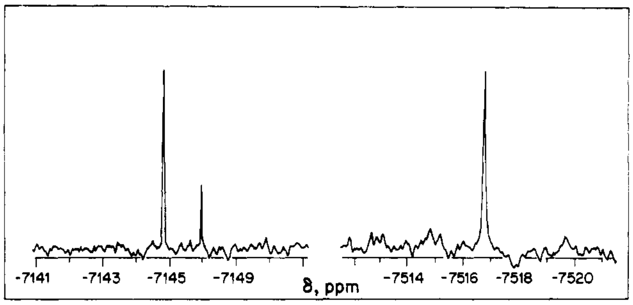

Figure 4. ^{195}Pt NMR spectrum of the Pt(II)–G_3 complexes. Referenced to K_2PtCl_6 at 0 ppm. $[Pt]_T = 0.25$ M, $[G_3]_T = 0.38$ M in D_2O, and pD = 6.0.

Cyanide is considered a very strong σ donor.[37] The chemical shift of $Pt^{II}(CN)_4^{2-}$ is −4725 ppm (upfield of K_2PtCl_6).[34] The three Pt^{II}–G_3 complexes appear at −7144, −7146, and −7517 ppm. This suggests coordination to donors much stronger than that of CN^-. The ^{195}Pt NMR spectrum of the three complexes is shown in Figure 4. No other ^{195}Pt lines were found in the range of 1000 to −10 000 ppm.

By comparison of the chemical shifts of $Pt^{II}Cl(H_2O)_3^+$, $Pt^{II}OAc(H_2O)_3^+$, and $Pt^{II}(OH)_4^{2-}$, (Table III), it is possible to assign the ^{195}Pt lines of the triglycine complexes to $Pt^{II}(H_{-2}G_3)^-$ (−7144 ppm), $Pt^{II}(H_{-2}G_3)OH^{2-}$ (−7146 ppm), and $Pt^{II}(H_{-2}G_3)Cl^{2-}$ (−7517 ppm).

From the data in Table III, the chemical shift values (δ, in ppm from $PtCl_6^{2-}$) per donor group can be estimated on the basis of the assumption that chemical shift varies linearly with the number of equivalent donors.[36] The values are as follows: H_2O, +6; OH^-, −41; Cl^-, −368; peptide amine, −738; carboxylate, −39. Thus, the effect of deprotonated peptide nitrogen is −3184 ppm, which is much greater than the effect due to CN^-, −1181 ppm.

The predicted ^{195}Pt NMR chemical shifts of $Pt^{II}(H_{-2}G_3)OH^{2-}$ and $Pt^{II}(H_{-2}G_3)Cl^{2-}$ were calculated by using the above values and are −7147 ppm and −7474, respectively. These are in good agreement with the experimental values from Table III.

Conclusions

Reaction of tripeptides with $PtCl_4^{2-}$ produces complexes containing cis-deprotonated-N peptide bonds to platinum(II). Three products, as identified by HPLC and ^{195}Pt NMR, form when G_3^- is the tripeptide. The pK_a of the deprotonated peptide nitrogens is estimated to be between 1 and 2 in the presence of 3.7×10^{-4} M Cl^- ion.

Chloride determination of the G_3^- complexes indicates that 70% of the platinum is still coordinated to one Cl^- ion, so $Pt^{II}(H_{-2}G_3)Cl^{2-}$ is proposed as the major product.

NMR data (^1H and ^{13}C) show that 22% of the platinum is coordinated to the peptide carboxylate. Therefore, $Pt^{II}(H_{-2}G_3)^-$ is the next most abundant product.

The remaining species may have H_2O or OH^- coordinated in the fourth position. Titration data indicate that 7% excess hydroxide was consumed during formation of the complexes, suggesting that $Pt^{II}(H_{-2}G_3)OH^{2-}$ is the minor product.

The ^{195}Pt NMR data show that a deprotonated peptide nitrogen is a much stronger σ donor than cyanide ion.

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Volume Profile for the Trans ⇌ Cis Isomerization of the Chloroaquabis(ethylenediamine)cobalt(III) Ion

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Activation volume ($\Delta V^* = 5.1 \pm 0.3$ cm^3 mol^{-1} in 0.01 M $HClO_4$) and reaction volume ($\Delta V = -2.9 \pm 0.2$ cm^3 mol^{-1} in 0.039 M $HClO_4$) have been obtained at 31.5 °C for the trans ⇌ cis isomerization of $Co(en)_2Cl(OH_2)^{2+}$. These are almost independent of ionic strength or temperature. A tetragonal-pyramidal transition state with one water molecule outside the coordination sphere can be inferred on the basis of these ΔV^* and ΔV values. It has been also found that the partial molal volumes of the trans and the cis isomers are almost equal for $Co(en)_2(OH_2)_2^{3+}$, $Co(en)_2Cl(NO_2)^+$, and $Co(en)_2(NO_2)(OH_2)^{2+}$.

Introduction

Positive values (7–14 cm^3 mol^{-1}) of ΔV^* were known hitherto for four trans → cis isomerization reactions of Co(III) complexes:

$$trans\text{-}Co(en)_2(OH_2)_2^{3+} \rightarrow cis\text{-}Co(en)_2(OH_2)_2^{3+} \qquad (1)$$[2]

$$trans\text{-}Co(en)_2(SeO_3H)OH_2^{2+} \rightarrow cis\text{-}Co(en)_2(SeO_3H)OH_2^{2+} \qquad (2)$$[3]

$$trans\text{-}Co(en)_2(SeO_3)OH_2^{+} \rightarrow cis\text{-}Co(en)_2(SeO_3)OH_2^{+} \qquad (3)$$[3]

$$trans\text{-}Co(en)_2(CH_3COO)OH_2^{2+} \rightarrow cis\text{-}Co(en)_2(CH_3COO)OH_2^{2+} \qquad (4)$$[3]

These ΔV^* were interpreted according to the postulate given by Stranks that the intrinsic partial molal volume of the five-coordinate intermediate is equal to that of the six-coordinate precursor.[4] However, the inappropriateness of this postulate has been repeatedly pointed out in recent years.[5-7] On the other hand, ΔV was considered to be negligible for reactions 1 and 4 because the final spectra of these reactions were almost pressure independent.[2,3] This near-zero magnitude of ΔV might be just for reaction 4, where the final composition is 75% cis and 25% trans.[3] However, it is rather unreliable for reaction 1, where the final composition is one-sided (98.3% cis and 1.7% trans).[2]

In this work, ΔV^* and ΔV have been obtained for another isomerization:

$$trans\text{-}Co(en)_2Cl(OH_2)^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} cis\text{-}Co(en)_2Cl(OH_2)^{2+} \qquad (5)$$[8]

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Table I. Rate Constant ($k_1/10^{-5}$ s^{-1}), Equilibrium Constant, and Volume Profile (cm^3 mol^{-1}) for the Trans ⇌ Cis Isomerization of $Co(en)_2Cl(OH_2)^{2+}$

	run 1 (38 °C; 0.01 M HNO_3)		run 2 (38 °C; 0.01 M $HClO_4$)		run 3 (31.5 °C; 0.01 M $HClO_4$)		run 4 (31.5 °C; 0.01 M $HClO_4$, 0.5 M $NaClO_4$)		run 5 (25 °C; 0.01 M $HClO_4$)
P/bar	k_1	K	k_1	K	k_1	K	k_1	K	k_1
1	47.6	2.76	47.9	3.20	18.4	3.81	19.1	3.03	7.00
	48.4	3.11	48.7	3.27	18.2	3.48	18.9	3.67	7.22
	45.1	2.87	53.1	3.35	18.6	3.40	19.1	3.23	6.77
	45.4	3.06	50.1	3.59	18.5	3.46	18.5	3.53	7.02
400	44.1	2.96	47.8	3.53	18.1	3.84	18.8	3.39	6.38
	44.8	3.33	47.2	3.60	18.3	3.40	18.6	3.50	6.91
800	44.1	3.00	43.7	3.33	17.0	3.65	17.5	3.91	5.46
	42.7	3.04	44.4	3.54	17.0	3.66	17.5	3.88	6.44
1200	37.8	2.72	38.6	3.73	15.1	3.68	15.6	3.84	5.41
	39.9	3.18	39.1	3.79	14.6	4.53	15.9	3.85	5.85
1600	35.6	3.19	36.5	3.95	13.7	4.02	13.9	3.81	5.01
	35.5	3.16	36.3	3.93	13.8	3.96	14.1	3.55	4.94
2000	32.2	3.30	32.5	4.05	12.3	3.89	12.4	4.24	4.50
	32.2	3.22	32.2	4.18	12.5	4.22	12.7	3.90	3.97
$\Delta V^{\ddagger}$	4.7 ± 0.3		5.6 ± 0.3		5.1 ± 0.3		5.2 ± 0.4		5.9 ± 0.5
ΔV	−0.9 ± 0.8		−2.6 ± 0.4		−1.9 ± 0.4		−2.2 ± 0.4		
$\Delta V^{\ddagger} - \Delta V$	5.6 ± 1.1		8.2 ± 0.7		7.0 ± 0.7		7.4 ± 0.8		

The proximity of the partial molal volumes of the geometrical isomers of Co(III) complexes has been considered, and the apparent molal volumes, (ϕ_v), have been measured at low ionic strength (μ) for isomers of $Co(en)_2(OH_2)_2^{3+}$, $Co(en)_2Cl(NO_2)^+$, and $Co(en)_2(NO_2)OH_2^{2+}$. The mechanism of reactions 1–5 is discussed on the basis of their volume profiles.

Experimental Section

The complexes *trans*-[$Co(en)_2Cl(OH)$]$Cl{\cdot}H_2O$,[8,9] *cis*-[$Co(en)_2Cl(OH_2)$]$SO_4{\cdot}2H_2O$,[10] and *trans*-[$Co(en)_2(OH_2)(OH)$]$(ClO_4)_2$[11] were obtained according to the literature, twice recrystallized, and identified by elemental analysis and UV absorption spectroscopy. UV absorptions, λ_{max} (ϵ): *trans*-[$Co(en)_2Cl(OH)$]$Cl{\cdot}H_2O$ in 0.01 M HNO_3, 588 (31.5), 441 (30.7);[8,12] *cis*-[$Co(en)_2Cl(OH_2)$]$SO_4{\cdot}2H_2O$ in 0.01 M HNO_3, 514 (86.8), 372 (69.9);[13] *trans*-[$Co(en)_2(OH_2)(OH)$]$(ClO_4)_2$ at pH 3 ($HClO_4$), 552 (32), 435 (35.8), 345 (53.4).[2] *trans*-[$Co(en)_2Cl(NO_2)$]NO_3 and *cis*-[$Co(en)_2Cl(NO_2)$]Cl were obtained and identified in a previous work.[14]

The kinetic and equilibrium experiments under high pressure were performed with use of a thermostated (±0.1 °C) Hawley and Chase type high-pressure cell.[14,15]

The dilatometry was carried out by using a bulb fitted with a capillary immersed in a well-controlled (±0.001 °C) thermostat.[14]

The density measurement was carried out with a digital densimeter (Shibayama Scientific Co., Ltd. Model SS-D-200) equipped with a well-controlled (±0.002 °C) thermostat.[16]

Results

Pressure Effects on the Velocity and Equilibrium of Reaction 5. *trans*-[$Co(en)_2Cl(OH)$]$Cl{\cdot}H_2O$ was dissolved in acid solution (5 mM). The changes in the absorption spectra (340–700 nm) of this solution were followed at a certain pressure. Four isosbestic points were clearly maintained. The $k_1 + k_2$ value was calculated from the optical density (D_t) at 510 nm by the ln ($D_\infty - D_t$) vs. t plot (run 1) or by the Guggenheim method up to 2 half-lives (runs 2–5). In runs 1–4, the equilibrium constant K = [cis]/[trans] = k_1/k_2 was calculated at each pressure from D_∞ at 510 nm by

$$K = \frac{\epsilon_t D_{iso} - \epsilon_{iso} D_\infty}{\epsilon_{iso} D_\infty - \epsilon_c D_{iso}} \qquad (6)$$

Table II. Dilatometrically Obtained ΔV for the Trans ⇌ Cis Isomerization of $Co(en)_2Cl(OH_2)^{2+}$

t/°C	c/mM[a]	solvent	ΔV/cm^3 mol^{-1}
25	10	0.021 M $HClO_4$	−3.7, −3.3, −2.9
31.5	25	0.039 M $HClO_4$	−3.1, −2.7

[a] Complex concentration.

Equation 6 can be derived by assuming the pressure independence of ϵ_t, ϵ_c, and ϵ_{iso}, where ϵ_t and ϵ_c are the absorption coefficients at 510 nm of the trans (11.6) and of the cis (86.4) isomers and ϵ_{iso} is that at an isosbestic point (31.6 at 584 nm, 29.0 at 456 nm, 37.2 at 406 nm, and 57.0 at 357 nm), respectively. In runs 2–4, D_∞ was calculated from D_t's. D_{iso} is the time-independent optical density at an isosbestic point. The four K values derived from the four D_{iso} values coincided within ±5%. The average K is shown in Table I. In run 5, K was estimated by ln $(K/K_0) = -(\Delta V)P/RT$, where $K_0 = 3.73$ and $\Delta V = -3.3$ cm^3 mol^{-1}. The resultant k_1 and K were fitted to the linear approximations ln $k_1 = aP + b$ and ln $K = AP + B$. $\Delta V^{*} = \bar{V}^{*} - \bar{V}_{trans}$ and $\Delta V = \bar{V}_{cis} - \bar{V}_{trans}$ were calculated by $\Delta V^{*} = -RT\text{d} \ln k_1/\text{d}P = -RTa$ and $\Delta V = -RT\text{d} \ln K/\text{d}P = -RTA$.

Dilatometric Results. The volume change of a 39.2 cm^3 solution of *trans*-[$Co(en)_2Cl(OH)$]$Cl{\cdot}H_2O$ was followed by observing the movement of the meniscus height (h_t) in a capillary (diameter = 0.0404 or 0.0202 cm) from 0.2 to 2.3 half-lives. The $h_0 - h_\infty$ value was obtained from the intercept at $t = 0$ of the Guggenheim plot. From $K = 3.73$ at 25 °C and $K = 3.54$ at 31.5 °C, ΔV was calculated (Table II). The resulting ΔV at 31.5 °C is quite close to the corresponding value (−1.9 ± 0.4 cm^3 mol^{-1}) in Table I, which guarantees the exactness of both measurements.

Densimetric Results. *trans*-[$Co(en)_2(OH_2)(OH)$]$(ClO_4)_2$ was dissolved (10–20 mM) in aqueous $HClO_4$ (60–70 mM). The time variation of the density of this solution was slow enough at 25 °C. So, the mean density until 1 hr after the dissolution was regarded as the initial density (d_0). The density of this solution was measured again after the completion of the isomerization (d_∞). The initial and final ϕ_v's were calculated from d_0 and d_∞ according to the literature.[17] The resulting ϕ_v's were independent of the complex concentration, and the means of three determinations are shown in Table III. ΔV of reaction 1 was obtained by $\Delta V = (\phi_{v,final} - \phi_{v,initial})/0.98$ (Table IV).

The density (d_t) of an aqueous solution of *trans*-[$Co(en)_2Cl(NO_2)$]NO_3 or *cis*-[$Co(en)_2Cl(NO_2)$]Cl was followed at 10 °C up to 1.2 or 0.2 half-lives of the aquation. The density was also

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Table III. Apparent Molal Volumes ($cm^3\ mol^{-1}$)

complex	*trans*-$[Co(en)_2(OH_2)_2](ClO_4)_3$	*cis*-$[Co(en)_2Cl(NO_2)]Cl$	*trans*-$[Co(en)_2Cl(NO_2)]NO_3$
solvent	50 mM $HClO_4$	water	water
t/°C	25	10	10
$\phi_{v,initial}$	251.0 ± 0.6	160.2 ± 0.1	171.2 ± 0.0
$\phi_{v,final}$	250.0 ± 0.6	169.9 ± 0.2	178.5 ± 0.3

Table IV. Volume Profile ($cm^3\ mol^{-1}$) for the Trans → Cis Isomerization of $Co(en)_2XY^{n+}$

a	complex	$\Delta V^{\ddagger}$	ΔV
1	$Co(en)_2(OH_2)_2^{3+}$	14.3 ± 0.2 (34.5 °C, 0.05 M $HClO_4$)[b]	−1.0 ± 1.2 (25 °C, 0.05 M $HClO_4$)[c]
2	$Co(en)_2(SeO_3H)OH_2^{2+}$	7.2[d]	
3	$Co(en)_2(SeO_3)OH_2^{+}$	7.3[d]	
4	$Co(en)_2(CH_3COO)OH_2^{2+}$	7.9 ± 0.3 (45.2 °C, 0.05 M $HClO_4$)[d]	0[d]
5	$Co(en)_2Cl(OH_2)^{2+}$	5.1 ± 0.3 (31.5 °C, 0.01 M $HClO_4$)[c]	−2.9 ± 0.2 (31.5 °C, 0.039 M $HClO_4$)[c]
	$Co(en)_2Cl(NO_2)^{+}$		−0.9 ± 0.1 (10 °C, in water)[c]
	$Co(en)_2(NO_2)OH_2^{2+}$		1.5 ± 0.5 (10 °C, in water)[c]
	$Co(en)_2(NO_2)_2^{+}$		0.4 ± 1.9[e]
	$Co(en)_2Cl_2^{+}$		2.8 (25 °C)[f]

[a] Reaction number. [b] Reference 2. [c] This work. [d] Reference 3. [e] At low μ. Rindermann, W. Ph.D. Thesis, Frankfurt University, 1982; p 74. [f] At low μ. Daffner, G.; Palmer, D. A.; Kelm, H. *Inorg. Chim. Acta* **1982**, *61*, 57.

measured after completion of aquation (d_∞).[18] The initial density (d_0) was obtained from the intercept of the linear ln $(1/d_t - 1/d_\infty)$ vs. t plot. The apparent molal volume, ϕ_v, of the reactant or of the product was calculated from d_0 or d_∞.[16] These ϕ_v's are independent of the complex concentration (11–30 mM), and the mean ϕ_v's of five or six determinations are shown in Table III. From $\bar{V}^{\circ}_{conv}(Cl^-) = 17.2\ cm^3\ mol^{-1}$ and $\bar{V}^{\circ}_{conv}(NO_3^-) = 27.3\ cm^3\ mol^{-1}$ at 10 °C,[19] $\Delta V = \bar{V}_{cis} - \bar{V}_{trans}$ was obtained for $Co(en)_2Cl(NO_2)^+$ and $Co(en)_2(NO_2)OH_2^{2+}$ (Table IV). From Table III, the ΔV of aquation can be known as −9.9 ± 0.3 and −7.5 ± 0.3 $cm^3\ mol^{-1}$ for *trans*- and *cis*-$Co(en)_2Cl(NO_2)^+$, respectively. These ΔV's are quite close to the corresponding −10.4 $cm^3\ mol^{-1}$ at 15 °C and −9.3 $cm^3\ mol^{-1}$ at 25 °C obtained dilatometrically in previous work.[14]

Discussion

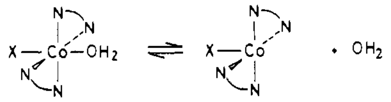
As shown in Table I, k_1 decreases and K increases with the increase of pressure. Accordingly, $\Delta V^{\ddagger}$ is definitely positive and ΔV is slightly negative. Both are almost independent of μ or reaction temperature. The activation volume of the reverse (cis → trans) process can be given as $\Delta V^{\ddagger} - \Delta V$, and this is again definitely positive. Thus, in reaction 5, $\bar{V}^{\ddagger}$ is larger by 5–8 $cm^3\ mol^{-1}$ than $\bar{V}$ of the trans or the cis isomer.

By comparison with the volume profiles of analogous reactions, it can be noticed that the magnitude of $\Delta V^{\ddagger}$ for reaction 5 is quite similar to those of reactions 2–4 (Table IV). Thus, reaction 5 and reactions 2–4 will have common mechanisms. Another interesting feature is that all seven ΔV's of isomerization are close to zero, irrespective of the charge on the complex. It seems that the partial molal volume of a Co(III) complex is determined mainly by the kinds of constituent ligands and affected little by their geometrical arrangement.

Hence, in the case of the twist mechanism, a near-zero $\Delta V^{\ddagger}$ should be expected, since in this mechanism bond breakage does not occur and only the change of the bond angles is realized in going to the transition state.[20] Thus, the twist mechanism cannot explain the definitely positive $\Delta V^{\ddagger}$ of reactions 1–5. A certain bond should be broken in the transition state of reactions 1–5. Co–SeO_3H, Co–SeO_3, Co–CH_3COO, or Co–Cl bond breakage is improbable, since bond re-formation would rarely occur. Co–en bond rupture is also improbable, since it occurs only under alkaline conditions.[21,22] Co–OH_2 bond breakage should be most probable. This expectation can be justified by the coincidence of the $\Delta V^{\ddagger}$ values of reactions 2–5 with that (5.9 ± 0.2 $cm^3\ mol^{-1}$ at 35 °C, μ = 2.0 M) of the aqua-exchange reaction[23]

$$trans\text{-}Co(en)_2(O^*H_2)_2^{3+} + 2H_2O \rightarrow trans\text{-}Co(en)_2(OH_2)_2^{3+} + 2H_2O^* \quad (7)$$

Reaction 7 is stereoretentive, and the transition state should have a tetragonal-pyramid geometry with one water molecule outside the coordination sphere (mechanism I).

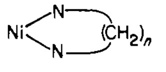


(I)

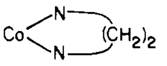
In mechanism I, $\Delta V^{\ddagger}$ should result from two contributions: one ($\Delta V^{\ddagger}_d$) due to the difference in the $\bar{V}$ of H_2O outside and inside the coordination sphere and the other ($\Delta V^{\ddagger}_c$) due to the Co–N bond contraction accompanied by the reduction of the coordination number.[24] $\Delta V^{\ddagger}_d$ and $\Delta V^{\ddagger}_c$ can be estimated from the analogy to the spin-state equilibrium of the Ni(II) complex[25]

$$Ni(cyclam)(OH_2)_2^{2+} = Ni(cyclam)^{2+} + 2H_2O \quad (8)$$

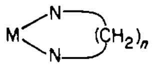
In reaction 8, $\bar{V}$ of the coordinated water has been obtained as 13.4 $cm^3\ mol^{-1}$. Then, $\Delta V^{\ddagger}_d$ will be 18.1 − 13.4 = 4.7 $cm^3\ mol^{-1}$. It has also been estimated that the volume of the $Ni(cyclam)^{2+}$ cylinder contracts by 8.1 $cm^3\ mol^{-1}$ when the coordination number is reduced from 6 to 4. The cyclam ligand forms four



rings, whereas the $(en)_2$ ligand forms two



rings. It may be assumed that the number of



rings in a complex is critical for volume contraction, and the volume contraction due to the coordination number reduction from 6 to 5 is half of that from 6 to 4. Then, $\Delta V^{\ddagger}_c$ will be −8.1 × $^1/_2$

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$\times\ ^{1}/_{2} = -2.0$ cm^3 mol^{-1}. Thus, for mechanism I, ΔV^{*} can be expected as $4.7 - 2.0 = 2.7$ cm^3 mol^{-1}. This magnitude is comparable to the experimental ΔV^{*} values of reactions 2–5. Consequently, mechanism I can be inferred for reactions 2–5.

In the case of reaction 1, ΔV is quite similar to those of reactions 4 and 5. So, if the construction of the transition state were the same as that for reactions 4 and 5, the magnitude of ΔV^{*} of reaction 1 would also be similar to those of reactions 4 and 5. Thus, the significantly large ΔV^{*} of reaction 1 seems incompatible with mechanism I. As indicated by Kruse and Taube, a mechanism to form the trigonal-bipyramid transition state may be more appropriate for reaction 1.[11]

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Electronic and Structural Properties of a Reactive Metalloporphyrin with *N*-Oxide Axial Ligands. Crystal and Molecular Structure of Bis(2,6-lutidine *N*-oxide)(tetraphenylporphinato)manganese(III) Perchlorate

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Manganese and iron porphyrins are known to catalyze the transfer of oxygen from amine *N*-oxides to hydrocarbon substrates, yet no reactive metalloporphyrin complex containing amine *N*-oxide axial ligands has been structurally characterized to date. An aromatic amine *N*-oxide, 2,6-lutidine *N*-oxide, has been found that forms relatively stable, isolable, soluble, and crystalline metalloporphyrin complexes. Treatment of $Mn^{III}TPP(ClO_4)$ with 2.5 equiv of 2,6-lutidine *N*-oxide in toluene solution followed by the addition of *n*-heptane produces two solvated crystalline modifications of the six-coordinate cationic metalloporphyrin complex bis(2,6-lutidine *N*-oxide)(tetraphenylporphinato)manganese(III) perchlorate (**1**). The magnetic moment (4.9 μ_B at 25 °C), electronic spectrum (λ 325–700 nm), and ^{1}H NMR spectral characteristics from −40 to +60 °C of **1** clearly establish the ground electronic state of the complex to be a d^4 high-spin ($S = 2$) Mn^{III} system in contrast to the Mn porphyrin iodosylbenzene species characterized previously. The magnitudes, alternating signs, and temperature dependencies of the isotropic shifts of the axial *N*-oxide hydrogen atoms indicate clearly that these shifts are primarily contact in origin and arise through a π-delocalization mechanism. Complex **1** crystallizes in the purple-red prism habit as a heptane solvate in the monoclinic space group $C2/c$, with $Z = 8$. The unit cell has $a = 36.644$ (12) Å, $b = 12.3158$ (15) Å, $c = 24.096$ (6) Å, $\alpha = 89.976$ (16)°, $\beta = 95.807$ (23)°, and $\gamma = 90.073$ (20)°. The Mn atom is effectively in the mean plane defined by the 24-atom porphyrin core, and the $d_{\text{Mn-N(Por)}}$ values are typical for a $S = 2$ Mn^{III} porphyrin complex. The bonds to the axial oxygen atoms are very long, $d_{\text{Mn-O}} = 2.263$ (4) and 2.264 (4) Å, in accord with the axial σ-antibonding character of a d^4 high-spin complex, and the N–O bonds of *N*-oxide moieties are minimally perturbed upon complexation to manganese, $d_{\text{N-O}} = 1.331$ (7) and 1.330 (6) Å. Complex **1** is six-coordinate both in the solid state and in solution from −40 to +60 °C.

Introduction

One of the most active areas of chemical research in the last few years has been metalloporphyrin-catalyzed hydrocarbon oxidation processes.[1-6] Synthetic metalloporphyrins have been able to mimic various aspects of the catalytic cycle for hydrocarbon oxidation by the most powerful organic oxidant in nature, cytochrome P-450.[1-7] Several synthetic metalloporphyrin systems as well as cytochrome P-450 itself can catalyze the epoxidation of alkenes and the hydroxylation of alkanes by a source of reduced oxygen such as an iodosylarene, an amine *N*-oxide, or hypochlorite in place of dioxygen and a reducing agent. Substantial experimental evidence suggests that an oxometalloporphyrin 2 electron equivalents more oxidized than the trivalent reactant metalloporphyrin is the actual oxidant that attacks the hydrocarbon substrates both in the enzymic system[7] and in most of the synthetic metalloporphyrin systems.[1-6] The complexes that are formally oxoiron(V) and oxomanganese(V) are kinetically the most competent oxidants for organic substrates that have been encountered in the metalloporphyrin systems examined to date and the only species that attack unactivated alkane C–H bonds at or below 25 °C. Unfortunately, both the formal oxoiron(V) and oxomanganese(V) species are sufficiently reactive that they are not likely to be structurally characterized by X-ray crystallography in the near future. Much progress has been made on the char-

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