Inorganica Chimica Acta, 53 (1981) L155–L156
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Conformational Properties of the Nickel(II)–1,5,9,13-Tetraazacyclohexadecane Moiety

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Received November 4, 1980

As a consequence of their peculiar reactivity properties, macrocyclic complexes often offer significant examples for studying the conformational properties of the molecules [1–4]. Recent developments in the synthesis of unsubstituted polyazacycloalkanes [5] have provided the ideal ligands for investigating the effects of the size and sequence of the chelate rings on the conformation properties of metal complexes formed by multidentate ligands. In this respect, the metal complexes formed by fourteen- and fifteen-membered tetraazacycloalkane ligands have been extensively investigated [6, 7]. The results of an isotropic shift study on paramagnetic nickel(II) derivatives of the sixteen-membered 1,5,9,13-tetraazacyclohexadecane ([16]aneN$_4$) are here reported and information on the conformational properties of this nickel(II)–macrocyclic moiety is given.

In theory, if the [16]aneN$_4$ ligand is planarly coordinated around a metal ion, four basic structural conformers can exist, as determined by the possible distribution of nitrogen atom configurations. They are schematically shown in Fig. 1, the '+' or '–' signs indicating secondary amine protons above or below the metal-four nitrogen plane. Therefore, as the conformational character, *i.e.* pseudo-axial, pseudo-equatorial or isoclinal, of the methylenic protons is considered, symmetry considerations indicate that for the isomers (a) through (d) there are seven, eleven, four and three sets of nonequivalent protons, respectively. Theoretical strain energy calculations for *trans*-[Co([16]aneN$_4$)Cl$_2$]$^+$ isomers suggest that (a) and (b) conformers are to be expected as the most stable [6].

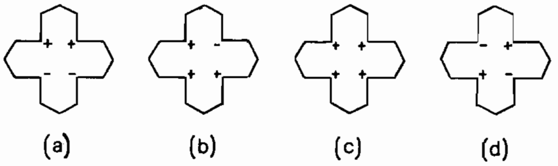

Fig. 1. Possible configurational isomers for the [16]aneN$_4$ ligand in *trans*-octahedral M([16]aneN$_4$)X$_2$ derivatives.

The ^{1}H NMR spectrum at 34 °C of a CDCl$_3$ solution of the paramagnetic Ni([16]aneN$_4$)Cl$_2$ is shown in Fig. 2. The observed resonance line pattern, which does not vary within a period of weeks, can be explained only by assuming the existence of more than one conformer at the equilibrium. All attempts to separate the different conformers through fractional crystallization were unsuccessful; however if one considers the different intensity ratios of the resonance signals, it is apparent that the different conformers exist in different percentages and the spectra of the mixture provide useful information for their configurational characterization.

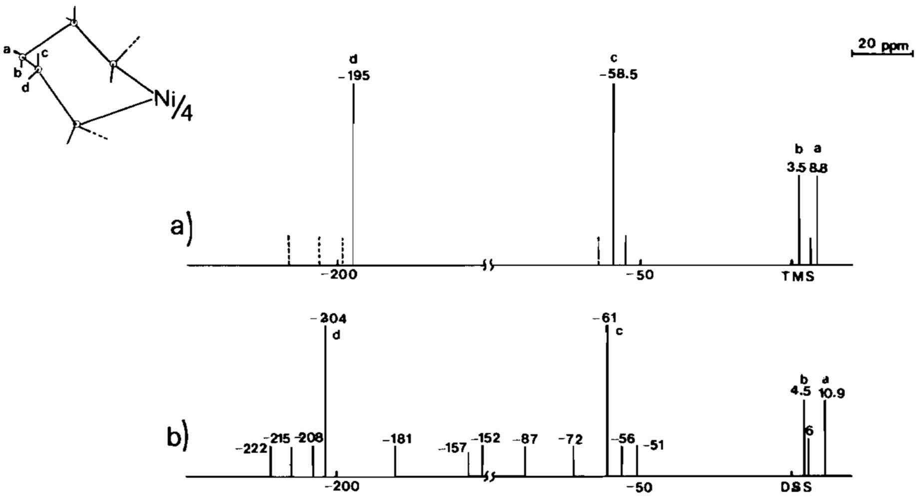

Fig. 2. Schematic representation of ^{1}H NMR spectra of Ni([16]aneN$_4$)Cl$_2$ in a) CDCl$_3$ and b) D$_2$O at 34 °C.

The predominant isomer exhibits four resonance signals, two located downfield and two upfield as referred to TMS; the downfield resonances are twice as intense than those upfield. The assignment of these signals can be carried out on the basis of similar considerations successfully used in previous studies on the conformational characterization of nickel(II)–macrocyclic complexes [4]. The α methylenic protons of the propylenic chains are expected to experience downfield shifts, as referred to their diamagnetic positions, whereas the β-methylenic protons are expected to shift upfield, because of spin polarization mechanisms [8, 9]. Furthermore axial protons are expected to experience smaller contact shifts than the equatorial protons because of the well known angular dependence of the hyperfine coupling constant [10]. Given these considerations, therefore, the resonance signals at –195 and –58.5 ppm are to be assigned to the equatorial and axial α-methylenic protons, respectively, whereas the signals at +8.8 and +3.5 ppm are to be attributed to the equatorial and axial β-methylenic protons.

The ligand-field spectra of the investigated compound are consistent with a *trans*-octahedral structure of the chromophore [11, 12]. Further support of this hypothesis is given by the comparison between the observed pattern of the resonances and that of the *cis*-octahedral $[Ni([16]aneN_4)(acac)]ClO_4$ derivative (acac = acetylacetonate). The spectrum of the latter compound is completely different and characterized by large line-width signals, as already observed in previous studies on *cis*-octahedral nickel(II)–tetraazamacrocyclic complexes [13]. Therefore, according to the considerations mentioned above, it can be concluded that the configuration (c) has to be assigned to the predominant conformer.

The pattern of the weak signals, which appear in the spectrum reported in Fig. 2, could be consistent with the presence either of (a) or (b) conformers or both. No definite conclusion can be reached here because of the low intensity of the signals and their intrinsic large line-width. As far as the spectrum of the same compound in D_2O is concerned (Fig. 2), more definite information is obtained. Again, as the equilibrium between the different conformers is reached, the (c) configuration has to be assigned to the predominant isomer. Furthermore six signals of similar intensity are detected in the range –150/–220 ppm, where resonances due to α-methylenic pseudoequatorial protons are expected. Signals due to the axial counterparts and β-methylenic protons are not resolved because of their large line-width and/or overlap with the resonances of the predominant isomer. This would suggest that both (a) and (b) conformers coexist as the equilibrium, although in smaller concentrations than the (c) conformer.

These results, therefore, indicate that the [16]-$aneN_4$ ligand, if coordinated, preferably adopts the four chair (c) conformation. Isomers (a) and (b), containing two chair and two twist chelate rings, are less stable. Again, a highly unfavourable conformational energy can be suggested for the four twist (d) conformation. These findings contrast with the results of strain energy calculations [6], which suggest, as mentioned above, a different pattern of stability for these conformers.

Experimental

The $Ni([16]aneN_4)Cl_2$ was prepared as previously described [11].

Proton magnetic resonance spectra were recorded on a Varian EM 390 spectrometer at 90 MHz. Shifts were calibrated from internal tetramethylsilane (TMS) or 4,4-dimethyl-4-silapentane-1-sulfonate (DSS). Deuteriochloroform and deuterium oxide (Merck, 99.8%) were used as solvents.

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