1166 (in-plane CH bending); 1025 (ring breathing); 895 (out-of-plane CH bending); 680, 650 (CC, CN torsion); 575 (FeCN bending); 482 (FeN stretching); 430 (Fe(py) stretching).

Above pH 7, the vibrational peaks associated with the iron(II)–diimine chromophore at 1618 and 1560 cm^{-1} decrease dramatically in intensity, as one can see in Figure 3C. A new, strongly enhanced peak grows at 1509 cm^{-1}, while the pyridine vibrations remain practically unchanged at 1480, 1308, 1232, 1162, 1030, 910, and 683 cm^{-1}. The excitation profiles also follow very closely the visible absorption spectra, as shown in Figure 1C. The complete decay of the characteristic diimine vibrational bands at pH 10 implies that the deprotonation of the oxime group has a pronounced effect on the conjugated chromophore. On the other hand, the new peak at 1509 cm^{-1} is in the range of 1570–1495 cm^{-1} characteristic of the N=O stretching vibration in aromatic and aliphatic nitroso compounds.[9]

Therefore, the RR spectrum of the oxime complex at pH 10 is consistent with the formation of a nitroso species. Nitroso complexes have also been detected[10] in the addition reactions of acetylpyridines to the nitrosyl ligand in the nitroprusside complex, $[Fe(CN)_5NO]^{2-}$. In these systems, a NO stretching peak has been observed around 1500 cm^{-1}. When the pH is lowered, oximes have been isolated in a high yield.

Acknowledgment. We thank the FAPESP, CNPq, and FINEP for financial support.

Registry No. $[Fe(CN)_4pyCHNOH]^{2-}$, 109585-62-8; $[Fe(CN)_4pyCHNO]^{3-}$, 109585-63-9; $[Fe(CN)_4pyCHNH]^{2-}$, 91730-48-2.

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Effect of Ligand Geometry on ^{59}Co NMR Relaxation in Hexakis(phosphite)cobalt(III) Complexes

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Cobalt-59 NMR spectroscopy has been shown to be a useful probe of the static and dynamic properties of octahedral cobalt(III) complexes.[3] Recently we described how ^{59}Co NMR can be used to quantify the ligand field in complexes of the type $[CoL_6]^{3+}$ for a series of phosphorus donor ligands L having different steric and electronic properties.[4,5] In these complexes, ^{59}Co–^{31}P spin–spin couplings were observed in the ^{59}Co NMR spectra only for complexes of phosphite ligands having 3-fold symmetry or chelating diphosphonite ligands possessing 2-fold symmetry. This result suggested that the geometry of the ligands influences the relaxation of the ^{59}Co nucleus. It therefore became of interest to measure the longitudinal relaxation of several of these complexes to determine the extent of such an effect.

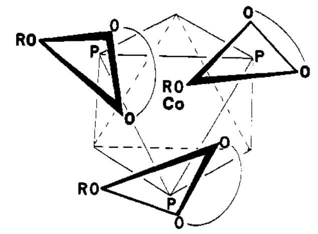

Figure 1. Schematic representation of the packing of monocyclic phosphite ester ligands around the octahedral Co^{3+} ion in one of the diastereomers of the $[CoL_6]^{3+}$ complex. The triangle in each ligand depicts the plane of the three esteratic oxygens while the curve denotes the ring carbons. The phosphorus atom is below the triangular plane. In the other diastereomer, the ligands around the bottom triangular face are rotated by 180° around the P–Co bonds.

Some ^{59}Co T_1 studies have been reported.[6-13] Since the ^{59}Co nucleus is spin $^7/_2$ and has a moderately large quadrupole moment, the longitudinal and transverse relaxation times of the magnetization of the ^{59}Co nucleus are expected to be dominated by the interaction of the nuclear electric quadrupole moment with fluctuating electric field gradients (quadrupole relaxation).[9,12] In the extreme narrowing limit with an axial electric field gradient at the quadrupolar nucleus, the quadrupolar relaxation rate, R_q, is given by

$$R_q = \left(\frac{3}{40}\right)\frac{(2I+3)}{I^2(2I-1)}\left(\frac{e^2Qq}{\hbar}\right)^2\tau_E \qquad (1)$$

where eQ is the nuclear quadrupole moment, τ_E is the correlation time for the reorientation for the electric field gradient, eq, at the observed nucleus, and the rest of the symbols have their usual meaning.[9,14] Recently it has been reported that ^{59}Co NMR relaxation times shorten and line widths broaden with increasing applied field strength for six-coordinate cobalt(III) complexes of low symmetry, suggesting that chemical shift anisotropy also makes a contribution to the relaxation in these complexes.[6]

Here we show that (1) T_1 of ^{59}Co in phosphite ester complexes of the type $[CoL_6]^{3+}$ decreases when reducing the symmetry of the ligands, (2) the variation in the ^{59}Co T_1 values is not due to differences in rotational correlation times of the complexes, (3) the appearance of the ^{31}P NMR spectra in these complexes is determined by the magnitudes and fluctuation times of the cobalt electric field gradients and the ^{59}Co–^{31}P spin–spin couplings, and (4) as the exocyclic group in a monocyclic phosphite ligand is enlarged in these complexes, a decrease of ^{59}Co–^{31}P spin–spin coupling constants accounts for the observed ^{31}P NMR line shapes.

Experimental Section

All cobalt complexes discussed were prepared as BF_4 salts as previously described.[15] Cobalt-59 (70.85 MHz), phosphorus-31 (121.51 MHz), and carbon-13 (75.47 MHz) NMR spectra were recorded on a Bruker WM-300 spectrometer operating in the pulse Fourier transform mode while locked on the ^{2}H resonance of deuteriated solvents. The T_1 relaxation times were measured by the inversion recovery technique as described by Becker[14] on nondegassed 0.1 M solutions in CD_3CN. The T_1 measurements were reproducible to ±10%.

Results and Discussion

^{59}Co Relaxation Times. In Table I we list ^{59}Co T_1 values and line widths for the series of $[CoL_6]^{3+}$ complexes studied here. When L is a monocyclic phosphite ester, the ^{59}Co T_1 values are an order of magnitude smaller than in the analogous complexes

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Table I. T_1 of ^{59}Co and ^{13}C in $[Co\{P(OR)_3\}_6](BF_4)_3$ Complexes in CD_3CN

	M_r of cation	temp, K	$T_1(^{59}Co)$, ms	$W_{1/2}(^{59}Co)$, Hz	$T_1(^{13}C)$,[a] s	$10^{11}\tau_R$, s
$[Co\{P(OCH_2)_3CEt\}_6](BF_4)_3$	1032	240	1.0		0.10	23
		275	2.8		0.21	11
		298	3.6	88	0.30	7.5
		343	7.3		0.41	5.6
$[Co\{P(OMe)_3\}_6](BF_4)_3$	803	275	1.4	170	...	...
$[Co(MeO\overline{POCH_2CH_2O})_6](BF_4)_3$	791	275	0.19	2.9×10^3	0.25	9.1
$[Co(EtO\overline{POCH_2CH_2O})_6](BF_4)_3$	875	275	0.15	2.8×10^3	0.24	9.6
$[Co(i\text{-}PrO\overline{POCH_2CH_2O})_6](BF_4)_3$	959	275	0.23	2.3×10^3	0.26	8.9
$[Co\{(MeO)_{eq}\overline{POCH(CH_3)_{eq}CH_2CH_2O}\}_6](BF_4)_3$	959	275	0.077	ca. 5×10^3	0.19	12

[a] T_1 of ring OCH_2 carbons measured.

of $P(OMe)_3$ and $P(OCH_2)_3CEt$. The relatively faster longitudinal relaxation rates for ^{59}Co in the monocyclic ester complexes can be ascribed mainly to the low symmetry of the ligands (C_s at best). Moreover, these ligands are apparently restricted to conferring the diastereomeric configurations depicted in Figure 1 on the $[CoL_6]^{3+}$ complexes.[15] For two such complexes, we have shown that these diastereomers are in a temperature-dependent equilibrium in solution.[15] The more than 10-fold longer T_1 for the ^{59}Co nucleus of $[Co\{P(OCH_2)_3CEt\}_6]^{3+}$ at 275 K compared to that for the analogous complexes of the monocyclic ligands is undoubtedly due to the higher symmetry of the ligand (C_{3v} for the bicyclic moiety). The ^{59}Co T_1 value for $[Co\{P(OMe)_3\}_6]^{+3}$ is approximately half as long as that for the $P(OCH_2)_3CEt$ complex. Numerous solid-state structural studies of $P(OMe)_3$ complexes reveal that the coordinated ligands have a variety of conformations. Generally, the ligand symmetry is C_1, sometimes C_3 or C_s, but it is never C_{3v}.[16] In solution, rotations of the OMe arms of the ligand may bring the average ligand symmetry close to C_3. The increase in the rate of T_1 relaxation thus seems to be associated with rising quadrupolar interaction and chemical shift anisotropy as the ligand asymmetry augments.

In an ideally rigid octahedral or tetrahedral molecule, the electric field gradient at the central atom is zero and thus the rate of quadrupolar relaxation should also be zero. This has not been found to be the case, however, for real molecules in solution.[17] In octahedral complexes, for example, it has recently been demonstrated that substantial changes in the relaxation rate of ^{59}Co can only be due to perturbations in the first coordination sphere,[6,8,9,18,19] although in complexes of lower symmetry, second-sphere hydrogen-bonding effects were noted.[19] In accord with these results it was reported by Doddrell that T_1 of ^{59}Co decreases as the size of the complex increases in a series of tris-chelate cobalt(III) complexes of D_3 symmetry. The differences in T_1, which were found not to be due to differences in molecular rotational correlation times, were attributed to solvent-assisted asymmetric vibrations in the larger complexes, thereby causing fluctuations of the electric field gradient of the ^{59}Co nucleus.[7] The ^{59}Co T_1 values obtained in the present study demonstrate that ligand symmetries, in addition to ligand sizes, have a strong effect on T_1 of the cobalt nucleus in octahedral complexes; as expected, asymmetric ligands reduce the molecular symmetry and hence induce more efficient relaxation.

In order to confirm that the variation in the T_1 values of ^{59}Co in our complexes is not due to differences in molecular rotational correlation times, estimates of this parameter were made by ^{13}C NMR spectroscopy. Assuming (1) the extreme narrowing limit, (2) that ^{13}C relaxation is dominated by dipole–dipole interaction with bound protons and (3) that the rotational correlation time τ_R of the dipole–dipole interaction of the C–H vector is dominated by rotational motion of the complex, then the ^{13}C relaxation is given by

$$\frac{1}{T_1} = \frac{N\gamma_C^2\gamma_H^2\hbar^2}{r_{C\text{-}H}^6}\tau_R \qquad (2)$$

where γ_C and γ_H are the magnetogyric ratios of carbon and hydrogen, respectively. In eq 2, N is the number of hydrogens bound to carbon and $r_{C\text{-}H}$ is the carbon hydrogen distance.[7,9,20] By measuring the T_1 values for the ^{13}C of the ring methylene carbons in our complexes,[21] we made estimates of τ_R (Table I)

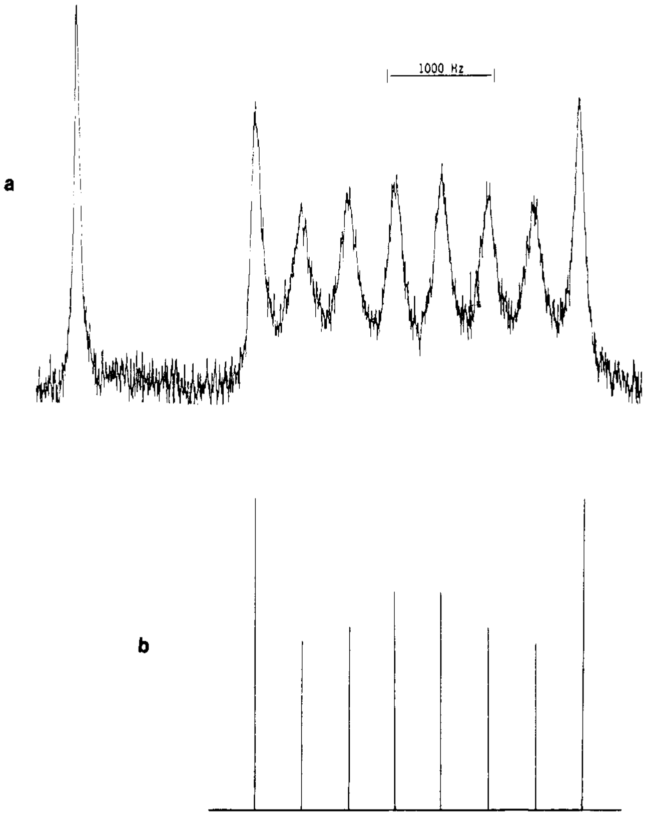

Figure 2. (a) ^{31}P NMR spectrum (121.5 MHz) of $[Co\{P(OCH_2)_3CEt\}_6](BF_4)_3$ (the symmetrical multiplet) and $[Co\{P(OCH_2)_3CEt\}_5]BF_4$ (the single downfield peak) at 343 K in CD_3CN. (b) Calculated Z NMR spectrum of a hypothetical octahedral YZ_6 molecule where Z has spin $^1/_2$, Y has spin $^7/_2$ and the broadening of Z is less than the spin–spin coupling.[24] The ratios of the peak heights in such a spectrum are 1.00:0.538:0.583:0.699:0.699:0.583:0.538:1.00.

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Table II. ^{31}P NMR of $[Co\{P(OR)_3\}_6](BF_4)_3$ Complexes in CD_3CN

	temp, K	δ^a	$W_{1/2}$,^{b} Hz	$T_1(^{31}P)$, s
$[Co\{P(OCH_2)_3CEt\}_6](BF_4)_3$	240	...	...	1.1
	298	...	...	2.1
	343	113.1	80	4.4
$[Co(MeO\overline{POCH_2CH_2O})_6](BF_4)_3$	275	131.4	ca. 1700	
$[Co(EtO\overline{POCH_2CH_2O})_6](BF_4)_3$	275	136.2	ca. 2100	0.9
$[Co(i\text{-}BuO\overline{POCH_2CH_2O})_6](BF_4)_3$	298	122.8	ca. 2000	
$[Co(i\text{-}PrO\overline{POCH_2CH_2O})_6](BF_4)_3$	275	121.2	225	2.6
$[Co(dl\text{-}MeO\overline{POCHCH_3CHCH_3O})_6](BF_4)_3$	298	126.5	ca. 2000	
$[Co(dl\text{-}EtO\overline{POCHCH_3CHCH_3O})_6](BF_4)_3$	298	128.2	814	
$[Co(dl\text{-}n\text{-}PrO\overline{POCHCH_3CHCH_3O})_6](BF_4)_3$	298	120.4	312	
$[Co\{(MeO)_{ax}\overline{POCH(CH_3)_{eq}CH_2CH(CH_3)_{eq}O}\}_6](BF_4)_3$	298	101.0	ca. 2100	
$[Co\{(MeO)_{eq}\overline{POCH(CH_3)_{eq}CH_2CH(CH_3)_{eq}O}\}_6](BF_4)_3$	298	101.9	ca. 2000	
$[Co\{(MeO)_{ax}\overline{POCH(CH_3)_{eq}CH_2CH_2O}\}_6](BF_4)_3$	298	104.5	ca. 2000	
$[Co\{(n\text{-}PrO)_{ax}\overline{POCH(CH_3)_{eq}CH_2CH_2O}\}_6](BF_4)_3$	298	100.8	554	
$[Co\{(MeO)_{eq}\overline{POCH(CH_3)_{eq}CH_2CH_2O}\}_6](BF_4)_3$	*c*	107.5	ca. 2000	1.6

^{a}Downfield from 85% H_3PO_4. ^{b}Line width at half of the peak height. ^{c}Line width and chemical shift measured at 298 K. T_1 measured at 275 K.

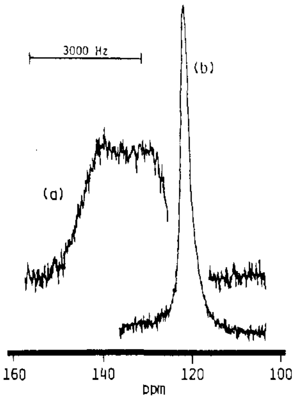

Figure 3. ^{31}P NMR spectrum (121.5 MHz) of (a) $[Co\{MeO\overline{POCH_2CH_2O}\}_6](BF_4)_3$ and (b) $[Co\{i\text{-}PrO\overline{POCH_2CH_2O}\}_6](BF_4)_3$ at 275 K in CD_3CN.

using eq 2. It can be seen that the relatively small dispersion in τ_R cannot account for the variation in ^{59}Co T_1 values on the basis of molecular reorientation fluctuations. It must be noted, however, that the somewhat irregular relationship between the ^{13}C T_1 values and the molecular weights of the complexes suggests that assumption 3 is not entirely valid.

^{31}P NMR Spectra of $[Co\{P(OR)_3\}_6]^{3+}$ Complexes. Although phosphorus ligand complexes of the type $[CoL_6]^{3+}$ have long been known,[15] until recently no reports of the ^{31}P NMR spectra of these complexes have appeared in the literature.[5,22] It is expected that the ^{31}P NMR resonances of these complexes would be broadened because of scalar interaction of the second kind with the quadrupolar ^{59}Co nucleus.[13,14] This effect is apparent in the ^{31}P NMR spectra of the $[CoL_6]^{3+}$ complexes studied here (see Figures 2–4 and Table II). According to Suzuki and Kubo the appearance of the NMR spectrum of a spin-$^1/_2$ nucleus that is coupled to a nucleus undergoing quadrupolar relaxation is determined by the dimensionless parameter α of eq 3 where T_1 is the longitudinal relaxation time of the quadrupolar nucleus.[23]

$$\alpha \equiv \frac{(e^2qQ)^2\tau_E}{Jh} \sim (T_1J)^{-1} \qquad (3)$$

When the line width due to lifetime broadening of the coupled spins is less than the coupling constant J (small α) and the spin of the quadrupolar nucleus is $^7/_2$, then the eight-line pattern that is observed in the ^{31}P NMR spectrum of $[Co\{P(OCH_2)_3CEt\}_6]^{3+}$ measured in CD_3CN at 343 K is predicted for the NMR spectrum of the spin-$^1/_2$ nucleus (Figure 2).[24] This pattern has also been observed in the ^1H NMR spectrum of $[HV(CO)_5]^{2-}$ in liquid ammonia at 223 K,[25] in the ^{15}N NMR spectrum of $[Co(^{15}NH_3)(NH_3)_5]^{3+}$ in D_2O at 328 K,[26] and in the ^{13}C NMR spectrum of $[Co(CN)_6]^{3+}$ in D_2O at 296 K.[10] As α increases, the theoretical spectrum broadens and eventually becomes a narrow peak for large α.[23] Thus as expected, lowering the temperature of a CD_3CN solution of $[Co\{P(OCH_2)_3CEt\}_6]^{3+}$ increases the correlation time of the electric field gradient fluctuations, and the resolution of ^{59}Co–^{31}P spin–spin coupling is lost as the ^{31}P NMR signal alters its shape (Figure 4). The T_1 values of ^{59}Co in the $[CoL_6]^{3+}$ complexes of the monocyclic ligands are much shorter than that of $[Co\{P(OCH_2)_3CEt\}_6]^{3+}$ (Table I). This is indicative of larger electric field gradients and/or longer fluctuation times (τ_E) in the former complexes and hence broad ^{31}P NMR signals. The ^{31}P T_1 values reported in Table II are only slightly shorter than those previously measured for phosphine, phosphinito, and phosphito complexes of Pt(II).[27] The differences can be accounted for in terms of temperature and molecular size. The data illustrate that interaction between a spin-$^1/_2$ nucleus and a rapidly relaxing quadrupolar nucleus will shorten T_2 of the spin-$^1/_2$ nucleus but will not affect its T_1 value, except in rare instances where the

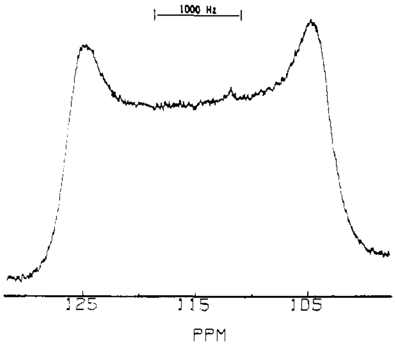

Figure 4. ^{31}P NMR spectrum (121.5 MHz) of $[Co\{P(OCH_2)_3CEt\}_6](BF_4)_3$ at 240 K in CD_3CN.

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resonance frequencies of the two nuclei are approximately equal.[14]

The line widths of the ^{31}P NMR peaks of $[Co(i\text{-}PrOPOCH_2CH_2O)_6]^{3+}$, $[Co(dl\text{-}n\text{-}PrOPOCHCH_3CHCH_3O)_6]^{3+}$, and $[Co\{(n\text{-}PrO)_{ax}POCH(CH_3)_{eq}CH_2CH_2O\}_6]^{3+}$ are narrow compared to those of complexes with less sterically demanding exocylic alkoxy groups of the ligand (see Table II and Figure 3). The narrower line widths in complexes with sterically demanding exocyclic groups are consistent with reduced ^{59}Co–^{31}P spin–spin coupling constants. Evidence for this are the similar ^{59}Co T_1 values for the four cobalt(III) complexes of the five-membered ring monocyclic phosphites (see Table I and eq 3). Recently we obtained UV and ^{59}Co NMR evidence for significant ligand–ligand repulsion in $[Co(i\text{-}PrOPOCH_2CH_2O)_6]^{3+}$, $[Co(dl\text{-}n\text{-}PrOPOCHCH_3CHCH_3O)_6]^{3+}$, and $[Co\{(n\text{-}PrO)_{ax}POCH(CH_3)_{eq}CH_2CH_2O\}_6]^{3+}$.[5] The ligand–ligand repulsions in these complexes may be sufficiently strong to lengthen the cobalt–phosphorus bonds and thereby reduce the ^{59}Co–^{31}P spin–spin coupling constants. The relatively small $^{1}J(^{59}Co\text{–}^{31}P)$ of $[Co\{P(OMe)_3\}_6]^{3+}$ (414 Hz)[28] compared with that of $[Co(PF_3)_4]^-$ (1225 Hz)[29] has been attributed to bond weakening arising from ligand repulsive interactions in addition to the smaller s character of the bonding electrons in the six-coordinate complex.[28,30] It is interesting in this respect to note that ^{195}Pt–^{31}P spin–spin coupling constants decrease substantially with increasing platinum–phosphorus distance in Pt(II) complexes of phosphorus ligands.[31]

In comparison to the broad signals observed in the ^{31}P NMR spectra of the $[CoL_6]^{3+}$ complexes studied here, the line widths of $[CoL_5]^+$ signals are relatively narrow as illustrated in Figure 2. The low-temperature line widths of the latter complexes are, in fact, comparable to ^{31}P NMR resonances where phosphorus is not coupled to a quadrupolar nucleus.[32] These narrower lines in the ^{31}P NMR spectra of the cobalt(I) complexes probably stem from the much faster relaxation times of ^{59}Co expected for the trigonal-bipyramidal symmetry of these complexes. The ^{59}Co in these five-coordinate complexes can be thought of as being "self-decoupled" from ^{31}P.[33]

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¹H NMR Evidence for the *R,S,R,S* Isomer of the (1,4,8,11-Tetraazacyclotetradecane)nickel(II) Ion

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The *R,R,S,S* or trans-III[1,2] isomer and the *R,S,R,S* or trans-I isomer of nickel(II) tetramethylcyclam (tetramethylcyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) were prepared by Barefield and co-workers[3] some years ago. Recently Lincoln[4] reported the observation of the *R,S,R,R* or trans-II isomer by NMR in nitromethane.

For a labile metal ion such as Ni(II), N-substitution of methyl groups on the cyclam macrocycle appears to make isomerization reactions more sluggish and aids in the isolation of less stable isomers such as the trans-I. For Ni(II) complexes of the unsubstituted macrocycle, only the trans-III isomer has been observed in aqueous solution although very recently we reported the isolation of the kinetically unstable trans-V isomer, which can be prepared via the "folded" cis-V isomer, $cis\text{-}[Ni(cyclam)(H_2O)_2]^{2+}$.[5,6]

We now report the observation, by proton NMR spectroscopy, of a further conformational isomer of $Ni(cyclam)^{2+}$, to which we assign the trans-I geometry. In aqueous solution this isomer is in equilibrium with the trans-III isomer and constitutes approximately 15% of the total complex at 25 °C.

Experimental Section

Synthesis. $Ni(cyclam)(ClO_4)_2$ and cyclam were prepared according to Barefield et al.[7] The chloro complex was prepared by mixing ethanol solutions of $NiCl_2{\cdot}6H_2O$ and ligand. Both the perchlorate and chloro complexes were recrystallized from aqueous solution.

NMR Measurements. Proton NMR spectra were recorded on a Varian XL300 spectrometer using a 5 mm broad-band probe. A typical sample consisted of 15–20 mg of the complex dissolved in 0.5 mL of D_2O (Aldrich). The pD was adjusted with DCl or NaOD. When pD values between 7 and 8 were desired, the complex was dissolved in 3 mM phosphate buffer solution. In general, 64 transients were accumulated for each spectrum, with a total acquisition time of approximately 1 min. The final pD was measured with a glass electrode by using the relationship pD = pH + 0.4.[8]

Kinetic measurements were made by acquiring successive spectra over a period of hours. The chloro complex was used for these studies because of its ease of dissolution. The perchlorate complex gave identical results. Data were acquired at the ambient spectrometer temperature (18 ± 1 °C). The spectra were integrated by computer and *R*, the ratio of the diamagnetic integral to total complex integral, was plotted vs. time. In nearly all cases, the isomerization was sufficiently rapid to permit determination of the final *R* value; *R* was independent of pD over the range 7.4–9.0 (nine measurements). Plots of $\ln(R_\infty - R_t)$ vs. t were linear, and the first-order rate constant was obtained by linear regression.

Temperature dependence of the equilibrium was investigated for a sample of approximately 20 mg of the perchlorate complex in 0.5 mL of D_2O adjusted to pH 9.0. The NMR temperature probe was calibrated by using standard techniques.[9] The temperature of the sample was varied; after an equilibration period of $^1/_2$ h a spectrum was recorded. R', the ratio of diamagnetic integral to paramagnetic integral, was determined. Plots of $\ln R'$ vs. $1/T$ were linear, and $\Delta H°$ and $\Delta S°$ were determined by linear regression.

Molecular mechanics calculations were performed by using a locally modified version of MODEL, a program utilizing Allinger's MM2 force field.[10] The parameters for Ni–N bonding, C–N–Ni and H–N–Ni bending were taken from the literature.[11] No attempt was made to account for charge–dipole or solvent interactions.

For the trans-octahedral complexes, dummy atoms were added to the axial coordination sites.[12] It was found that minimization with and without the dummy atoms gave essentially identical results and the

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