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The Tris[(±)-trans-1,2-cyclohexanediamine]cobalt(III) System

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The isomers $[\text{Co}((\pm)\text{chxn})_3]\text{Cl}_3$ (chxn = trans-1,2-cyclohexanediamine) comprise two catoptric series with the configurations Δ and Λ around the metal ion. The chelate rings formed by the ligands (-)-R,R-chxn and (+)-S,S-chxn have the conformations λ and δ , respectively. For each of the configurational series the possible ligand conformations give rise to four diastereoisomers which have been named lel_3 , lel_2ob , ob_2lel , and ob_3 . These eight isomers have been isolated and characterized. The equilibrium between the isomers has been established at 100 °C and the standard free energies for the interconversion between the diastereoisomers have, after a statistical correction, been interpreted in a ring-pair relationship model whose two parameters fully account for the equilibrium data.

Introduction

The two isomers of tris[(-)-*trans*-1(*R*),2(*R*)-cyclohexanediamine]cobalt(III) chloride, $[\text{Co}((-)\text{chxn})_3]\text{Cl}_3$, have been known¹ for some time and the corresponding isomers of rhodium(III),² iridium(III),³ and chromium(III)⁴ have recently been isolated. The stereochemical difference between the two isomers may be characterized as an interplay of the conformation of the five-membered chelate rings and the configuration around the central metal ion. The chelate ring formed by the ligand, (-)chxn, has the conformation λ , which when associated with the configurations Δ and Λ gives rise to the diastereoisomer ions $\Delta\text{-}[\text{Co}((-)\text{chxn})_3\text{-}\lambda\lambda\lambda]^{3+}$ and $\Lambda\text{-}[\text{Co}((-)\text{chxn})_3\text{-}\lambda\lambda\lambda]^{3+}$.

The discussion of the isomerism and nomenclature of tris(diamine) complexes^{5,6} containing racemic chxn will be summarized briefly.

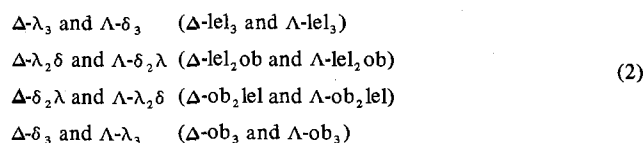
The diastereochemical relationship between the conformation of each chelate ring and the configuration of the tris complex can be characterized by the symbols lel and ob defined by

$$\text{lel} \equiv \lambda(\Delta) \text{ or } \delta(\Lambda) \quad (1)$$

$$\text{ob} \equiv \delta(\Delta) \text{ or } \lambda(\Lambda)$$

The symbols lel and ob refer to the direction of the bond between the carbon atoms attached to the ligating nitrogen atoms, being almost parallel and oblique, respectively, to the threefold axis defined by the three edges of the octahedron which are spanned by the chelate rings. Thus the symbol $\lambda(\Delta)$, for example, means the conformation λ in the configuration Δ . If symmetry operations are applied to the entries of eq 1, it is seen that the symbols lel and ob are invariant to proper as well as to improper rotations,⁶ whereas the chirality symbols are changed into their catoptric (= enantiomeric) forms under the latter operations. For example, application of an improper rotation to the lel system $\lambda(\Delta)$ yields $\delta(\Lambda)$, which is also lel . It follows that the complexes mentioned above can be characterized⁷ as $\Delta\text{-lel}_3$ and $\Lambda\text{-ob}_3$, respectively. Originally, Corey and Bailar⁸ used the designation lel and ob for such isomers, but this notation is not sufficient for the present purpose and has accordingly been modified⁷ because we want to consider complexes which simultaneously contain chelate rings of lel and ob type.

In the case when $[\text{Co}(\text{chxn})_3]^{3+}$ is prepared from racemic trans-1,2-cyclohexanediamine, one obtains four racemic pairs of complexes



In the present work the eight isomers have been separated, the equilibrium ratios have been determined, and the circular dichroism spectra have been measured.

The two isomers $\Delta\text{-lel}_3$ and $\Lambda\text{-ob}_3$ that can be formed from (-)chxn can easily be separated by recrystallization from boiling water by addition of hydrochloric acid, since the lel_3 isomer and the ob_3 isomer have solubility minima in ca 0.4 and ca. 4 M hydrochloric acid, respectively.

A rather special technique is employed for the separation of all eight isomers. A cation exchanger is used with sodium ions as eluting agents but with a suitable anion to effect the separation. Phosphate ions are used in the separation of the four racemic pairs which are eluted in the sequence of (2) with the lel_3 catoptromers leaving the column first. Each racemic pair is then sorbed separately on a new column and separated by the method of Yoshikawa and Yamasaki⁹ using ammonium (+)-tartrate. In each case the Λ catoptromer leaves the column first, as also found⁹ for the tris(ethylenediamine)cobalt(III) system. The column separations are analogous to those of the tris[(±)-1,2-propanediamine]cobalt(III) system.⁵

Experimental Section

trans-1,2-Cyclohexanediamine was resolved as described by Galsbol, Steenbol, and Sorensen.²

$\Delta\text{-}[\text{Co}(+)\text{chxn})_3\text{-}\delta\delta\delta]\text{Cl}_3 \cdot 4\text{H}_2\text{O}$ and $\Lambda\text{-}[\text{Co}(+)\text{chxn})_3\text{-}\delta\delta\delta]\text{Cl}_3 \cdot 1.5\text{H}_2\text{O}$. A 170-g sample of trans- $[\text{Co}(\text{py})_4\text{Cl}_2]\text{Cl} \cdot 6\text{H}_2\text{O}$ (0.29 mol) was dissolved in 400 ml of methanol at 40 °C and mixed into a solution of 100 g of (+)chxn (0.88 mol) dissolved in 600 ml of methanol at 40 °C. While being stirred the mixture was allowed to cool and was then filtered. The precipitate was washed with methanol and dried; yield 130 g of tris complex, mainly $\Lambda\text{-lel}_3$.

Before the separation of the two isomers $\Lambda\text{-lel}_3$ and $\Delta\text{-ob}_3$ it is convenient to establish the equilibrium between them. Accordingly 130 g of the tris complex was dissolved in 1450 ml of water at 100 °C, ca. 1 g of (+)chxn was added, and then the pH was adjusted to 7. After addition of 8 g of charcoal and refluxing for 2 h the hot solution was filtered and partially evaporated in vacuo to yield ca. 100 g of $\Lambda\text{-lel}_3$. The residue which contains ca. 9 g of $\Delta\text{-ob}_3$ (cf. Table II) was also evaporated to dryness.

The crude $\Lambda\text{-lel}_3$ isomer was reprecipitated using the following general procedure. x g of $\Lambda\text{-lel}_3$ was dissolved in ca. 8x ml of water at 100 °C. After filtration 0.8x ml of 4 M hydrochloric acid was added and the solution was cooled on ice and filtered. The precipitate

Table I. Spectral Data of Δ -[Co(chxn)₃]Cl₃^a

Δ -lel ₃		Δ -lel ₂ ob		Δ -ob ₂ lel		Δ -ob ₃	
Abs $\bar{\nu}_{\max}$ (ε)	CD $\bar{\nu}_{\text{ext}} (\epsilon_1 - \epsilon_d)$	Abs $\bar{\nu}_{\max}$ (ε)	CD $\bar{\nu}_{\text{ext}} (\epsilon_1 - \epsilon_d)$	Abs $\bar{\nu}_{\max}$ (ε)	CD $\bar{\nu}_{\text{ext}} (\epsilon_1 - \epsilon_d)$	Abs $\bar{\nu}_{\max}$ (ε)	CD $\bar{\nu}_{\text{ext}} (\epsilon_1 - \epsilon_d)$
21.19 (101)	20.04 (-2.45) 22.5 (+0.77)	21.14 (102)	20.20 (-2.76) 23.9 (0.0)	21.14 (102)	20.49 (-3.51) 25.6 (-0.05)	21.14 (101)	20.88 (-4.45)
29.24 (94)	28.7 (-0.20)	29.24 (98)	28.2 (-0.22)	29.24 (98)	27.7 (-0.14)	29.15 (93)	<i>b</i> 29.1 (+0.03) 31.5 (-0.03) 33.9 (-0.01) 37.6 (-0.1) 43.9 (+17)
44.76 (2.79 × 10 ⁴)	44.1 (+48)	44.61 (2.89 × 10 ⁴)	43.7 (+38)	44.55 (2.89 × 10 ⁴)	43.7 (+28)	44.50 (2.95 × 10 ⁴)	49.5 (-7)
	~51 (-1)		~51 (-4)		~50 (-6)		

^a The measurements were carried out on Δ -lel₃, Δ -lel₂ob, Δ -ob₂lel, and Δ -ob₃. The concentrations, ca. 10⁻² M (visible) and ca. 4 × 10⁻⁵ M (ultraviolet) in water, were determined by atomic absorption. The molar absorptivity ϵ at the maxima of the absorption spectra and the molar circular dichroism $\epsilon_1 - \epsilon_d$ at the extrema of the CD spectra are given in parentheses following the corresponding positions $\bar{\nu}_{\max}$ and $\bar{\nu}_{\text{ext}}$ in units of 1000 cm⁻¹. The spectra are qualitatively similar to those of the Δ -[Co(pn)₃]Cl₃ system (ref 5, Figure 4) and the present table is built up in the same way as Table II of ref 5. At 50 000 cm⁻¹, ϵ is ≈ 10⁴ for all isomers. ^b In comparison with the Δ -[Co(pn)₃]Cl₃ system, no distinct extrema were found in the CD spectra of the Δ -[Co(chxn)₃]Cl₃ system at these positions.

was washed with water at 0 °C and dried in the air; yield ca. 0.75 g of Δ -lel₃. After three reprecipitations the CD spectrum was constant; yield 45 g of Δ -[Co((+)chxn)₃- $\delta\delta\delta$]Cl₃·~4H₂O (the content of H₂O varies between 3.5 and 4.5).

The Δ -ob₃ isomer was recovered in the following way from the 30 g of residue mentioned above. y g of Δ -ob₃ (vide infra) was dissolved in ca. 23 y ml of water at 100 °C. After filtration 11 y ml of 12 M hydrochloric acid was added and the solution was cooled in ice and filtered. The precipitate was washed with 4 M hydrochloric acid and dried in the air; yield ca. 0.8 y g of Δ -ob₃. In the first reprecipitation y denotes the amount of Δ -ob₃ to be expected (~9 g) and in the next reprecipitations y equals the actual amount of precipitate. After three such reprecipitations the CD spectrum was constant; yield 4 g of Δ -[Co((+)chxn)₃- $\delta\delta\delta$]Cl₃·1.5H₂O. The catoptomers, Δ -lel₃ and Δ -ob₃, were also prepared.

The particular sample of Δ -lel₃ prepared in this work has been used in the correlation¹² of the absolute configuration¹⁰ of the optically active complexes [M^{III}(chxn)₃-lel₃]³⁺, where M = Cr, Co, Rh, and Ir, by means of x-ray powder photographs of the active racemates.

Crystals of the present samples of Δ -lel₂ob and Δ -ob₃ have been used in the x-ray determination of the absolute configuration^{11,17} of Δ -[Co((+)chxn)₂(-)chxn- $\delta\delta\delta$]Cl₃·5H₂O and Δ -[Co((-)chxn)₃- $\lambda\lambda\lambda$]Cl₃·1.5H₂O, respectively.

Preparation, Separation, and Resolution of Racemic Complexes. Racemic [Co(chxn)₃-lel₃]Cl₃·H₂O was prepared by precipitation of equal amounts of the optically active forms. Recrystallization from 0.5 M hydrochloric acid was necessary to ensure a vanishing CD spectrum. Equilibrium between the eight isomers [see (2)] was established by use of charcoal as described above. The four racemic pairs were separated⁵ on a column using Sephadex SE-C25 cation exchanger and 0.2 M trisodium phosphate as eluent.

Each pair off the column was purified as follows. The sample was neutralized with hydrochloric acid, diluted with water, resorbed on a new column, washed with water, and eluted with 1 M hydrochloric acid. The eluate was evaporated to dryness and the complex was recrystallized from 0.5 M hydrochloric acid. It turns out that the content of water in the crystals varies somewhat. On an average we have found for the racemic chlorides: lel₃·H₂O, lel₂ob·2H₂O, ob₂lel·4H₂O, and ob₃·2H₂O.

The resolution of each racemic pair was made⁵ by using 0.1 M (NH₄)₂(+)tart as eluent, and the A fraction was the first one eluted. Purification was made as described for the racemic pairs. The optically active lel₂ob and ob₂lel chlorides contain around 1 mol of water of crystallization.

Analyses. Cobalt analyses were carried out with a Perkin-Elmer 403 atomic absorption spectrophotometer to an accuracy of ≤1%. Analyses for C, H, N, and Cl were carried out at the microanalytical laboratory of the H. C. Orsted Institute. The ratio C:N:Cl was found to be in agreement with the formulas whereas the content of water was found to vary.

Absorption and Circular Dichroism Spectra. Spectra were measured on aqueous solutions with a Cary 14 spectrophotometer and a Jouan Dicrographe 2B. In order to provide reliable figures for the molar absorptivity the cobalt concentrations were determined by atomic

absorption. The spectral results are given in Table I.

Determination of Relative Equilibrium Constants. a. Racemic Complexes. A 0.7-mmol amount of racemic [Co(chxn)₃-lel₃]Cl₃ was dissolved in 10 ml of water. A 10-ml aliquot of 0.105 M racemic chxn·2HCl was added and pH was adjusted to 7.0 with 2 M sodium hydroxide. A 10-mg sample of charcoal (Medicinsk A, Struers⁵) was added and the mixture was refluxed for 30 min. While the mixture was hot, the equilibrium was quenched with 2 ml of 1 M hydrochloric acid.¹⁸ In two experiments the acid was added to the reaction mixture which was then filtered (indicated by footnote *a* in Table II), and in two other experiments the hot reaction mixture was filtered into the acid. The four racemic pairs were then separated on a column. The content of cobalt in each fraction off the column was measured relative to the solution placed on the column. The results of the four independent experiments are given in Table IIa.

b. Complexes with (-)chxn. A 0.7-mmol sample of Δ -[Co((-)chxn)₃]Cl₃ and 1.05 mmol of (-)chxn·2HCl were brought to equilibrium on charcoal (pH 7.0, 100 °C), quenched and separated as described in part a. The results of four independent experiments are given in Table IIb.

c. Ratio of Free Diamine, [(-)chxn]/[(+)chxn] = 2.01, at Equilibrium. The philosophy behind this experiment has been described⁵ previously. By use of the equilibrium constants of Table IIc one can prearrange the experimental conditions in such a way that the ratio between the concentrations of free (-)chxn and (+)chxn at equilibrium is equal to 2. A 4.99-mmol sample of Δ -[Co((-)chxn)₃]Cl₃, 1.40 mmol of (-)chxn·2HCl, and 6.10 mmol of (+)chxn·2HCl were dissolved in 140 ml of water, mixed with 70 mg of charcoal, and refluxed for 30 min. After quenching, the isomers were separated and resolved and the content of cobalt was measured in each fraction. The results are presented in Table III.

Adsorption on Charcoal. In order to assess the influence of the charcoal on the equilibrium data, the amount of charcoal was increased. A 2.5-g sample of Δ -[Co((-)chxn)₃]Cl₃ and 1.0 g of (-)chxn·2HCl were dissolved in 100 ml of H₂O. A 2.5-g amount of charcoal was added, pH was adjusted to 7.0, and the mixture was refluxed for 30 min. The boiling mixture was then poured into liquid nitrogen and placed on a glass filter. The solution was removed by suction as it melted to give 75 ml that contained 1.46 g of complex with the composition Δ -ob₃: Δ -lel₃ = 0.067. The charcoal was extracted with water to give 0.94 g of complex with the composition Δ -ob₃: Δ -lel₃ = 0.034.

Discussion

The equilibrium between the isomers in the [Co(chxn)₃]³⁺ system was established on charcoal at 100 °C and pH 7.0. Then the equilibrium was quenched in two ways, either by adding acid before the charcoal was removed or vice versa. It can be seen from Table II that there is no detectable difference between the two procedures. This is as one would expect since an experiment showed that, under the conditions at which the equilibria of Tables II and III were established, only approximately 0.8% of the complex is adsorbed on the

Table II. Equilibrium Isomer Distribution in the [Co(chxn)₃]³⁺ System at 100 °C

a. Equilibria Involving Racemic Cyclohexanediamine ^b				
Isomer	Composition, %			
	Expt 1 ^a	Expt 2	Expt 3 ^a	Expt 4
Δ,Δ-lel ₃	46.74	46.52	46.67	47.41
Δ,Δ-lel ₂ ob	34.69	34.19	34.44	35.10
Δ,Δ-ob ₂ lel	13.76	13.68	14.35	14.51
Δ,Δ-ob ₃	3.22	3.29	3.26	3.27
b. Equilibrium Involving (-)-Cyclohexanediamine ^c				
Isomer	Composition, %			
	Expt 5 ^a	Expt 6	Expt 7 ^a	Expt 8
Δ-lel ₃	91.85	94.13	93.37	92.69
Δ-ob ₃	6.70	6.89	6.96	6.57
c. Equilibrium Constants ^d				
K	Mean value	Std dev	Correln coeff ^e	
[lel ₂ ob]/[lel ₃]	0.742	0.007		
[ob ₂ lel]/[lel ₃]	0.302	0.003	0.47	
[ob ₃]/[lel ₃]	0.0712	0.0008	0.23	0.23

^a The equilibrium was quenched with hydrochloric acid before filtering the solution from the charcoal; see the text. ^b Relative isomer distribution in four equilibrium mixtures of the composition (+)chxn:(-)-chxn = 1.00 and Co:chxn = 1:4.5. ^c Relative isomer distribution in four equilibrium mixtures of the composition Co:(-)-chxn = 1:4.5. ^d The equilibrium constants were calculated from the data given in parts a and b and were obtained by assuming that the weight of the figures for the ob₃ isomers is half of that of the other figures. ^e The three numbers given here are the correlation coefficients set up as the part of the correlation matrix below the diagonal.

Table III. Equilibrium Isomer Distribution at 100 °C of an Equilibrium Mixture Having a Ratio of Free (i.e., Not Complex Bound) Diamine, (-)chxn:(+)chxn, Equal to 2.01^a

Isomer	Mixture composition, %	
	Exptl	Calcd ⁵
Δ-lel ₃	6.2	6.2
Δ-lel ₂ ob	50.6	50.5
Δ-lel ₂ ob	8.7	9.3
Δ-lel ₂ ob	17.5	18.6
Δ-ob ₂ lel	7.7	7.6
Δ-ob ₂ lel	3.2	3.8
Δ-ob ₃	3.0	3.6
Δ-ob ₃		0.4

^a The composition of the initial mixture, which has been calculated (cf. ref 5) by means of the constants from Table IIc, is Co:(-)-chxn:(+)chxn = 1:3.28:1.22 and Co:chxn = 1:4.5.

charcoal, so that the fact that the ratio of lel₃ to ob₃ is twice that in the solution does not influence the equilibrium data determined.

The equilibrium constants for the [Co(chxn)₃]³⁺ system, Table IIc, have been transformed into the standard free energies ($T = 373$ K) shown in Table IVa. For comparison the corresponding set of data for the [Co(pn)₃]³⁺ system has been recalculated from the data in Table I, column 1, of ref 5.

The ΔH° terms of Table IVb are obtained by correcting the ΔG° values for that part of the entropy term, $T\Delta S^\circ$, which arises from lel₂ob and ob₂lel being 3 times more probable than lel₃ and ob₃. This correction⁵ corresponds to the statistical effect of Bjerrum¹³ and Bjerrum.¹⁴

The different stability of the isomers can be rationalized in terms of the mutual interactions between the ligands by means of the ring-pair relationship model.⁵ In this model the ob₃ and lel₃ complexes are characterized by containing three ob-ob and three lel-lel relationships, respectively. Similarly, the ob₂lel and the lel₂ob complexes have two lel-ob relationships

Table IV. Energy Differences between the Isomers: a Comparison between the Tris(*trans*-1,2-cyclohexanediamine)cobalt(III) and Tris(1,2-propanediamine)cobalt(III)⁵ Systems at 373 K

	Part a ^a							
	[Co(chxn) ₃] ³⁺				[Co(pn) ₃] ³⁺			
	Std				Std			
	Exptl	dev	Calcd	Diff	Exptl	dev	Calcd	Diff
ΔG° (lel ₂ ob → lel ₃)	-0.93	0.03	-0.96	+0.03	+0.49	0.04	+0.34	+0.15
ΔG° (ob ₂ lel → lel ₃)	-3.72	0.03	-3.70	-0.02	-2.09	0.04	-2.01	-0.08
ΔG° (ob ₃ → lel ₃)	-8.20	0.03	-8.22	+0.02	-6.85	0.07	-7.05	+0.20
	Part b ^b							
	[Co(chxn) ₃] ³⁺				[Co(pn) ₃] ³⁺			
	Calcd	Std dev			Calcd	Std dev		
ΔH° (lel ₂ ob → lel ₃)	-4.34	0.03			-2.92	0.04		
ΔH° (ob ₂ lel → lel ₃)	-7.13	0.03			-5.50	0.04		
ΔH° (ob ₃ → lel ₃)	-8.20	0.03			-6.85	0.07		
	Part c ^c							
	[Co(chxn) ₃] ³⁺				[Co(pn) ₃] ³⁺			
	Calcd	Std dev			Calcd	Std dev		
ΔH° (lel-ob → lel-lel)	-2.18	0.02			-1.5	0.1		
ΔH° (ob-ob → lel-lel)	-2.74	0.02			-2.3	0.1		

^a Experimental ΔG° values with standard deviations together with ΔG° values as calculated by means of eq 3 and the parameters of part c. The differences between experimental and calculated ΔG° values are also recorded. Units: kJ/mol of Co. ^b $\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$, where $T\Delta S^\circ$ (lel₂ob → lel₃) = $T\Delta S^\circ$ (ob₂lel → lel₃) = $RT \ln(1/3)$ and $T\Delta S^\circ$ (ob₃ → lel₃) = 0. Units: kJ/mol of Co. ^c The parameters in the ring-pair relationship model. Units: kJ/ring pair.

in common and differ in that ob₂lel has an extra ob-ob and lel₂ob and extra lel-lel relationship. Explicitly, one can express the ΔH° values from Table IVb in terms of two model parameters

$$\begin{aligned} \Delta H^\circ(\text{lel}_2\text{ob} \rightarrow \text{lel}_3) &= 2\Delta H^\circ(\text{lel-ob} \rightarrow \text{lel-lel}) \\ \Delta H^\circ(\text{ob}_2\text{lel} \rightarrow \text{lel}_3) &= 2\Delta H^\circ(\text{lel-ob} \rightarrow \text{lel-lel}) \\ &+ \Delta H^\circ(\text{ob-ob} \rightarrow \text{lel-lel}) \\ \Delta H^\circ(\text{ob}_3 \rightarrow \text{lel}_3) &= 3\Delta H^\circ(\text{ob-ob} \rightarrow \text{lel-lel}) \end{aligned} \quad (3)$$

The results of a linear regression analysis based upon eq 3 are shown in Table IVc, and the ΔG° values calculated from these parameters are listed in Table IVa.

One may consider a similar analysis based upon a one-parameter model, i.e., a model where the chelate rings are independent of one another. Such a model can be expressed by

$$\begin{aligned} \Delta H^\circ(\text{lel}_2\text{ob} \rightarrow \text{lel}_3) &= \Delta H^\circ(\text{ob} \rightarrow \text{lel}) \\ \Delta H^\circ(\text{ob}_2\text{lel} \rightarrow \text{lel}_3) &= 2\Delta H^\circ(\text{ob} \rightarrow \text{lel}) \\ \Delta H^\circ(\text{ob}_3 \rightarrow \text{lel}_3) &= 3\Delta H^\circ(\text{ob} \rightarrow \text{lel}) \end{aligned} \quad (4)$$

However, a comparison of the two models shows¹⁵ that the latter model, eq 4, can be rejected.

The stepwise transformation of ob₃ into the more stable lel₃ can be described in terms of a usual consecutive complex formation. In Table V the ΔH° for each step and the corresponding statistically corrected equilibrium constants, $K(\text{cor})$, are given. It is seen that for both the systems considered the consecutive constants increase, corresponding to a negative ligand effect,¹⁴ or in other words an increase in the binding of lel as the number of lel already present increases. We have

Table V. Statistically Corrected Consecutive Complexity Constants for the Process $ob_3 \rightarrow lel_3^a$

	[Co(chxn) ₃] ³⁺		[Co(pn) ₃] ³⁺	
	ΔH° , kJ	K(cor)	ΔH° , kJ	K(cor)
$ob_3 \rightarrow ob_2lel$	-1.07	1.41	-1.35	1.55
$ob_2lel \rightarrow lel_2ob$	-2.79	2.45	-2.58	2.30
$lel_2ob \rightarrow lel_3$	-4.34	4.05	-2.92	2.56

^a Based upon the data from Table II. The relation $\Delta H^\circ = -RT \ln [K(\text{cor})]$, $T = 373$ K, has been employed.

in these systems well-defined equilibrium constants with a magnitude of 1-4 corresponding to standard free energies of 0-4 kJ/mol, i.e., quantities that are small even in comparison with van der Waals energies and yet varying in a highly systematic way. The fact that intramolecular considerations lead to such regularities means that the free energy of solvation of the isomers is almost invariant or at least varies monotonically through the series ob_3 , ob_2lel , lel_2ob , lel_3 . Further, it is remarkable that the two tris(diamine) systems resemble one another as far as to the deviations between the experimental results and the pair relationship model.

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Registry No. Δ -[Co((+)chxn)₃- $\delta\delta\delta$]Cl₃, 59671-81-7; Δ -[Co((+)chxn)₃- $\delta\delta\delta$]Cl₃, 59727-64-9; Δ -[Co((+)chxn)₂(-)chxn- $\delta\delta\lambda$]Cl₃,

59727-65-0; Δ -[Co((+)chxn)₂(-)chxn- $\delta\delta\lambda$]Cl₃, 59727-63-8; Δ -[Co((-)chxn)₂(+)chxn- $\lambda\lambda\delta$]Cl₃, 59727-66-1; Δ -[Co((-)chxn)₂(+)chxn- $\lambda\lambda\delta$]Cl₃, 59727-62-7; Δ -[Co((-)chxn)₃- $\lambda\lambda\lambda$]Cl₃, 34369-95-4; Δ -[Co((-)chxn)₃- $\lambda\lambda\lambda$]Cl₃, 31537-08-3; *trans*-[Co(py)₄Cl₂]Cl, 27883-34-7.

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Exchange of *N,N*-Dimethylacetamide on Dioxopentakis(*N,N*-dimethylacetamide)uranium(VI) Ion. Proton Magnetic Resonance Study

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The species $UO_2(DMA)_5^{2+}$ is shown from ¹H NMR studies to be the greatly predominant dioxouranium(VI) species existing in a series of dilute *N,N*-dimethylacetamide (DMA) solutions in CD₂Cl₂ diluent. Complete line shape analyses of exchange-modified ¹H NMR DMA line shapes show the rate law for DMA exchange to be $5k_{ex}[UO_2(DMA)_5^{2+}]$ over a 24.05-fold variation of [DMA]. The mechanism of the DMA exchange is considered to be of the D type. A typical set of rate parameters are $k_{ex}(260\text{ K}) = 81 \pm 2\text{ s}^{-1}$, $\Delta H^\ddagger = 10.2 \pm 0.2\text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -10.4 \pm 0.7\text{ cal deg}^{-1}\text{ mol}^{-1}$ for a solution in which $[UO_2(DMA)_5^{2+}]$, [DMA], and [CD₂Cl₂] are respectively 0.1518, 0.7108, and 14.15 M.

The coordination number of uranium(VI) in dioxouranium(VI) species ranges from 6 or 7 with monodentate oxygen donor equatorial ligands to 8 with oxygen donor bidentate ligands, and the axial uranium(VI) to oxygen bonds are usually close to collinearity as shown in a number of solid-state studies.¹⁻⁶ Similar geometries appear to exist for monomeric dioxouranium(VI) species in solution, but it is only recently that NMR solution studies have determined the stoichiometry of the complex ions⁷⁻⁹ $UO_2(H_2O)_4^{2+}$, $UO_2(DMSO)_4^{2+}$, and $UO_2(DMF)_5^{2+}$, where DMSO and DMF are dimethyl sulfoxide and *N,N*-dimethylformamide, respectively. The inert nature^{10,11} of the axial oxygens presents the unusual situation where, in dioxouranium(VI) species, the processes of ligand substitution are likely to be restricted to

rearrangements in a single plane during the formation of the transition state. Mechanistic interpretation is simplified by the absence of overall geometric and stoichiometric change accompanying identical ligand-exchange processes, and accordingly the exchange of *N,N*-dimethylacetamide (DMA) on $UO_2(DMA)_5^{2+}$ has been selected as a simple process through which to study ligand-substitution processes on dioxouranium(VI).

Experimental Section

Dioxopentakis(*N,N*-dimethylacetamide)uranium(VI) perchlorate was prepared under dry nitrogen by refluxing hydrated dioxouranium perchlorate (G. Frederick Smith) (2.5 g) with triethyl orthoformate^{12,13} (4.0 g) at 320-330 K for 1 h. Dry *N,N*-dimethylacetamide (2.0 g) was then added at room temperature and the resultant yellow crystals