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[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

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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-

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(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).

TABLE I

METAL (ALKYLPYRIDINE)$_4$-(SCN)$_2$ CLATHRATES

Metal	Alkyl	Foreign molecule	Mole foreign molecule per mole metal complex	Composition of clathrated material
Ni^{++}	3-Methyl	Dichlorobenzenes	No clathrate	
Ni^{++}	3-Methyl	Methylstyrenes	No clathrate	
Ni^{++}	4-*n*-Propyl	Methylstyrenes	No clathrate	
Ni^{++}	4-Methyl	Dichlorobenzenes	0.76	90.5% *p*-, 9.5% *o*-
Ni^{++}	4-Methyl	Methylstyrenes	.60	90.0% *p*-, 10.0% *o*-
Fe^{++}	4-Methyl	Methylstyrenes	.94	82.3% *p*-, 17.7% *o*-
Co^{++}	4-Methyl	Methylstyrenes	.86	82.5% *p*-, 17.5% *o*-

rous complex seems to have the highest capacity for accepting alien molecules into its lattice. The proportion of benzene derivative to Werner complex approaches a one-to-one molar ratio which is observed for the nickel ammonia cyanide clathrate with benzene.

The crystal structure of the clathrate of benzene and dicyanoamminenickel(II) is an extended two-dimensional flat network of alternating nickel and cyanide groups.[4] Attachment of the coördinated ammonia molecules at right angles to this network provides a "box" which captures benzene molecules. Ammoniacal solutions of nickel cyanide will also form clathrates with pyrrole, furan and thiophene but not with the xylenes. Somewhat the same situation may occur with the metal tetra-(4-methylpyridine)-dithiocyanates. Insertion of the longer 4-methylpyridine molecule increases one dimension of the "box" allowing the entrapment of molecules of larger dimensions.

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

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE STATE UNIVERSITY, AND THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Stereochemistry of Complex Inorganic Compounds. XXI. The Resolution of Racemic Substances through Optically Active Complex Inorganic Compounds[1,2]

BY STANLEY KIRSCHNER, YUNG-KANG WEI AND JOHN C. BAILAR, JR.

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Apparently only two of the possible isomers of the $[Co(pn)_3]^{+++}$ ion (D-$[Co(d\text{-}pn)_3]^{+++}$ and L-$[Co(l\text{-}pn)_3]^{+++}$) are sufficiently stable to be isolated, and it has therefore been suggested that asymmetric complex ions react preferentially with certain favorably oriented stereoisomers of attacking coördinating agents. In addition, ethylenediamine has been reported to displace the ligand of the D-$[Co(edta)]^-$ ion with some retention of configuration to give the D-$[Co(en)_3]^{+++}$ cation. Consequently, D-$[Co(edta)]^-$ ion was treated with racemic propylenediamine to determine whether preferential displacement of the coördinated ligand by one stereoisomer of propylenediamine occurs, leaving the other isomer in solution. This is expected to take place if an asymmetric central ion of a complex influences the rate of attack of asymmetric ligands, provided that this complex ion retains its configuration during the displacement. Such preferential displacement is actually found to occur, with *d*-propylenediamine reacting more rapidly than the levo isomer, thereby effecting a partial resolution of *rac*-propylenediamine. Furthermore, treatment of D,L-$[Co(edta)]^-$ with *l*-propylenediamine results in a preferential reaction of the amine with L-$[Co(edta)]^-$, giving a partial resolution of the racemic complex ion. The mechanism by which this displacement occurs has been studied, and the reaction of *l*-propylenediamine with D-$[Co(edta)]^-$ ion, which results in an inversion of configuration of the complex to give L-$[Co(l\text{-}pn)_3]^{+++}$, supports the conclusion that the process is a stepwise displacement of the hexadentate ethylenediaminetetraacetate ligand by three bidentate groups. It is concluded that attack on the asymmetric complex ion by the stereoisomer of preferential configuration of the ligand occurs more rapidly than attack by the opposite isomer, and that attack by this opposite isomer causes an inversion of configuration of the complex resulting in the formation of a stable stereoisomer of the product.

Introduction

Smirnoff[3] and Jaeger[4] reported that only two of the possible stereoisomers of the $[Co(pn)_3]^{+++}$ ion[5] are apparently sufficiently stable to be isolated. These are the D-$[Co(d\text{-}pn)_3]^{+++}$ and L-$[Co(l\text{-}pn)_3]^{+++}$ ions.[6] The other possible combinations of cobalt(III) with propylenediamine (such as [D-(lll)]$^{+++}$, [D(lld)]$^{+++}$, [D(ldd)]$^{+++}$, [L(ddd)]$^{+++}$, [L(ddl)]$^{+++}$, and [L(dll)]$^{+++}$), if formed at all, apparently rearrange to the two stable stereoisomers.

In 1952 Bailar and his co-workers[7,8] partially resolved *rac*-tartaric, α-chloropropionic and lactic acids by treatment with $[Co(l\text{-}pn)_2CO_3]Cl$. In each case one enantiomer of the racemic acid displaced the carbonate preferentially, resulting in a

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[1] Presented in part before the Division of Inorganic Chemistry, 131st Meeting, American Chemical Society, Miami, Florida, April 7-12, 1957.

[2] Taken in part from the Doctoral Dissertation of S. K., University of Illinois, 1954, and the Master of Science thesis of Y. K. W., Wayne State University, 1957.

[3] A. P. Smirnoff, *Helv. Chim. Acta*, **3**, 177 (1920).

[4] F. M. Jaeger, "Optical Activity and High Temperature Measurements," McGraw-Hill Book Co., Inc., New York, N. Y., 1930, p. 158.

[5] The coördinating agents are designated as follows: en = ethylenediamine, pn = propylenediamine, edta = ethylenediaminetetraacetate anion.

[6] "D" and "L" represent dextrorotatory and levorotatory complex ions, respectively, and "*d*" and "*l*" represent dextrorotatory and levorotatory coördinating agents, respectively.

[7] J. C. Bailar, Jr., H. B. Jonassen and A. D. Gott, THIS JOURNAL, **74**, 3131 (1952).

[8] A. D. Gott and J. C. Bailar, Jr., *ibid.*, **74**, 4820 (1952).