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Pmr Investigation of Paramagnetic Triazene 1-Oxide Complexes of Nickel(II)

P. S. ZACHARIAS and A. CHAKRAVORTY*
Department of Chemistry Indian Institute of Technology Kanpur-208016, India

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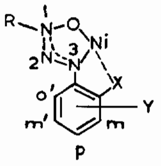
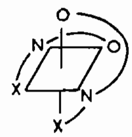
Paramagnetic nickel(II) complexes derived from potentially tridentate triazene 1-oxide ligands show pmr contact shifts. The pmr spectra can be assigned unambiguously. When two triazene 1-oxide complexes are mixed together in solution, ligand exchange occurs and the mixed complex contributes to solution composition. This is neatly demonstrated by pmr spectra. Using intensity data of pmr signals equilibrium constants for several equilibria are determined. Only when the ligands are very similar are their redistribution statistical. The structures of the mixed-ligand complexes are discussed.

Introduction

Triazene 1-oxides form bis complexes of the type I with nickel(II). The dotted line in I is used to mean that the group X may or may not be coordinated to the metal atom. Thorough magnetic and spectral studies[1–4] have shown that the solution behaviour of I depends on the nature of X. When X = OR (R = alkyl), the complexes are fully paramagnetic and octahedral (II) in solution.[2] When X = halogen, planar $\rightleftharpoons$ octahedral equilibria occur.[1,2] In the planar form (III), X is not coordinated. Lastly when X = H or alkyl only the planar form results.[3] We now wish to report that the structural type II shows sizable pmr contact shifts.[5]



I



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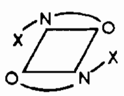


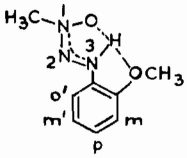
III

This phenomenon is utilized to study the formation of mixed-ligand complexes that result when two different chelates of type I are taken together in solution. The pmr technique has been used before for the study of other mixed complex systems.[6] In what follows I will be abbreviated as (R-Y-X)$_2$Ni. When Y = H, the abbreviation will simply be (R-X)$_2$Ni.

Results and Discussion

Paramagnetic Shifts in Complexes I

The free triazene 1-oxide ligands show expected pmr spectra. For example, the ligand IV has the following chemical shifts (ppm) downfield from tetramethylsilane in deuterochloroform: NCH$_3$, 4.00; OCH$_3$, 4.09; aromatic protons, 7.23 (centre of gravity of a complexes pattern of signals); NH, 10.70. Other ligands give rise to similar spectra which will not be discussed any further here.



IV

The complexes give rise to wellseparated lines for every type of proton. First-order spin–spin splitting is neatly observable for aromatic protons in each case. The spectrum of (CH$_3$-*m'*-CH$_3$-OCH$_3$)$_2$Ni is illustrated in Figure 1. The assignments shown in Figure 1 are unambiguous and were arrived at on the basis of the spin–spin structures and comparison of this spectrum with that of (CH$_3$-OCH$_3$)$_2$Ni.[7] Contact shifts Δf_i for the ith proton were computed by the relation (1), where f^c_i and f^l_i are respectively the chemical

$$\Delta f_i = f^c_i - f^l_i \qquad (1)$$

shifts of the ith proton in the complex and in the free ligand. In computing Δf_i of aromatic protons the centre of gravity of the free ligand aromatic signals was taken as f^l_i. Where f^c_i and/or f^l_i are spin multiplets, the centres of the multiplets were used for computation of Δf_i. Contact shift data for the complexes are displayed in Table I.

In the aromatic ring the contact shifts alternate in sign. The *o'*- and *p*-protons get positive shifts while the *m*- and *m'*-protons are shifted down-field. This alternation is suggestive of the existence of unpaired

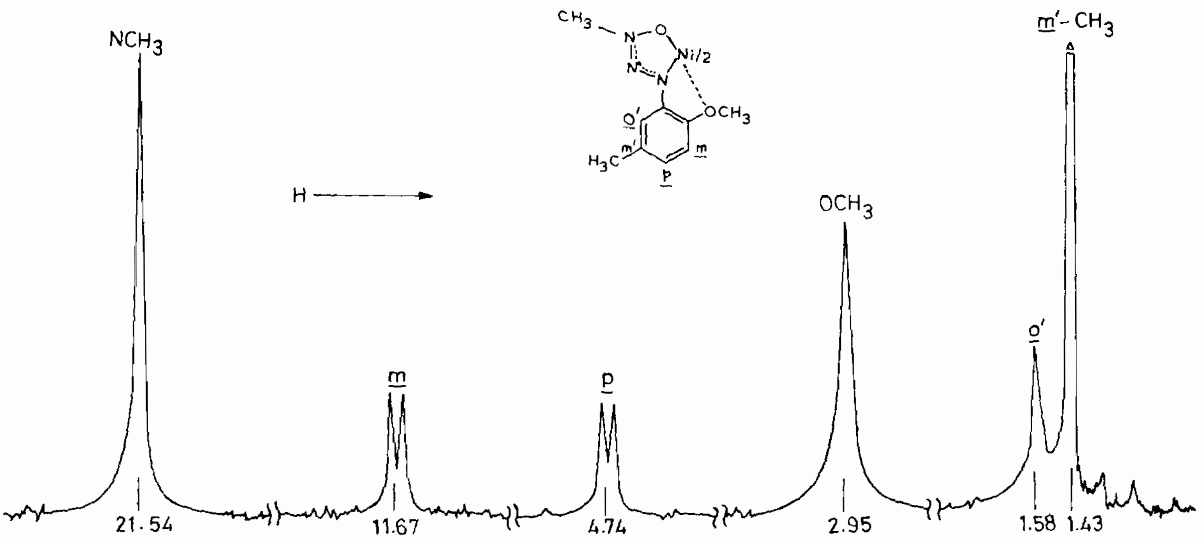


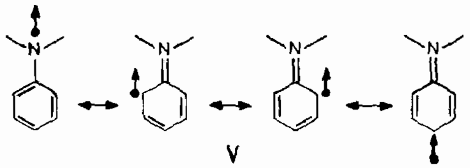
Figure 1. PMR spectrum of $(CH_3\text{-}m'\text{-}CH_3\text{-}OCH_3)_2Ni$ in $CDCl_3$. Chemical shifts are in ppm downfield from tetramethylsilane.

TABLE 1. Contact Shift Data ($CDCl_3$, 305° K).

Compound	μ_{eff}[a]	Contact Shifts (ppm)					
		m–H	p–H	m'–H	o'–H	N–CH_3	Others
$(CH_3\text{–}OCH_3)_2Ni$	3.28	–8.87	+0.65	–22.63	+5.87	–24.95	OCH_3, +0.25
$(CH_3\text{–}OC_2H_3)_2Ni$	3.21	–8.85	+0.82	–22.95	+4.83	–24.93	OCH_2CH_3, –6.80; OCH_2CH_3, +6.74
$(C_2H_5\text{–}OCH_3)_2Ni$	b	–9.48	+1.96	–23.11	+7.90	–	OCH_3, –0.22; NCH_2CH_3, –22.11; NCH_2CH_3, +7.27
$(nC_3H_7\text{–}OCH_3)_2Ni$	b	–9.40	+1.41	–23.38	+7.27	–	OCH_3, –0.37; NCH_2-CH_2CH_3, –23.10; $NCH_2CH_2CH_3$, +7.49; $NCH_2CH_2CH_3$, +2.81
$(CH_3\text{–}m'\text{–}CH_3\text{–}OCH_3)_2Ni$	3.26	–4.91	+2.02	–	+5.18	–17.84	OCH_3, +0.85; m'–CH_3, +0.80
$(CH_3\text{–}Cl)_2Ni$	1.35	–3.78	+3.08	–7.52	+2.99	–6.88	
$(CH_3\text{–}m'\text{–}CH_3\text{–}Cl)_2Ni$	b	–2.68	+2.37	–	+2.13	–4.90	m'–CH_3, +1.60
$(CH_3\text{–}Br)_2Ni$	1.42	–4.15	+2.92	–8.60	+1.62	–6.40	

[a] Solution data in benzene at 305° K. [b] Measurements not made.

spin-density in a π-orbital of the ligand. If spin-delocalization occurs *via* N(3) the valence bond description, V is in qualitative agreement with the sign of contact shifts of the aromatic protons of $(R\text{-}X)_2Ni$



V

complexes. In $(R\text{-}X)_2Ni$, the m'-H shift is negative while in $(R\text{-}m'\text{-}CH_3\text{-}X)_2Ni$, the m'-CH_3 shift is positive. This again supports the occurrence of spin delocalization in a π-orbital. Beyond this it has not been possible to understand the trends of shift data quantitatively even though several models of spin delocalization were examined.[8]

The paramagnetic complexes (I) are dissymetric at the metal and consequently two optical isomers are possible. If in addition the ligand has an optically active centre several diastereoisomers can arise. If all the diastereoisomers are stereochemically stable on the pmr time-scale, it should be possible in principle to observe separate signals for the diastereoisomers. This has been observed in tetrahedral complexes.[9] In order to verify whether the same applies to triazene 1-oxide complexes, $(R\text{-}X)_2Ni$ with $R = sec\text{-}C_4H_9$ was examined. Separate signals from the diastereoisomers were not obtained – each kind of proton gave rise to one characteristic signal only. The Δf_i data ($CDCl_3$, 305°K) are $X = OCH_3$, *m*-H, –9.66; *p*-H, +2.89; *m'*-H, –23.54; *o'*-H, +8.93; X = Cl, *m*-H, –3.10; *p*-H, +3.36; *m'*-H, –5.75 and *o'*-H, +3.70 ppm. The non-bonded interactions of the optically active sites are probably too small to produce observable chemical shift differences among diastereoisomers of $(R\text{-}X)_2Ni$.

Mixed Complex Formation

When two triazene 1-oxide complexes are mixed together in solution, ligand exchange occurs and the mixed complex contributes to solution composition. The general reaction is

$$A_2Ni + B_2Ni \rightleftharpoons 2ABNi \quad (2)$$

where A and B are two different triazene 1-oxide ligands. The occurrence of equilibrium (2) is neatly demonstrated by pmr spectra. The signals from the original species are identified from frequency (Table I) and intensity (*i.e.* which signal grows with increment of which component) data. The contact shifts of the mixed complex are quite different from those of the parent species and in addition the two chelate rings usually give widely separated signals. The spectrum of the mixture of $(CH_3\text{-}OCH_3)_2Ni$ and $(CH_3\text{-}Cl)_2Ni$ is illustrated in Figure 2. Shift data for several ABNi species can be found in Table II. The equilibrium constant K for reaction (2) is

$$K = \frac{4x^2}{(p-x)(q-x)} \quad (3)$$

where (p) and (p–x) are respectively the initial and equilibrium concentrations of A_2Ni. Similarly (q) and (q–x) refer to B_2Ni; x is the equilibrium concentration of ABNi. The values of the parameters needed for calculation of K could be readily obtained from relative intensity data (area under peaks) of pmr signals. As many signals as possible were used for the computation of the same K. A typical set of results are shown in Table II. The values of K are estimated to be good to within 10%.

If ligand redistribution is completely random among nickel sites, K becomes equal to 1. This is indeed true for the mixture $(CH_3\text{-}OCH_3)_2Ni + (CH_3\text{-}OC_2H_5)_2Ni$. In this case the two ligands are very similar to each other. In the mixture $(CH_3\text{-}OCH_3)_2Ni + (CH_3\text{-}Cl)_2Ni$ measurable ligand discrimination occurs (K ~0.7). Finally for $(CH_3\text{-}OCH_3)_2Ni + (CH_3\text{-}H)_2Ni$, the two ligands appear to be vastly different (K ~0.1). The thermodynamic implication of K <1 is that

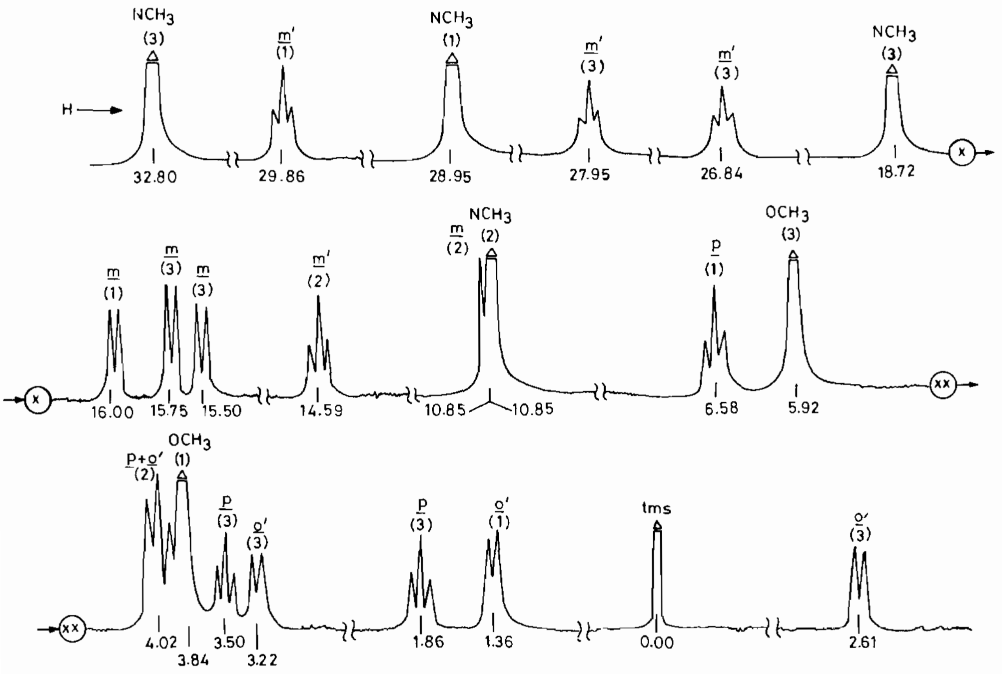


Figure 2. PMR spectrum of a mixture of $(CH_3\text{-}OCH_3)_2Ni$ and $(CH_3\text{-}Cl)_2Ni$ in $CDCl_3$. Chemical shifts are in ppm from tetramethylsilane (tms). The numbers in parentheses have the following meanings: (1), $(CH_3\text{-}OCH_3)_2Ni$; (2), $(CH_3\text{-}Cl)_2Ni$; (3), mixed complex $(CH_3\text{-}OCH_3)(CH_3\text{-}Cl)Ni$.

TABLE II. Contact Shifts and Equilibrium Constants of Mixed Complexes ($CDCl_3$, 305 °K).

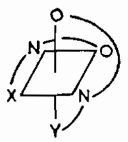
Mixture	Contact Shifts (ppm)				Data on Equilibria[c]			
	m–H	*p*–H	*m'*–H	*o'*–H	p	q	x	K
$(CH_3–OCH_3)_2Ni+(CH_3–OC_2H_5)_2Ni$	–7.63	+0.66	–21.83	+5.35	0.0978	0.1053	0.0338	0.98
	–7.63	+1.27	–22.34	+5.35				
$(CH_3–OCH_3)_2Ni+(CH_3–Cl)_2Ni$	–8.35	+3.65	–19.69	+3.93	0.1046	0.1076	0.0306	0.66
	–8.60	+5.29	–20.80	+9.76				
$(CH_3–OCH_3)_2Ni+(CH_3–m'–CH_3–Cl)_2Ni$	–8.09	+3.56[a]	–20.16[a]	+3.69	0.1016	0.1086	0.0314	0.73
	–8.56[a]	+5.38	–	+9.34[a]				
$(CH_3–OCH_3)_2Ni+(CH_3–H)_2Ni$	–4.70	+4.31	–6.39	b	0.1446	0.2606	0.016	0.06
	–6.39	+6.64	–9.60	+11.74				

[a] This signal belongs to *o*-methoxyl ligand of the mixed complex. [b] The signal could not be located. [c] Meaning of symbols as in text.

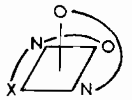
$$F°_{ABNi} > {}^1/_2\,(F°_{A_2Ni} + F°_{B_2Ni})$$

where $F°_p$ is the standard free energy of the species P.

We can make some reasonable speculations about the structure of the mixed complexes. It is noted that in the fully paramagnetic complexes the *m'*-H signal systematically has a contact shift of ~ –22 ppm (Table I). The magnitude of this shift in partially paramagnetic systems is lower. The mixed complex $(CH_3\text{-}OCH_3)(CH_3\text{-}OC_2H_5)Ni$ may be expected to be fully paramagnetic since the two parent complexes are so. Its expected structure is then VI ($X = OCH_3$, $Y = OC_2H_5$). Indeed the two *m'*-H shifts of this complex lie close to –22 ppm (Table II).



VI



VII

On the basis of *m'*-H shifts, the complex $(CH_3\text{-}OCH_3)(CH_3\text{-}Cl)Ni$ is also believed to exist more or less completely as VI ($X = OCH_3$, $Y = Cl$). This is to be contrasted with the behaviour of $(CH_3\text{-}Cl)_2Ni$ in solutions of which the structure II is only partially populated (Table I). The complex $(CH_3\text{-}OCH_3)(CH_3\text{-}H)Ni$ is probably not fully paramagnetic; the paramagnetic form may have the pentacoordinated structure VII. High-spin pentacoordinated nickel(II) shows electronic bands in the near-ir region.[10] In this context it may be significant that the mixture $(CH_3\text{-}OCH_3)_2Ni$ + $(CH_3\text{-}H)_2Ni$ shows an increase (over the pure component values) absorption at ~7050 cm^{-1}.

Experimental Section

The synthesis and characterization of the complexes have been reported before.[2,3] Pmr spectra were recorded at 100 MHz using a Varian HR–100 spectrometer. Tetramethylsilane was uniformly used as the internal standard. Frequencies were determined by the side-band technique. The temperature of the probe was determined by measuring the separation of the signals of a standard methanol sample. Area measurements were done planimetrically. Magnetic susceptibility data and electronic spectra were obtained as previously.[2]

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