TABLE IX

*p*H RESULTS OF SOME METAL COMPLEXES, 25°

Complex	log k_1 u = 0.16–0.19	log k_1, as reported in lit.	log k_1 (ion-exchange results, this investigation) u = 0.16
Mn^{++}-malonate	2.24	3.29 (u = 0.04)[25]	2.30
UO_2^{++}-glycolate	2.75	2.42 (u = 1,20°)	2.78
log k_2:	1.52	1.53 (u = 1.20°)	1.30
Co^{++}-acetate	1.10		0.91
glycolate	1.62		1.64
malonate	2.85	3.72 (u = 0.04)[25]	2.85

ever are again about 1 log unit smaller than that reported by Stock and Davies,[25] log k_1 = 2.49 (u = 0.04). Part of the difference between the ion-exchange and *p*H values on the one hand, and the colorimetric value on the other hand, is probably due to the difference in ionic strength.

All the values of log k_1, determined by the *p*H method in this investigation, are in good agreement with those determined by the ion-exchange method. For these complexes therefore, two conclusions may be made: (1) the complex itself is not taken up by the resin to any noticeable extent, and (2) the nature and stability of complexes of radioactive metal cations are identical with complexes of non-radioactive metal cations.

Ahrland,[26] *et al.*, have shown that the complex formation curve is dependent on concentration of metal ion, if polynuclear complexes exist; while if the complex formation curve is independent of metal ion concentration, the complex is mononuclear. The difference in the metal ion concentration used in ion-exchange and *p*H methods is clearly very great, and the agreement in the formation constant values obtained by the two methods must mean therefore that the Mn(II), uranyl and Co(II) complexes listed in Table IX are mononuclear.

Acknowledgment.—The authors are indebted to Dr. K. E. Wilzbach of Argonne National Laboratory for the preparation and analysis of tritium-labeled acetate.

[26] S. Ahrland, R. Larsson and K. Rosengren, *Acta Chem. Scand.*, **10**, 705 (1956).

LEMONT, ILL.
PITTSBURGH 19, PA.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION OIL COMPANY OF CALIFORNIA]

Separation of Xylenes, Cymenes, Methylnaphthalenes and Other Isomers by Clathration with Inorganic Complexes

BY WILLIAM D. SCHAEFFER, W. S. DORSEY, DAVIS A. SKINNER AND C. G. CHRISTIAN

RECEIVED JUNE 18, 1957

Xylenes, cymenes, methylnaphthalenes and other isomers have been separated from mixtures by clathration with appropriate inorganic complex compounds. *p*-Xylene concentrates have been recovered from either C_8 aromatic hydrocarbons or from gasolines by single step operations. Each of the C_8 aromatic hydrocarbons has been preferentially clathrated by selection of the proper complex. High selectivity and recovery have been achieved by proper selection of complex and manipulative conditions for the separation at hand. Many new complexes of inorganic salts and basic nitrogen compounds have been prepared.

The use of urea, thiourea, 4,4′-dinitrodiphenyl, hydroquinone and various other materials for selective inclusion in a solid phase of various types of compounds is now widely recognized and documented.[1,2] This phenomenon which has more recently been dubbed "clathration" by Powell[3] has developed into a powerful tool for the separation and purification of organic compounds.

Prior to this report the only reported inorganic complex compound known[4] to form clathrates with organic compounds was the mono-ammino complex of nickel cyanide, $Ni(NH_3)(CN)_2$. This compound forms crystals in the presence of certain organic molecules, which contain both the components of the complex and the organic molecule. Organic molecules clathrated by this inorganic compound include thiophene, benzene, phenol, aniline and furan, all of which occupy about the same molecular volume. The molecular volume appears to be the basis for the selective clathration.[3,4]

It has now been discovered[5] that other inorganic complex compounds will form clathrate compounds with organic compounds. This new class of clathrate formers exhibits a sharp selectivity for forming crystals containing certain organic molecules, the selectivity being based, apparently, on the shape rather than on the molecular volume occupied by the organic moiety. By means of these complexes good separation of isomers such as the xylenes, cymenes, methylnaphthalenes and others has been realized.[5] The complexes employed here are also of the Werner type but differ from the $Ni(NH_3)(CN)_2$ complex in that a plurality of neutral molecules (usually four) plus anions, are coordinated with the metal ion.

The three constituents of these complexes (the metal atom, a basic nitrogen compound and the

---

(1) F. D. Cramer, *Rev. Pure Appl. Chem.*, **5**, 143 (1955); G. Montel, *Bull. soc. chim. France*, 1013 (1955); F. D. Cramer, "Einschlussverbindungen," Springer-Verlag, Berlin, 1954; H. M. Powell, *J. Chem. Soc.*, 2658 (19-4).

(2) M. Martinette, *J. Chem. Ed.*, **30**, 628 (1953); N. J. Ambs, *Mendel Bull.*, **17**, 26 (1953); C. V. Truter, *Research*, **6**, 320 (1953); W. Schlenk, Jr., *Fortschr. chem. Forsch.*, **2**, 92 (1951).

(3) H. M. Powell, *Nature*, **163**, 566 (1949).

(4) K. A. Hofmann, *Z. anorg. Chem.*, **15**, 204 (1897).

(5) W. D. Schaeffer, Belgian patent 553,481, June 17, 1957, U. S. patent 2,798,891 (July 9, 1957); C. G. Christian, U. S. patent 2,774,802 (December 18, 1956); W. D. Schaeffer, *et al.*, U. S. patent 2,798,103 (July 2, 1957); U. S. patent 2,798,102 (July 2, 1957); and others pending.

anion) all contribute to the ability of the complex to form clathrates as well as determine the type or types of organic molecules that will be clathrated. As will be seen from the examples, many of the transition elements are suitable metals. In particular, nickel, cobalt, manganese, iron, copper and zinc have been tested. A variety of basic nitrogen compounds such as the substituted pyridines and quinolines are suitable. The anion may be a simple mono-atomic ion such as chloride or bromide, or it may be a poly-atomic ion such as thiocyanate, formate, cyanate, cyanide or nitrite.

The complexes reported herein are for the most part characterized by very rapid formation—reaction times well under one minute when the appropriate reagents are mixed—and by nearly quantitative yield of synthesis. Many previously unreported complexes were prepared in the course of this study and are detailed in the experimental reaction. The amount of analytical data obtained varied and the formulas for some of the complexes were inferred from stoichiometry and similarity of properties. The analyses were sometimes less precise than those encountered in many types of work, but were considered adequate where the primary objective was the separation to be realized rather than purity of the complex. Part of the variation is believed to result from coexistence of equilibria[6] such as

$$M^{++} + 2Py \rightleftharpoons M(Py)_2^{++} \qquad (1)$$

$$M(Py)_2^{++} + 2Py \rightleftharpoons M(Py)_4^{++} \qquad (2)$$

coupled with the problem of washing excess base from the complex.

The importance of these equilibria is further demonstrated in clathration experiments. Most of the complex compounds that proved to have clathration properties had four molecules of the nitrogen base coördinated with the metal atom. For this reason it was found desirable in clathration experiments to include a small excess of the nitrogen base to help maintain the complex as the tetra-coördinated species.

Three primary methods were employed for preparation of the clathrate from the complex and the feed mixture: (1) stirring of the complex as a suspension in the liquid feed mixture, (2) contacting of the feed mixture with a solution of the clathrate former in a solvent at an elevated temperature, then cooling and filtering, and (3) contacting a suspension of the complex in an organic fluid (which did not dissolve the complex and which did not enter into the clathrating reaction) with the feed mixture. The particular technique employed is indicated in the tables of results, designating (1) and (3) as "suspension" technique, and (2) as "solution" technique. The best technique for a particular separation depends on the materials to be separated, the complex which is used and the circumstances of manipulation.

Three primary methods were employed for recovery of the desired constituent from the clathrate.

The first of these was a simple solution of the clathrate in aqueous acid. When the clathrated compound was not appreciably soluble in aqueous acid solution, it separated as a separate phase and was readily recovered. This technique was used for much of the screening work.

A second method was by steam stripping the clathrate. This method was tested on the removal of xylenes from the clathrate formed with tetra-(4-methylpyridino)-nickel dithiocyanate. Table I demonstrates that hydrocarbon recovery was not complete by this method and that relatively large amounts of steam were required per unit of xylene recovered.

TABLE I

STEAM STRIPPING OF XYLENE FROM CLATHRATE WITH $Ni(4\text{-METHYLPYRIDINE})_4(SCN)_2$

		Compn. of xylenes in clathrate compd., vol. %					
Run no.	Sample[a]	*p*-Xylene	*m*-Xylene	*o*-Xylene	Ethylbenzene	G. of steam per g. of complex	Removal[b]
1	Before	44.4	17.8	..	37.8	...	..
	After	70.4	6.6	..	23.0	0.393	60.0
2	Before	65.0	20.5	..	14.1	...	..
	After	86.0	0.5	..	13.5	0.875	67.5
3	Before	64.6	13.7	0.4	21.6	...	..
	After	83.5	1.8	..	12.8	...	..

[a] Before or after steam stripping. [b] Volume % of initial xylene content of clathrate which was removed by stripping.

Simple application of a vacuum did not remove xylene from the clathrate until a pressure–temperature combination was reached at which the complex as well as the clathrate dissociated.

The third method employed the high solubility–temperature coefficient of some of these complexes in various solvents. The clathrate was suspended in the solvent and the mixture heated until solution resulted. Because these complexes show no attraction for organic molecules when in molecular solution the formerly clathrated species could be removed by distillation or by means of liquid–liquid extraction.

Table II shows the separation of *p*-xylene by various complexes. Concentration of *p*-xylene from 19.4 volume % in the feed to 50.0% in the product may be noted. Table III shows the results obtained for the resolution of xylene isomer mixtures (more broadly, C_8 aromatic isomer mixtures). A number of items may be noted which demonstrate the great effect of the exact composition of the complex on the results achieved, or conversely, the manner in which the complex may be tailored to achieve the best results for the separation at hand. For example, at least one complex is known with a selectivity for each of the four C_8 aromatic isomers. Concentration increases from feed to product of 19.9 to 75.9 volume % for *p*-xylene, 45.5 to 56.9 volume % for *m*-xylene, 19.3 to 53.1 volume % for *o*-xylene and 15.3 to 54.6 volume % for ethylbenzene may be noted. With regard to the metal ions it will be seen that the nickel and cobalt complexes produce superior results for *p*-xylene recovery as compared to the iron and manganese com-

---

(6) A. V. Logan and D. W. Carle, THIS JOURNAL, **74**, 5224 (1952); A. V. Logan, D. Bush and C. Rogers, *ibid.*, **74**, 4194 (1952); T. L. Davis and A. V. Logan, *ibid.*, **62**, 1276 (1940); **58**, 2153 (1936); T. L. Davis and C. W. Om, *ibid.*, **56**, 1061 (1934); T. L. Davis and H. R. Batchelder, *ibid.*, **52**, 4069 (1930); T. L. Davis and A. V. Logan, *ibid.*, **50**, 2493 (1928).

TABLE II

SEPARATION OF *p*-XYLENE

Complex[a]	Type of contacting[b,c]	Wt. ratios Complex/ xylene	Wt. ratios Solvent or thinner/ complex	Solvent or thinner	Vol. % *p*-Xylene in Feed	Vol. % *p*-Xylene in Hydrocarbons from crystals	Vol. % *p*-Xylene in Filtrate
$Ni(4\text{-}mepy)_4(SCN)_2$	Soln.	2.0	2.50	20% 4-Methylpyridine. 80% methyl cellosolve	19.4	50.0	4.9
$Ni(4\text{-}etpy)_4(SCN)_2$	Susp.	0.58	1.72	Excess xylene	22.3	43.9	19.7
$Ni(4\text{-}vipy)_4(SCN)_2$	Soln.	1.0	3.0	Chloroform	21.2	31.7	..
$Co(4\text{-}mepy)_4(SCN)_2$	Soln.	1.75	3.3	50% Butyl cellosolve. 50% methyl cellosolve	22.6	64.2	6.6
$Mn(4\text{-}etpy)_4(SCN)_2$	Susp.	0.28	3.5	Excess xylene	22.0	36.0	21.5
$Mn(4\text{-}etpy)_4(SCN)_2$	Soln.	2.0	2.5	20% 4-Ethylpyridine, 80% butyl cellosolve	19.4	38.8	8.0
$Fe(4\text{-}etpy)_4(SCN)_2$	Susp.	0.29	3.4	Excess xylene	23.0	46.5	20.5
$Fe(4\text{-}mepy)_4(SCN)_2$	Susp.	0.46	2.18	Excess xylene	20.2	31.7	17.5

[a] Abbreviations same as Table I. [b] Soln. = solution. [c] Susp. = suspension.

TABLE III

SEPARATION[a] OF C_8 AROMATIC ISOMERS BY SOLUTION[b,c] TECHNIQUE

Complex[d]	C_8 aromatic clathrated	Wt. ratio of complex/ aromatics	Wt. ratio of complex/ excess base[c]	Recovery, %	Clathrate C_8 aromatic compn. *para*	*meta*	*ortho*	Ethylbenzene	Reject C_8 aromatic compn. *para*	*meta*	*ortho*	Ethylbenzene
$Ni(3\text{-}NH_2py)_4(SCN)_2$	*p*-Xylene	0.75	1.5[e]	35.0	75.9	8.6	6.6	8.9	12.3	49.7	22.7	15.3
$Ni(4\text{-}etpy)_4(formate)_2$	*o*-Xylene	0.93	8.4	0.16	8.0	20.1	53.1	18.8	19.9	45.8	20.5	13.8
$Mn(4\text{-}etpy)_4Cl_2$	*o*-Xylene	0.75	3.0	0.032	14.9	39.4	37.9	7.8	19.4	46.5	19.2	14.9
$Mn(4\text{-}etpy)_4(CN)_2$	*o*-Xylene	1.75	16.	8.4	19.1	41.8	36.3	2.8	18.4	43.3	19.5	18.8
$Mn(4\text{-}etpy)_4(CNO)_2$	*o*-Xylene	1.75	16.	0.52	19.3	43.8	25.8	11.2	19.6	45.7	19.8	14.9
$Ni(3\text{-}et\text{-}4\text{-}mepy)_4(SCN)_2$	*m*-Xylene	0.46	0[f]	0.75	15.4	56.9	6.7	21.0	19.4	46.2	19.8	14.6
$Ni(4\text{-}acpy)_4(SCN)_2$	Ethylbenzene	0.47	20	22	11.5	23.5	10.4	54.6	..	..	..	..

[a] Feed: 19.9 vol. % *p*-, 45.5% *m*-, 19.3% *o*-xylene, and 15.3% ethylbenzene. [b] Solvent: methyl cellosolve with excess base. [c] Base was same as the base in the complex unless otherwise noted. [d] Abbreviations same as Table I. [e] Excess base was 4-methylpyridine. [f] No excess base was employed.

pounds. This sensitivity is to us quite remarkable when considered in the light of the principal apparent variable, the effective radii of the metal ions. Octahedral radii of manganese, iron, cobalt, nickel, copper and zinc range only from 1.23 through 1.39 A.,[7] a total range of only 0.16 Å.

Experiments were also made to assess the effect of molecule size of the compound taken up on the performance of the clathrate former tetra-(4-methylpyridino)-nickel dithiocyanate. Table IV shows that the selectivity is dependent not only on the complex but also on the material to be complexed. Thus *p*-xylene is clathrated in preference to toluene or benzene, benzene or toluene is clathrated in preference to *o*-xylene, and benzene is clathrated in preference to toluene. These data indicate that the clathrate former, the organic moiety clathrated and the clathrate compound are in dynamic equilibrium. The position of equilibrium is favored for the *p*-xylene clathrate with respect to the other compounds tested.

The great affinity of this complex compound for *p*-xylene was further demonstrated by contacting the complex with an aromatic-rich gasoline (reformate heart-cut). It was also used to process a straight-run gasoline heart-cut. The results and the properties of the feeds are shown in Table V. *p*-Xylene concentrations as high as 70.6 volume % of C_8 aromatic isomers in the product may be noted at a *p*-xylene recovery of 60.3 volume % of feed. It can be seen that the complex demonstrates a sharp selectivity for *p*-xylene even out of this welter of compounds.

TABLE IV

SEPARATION[a] OF AROMATIC HYDROCARBONS, C_6 THROUGH C_8 WITH $Ni(4\text{-}METHYLPYRIDINE)_4(SCN)_2$

Hydrocarbon feed mixture	Sample	Analyses of sample, vol. % *p*-Xylene	*o*-Xylene	Toluene	Benzene	Wt. ratio[b] clathrate former to *p*-xylene
p-Xylene–toluene	Feed	48.7		51.3		5.8
	Crystals	64.5		35.5		
	Filtrate	35.8		64.2		
p-Xylene–benzene	Feed	47.9			52.1	
	Crystals	75.6			24.4	5.8
	Filtrate	33.4			66.6	
o-Xylene–benzene	Feed		55.1		44.9	
	Crystals		15.2		84.8	4.1[c]
	Filtrate		70.8		29.2	
o-Xylene–toluene	Feed		55.0	45.0		
	Crystals		21.1	78.9		4.1[c]
	Filtrate		64.9	35.1		
Benzene–toluene	Feed			49.4	50.6	
	Crystals			38.9	61.1	3.4[d]
	Filtrate			60.4	39.6	

[a] Solution technique; solvent 90 vol. % methyl cellosolve, 10 vol. % 4-methylpyridine. Weight ratio solvent/clathrate former = 2.0. [b] For initial solution. [c] Clathrate former to *o*-xylene. [d] Clathrate former to toluene.

The complex, tetra-(4-methylpyridino)-nickel dithiocyanate, was tested with mixtures of ethyltoluene, cymene and diethylbenzene isomers. The results are given in Table VI together with experiments with the xylene isomers (compare Table III). It will be observed that the concentration increase achieved and the amount of recovery experienced is lower for each of these isomers than for the mixed xylene isomers. However, product concentrations

---

[7] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. 1, Oxford University Press, 1950, pp. XXIX.

Table V

Recovery of *p*-Xylene from Gasolines

Type of contacting	Gasoline	Wt. ratio of clathrate former/ *p*-Xylene	Sample	Aromatics content of gasoline, vol. %	Xylenes analyses,[b] vol. %				
					p-Xylene	*m*-Xylene	*o*-Xylene	Ethylbenzene	Recovery[c]
Solution[a]	Reformed[d]	6.2	Feed	51.7	18.8	44.0	21.8	15.4	..
			Unwashed crystals		60.7	15.7	7.7	15.9	67.0
			Washed crystals		70.6	10.9	4.4	14.1	60.3
			Filtrate		8.0	48.8	25.5	17.7	31.2
Solution[a]	Reformed[d]	12.3	Feed	51.7	18.8	44.0	21.8	15.4	..
			Unwashed crystals		53.0	17.6	8.2	21.2	83.0
			Washed crystals		65.7	9.7	4.3	20.3	72.0
			Filtrate		3.9	54.9	27.6	13.6	12.1
Suspension[f]	Straight run[e]	10.0	Feed	14.3	13.8	44.1	21.1	16.0	..
			Unwashed crystals		55.3	15.3	4.6	24.8	69.0
			Filtrate		4.0	57.4	24.5	14.1	..

[a] Ni(4-methylpyridine)$_4$(SCN)$_2$ in 20 vol. % 4-methylpyridine, 80% methyl cellosolve. Weight ratio solvent/complex = 2.0. [b] Of C_8 aromatic hydrocarbons, normalized to 100%. [c] Volume % of *p*-xylene charged as feed recovered in that sample. [d] Heart cut with overhead temperatures 130 to 145° inclusive, taken with 20 plates and 10 to 1 reflux ratio from a catalytically reformed gasoline prepared from a Western light straight-run gasoline stock. [e] Heart cut with overhead temperatures 125 to 151° inclusive, taken with 20 plates and 10 to 1 reflux ratio from a Western straight-run gasoline. [f] Thinner was 1 volume of isoöctane per 2.2 volumes of gasoline.

Table VI

Separation[a] of Aromatic Hydrocarbon Mixtures, C_8 through C_{10} with Ni(4-Methylpyridine)$_4$(SCN)$_2$

Hydrocarbon feed mixture	Sample	Analyses of sample, vol. %					Wt. ratio,[b] clathrate former to *p*-isomer
		p-Isomer	*m*-Isomer	*o*-Isomer	Ethylbenzene	Recovery	
Ethyltoluenes	Feed	33.4	47.3	19.0	..	..	
	Crystals	58.4	25.1	16.5	..	25.8	6.4
	Filtrate	28.2	51.6	20.2	..	74.2	
Cymenes	Feed	50.0	14.7	35.3	..	..	
	Crystals	69.0	9.0	22.0	..	24.5	1.9
	Filtrate	35.6	13.8	50.6	..	75.5	
Diethylbenzenes	Feed	15.7	71.4	12.9	..	..	
	Crystals	29.3	67.4	3.3	..	17.5	9.3
	Filtrate	13.0	75.5	11.5	..	82.5	
Xylenes	Feed	78.7	9.2	1.8	10.3	..	
	Washed crystals	97.7	0.7	0.7	2.3	70.5	5.8
	Filtrate	46.7	25.9	2.2	25.2	29.5	
Xylenes	Feed	26.9	50.7	22.2	..	..	
	Unwashed crystals	68.0	22.8	8.4	..	83.2	8.1
	Filtrate	8.8	62.1	29.0	..	16.7	
	Washed crystals	84.2	12.3	3.5	..	79.7	
	Wash filtrate	24.7	51.9	23.4	..	3.8	

[a] Solution technique; solvent 90 vol. % methyl cellosolve, 10 vol. % 4-methylpyridine. Weight ratio solvent/clathrate former = 2.0. [b] For initial solution.

of *para* isomer of 58.4, 69.0, 29.3, 97.7 and 84.2 volume % were achieved for ethyltoluenes, cymenes, diethylbenzenes, xylenes and xylenes, respectively. The product *para* isomer concentrations are 313, 186 and 175% greater than the feed concentrations for the last xylene mixture, the diethylbenzenes and the ethyltoluenes, respectively. In each case a definite selectivity is indicated for the *para* isomer.

In order to assess the importance of functional groups on clathrate performance a series of experiments were carried out with the chlorotoluenes, nitrotoluenes, methoxytoluenes, aminotoluenes and dichlorobenzenes employing tetra-(4-methylpyridino)-nickel dithiocyanate as the clathrate former. The results given in Table VII show that the *para* isomer of each of these mixtures is selectively clathrated. Product *para* isomer concentrations of 91.4, 93.0, 68.4, 73.5 and 94.4 weight % were obtained, respectively, for chlorotoluenes, dichlorobenzenes, toluidines and methylanisoles. For the chlorotoluenes and methylanisoles, the product *para* isomer concentration was over 180% of the feed concentration.

The possibility of clathration of polycyclic isomers was tested on four mixtures: naphthalene–diphenyl, 1- and 2-methylnaphthalene, diphenyl oxide–phenanthrene and anthracene–phenanthrene. The results given in Table VIII demonstrate that naphthalene, 1-methylnaphthalene, diphenyl oxide and anthracene are taken up from the respective mixtures. Product concentrations of one compound ran from 74.4 to 85.6 weight % from treatment of binary mixtures of roughly 50–50 composition. For anthracene, the product concentration was 97.9 weight % from a feed mixture containing

Table VII

Separation of Di-substituted Benzene Isomer Mixtures with Ni(4-Methylpyridine)$_4$(SCN)$_2$

Isomeric mixture	Wt. ratio of clathrate former to *p*-isomer	Sample	Analyses of samples, wt. % *p*-Isomer	*o*-Isomer	*m*-Isomer	Recovery[a]
Chlorotoluenes	7.67	Feed	50.2	45.0	4.8	..
		Washed crystals[b]	91.4	7.8	0.8	35
		Filtrate	38.6	56.7	4.7	65
Dichlorobenzenes	3.08	Feed	52.8	47.2	0	..
		Washed crystals[b]	93.0	7.0	..	34.8
		Filtrate	37.5	62.5	..	65.2
Toluidines	4.16	Feed	49.1	50.9	0	..
		Washed crystals[b]	68.4	31.6	..	10.1
Nitrotoluenes	3.47	Feed	50.0	50.0	0	..
		Washed crystals[b]	73.5	26.5	..	7.0
		Filtrate	47.6	52.4	..	93.0
Methylanisoles	2.57	Feed	52.2	47.8	..	..
		Washed crystals[b]	94.4	5.6	..	25.5
		Filtrate	39.3	60.7	..	74.5

Solvent (vol. %), 10% 4-methylpyridine, 90% methyl cellosolve in all experiments.

$\frac{\text{Solvent}}{\text{Clathrate former}}$ (weight ratio) = 2.0 in all experiments.

[a] Weight % of the *p*-isomer introduced as feed recovered in that phase. [b] Clathrate crystals were washed once with fresh solvent before recovering the clathrated product contained therein.

Table VIII

Separation of Polycyclic Compounds with Ni(4-Methylpyridine)$_4$(SCN)$_2$

Type of contacting	Feed Compd. 1	Compd. 2	Sample	Analyses, wt. % Compd. 1	Compd. 2	Recovery, %	Wt. ratio, clathrate former to compd. 1	Soln. temp., °C.	Filtration temp., °C.
Solution[a]	Naphthalene	Diphenyl	Feed	48.6	51.4	..	3.0	108	25
			Washed crystals	85.6	14.4	83			
			Filtrate	14.8	85.2	17			
Solution[a]	1-Methylnaphthalene	2-Methylnaphthalene	Feed	58.3	41.7	..	2.6	105	21
			Washed crystals	81.3	18.7	43			
			Filtrate	45.5	54.5	57			
Solution[a]	Anthracene	Phenanthrene	Feed	33.3	66.7	..	10.0	94	25
			Washed crystals	97.9	2.1	..			
			Filtrate	20.2	79.8	..			
Solution[a]	Diphenyl oxide	Phenanthrene	Feed	54.1	45.9	..	3.3	81	30
			Washed crystals	83.7	16.3	..			
			Filtrate	50.8	49.2	..			
Suspension[b]	Naphthalene	Diphenyl	Feed	50.0	50.0	..	4.0	20	20
			Washed crystals	74.4	25.6	..			
			Filtrate	23.4	74.4	..			

[a] Solvent: 90 vol. % methyl cellosolve, 10 vol. % 4-methylpyridine. [b] *n*-Heptane as diluent.

33.3%. The selectivity displayed here for 1-methylnaphthalene is substantially higher than that of the other methods in the literature for resolution of the 1- and 2-methylnaphthalenes.

It is apparent that the number of possible compounds which might be studied for clathration purposes is at least several thousand and possibly much larger.

The authors regard the techniques described here as a highly practical tool for separation and as a theoretical problem in structural chemistry of great significance. We hope as the study progresses to reduce the phenomenon to a sufficiently scientific level to permit prediction of the specific compounds which will be selectivity clathrated by any given complex. However, a few minutes spent with molecular models of, say, tetra-(4-methylpyridino)-nickel dithiocyanate in an attempt to conceive of the lattice in which the molecules of complex lie and the interstices into which molecules such as *p*-xylene fit to the rejection of other xylene isomers will, we believe, convince the reader that a great amount of work remains to be done before this type prediction can be made with any certainty. The fact that tetra-(4-methylpyridino)-nickel dithiocyanate clathrates, depending on the feed, *p*-xylene, toluene, naphthalene, 1-methylnaphthalene, diphenyl oxide and anthracene while also displaying the selectivity sufficient to extract *p*-xylene from so broad a mixture as gasoline will bear out this impression.

The potential uses of this discovery lie in many fields: the recovery of *p*-xylene or *p*-cymene for the preparation of terephthalic acid, the recovery of *m*-xylene for the production of isophthalic acid, the separation of methylnaphthalene isomers, and in separation problems of synthetic organic chemistry. Further, the technique may be of analytical value in separation and characterization of complex mixtures such as petroleum products.

We predict that for many problems where separation of isomers or compounds of different sizes and/or shapes is required, the present work may be extended to provide one or more complexes suitable for the separation at hand. We hope at a later date to present information on this topic beyond this initial report.

Experimental

Preparation of Complexes.—The various complexes were prepared by variation of a basic method. The basic method may be exemplified as follows.

Preparation of Tetra-(4-methylpyridino)-nickel Dithiocyanate.—To 216 g. (0.911 mole) of nickelous chloride hexahydrate dissolved in 1700 ml. of water was added 178 g. (1.82 moles) of potassium thiocyanate. To the resulting green solution was added slowly and with constant stirring 340 g. (3.64 moles) of 4-methylpyridine. As the 4-methylpyridine was added to the nickel solution, a blue precipitate formed. The addition of 4-methylpyridine was extended over a period of five minutes. The entire operation was carried out at room temperature. After all of the 4-methylpyridine had been added, the mixture was stirred an additional 15 minutes to allow the system to come to equilibrium and the mixture was then filtered. The clear and colorless filtrate was discarded. The blue residue on the filter was removed and air-dried for 24 hours. The dried complex weighed 480 g., giving a net yield of 96% of theoretical.

The variations of this scheme included solution of the basic nitrogen compound in water prior to mixing, use of ammonium thiocyanate solution as a source of thiocyanate ion and addition of the basic nitrogen compound to an aqueous solution of nickelous chloride followed by addition of a solution containing thiocyanate ion. All of these methods produced the desired product and any of these methods were satisfactory for preparing complexes which were insoluble in water. Stoichiometric amounts of reactants were employed, except that a 1 or 2 mole % excess of nitrogen base usually was added.

Many of the water-insoluble complexes showed a large solubility in chloroform and extraction of the precipitated phase into chloroform provided a convenient method for purification. The purified complex could then be recovered from the chloroform solution by the evaporation of chloroform.

Preparation of Water-soluble Complexes.—Water-soluble complexes were prepared by simple mixing of the components followed by evaporation of the aqueous solution. The method is exemplified as follows.

Preparation of Tetra-(4-methylpyridino)-nickel Dichloride.—To 216 g. (0.911 mole) of nickelous chloride hexahydrate dissolved in 1700 ml. of water was added with constant stirring 340 g. (3.64 moles) of 4-methylpyridine. The resulting blue-green solution was transferred to an evaporating dish and the water evaporated in a slow air stream. The dried complex weighed 434 g. giving a net yield of 95% of theoretical.

Preparation of Clathrate Compounds.—Preparation of the clathrate compounds is exceedingly simple. All that is required is simple mixing of the solid complex with the feed mixture. Reaction rates are rapid—generally less than five minutes—and filtration serves to separate the clathrate from the liquid phase containing the non-clathrated components of the feed mixture. Two examples follow: one demonstrating the "suspension" process and the second demonstrating the "solution" process.

"Suspension" Process.—To a 150-ml. beaker containing 20.0 g. (0.0365 mole) of tetra-(4-methylpyridino)-nickel dithiocyanate was added 55 ml. of *n*-heptane and 3.0 ml. of 4-methylpyridine. The resulting two-phase system was stirred by means of a stirring rod while 16.5 ml. (0.134 mole, 20.1% *p*-xylene) of mixed xylene isomers was added. The mixture was stirred for two minutes and then filtered on a Büchner funnel. A 10.0-g. aliquot of the crystals on the filter was dissolved in 60.0 ml. of 1:1 HCl and the hydrocarbon phase which separated was extracted into 30.0 ml. of *n*-heptane. After separation of the liquid phase the hydrocarbon phase was washed twice with 30-ml. portions of 1:1 HCl and then analyzed by means of ultraviolet spectroscopy. The analysis showed the *p*-xylene content in the xylenes present to be 57.2%.

The remainder of the crystals on the filter were washed with 40 ml. of *n*-heptane by reslurrying and refiltering. Acid decomposition of the washed crystals and ultraviolet examination of the xylene phase, as above, showed the *p*-xylene content in the xylenes present to be 68.3%.

The combined filtrates were washed twice with 50-ml. portions of 1:1 HCl and ultraviolet examination of the washed hydrocarbon phase showed the *p*-xylene content to be 4.3% of the xylenes present.

"Solution" Process.—To a 150-ml. beaker containing 20.0 g. (0.0365 mole) of tetra-(4-methylpyridino)-nickel dithiocyanate was added 38.0 ml. of methyl cellosolve and 4.0 ml. of 4-methylpyridine. The mixture was heated on a hot plate to about 105° until solution was obtained. To the hot solution was added 16.5 ml. (0.134 mole, 20.1% *p*-xylene) of mixed xylene isomers and the solution was then cooled in an ice-bath with continuous stirring. As the mixture cooled blue crystals of the clathrate compound separated. When cooled to about room temperature the mixture was filtered on a Büchner funnel. A 10.0-g. aliquot of the crystals on the filter was dissolved in 60.0 ml. of 1:1 HCl and the hydrocarbon phase which separated was extracted into 30.0 ml. of *n*-heptane. After separation of the liquid phases the hydrocarbon phase was washed twice with 30-ml. portions of 1:1 HCl and then analyzed by means of ultraviolet spectroscopy. Analysis showed the *p*-xylene content in the xylenes present to be 61.8%.

The remainder of the crystals on the filter were washed with 40.0 ml. of methyl cellosolve by reslurrying and refiltering. Acid decomposition of the washed crystals and ultraviolet examination of the xylene phase, as above, showed the *p*-xylene content in the xylenes present to be 70.2%.

The combined filtrates were diluted with 50 ml. of *n*-heptane and washed three times with 40.0-ml. portions of dilute HCl. Ultraviolet examination of the washed hydrocarbon phase showed the *p*-xylene content in xylenes present to be 3.7%.

Complexes Prepared.—Many complexes were prepared, some of them previously unreported. The following abbreviations have been used in listing them: Py, pyridine; Isoq, isoquinoline; Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl; Bz, benzyl; Ac, acetyl; NH_2, amino; Cy, cyano; Hyme, hydroxymethyl; Vi, vinyl; i, iso; n, normal.

Arranged in order of increasing atomic number of the metal and increasing number of carbon atoms in nitrogen bases, the complexes prepared were: formula, color, melting point (if observed); $\mathrm{Mn(4\text{-}MePy)_4(SCN)_2}$, white; $\mathrm{Mn(4\text{-}EtPy)_4(SCN)_2}$, white; $\mathrm{Mn(4\text{-}EtPy)_4(CNO)_2}$, tan, 126; $\mathrm{Mn(4\text{-}EtPy)_4Cl_2}$, pink, 164° dec.; $\mathrm{Mn(Isoq)_4(SCN)_2}$, light yellow; $\mathrm{Ni(Py)_4(SCN)_2}$, blue; $\mathrm{Ni(Py)_4Cl_2}$, blue; $\mathrm{Ni(3\text{-}MePy)_4(SCN)_2}$, blue; $\mathrm{Ni(4\text{-}MePy)_2(SCN)_2}$, green; $\mathrm{Ni(4\text{-}MePy)_4(SCN)_2}$, blue; $\mathrm{Ni(4\text{-}MePy)_4(N_3)_2}$, green-blue; $\mathrm{Ni(4\text{-}MePy)_4Cl_2}$, blue; $\mathrm{Ni(4\text{-}MePy)_4(formate)_2}$, blue, 202° dec.; $\mathrm{Ni(4\text{-}MePy)_4(NO_2)_2}$, blue, 170° dec.; $\mathrm{Ni(4\text{-}EtPy)_4(SCN)_2}$, blue; $\mathrm{Ni(4\text{-}EtPy)_4(formate)_2}$, pale blue, 161°; $\mathrm{Ni(4\text{-}ViPy)_4(SCN)_2}$, blue; $\mathrm{Ni(4\text{-}\mathit{n}\text{-}PrPy)_4(SCN)_2}$, blue; $\mathrm{Ni(3\text{-}Et\text{-}4\text{-}MePy)_4(SCN)_2}$, gray, 141°; $\mathrm{Ni(4\text{-}\mathit{n}\text{-}BuPy)_4(SCN)_2}$; blue, $\mathrm{Ni(4\text{-}BzPy)_4(SCN)_2}$, blue, 200°; $\mathrm{Ni(4\text{-}AcPy)_4(SCN)_2}$, pale blue, 289°; $\mathrm{Ni(3\text{-}NH_2Py)_4(SCN)_2}$, blue, 231°; $\mathrm{Ni(4\text{-}NH_2Py)_4(SCN)_2}$, gray blue, 252°; $\mathrm{Ni(3\text{-}BrPy)_4(SCN)_2}$, blue; >300°; $\mathrm{Ni(3\text{-}CyPy)_4(SCN)_2}$, blue, 212° dec.; $\mathrm{Ni(4\text{-}CyPy)_4(SCN)_2}$, blue, 296° dec.; $\mathrm{Ni[4(Hyme)Py]_4(SCN)_2}$, blue, 237°; $\mathrm{Ni(Nicotinamide)_4(SCN)_2}$, blue, 194° dec.; $\mathrm{Ni(Me\ isonicotinate)_4(SCN)_2}$, blue, 238° dec.; $\mathrm{Ni(Et\ isonicotinate)_4(SCN)_2}$, purplish blue, 270° dec.; $\mathrm{Ni(\mathit{i}\text{-}nicotinic\ acid\ thioamide)_4(SCN)_2}$, brown, 186°; $\mathrm{Ni(isonicotinamide)_4(SCN)_2}$, purple, 260°; $\mathrm{Ni(Isoq)_4(SCN)_2}$, blue; $\mathrm{Ni(Isoq)_4Cl_2}$, blue; $\mathrm{Co(Py)_4(SCN)_2}$, bright pink; $\mathrm{Co(4\text{-}MePy)_4(SCN)_2}$, pink; $\mathrm{Co(4\text{-}EtPy)_4(SCN)_2}$, pink; $\mathrm{Fe(4\text{-}MePy)_4(SCN)_2}$, brown; $\mathrm{Fe(4\text{-}EtPy)_4(SCN)_2}$, yellow; $\mathrm{Cu(Py)_4(SCN)_2}$, green; $\mathrm{Cu(4\text{-}MePy)_4(SCN)_2}$, green; $\mathrm{Zn(4\text{-}MePy)_2Cl_2}$, white.

Most complexes were analyzed. For the analyses indicated the mean deviations (weight % of theoretical) and range of constituent content (weight %) were: metal, 1.0, 6.9 to 11.9; anion, 1.5, 12.8 to 32.1; carbon, 3.2, 47.1 to 70.5; hydrogen, 0.3, 3.9 to 6.7; nitrogen, 1.7, 9.7 to 25.4.

Acknowledgments.—We are indebted to Mr. Fred L. Hartley, present vice president in charge of Research, the Union Oil Company of California, for permission to publish these findings. We also are indebted to Mr. C. E. Swift, vice president retired, for his encouragement and support of this project in its early stages. It is a pleasure to acknowledge the constructive discussions and assistance of Messrs. H. C. Huffman, A. C. McKinnis, J. D. Wordie, H. R. Emmerson and H. F. Keller. The careful experimental work of Messrs. L. C. Smith and A. A. Fawver contributed substantially to the project. Finally, we are indebted to Messrs. W. C. Merrill, W. E. Ferguson, D. Alford, A. Grenall and others of the Analytical Group of this Department for their unstinting coöperation in the many analytical features of this study.

BREA, CALIFORNIA

[CONTRIBUTION FROM THE MONSANTO CHEMICAL CO., CHEMICAL RESEARCH DEPARTMENT, RESEARCH AND ENGINEERING DIVISION]

Clathrate Compounds of Werner Complexes with *p*-Disubstituted Benzene Derivatives

BY FORREST V. WILLIAMS

RECEIVED JULY 26, 1957

Iron, cobalt and nickel tetra-(4-methylpyridine)-dithiocyanates have been found to form clathrate compounds with the dichlorobenzenes and the methylstyrenes. *Para* derivatives are clathrated in preference to *ortho* isomers. The 3-methylpyridine, 4-*n*-propylpyridine and quinoline complexes of these metals do not form clathrate compounds. These effects have been explained in terms of the steric requirements of the voids in the crystal lattice of the Werner complex.

Introduction

Considerable evidence has been accumulated in recent years which indicates that several types of crystals can accommodate foreign molecules in their lattice. Among well known examples which may be mentioned are the urea and thiourea adducts, the choleic acids, the complexes of hydroquinone and the clathrate of benzene with dicyanoamminenickel(II). Apparently, voids exist in the crystal lattice of the parent compound into which only molecules of certain dimensions can be inserted. The term clathrate has been given to those complexes in which the foreign molecules have been entrapped by a void in three dimensions.[1]

In this paper are described some results on clathrate formation between some Werner complexes and certain disubstituted benzene derivatives.

Experimental

Materials.—All of the inorganic salts were reagent grade. The substituted pyridines were obtained from Eastman Kodak Co. The sample of mixed methylstyrenes was obtained from American Cyanamid Co. This sample of methylstyrenes had a composition of 72% *p*- and 28% *o*-methylstyrene. The sample of dichlorobenzenes was obtained from the Monsanto Chemical Co. The composition of the dichlorobenzenes was 74% *o*-, 1.9% *m*- and 24.1% *p*-dichlorobenzene.

Preparation of Clathrates.—Formation of the clathrates can be accomplished in two ways: (1) By dissolving the solid Werner complex and the benzene derivative in a suitable solvent by warming and then allowing the complex to recrystallize. The Werner complexes are soluble in chloroform and alcohols. Details of the preparation of the nickel complexes have been described previously.[2] When the nickel complexes alone are recrystallized from chloroform, octahedra are obtained. When the nickel clathrates are obtained from chloroform, considerable habit modification is evident. Instead of octahedra, ten-sided crystals usually are obtained. (2) By titrating an aqueous solution of the metal thiocyanates with a solution of the benzene derivative and the pyridine base. In place of the metal thiocyanates, solutions of metal nitrate or chloride and sodium thiocyanate are convenient. When the ratio of benzene derivative to nickel complex is large, the clathrates are obtained as gummy masses which can be filtered easily and then washed free of occluded material with hydrocarbon solvents such as pentane or hexane.

Analyses.—The composition of the entrapped material was determined by dissolving a known weight of the clathrate in 1:1 HCl and extracting with either carbon disulfide (for the dichlorobenzenes) or cyclohexane (for the methylstyrenes). The extracts were washed with saturated $NaHCO_3$ solution and distilled water, then dried over $CaSO_4$ and diluted to a known volume. The isomer compositions of the dichlorobenzene extracts were determined by a vapor chromatography technique (Burrell Kromo-Tog, Burrell Corp., Pittsburgh, Pa.). This analysis has been described.[3] The isomer compositions of the methylstyrene extracts were analyzed by an infrared technique. A calibration curve of concentration *versus* absorbance at 12.20 μ was prepared, using a sample of pure *p*-methylstyrene. The *ortho* band occurs at 13.03 μ.

Results and Discussion

The pertinent data are presented in Table I. It is evident that a 4-substituted pyridine is a necessary condition for clathrate formation. Apparently, introduction of a methyl group in the 3-position of pyridine alters the geometry of the voids sufficiently to prevent the incorporation of the benzene derivatives into the crystal lattice. The same results were also obtained with the quinoline complexes. Construction of molecular models showed that 4-*n*-propylpyridine has somewhat the same steric requirements as 3-methylpyridine. *Para* isomers are clathrated in preference to *ortho* isomers. The dimensions of the voids in the crystal lattice of the metal complexes must be such that molecules with a "width" of one benzene ring are preferred for clathration. This is confirmed by the fact that the 3-methylpyridine complexes do not form clathrates. In addition, bulky groups in the *para* position can prevent clathrate formation. Thus, neither biphenyl derivatives nor *p*-chloronitrobenzene would form clathrates with the nickel complex. Clathrates between the nickel complex and styrene also have been prepared. Generally, as the amount of material which is incorporated into the lattice is increased, the efficiency of separation of *para* from *ortho* isomers is decreased. The fer-

---

[1] H. M. Powell, *J. Chem. Soc.*, 63 (1948).

[2] A. V. Logan and D. W. Carle, THIS JOURNAL, **74**, 5224 (1952).

[3] R. H. Munch, *Rec. Chem. Prog.*, **18**, 96 (1957).