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^{1}H NMR Characterization of Paramagnetic Dinuclear Nickel(II) Macrocyclic Derivatives

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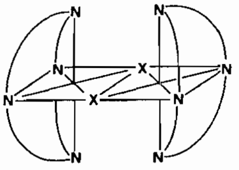
^{1}H NMR is in principle a powerful tool for investigating the nature of metal–metal interactions, since it can provide information on the effect of a metal ion on both the energetics and the relaxation properties of the neighbouring metal ion. Despite the potential interest existing in this field, the contributions on the subject are not numerous [1–6]. This is partly due to the difficulties involved in fully understanding the observed spectral parameters.

In dinuclear complexes a ligand proton is under the influence of two paramagnetic centers. It is of interest to elucidate the conditions determining the relaxation properties of the proton as well as their dependence on the electronic properties of the couple in the metal ions.

In this communication we report the results of a ^{1}H NMR investigation on some dinuclear nickel(II) complexes formed by the macrocyclic ligand *dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*dl*-$Me_6[14]aneN_4$). The observed spectral parameters are compared with those of two mononuclear *cis*- and *trans*-octahedral complexes.

Results and Discussion

The three compounds of the general formula [Ni(*dl*-$Me_6[14]aneN_4)X]ClO_4$ (X = Cl, SH, $C_2O_4/2$) are postulated to contain dinuclear [Ni(*dl*-$Me_6[14]aneN_4)X]_2^{2+}$ cations, where the X groups act as bridging ligands between the two pseudooctahedral nickel(II) ions, according to Scheme 1 [7, 8]. All the observed properties of these complexes as well as the ^{1}H NMR spectra, support this statement. In



Scheme 1.

TABLE I. Isotropic Shift Data (ppm)[a] and Spectral Assignments for [Ni(*dl*-$Me_6[14]aneN_4)X]_2(ClO_4)_2$ Complexes and Monomeric Reference Compounds at 34 °C.[b,c]

	Solvent	5-Membered chelate rings		NH/SH	6-Membered chelate rings					
		CH_{ax}	CH_{eq}		α-CH_{ax}	β-CH_{ax}	β-CH_{eq}	Me_{1eq}	Me_{2ax}	Me_{3eq}
[Ni(*dl*-$Me_6[14]aneN_4)(C_2O_4)_{1/2}]_2(ClO_4)_2$	CD_3CN	b	−160	+185 +165	b	b	+16	−10	+3[b]	−10
[Ni(*dl*-$Me_6[14]aneN_4)SH]_2(ClO_4)_2$	$(CD_3)_2SO$	−32 −11	−228 −225	+270 +275	−45	+8	+17	−20	+1	−6
[Ni(*dl*-$Me_6[14]aneN_4)Cl]_2(ClO_4)_2$	CD_3CN	−26 −20	−225 −193	+148 +261	−37	+7	+17	−19	−1	−7
[Ni(*dl*-$Me_6[14]aneN_4)NO_3]ClO_4$	CD_3CN	−20[b]	−195 −147	+180	−42	b	+18	−13	+3[b]	−11
Ni(*meso*-$Me_6[14]aneN_4)(Cl_2)$[d]	$CDCl_3$	−30 −20	−189 −180	+202	−55	+5	+14	−20	+4	−14

[a] The isotropic shift are determined relative to the shifts of the free ligands: –CH = –2.8 (average), –CH = –1.7 (average), Me = –1.1 ppm (average). Estimated error in isotropic shift data: 1 ppm. [b] Tentative value or not detected because of the overlap with other signals. [c] Key: ax = axial, eq = equatorial. Me_1 and Me_2 are the geminal methyl groups. [d] From ref. [13].

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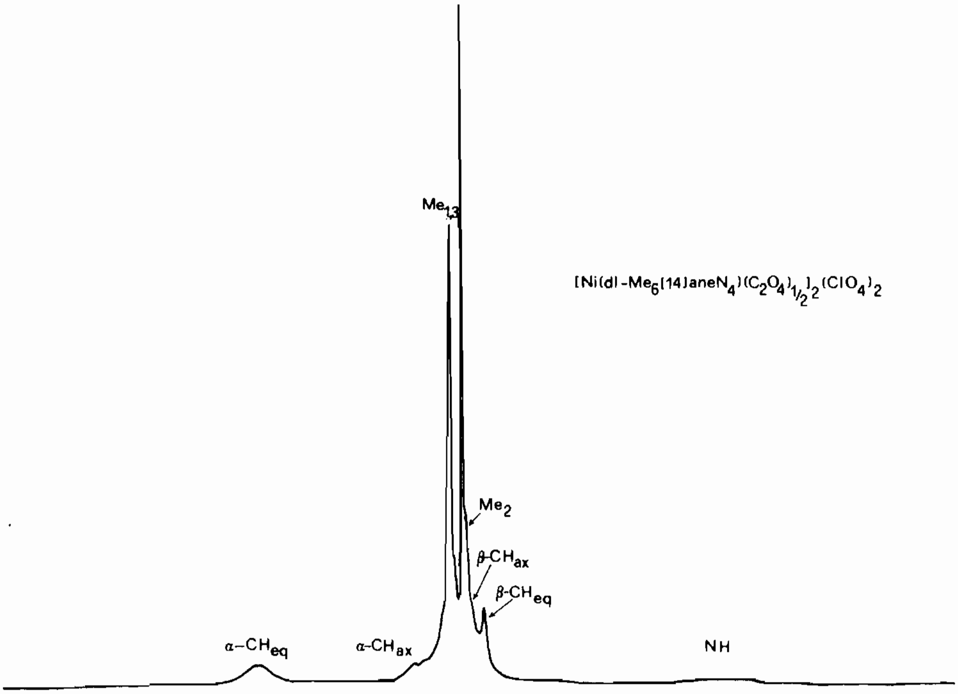


Fig. 1. ^{1}H NMR spectrum of [Ni(*dl*-Me_6[14]aneN_4)(C_2O_4)$_{1/2}$]$_2$(ClO_4)$_2$ in CD_3CN at 34 °C.

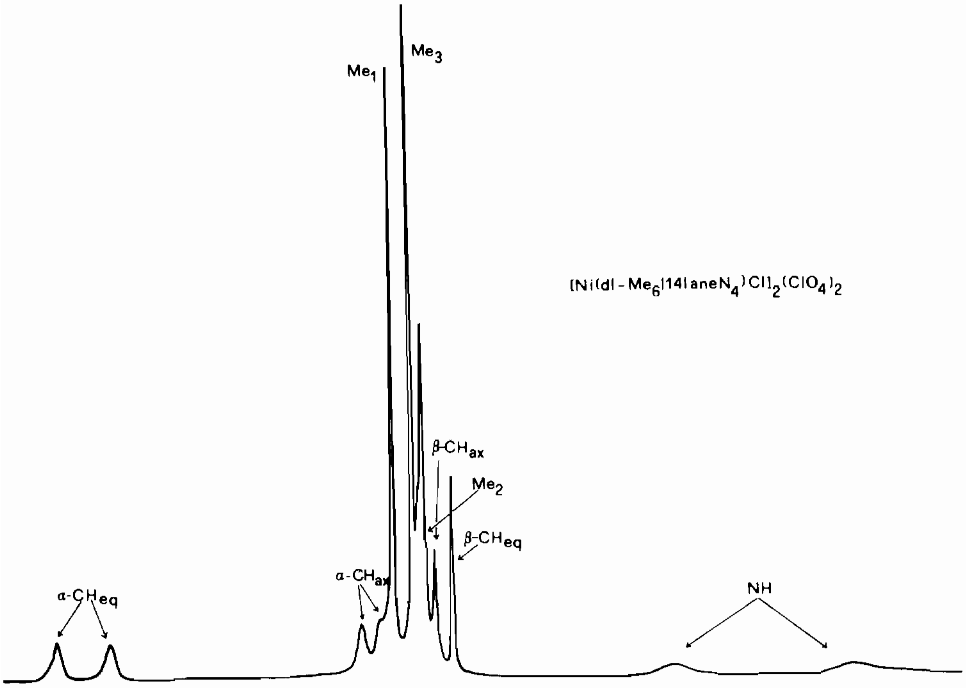


Fig. 2. ^{1}H NMR spectrum of [Ni(*dl*-Me_6[14]aneN_4)(SH)]$_2$(ClO_4)$_2$ in $(CD_3)_2SO$ at 34 °C.

particular the electronic spectra are as would be expected for *cis*-octahedral chromophores [9].

It has been shown that in the oxalato derivative the two metal ions experience antiferromagnetic coupling [10], the observed coupling constant J being -18 cm^{-1} if the magnetic interaction is assumed to be described by the isotropic spin hamiltonian $\mathbf{H} = -2\mathbf{J}\mathbf{S}_1\mathbf{S}_2$. No evidence of magnetic coupling has been observed for the chloro- and hydrogenosulphido-derivatives, the observed magnetic

TABLE II. T_{1M} Values (ms) of $[Ni(dl\text{-}Me_6[14]aneN_4)X]_2(ClO_4)_2$ Complexes and Monomeric *cis*- and *trans*-Reference Compounds.[a]

Averaged Ni–H distance[b] (Å)	5-Membered chelate rings		6-Membered chelate rings					
	CH_{ax} 3.2	CH_{eq} 3.8	α-CH_{ax} 3.3	β-CH_{ax} 3.4	β-CH_{eq} 4.2	Me_{1eq} 4.5	Me_{2ax} 3.6	Me_{3eq} 4.5
$[Ni(dl\text{-}Me_6[14]aneN_4)(C_2O_4)_{1/2}]_2(ClO_4)_2$	c	0.7	c	c	1.2	1.4	0.8[c]	1.4
$[Ni(dl\text{-}Me_6[14]aneN_4)(SH)]_2(ClO_4)_2$	2.5	2.3	2.5	4.5	7.8	11	c	16
$[Ni(dl\text{-}Me_6[14]aneN_4)(Cl)]_2(ClO_4)_2$	0.7	0.8	0.8	2.3	6.5	9	2.6	11
$[Ni(dl\text{-}Me_6[14]aneN_4)(NO_3)]ClO_4$	0.5	0.5	0.5	c	2	3	0.8[c]	4
$Ni(meso\text{-}Me_6[14]aneN_4)Cl_2$[d]	0.9	6.4 9.2	0.9	c	10.2	22	2.4	25

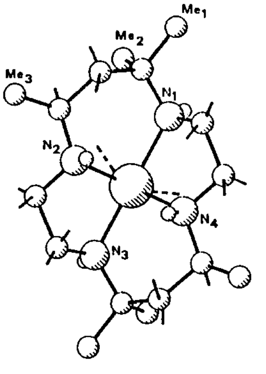
[a] Estimated error: ±10%. [b] Calculated according to X-ray data (Ref. [14]). Estimated error: 0.1 Å. [c] Tentative value or not detected because of the overlap with other signals. [d] From ref. [17].

moments of the two compounds being constant within the experimental error in the range 80–293 K ('Experimental').

The ^1H NMR traces of solutions of the oxalato- and hydrogenosulphido- complexes in the range −300–+300 ppm (TMS reference) are shown in Figs. 1, 2. The isotropic shift data for the three dinuclear complexes as well as those of the monomeric *cis*-octahedral $[Ni(dl\text{-}Me_6[14]aneN_4)NO_3]ClO_4$ [11], and *trans*-octahedral $Ni(ms\text{-}Me_6[14]aneN_4)Cl_2$, are reported in Table I.

The assignment of the resonances has been made following the same considerations previously utilized for similar systems [12, 13]. For methyl groups the proposed assignment is supported by the spectra of samples containing selectively deuterated substituents.

The observed patterns of resonances are consistent with the existence of only one stereoisomer in solution for any given complex. These suggestions agree well with the findings of single crystal X-ray diffraction studies on three monomeric *cis*-octahedral nickel(II) complexes of this ligand [14–16]. In these studies it has been shown also that the macrocycle folds about N(1)–Ni–N(3) (Scheme 2). If a similar arrangement of the ligand in our dinuclear derivatives is assumed, the following considerations can be made.



Scheme 2.

The resonance signals of the two sets of inequivalent NH protons of the μ-dichloro and μ-dihydrogenosulphido derivatives are split by more than 100 ppm. In the spectra of the other compounds the same protons generate only one broad signal falling into the range of 180–200 ppm. In the μ-dichloro and dihydrogenosulphido derivatives the two sets of protons experience either upfield and downfield shifts with respect to the above values and this behavior appears to be also transmitted to the protons of the aliphatic chains. For instance, pseudo-equatorial Me_1 and Me_3 methyl groups, which generate overlapping signals in the nitrato and oxalato derivatives, are also split significantly, experiencing either larger or smaller downfield shifts with respect to the expected values. Therefore, as it is assumed that the macrocycle is folded about N(1)–Ni–N(3), it could be suggested that the NH protons lying outside the plane containing the two nickel(II) ions and the bridging donors experience larger upfield shifts using the hypothesis that a spin polarization mechanism is operative [12, 13]. To our knowledge, this is the first time that this behavior has been observed and it can be considered as an important finding for the analysis of the NMR spectra of polynuclear metal complexes, showing that large shifts can be induced by the presence of a second metal ion.

The lattice spin nuclear relaxation times T_1, obtained by the inversion recovery method, are reported in Table II together with the estimated Ni–H distances. As previously observed [17], any quantitative analysis of these data by means of the Solomon–Bloembergen–Morgan equation is unsuccessful, because of the existence of a significant ligand centered contribution [18, 19]. However, even considering the pitfalls of a quantitative approach, in the assumption that an electron nuclear dipolar mechanism determines the proton relaxation rates, it would be expected that protons or methyl substituents having pseudoaxial character, would exhibit greater relaxation rate enhancements than their pseudoequatorial counterparts, since the former protons are closer to the paramagnetic center. This expectation has been shown to hold [17] for *trans*-octahedral derivatives as the Ni(*ms*-Me$_6$[14]aneN$_4$)Cl$_2$ complex (see Table II). For the *cis*-octahedral complexes this expectation is observed to hold only for the substituents of six-membered chelate rings. The axial and equatorial protons of the ethylenic chains experience, on the contrary, the same relaxation rates independently of their conformational character. T_1 ratio values of about 3 would be expected for each couple of geminal protons if a pure dipolar mechanism is operative.

The inspection of data reported in Table II shows that the ligand protons of the monomeric *cis*-nitrato derivative exhibit greater relaxation rate enhancements with respect to those of the monomeric *trans*-dichloro derivative, thus indicating that the electron spin lattice relaxation time in the former compound is longer than that which characterizes the latter. This difference must be attributed to the different electronic properties of the nickel(II) ion in the two coordination geometries. Similar results were found for all the *cis*- and *trans*-octahedral nickel(II) complexes formed by macrocyclic ligands we have investigated [20].

The inspection of the ^{1}H NMR traces shows that the signal line widths of the μ-dichloro and of the μ-dihydrogenosulphido complexes are significantly smaller than those of the other *cis*-complexes. As an example, we found half-width values of 35 and 30 Hz for the pseudoequatorial Me$_1$ and Me$_3$ methyl groups in the μ-dichloro derivative, whereas values of about 200 Hz are found for the same substituents in the oxalato derivative. The T_1 data are consistent with this, showing that the μ-dichloro and μ-dihydrogenosulphido complexes exhibit smaller relaxation rate enhancements than the monomeric nitrato. The oxalato derivative on the other hand exhibits a proton relaxation rate T_{1M}^{-1} of the same order of magnitude of the monomeric nitrato. This is an unexpected results since the theory predicts [21] that a magnetically coupled system would exhibit a larger electronic relaxation rate than that of an uncoupled one.

A possible reason of this discrepancy may be bound to the assumption that in the μ-dichloro and μ-dihydrogenosulphido derivatives the electronic relaxation time of the individual metal ion should be similar to that of the nitrato complex.

Experimental

The complexes [Ni(*dl*-Me$_6$[14]aneN$_4$)X]ClO$_4$ (X = NO$_3$, Cl, C$_2$O$_4$/2) were prepared according to literature methods [7, 8, 11].

The complex [Ni(*dl*-Me$_6$[14]aneN$_4$)SH]ClO$_4$ was prepared by adding sodium sulphide to an aqueous solution of the Ni(*dl*-Me$_6$[14]aneN$_4$)(ClO$_4$)$_2$. Green crystals appear immediately. They were filtered and dried *in vacuo*.

All the complexes were satisfactorily analysed for C, H, and N.

Physical Properties

[Ni(dl-Me$_6$[14]aneN$_4$)Cl]$_2$(ClO$_4$)$_2$

(μ_B) = 3.14 (293 K), 3.17 (80 K). Absorption maxima (kK) in CH$_3$CN (ϵ_{molar} in parentheses): 8.5(14), 16.0(36), 26.3(98), (shoulder at 9.4).

[Ni(dl-Me$_6$[14]aneN$_4$)SH]$_2$(ClO$_4$)$_2$

(μ_B) = 3.18 (293 K), 317 (80 K). Absorption maxima (kK) in CH$_3$CN (ϵ_{molar} in parentheses): 8.7(11.5), 16.0(68), 21.3(30).

^{1}H NMR Measurement

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 non-linear least squares fitting program. Hexadeuterodimethylsulphoxide and trideuteroacetonitrile were used as solvents.

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