# Reactions of Coordinated Ligands. IX. Utilization of the Template Hypothesis to Synthesize Macrocyclic Ligands in Situ

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A kinetically operating coordination template hypothesis has been stated to derive from the ability of an inert ion to hold reactive groups in proper array to produce sterically highly selective multistep reactions. The hypothesis has been substantiated by the use of planar nickel(II) to hold terminal mercapto groups of linear tetradentate ligands in cis-planar positions during the course of two-step reactions with alkyl dihalides. The products of the reactions are complexes in which the metal ion is enclosed by tetradentate macrocyclic ligands. The new complexes have been characterized by a variety of physical measurements. Their chemical properties are unusual as is expected for complexes of macrocyclic ligands.

## Introduction

The reactions of coordinated ligands have been studied sporadically since before the time of Werner. Only recently, however, has it been recognized that a great deal may be learned about catalysis and reaction mechanisms in general by the study of this type of process. Recent reviews[1,2] partially reveal the scope of the subject.

The presence of the metal ion during the course of an organic chemical reaction may lead to a variety of electronic effects, special steric effects, and energy transfer phenomena. For example, the basic hypothesis of the work summarized here assumes that the coordination sphere of the metal ion may serve as a template to hold reactive groups in proper position for sterically highly selective, multistep reactions. The example chosen to justify this hypothesis involves the formation of macrocyclic ligands which completely enclose a planar central metal ion as shown (for example) in eq. 1.[3] For reactions of the type given by
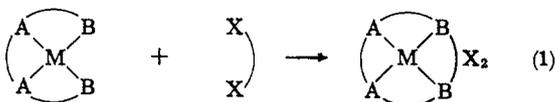


eq. 1, three requirements are prerequisite to such a synthesis. (1) The original ligand must be tetradentate and chelate in a planar or other suitable fashion (cis-octahedral would fail but tetrahedral would be suitable). (2) The terminal groups (B) must undergo a characterized addition reaction with ring-forming groups. (3) Suitable reagents must be available to provide the final ring-forming linkage. Equation 1 also suggests that the metal ion may stabilize macrocyclic organic molecules not otherwise stable.

Reactions of the coordinated donor atom were considered to be the most promising with which to test the template hypothesis. This was adjudged because the effect of the metal ion on the kinetics and mechanism of the reaction and the structure of the product are expected to be greater in this case than in other classes of ligand reaction.

Having defined the specific model for study, it was necessary to choose a donor atom which is reactive but remains coordinated during reaction and upon completion of reaction. For ease of study, the reaction

should be simple, preferably leading to one product. In order to predict the effect of the metal ion, it was necessary that the ligand reaction be well characterized.

The coordinated sulfur atom was considered to be most promising for the purposes of these investigations. Coordinated sulfur is most often in the divalent state and the organic chemistry of divalent sulfur has been thoroughly investigated. Extensive investigations in these laboratories[4,5] have shown the generality of the alkylation of coordinated mercapto groups by alkyl halides. For example, the reaction of bis(mercaptoethylamine)nickel(II) with methyl iodide produces an octahedral complex containing the thioether (eq. 2). Kinetic studies[5] of this and a number of re-

$$\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})_2 + 2\text{CH}_3\text{I} \longrightarrow$$
$$\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{SCH}_3)_2\text{I}_2 \quad (2)$$
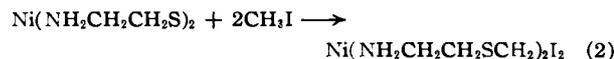
lated reactions have added strong support to the contention that the mercaptide function remains coordinated to the metal ion during the course of the alkylation reaction. This is of considerable significance, for it suggests that the orientation of two or more sulfur atoms with respect to each other in the coordination sphere may be put to use in testing the template hypothesis (eq. 1). From the foregoing considerations it may be expected that difunctional alkylating agents would react with two sulfur atoms coordinated at cis positions to form a new chelate ring. Such a reaction would provide an example of the controlled formation of chelate rings without substitution at the metal atom, since the donor atoms would remain coordinated during the process. This is shown diagrammatically in eq. 3. Presumably, the bond angles and bond distances
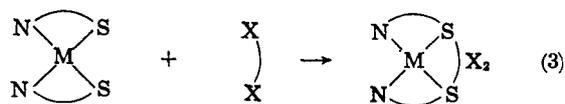


would be altered during the course of such a reaction. Otherwise, the original groups, other than the reacting atoms, would remain generally unaltered within the complex during the transformation. Consequently, the coordination sphere of the metal ion may be described as a slightly flexible template which may serve to hold the reactive functional groups of a ligand in

(1) D. H. Busch, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p. 1.

(2) M. M. Jones and W. A. Conner, Ind. Eng. Chem., 55, No. 9, 14 (1963).

(3) A preliminary report on these experiments appeared in Chem. Eng. News, 40, 57 (Sept. 17, 1962).

(4) D. H. Busch, D. C. Jicha, M. C. Thompson, J. W. Wrathall, and E. L. Blinn, J. Am. Chem. Soc., 86, 3642 (1964).

(5) D. H. Busch, J. A. Burke, Jr., D. C. Jicha, M. C. Thompson, and M. L. Morris, ref. 1, p. 125.

proper position to direct the steric course of complex multistep reactions. During these investigations reactions of the type shown in eq. 3 have been performed.

At this point, the application of the template hypothesis, in systems of sulfur complexes, to the synthesis of macrocyclic ligands depends on the availability of the proper tetradentate ligand. The family of complexes containing Schiff base ligands derived from α-diketones and β-mercaptoethylamine (structure I)[6,7] are well designed to give macrocyclic ligands by reaction with difunctional alkylating agents.


I
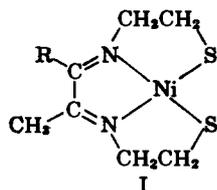
Among the complexes of this type available are those prepared from biacetyl (R = $CH_3$), Ni(BE); 2,3-pentanedione (R = $C_2H_5$), Ni(PE); and 2,3-octanedione (R = $C_6H_{11}$), Ni(OE).

The studies reported here describe the reaction of these α-diketobismercaptoethylimine complexes with difunctional alkylating agents to produce complexes in which the metal ion is completely enclosed by macrocyclic ligands (eq. 1). The products have been characterized by a variety of physical measurements including infrared and electronic spectra, magnetic moments, molecular weights, elemental analyses, and conductivities.

## Experimental

**Materials.**—α,α'-Dibromo-o-xylene (Matheson Coleman and Bell), 1,2-dibromoethane (Eastman), 1,3-dibromopropane (Eastman), 1,3-diiodopropane (Eastman), hydrogen chloride gas (Matheson), and β-mercaptoethylamine hydrochloride (Evans Chemetics, Inc., in 97–99.7% purity) were used without further purification. Bis(2-aminoethanethiolo)nickel(II) was prepared according to the procedure of Jicha and Busch.[8] Biacetylbis(mercaptoethylimino)nickel(II), 2,3-pentanedionebis(mercaptoethylimino)nickel(II), and 2,3-octanedionebis(mercaptoethylimino)nickel(II) were prepared according to the procedure of Thompson and Busch.[7] Anhydrous nickel(II) chloride was prepared according to the method of Pray.[9] Anhydrous nickel(II) bromide was prepared by dissolving nickel(II) hydroxide in hydrobromic acid and evaporating to dryness in vacuo. 1,2-Dichloroethane was dried and distilled over calcium hydride. All other chemicals were reagent grade.

**Reaction of Bis(2-aminoethanethiol)nickel(II) with α,α'-Dibromo-o-xylene.**—To a suspension of 2.11 g. (0.01 mole) of bis(2-aminoethanethiolo)nickel(II) in dimethylformamide (100 ml.) was added 2.64 g. (0.01 mole) of α,α'-dibromo-o-xylene and the mixture was refluxed until all the light green solid vanished, leaving a very light blue material. This product was filtered and washed with cold ethanol. The product was recrystallized from hot methanol (200 ml.) and dried in vacuo over $P_2O_5$. The product was a light blue powder, soluble in water, slightly soluble in methanol, and insoluble in ethanol; yield 60.5%. Anal. Calcd. for $Ni(C_{12}H_{20}N_2S_2)Br_2$: C, 30.34; H, 4.24; N, 5.90; S, 13.50; Br, 33.65. Found: C, 30.63; H, 4.43; N, 5.92; S, 13.61; Br, 33.96.

**Preparation of 2,2'[o-Phenylenebis(methylenethio)]bis[ethylamine].**—A solution of 0.02 mole of $NH_2CH_2CH_2SNa$ was prepared by adding 2.25 g. (0.02 mole) of β-mercaptoethylamine

hydrochloride to a solution formed from 0.92 g. (0.04 g.-atom) of sodium and 75 ml. of absolute methanol and removing the sodium chloride by filtration. To this solution was added 2.64 g. (0.01 mole) of α,α'-dibromo-o-xylene, and the solution was stirred at room temperature for 30 min. The sodium bromide which formed was removed by filtration and hydrogen chloride gas was passed through the solution until it was saturated. After cooling several hours, white crystals of the dihydrochloride precipitated. These were filtered, washed with cold ether, and dried in vacuo over $P_2O_5$. The infrared spectrum showed all the expected characteristics, so the substance was used without further treatment or analysis; yield 85.4%.

**Preparation of Dichloro-2,2'-[o-phenylenebis(methylenethio)]bis[ethylamine]nickel(II), Ni(EX)Cl₂·H₂O.**—2,2'-[o-Phenylenebis(methylenethio)]bis[ethylamine dihydrochloride] (1.65 g., 0.005 mole) was added to 50 ml. of ethanol containing 0.20 g. (0.01 g.-atom) of sodium and the sodium chloride was removed by filtration. To this solution was added 1.30 g. (0.005 mole) of anhydrous nickel(II) chloride with heating and stirring. At first, the solution turned green, then slowly changed to blue as a light blue solid was formed. This solid was isolated and recrystallized from methanol. The product was dried in vacuo over $P_2O_5$; yield 90.3%. Anal. Calcd. for $Ni(C_{12}H_{20}N_2S_2)Cl_2·H_2O$: C, 35.67; H, 5.49; N, 6.93; S, 15.87; Cl, 17.55. Found: C, 35.99; H, 5.35; N, 6.88; S, 15.85; Cl, 17.55.

**Preparation of Dibromo-2,2'[o-phenylenebis(methylenethio)]bis[ethylamine]nickel(II), Ni(EX)Br₂.**—This compound was prepared in an analogous manner to the chloro compound except that anhydrous nickel(II) bromide was used instead of the chloride. The compound was light blue and exhibited an infrared spectrum identical with that of the chloro compound.

**Reaction of Biacetylbis(mercaptoethylimino)nickel(II), Ni(BE), with α,α'-Dibromo-o-xylene.**—Ni(BE) (1.30 g., 0.005 mole) was dissolved in 50 ml. of 1,2-dichloroethane and 1.32 g. (0.005 mole) of α,α'-dibromo-o-xylene was added to the solution. As the solution was stirred (30 min.), it turned dark brown and a dark brown solid separated. The solid was filtered under dry nitrogen and dried in vacuo over $P_2O_5$. Anal. Calcd. for $Ni(C_{16}H_{22}N_2S_2)Br_2$: C, 36.60; H, 4.22; N, 5.34; S, 12.22; Br, 30.44. Found: C, 36,18; H, 4.25; N, 5.27; S, 11.96; Br, 30.17.

**Reaction of Biacetylbis(mercaptoethylimino)nickel(II), Ni(BE), with 1,2-Dibromoethane.**—Ni(BE) (1.30 g., 0.005 mole) was dissolved in 50 ml. of chloroform and 0.94 g. (0.005 mole) of 1,2-dibromoethane was added to the solution. The solution was stirred 3 or 4 hr. and cooled, yielding a dark brown solid. The solid was filtered, recrystallized from ethanol, and dried in vacuo over $P_2O_5$. Anal. Calcd. for $Ni(C_8H_{14}N_2S_2)$: C, 36.81; H, 5.41; N, 10.73; S, 24.57. Found: C, 34.87; H, 5.56; N, 9.60; S, 22.86; Br, 3.20.

**Reaction of Biacetylbis(mercaptoethylimino)nickel(II), Ni(BE), with 1,3-Dibromopropane and 1,3-Diiodopropane.**—These reactions were analogous to the previous one except that 1.01 g. (0.005 mole) of 1,3-dibromopropane and 1.50 g. (0.005 mole) of 1,3-diiodopropane, respectively, were the alkylating agents. Filtration of the solutions gave black, tarry masses which were insoluble in all common solvents. The infrared spectrum gave no clearly definable absorptions. On cooling a brown-black solid formed, which was filtered, recrystallized from ethanol, and dried in vacuo over $P_2O_5$. Anal. Calcd. for $Ni(C_{11}H_{20}N_2S_2)Br_2$: N, 6.05. Found: N, 6.25. Calcd. for $Ni(C_{11}H_{20}N_2S_2)I_2$: C, 23.72; H, 3.62; N, 5.03; S, 11.51; I, 45.58. Found: C, 25.61; H, 4.02; N, 5.10; S, 14.25; I, 31.33.

**Reaction of 2,3-Octanedionebis(mercaptoethylimino)nickel(II), Ni(OE), with α,α'-Dibromo-o-xylene.**—Ni(OE) (1.58 g., 0.005 mole) was dissolved in 50 ml. of 1,2-dichloroethane and 1.32 g. (0.005 mole) of α,α'-dibromo-o-xylene was added to the solution. The solution was stirred for 30 min., as the color turned dark brown. The solution was concentrated almost to dryness, yielding a dark brown solid which was filtered under dry nitrogen and dried in vacuo over $P_2O_5$. Anal. Calcd. for $Ni(C_{20}H_{30}N_2S_2)Br_2$: C, 41.34; H, 5.20; N, 4.82; S, 11.04; Br, 27.51. Found: C, 41.11; H, 5.51; N, 4.79; S, 11.28; Br, 27.31.

**Reaction of 2,3-Pentanedionebis(mercaptoethylimino)nickel(II), Ni(PE), with 1,3-Dibromopropane.**—Ni(PE) (1.37 g., 0.005 mole) was dissolved in 50 ml. of chloroform and 1.01 g. (0.005 mole) of 1,3-dibromopropane was added to the solution. The solution was stirred 3–4 hr. Filtration of the solution gave a black, tarry mass which was insoluble in all common solvents. The infrared spectrum gave no clearly definable absorptions. On

(6) M. C. Thompson and D. H. Busch. *J. Am. Chem. Soc.*, **84**, 1762 (1962).

(7) M. C. Thompson and D. H. Busch. *ibid.*, **86**, 213 (1964).

(8) D. C. Jicha and D. H. Busch, *Inorg. Chem.*, **1**, 872 (1962).

(9) A. R. Pray, *Inorg. Syn.*, **5**, 153 (1957).

cooling a dark brown solid formed which was filtered, recrystallized from ethanol, and dried *in vacuo* over $P_2O_5$. *Anal.* Calcd. for $Ni(C_{12}H_{22}N_2S_2)Br_2$: C, 30.22; H, 4.65; N, 5.87; S, 13.45; Br, 33.51. Found: C, 27.82; H, 4.81; N, 5.87; S, 13.75; Br, 33.83.

**Reaction of 2,3-Pentanedionebis(mercaptoethylimino)nickel-(II), Ni(PE), with α,α'-Dibromo-o-xylene.**—Ni(PE) (1.37 g., 0.005 mole) was dissolved in 50 ml. of 1,2-dichloroethane and 1.32 g. (0.005 mole) of α,α'-dibromo-o-xylene was added to the solution. The solution was stirred 30 min., and the color of the solution changed to dark brown. The solution was concentrated almost to dryness, yielding a dark brown solid which was filtered under dry nitrogen and dried *in vacuo* over $P_2O_5$. *Anal.* Calcd. for $Ni(C_{17}H_{24}N_2S_2)Br_2$: C, 37.87; H, 4.49; N, 5.20; S, 11.90; Br, 29.65. Found: C, 37.79; H, 4.77; N, 5.31; S, 12.20; Br, 29.80.

**Magnetic Measurements.**—Magnetic measurements were made by the Gouy method at room temperature. The susceptibilities of ligands and anions were calculated from Pascal's constants, except for the tetraphenylborate anion which was measured in the form of the sodium salt. The standard used was $Hg[Co(NCS)_4]$. The balance used was a Sauter Monopan with a capacity of 200 g. On several samples, measurements were made at field strengths of approximately 5 and 8 kgauss and the resulting moments were found to be the same within ±0.5 B.M.

**Electrical Conductance.**—Conductivities were obtained using an Industrial Instruments, Inc., Model RC 16B conductivity bridge. Measurements were all made at 25° on 0.001 $M$ solutions at a frequency of 1000 c.p.s.

**Infrared Spectra.**—The infrared absorption spectra were obtained by using Perkin-Elmer Models 21 and 337 recording spectrophotometers. Nujol mull and potassium bromide pellet techniques were employed. Polystyrene spectra were used for calibration.

**Electronic Spectra.**—Electronic spectra were obtained by using a Cary Model 14 recording spectrophotometer with 1-cm. and 5-cm. matched, fused silica cells.

**Molecular Weight Measurements.**—Molecular weights were determined in chloroform and 1,2-dichloroethane at 37° with a Mechrolab, Inc., vapor pressure osmometer, Model 301A, calibrated with benzil. Concentrations of solutions were approximately $10^{-1}$ $M$. The results were reproducible to ±1% in most cases.

**Analyses.**—Analyses except for nitrogen were performed by Galbraith Microanalytical Laboratories and Schwarzkopf Microanalytical Laboratories. A majority of the nitrogen analyses were obtained in these laboratories by using a Coleman Model 29 nitrogen analyzer.

## Results and Discussion

Establishing the validity of the coordination template hypothesis is the basic aim of this investigation. According to this hypothesis, the coordination sphere of a metal ion may serve as a template to hold reactive groups in proper position for sterically highly selective, multistep reactions. The conditions necessary to the application of the template hypothesis to the synthesis of macrocyclic ligands reported here were developed in the Introduction. The nature of the reactions was prescribed by eq. 1 and 3.

**Closing of Chelate Rings.**—Prior to the application of the template hypothesis to the formation of macrocyclic ligands, it is desirable to prove that a difunctional alkylating agent will react with *cis*-coordinated sulfur atoms to form a new chelate ring in simpler systems.

Bis(mercaptoethylamino)nickel(II) has been shown to exist only as the *cis* isomer, by theoretical arguments and by demonstrating that the complex acts as a bidentate ligand, in the presence of transition metal ions, to form complexes such as tetrakis(mercaptoethylamino)-trinickel(II) chloride.[8,10] Bis(mercaptoethylamino)-nickel(II) reacts with alkylating agents as shown in

(10) D. C. Jicha and D. H. Busch, *Inorg. Chem.*, **1**, 878 (1962).

eq. 2. Therefore, this complex was deemed appropriate for attempts to form new chelate rings by reactions with difunctional alkylating agents.

The reaction of bis(mercaptoethylamino)nickel(II) with α,α'-dibromo-o-xylene was carried out in dimethylformamide (DMF) to give a light blue product that is insoluble in DMF, but can be recrystallized from methanol. This product was found to be identical with that formed by reaction of the pure ligand (separately prepared) with anhydrous nickel(II) bromide. Reaction of pure ligand with anhydrous nickel(II) chloride resulted in a more intensely blue-colored complex whose infrared spectrum was identical with those of the two previous products. All three complexes are soluble in water and methanol but insoluble in organic solvents. Elemental analyses show identical C, N, S, halide ratios for the chloride and the bromide from ligand reaction, proving that the same ligand is present in the two complexes. Magnetic susceptibilities of the three compounds listed in Table I all correspond to triplet ground states. The susceptibility of the product from ligand reaction was measured with a sample several months old and its purity is not assured. It is interesting to note that the magnetic measurements indicate octahedral structures as have been observed in reactions of the same complex with monofunctional alkylating agents.[4] It may be concluded that structure II is appropriate for these substances.

### TABLE I

### MAGNETIC SUSCEPTIBILITIES OF S,S'-o-XYLYLBIS(MERCAPTOETHYLAMINE) COMPLEXES

| Compound[a] | $T$, °K. | $\chi_m \times 10^6$ | $\mu_{eff}$ |
|---|---|---|---|
| $Ni(EX)Cl_2 \cdot H_2O$ | 298.0 | 3880 | 3.15[b] |
| $Ni(EX)Br_2$ | 298.0 | 3727 | 3.10[b] |
| $Ni(EX)Br_2$ | 302.5 | 4517 | 3.4[c] |

[a] Abbreviations are: EX = S,S'-o-xylylbis(mercaptoethylamine). [b] Prepared by reaction of ligand with metal salt. [c] Prepared by alkylation of complex.

Thus, the reaction giving the product shown in structure II demonstrates the feasibility of chelate



II
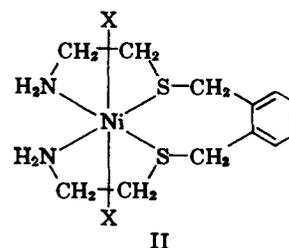
ring formation by ligand reactions of this kind. Further, the results indicate that α,α'-dibromo-o-xylene is a reagent well suited to react with *cis* sulfur atoms to produce rings.

**Formation of Macrocycles.**—Having illustrated the reactivity of the mercapto groups in biacetylbis(mercaptoethylimino)nickel(II), Ni(BE); 2,3-octanedionebis(mercaptoethylimino)nickel(II), Ni(OE); and 2,3-pentanedionebis(mercaptoethylimino)nickel(II), Ni(PE), toward monofunctional alkylating agents[4] and the feasibility of formation of new chelate rings (above) by ligand reactions, through the reaction of bis(mercaptoethylamino)nickel(II) with α,α'-dibromo-

o-xylene, it was possible to perform the critical experiments necessary to test the template hypothesis stated earlier and demonstrate the formation of macrocyclic ligands *in situ*. In order to accomplish this the appropriate bifunctional reagents are necessary. In this regard, it should be realized that the actual structures of complexes, such as Ni(BE), Ni(OE), and Ni(PE), are not expected to be simply *square*-planar, despite the usual manner of reference to such geometries. The presence of three fused, relatively confining five-membered chelate rings in the complex should produce a trapezoidal structure. Such distortions have been proven to exist in the plane containing three fused rings in hexadentate ethylenediaminetetraacetato-cobaltate(III).[11]

Previously discussed experiments illustrated that α,α'-dibromo-o-xylene is a quite reactive difunctional alkylating agent, sterically well suited to close chelate rings. In addition, it is noted that the seven-membered rings formed with this reagent are relatively large. Thus, reaction of Ni(BE), Ni(OE), and Ni(PE) with α,α'-dibromo-o-xylene should lead to complexes containing a macrocyclic ligand. As reported earlier,[4] the products of reaction of Ni(BE), Ni(OE), and Ni(PE) with monofunctional alkyl halides are di-univalent electrolytes in water and exhibit moments of the usual magnitude associated with two unpaired electrons. The macrocyclic compounds are expected to exhibit monomeric molecular weights. Also, in order to demonstrate that both sites have reacted, the compounds must be di-univalent electrolytes in highly polar solvents. The formation of the fourth chelate ring may be presumed to constrain the nitrogen and sulfur donors to a single plane and, further, the bond distance in the nickel–sulfur linkage may be shortened by the steric requirements of the macrocyclic ligand. This, in turn, should lead to enhanced ligand field strength in the unique plane, a factor which might lead to spin pairing.[12] Further, these macrocyclic complexes may be expected to exhibit unusual stability, as is true in the case of phthalocyanines and other recently reported macrocyclic complexes.[13,14]

The reaction of Ni(BE), Ni(OE), and Ni(PE) with α,α'-dibromo-o-xylene proceeds rapidly in 1,2-dichloroethane to form high yields of a single product. Due to the low solubility in 1,2-dichloroethane of the product formed by the reaction of Ni(BE), a major portion of it precipitates during reaction. In the cases of Ni(OE) and Ni(PE) it is necessary to concentrate the solutions almost to dryness in order to obtain the solid complex.

**Physical Properties of Macrocyclic Complexes.**— Molecuar weight data in chloroform and 1,2-dichloroethane for the more soluble products formed from Ni(OE) and Ni(PE), respectively, indicate they are monomeric in these solvents (Table II), conforming to a formulation with the bromides coordinated.

Molar conductivities of the three compounds (Table III) show them to be di-univalent electrolytes in water. This demonstrates that both bromide ions have been displaced from the o-xylyl group by reaction with the

(11) H. A. Weakkleim and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 550 (1959).

(12) C. J. Ballhausen and A. D. Liehr, *ibid.*, **81**, 538 (1959).

(13) G. A. Melson and D. H. Busch, *Proc. Chem. Soc.*, 223 (1963).

(14) D. A. House and N. F. Curtis, *J. Am. Chem. Soc.*, **84**, 3248 (1962).

### TABLE II
### MOLECULAR WEIGHTS OF
S,S'-o-XYLYL-α-DIKETOBIS(MERCAPTOETHYLIMINE) COMPLEXES

| | Molecular weight | |
|---|---|---|
| Compound[a] | Theoretical | Found |
| Ni(PEX)Br₂ | 539 | 542[b] |
| Ni(OEX)Br₂ | 555 | 581[c] |

[a] Abbreviations are as in Table III. [b] Solvent 1,2-dichloroethane. [c] Solvent chloroform.

sulfur atoms. Conductivities in DMF and methanol (Table III) show that the polarity of the solvent is quite important. In DMF the molar conductance values are between di-univalent and uni-univalent[15] while in methanol they correspond to uni-univalent electrolytes; however, on standing the methanol solutions change to give values more indicative of di-univalent electrolytes.

### TABLE III
### MOLAR CONDUCTIVITIES OF
S,S'-o-XYLYL-α-DIKETOBIS(MERCAPTOETHYLIMINE) COMPLEXES

| | Molar conductivity, ohm⁻¹ | | |
|---|---|---|---|
| Compound[a] | H₂O | DMF[b] | Methanol |
| Ni(BEX)Br₂ | 230 | 97 | 78.7 |
| Ni(OEX)Br₂ | 201 | 89 | 74.4 |
| Ni(PEX)Br₂ | 216 | 97 | 78.4 |

[a] Abbreviations are: BEX = S,S'-o-xylylbiacetylbis(mercaptoethylimine), OEX = S,S'-o-xylyl-2,3-pentanedionebis-(mercaptoethylimine), and PEX = S,S'-o-xylyl-2,3-pentanedionebis(mercaptoethylimine). [b] Value for uni-univalent 70, value for di-univalent 140–150, see ref. 15.

The values of the molecular weights and conductivities eliminate the possibility of polymers as products, as well as militating against either a distorted tetrahedral or square-planar structure.

The magnetic susceptibilities show the singlet to be the ground state in these complexes. The corrected susceptibilities of the nickel(II) in the products show small positive values. If the samples are not properly handled, substantial enhancement of the positive susceptibility may occur. This is believed to result from displacement of bromide by water molecules resulting in the formation of such paramagnetic ions as Ni(PEX)(H₂O)₂²⁺. The effect of extraplanar ligands on the magnetic properties of these substances is the subject of continuing investigations.

On the basis of the properties reported it is concluded that the substances are macrocyclic complexes as shown in structure III. For convenience, the coordinated bromides are improperly represented in structure III.



III
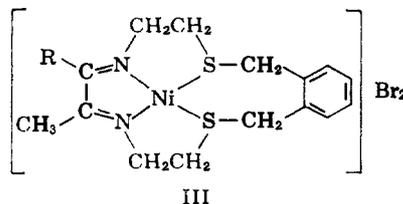
The compounds Ni(BEX)Br₂, Ni(PEX)Br₂, and Ni(OEX)Br₂ exhibit singlet ground states. Tables IV and V report their spectra in 1,2-dichloroethane and

(15) P. G. Simpson, A. Vinciguerra, and J. V. Quagliano, *Inorg. Chem.*, **2**, 282 (1963).

DMF, respectively. The first three bands, in both solvents, are of the same origin; however, a difference

| Band | | Ni(PEX)Br₂ | Ni(OEX)Br₂ |
|---|---|---|---|
| I | $\lambda_{max}$, m$\mu$ | 1,110 | 1,105 |
| | $\bar{\nu}$, cm.$^{-1}$ | 9,010 | 9,050 |
| | $\epsilon_{max}$ | 21.2 | 33.1 |
| II | $\lambda_{max}$, m$\mu$ | 985 | 983 |
| | $\bar{\nu}$, cm.$^{-1}$ | 10,200 | 10,200 |
| | $\epsilon_{max}$ | 16.4 | 29.0 |
| III | $\lambda_{max}$, m$\mu$ | 619 (sh) | 602 (sh) |
| | $\bar{\nu}$, cm.$^{-1}$ | 16,200 | 16,600 |
| | $\epsilon_{max}$ | 68.4 | 104 |
| IV | $\lambda_{max}$, m$\mu$ | 440 (sh) | 450 (sh) |
| | $\bar{\nu}$, cm.$^{-1}$ | 22,700 | 22,200 |
| | $\epsilon_{max}$ | 284 | 300 |
| V | $\lambda_{max}$, m$\mu$ | 290 | 294 |
| | $\bar{\nu}$, cm.$^{-1}$ | 34,500 | 34,000 |
| | $\epsilon_{max}$ | 6,850 | 6,330 |
| VI | $\lambda_{max}$, m$\mu$ | 269 | 269 |
| | $\bar{\nu}$, cm.$^{-1}$ | 37,200 | 37,200 |
| | $\epsilon_{max}$ | 7,060 | 6,470 |

[a] Abbreviations are the same as in Table III.

in the charge-transfer bands in DMF obscures a fourth band which appears in 1,2-dichloroethane. All three bands remain at about the same position in the two solvents. The first one occurs at 9000–9200 cm.$^{-1}$ and is assigned to the transition $^1A_1 \rightarrow {}^3B_1$. The second band, occurring at 10,000–10,300 cm.$^{-1}$, is assigned to

| Band | | Ni(BEX)Br₂ | Ni(OEX)Br₂ | Ni(PEX)Br₂ |
|---|---|---|---|---|
| I | $\lambda_{max}$, m$\mu$ | 1,087 | 1,085 | 1,104 |
| | $\bar{\nu}$, cm.$^{-1}$ | 9,200 | 9,217 | 9,060 |
| | $\epsilon_{max}$ | 12.7 | 28.7 | 11.1 |
| II | $\lambda_{max}$, m$\mu$ | 969 (sh) | 985 | 993 |
| | $\bar{\nu}$, cm.$^{-1}$ | 10,300 | 10,200 | 10,100 |
| | $\epsilon_{max}$ | 12.9 | 27.2 | 7.7 |
| III | $\lambda_{max}$, m$\mu$ | 572 (sh) | 624 | 544 |
| | $\bar{\nu}$, cm.$^{-1}$ | 17,500 | 16,000 | 18,400 |
| | $\epsilon_{max}$ | 271 | 322 | 282 |
| IV | $\lambda_{max}$, m$\mu$ | .... | 435 (sh) | .... |
| | $\bar{\nu}$, cm.$^{-1}$ | .... | 23,000 | .... |
| | $\epsilon_{max}$ | .... | 1,470 | .... |
| V | $\lambda_{max}$, m$\mu$ | 397 | 401 | 398 |
| | $\bar{\nu}$, cm.$^{-1}$ | 25,200 | 24,900 | 25,100 |
| | $\epsilon_{max}$ | 1,060 | 1,690 | 2,310 |
| VI | $\lambda_{max}$, m$\mu$ | 322 (sh) | 326 (sh) | 323 (sh) |
| | $\bar{\nu}$, cm.$^{-1}$ | 31,100 | 30,700 | 31,000 |
| | $\epsilon_{max}$ | 2,780 | 2,550 | 3,810 |

[a] Abbreviations are the same as in Table III.

the transition $^1A_1 \rightarrow {}^3B_1'$. The third band, occurring at 16,000–18,400 cm.$^{-1}$ is assigned to the transition $^1A_1 \rightarrow {}^3B_2$. All of these bands are spin-forbidden, so they exhibit relatively low intensities compared to the singlet–singlet transition ($^1A_1 \rightarrow {}^1B_1$). The spin-permitted $^1A_1 \rightarrow {}^1B_1$ absorption occurs at around 22,500 cm.$^{-1}$ in 1,2-dichloroethane, but is obscured by the higher energy neighboring band in DMF except in Ni(OEX)Br₂, which shows a shoulder at 23,000 cm.$^{-1}$.

The next higher energy bands in Ni(BEX)Br₂ and Ni(PEX)Br₂ are unsymmetrical, an observation suggesting that the absorption of immediate interest is overlapped by the succeeding band. These assignments are consistent with those made by Maki[16] on diamagnetic pyridine solutions of Ni(sal)(en).

The agreement of the spectra with expectation for six-coordinate tetragonal, low-spin nickel(II) lends further support to the assigned structures.

**Chemical Properties of Macrocyclic Complexes.**—As expected, these macrocyclic compounds exhibit unusual stability. The nickel cannot be extracted by dimethylglyoxime or S$^{-2}$. Indeed, sulfide ion seems to replace the two bromide ions to form a complex. The compounds of structure III are not decomposed by acid or base. In fact, even cold concentrated nitric and sulfuric acids dissolve the complexes, giving characteristically colored solutions. In the presence of warm nitric or sulfuric acid a reaction occurs. Boiling Ni(BEX)Br₂ in basic solution results in a new complex which exhibits a very sharp absorption at about 3600 cm.$^{-1}$ in its infrared spectrum. The remainder of the spectrum is not well resolved, but indicates that the ligand is present. This behavior may be similar to that observed by Melson,[17,18] in which macrocyclic ligands formed by self-condensation of *o*-aminobenzaldehyde add water across the C=N in basic solution.

Attempts to close the remaining open side of Ni(BE) and Ni(PE) with ethylene dibromide resulted in slow reactions leading to materials of uncertain composition which, from their intractable nature, are suspected of being polymeric. 1,3-Diiodopropane and 1,3-dibromopropane were found to give materials tentatively identified as the expected products and also products suspected of being polymers. These reactions were, also, quite slow. These reactions support the necessity for a relatively large chelate ring to complete the organic macrocycle as predicted from the expected trapezoidal structure of the starting material.

### Conclusions

The synthesis of these macrocyclic chelate compounds from Ni(BE), Ni(PE), and Ni(OE) by reaction with $\alpha,\alpha'$-dibromo-*o*-xylene constitutes the first deliberate utilization of reactions of the coordinated donor atom to close chelate rings and, of greater significance, to produce completely encycled complexes. Further, the technique involved represents a method for the synthesis of large organic ring structures.

This type of reaction in which a metal ion holds reactive groups within a substitution-inert complex in proper array to facilitate a stereochemically selective multistep reaction may be referred to as a *kinetic template reaction* for the succession of reaction steps is determined by the metal ion. The preparation of the starting materials Ni(BE), Ni(OE), and Ni(PE) constitutes a second class of template reaction as discussed in earlier reports.[6,7]

Recently, other examples of cyclization reactions have been reported.[14,19,20] The cyclization reaction reported independently by Schrauzer[19] and by Umland and Thierig,[20] and represented by eq. 4 is clearly an

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(17) G. A. Melson and D. H. Busch, unpublished results.
(18) D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **78**, 1137 (1956).
(19) G. N. Schrauzer, *Ber.*, **95**, 1438 (1962).
(20) F. Umland and D. Thierig, *Angew. Chem.*, **74**, 388 (1962).

$$2BX_3 + Ni(DMG)_2 \longrightarrow X_2B \text{(structure)} + 2HX \quad (4)$$

example of a *kinetic template reaction*. The general subjects of template reactions and complexes containing macrocyclic ligands have been reviewed elsewhere.[21]

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[CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

# Stereochemistry of Complex Inorganic Compounds. XXVIII.[1] The Walden Inversion in the Base Hydrolysis of Optically Active Cobalt(III) Complexes

BY L. J. BOUCHER, E SHIN KYUNO, AND JOHN C. BAILAR, JR.

The base hydrolysis of optically active *cis*-dichlorobis(ethylenediamine)cobalt(III) cation in concentrated aqueous solution leads to an inversion of configuration in the formation of the product. It is shown that the inversion takes place in the first step of the hydrolysis. Additional information about the same process in dilute solutions in the presence of silver ion is also given. Mechanisms are proposed for the reactions which take place in the presence and in the absence of silver ion.

## Introduction

In comparison to the large number of substitution reactions in octahedral complexes which are known, examples of those that proceed with inversion of configuration are rare. The first example which was thoroughly studied involved the transformation of the optically active *cis*-dichlorobis(ethylenediamine)cobalt(III) ion into the optically active carbonatobis(ethylenediamine)cobalt(III) ion.[2]

$$(+)D\text{-}cis\text{-}[Co(en)_2Cl_2)]^+ \xrightarrow[\text{Ag}_2CO_3]{\text{K}_2CO_3} \begin{cases} (+)D\text{-}[Co(en)_2CO_3]^+ \\ (-)D\text{-}[Co(en)_2CO_3]^+ \end{cases}$$

It has been deduced from rotatory dispersion studies that the *cis*-[Co(en)$_2$Cl$_2$]$^+$, *cis*-[Co(en)$_2$ClH$_2$O]$^{2+}$, and [Co(en)$_2$CO$_3$]$^+$ that are dextrorotatory at the Na D-line, (+)D, have the same configuration.[3] It is then apparent that inversion takes place in the reaction involving silver ion. The reactions were carried out by grinding the metal carbonate with the complex ion in a small amount of water to form a paste, followed by the extraction of the soluble products with water. Similar reactions with mercury(I) carbonate and silver oxalate did not give inverted products. However, when a large excess of potassium carbonate was used, an inverted product was formed.[4]

It has been suggested recently that in the reaction involving silver carbonate, the hydroxide and bicarbonate ions which are present play an important role. Further, when the base hydrolysis of (+)D-*cis*-[Co(en)$_2$Cl$_2$]$^+$ was carried out in the presence of silver ion, an inverted product was formed. Stable materials were formed by acidification of the reaction mixture and addition of bicarbonate ion.[5] The following

reaction sequence summarizes the reported data on the formation of optically active [Co(en)$_2$CO$_3$]$^+$.[6]

$$\Lambda\text{-}cis\text{-}[Co(en)_2Cl_2]^+ \xrightarrow{H_2O} \Lambda\text{-}cis\text{-}[Co(en)_2ClH_2O]^{2+} ?$$



Under the conditions used, the presence of silver ion is necessary for an inversion process to occur in the base hydrolysis of $\Lambda$-*cis*-[Co(en)$_2$Cl$_2$]$^+$. Efforts to substitute other ions for silver, *i.e.*, Hg$^{2+}$, Pb$^{2+}$, or Tl$^+$, were unsuccessful.[5]

An example of an inversion reaction that does not require the presence of silver ion is the ammonation of $\Lambda$-*cis*-[Co(en)$_2$Cl$_2$]$^+$ to form $\Delta$-*cis*-[Co(en)$_2$NH$_3$Cl]$^{2+}$ in liquid ammonia at $-77°$.[8] No analogous reaction has been reported to take place in aqueous solution.

We wish to report here additional information on the inversion reaction observed in the base hydrolysis of $\Lambda$-*cis*-[Co(en)$_2$Cl$_2$]$^+$ in aqueous solution in the presence of silver ion, and the discovery of the conditions necessary for the same inversion reaction in the absence of silver ion.

## Results

The base hydrolysis of *cis*-[Co(en)$_2$Cl$_2$]$^+$ by addition of one equivalent of hydroxide into a solution of the complex gives, in addition to the expected *cis*- and *trans*-[Co(en)$_2$ClOH]$^+$, both *cis*-[Co(en)$_2$(OH)$_2$]$^+$ and unchanged *cis*-[Co(en)$_2$Cl$_2$]$^+$.[9] However, when a 2:1

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(3) J. P. Mathieu, *Bull. Soc. Chim. France*, **3**, 476 (1936).

(4) J. C. Bailar, Jr., and J. P. McReynolds, *J. Am. Chem. Soc.*, **61**, 3199 (1939).

(5) F. P. Dwyer, A. M. Sargeson, and I. K. Reid, *ibid.*, **85**, 1215 (1963).

(6) The (+)D-[Co(en)$_3$]$^{3+}$ ion has been assigned a lambda, A, absolute configuration. A and $\Delta$ refer to an isomer with a natural screw form which is left-handed and right-handed, respectively. For the original assignment see T. S. Piper, *J. Am. Chem. Soc.*, **83**, 3908 (1961). Further, the configuration of the (+)D-[Co(en)$_2$Cl$_2$]$^+$ ion has been related to that of the (+)D-[Co(en)$_3$]$^+$ ion by rotatory dispersion studies: T. E. MacDermott and A. M. Sargeson, *Australian J. Chem.*, **16**, 334 (1963).

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