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Kinetic Rate Studies and Related Properties of Some Werner-Complex Clathrates

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KINETIC RATE STUDIES AND RELATED PROPERTIES
OF SOME WERNER-COMPLEX CLATHRATES

by

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B.S. Hongkong Baptist College

A Thesis

Submitted in Partial Fulfillment of the
Requirements for the Degree of
Master of Arts in Chemistry

School of Graduate Studies
Northern Michigan University

Marquette, Michigan

January 1970

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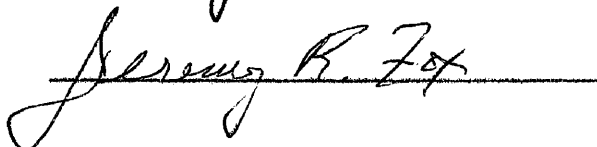
by

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This thesis is recommended for approval
by the student's thesis committee:


Chairman





Approved by , Dean of Graduate Studies.

Submitted in Partial Fulfillment of the
Requirements for the Degree of
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January 1970

ABSTRACT

A brief outline of the history of clathrate compounds is presented. A study of the relationship between the size of the vacancy within the Werner complex and the size of the guest molecule was carried out for first row transition elements. The size of the guest molecule varied from benzene(molecular volume=88.8cc/mole) to 4-ethyltoluene(molecular volume=139.8cc/mole). A definite relationship was found between the size of the host vacancy and the size of the guest molecule. This relationship was established through kinetic rate studies, X-ray powder diffraction patterns, and gravimetric analyses.

A lattice change from complex to clathrate is confirmed by X-ray powder diffraction patterns. Also, evidence in support of a charge-transfer type complex was obtained when no clathrates could be formed using cyclopentane and cyclohexane as guest molecules. A model of the clathrate was constructed in order to show the possible "sandwich" type interaction between the nitrogen base of the complex and the guest molecule.

ACKNOWLEDGMENTS

The author wishes to express his deepest appreciation to Dr. Gerald D. Jacobs for his constant encouragement, guidance and whole-hearted support which he so generously gave during this research program, and to the faculty and graduate students in the Department of Chemistry for their useful help and discussions.

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HISTORICAL BACKGROUND

HISTORICAL BACKGROUND

The word "clathrate" was first introduced into chemistry by H. M. Powell following his x-ray studies on a series of molecular compounds (31). Powell was able to show that these compounds were capable of "trapping" other molecules within their crystalline lattices, and hence he proposed the term clathrate (from the Latin "clathratus" meaning enclosed or protected by the cross-bars of a grating). Following the x-ray work of Powell, other investigators began intensive studies on this new type of compound. The early work was concentrated in three areas:

1. gas hydrates
2. quinol complexes
3. $\text{Ni}(\text{CN})_2 \cdot \text{NH}_3 \cdot \text{M}$ (M= organic adduct)

1. Gas Hydrates

The first gas hydrate reported was that between chlorine and water. It was prepared by H. Davy in 1810 (7) by cooling a saturated solution of chlorine in water to below 9°C . M. Faraday proposed the formula $\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ (15) and further work by M. von Stackelberg and others (51-64) clarified the nature of these compounds. More recent work by C. Lowing (23), M. Broneman(3), M. Mannere(24), G. Chancel and F. Parmentier(4), H.Z. Roozeboom(42), P. Villard (44-47) and many others, showed that this type of hydrate

can be formed with a large number of gases or volatile liquids, such as Cl_2 , Br_2 , H_2S , CO , SO_2 , CH_3Cl , CHCl_3 , CH_4 , Ar , Kr , and Xe .

An x-ray structural study of gas hydrates was carried out by L. Pauling and R.E. Marsh. (30) According to their x-ray analysis, all gas hydrates crystallize in cubic structures and are believed to be solid solutions. The guest molecules are situated in cavities formed by a framework of water molecules (the host) linked together by hydrogen bonds.

2. Quinol complexes

More than a century ago, the hydroquinone complexes with H_2S and SO_2 were reported by K. Wohler(66) and Clemm(4). However, most of the work in this area has been done since Powell reported the structure of several quinol complexes—based upon x-ray analysis. (27-28; 31-37) He proposed that hydroquinone molecules were linked by means of hydrogen bonds to form a pair of interlocking three dimensional networks. The networks do not, however, completely fill the available space. The cavities which result are roughly spherical and about 4 ⁰ A in diameter. Each cavity is bounded by two circles of six hydrogen

bonded hydroxyl groups and by the benzene rings of six quinol molecules. The guest molecules lie trapped in these cavities.

Thermodynamic values for quinol complexes, as well as other properties, have been determined by D.F. Evans and R.E. Richards, (11-14) T.S. Dryden, (8-10) Van der Walls, (48-51) R.M. Nexter and Goldfarb, (20) J.C. Platteuw, (39-40) and many other workers.

3. $\text{Ni}(\text{CN})_2\text{NH}_3$ complex

The clathrate formed between this inorganic complex and benzene was first reported in 1897, (18) although the exact structure was not known. In 1952, J.H. Rayner and H.M. Powell reported the crystal structure of the $\text{Ni}(\text{CN})_2\text{NH}_3$ benzene clathrate by x-ray analysis. (39) Since that time a large number of other Werner complexes have been shown to function as hosts. W.D. Schaeffer and F. Williams (42; 66) reported a large number of these compounds and the one utilizing $\text{Ni}(\text{4-methylpyridine})_4(\text{SCN})_2$ as host was studied by M.I. Hart, M.J. Minton and N.D. Smith. (17,18,24,25) They have published thermodynamic constants, kinetic rate data, infrared spectra and phase diagrams for several clathrates. A single crystal study on some clathrates of tetra-(4-methylpyridine)-nickel(II) and cobalt (II) dithiocyanates has been published by D.

Belitskus, et. al. (1)

It soon became obvious that not all of the substances under study were "clathrates" by the definition of Powell. A classification scheme thus became necessary, and the following scheme was proposed:

I. Complex molecules

A. Coordination Compounds

B. Inorganic Polymers

C. ...

D. Molecular Compounds

1. Inclusion compounds

	<u>nature of cavity</u>
a. Urea and Thiourea Adducts	channels
b. Zeolite Complexes	channels
d. Graphite and Silica Complexes	layers
d. Dextrin-Iodine Type Complexes	solution
e. Clathrates	cages

At the present time there is some indication that this classification scheme is not inclusive and will require modification. (2)

INTRODUCTION

INTRODUCTION

In 1957, Schaeffer and co-workers published a paper entitled "Separation of Xylenes, Cymenes, Methyl-naphthalenes and Other Isomers by Clathration with Inorganic Complexes" (42). Since that time a large number of inorganic complexes (Werner Complexes) have been prepared and their physical and chemical properties studied including unit cell dimensions for the crystals. According to the paper by Schaeffer(42), more than 40 complexes utilizing first row transition metals are capable of forming clathrates. Fourteen of these were utilized in studying the separation of isomers of p-xylene. The clathrates were prepared by two different methods, the suspension process and the solution process. The work by Schaeffer was apparently of an analytical nature only, since his paper deals exclusively with the enrichment of petroleum fraction. Preliminary studies in this laboratory indicate failure of clathration for several of the complexes listed in his paper. Up to now the only one of these complexes which has been studied in detail is Ni-(4-methylpyridine)₄(SCN)₂. Hart, in his thesis,(18) presented infrared spectra, phase diagrams and calorimetric data for clathrates of Ni(4-methylpyridine)₄(SCN)₂. Minton

in her thesis(25), presented the results of further kinetic, phase and calorimetric studies. X-ray studies by Hart(18) also indicated a difference between the crystal structure of the complex and clathrate. The suspected octahedral configuration of the complex was confirmed by magnetic susceptibility measurements and visible absorption spectra. Later, x-ray single crystal studies by Belitskus (1) also indicated an octahedral configuration(space group $I4_1/a$).

The heat of clathration at 25°C was measured and found to be 15-20 Kcal mole⁻¹ for p-xylene, p-dichlorobenzene, ethylbenzene, and toluene with host molecule Ni-(4-methylpyridine)₄(SCN)₂.(18,25) So far a limited theoretical interpretation has been presented, but no systematic experiments have been performed to support the theory.

In this thesis, experiments were designed that would test current theories. This included kinetic rate studies of clathration using first row transition elements from Mn²⁺ to Cu²⁺ with the same ligands, SCN⁻ and 4-mepy, and different sizes of guest molecules; interpretation of x-ray powder diffraction patterns and quantitative analysis. One section is devoted to a study of "sandwich" type interaction between guest molecule and nitrogen base of the host molecule. In addition, a twin calorimeter similar to Hart's (18) was constructed.

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SPECIAL REQUIREMENTS

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INSTRUMENTATION

Temperature

A constant temperature bath capable of regulation to $\pm 0.1^{\circ}\text{C}$ was used for all the kinetic rate studies. Temperature measurements were made with a thermometer calibrated and certified by the United States National Bureau of Standards.

X-ray Measurements

The x-ray powder diffraction patterns were obtained on a Siemens Kristalloflex 4, X-ray Diffractometer, using copper K-alpha radiation. A Siemens two radian camera was used and line measurements were made with a coincidence scale having an accuracy of ± 0.01 mm.

Spectral Measurements

Ultraviolet spectra were obtained on a Beckman DB-G Grating Spectrophotometer, using Beckman silica cells. A Sargent Model SR Recorder was used to record the spectra.

Analytical Measurements

An Ainsworth Type 21N single pan automatic balance was used for all weighings. A Sargent-Slowin Electrolytic Analyser and platinum electrodes were used for the quantitative analysis of cobalt and copper.

Gas Chromatography Measurements

A Varian Series 1700 Gas Chromatograph was used for kinetic rate studies involving cyclopentane and cycloheptane. A Sargent Model SR0 Recorder was used to record the chromatograms.

EXPERIMENTAL

EXPERIMENTAL

Preparation of Werner Complexes

To 0.228 moles of each of the following hydrates dissolved in 3 liters of water was added 0.456 moles of KSCN.



After complete solution of the metal salt and thiocyanate, 0.910 moles of 4-methylpyridine was added slowly with constant stirring. The mixture was then stirred for an additional half hour before filtering. The precipitate was air dried for four hours and then transferred to a desiccator and stored over solid potassium hydroxide. Removal of all moisture required approximately one week. Materials used in this preparation were of analytical reagent grade. The large amount of water used in the preparation was necessary to prevent excess SCN^- from co-precipitating.

A quantitative determination of the percent of metal in each of the complexes was used as an indication of purity. The results are shown in Table I, page 21.

Purification of solvent

It was necessary to purify reagent grade heptane before using it as a suspension medium in the kinetic rate studies. Later spectral studies showed that the purified heptane was of the same purity as commercially available "Spectroquality" grade.

The procedure used in the purification was as follows. First, the heptane was extracted using sulfuric acid. This was accomplished in a large separatory funnel with occasional shaking over a twenty four hour period. Next, the heptane layer was neutralized by shaking with a 10% sodium carbonate solution and a salting out process was followed by using saturated sodium chloride solution. The heptane was dried by passing it through a column of anhydrous calcium chloride and then fractionally distilled. The purity of the heptane was determined from ultraviolet spectra.

Kinetic rate studies

The kinetic rate studies were carried out in a constant temperature bath capable of regulation to $\pm 0.1^{\circ}\text{C}$.

A 500 ml reaction flask containing 300 ml of purified heptane was placed in the constant temperature bath and allowed to come to equilibrium. Ten milliliters of the guest component was then introduced and the solution stirred by means of a magnetic stirrer located beneath the bath. Once thermal equilibrium had been established 1 ml.

of the sample solution was withdrawn by means of a filter stick. A microliter pipette was then used to accurately measure 0.1 ml of the withdrawn sample. This sample was placed in a 25 ml volumetric flask and diluted with purified heptane.

Following the withdrawal of the initial sample the solid Werner complex was introduced into the reaction flask. An amount to yield slightly less than a 1:1 mole ratio of host:guest was used. The initial time for a kinetic run was taken as the time the complex was added to the solution

Using preselected time intervals, 1.0 ml samples of solution were withdrawn from the reaction flask by means of the filter stick. Exactly 0.1 ml of each of these samples was then transferred to a 25 ml volumetric flask and diluted with purified heptane.

Each of the kinetic rate studies was allowed to proceed for no less than 48 hours. The decrease in the amount of guest component present as a function of time was determined spectrophotometrically using a Beckman DB-G Spectrophotometer operating in the ultraviolet region at pre-selected wavelengths. Following each of the kinetic runs the contents of the reaction flask were

filtered and the solid material air-dried. The solid was then used in obtaining x-ray powder diffraction patterns and a quantitative analysis.

X-ray Diffraction Patterns

Samples of each of the complexes and the material obtained from the kinetic runs were used for powder diffraction x-ray patterns. The samples were prepared by mixing the powdered sample with collodion (or Vaseline in the case of Co) and extruding the partially dried sample from a 0.5 mm diameter capillary tube. Patterns were obtained on a standard two radian camera using copper K-alpha radiation and exposure times of 1/2 to 1 1/2 hours.

Quantitative Analysis

The determination of the percent metal in the complexes and clathrates followed standard analytical procedures. In the clathrate cases dilute hydrochloric acid was used to break down the compounds with Mn, Fe, and Ni while heat was used for those of Co and Cu.

The percent Mn^{++} was determined gravimetrically by precipitation and consequent conversion to $Mn_2P_2O_7$. The percent of Fe^{++} was determined volumetrically by titration with a standardized solution of $KMnO_4$. Ni^{++} was

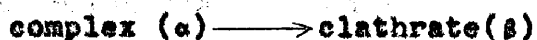
converted to nickel dimethylglyoxime and determined gravimetrically. Both Cu^{++} and Co^{++} were determined electrolytically by plating of the metal onto a platinum electrode.

DISCUSSION

DISCUSSION

Kinetic studies

The first kinetic rate studies on Werner-complex clathrates were reported by G. Gawalek, et. al. (16) As a result of their studies it was reported that the time required for clathrate formation was less than 15 minutes and that the solubility of the complex in the hydrocarbon greatly effects the rate of formation of clathrate. Further kinetic studies have been done by Minton and Smith (24, 25) who reported an initial increase in guest concentration and attributed the increase to either adsorption or absorption by the complex. They also reported that the reaction appeared to follow first order, reversible, kinetics. According to the work of Hart and Smith (17, 18) a lattice change occurs during the clathration process. Using the symbol α for the complex lattice and β for the lattice of the clathrate, the following equation represents the clathration process:



In the work of Minton (24, 25) the clathration reaction was reported to be complete in four to six hours, depending upon the particular guest molecule. The process

was described as follows: " the clathration reaction would not begin until the guest molecule could displace solvent molecules, come in contact with the complex, dissolve it to some extent and bring about the lattice change by precipitation. Then, when the lattice change was at least partially accomplished, the guest molecules could move into the host."

The results from initial studies in this laboratory showed both agreement and disagreement with previously published data. As a consequence it was decided that further, more extensive experiments should be performed in an attempt to clarify the rate process of clathration. The first trials were made using Werner complexes of the type $M(4\text{-methylpyridine})_x\text{Cl}_y$ (where M was either Ni^{2+} or Zn^{2+} and x and y in general had the values 4 and 2 respectively). These host structures failed to form clathrates with either p-xylene or benzene. This was confirmed by comparison of x-ray powder patterns of the host before attempted clathration and of the solid material remaining after the completion of the kinetic run. In each case there was no shift of line positions or in line intensities. Further evidence against clathration was provided by gravimetric analyses for the

percent of M in each sample both before and after the attempt to form a clathrate.

The same type of studies were carried out on the complex $\text{Ni}(4\text{-mepy})_4(\text{CNO})_2$ with p-xylene and benzene as possible guest molecules. Again no clathrates were found as evidenced by the results of kinetic studies, x-ray powder patterns, and gravimetric analyses.

A re-determination of the published data on the rate of clathrate formation between $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$ and p-xylene was then undertaken. The results from the rate studies, x-ray powder patterns, and gravimetric metal analyses were in total agreement with the earlier work of Minton(24,25) and Belitskus(1) which supported clathrate formation.

With renewed confidence in the method, kinetic runs were carried out at several different temperatures (21.02°C, 30.04°C, and 41.60°C) on the Werner complex $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$ utilizing different guest molecules. The results of the gravimetric analyses are shown in Table I. The change in guest concentration with time during the clathration process is shown in Table II, and Figure 1 presents graphically the results of the kinetic rate studies.

Table I
GRAVIMETRIC ANALYSES FOR N1
IN THE COMPLEX $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$ AND P-XYLENE CLATHRATES

	PERCENT N1			
	COMPLEX	CLATHRATE I*	II*	III*
Trial 1	10.63	9.20	9.05	9.02
2	10.66	9.18	9.24	9.16
3	10.47	9.19	9.11	9.06
Average	10.59	9.19	9.13	9.08
Theoretical	10.73			
Mole ratio(guest/host)		0.861	0.899	0.935

* Clathrate I, II, III refers to the clathrate formed at 21°C, 30°C, and 42°C respectively.

Table II
 CHANGE OF GUEST CONCENTRATION WITH TIME
 DURING THE CLATHRATION REACTION BETWEEN
 $N1(4\text{-mepy})_4(\text{SCN})_2$ and p-XYLENE

TIME(hour)	ABSORBANCE OF p-XYLENE AT 275m μ		
	SAMPLE I(21°C)	SAMPLE II(30°C)	SAMPLE III(42°C)
0	0.95	0.95	0.94
1/4	0.93	0.95	0.93
1/2	0.86	0.925	0.925
3/4	0.72	0.87	0.915
1	0.66	0.80	0.905
1 1/2	0.56	0.64	0.84
2	0.51	0.545	0.71
4	0.382	0.36	0.38
6	0.335	0.302	0.29
8	0.309	0.272	0.26
10	-	-	0.255
11	0.294	0.25	-
13	0.29	0.24	-
25	-	-	0.23
27	-	0.225	-
52	0.26	0.205	0.238

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

Fig 1
KINETIC RUN

Host molecule	Ni(4-mepy) ₄ (SCN) ₂
Guest molecule	p-Xylene
	21.0°C
	30.0°C
	41.6°C

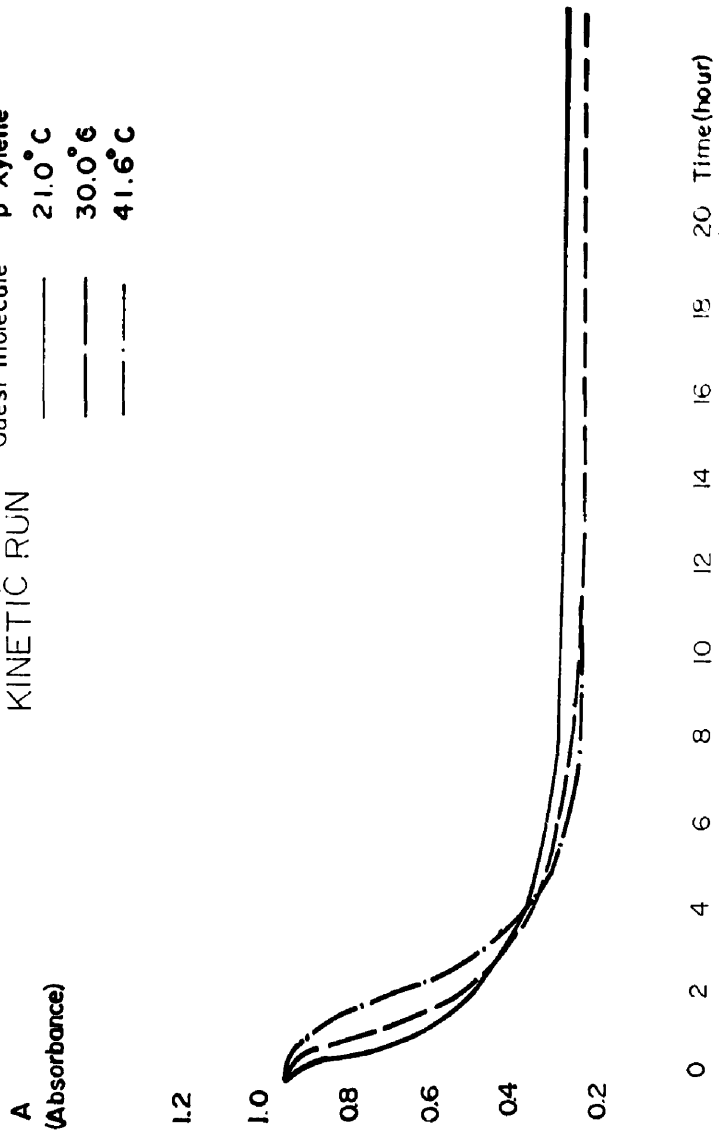


Fig 1

No initial increase in guest concentration was found in any of the kinetic runs. A plot of $-\log (A_t - A_e)$ vs. time was drawn and is shown in Figure 2. From the curve obtained it is evident that the reaction is not reversible, first order as proposed by Minton (24). The results do support the thermodynamic studies of Minton(24) and Hart(18) which showed that the clathration reaction is endothermic. In addition the x-ray powder patterns of complex and clathrate are definitely different as shown in Table III and thus support the theory that the lattice of the host structure undergoes a change during clathration ($\alpha \rightarrow \beta$). An additional experiment was performed using unpurified heptane as the suspension medium in an attempt to duplicate the work of Minton on the initial rise in guest concentration. However, the initial rise was again undetected.

The experimental work was next extended to determine whether or not a relationship could be found between the size of the guest molecule and the ease of clathration. For this study, divalent, first row transition metal ions from Mn^{2+} to Cu^{2+} were used. The common anion was SCN^- and the basic nitrogen compound was 4-methylpyridine. Guest molecules varied from benzene

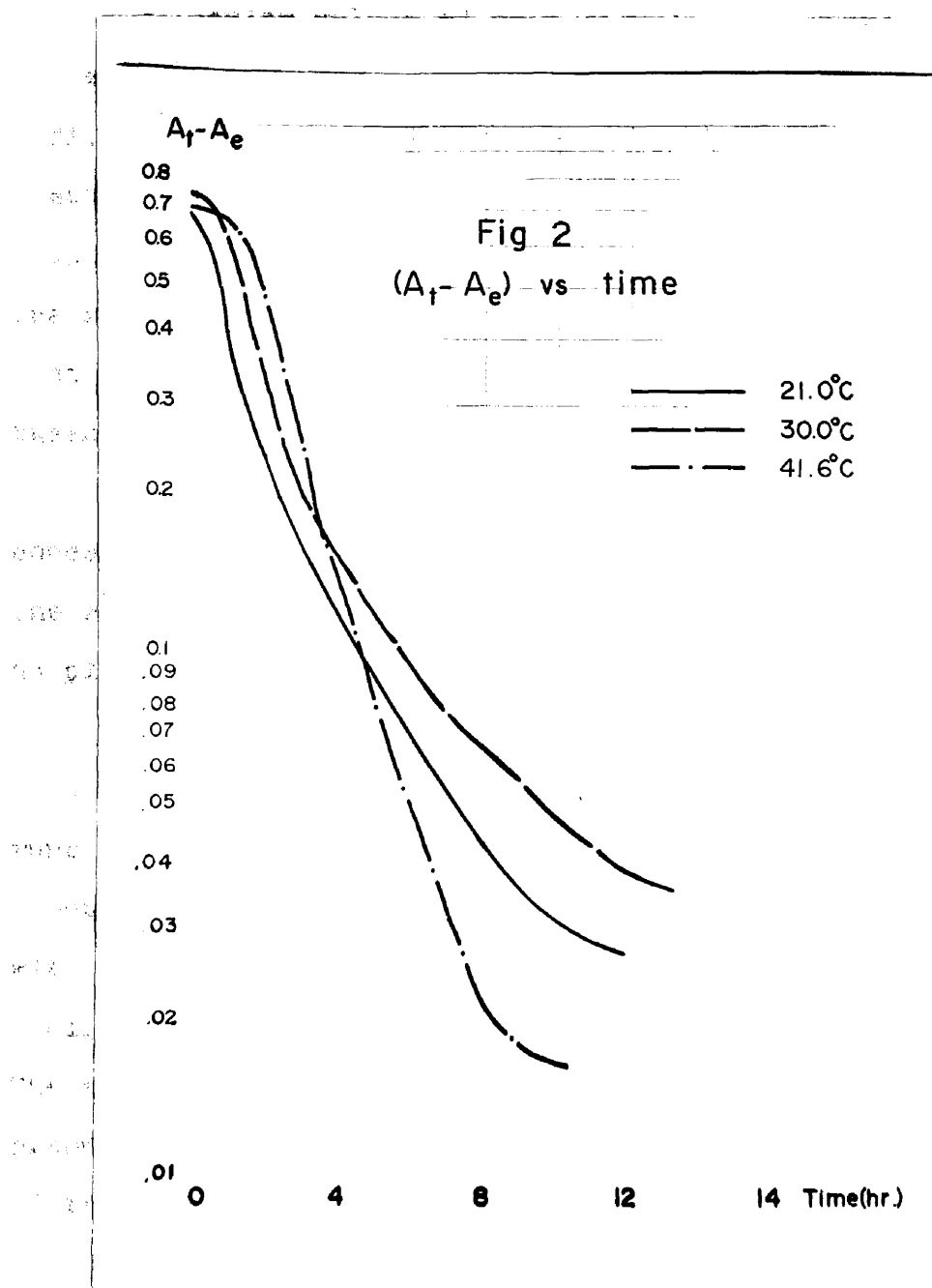
Table III
 INTERPLANAR DISTANCES (A) FOR THE MORE PROMINENT
 REFLECTIONS FROM THE $Ni(4\text{-mepy})_4(SCN)_2$ COMPLEX AND THE
 p-XYLENE CLATHRATE

COMPLEX		CLATHRATE		
d_{obsd}	$d_{\text{lit}}^{\#}$	d_{obsd}	$d_{\text{lit}}^{\#}$	d_{calcd}^{**}
	8.64s	13.77	13.34m	13.43
8.55	8.37vs	8.50	8.36vs	8.39
7.56	7.56m	7.30	7.14s	7.12
6.80	7.34w	6.01		
	5.17w	5.49	5.41s	5.43
5.08	5.03s	5.25	5.23s	5.23
	4.98m			
4.82	4.85m		4.86w	4.80
4.54	4.50s	4.61	4.60s	4.66, 4.56
4.32	4.36s			
	4.27s			
4.08	4.08m			
	4.05m			
3.91	3.90m	3.99	4.02w	4.01
	3.85m		3.95m	3.95
3.68	3.65w	3.83	3.80m	3.85, 3.75
3.56	3.55w	3.65	3.65s	3.57

3.27w		3.62m	3.56
3.16	3.15w	3.61m	3.56
		3.32w	3.32
		3.19w	3.22,3.16

* M.I. Hart and N.O. Smith, J. Am. Chem. Soc. 84, 1816(1962).

** D. Belitskus, et. al., Inorg. Chem.,2, 873(1963).



with a molecular volume of 88.8 cc/mole to p-ethyltoluene with a molecular volume of 139.8 cc/mole. In addition to these, in the case of the Ni^{2+} complex, 4-ethylpyridine was used as the basic nitrogen compound in combination with various size guest molecules. The most conclusive result from all of these studies is that there appears to be a very definite relationship between molecular size and the formation of a clathrate.

Tables IV through VII show the change in guest concentration with time for the complexes under study. The rates of formation are shown in Figures 3 through 5 as plots of absorbance against time.

Contrary to our previous results, an initial rise in absorption was observed for most of the kinetic runs. This rise was shown to be due to existence of free 4-methylpyridine in solution. If the solution is extracted with 6 N HCl and dried by passing it through anhydrous CaCl_2 , the initial increase in absorbance can be eliminated. The excess was probably carried along from the initial preparation but could have been due to some decomposition of the complex.

Table IV
 CHANGE OF GUEST CONCENTRATION WITH TIME
 DURING CLATHRATION REACTION
 BETWEEN $Mn(4\text{-mep})_4(SCN)_2$ and BENZENE, TOLUENE AND p-XYLENE

Time (hour)	Absorbance (A)		
	Benzene (at $\lambda=255m\mu$)	Toluene (at $\lambda=263m\mu$)	p-Xylene (at $\lambda=275m\mu$)
0	0.23	0.30	0.63
1/2	0.24	0.31	0.63
1	0.25	0.31	0.63
1 1/2	0.24	0.31	0.62
2	0.235	0.31	0.61
3	0.245	0.31	0.60
5	0.245	0.31	0.49
8	0.236	0.31	-
9	-	-	0.33
10	0.235	-	-
12	-	0.30	0.32
24	0.24	0.29	0.305
36	0.25	0.28	0.295
48	0.245	0.26	0.285

Table V
 CHANGE OF GUEST CONCENTRATION WITH TIME
 DURING CLATHRATION REACTION
 BETWEEN $\text{Fe}(\text{4mepy})_4(\text{SCN})_2$ and BENZENE AND p-XYLENE

Time(hour)	Absorbance(A)	
	Benzene(at $\lambda=255\text{m}\mu$)	p-Xylene(at $\lambda=275\text{m}\mu$)
0	0.300	0.615
1/2	0.298	0.600
1	0.280	-
1 1/2	0.270	0.480
2	-	0.410
2 1/4	0.248	-
3	-	0.325
3 1/2	0.228	-
5	0.214	0.245
9	0.212	0.213
12	0.208	-
12 1/4	-	0.208
24	0.195	-
25	-	0.200
35	0.195	-
36	-	0.210
48	0.187	0.200

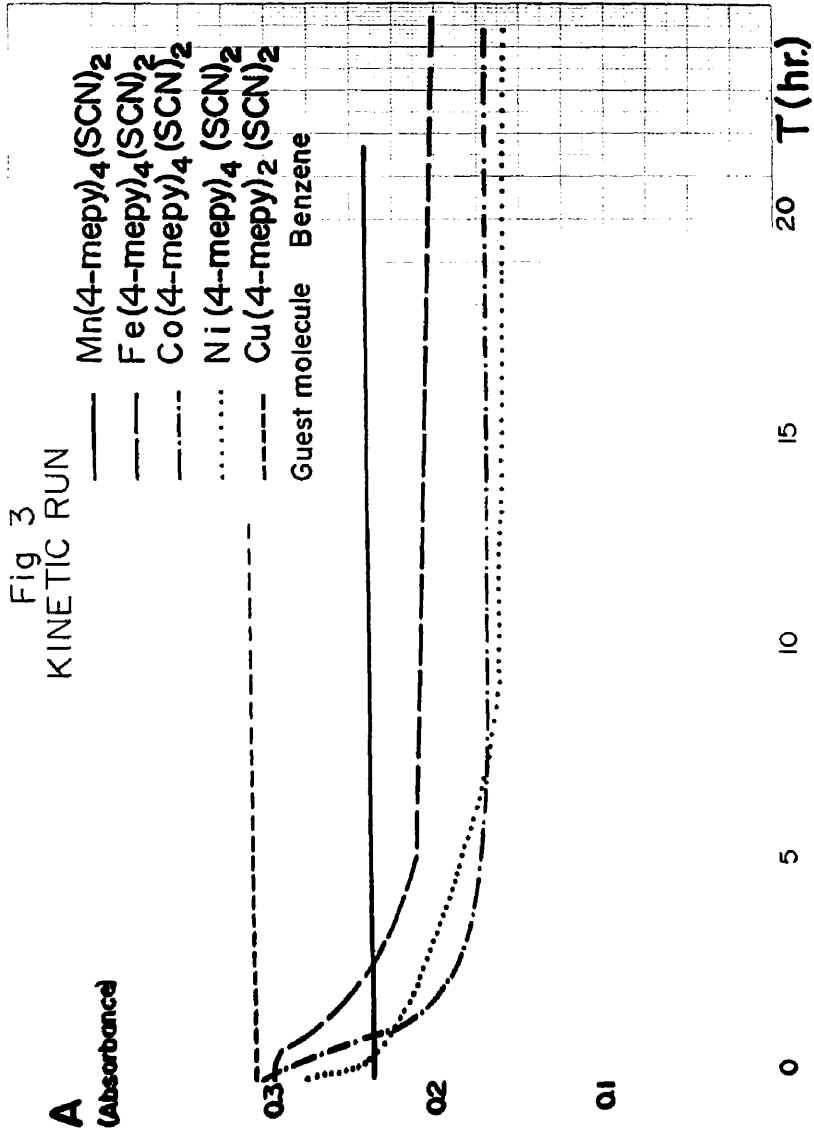
Table VI
 CHANGE OF GUEST CONCENTRATION WITH TIME
 DURING CLATHRATION REACTION
 BETWEEN $\text{Co}(4\text{-mepy})_4(\text{SCN})_2$ and BENZENE, p-XYLENE

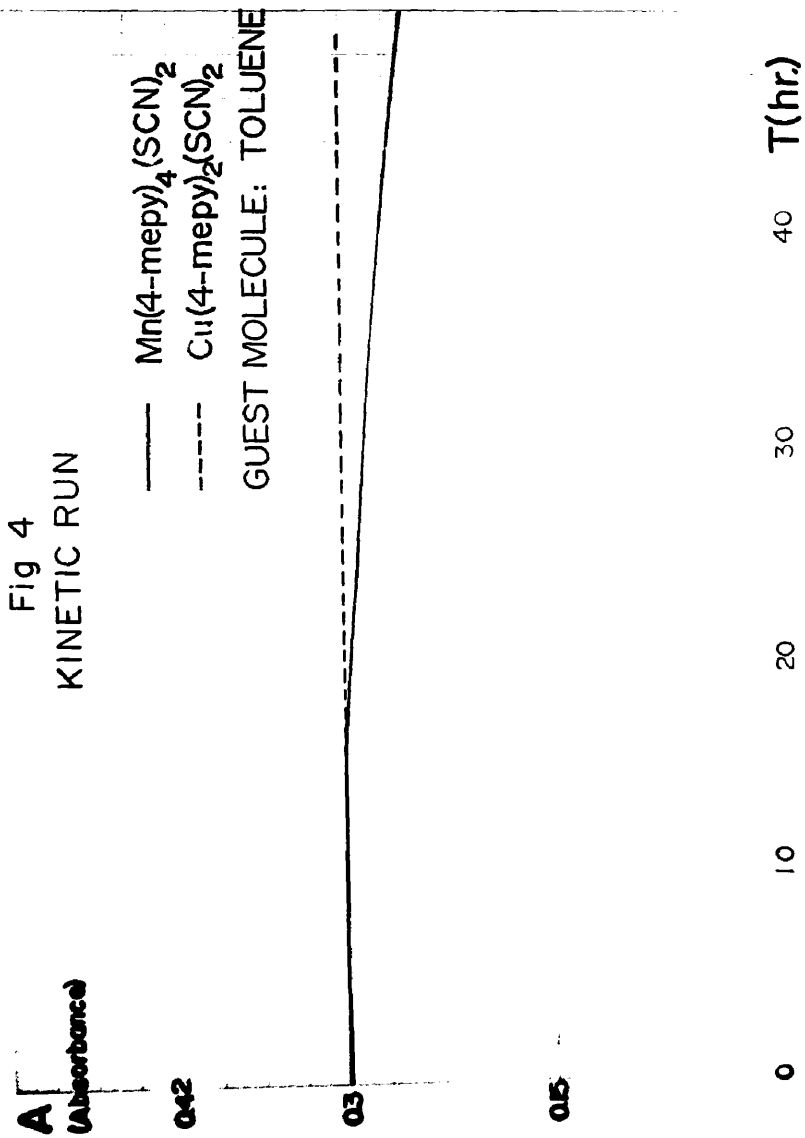
Time(hour)	Absorbance(A)	
	Benzene(at $\lambda=255\text{m}\mu$)	p-Xylene(at $\lambda=275\text{m}\mu$)
0	0.306	0.628
1/2	0.280	0.375
1	0.240	0.295
1 1/2	0.209	-
2	0.200	0.257
3	0.198	-
3 1/2	-	0.240
5	0.175	0.237
8	-	0.240
11	0.170	-
11 1/2	-	0.240
24	0.170	0.235
36	0.170	0.235
48	0.180	0.235

Table VII
 CHANGE OF GUEST CONCENTRATION WITH TIME
 DURING CLATHRATION REACTION
 BETWEEN $Ni(4-mepy)_4(SCN)_2$ and BENZENE, p-XYLENE

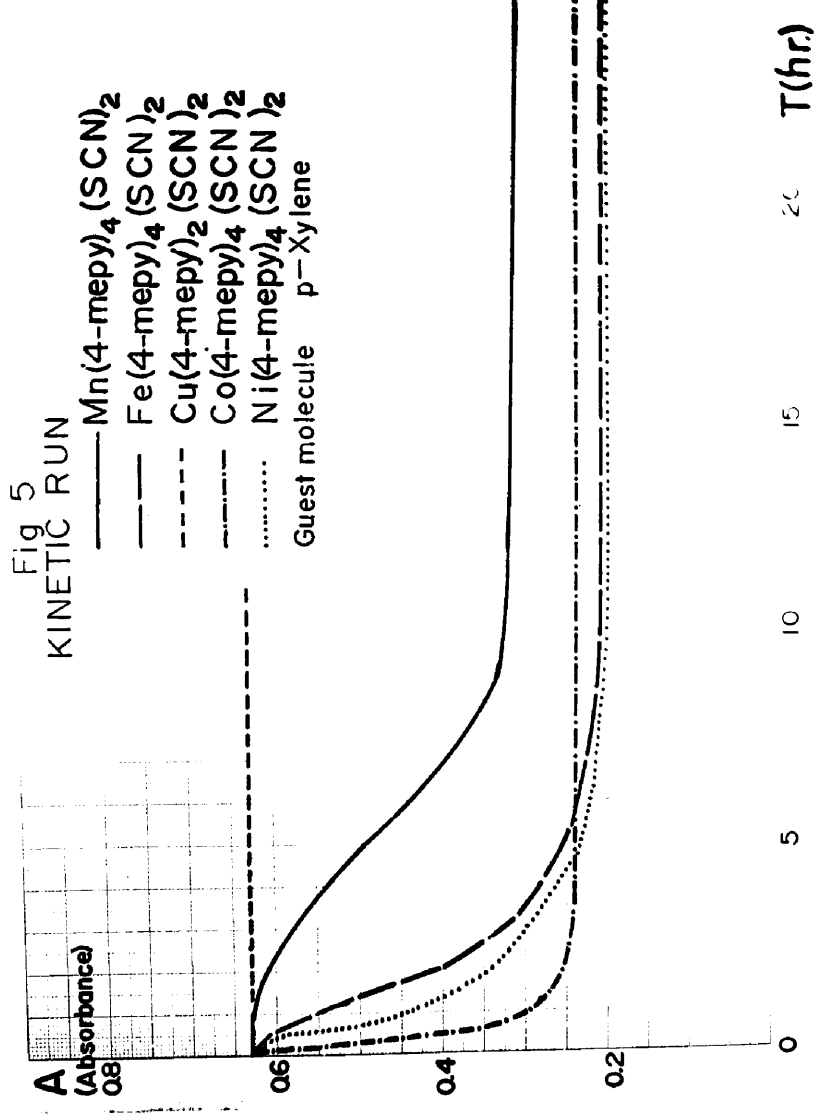
Time (hour)	Absorbance (A)	
	Benzene(at $\lambda=255m\mu$)	p-Xylene(at $\lambda=275m\mu$)
0	0.280	0.950
1/4	0.250	0.930
1/2	0.250	0.860
3/4	0.240	0.720
1	-	0.660
1 ¹ / ₄	0.230	-
1 ¹ / ₂	-	0.560
2	0.215	0.510
3	0.210	-
4	-	0.382
5	0.187	-
6	-	0.335
8	0.165	0.309
11	-	0.294
12 ¹ / ₄	0.164	-
13	-	0.290
24	0.157	-
36	0.155	-
48	0.155	0.265

Fig 3
KINETIC RUN





100
 90
 80
 70
 60
 50
 40
 30
 20
 10
 0



X-ray powder diffraction patterns again confirmed a change in lattice structure in going from complex to clathrate ($\alpha \rightarrow \beta$). The interplanar spacings are listed in Tables VIII through XII. Only in the cases of certain benzene clathrates were the patterns identical and this was probably due to a highly reversible reaction for this small guest molecule.

complex (α) \rightleftharpoons clathrate (β)

Gravimetric analysis supported this conclusion. The results of the gravimetric analyses are shown in Table XIII.

In addition to molecular volume, the effects of ionic radius of the metal ion and the ligand stability energy were investigated. A plot of the effect of ionic radius is shown in Figure 6. The graph shows that the larger the ionic radius the larger must be the guest molecule to form a clathrate. Mn^{2+} , with a configuration of $t_{2g}^3 e_g^2$, has the largest ionic radius due to a spherical (uniform) distribution of "d" electron density around the metal ion. Going from Mn^{2+} to Ni^{2+} the additional electron(s) is added to t_{2g} regions of space away from

Table VIII
INTERPLANAR SPACINGS (Å) FOR THE COMPLEX $\text{Na}(4\text{-mepy})_4(\text{SCN})_2$
AND ITS CLATHRATE WITH p-XYLENE

Complex	Toluene	p-xylene Clathrate
13.80s	13.80s	14.07s
10.21m	10.21m	10.01w
8.21s	8.21s	8.57vs
		7.28m
6.94s	6.94s	
5.52m	5.52m	
5.29m	5.29m	5.38s
4.94m	4.94m	4.94w
4.62s	4.62s	4.65s
4.20vs	4.20vs	4.27w
		4.03w
		3.66s
		3.37m
		3.18s

Table IX
INTERPLANAR SPACINGS (Å) FOR THE COMPLEX $\text{Fe}(\text{4-mepy})_4(\text{SCN})_2$
AND ITS CLATHRATE WITH P-XYLENE

Complex	Benzene Clathrate	p-Xylene Clathrate
13.94s	13.94s	13.92s
		10.07m
8.53vs	8.53vs	8.16vs
7.30s	7.30s	6.96s
6.01w	6.01w	5.66m
5.35s	5.35s	5.27w
4.95w	4.95w	4.91w
4.65s	4.65s	4.60m
4.01s	4.01s	4.20s
3.81w	3.81w	
3.64m	3.64m	
3.39m	3.39m	
3.14m	3.14m	

Table X
INTERPLANAR SPACINGS (Å) FOR THE COMPLEX $\text{Co}(\text{4mepy})_4(\text{SCN})_2$
AND ITS CLATHRATES WITH BENZENE AND p-XYLENE

Complex	Benzene Clathrate	p-Xylene clathrate
8.58vs	13.98n	13.98m
8.58vs	8.52vs	8.52vs
7.69w	7.29w	7.29w
6.88w		
	5.56m	5.56m
	5.33s	5.33s
5.09s	4.92w	4.92w
4.55s	4.64s	4.64s
4.37m		
4.10m	4.01s	4.01s
3.88w	3.80w	3.80w
3.61w	3.64m	3.64m
	3.34w	3.34w
3.14w	3.14m	3.14m
2.99w		

Table XI
INTERPLANAR SPACINGS (Å) FOR THE COMPLEX Ni(4-mepy)₄(SCN)₂
AND ITS CLATHRATES WITH BENZENE AND p-XYLENE

Complex	Benzene Clathrate	p-Xylene Clathrate
	13.61(s)	13.77m
8.55vs	8.45vs	8.50vs
7.56s	7.17m	7.30s
6.80w	6.00m	6.01w
	5.38m	5.49s
5.08s	5.16s	5.25s
4.82s	4.87w	4.61s
4.54s	4.61s	4.61s
4.32s		
4.08s		
3.91s	3.98s	3.99w
	3.79w	3.83m
3.68w	3.70s	3.65s
3.56m		
3.27w	3.30w	
3.16m	3.20m	

Table XII

INTERPLANAR SPACINGS (Å) FOR THE COMPLEX $\text{Cu}(4\text{-mepy})_2(\text{SCN})_2$

Complex

8.84s

7.68vs

6.68w

5.44w

4.87s

4.16s

3.86m

3.44m

3.20m

3.00m

2.90m

2.70w

2.54m

2.41m

2.32m

2.21w

Table XIII
GRAVIMETRIC ANALYSES FOR THE METAL ION IN COMPLEXES
OF THE TYPE $M(4\text{-mepy})_4(\text{SCN})_2$ AND SOME CLATHRATES

	Complex		Clathrates		
	Experimental	Theoretical	Benzene	Toluene	p-Xylene
%Mn ²⁺	8.92	9.90	10.11	9.71	8.90
%Fe ²⁺	10.55	10.26	10.41	-	9.31
%Co ²⁺	10.66	10.76	9.57	-	8.88
%Ni ²⁺	10.59	10.72	9.20	-	9.19
%Cu ²⁺	18.73	19.03*	18.58	19.03	18.50

* based on the complex $\text{Cu}(4\text{-mepy})_2(\text{SCN})_2$

The results show that the abundance of the ions is in the order:

$Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+} > Cu^{2+} > Zn^{2+}$

where

$Mn^{2+} > Fe^{2+}$

and the

order is

region

affected

Aluminum

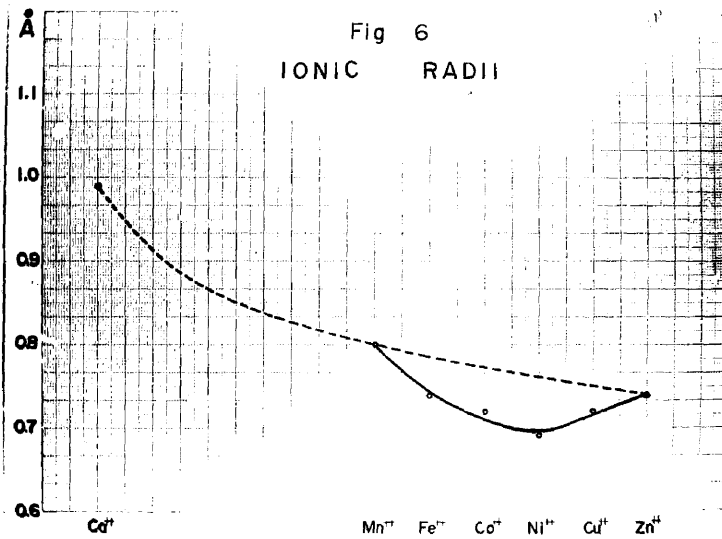
oxide

precipitates

precipitates

precipitates

precipitates



precipitates of various metal hydroxides, etc.

precipitates of various metal hydroxides, etc.

precipitates of various metal hydroxides, etc.

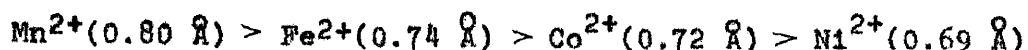
precipitates of various metal hydroxides, etc.

precipitates of various metal hydroxides, etc.

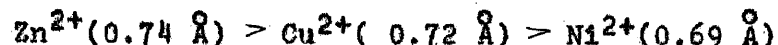
precipitates of various metal hydroxides, etc.

precipitates of various metal hydroxides, etc.

the metal-ligand bond axes, thus the effect of screening is abnormally low and the radii fall in the following order:



Going from Ni^{2+} to Zn^{2+} , electron(s) are added to e_g , regions of space on the metal-ligand axes, thus the effect of screening is quite high and the order is:



Although Cu^{2+} has about the same ionic radius as Co^{2+} , the copper ion will be expected to form a comparatively large cage due to the Jahn-Teller effect(21). Experimentally we were unable to form a clathrate using copper as the metal ion. This is apparently due to the Jahn-Teller effect in that Cu^{2+} will only form a tetra coordinated complex with 4-methylpyridine.(68)

According to Graddon's results(22) on Zn^{2+} compounds of the type ZnB_2X_2 predominate with B being a heterocyclic base and X a halogen. Our studies supported this since no clathrate formation was observed with Zn^{2+} complexes of this type. This result is also in agreement with the order of Irving-Williams (21).

Our studies and those of others who have been cited supported the postulate that the formation of a clathrate is dependent upon the molecular size of the guest component.

Additional experimental work was carried out using 4-ethyltoluene as a possible guest component. This compound has a computed molecular volume of 139.8 cc/mole and according to Schaeffer, et. al.(43) forms a clathrate with $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$. However, two independent, kinetic runs in this laboratory using the suspension method and times of 48 hours failed to confirm the results reported by Schaeffer. The lack of clathrate formation is based on ultraviolet spectra, X-ray diffraction patterns and gravimetric analyses. An attempt to form a clathrate using $\text{Mn}(4\text{-mepy})_4(\text{SCN})_2$ as the host structure was also unsuccessful even though the cavity in this complex should be larger than in the nickel complex. The next closest molecule in molecular volume to 4-ethyltoluene which is reported to form a clathrate with $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$ is 4-methylstyrene (molecular volume 131.3cc/mole). This highly conjugated system was reported on by Williams(67). In a recent paper by F. Casellato and B. Casu(71) evidence for the non-clathration of tertiary-butylbenzene(molecular volume

154.8 co/mole), by itself, is presented.

The conclusion which we draw from the above evidence is that molecules with a molecular volume equal to or greater than that of 4-ethyltoluene are too large to be accommodated in the β -lattice of $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$. This provides further support for the theory of clathration that emphasizes the relationship between the size of the cavity in the host structure and the molecular volume of the guest molecule.

A further test of the theory was provided by increasing the size of the basic nitrogen compound in the Werner complex. In this experiment, 4-ethylpyridine was used in place of 4-methylpyridine in order to provide a larger cavity in the β -lattice. No evidence of clathration was found using benzene, toluene, p-xylene, and 4-ethyltoluene as possible guest components. Results of these studies are shown in Table XIV and XV. Size relationships alone can be used to explain these results. However, there is also strong evidence in support of some type of pi-electron interaction in these clathrates and this is discussed in next section of this thesis.

Table XIV
INTERPLANAR SPACINGS (\AA) FOR THE COMPLEX $\text{Ni}(4\text{-ethylpy})_4(\text{SCN})_2$

Complex

9.68vs

7.30s

6.40w

5.87w

5.63m

5.06s

4.87m

5.57s

4.29m

4.13s

3.96w

3.71w

3.53w

3.29m

3.09m

3.04w

2.86w

Table IV
GRAVIMETRIC ANALYSIS FOR NI ION IN THE
COMPLEX OF $\text{Ni}(\text{4-ethylpy})_4(\text{SCN})_2$ BEFORE AND AFTER KINETIC RUN

Trial	COMPLEX	PERCENT NI			
		AFTER KINETIC RUN			
		WITH POSSIBLE GUEST MOLECULE			
		BENZENE	TOLUENE	p-XYLENE	4-ETHYL TOLUENE
1	9.44	-	9.44	9.51	9.46
2	9.35	9.47	9.53	9.61	9.50
3	9.44	9.47	9.48	9.61	9.54
Average	9.41	9.47	9.48	9.54	9.50
Theoretical	9.73				

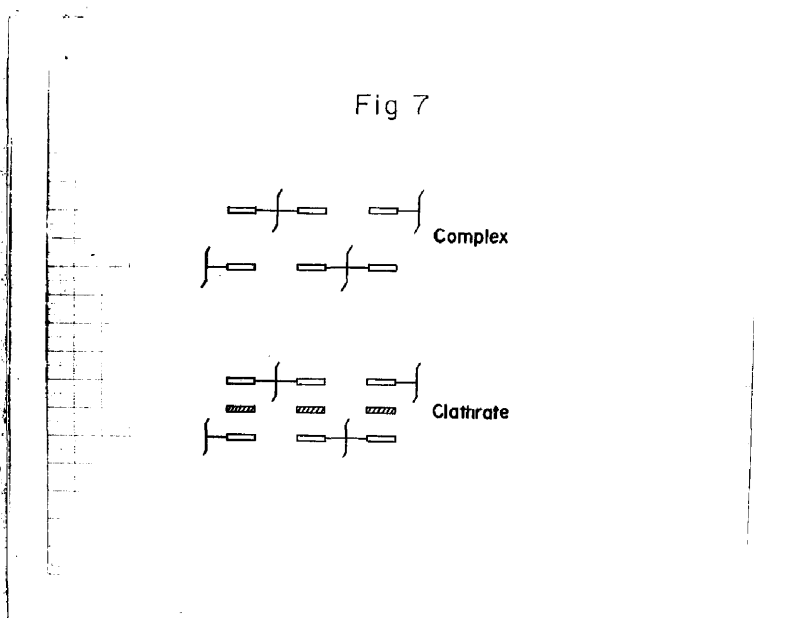
p1-ELECTRON INTERACTION

pi-ELECTRON INTERACTION

Clathrate formation with Werner complexes evidently is not only affected by the size of both the hole provided by β -form structure of the host molecule and the size of guest molecule, but is also believed to be affected by the pi-electrons in the nitrogen base and the pi-electrons of the guest molecule. The simplest way to picture this type of bonding is as a "sandwich" in which the pi-electrons from both the nitrogen base and the guest molecule are involved. The "sandwich" type interaction was first suggested by De Radzitsky and co-workers based upon preliminary X-ray diffraction studies on the clathrate-forming complex $Ni(NCS)_2(\alpha\text{-methyl-p-bromobenzyl-amine})_4$ (72). This model has now been applied to 4-methylpyridine type clathrates by Casellato and Casu in their recent paper(71). Based upon I.R. spectral shifts, weak charge transfer interaction between the components of the clathrate was postulated. A simple model was used in the paper as shown in Figure 9. The relative orientations of the basic nitrogen compound and guest molecule are not known but was proposed as shown in Figure 8 and Figure 9 according to a "sandwich" type interaction and definite size relationships obtained in this laboratory.

Figure 7

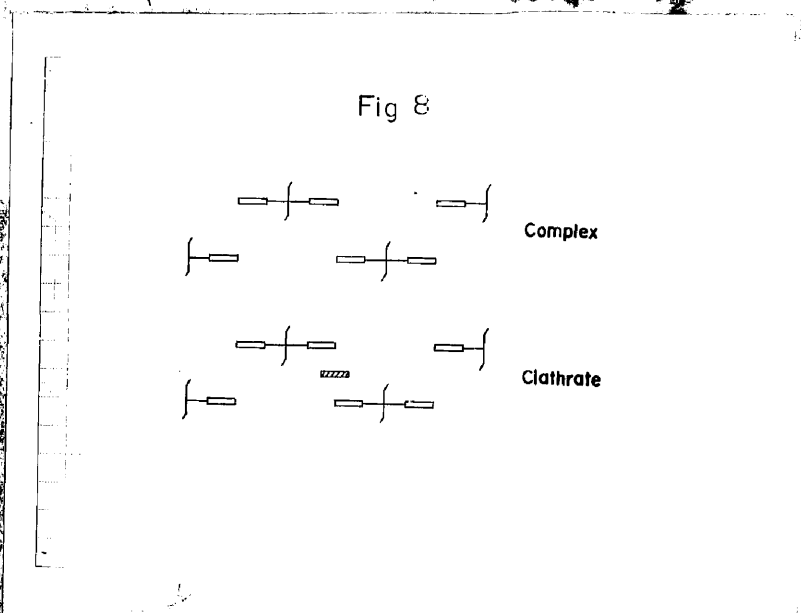
A planar projection of the probable arrangement of host units in the β -lattice of $\text{Ni}(\text{4-mepy})_4(\text{SCN})_2^*$



— represent 4-methylpyridine
▨ represent guest molecule

* Casaleato, F. and B. Casu, Spectrochimica Acta, Vol. 25, No. 8, 1407(1969)

Figure 8
 A Planar Projection of The Proposed
 Arrangement of The Host Units In
 The β -lattice of $Ni(4\text{-mepy})_4(SCN)_2$



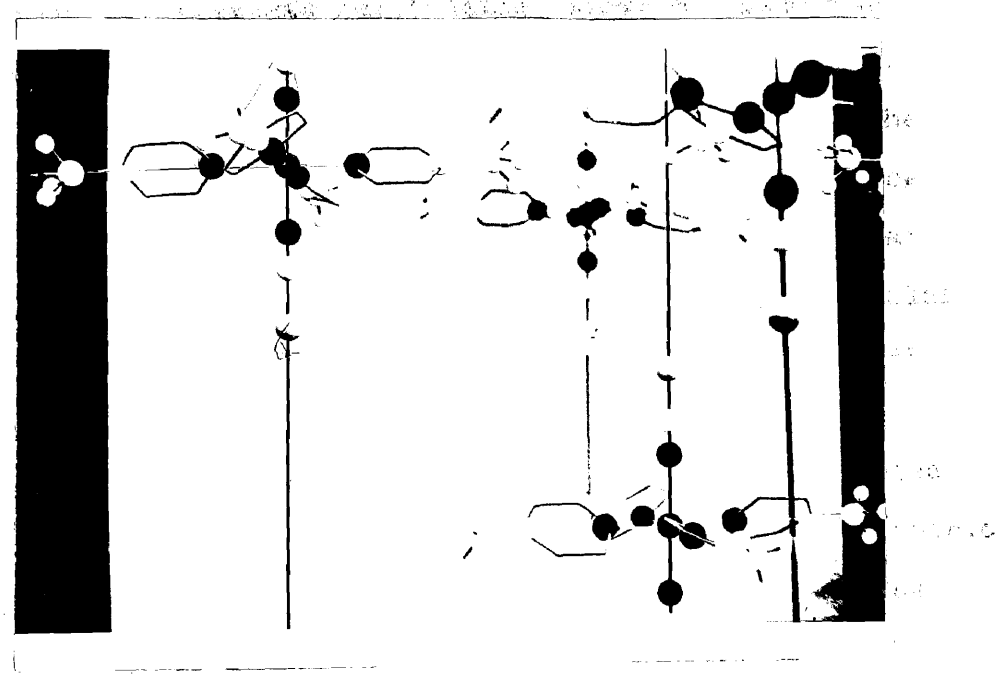
All the 4-mepy and guest molecules are tilted due to steric interaction between the 4-mepy rings of the same complex molecule. (represents guest molecule and represents 4-mepy ring.)

20 2770

Le

Figure 9

A model of proposed arrangement of
the host units in the β -lattice
of $\text{Ni}(\text{4-mepy})_4(\text{SCN})_2$ with p-xylene as guest molecule



As shown in the proposed model, the guest molecule is able to interact with the nitrogen bases on two different complexes. This interaction was shown as an I. R. shift of the C-H bond in the nitrogen base by Casellato and Casu(71). According to this proposed model, the lack of formation of a clathrate between $\text{Ni}(4\text{-ethylpy})_4(\text{SCN})_2$ and p-xylene at room temperature is easily explained in terms of increased cavity size, since pi-electrons interaction is no longer probable.

The evidence for involving pi-electron of the guest molecule in forming a clathrate is shown by using a guest molecule such as cyclopentane, with a molecular volume of 93.6 cc/mole, and cyclohexane, with a molecular volume of 110.5 cc/mole. Both fall into the right guest molecule size range for $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$, but no clathrates were found, presumably due to the lack of pi-electrons in the guest molecule. The results of the gravimetric analysis for nickel in the complex $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$ before and after kinetic runs with cyclopentane and cyclohexane are shown in Table XVI.

Table XVI
GRAVIMETRIC ANALYSIS FOR THE Ni ION
IN THE COMPLEX OF Ni(4-mepy)₄(SCN)₂ BEFORE
AND AFTER KINETIC RUNS WITH CYCLOPENTANE AND CYCLOHEXANE
AS POSSIBLE GUEST MOLECULE

		PERCENT Ni		
COMPLEX		AFTER KINETIC RUN		
		WITH POSSIBLE GUEST MOLECULE		
		CYCLOPENTANE	CYCLOHEXANE	
Trial	1	10.63	10.36	10.52
	2	10.66	10.35	10.61
	3	10.47	-	10.53
Average		10.59	10.36	10.55
Theoretical		10.72		

GENERAL SUMMARY

GENERAL SUMMARY

A summary of the experimental data is presented in Table XVII. A study of the table reveals a number of very interesting points. First, all clathrates formed using aromatic hydrocarbons as "guest" and complexes of the type, $M(\text{ENC})_4(\text{X})_2$, as "host", have definite size limitations on the molecular volume of the guest which may be accommodated. For example, the molecular volume of a guest molecule must be in the range 106 cc/mole to 132 cc/mole if it is to form a clathrate with the host, $\text{Mn}(4\text{-mepy})_4(\text{SCN})_2$. The same limitation is true for the complexes of Fe^{2+} , Co^{2+} , and Ni^{2+} . It is apparent, therefore, that the size of the guest molecule is a critical factor in the formation of clathrates. The second point which is apparent from Table XVII is that the size of the guest molecule which is accommodated increases in proportion to the increase in ionic radius of the central metal ion, from Ni^{2+} (0.69 Å) to Mn^{2+} (0.80 Å). Thus, a clathrate was formed between benzene (88.8 cc/mole) and the complex $\text{Ni}(4\text{mepy})_4(\text{SCN})_2$. Whereas no clathrate was observed with $\text{Mn}(4\text{-mepy})_4(\text{SCN})_2$. This leads to the conclusion that the size of the "hole" in the host complex is also a main factor in clathrate formation. A third point observed is

that although cyclopentane and cyclohexane both have a molecular volume in the right range, neither formed a clathrate with the host $\text{Ni}(4\text{-mepy})_4(\text{SCN})_2$. This latter finding would suggest that pi-electrons in the guest molecule are also an important factor in clathrate formation. Recent finding in other laboratories(71) seem to confirm the concept of a "sandwich-type" interaction in these Werner-type complex clathrates.

The results of the X-ray powder diffraction measurements confirm the lattice change ($\alpha \rightarrow \beta$) in going from complex to clathrate. Closer examination of the interplanar spacings in the complex and clathrate suggest a lattice expansion in the $\alpha \rightarrow \beta$ transformation.

Table IVII GENERALIZED TABLE

HOST MOLECULE	GUEST MOLECULE		cyclo-pentane	cyclo-hexane	benzene	toluene	p-xy-lene	4-methyl styrene	4-ethyl toluene
	Molec. Vol. cc/mole	ionic radius (Å)*							
	93.6		110.5	88.8	106.3	123.3	131.3	139.6	
M1(4mepy) ₄ (SCN) ₂	0.69	(-)	(-)	(+)	(+)	(+)	(+)	+(67)	(-)(43)
Co(4mepy) ₄ (SCN) ₂	0.72	-	-	(+)	(+)	(+)	(+)	+(67)	-
Fe(4mepy) ₄ (SCN) ₂	0.74	-	-	(+)	(+)	(+)	(+)	+(67)	-
Mn(4mepy) ₄ (SCN) ₂	0.80	-	-	(-)	(+)	(+)	(+)	+	(-)
Cu(4mepy) ₂ (SCN) ₂	0.72	-	-	(-)	(-)	(-)	(-)	-	-
Zn(4mepy) ₂ (SCN) ₂	0.74	-	-	(-)	(-)	(-)	(-)	-	-
M1(4etpy) ₄ (SCN) ₂	0.69	-	-	(-)	(-)	(-)	(-)(43)	-	(-)

+ evidence supports clathrate formation
 - evidence supports no clathrate formed
 ○ supported by kinetic rate study
 () reference number; work performed in other laboratories
 * central metal ion

note: p-diethylbenzene, molecular volume 155.5cc/mole, has been found to form a clathrate with M1(4-mepy)₄(SCN)₂.(43)

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