
			1980		
3366m, s	1860wk, s	1818m	1828	3200wk, br	3220m, s
			1836		
3306m, m	1479i, s	1482i	1478	1615i, br	1624i, m
2620v wk, m	1147–1172wk, br	1148–1168wk, br			1603i, s
2161i, s	1167i, s	1173wk, br		1493m, s	1501i, s
1608m, m	1037i, s	1039i	1036	1311v wk, m	1311wk, s
1230i, s	705i, s	682i	687	1286m, m	1276i, m
1127wk, br				1192m, s	
1147wk, br				1177wk, s	1177m, s
937v wk, m				1154wk, s	1157wk, s
720v wk, m				1102wk, br	1052wk, br
				1037wk, br	1027m, s
				888wk, m	883,m, m
				768i, m	755i, m
				700m, s	695i, s

Pyrrole in clathrate	Pyrrole (liquid)	Thiophene in clathrate	Thiophene (liquid)
3421i, m	3389i, s	3550v wk, s	
1528m, s	1530m, s	3094wk, m	3046m, s
Nujol	1471m, s		
1416m, s	1418m, s	1398wk, s	1408i, s
		1252sh	
1281v wk, s	1286wk, s	1161s, s	1252i, s
1175i, s		1084wk, s	1082i, s
1137wk, s	1140m, s	1032wk, s	1035i, s
1077m, s	1077i, s	834med, s	834i, s
1047i, s	1047i, s	745i, s	
1017i, s	1017i, s	712wk, s	700–730i, br
868v wk, s	868wk, s		
755i, s	735i, m		

[a] The first symbol listed refers to the band intensity: i = intense, m = medium, wk = weak, v wk = very weak. The second refers to band width: s = sharp, m = medium, br = broad. The symbol sh. refers to shoulder. [b] The values for the pure organic liquids reported in the above table are only those lines which can be distinguished in the clathrate compounds. Many weak bands of the organic liquids disappear because the absorption is much weaker in the clathrate. The disappearance of intense lines is not observed. The absorption due to dicyanoammine-nickel(II) appears in all the clathrate compounds but these values have only been listed in the first column. The 2600 cm.$^{-1}$ peak is very weak and is not always observed. [c] Spectra were obtained on at least two and in most instances three different samples of the clathrates reported above. Excellent agreement between the samples was found. The spectrometer employed was calibrated and the corrected frequencies have been reported. The spectra reported on the pure materials have been measured on our instrument to afford an accurate means of comparison.

tron pair donors were undertaken to provide additional information. The spectral data indicate the presence of water in all the clathrates examined. Shifts in absorption frequency of the trapped molecules were observed only for those peaks attributed to out-of-plane vibrations of the atoms.

The absence 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.[2,6] In order to examine the caging material without anything included, $Ni(CN)_2NH_3 \cdot xH_2O$ 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 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.[7] The Karl Fischer reagent is capable of analyzing both coördinated and uncoördinated water.[8]

Results and Discussion

(A) Infrared Spectra.[9]—The results of the infrared investigations are summarized in Table I.

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[6] W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, Cambridge, England, 1954, p. 561.

[7] J. Mitchell, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948.

[8] M. Chamberlain, Ph.D. Thesis, University of Illinois, 1956.

[9] The infrared spectrum of the benzene clathrate was reported subsequent to the completion of this study by: E. E. Aynsley, W. A. Campbell and R. D. Dodd, *Proc. Chem. Soc.*, 210 (1957). These authors were mainly concerned with the intensity of the absorption and the treatment does not parallel the one in the present study. The reported frequencies for trapped benzene are 1481, 1166, 1037 and 707 cm.$^{-1}$, all in excellent agreement with those found in this study.

[10] Reference for these results: R. L. Mair and D. F. Hornig, *J. Chem. Phys.*, **17**, 1236 (1949).

TABLE II

Sample no.		1	1b	2	3	3b	4
Moles of trapped molecules/g. formula wt. of $Ni(CN)_2NH_3{}^1/_3H_2O$		$^1/_2C_6H_6$	$^1/_{20}C_6H_6$	$^1/_3C_6H_6$	$^1/_2C_6H_6$	$^1/_{20}C_6H_6$	$^2/_5C_2H_5NH_2$
Molecular weight		172.8	137.7	159.8	172.8	137.7	171.0
Magnetic moment (Bohr magnetons)		2.0	2.2	2.0	2.0	2.0	2.36
Anal. results, %	Theor. Ni	33.96	42.63	36.73	Same	Same	34.33
	C	34.75	20.35	30.06	as	as	30.88
	H	3.89	2.88	3.54	sample	sample	3.78
	N	24.31	30.50	26.28	1	1b	27.87
	Found Ni	34.5	43.6	33.3	...	44.3	34.2
	C	35.29	20.87	30.25	34.37	20.79	31.47
	H	3.66	2.42	3.26	3.67	2.64	3.80
	N	22.90	29.22	25.89	...	31.24	26.98

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

3623 cm.$^{-1}$ to O–H stretch (water);[11]
3366, 3280 and 2600 cm.$^{-1}$ to N–H stretch;[12]
1608 cm.$^{-1}$ to antisymmetric NH_3 deformation;[12]
1230 cm.$^{-1}$ to symmetric NH_3 deformation;[12]
720 cm.$^{-1}$ to an NH_3 rocking mode;[12] and
2161 cm.$^{-1}$ to C≡N stretch[11]

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.

(B) **Magnetic Measurements.**—The magnetic moments expressed in Bohr magnetons (B.M.) are listed in Table II.[15]

Samples 1b and 3b were produced by placing samples 1 and 3 in vacuum over phosphorus pentoxide for three days. Nearly all the benzene was lost but Karl Fischer analysis[16] indicated one-third of a mole of water per nickel atom remained. The similarity in the magnetic moments of 1 and 1b and of 3 and 3b is good evidence for the absence of coördination of benzene. If benzene were coordinated, the magnetic moment of sample 1 would be 0.4 B.M. greater than 1b, as will be subsequently shown. Thus, the shifts observed in the spectrum of benzene are probably due to crystal lattice effects.

Before the magnetic data can be interpreted to provide definite conclusions regarding the presence of diamagnetic nickel atoms or coördinated water, the absence of an orbital contribution to the magnetic moment of nickel must be demonstrated. A study of the magnetic susceptibility of the benzene clathrate as a function of temperature indicates it is an ideal paramagnetic substance, *i.e.*, it obeys the Curie–Weiss law.[17] Dicyanodiaquonickel(II) and anhydrous nickel cyanide are also ideal paramagnetic substances with a moment of 2.73 B.M. for the hydrated material which decreases to a small residual moment as water is lost and the anhydrous material is produced.[18] In view of the above findings, it is logical to assume the absence of an orbital contribution to the moment and to use a value of 2.73 B.M. for the moment of the octahedral nickel atoms in the calculation of the theoretical moment to be expected for various structures.

If the water present in these clathrates is not coördinated, the structure of the caging material can be represented as a hybrid of structure A, structure B, and structures which represent combinations of these two (see Fig. 1).

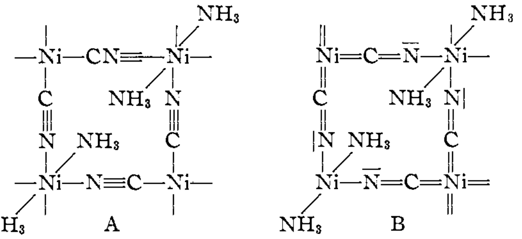

Fig. 1.

The addition, as coördinated water, of approximately one-third of a mole of water[19] per gram

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(11) A. Weissberger, "Techniques of Organic Chemistry," Vol. IX, Interscience Publishers, Inc., New York, N. Y., 1956.

(12) G. M. Barrow, R. H. Krueger and F. Basolo, *J. Inorg. Nuclear Chem.*, **2**, 340 (1956).

(13) K. S. Pitzer and D. W. Scott, THIS JOURNAL, **65**, 803 (1943).

(14) P. Mirone, *Gazz. chim. ital.*, **86**, 165 (1956); Lord and Miller, *J. Chem. Phys.*, **10**, 328 (1942).

(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_3 could be lost by this treatment, water content is best determined for 1b and 3b by the Karl Fischer method.

(17) L. Cambi, A. Cagnasso and E. Tremolada, *Gazz. chim. ital.*, **64**, 758 (1934). The value of the magnetic moment calculated from this study is in doubt because a complete elemental analysis on the sample was not reported and the authors employed a molecular weight calculated from the formula $Ni(CN)_2NH_3C_6H_6$. In view of the nonstoichiometry of these materials utilization of this incorrect molecular weight could cause the magnetic moment to be high by as much as 0.2 B.M.

(18) R. A. Fereday, *Proc. Phys. Soc.* (*London*), **44**, 279 (1932); **46**, 214 (1934).

(19) 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 (*i.e.*) $Ni(CN)_2(NH_3 \cdot {}^1/_3H_2O \times C_6H_6)$ 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 coördination 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 coördinated.

Though the magnetic data do not distinguish between coördinated 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 presented 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 $d\pi - p\pi$ interaction are possible. The water has not been indicated in this figure, but if it is coördinated, there are probably two molecules on one out of every three or four planar nickel atoms.

ADDED IN PROOF.—These results indicate that conclusions regarding the coördination of ligands to metal ions, based upon changes of the infrared spectra of solid materials are not reliable. In this work, shifts of the order of magnitude of 50 cm.$^{-1}$ were observed when the organic molecule was placed in the crystal lattice of the clathrate. Similarly, many of the spectral changes observed upon coördination of a ligand to a metal ion could be caused by similar interactions.

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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[20] The approximate theoretical magnetic moment (μ mean) was calculated by taking the root mean square of the magnetic moments of the various nickel atoms. For example, consider the compound $Ni(CN)_2NH_3{}^1/_3H_2O$, μ mean $= [(3\mu_1^2 + 2\mu_2^2 + 1\mu_3^2)/6]^{1/2}$ where μ_1 is the moment for each of the three nickel atoms with two ammonias (2.73 B.M.), μ_3 for the one with two waters (2.73 B.M.) and μ_2 for each of the two planar diamagnetic nickel atoms (0.0 B.M.).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE, AND VARIAN ASSOCIATES]

Structures of Halogen Substituted Boranes

BY RILEY SCHAEFFER,[1] JAMES N. SHOOLERY[2] AND ROBERT JONES

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The nuclear magnetic resonance spectra of several halogen substituted boranes have been observed and used to establish conclusively the structures. Both a monoiodide and a monobromide of pentaborane-9 have been shown to be apex substituted. A monoiodide and a monobromide of decaborane have been shown to be substituted at the B-2 positions. A second monoiodide 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 ($B_{10}H_{12}I_2$) has been established.[3] The method of preparation of $B_{10}H_{12}I_2$ 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_5H_8Br (m.p. 32–34°), B_5H_8I (m.p. 53°), $B_{10}H_{13}Br$ (m.p. 105°), $B_{10}H_{13}I$ (m.p. 116°) and $B_{10}H_{13}I$ (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 $B_{10}H_{12}I_2$ 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 B^{11} 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 30.0013 and 9.6257 Mc./sec. The effect of the latter method is to interrupt the spin orientations of the B^{11} nuclei frequently enough so that the H^1 nuclei see only the average value of zero and the multiplet structure collapses.[5] All spectra are shown with field strength increasing toward the right.

Results

Figure 1 compares the proton resonance spectrum of B_5H_8Br and B_5H_8I with that of B_5H_9. The

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[1] Department of Chemistry, Iowa State College, Ames, Iowa. Requests for reprints should be addressed to this author at Department of Chemistry, Indiana University, Bloomington, Indiana.

[2] Varian Associates, Palo Alto, California.

[3] R. Schaeffer, THIS JOURNAL, **79**, 2726 (1957).

[4] For the suggestion that electrophilic substitution may occur in boranes see W. N. Lipscomb, *J. chim. phys.*, **53**, 515 (1956). For a discussion of charge distribution in boranes see W. H. Eberhardt, B. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

[5] (a) A. L. Bloom and J. N. Shoolery, *Phys. Rev.*, **97**, 1261 (1955); (b) J. N. Shoolery, *Disc. Faraday Soc.*, **19**, 215 (1955).