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Thermodynamics and Structure of the *p*-Xylene and *p*-Dichlorobenzene Clathrates of Tetra-(4-methylpyridine)-nickel(II) Thiocyanate[1]

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Measurements of the enthalpy change accompanying the clathration by the host, $Ni(4\text{-mepy})_4(SCN)_2$, of the guests, *p*-$C_6H_4(CH_3)_2$ and *p*-$C_6H_4Cl_2$ in various guest-to-host ratios were made by means of a twin calorimeter. The maximum value of this ratio is unity. Unexpectedly large exothermic heat effects were observed. X-ray and density studies showed that the lattice of the original complex is different from that of the complex when it is acting as host. The difference in the lattice energies of the two was determined. Infrared absorption and magnetic susceptibility measurements indicate that the complex is largely unaffected by clathration. The same is true for the two guests. Phase studies in the system guest–host–*n*-heptane were conducted and the heat capacities of complex and clathrates determined. The energy change accompanying clathration, although large and partly the result of changes of translational and rotational motion, is still attributable principally to the operation of van der Waals forces.

Introduction

The name clathrate was first introduced in 1948 by Powell[2], who gave the name to a type of intermolecular compound which involved the complete enclosure of a molecule of one component by one or more molecules of another component. More recently, van der Waals and Platteeuw[3] gave a statistical treatment of the hydroquinone and gas hydrate clathrates, in which the clathrate was considered to be a form of solid solution. Supported by X-ray and calorimetric studies they assumed that the spectrum of the host lattice is not affected by the presence of the solute or guest, that the enclosed molecules are localized in the cavities of the host lattice and that a cavity can never hold more than one guest molecule. They further assumed the free rotation of the solute molecule in the cavity. Mandelcorn,[4] in a review article, also considered the clathrate to be a solid solution and stated that the guest molecule loses not only translational energy but also some rotational and vibrational modes, due to interaction with the host lattice.

Evans and Richards[5] made calorimetric measurements of the heats of formation of various hydroquinone clathrates and of the difference in energy of the two crystalline forms of the hydroquinone molecule. A few years later Schaeffer[6] and Williams[7] undertook an investigation of the various clathrates formed by the type of complexes MP_4X_2, where M is a transition metal ion, P a pyridine derivative and X a halide or pseudohalide such as SCN^-. This type of complex has been extensively investigated by Logan and others.[8] Recently, de Radzitzky and Hanotier[9] have extended the number of clathrates of this type to include those in which P is a substituted benzylamine.

It was the purpose of the work here reported to determine some of the fundamental properties of the *p*-xylene and *p*-dichlorobenzene clathrates of tetra-(4-methylpyridine)-nickel(II) thiocyanate ($Ni(4\text{-mepy})_4(SCN)_2$). Current interest in the use of the phenomenon of clathration for the separation of otherwise difficultly separable isomers, and for other purposes, provided a further stimulus for this study.

Experimental

The complex to be used as host, $Ni(4\text{-mepy})_4(SCN)_2$, was prepared by precipitation from a very dilute aqueous solution of nickel chloride and 4-methylpyridine by the addition of potassium thiocyanate solution. It was not recrystallized, for all solvents tried were found to coprecipitate with it. It was analyzed for nickel (gravimetrically with dimethylglyoxime) and for sulfur and nitrogen (by the usual methods). The clathrates were prepared from the complex by suspending the latter in a solution of the desired guest in *n*-heptane, the extent of clathration being determined by the concentration of the guest. The products were analyzed gravimetrically for nickel, and the guest content computed by difference.

The heats of formation were found using a twin calorimeter similar to that used by Evans and Richards.[5] It consisted of two similar Dewar flasks, each equipped with heater, stirrer, sample holder and thermel of 21 chromel–constantan junctions. The emf of the thermel was determined by means of a potentiometer, either a Sargent recorder or a Leeds and Northrup Type K. The sample bulbs, each containing equivalent amounts of complex and clathrate, were broken simultaneously in their respective Dewars in a solution of 1:1 HCl, and the e.m.f. change recorded as a function of time. The e.m.f. change was then compared to a similar change produced by the heating of the contents of the Dewar by passing a known current through the heater of known resistance. The heat thus measured gave the energy difference between the complex and the clathrate. Measurements were performed in the same way using clathrates with less than the maximum guest content but nevertheless of the single X-ray pattern variety. (This matter will be discussed at greater length below.) The accuracy of the calorimeter was assessed by determining the heat of solution of KCl and comparing this with the literature values. Agreement was within 1.2%.

Heat capacity measurements of the complex and clathrates were made at 28° ± 1, in a copper calorimeter enclosed, except for the top, in an evacuated, silvered glass chamber. A Beckmann thermometer was used to measure the temperature changes. The heat capacity of the calorimeter was determined with KCl, NaCl and benzoic acid as standards.

The infrared spectra of the complex and clathrates were recorded on a Perkin Elmer Model 21 spectrophotometer with sodium chloride optics. Potassium bromide pellets were used for these spectra. Differential spectra were also recorded with clathrate in one beam and an equiva-

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(1) Taken from the Ph.D. thesis of M. I. Hart, Jr., Fordham University, February, 1962. Portions of this work were reported to the Division of Physical Chemistry of the American Chemical Society in New York, September, 1960 and in Chicago, September, 1961.

(2) H. M. Powell, *J. Chem. Soc.*, 61 (1948).

(3) J. H. van der Waals and J. C. Platteeuw, "Advances in Chemical Physics," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1959, p. 2.

(4) L. Mandelcorn, *Chem. Revs.*, **59**, 827 (1959).

(5) D. F. Evans and R. E. Richards, *Proc. Roy. Soc.* (London), **A223**, 238 (1959); *J. Chem. Soc.*, 3932 (1952).

(6) W. D. Schaeffer, W. Dorsey, D. A. Skinner and C. G. Christian, *J. Am. Chem. Soc.*, **79**, 5870 (1957).

(7) F. V. Williams, *ibid.*, **79**, 5876 (1957).

(8) A. V. Logan and D. W. Carle, *ibid.*, **74**, 5224 (1952).

(9) P. de Radzitzky and J. Hanotier, *Ind. Eng. Chem., Process Design & Development*, **1**, 10 (1962).

lent quantity of complex in the other. Visible spectra of the complex in ethanol were taken with a Perkin Elmer Model 4000 Spectracord.

The densities of the complex and clathrates were determined by means of a vacuum-jacketed pycnometer thermostated at 25° ± 0.1. The liquid used was *n*-heptane for the complex and a solution of the guest in *n*-heptane for the clathrates.

The complex and the clathrates were subjected to X-ray powder diffraction analysis using a Norelco unit and copper K alpha radiation, and their magnetic susceptibilities were determined with a Gouy-type magnetic balance, calibrated with $HgCo(SCN)_4$.

Attempts were also made to determine whether a clathrate with less than the maximum guest content is a solid solution of completely clathrated material in complex or a mechanical mixture of these two by application of the following principle: Isothermal addition of guest to a suspension of complex in *n*-heptane should give a supernatant liquid with continuously changing composition if the solid is a solution but show a halt in composition if the solid is a mixture, since invariance would then be required by the phase rule. (In experiments of this type van der Waals and Platteeuw[3] had found invariance in the system hydroquinone–methanol–1-propanol). The appearance of such a halt would also enable the composition of the pure clathrate to be determined if both the total composition of the system and that of the invariant liquid were known. The index of refraction of the liquid was taken as a convenient measure of its concentration, after first determining the relation between the two. As carried out, separate complex–heptane–guest mixtures were used for each refractive index measurement, and the mixtures agitated at 25° ± 0.1 for 15 hr. before withdrawing a sample of the liquid for analysis. Three such series of runs were conducted with p-xylene and one for p-dichlorobenzene.

Results

Analysis of the complex gave the following satisfactory results (in wt. %): Found: Ni, 10.73, 10.69, 10.72; N, 15.24; S, 11.28. Calcd.: Ni, 10.73; N, 15.36; S, 11.72. Both complex and clathrate are the same color, *viz.*, blue.

The heats of formation for clathrates of various compositions are given in Table I and are plotted in Fig. 1. The mole ratios are believed accurate to 3%, the heat quantities to within 0.15 kcal. Most of the quantities quoted are the means of two to four separate experiments having the indicated average deviations.

Table I

Heats of Formation

p-Xylene clathrate		p-Dichlorobenzene clathrate	
Mole ratio Guest/ complex	$-\Delta H^0_{298.2}$ (kcal. mole^{-1} complex)	Mole ratio Guest/ complex	$-\Delta H^0_{298.2}$ (kcal. mole^{-1} complex)
0.612	5.32 ± 0.05	0.656	2.13 ± 0.07
.671	5.68 ± .04	.694	2.08 ± .10
.817	6.69	.793	2.67 ± .05
.884	7.23 ± .08	.949	3.84 ± .02
.956	7.89 ± .11	1.000	3.87
.959	8.08		

Heat capacities were determined to be 175 ± 5 cal. mole^{-1} deg.$^{-1}$ for the complex, 237 ± 7 cal. mole^{-1} deg.$^{-1}$ for the p-xylene clathrate (mole ratio 1.00), and 221 ± 6 cal. mole^{-1} deg.$^{-1}$ for the p-dichlorobenzene clathrate (mole ratio 1.00).

There was little change in the infrared spectrum of the complex upon formation of the clathrate with either p-xylene or p-dichlorobenzene except for a possible slight reduction of intensity of an absorption at 3400 cm.$^{-1}$ due to the SCN group.

It was difficult to interpret the spectrum of the clathrated p-xylene since it was weak and resembled the spectrum of 4-methylpyridine closely. A marked reduction in the intensity of the 1100 cm.$^{-1}$ band was found. The band is believed to be due to the in-plane bending vibration of the methyl group. Other than this there was no clear cut change.

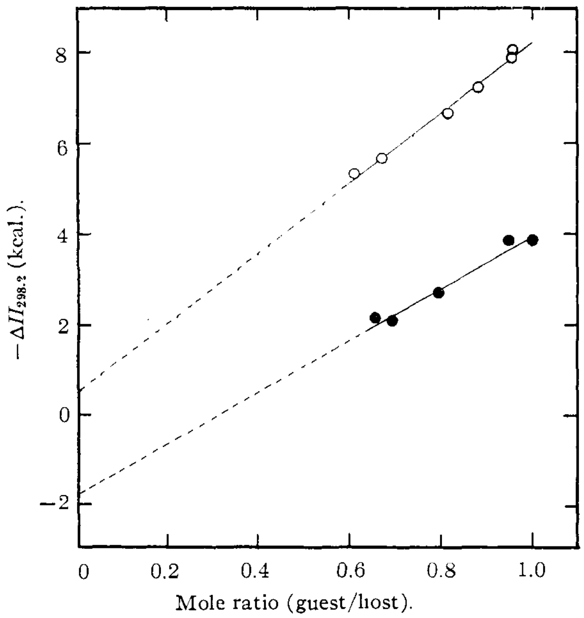

Fig. 1.—Heat of formation of clathrate (per mole of complex) at 25° as a function of guest content: p-xylene, -○-; p-dichlorobenzene, -●-.

The spectrum of the clathrated p-dichlorobenzene closely resembled the spectrum of p-dichlorobenzene in solution. In the few cases where there was a difference between these two spectra, it could be related to the spectrum of p-dichlorobenzene in either the solid or the vapor state.[10]

The visible region spectrum of the complex in ethanol showed maxima at the following values of wave number (cm.$^{-1}$): 10,500, 16,500, 26,700. These would conventionally be labelled ν_1, ν_3, and ν_4, respectively, so that ν_3/ν_1 would equal 1.62. The spectrum for an octahedral complex would be expected to yield a value of about 1.8 for this ratio.[11]

The mean densities and molar volumes, at 25° ± 0.1, in g. ml.$^{-1}$ and ml. mole^{-1}, respectively, were found to be as follows: Complex: 1.270 ± 0.001, 431.0; p-xylene clathrate (1:1): 1,260 ± 0.003, 518.7; p-dichlorobenzene clathrate (1:1): 1.339 ± 0.002, 518.6.

Interplanar distances for the more prominent X-ray reflections of the complex and clathrates are listed in Table II. Moreover, other guest molecules were also found to be coprecipitated with the complex when attempts were made to recrystallize the latter. In addition to the types formed by the inclusion of p-xylene and p-dichlorobenzene, seemingly distinct types were formed by the inclusion of each of the following: chloroform, methanol, butyl cellosolve, 2-propanol. Methyl cellosolve

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[10] A detailed comparison of the differential infrared spectra of each guest in the clathrated and unclathrated forms will be found in the Ph.D. dissertation of M.I.H. (see ref. 1).

[11] W. Manch and W. C. Fernelius, *J. Chem. Educ.*, **38**, 192 (1961).

TABLE II

INTERPLANAR DISTANCES FOR THE MORE PROMINENT REFLECTIONS FROM THE COMPLEX AND *p*-XYLENE AND *p*-DICHLOROBENZENE CLATHRATES (A.)

Complex	*p*-Xylene clathrate	*p*-Dichlorobenzene clathrate
	13.34 m	
8.64 s		8.63 s
8.37 vs	8.36 vs	
7.56 m		
7.34 w		
	7.14 s	
	5.41 s	5.41 m
5.17 w	5.23 s	5.14 m
5.03 s		
4.98 m		4.93 w
4.85 m	4.86 w	
	4.60 s	4.70 m
4.50 m		
4.36 s		
4.27 s		
4.08 m		
4.05 m	4.02 w	4.05 w
	3.95 m	3.94 s
3.90 m		
3.85 m		3.87 m
	3.80 m	
3.65 w	3.65 s	3.67 s
	3.62 m	
3.55 w	3.61 m	
	3.32 w	
	3.19 w	3.19 w
3.15 w		3.15 w
		3.08 w

gave the same type pattern as chloroform and 4-methylpyridine the same as *p*-xylene.

It was also observed that the X-ray pattern, which we shall designate as beta, given by compositions with about 0.6 to 1.0 mole ratio of guest to host was quite different from that of the original complex, designated as alpha. On the other hand, compositions with a small mole ratio gave, at least with *p*-xylene, the alpha pattern superimposed on the beta. It appears, therefore, that unoccupied complex can exist in two different lattices, alpha and beta, only the beta being able to accommodate a guest.

The experimental magnetic susceptibilities (c.g.s. units $\times 10^6$) and magnetic moments (B.M.) were found to be 7.18 and 3.07 for the complex, 5.90 and 3.04 for the *p*-xylene clathrate and 5.61 and 3.05 for the *p*-dichlorobenzene clathrate, respectively. The presence of two unpaired electrons in the complex is indicated by the nearness of the observed moment of 3.07 to the calculated value (2.83). The observed specific susceptibilities for the clathrates may be compared with those calculated from the observed values for the complex (7.18×10^{-6}) and the literature values for *p*-xylene,[12] -0.7232×10^{-6}, and *p*-dichlorobenzene,[13] -0.5559×10^{-6}, assuming additivity. Such a calculation gives 5.90×10^{-6} and 5.56×10^{-6} for the susceptibilities of the *p*-xylene and *p*-dichlorobenzene clathrates, respectively. The reasonable agreement of these figures with the experimental ones gives support to the postulate of no interaction between the nickel and the guest molecule.

The phase studies revealed an invariant liquid in both clathrate systems, since the refractive index of the supernatant was constant over a considerable range of total composition. That this is so is seen by the following representative succession of refractive indices ($n^{25}\text{D}$) for a series of samples of increasing *p*-xylene content: 1.3862, 1.3859, 1.3859, 1.3863, 1.3877, 1.3899, 1.3920. The over-all mole per cent *p*-xylene in each of these experiments was, respectively, 1.089, 3.197, 5.217, 7.15, 9.01, 10.80, 12.53. The same behavior was found for *p*-dichlorobenzene. The rise in value after the period of constancy marks, of course, entry into a univariant region where only one solid phase is present. It is concluded, therefore, that the *p*-xylene and *p*-dichlorobenzene clathrates both form a mechanical mixture at equilibrium with whatever form of the complex is present. That this is the alpha form for the *p*-xylene system, and possibly also for the *p*-dichlorobenzene system, was indicated by the X-ray patterns of the solid phases obtained before the liquid phase ceased to be invariant. It should be emphasized that these two-phase solids were thus different from the completely beta-type materials used in the calorimetric work and made by a different method.

The composition of the solid phase beyond which, in the above study, the liquid ceased to be invariant, was obtained by algebraic extrapolation of the liquid and total compositions (at that point) to zero per cent heptane. For the *p*-xylene and *p*-dichlorobenzene systems the invariant liquids were found to contain, respectively, 1.12 ± 0.12 and 0.73 mole % guest and negligible quantities of complex. The corresponding extrapolations gave 49.0 ± 0.7 mole % *p*-xylene and 49.6 mole % *p*-dichlorobenzene in the solid phase. It is seen that both clathrates have the 1:1 molar composition within experimental error.

Discussion

In the formation of the clathrate from the complex, there is a definite structural change in the lattice of the host. This was evident not only from the X-ray powder diffraction studies, phase studies and densities of the materials but also from the microscope appearance of the crystals of the complex and clathrates. The latter could, of course, be a mere change of habit, but together with the above information the results indicate a change of structure. The case of the structures of the two clathrates is slightly different, however for though the X-ray powder diffraction spectra are different, the molar volumes of the two clathrates are the same. This may be merely chance, since, as seen below, the experimental heats of transition for the change of the alpha to the beta lattice are different for the two clathrates.

The infrared study showed that since only minor changes in the spectrum of the complex were detected, the change of lattice structure in the formation of the clathrates cannot affect the complex

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(12) S. Broersma, *J. Chem. Phys.*, **17**, 873 (1949); V. C. G. Trew, *Trans. Faraday Soc.*, **49**, 604 (1953).

(13) M. A. Luferova and Ya. K. Syrkin, *Izvest. Akad. Nauk S.S.S.R Otdel. Khim. Nauk*, 380 (1954).

too severely. Furthermore, the spectra of the clathrated *p*-xylene and *p*-dichlorobenzene do not appear to give support to the idea of a strong chemical association formed between the host and the guests. The changes that do occur are probably those that occur upon the change of physical state of the guests, such as entering upon solution.

Although it has been suggested by some that these clathrates may be a form of pi complex, in addition to or instead of being an inclusion compound, the results of the present investigation do not show any indication of any form of chemical bond. Magnetic susceptibility measurements rule out the possibility of a bond to the nickel atom, and the infrared spectra do not show any changes that might result from the formation of a chemical bond.

The results of the extrapolation in the phase studies are seen to show that one mole of complex will accommodate a maximum of one mole of guest. Moreover, the existence of an invariant liquid shows the presence of two solid phases when the guest content is less than this maximum. These solids, however, even when high in overall guest content, gave, at least for the *p*-xylene clathrate, the X-ray pattern of a mixture of alpha and beta structures, thus not showing whether the one-pattern, high-guest content solids used in the calorimetric studies were mixtures or solid solutions. The fact that the latter solids did give a single pattern, however, suggests that they were solid solutions of complex in 1:1 clathrate rather than mixtures.

The least-squares lines in Fig. 1 have been drawn on the assumption that the heat of clathration per mole of complex is a linear function of the mole ratio. This would be expected if, as it appears from the above, the clathrate and beta form of the complex form a solid solution and if the guest molecules do not interact appreciably with each other in the clathrate. The intercepts of the lines give the heat of transition per mole of the complex from the alpha to the beta lattice, and their slopes give the heat of formation per mole of the clathrate from the beta complex and the guest. These quantities, combined with the heat of vaporization of *p* - xylene (10.1 kcal. mole^{-1})[14] and the heat of sublimation of *p*-dichlorobenzene (15.5 kcal. mole^{-1}),[15] lead to the following equations, in which beta refers to the complex which can accommodate *p*-xylene and beta′ that which can accommodate *p*-dichlorobenzene

$$(1)\quad \text{Complex}_{(\text{s, alpha})} \longrightarrow \text{complex}_{(\text{s, beta})} \qquad \Delta H^0_{298.2} = -0.51 \text{ kcal.}$$

$$(2)\quad \text{Complex}_{(\text{s, alpha})} \longrightarrow \text{complex}_{(\text{s, beta}')} \qquad \Delta H^0_{298.2} = 1.80 \text{ kcal.}$$

$$(3)\quad \text{Complex}_{(\text{s, beta})} + p\text{-xylene}_{(\text{g})} \longrightarrow \text{clathrate}_{(\text{s})} \qquad \Delta H^0_{298.2} = -17.8 \text{ kcal.}$$

$$(4)\quad \text{Complex}_{(\text{s, beta })} + p\text{-dichlorobenzene}_{(\text{g})} \longrightarrow \text{clathrate}_{(\text{s})} \qquad \Delta H^0_{298.2} = -21.3 \text{ kcal.}$$

One may estimate that the accumulated error in these last two enthalpy changes is no larger than 0.8 kcal. Allowing for this, and also for a likely loss of some 2 kcal. translational and rotational energy accompanying the clathration process, there is still a sizeable drop in energy when the clathrate is formed. For lack of further information this must at present be ascribed to the operation of van der Waals-type forces between host and guest. The difference between the heat effects in (3) and (4), amounting to 3 or 4 kcal. is probably real, and may be related to the differences between the electron donating ability of the two guests, or to a difference in their position in the clathrate lattice. It may be pointed out, too, that the lattices themselves appear to be different for the beta forms of the two complexes.

An interpretation of the heat capacity data is difficult. It is interesting to be able to compare the experimental heat capacities of the clathrate with the sums of the heat capacities of the complex and gaseous host, even with the former in the alpha lattice, as measured. The heat capacity of gaseous *p*-xylene has not been measured at 298° K. but has been calculated[14] as 30 cal. mole^{-1} deg.$^{-1}$ at this temperature. If one deducts 6 cal. for loss of translational and rotational modes, one may add the resulting 24 cal. to the heat capacity for the complex (175) giving a value of 199 for an estimated heat capacity of the *p*-xylene clathrate. This is 16% below the observed value. For the *p*-dichlorobenzene clathrate a corresponding difference of 11% is obtained using the value of 27 cal. mole^{-1} for the heat capacity of *p*-dichlorobenzene vapor at 298°K., as calculated by Godnev and Sverdlin.[16] Whether these differences can be ascribed to interactions of the complex with the guest, recognizing that the measured value for the complex is for the alpha form and not for the beta which is actually present, cannot be decided. It may here be pointed out that even for *p*-xylene itself there is the anomaly that the calculated heat capacity of the gaseous form is smaller than the experimental value of 44 cal. mole^{-1} deg.$^{-1}$ for the liquid.[17]

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[14] K. S. Pitzer and D. W. Scott, *J. Am. Chem. Soc.*, **65**, 803 (1943).

[15] P. N. Walsh and N. O. Smith, *J. Chem. Eng. Data*, **6**, 33 (1961).

[16] I. N. Godnev and A. S. Sverdlin, *Zhur. Fiz. Khim.*, **24**, 670 (1950).

[17] R. J. Corruccini and D. C. Ginnings, *J. Am. Chem. Soc.*, **69**, 2291 (1947).