magnitude as $g\beta H$ it is necessary to use the magnetization expression[16]

$$M = \frac{Ng\beta \sinh (g\beta H/kT)}{\exp(-2J/kT) + 2 \cosh (g\beta H/kT) + 1} \qquad (2)$$

A best least-squares fit of the data to this equation gives $g = 1.98$ and $2J = -4.38\ \text{cm}^{-1}$, MFD = 0.067. At this point, an attempt was made to improve the agreement by taking into account the weak-exchange interaction between pairs in the molecular field approximation using the method of Friedberg and coworkers.[16] By setting $H = H_0 + \gamma M$, where H_0 is the external field and H is the effective field, eq 2 becomes a self-consistent equation that may be solved by repeated iteration. A best least-squares fit to this equation gives a $2J$ value of $-4.3\ \text{cm}^{-1}$ with $g = 2.13$ and $\gamma = -1.9$. This g value is more reasonable for copper(II) than the value of 1.98 obtained when only the external field is considered and is in good agreement with the average value of 2.17 obtained from EPR studies.[17] By using the equation[16,18]

$$J' = \gamma N g^2 \beta^2 k/2Z$$

where Z is the number of nearest neighboring dimers (in this case there are four) a value of $-0.20\ \text{cm}^{-1}$ is obtained for the lattice interaction parameter J'. Small values of J' are common for copper(II) dimers.[19] The theoretical curve for this model, where $\chi_m = M/H_0$, is indicated by the solid line in Figure 1; the MFD for this fit is 0.041.

The results of this investigation, therefore, support the hypothesis that the value of the singlet–triplet splitting, $2J$, is small for dimeric systems in which the bridging atom occupies an apical site on the metal and demonstrate the necessity of using the magnetization expression for cases where $2J$ is of the same order of magnitude as $g\beta H$.

Acknowledgment. This research was supported by the Materials Research Center of the University of North Carolina through Grant No. GH 33632 from the National Science Foundation and by the National Science Foundation through Grant No. MPS73-08703 A02.

Registry No. $[Cu[(C_6H_5)CONHCH_2COO]_2(H_2O)_2]_2 \cdot 4H_2O$, 40215-14-3.

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Study of the Ring Conformations in Tris(ethylenediamine)metal Complexes Using Solid-State Vibrational Spectroscopy

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Received February 13, 1975 AIC50109+

One of the most interesting features of chelate–metal complexes is the possibility of conformational isomerism for the five-membered ring systems found in such compounds. The relatively simple tris(ethylenediamine) complexes, for example, have four possible conformers, and because of the chiral metal center each of these four has an enantiomeric partner. There are then eight allowed isomers: Λδδδ, Λδδλ, Λδλλ, Λλλλ, Δλλλ, Δλλδ, Δλδδ, Δδδδ.[2] Absolute configuration about the metal has been designated Λ or Δ where the view down the threefold axis of the complex forms a left-handed or right-handed propeller, respectively. In the Λ configuration, the δ ring conformation is achieved when the carbon–carbon bond is nearly parallel to the threefold axis and the λ ring conformation is assigned where this bond forms an obtuse angle with the C_3 axis. Due to identical conformational stabilities of their mirror image set, the following discussion will be limited to only the first set of four conformers in the above list.

Corey and Bailar[3a] first calculated the relative energies of the Λδδδ and Λλλλ conformations based on a comparison of the nonbonded interactions in the systems and predicted the Λδδδ form to be 1.8 kcal mol^{-1} lower in energy. A more complete study which included entropy effects by Gollogy, Hawkins, and Beattie[3b] suggested that Λδδλ would be nearly equal in stability with the Λδδδ conformation. In agreement with these theoretical arguments, the large majority of X-ray structure determinations on tris(ethylenediamine)metal complexes have revealed Λδδδ while only a few, as indicated in Table I, have shown Λλλλ or one of the mixed conformer ring systems. Thus far, the structural differences in these isomers have been detected only by arduous experiments requiring complete X-ray techniques. In this work we have attempted systematically to identify the individual conformer ring systems for tris(ethylenediamine) complexes using the solid-state vibrational spectroscopy of compounds whose ring conformations have been determined by X-ray methods.

Experimental Section

Preparation of Compounds. Several of the compounds used in this study were prepared following standard synthetic procedures. Among these are $[Co(en)_3]Cl_3 \cdot 3H_2O$,[15a] $[Cr(en)_3]Cl_3 \cdot 3.5H_2O$,[15b] and $[Cr(en)_3][Ni(CN)_5] \cdot 1.5H_2O$.[15c] Synthesis of the compounds $[Cr(en)_3][Co(CN)_6] \cdot xH_2O$,[16] $[Co(en)_3][Cr(CN)_5NO] \cdot 2H_2O$,[13] $[Co(en)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$,[17] $[Ni(en)_3][(C_6H_5)_4B]_2$,[18] and $[Ni(en)_3](C_2H_3O_2)_2 \cdot 2H_2O$[19] followed recent literature references and resulted in good yields. The infrared spectra from 4000 to 600 cm^{-1} were obtained for each of these compounds and were in good agreement with literature values. Other methods of characterization for some of the compounds included conductivity measurement, elemental and hydrate analysis, and X-ray crystallographic determination.

Spectroscopic Studies. All infrared spectra were obtained as Nujol mulls on NaCl plates using a Beckman IR-10 or a Perkin-Elmer 180 spectrophotometer. Duplicate and triplicate spectra were taken to ensure reproducibility. We were able to achieve greater resolution on the Perkin-Elmer instrument as illustrated in Figure 1 where the same sample has yielded spectrum 1c on the IR-10 and spectrum 1d on the Model 180. Hence, all other spectra shown in Figure 1 and those in Figure 2 were obtained on the Perkin-Elmer 180.

Raman wave number shifts were recorded on a Cary 82 laser Raman spectrophotometer using the 5145-Å exciting line of an argon ion laser. Thermal decomposition of the highly colored solids due

Table I. Observed Ring Conformations from X-Ray Crystallographic Data

Compd	Formula	Conformn[a]	Ref
1	$[Ni(en)_3](NO_3)_2$	δδδ	4
2	$[Ni(en)_3]SO_4$	δδδ	5
3	$[Cu(en)_3]SO_4$	δδδ	6
4	$[Co(en)_3](NO_3)_3$	δδδ	7
5	$[Co(en)_3]_2(HPO_4)_3$	δδδ	8
6	$[Co(en)_3]Cl_3 \cdot 3H_2O$	δδδ	9
7	$[Cr(en)_3]Cl_3 \cdot 3.5H_2O$	δδδ	10
8	$[Ni(en)_3](C_2H_3O_2)_2 \cdot 2H_2O$	δδδ	11
9	$[Cr(en)_3][Ni(CN)_5] \cdot 1.5H_2O$	δλλ, δδλ	12
10	$[Cr(en)_3][Co(CN)_6] \cdot 6H_2O$	λλλ	12
11	$[Co(en)_3][Cr(CN)_5NO] \cdot 2H_2O$	δλλ	13
12	$[Co(en)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$	δλλ	14

[a] For Λ metal configuration.

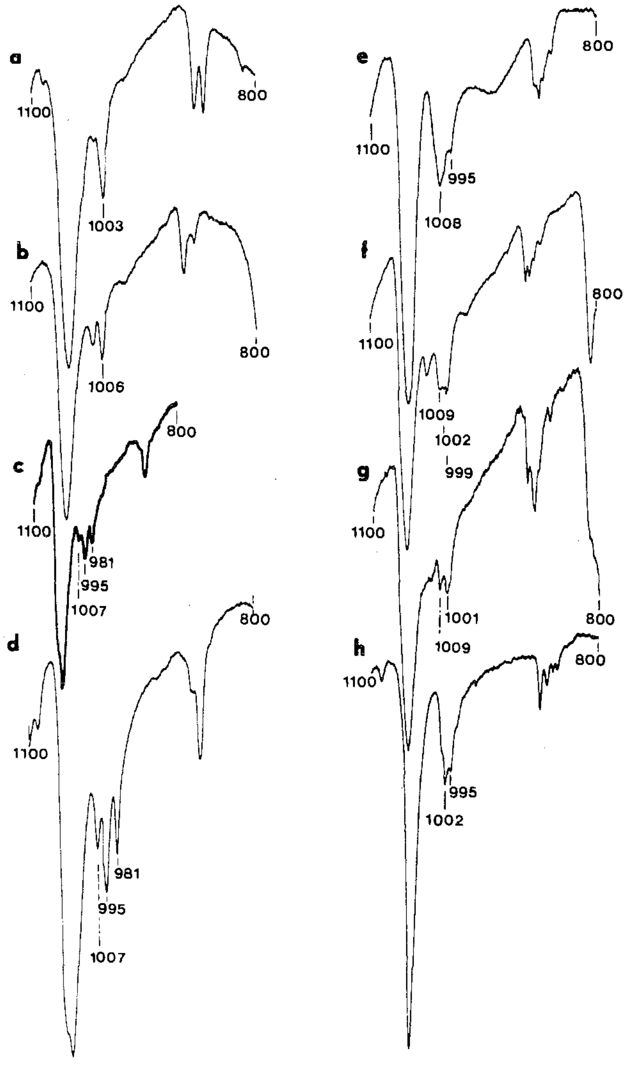

Figure 1. Infrared spectra from 1100 to 800 cm^{-1} for (a) $[Cr(en)_3]Cl_3 \cdot 3.5H_2O$, (b) $[Co(en)_3]Cl_3 \cdot 3H_2O$, (c) $[Cr(en)_3][Co(CN)_6] \cdot xH_2O$, $x \approx 1.5$, taken on the IR-10, (d) $[Cr(en)_3][Co(CN)_6] \cdot xH_2O$, $1.5 < x < 6.0$, (e) $[Cr(en)_3][Ni(CN)_5] \cdot 1.5H_2O$, (f) $[Co(en)_3][Cr(CN)_5NO] \cdot 2H_2O$, (g) $[Co(en)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$, and (h) $[Cr(en)_3][Co(CN)_6] \cdot xH_2O$, $x \approx 0$.

to absorption of the 400–600-mW beam was minimized by spinning the samples through the laser beam.

Results and Discussion

It has been established[20] that for the Λδδδ conformation of the $[M(en)_3]^{n+}$ ion, in D_3 symmetry, only one carbon–carbon infrared stretching vibration is to be expected

$$\Gamma_{\nu(\mathrm{C-C})}^{D_3} = \mathrm{A_1(R) + E(ir, R)}$$

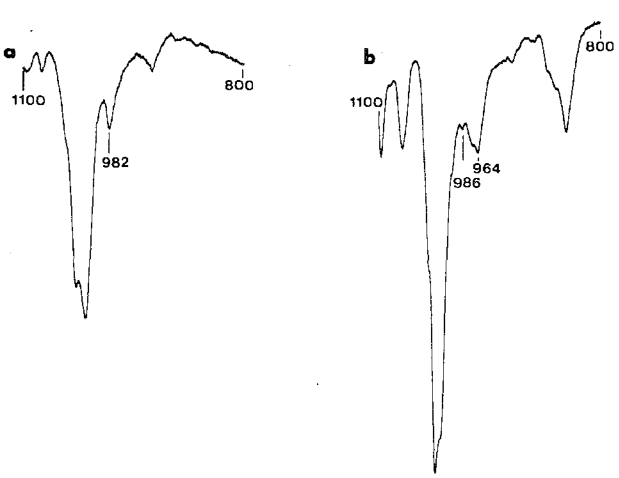

Figure 2. Infrared spectra from 1100 to 800 cm^{-1} for (a) $[Ni(en)_3](CH_3COO)_2 \cdot 2H_2O$ and (b) $[Ni(en)_3][(C_5H_6)_4B]_2$.

For the mixed ring conformations δδλ and δλλ the symmetry is lowered to C_2 and the number of infrared absorptions to be found for the carbon–carbon stretching vibration is 3

$$\Gamma_{\nu(\mathrm{C-C})}^{C_2} = \mathrm{2A(ir, R) + B(ir, R)}$$

The first requirement is to determine the frequency of the C–C stretching vibration. This mode has been assigned to a band at 980 cm^{-1} for free ethylenediamine,[21] and for halide salts of $M(en)_3^{n+}$, M = Rh(III), Ir(III), and Pt(IV), a band of weak to medium intensity near 1000 cm^{-1} has been assigned[20] to C–C stretching. Nakagawa[22] also assigned a band in this region to C–C stretching in the detailed analysis of *trans*-$[Co(en)_2Cl_2]^+$. We are thus interested in bands of weak to medium intensity at about 1000 cm^{-1}. Accordingly the infrared region from 1100 to 800 cm^{-1} was examined and the results are presented in Figure 1.

A band assigned as the C–C stretch appears at 1003 cm^{-1} in Figure 1a for the δδδ conformation of $[Cr(en)_3]Cl_3 \cdot 3.5H_2O$ but broadens (1008, 1002 (sh) cm^{-1}) and picks up a shoulder at 995 cm^{-1} in Figure 1e for $[Cr(en)_3][Ni(CN)_5] \cdot 1.5H_2O$ which contains both δλλ and λδδ conformations. Similarly, D_3 symmetry of $[Co(en)_3]Cl_3 \cdot 3H_2O$ yields one sharp absorption at 1006 cm^{-1} in Figure 1b, while in Figure 1f the C_2 symmetry of the δλλ conformation in $[Co(en)_3][Cr(CN)_5NO] \cdot 2H_2O$ splits this band into three definite peaks at 1009, 1002, and 999 cm^{-1}. The spectrum of another cobalt complex which also has δλλ conformation and C_2 symmetry, $[Co(en)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$, is shown in Figure 1g. Two peaks, at 1009 and 1001 cm^{-1}, are discernible. This small but significant experimental difference substantiates the theoretical treatment and indicates that it is possible to detect mixed ring conformations by infrared spectroscopy.

In the case of $[Cr(en)_3][Co(CN)_6] \cdot xH_2O$ an apparent contradiction arises since the infrared spectrum (Figure 1d) shows three peaks at about 1000 cm^{-1} but the X-ray results identified the λλλ conformation which belongs to the D_3 point group. This inconsistency can be resolved by noting that the X-ray structure was carried out on the hexahydrate which is "obtained only at low temperatures and rapidly effloresces when opened to the air".[16] In our experiment no precautions were taken to prevent efflorescence and thus the hydrate number of the solid used in obtaining spectra 1c and 1d was definitely less than 6. The weight loss on heating some of this product several days at 124° corresponded to a hydrate value of 1.5; a change in the crystalline appearance also occurred on heating. The observed spectra indicate that the efflorescent reduction from $x = 6$ to $x = 1.5$ in the number of waters of hydration manifests itself as a conformational transition from the highest energy form to a mixed arrangement, δλλ or λδδ,

Table II. Raman Shifts for N-H and C-H Stretching Modes in Various $[M(en)_3]^{n+}$ Conformations

	Compd and conformn					
Assignment	Ethylenediamine[a]	**6**,[b] δδδ	**7**, δδδ	**11**, δλλ	**10**, δλλ, δδλ	9, δλλ, δδλ
$\Delta\nu(CH_2)$, cm^{-1}	2860 s	2908 m	2904 m	2905 m	2913 m	2898 w
	2930 s	2975 s	2964 s	2965 s	2975 m	2964 m
$\Delta\nu(NH_2)$, cm^{-1}		3105 vw	3085 vw	3235 vw		
	3300 vs	3216 m	3210 m	3285 m	3255 w	3287 w
$\nu(NH_2)$, cm^{-1} (ir)		3175	3170	3225	3230	3220

[a] 98–100% liquid in capillary sample tube. Abbreviations: s, strong; m, medium; w, weak; v, very. [b] See Table I for compound identification.

either of which has C_2 symmetry. Moreover, the product after the thermally induced dehydration from $x = 1.5$ to $x \simeq 0$ yields the spectrum shown in Figure 1h in which the ν(C–C) vibration band near 1000 cm^{-1} now has a dramatically reduced splitting. This strongly suggests that the loss of H_2O molecules from the lattice initiates a structural change in $[Cr(en)_3]^{3+}$ which takes it from D_3 to C_2 to nearly complete D_3 symmetry by eliminating the high-energy λλλ conformer in favor of λλδ and λδδ and finally toward the lowest energy δδδ conformer.

Efforts to obtain spectra of a freshly prepared precipitate of the hexahydrate by mulling it in its aqueous mother liquor yielded intensities only one-fourth those shown in Figure 1. A single band near 1000 cm^{-1} was observed as long as the mull was still moist but after 30 min to 1 hr in the infrared beam this region for the dry sample began to broaden and develop an additional peak. Further drying, however, did not produce the resolved fine structure shown in Figure 1d and the general low quality of the spectra prevent making a conclusion based solely on these results.

Raymond, Corfield, and Ibers have postulated[12] that the large number of potential hydrogen bonding sites on anions like $[Co(CN)_6]^{3-}$ stabilize and thus induce λ ring conformations in $[M(en)_3]^{n+}$ systems because in this geometry more amino hydrogens are available for such interactions. However, in a recent publication[11] we have suggested that another parameter, namely, a size or bulk effect, is probably equally or more important than the H-bonding effect in determining which conformer will be observed in the solid state. In agreement with the latter argument, a decrease in lattice volume caused by the release of hydrate water molecules from $[Cr(en)_3][Co(CN)_6]\cdot xH_2O$ would select against the larger, more spherical geometry of the λλλ conformation in favor of the smaller, more cylindrical δδδ conformation.

In order to test this theory we have observed the infrared spectrum of $[Ni(en)_3][(C_6H_5)_4B]_2$. The tetraphenylborate anion should be large enough to isolate the tris complex, yet it should also be a weak hydrogen-bond acceptor. Therefore, we would predict the ν(C–C) band to have much more detail thus indicating a preference for λ rings and a mixed conformation because of the size effect alone. This is what is observed when comparing Figure 2a with 2b. The single peak at 982 cm^{-1} for the δδδ conformation of $[Ni(en)_3](C_2H_3O_2)_2\cdot 2H_2O$ is split for $[Ni(en)_3][(C_6H_5)_4B]_2$ into peaks at 986, 971 sh, and 964 cm^{-1}.

Additional data concerning the actual effect of the amino proton–anion hydrogen-bonding interaction may be obtained by investigating another region of the spectrum. In an X-ray crystal structure determination of $[Ni(en)_3](NO_3)_2$ Swink and Atoji[4] discussed the infrared spectrum and assigned two peaks at 3200 and 3300 cm^{-1} to N–H stretching according to the symmetric $\nu(NH_3)$ at 3337 cm^{-1} and the asymmetric $\nu(NH_3)$ at 3414 cm^{-1} found for ammonia. They attributed the shift to lower wave numbers mainly to anion–complex hydrogen-bonding interaction through the N–H groups but also noted that the interaction was bifurcated and thus would be weaker than an ordinary hydrogen bond. We have been able to observe a single broad peak for the $\nu(NH_2)$ stretching mode in the infrared spectra of several ethylenediamine complexes despite severe interference bands from water and Nujol. These assignments have been included in Table II in order to show their corroboration with the Raman data we have collected. The Raman spectra of the solid complexes are much simpler and are comprised essentially of the three main peaks assigned in Table II. There is good agreement between observed $\nu(CH_2)$ stretching frequencies among the complexes and between those of free ligand and each complex. However, a shift for the $\nu(NH_2)$ frequency similar to that recognized as due to hydrogen bonding by Swink and Atoji is evidenced by each complex. Furthermore, each complex exhibits a different shift from the free ethylenediamine value of 3300 cm^{-1}. Those complexes having δδδ conformation have been shifted nearly 90 cm^{-1} while those containing some λ rings have been shifted by less than 50 cm^{-1}. This may tend to suggest that the hydrogen-bonding interaction between anion and amine protons on the complex is stronger for the δ rings than it is for the λ rings. It is also interesting to note that when a complete mixture of possible ring conformations is present, as in compounds **10** and **11** or in free ethylenediamine which has trans plus both gauche forms, then a second very weak signal, found at lower frequency for compounds in which all or nearly all the rings are the same, is no longer observed. James and Nolan[20] were able to observe only one peak at 3230 cm^{-1} for the $\nu(NH_2)$ stretching mode in the Raman spectrum of $[Rh(en)_3]Cl_3\cdot 3H_2O$ which is known to have the δδδ conformation. In a detailed infrared study Csaszar[23] has observed the $\nu(NH_2)$ stretching mode for several $[Ni(en)_3]^{2+}$ complexes with different anions. The values of free ligand were given as 3335 and 3246 cm^{-1} and a comparison between the shifts from these values for the complexes where the anions are Cl^-, Br^-, and I^- and the shifts for $[Ni(en)_3][PtCl_6]$ shows that while each of the halide salts give nearly identical shifts the $\nu(NH_2)$ frequencies found for the platinate salt are not shifted as far. The large hexachloroplatinate anion may induce λ rings in $[Ni(en)_3]^{2+}$ and thus this series of tris(ethylenediamine) complexes can be rationalized to yield the same trend seen in Table II where the presence of δ rings effects a stronger N–H···A interaction and results in a lessening of the N–H bond order; hence the $\nu(NH_2)$ stretching frequency is lowered.

From conformational geometries previously determined through complete X-ray crystallographic techniques, we have been able to show how the vibrational spectroscopy of tris(ethylenediamine) complexes can be used to identify the presence of mixed ring conformations. The simplicity and advantages of this treatment are evident and we predict it will facilitate the discovery of other compounds of mixed conformation. The peculiar behavior of $[Cr(en)_3][Co(CN)_6]\cdot xH_2O$ discussed above suggests an interesting experiment involving high-pressure infrared spectroscopy. If the complex cation does undergo a structural rearrangement as lattice volume diminishes, then it seems possible that the same transformation will be induced under high pressures and could be recorded as changes in the infrared spectra similar to those observed in Figure 1d and 1h. Such experiments involving pressure-induced geometrical changes in $[Ni(CN)_5]^{3-}$ [24] and

$Ni[BzP(C_6H_5)_2]_2Br_2$[25] have recently been reported.

Registry No. $[Co(en)_3]Cl_3{\cdot}3H_2O$, 14883-80-8; $[Cr(en)_3]Cl_3{\cdot}3.5H_2O$, 16165-32-5; $[Cr(en)_3][Ni(CN)_5]{\cdot}1.5H_2O$, 20523-47-1; $[Cr(en)_3][Co(CN)_6]{\cdot}xH_2O$, 56114-36-4; $[Co(en)_3][Cr(CN)_5NO]{\cdot}2H_2O$, 55991-03-2; $[Co(en)_3]_2[Cu_2Cl_8]Cl_2{\cdot}2H_2O$, 28852-88-2; $[Ni(en)_3][(C_6H_5)_4B]_2$, 41685-81-8; $[Ni(en)_3](C_2H_3O_2)_2{\cdot}2H_2O$, 55991-04-3.

Supplementary Material Available. Tables III and IV, listing the observed Raman wave number shifts and infrared frequencies, respectively, for compounds **6**, **7**, **9**, **10**, and **11** (see Table I), will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC50109+-10-75.

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Nucleoside Complexing. Longitudinal Relaxation Studies of Metal Binding Sites in Adenosine and Cytidine

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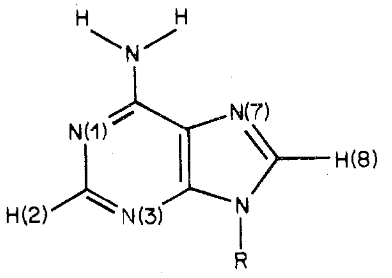
Received February 13, 1975 AIC501109

Our interest in finding specific metal-containing reagents for probing nucleic acid structures[2a] has led us to use PMR relaxation techniques[2b] as tools. One such technique, the line broadening induced by the Cu^{2+} ion, has been questioned recently, when Martin showed that this broadening was greatly influenced by scalar coupling.[3] Scalar coupling cannot occur unless a bond is formed.[2b] However, the extent of coupling may not diminish uniformly as the number of bonds between the paramagentic center and the resonating nucleus increases. The scalar coupling term influences longitudinal relaxation times (T_1) to a much smaller extent.[2b,3] For the Cu^{2+} ion, the relaxation is not exchange limited[3] and thus, T_{1P}^{-1} the difference between the T_1^{-1} of a resonance in the presence and the absence of the paramagnetic metal ion, is a measure of the inverse sixth power of the distance between the Cu^{2+} (or other paramagnetic centers) and the nucleus of concern.[2b] The *relative* values of T_{1P}^{-1} for different nuclei in a given ligand can be used to deduce the metal binding site.

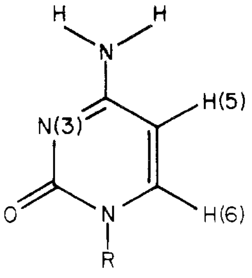
Line-broadening studies using the Cu^{2+} ion form a very important body of information in the coordination chemistry of nucleic acids and nucleic acid constituents. Good crystalline samples of the complexes of interest are difficult to obtain, and, consequently, few crystal structures, which might serve to verify the assignments, have been reported.[4] We have recognized for some time that line broadening may be complicated by scalar coupling. As part of our search for selective reagents, we have checked some binding site assignments by using longitudinal relaxation. Our assignments agreed with those of Eichhorn.[4,5] The report by Martin[3] prompts us to report our results.

Results and Discussion

The nucleic acid constituents which are most useful in our studies are the nucleosides, consisting of a ribose sugar and a heterocyclic base capable of permitting selective bonding.[2a] For two nucleosides, adenosine (I) and cytidine (II) (R = ribose for both), longitudinal relaxation studies have provided information not obtainable by line broadening. Adenosine (I) has two apparently similar binding sites for attachment of metals, one on the six-membered ring and one on the five-membered ring of the purine heterocycle.[5] From line-broadening studies it is fairly certain that the five-membered ring site is N(7).[5] The six-membered ring site could be either N(1) or N(3).[5] The evidence for these sites is the nearly equal broadening of the H(2) and H(8) resonances of adenosine in DMSO when the Cu^{2+} ion is added.[5] Because the broadening may be a result of scalar coupling,[3] it is not possible either to assign the six-membered ring bonding site or to estimate the relative importance of the binding to the six-membered ring and to the five-membered ring sites.



I



II

The addition of the Cu^{2+} ion to cytidine solutions causes the H(5) resonance to broaden almost beyond limits of observation.[5] The H(6) resonance does not broaden appreciably and remains a doublet, coupled with H(5). This result is clearly suggestive of a large scalar component in the broadening. Otherwise, as the H(5) resonance broadened, the coupling to H(6) would have disappeared. This analysis of the broadening effect was recently advanced in the literature,[6] and we had reached the same conclusion. Furthermore, crystal structures of the related cytosine complexes reveal that the H(5) and H(6)