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Conformational Characterization of Paramagnetic Nickel(II) Tetraazamacrocyclic Complexes through ^{1}H NMR Relaxation Studies

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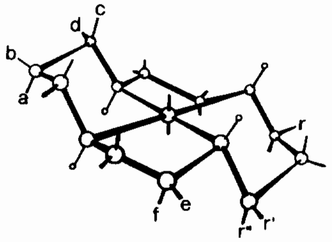
Isotropic shift studies can in principle provide a powerful tool for investigating the structure of paramagnetic molecules in solution, since both contact and dipolar shift contributions are related to the geometrical properties of the resonating protons with respect to the paramagnetic center [1]. However, because of the difficulties involved in separating these two contributions [2], the use of the technique is often limited only to the cases where one of the above quantities is believed to be significantly less important than the other. As a matter of fact, conformational studies on paramagnetic complexes have been extensively carried out only for six-coordinate nickel(II) complexes [3–6], since, on account of the fact that this octahedral metal ion is characterized by an orbitally non-degenerate electronic ground state, dipolar shifts are expected to be negligible.

In order to overcome this problem the analysis of the proton relaxation rates could be considered an alternative method for obtaining information on the detailed structure of the molecule around the paramagnetic metal ion [7, 8]. The well known Solomon–Bloembergen–Morgan (SBM) equation [9, 10] offers a basis for quantitative explanation of the observed spin–lattice nuclear relaxation rates, relating these quantities in a given paramagnetic system to the sixth power of the distance from the paramagnetic center of the relaxing nucleus. However, although this equation has been extensively applied to many paramagnetic chemical systems, mostly of biological interest, many complications may arise for a proper application. In particular there has been pointed out the importance of significant spin densities induced by the paramagnetic metal ion into the ligand orbitals, as required by the observed contact shifts [1]. Another cause of deviation from the SBM behaviour is that the unpaired spin density is associated with orbitals which have significant probability amplitude also at distances of the same order of magnitude as the metal ion–resonating nucleus distance [11, 12]. For these reasons, despite its large use, the SBM equation is expected to have a very limited application for the nuclei in close proximity of the metal ion [11–13]. However, even considering the pitfalls of a quantitative approach, it would appear useful to check whether the SBM equation may be applied in order to obtain qualitative information. With this in mind we have attempted to characterize through ^{1}H NMR relaxation measurements some closely related six-coordinate nickel(II) complexes formed by saturated tetraazamacrocyclic ligands. These complexes have been shown to provide stimulating examples for studying the conformational properties of the molecules, because of the high barrier of interconversion of their chelate ring systems.

The complexes which have been considered are the *trans*-octahedral dichloro nickel(II) derivatives of the 1,4,8,11-tetraazacyclotetradecane ([14]aneN_4), *meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane (Me_2[14]aneN_4), and *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (Me_6[14]aneN_4) ligands. According to the molecular scheme (I), in all of these complexes the conformation of the ligand is such that the six- and five-membered chelate rings are in a chair and gauche conformation, respectively, as supported by chemical reactivity, X-ray diffractometric analysis and ^{1}H NMR spectroscopic studies [6, 14–16]. The ^{1}H NMR spectra of $CDCl_3$ solutions of these complexes have been previously reported and assigned. The observed isotropic shift patterns agree with those expected on the basis of contact shift contributions occurring *via* spin-polarization mechanisms. INDO calculations of spin densities support this conclusion [17].



$r, r', r'' = \mathrm{H}$, [14]aneN_4

$r = \mathrm{CH}$; $r', r'' = \mathrm{H}$ Me_2[14]aneN_4

$r, r', r'' = CH_3$, Me_6[14]aneN_4

The spin–lattice nuclear relaxation times T_1, as obtained from *ca.* 10^{-2} *M* solutions at 34 °C in the same solvent by the inversion recovery method, are reported in Table I.

As a general conclusion it may be observed that protons or methyl substituents having pseudo axial character exhibit greater relaxation rate enhancements than do their pseudo-equatorial counter-

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parts. This can be easily understood if an electron nuclear dipolar mechanism is operative. Considering that the shorter the distance between a given nucleus and the paramagnetic center, the greater its relaxation rate enhancement is expected to be, since pseudo-axial substituents are closer than pseudo-equatorial ones, it is reasonable to expect that the former protons experience greater relaxation enhancements than the latter ones. The exception to this behaviour is given by the H_d protons which experience proton relaxation enhancements of the same order of magnitude as their axial counterparts H_c.

As predicted, any quantitative analysis of these data by means of the SBM equation is unsuccessful. According to this equation, the ratios of the T_{1M} values for any given couple of protons would approach the sixth power of the ratios of their distances from the paramagnetic metal ion. Although no detailed structural data have been reported for the complexes under investigation, reliable values of the $Ni-H_i$ distances can be estimated by comparison with the X-ray diffractometric data of some related compounds [18, 19]. These values are shown in Table I, their uncertainties being less than 0.1 Å. From these data T_1 ratio values of *ca.* 3 would be expected for any couple of geminal methylenic protons, but significant discrepancies between the calculated and the observed quantities are observed. For the geminal protons of the ethylenic chains ratio values of *ca.* 10 are actually found, whereas for the α and β methylenic couples of the propylenic chains ratio values of 1 and 2, respectively, are measured. Again significant discrepancies show up when one compares the relaxation enhancements of protons attached to different carbon atoms. The most representative example is given by the pseudo-equatorial protons of the methylenic groups directly attached to the nitrogen donor atoms: despite the similarity of the Ni–H distances the ethylenic protons experience relaxation rates one order of magnitude smaller than the propylenic ones.

Also the relaxation rates of the ethylenic pseudo-equatorial protons of the $Me_2[14]aneN_4$ and Me_6-$[14]aneN_4$ derivatives are very different from each other. The methyl substituent on carbons 5 and 12 of the cyclotetradecane ring renders inequivalent the two methylenic groups of the ethylenic chains. As a consequence the metal-to-nitrogen distances are different, being, as shown by X-ray diffractometric data, 2.06 and 2.02 Å for Cu–N(1) and Cu–N(4), respectively, in the $Cu(Me_6[14]aneN_4)(ClO_4)_2$ derivative [18]. The observed Cu–H distances in this compound for the ethylenic pseudo-equatorial protons are 3.84 Å for proton on C(2) and 3.82 Å for proton on C(3). The two protons in the nickel(II) derivative experience similar isotropic shifts [6], however their relaxation rates differ by more than 30%. One might reasonably suggest that the

TABLE I T_{1M} Values (ms) of Nickel(II) Tetraaza Macrocyclic Complexes in $CDCl_3$ at 34 °C [a]

	5-membered chel. rings		6-membered chelate rings						
Averaged Ni–H distance (Å) [b]	CH_{ax}(f) 3.2	CH_{eq}(e) 3.8	α-CH_{ax}(c) 3.3	α-CH_{eq}(d) 3.9	β-CH_{ax}(b) 3.4	β-CH_{eq}(a) 4.2	Me_{eq}(r) 4.5	Me_{eq}(r') 4.5	Me_{ax}(r') 3.6
$Ni([14]aneN_4)Cl_2$	0.4	4.3	0.4	0.4	1.1	2.3	–	–	–
$Ni(Me_2[14]aneN_4)Cl_2$	0.7	5.4, 7.2	0.6, 0.7	0.7	2.0	5.4	12.2	–	–
$Ni(Me_6[14]aneN_4)Cl_2$	0.9	6.4, 9.2	0.9	–	–	10.2	21.8	25.1	(2.4)[c]

[a] Estimated error: ±10%. [b] Calculated according to X-ray data (Refs. 18, 19). Estimated error: ±0.1 Å. [c] Approximate value, because of the overlap with β-CH_{ax} resonance.

faster relaxing proton is that adjacent to the nitrogen closer to the metal. In this respect the main conclusion is that relaxation rates provide a very sensitive tool for assigning proton resonances.

The failure of the SBM equation in interpreting these results may be attributed to the basic assumption that the unpaired electron spin is located on the metal ion and can be treated as a point dipole. Following the molecular orbital treatment of Gottlieb, Barfield and Doddrell [11] the spin lattice nuclear relaxation in a paramagnetic complex should be given by the sum of three contributions according to the relationship

$$T_1^{-1} = T_{1M}^{-1} + T_{1L}^{-1} + T_{1ML}^{-1}$$

where T_{1M}^{-1} is the metal centered relaxation contribution (similar to that described by the SBM equation), T_{1L}^{-1} is the ligand centered contribution arising from the delocalization of the unpaired electron in the ligand orbitals, and T_{1ML}^{-1} is a term arising from the time correlation of ligand and metal centered correlation matrix elements and is a consequence of the MO approach. From these data it should be concluded that the ligand centered contribution largely determines the relaxation of protons close to the paramagnetic metal ion.

Despite the difficulties involved in a simple theoretical analysis of the experimental results, it is noteworthy that the observed patterns of relaxation rates are quite regular among the series of the complexes under investigation. The general decrease of the relaxation rate enhancements on passing from the [14]aneN$_4$ derivative to the Me$_2$[14]aneN$_4$ and Me$_6$-[14]aneN$_4$ ones can be explained by assuming that the correlation time in these systems is largely determined by the orientational relaxation time τ_r due to Brownian rotational motion. This is not an unexpected result since τ_r values of *ca.* 10^{-11} s can be estimated from Stokes' law [20] for these systems, whereas the electronic relaxation time for nickel(II) in pseudooctahedral environments is expected to fall in the range 10^{-10}–10^{-11} s [21]. Therefore following Stokes' law the reorientation rate of the complex will decrease on increasing the effective radius of the tumbling system, thus justifying the experimental results.

The observed regularity of the relaxation rate patterns among the series of the complexes indicates a striking analogy in the spin-polarization terms induced by the paramagnetism of the metal ion. In this sense one can reasonably suggest that similar patterns should be anticipated for complexes formed by similar paramagnetic metal ions, neglecting contributions arising from magnetic anisotropy. This suggestion is a direct consequence of the fact that spin-delocalization contributions largely determine the relaxation rates of protons close to the paramagnetic center. These considerations can be compared with those suggested by Horrocks [22] in order to justify his "ratio method", and we believe that they can be usefully applied for understanding the isotropic shift patterns of nickel(II) analogues formed, for instance, by iron(II) and cobalt(II).

Experimental

The nickel(II) macrocyclic complexes were prepared as previously reported [6].

The ^{1}H NMR spectra were recorded at 34 °C on a Bruker CXP 100 spectrometer equipped with a 1.4 T Varian DA 60 magnet. Longitudinal relaxation times, T_1, were measured with the inversion recovery method using an appropriate nonlinear least-squares fitting program. Deuteriochloroform (Merck 99.8%) was used as solvent.

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