

TABLE IV
 SPECTRAL DATA FOR Pt(II) COMPLEXES

Compound	ν_{\max} , cm. ⁻¹	ϵ	Assignment	Energy, kcal.
PtCl ₄ ²⁻ ^a	21,000	15	b _{2g} → b _{1g}	Δ ₁ , 60
	25,500	59	a _{1g} → b _{1g}	Δ ₂ , 73
	30,200	64	e _g → b _{1g}	Δ ₃ , 87
	46,000	9580	C.t.	
C ₂ H ₄ PtCl ₃ ^{-b}	29,800	235	b ₂ → a ₁	Δ ₁ , 85
	33,700	725	a ₁ → a ₁	Δ ₂ , 96
	38,000	1905 ^c	b ₁ → a ₁	Δ ₃ , 103
	42,000	3390	C.t.	

^a Ref. 7. ^b From the Ph.D. thesis of John R. Joy, University of Cincinnati (1958). ^c The intensity is too large for this to be wholly a d-d band and charge transfer probably adds considerably to the intensity here (see ref. 7).

There is of course a substantial contribution to stability by the π -bond between Pt and C₂H₄.

The $\pi \rightarrow \pi^*$ transitions for ethylene and styrene occur at 165 and 292 m μ , corresponding to an energy spread of 173 and 98 kcal., respectively. With this information, the crude level diagram of Fig. 3 may be constructed. The broken lines in the platinum atomic

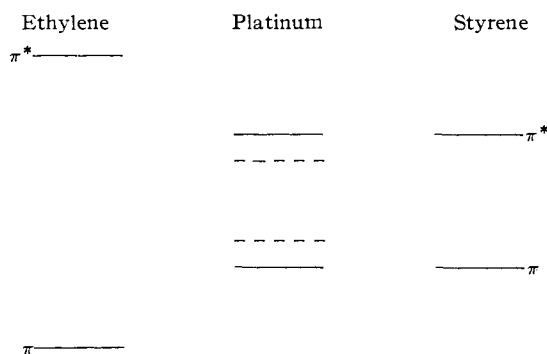


Fig. 3.—Energy levels of orbitals.

orbital diagram represent the d splitting in C₂H₄PtCl₃⁻ where the long wave length b₂ → a₁ band is at 336 m μ . It is important to report that the long wave length band in the spectrum of 1-(pyridine N-oxide)-3-ethylene-2,4-dichloroplatinum(II) occurs at 339 m μ

(ϵ 580), and thus in this compound the d splitting may be assumed to be similar to that in Zeise's salt. However, if this similarity exists, it is difficult to explain on the basis of Fig. 3 why in the competition of styrene and dodecene for a site in UnPtCl₃⁻, the dodecene is favored ($K = 37$), whereas in UnPtCl₂PyO the styrene is favored ($K = 0.052$, Table III). It may be that the PyO with its strong dipole in the direction of the Pt¹⁰ increases the overlap with the diffuse orbitals of styrene very effectively, whereas the overlap increase with the orbitals of dodecene is not as effective.

The "U" shape character of Fig. 1 is probably additional evidence for the double bond character of the UnPt bond and implies that all substituents on PyO favor dodecene in its competition with styrene ($X = H$). Substitution by the electron-releasing CH₃O group ($Z = CH_3O$ as compared to H) probably improves the energy matching of the dodecene-Pt orbitals, whereas the principal effect of $Z = NO_2$ is to encourage back donation from the styrene. When PyO is substituted by any group other than CH₃O, the styrene is favored regardless of the nature of the substituent on styrene (with the exception of $X = H$, $Z = NO_2$).

The effect of substitution on styrene is to compress the styrene levels and on this basis to improve the energy matching with the Pt orbitals. When $X = NO_2$, the styrene complex is always more favored than the dodecene complex. Perhaps solvation effects are important and operate to stabilize the styrene. The most stable styrene complex of all those reported here is the *p*-nitrostyrene complex with the parent PyO as partner.

All attempts at a Hammett σ - ρ correlation to fit all the data were unsuccessful. The work is being continued in an attempt to arrive at a consistent explanation.

Acknowledgment.—The authors wish to thank the Gulf Oil Company for a fellowship which made this work possible and Engelhard Industries for a generous supply of platinum.

(10) A. R. Katritzky, E. W. Randall, and L. E. Sutton, *J. Chem. Soc.*, 1769 (1957).

[A CONTRIBUTION FROM THE BIOLOGICAL INORGANIC CHEMISTRY UNIT, THE JOHN CURTIN SCHOOL OF MEDICAL RESEARCH, THE AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA, AUSTRALIA]

Stereospecific Influences in Metal Complexes Containing Optically Active Ligands. IX. The Equilibrium Ratios and Isolation of Some of the Isomers in the Mixture Tris-((±)-propylenediamine)-cobalt(III) Chloride

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The optical isomers D-bis((+)-propylenediamine)-(-)-propylenediaminecobalt(III) iodide and L-bis((-)-propylenediamine)-(+)-propylenediaminecobalt(III) iodide have been isolated and characterized. The equilibrium constants $D[Co(+)(pn)_3]^{3+}/L[Co(-)(pn)_3]^{3+}$, $L[Co(-)(pn)_3]^{3+}/D[Co(+)(pn)_3]^{3+}$, $L[Co(-)(pn)_2(+)(pn)]^{3+}/D[Co(+)(pn)_2(-)(pn)]^{3+}$, $D[Co(+)(pn)_2(-)(pn)]^{3+}/L[Co(+)(pn)_2(+)(pn)]^{3+} = 2.4$, and $D[Co(+)(pn)(-)(pn)]^{3+}/L[Co(-)(pn)(+)(pn)]^{3+}$, $L[Co(-)(pn)(+)(pn)]^{3+}/D[Co(+)(pn)(-)(pn)]^{3+} = 6.1$ were determined and the stabilities of the isomers have been rationalized with respect to the possible conformations which may be adopted by the propylenediamine rings.

Introduction

A previous paper in this series dealt with the conformational effects and the stabilities of the optical

(1) (a) Deceased. (b) *Notation for Optical Isomers:* D refers to the absolute configuration of the isomer relative to the D(+)[Co(en)₃]²⁺ ion, (+) refers to the sign of rotation of the optically active entity (either the base or the complex) in the Na D line. If the rotation is recorded at another wave length the latter appears as a subscript, *i.e.*, [α]₅₇₈. The literature associated with stereospecificity in metal complexes has denoted D(+)[Co(+)(pn)₃]³⁺ as *DDDD* in the past; in this paper *DDDD* and D[(+)(+)(+)] are equivalent.

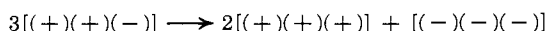
isomers of "tris"-cobalt(III) complexes containing ethylenediamine (en) and (-)-propylenediamine ((-)-pn). It was pointed out that both ethylenediamine

In the usage exemplified by *DDDD*, D referred to the sign of rotation in the Na D line of the complex and *d* was the sign of rotation of the base in the same wave length. Fortunately, in the cobalt(III) propylenediamine complexes the dextrorotatory isomers have the absolute configuration D so that D[*ddd*] is equivalent to D*d*[*ddd*], or D(+)[(+)(+)(+)] or D[(+)(+)(+)].

(2) F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *J. Am. Chem. Soc.*, **85**, 2913 (1963).

and propylenediamine molecules were statistically distributed about the Co(III) ions in all possible combinations, *i.e.* $[\text{Co}(\text{pn})_3]^{3+}$, $[\text{Co}(\text{pn})_2\text{en}]^{3+}$, $[\text{Co}(\text{pn})(\text{en})_2]^{3+}$, and $[\text{Co}(\text{en})_3]^{3+}$ and the difference in stability between optical isomers with the same constitution; for example, *D*- and *L*- $[\text{Co}(-)\text{pn}_2\text{en}]^{3+}$, arose because of the two possible conformations which the coordinated en molecules could adopt.³ Whereas en changed its conformation in going from the *D*→*L* complex configuration (*k*→*k'*) the (-)pn molecule was always constrained to have the methyl group equatorial in both *D*- and *L*-configurations (*k*').

A similar effect has now been observed with $[\text{Co}(\text{pn})_3]^{3+}$ complexes when both (+)- and (-)pn occur together around the Co(III) ion. It has been claimed in the past that these complexes are inherently unstable⁴ and that they disproportionate according to the scheme



but it was found that the "mixed" complexes once formed were quite as inert as the $[\text{Co}(\text{en})_3]^{3+}$ ion.

Results

The $[\text{Co}(\pm)\text{pn}_3]\text{Cl}_3$ reaction mixture was prepared by oxidizing CoCl_2 (1 mole), (\pm)pn (3 moles), and HCl (1 mole) with air in the presence of charcoal. The solid product was chromatographed on a cellulose column with $\text{BuOH-H}_2\text{O-HCl}$ to isolate quantities of the isomers and also on paper to estimate their relative concentrations. Three distinct bands were obtained: the fastest moving contained the racemic pair $\text{D}[\text{Co}(+)\text{pn}_3]\text{Cl}_3$, $\text{L}[\text{Co}(-)\text{pn}_3]\text{Cl}_3$, fraction 1; the middle band contained $\text{D}[\text{Co}(+)\text{pn}_2(-)\text{pn}]\text{Cl}_3$, $\text{L}[\text{Co}(-)\text{pn}_2(+)\text{pn}]\text{Cl}_3$, fraction 2; and the slowest moving band was a mixture of two racemic pairs $\text{D}[\text{Co}(+)\text{pn}(-)\text{pn}_2]\text{Cl}_3$, $\text{L}[\text{Co}(-)\text{pn}(+)\text{pn}_2]\text{Cl}_3$, and $\text{D}[\text{Co}(-)\text{pn}_3]\text{Cl}_3$, $\text{L}[\text{Co}(+)\text{pn}_3]\text{Cl}_3$, fraction 3.

The first and part of the third fractions were identified by chromatography on paper with authentic samples of $\text{D}[\text{Co}(+)\text{pn}_3]\text{Cl}_3$ and $\text{L}[\text{Co}(+)\text{pn}_3]\text{Cl}_3$. Fraction 2 was resolved as the chloride-(+)-tartrate and the less soluble diastereoisomer $\text{D}(+)\text{[Co}(+)\text{pn}_2(-)\text{pn}]\text{Cl}(+)\text{tartrate}$, $[\alpha]_{\text{D}} +91^\circ$, was converted to the chloride, $[\alpha]_{\text{D}} +125^\circ$, and to the iodide, $[\alpha]_{\text{D}} +80^\circ$. The isomer was identified by recovering the mixture of bases in benzene and it was shown that it contained pn with $[\alpha]_{\text{D}} +11.5^\circ$, *i.e.* one third the rotation of the pure isomer $[\alpha]_{\text{D}} +34.8^\circ$.⁵ The complex in the filtrate from the first diastereoisomer was then converted to the chloride(-)-tartrate salt and was isolated as the less soluble $\text{L}(-)\text{[Co}(+)\text{pn}(-)\text{pn}_2]\text{Cl}(-)\text{tartrate}$, $[\alpha]_{\text{D}} -90^\circ$. The corresponding iodide $[\alpha]_{\text{D}} -78^\circ$ gave $[\alpha]_{\text{D}} -11.2^\circ$ for the extracted propylenediamine in benzene. The sign and magnitude of the rotations of propylenediamine extracted from these optical isomers identify them clearly as $\text{D}(+)\text{[Co}(+)\text{pn}_2(-)\text{pn}]\text{I}_3$ and $\text{L}(-)\text{[Co}(-)\text{pn}_2(+)\text{pn}]\text{I}_3$. It could not be determined whether these isomers were *cis* or *trans* (due to the position of the methyl group) or whether they were a mixture of *cis* and *trans*.

A similar resolution procedure for fraction 3 gave a very soluble diastereoisomer from methanol. It was recrystallized several times to constant rotation $[\alpha]_{\text{D}} +205^\circ$, but the propylenediamine extracted from the corresponding iodide gave $[\alpha]_{\text{D}} -24^\circ$ in benzene which showed that the resolved sample contained both $\text{D}[\text{Co}(-)\text{pn}_2(+)\text{pn}]\text{I}_3$ and $\text{D}[\text{Co}(-)\text{pn}_3]\text{I}_3$ or

was imperfectly resolved $\text{D}[\text{Co}(-)\text{pn}_3]\text{I}_3$, $\text{L}[\text{Co}(+)\text{pn}_3]\text{I}_3$. The former is more likely as it will be shown later that most of fraction 3 is $\text{D}[\text{Co}(-)\text{pn}_2(+)\text{pn}]^{3+} + \text{L}[\text{Co}(+)\text{pn}_2(-)\text{pn}]^{3+}$. Numerous attempts to separate this fraction, by fractional crystallization of both the iodide and the chloride-(+)-tartrate and by chromatography with a variety of solvents, were all unsuccessful.

Discussion

Since the $\text{D}[\text{Co}(+)\text{pn}_3]^{3+}/\text{L}[\text{Co}(+)\text{pn}_3]^{3+}$ equilibrium constant was found to be 15,² the concentration of $\text{L}[(+)\text{pn}_3]^{3+}$ plus $\text{D}[-]\text{pn}_3]^{3+}$ in fraction 3 must be $1/16$ of fraction 1. It is possible now to determine the relative ratios of all the optical isomers in the equilibrated mixture even though fraction 3 could not be separated. The relative isomer concentrations are given in Table I. The difference between the stabilities of the $\text{D}[\text{Co}(+)\text{pn}_2(-)\text{pn}]^{3+}$ and $\text{L}[\text{Co}(+)\text{pn}_2(-)\text{pn}]^{3+}$ ions, which statistically are equally probable, arises largely from the conformational effects due to the propylenediamine units. The conformations in the *D*-isomer (in Corey and Bailar's notation³) would be *Dkkk'* and in the *L*-form *Lkkk'*. The *k*-conformation in the *D* ion is calculated to be more stable than the *k'* by about 0.6 kcal./mole³ and similarly the *k'* conformation in the *L*-configuration is more stable than the *k*-conformation. Thus, since the methyl group must always remain equatorial, in the change from the *D*→*L* configuration the conformations remain constant and *Dkkk'* should be more stable than *Lkkk'* by about 0.6 kcal./mole, which is roughly the amount observed, (Table I). A similar argument applies to the stability difference between the $\text{D}[\text{Co}(+)\text{pn}_3]^{3+}$ and $\text{D}[\text{Co}(+)\text{pn}_2(-)\text{pn}]^{3+}$ isomers: the conformations here are *kkk* and *kkk'*, respectively, and the energy difference again should be about 0.6 kcal./mole ($\Delta G_{\text{obsd}} = 0$). However, there is also a statistical factor involved in that the isomers containing both (+)- and (-)pn are preferred over those with only one optical form of pn in the ratio of 3/1 where $(+)\text{pn}/(-)\text{pn} = 1$. This effect raises the stability of the "mixed" isomer and was shown more clearly when the $(+)\text{pn}/(-)\text{pn}$ ratio was changed from 1 to 2, Table I; as the $(+)\text{pn}$ increased so the concentration of the $[\text{Co}(+)\text{pn}_3]^{3+}$ species increased.

In the following analysis the statistical term is treated solely as an entropy effect and the conformational effect as an enthalpy term. Also since the four "tris" and four "mixed" species cannot be differentiated statistically, only the equilibrium constant $K = \text{tris}/\text{mixed}$ is considered. For $(+)\text{pn}/(-)\text{pn} = 1$ the statistical factor gives $K = 0.33$ ($\Delta H = 0$ assumed) which leads to a $T\Delta S$ value of -0.66 kcal./mole at 25°.

An estimate of the conformational effect may be obtained from the reaction mixture $1\text{Co}:1(-)\text{pn}:2\text{en}^2$ where $[\text{Co}(-)\text{pn}_3]^{3+}$, $[\text{Co}(-)\text{pn}_2\text{en}]^{3+}$, $[\text{Co}(-)\text{pn}(\text{en})_2]^{3+}$ and $[\text{Co}(\text{en})_3]^{3+}$ formed in statistical proportions. Assuming $\text{L}[\text{Co}(-)\text{pn}_3]^{3+}$, $\text{L}[\text{Co}(-)\text{pn}_2\text{en}]^{3+}$, $\text{L}[\text{Co}(-)\text{pn}(\text{en})_2]^{3+}$, and $\text{L}[\text{Co}(\text{en})_3]^{3+}$, all with *k'k'k'* conformations, are equally stable, then $\text{D}[\text{Co}(-)\text{pn}(-)\text{pn}(-)\text{pn}]^{3+}$ (*k'k'k'*), $\text{D}[\text{Co}(-)\text{pn}(-)\text{pn}(\text{en})]^{3+}$ (*k'k'k*), $\text{D}[\text{Co}(-)\text{pn}(\text{en})(\text{en})]^{3+}$ (*k'kk*), and $\text{D}[\text{Co}(\text{en})(\text{en})(\text{en})]^{3+}$ (*kkk*) must be in the ratio 0.07, 0.13, 0.45, 1, respectively. This leads to a tris/mixed ratio of 1.07/0.58 and an enthalpy term of -0.36 kcal./mole. Combining both effects the free energy change for the equilibrium $\text{tris}/\text{mixed} = -0.36 + 0.66 = +0.30$ kcal./mole, which leads to an equilibrium constant $K = 0.60$ (found 0.76). When the $(+)\text{pn}/(-)\text{pn}$ ratio = 2 the statistical factor alters to 0.5 but the conformational effect is unchanged; hence $\Delta G = -0.36 + 0.41 = +0.05$ kcal./mole and

(3) E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).

(4) F. M. Jaeger, "Optical Activity and High Temperature Measurements," McGraw-Hill Book Co., Inc., New York, N. Y., 1930, p. 155.

(5) F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Am. Chem. Soc.*, **81**, 290 (1959).

TABLE I

THE CONCENTRATIONS (%) AND EQUILIBRIUM CONSTANTS FOR THE RACEMIC PAIRS IN THE REACTION MIXTURE $[\text{Co}(\pm)\text{pn}_3]\text{Cl}_3$

Racemic pairs	Isomer concn. (+)pn/(-)pn = 1	K_{20°	$\Delta G_{\text{obsd.}}$ kcal./mole	Isomer concn. (+)pn/(-)pn = 2
$\text{D}[\text{Co}(+)\text{pn}_3]^{3+}, \text{L}[\text{Co}(-)\text{pn}_3]^{3+}$	40.5	$\frac{\text{D}[\text{Co}(+)\text{pn}_3]^{3+}, \text{L}[\text{Co}(-)\text{pn}_3]^{3+}}{\text{D}[\text{Co}(+)\text{pn}_2(-)\text{pn}]^{3+}, \text{L}[\text{Co}(-)\text{pn}_2(+)\text{pn}]^{3+}} = 1$	0.0	48.5
$\text{D}[\text{Co}(+)\text{pn}_2(-)\text{pn}]^{3+}, \text{L}[\text{Co}(-)\text{pn}_2(+)\text{pn}]^{3+}$	40.3	$\frac{\text{D}[\text{Co}(+)\text{pn}_2(-)\text{pn}]^{3+}}{\text{L}[\text{Co}(+)\text{pn}_2(-)\text{pn}]^{3+}} = 2.4$	-0.52	36.0
$\text{D}[\text{Co}(+)\text{pn}(-)\text{pn}_2]^{3+}, \text{L}[\text{Co}(-)\text{pn}(+)\text{pn}_2]^{3+}$	16.5	$\frac{\text{D}[\text{Co}(+)\text{pn}(-)\text{pn}_2]^{3+}, \text{L}[\text{Co}(-)\text{pn}(+)\text{pn}_2]^{3+}}{\text{D}[\text{Co}(-)\text{pn}_3]^{3+}, \text{L}[\text{Co}(+)\text{pn}_3]^{3+}} = 6.1$	-1.1	12.3
$\text{D}[\text{Co}(-)\text{pn}_3]^{3+}, \text{L}[\text{Co}(+)\text{pn}_3]^{3+}$	2.7			3.2

$K = 0.92$ (found 1.07). Also, if it is assumed that the energy difference between conformations is ~ 0.5 kcal./mole, then the calculated values for the equilibrium constant are 0.58 and 0.89 for $(+)\text{pn}/(-)\text{pn} = 1$ and $(+)\text{pn}/(-)\text{pn} = 2$, respectively. From the agreement between the observed and calculated equilibrium ratios it would seem that the conformational factor and the statistical factor, where relevant, are the two principal contributions in determining the isomer ratios.

Experimental

Reaction Mixture.—Cobalt(II) chloride 6 hydrate (71 g.), HCl (60 ml., 5 N), and (\pm) -propylenediamine (74 g.) in water (1.5 l.) were oxidized in a stream of air in the presence of charcoal (30 g.) for 12 hr. The solution was filtered and made slightly acid with HCl, evaporated to dryness, and the dry *luteo* product finely powdered (125 g.).

Separation of the Isomers.—Whatman cellulose powder (500 g.) suspended in 1-butanol (water satd.) was packed in a column (14 in./3 in.). The *luteo* product (2 g.) in wet butanol (400 ml.) and HCl (1 ml., 10 N) was heated to 35° to effect dissolution and dry butanol (200 ml.) then added. This solution was adsorbed on the column and eluted with butanol (500 ml. of water satd.) and HCl (10 ml., 10 N). The fractions were extracted with water and evaporated to dryness at 40° . The procedure was repeated until sufficient sample was obtained for resolution (10 g.). The sample was then recrystallized from water with acetone.

D-(+)-Bis-(+)-propylenediamine(-)-propylenediaminecobalt(III) Iodide.—Fraction 2 (10 g.) was dissolved in warm water (50 ml.), $\text{Ag}_2(+)\text{-tartrate}$ (9 g.) added, and the mixture shaken for 10 min. Methanol was then added to the filtered solution and $\text{D}(+)\text{[Co}(+)\text{pn}_2(-)\text{pn}]\text{Cl}(+)\text{tartrate}$ crystallized out. The diastereoisomer was recrystallized several times from aqueous methanol to constant rotation $[\alpha]_{\text{D}} + 91^\circ$.

Anal. Calcd. for $\text{Co}(\text{C}_3\text{H}_{10}\text{N}_2)_3\text{ClC}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}$: C, 31.88; H, 8.20; N, 14.88. Found: C, 31.56; H, 7.7; N, 14.59.

It was treated with a little HCl (10 N) and the complex chloride was precipitated with acetone and recrystallized from aqueous

ethanol; $[\alpha]_{\text{D}} + 125^\circ$, $[\alpha]_{578} + 160^\circ$, $[\alpha]_{546} + 380^\circ$. The chloride was converted to the iodide by adding excess LiI to an aqueous solution of the chloride and the specific rotations for the complex iodide were $[\alpha]_{\text{D}} + 80^\circ$, $[\alpha]_{578} + 100^\circ$, and $[\alpha]_{546} + 246^\circ$.

The pn was extracted after decomposing the complex with Na_2S_2 and gave $[\alpha]_{\text{D}} + 11.5^\circ$ in benzene.

Anal. Calcd. for $[\text{Co}(\text{C}_3\text{H}_{10}\text{N}_2)_3]\text{I}_3$: C, 16.33; H, 4.57; N, 12.70. Found: C, 16.37; H, 4.98; N, 12.46.

L-(-)-Bis-(-)-propylenediamine-(+)-propylenediaminecobalt(III) Iodide.—The filtrate from the diastereoisomer above was reconverted to the chloride (5.2 g.) and then to the chloride(-)-tartrate with $\text{Ag}_2(-)\text{-tartrate}$ (4.6 g.). The pure diastereoisomer $\text{L}[\text{Co}(-)\text{pn}_2(+)\text{pn}]\text{Cl}(-)\text{tartrate}$, $[\alpha]_{\text{D}} - 90^\circ$, was obtained as above.

The iodide obtained from an aqueous solution of the diastereoisomer with LiI gave $[\alpha]_{\text{D}} - 78^\circ$, $[\alpha]_{578} - 100^\circ$, and $[\alpha]_{546} - 240^\circ$ and the extracted pn had a specific rotation $[\alpha]_{\text{D}} - 11.2^\circ$.

Anal. Calcd. for $[\text{Co}(\text{C}_3\text{H}_{10}\text{N}_2)_3]\text{I}_3$: C, 16.33; H, 4.57; N, 12.70. Found: C, 16.32; H, 4.60; N, 12.35.

Relative Concentrations of the Fractions.—A sample of the reaction mixture prepared at 20° was spread in a strip on Whatman 3 MM chromatography paper and eluted overnight with a 1-butanol- H_2O -HCl (60:30:10) mixture. The three fractions which separated were cut out and the complex eluted off the paper with water. The relative concentrations were then measured spectrophotometrically at 470 m μ .

fract. 1, $\text{D}[\text{Co}(+)\text{pn}_3]\text{Cl}_3, \text{L}[\text{Co}(-)\text{pn}_3]\text{Cl}_3$, fastest moving, 40.0–41%

fract. 2, $\text{D}[\text{Co}(+)\text{pn}_2(-)\text{pn}]\text{Cl}_3, \text{L}[\text{Co}(-)\text{pn}_2(+)\text{pn}]\text{Cl}_3$, 40.5–40%

fract. 3, $\text{D}[\text{Co}(+)\text{pn}(-)\text{pn}_2]\text{Cl}_3, \text{L}[\text{Co}(-)\text{pn}(+)\text{pn}_2]\text{Cl}_3, \text{D}[\text{Co}(-)\text{pn}_3]\text{Cl}_3, \text{L}[\text{Co}(+)\text{pn}_3]\text{Cl}_3$, slowest moving, 19.5–19%

The second set of values was obtained by repeating the whole procedure on another sample.

The reaction mixture prepared using $(-)\text{pn}/(+)\text{pn} = 2$ gave the following concentrations: fraction 1, 48.5%; fraction 2, 36.0%; fraction 3, 15.5%.

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[CONTRIBUTION FROM THE EVANS AND MCPHERSON CHEMICAL LABORATORIES, THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO]

The Reactions of Coordinated Ligands. VII. Metal Ion Control in the Synthesis of Chelate Compounds Containing Pentadentate and Sexadentate Macrocyclic Ligands

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The metal ion mediation of the Schiff base condensation reactions between 2,6-diacetylpyridine and two polyethylenepolyamines, triethylenetetraamine, and tetraethylenepentamine, has led to the synthesis of unique complexes containing macrocyclic chelate ligands that are, respectively, pentadentate and sexadentate. The ligands have been prepared in their highly crystalline spin-paired iron(III) complexes. The complexes have been characterized through magnetic, conductance, and spectral measurements.

Introduction

During the past few years, a number of dramatic examples have served to illustrate the ability of a metal ion to serve as a template in the course of reactions that

lead to the formation of macrocyclic organic ligands. Prime examples from these Laboratories have involved the reaction of alkyl dihalides with α -diketobis(mercaptoethyl)nickel(II) complexes² and the cyclic

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(2) M. C. Thompson and D. H. Busch, *Chem. Eng. News*, **40**, No. 38, 57 (1962).