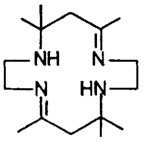
Spectroscopic Evidence for Non-planarity in Nickel(III) Complexes of Macrocyclic Ligands. Pulse Radiolysis and Electron Spin Resonance Studies in Aqueous Solution

By GUILLERMO FERRAUDI* and LARRY PATTERSON
(*Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana* 46556)

Summary The spectral and e.s.r. data obtained from the reaction of Ni^{II} macrocyclic with OH· radicals in aqueous solution show that oxidation takes place at the metal centre to form momentarily stable Ni^{III} species, and, depending on the degree of unsaturation in the ligand employed, strong absorption bands in the region associated with *d–d* transitions can occur which may be best explained by departures from planarity in the complex.

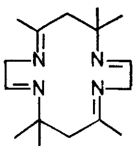
SEVERAL workers have reported the production of transient Ni^{III} mono- and bi-dentate complexes from reactions of OH· radicals in aqueous media.[1] Such identification rests largely on observation of long lifetimes, stability toward O$_2$, ability to oxidize I$^-$, and the similarity of transient spectra of complexes containing differing ligands. However, to date, e.s.r. data confirming such assignments of radiolytically generated species are limited.[2] Hence departure of spectral behaviour of OH·-generated transients from that of Ni^{III} in organic solvents[3–5] suggests ambiguity in the assignment of these transients and casts considerable doubt on any interpretation of such spectral data.

During pulse radiolysis studies on Ni^{II} macrocyclic complexes in aqueous solution, it has been found that the reaction of an OH· radical[6] with {Ni[14]dieneN$_4$}$^{2+}$ {[14]-dieneN$_4$ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (I)} produces a transient which, in addition to the intense band expected at *ca.* 300 nm, exhibits a well defined absorption (ϵ = 1500 l mol^{-1} cm^{-1}) at 535 nm.



[14]dieneN$_4$

(I)



[14]tetraeneN$_4$

(II)

Addition of Na$_2$SO$_4$ (0·1M) to the electrolyte causes the u.v. band to shift towards the red end of the spectrum while having no effect on the band at 535 nm. This type of behaviour for the band at 535 nm would normally be associated with a *d–d* transition but its intensity is uncharacteristic of Ni^{III} spectra observed in non-aqueous solvents.[3] In acetonitrile, for instance, the extinction coefficient of the comparable band is *ca.* 70 l mol^{-1} cm^{-1}. This intermediate has a half-life in neutral solution of 20 s and its rate of decay is first order. In the presence of O_2 this lifetime diminishes by one half which corresponds to a rate constant $k(\mathrm{int}+O_2)$ *ca.* 3 × 10^2 l mol^{-1} s^{-1}. Such observations may be contrasted with those made in the related $\{Ni[14]tetraeneN_4\}^{2+}$ {[14]tetraeneN_4 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-1,4,8,11-tetraene (II)} system which, as would be predicted from studies of Ni^{III} complexes in acetonitrile[3] gives only one band at 320 nm with a broad shoulder (ϵ *ca.* 10^2 l mol^{-1} cm^{-1}) extending beyond 500 nm. Additionally, the lifetime of the tetraene species is only 0·5 s when measured under conditions similar to those for the diene intermediate. The transient spectra of both species are given in Figure 1. Both were found to be good oxidants capable of undergoing electron transfer from I^-, Fe^{2+}, and most significantly, $[Ni(EDTA)]^{2+}$.

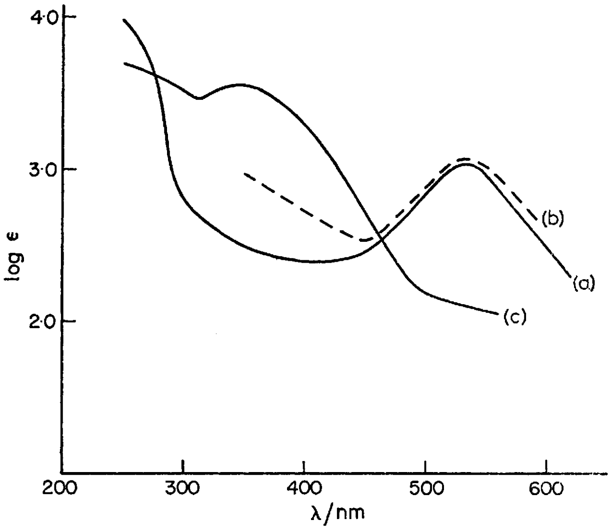


FIGURE 1. Transient spectra of Ni^{III} complexes in aqueous medium: (a) $\{Ni[14]dieneN_4\}^{3+}$ in neutral solution; (b) $\{Ni[14]dieneN_4\}^{3+}$ in 0·1 M Na_2SO_4 and 10^{-4} M $HClO_4$; (c) $\{Ni[14]tetraeneN_4\}^{3+}$ in 10^{-4} M $HClO_4$. Data were obtained by pulse radiolysis of N_2O-saturated solutions containing 2 × 10^{-4} M Ni^{II} complexes. Spectra were measured immediately after attack of the OH· radicals.

From the spectral data for $\{Ni[14]dieneN_4\}^{2+}$ it can be postulated that either an unusually long lived radical forms generated by attack of the OH· radical at a ligand site, or oxidation occurs at the metal centre which produces a species having significant structural differences compared to $\{Ni[14]dieneN_4\}^{3+}$ in acetonitrile. The comparative stability of this transient provides a unique opportunity for e.s.r. measurements which are not possible with other transients of this type having shorter life. Both Ni^{III} and Ni^{I} compounds are paramagnetic while the parent Ni^{II} compound is diamagnetic. Samples of $\{Ni[14]dieneN_4\}^{2+}$ saturated with N_2O were irradiated with pulses of high energy electrons for 10 ms and then were plunged into liquid N_2 1 s after irradiation. The e.s.r. spectrum obtained from such samples is given in Figure 2, and shows a well defined anisotropic signal at $g_\perp = 2·22$ and $g_{||} =$ *ca.* 2·002, which are the positions reported for Ni^{III} complexes in non-aqueous solvents.[6] This signal disappeared when the sample was warmed and then again frozen. Identification of the transient species as having a Ni^{III} metal centre follows from this observation. Thus differences in the intensity of the band at 535 nm observed for $\{Ni[14]dieneN_4\}^{3+}$ in aqueous and non-aqueous solvents may not be due to generation of a radical in the ligand system. The occurrence of the band in both solvents as well as its insensitivity to the added electrolyte strongly suggests that this absorption could arise owing to a *d–d* transition. It follows that differences between the π-electron character of the diene and tetraene complexes alone are not sufficient to account for the differences in this transition observed in H_2O. It is more probable that the arrangement of the [14]dieneN_4 ligand about the Ni^{III} metal centre, in H_2O, possesses a symmetry that is absent either when the more rigid tetraene ligand is present or when the solvent is acetonitrile. Associated contributions to the removal of the D_{4h} symmetry centre from such perturbations may well account for increasing the allowed character of the *d–d* transition at 535 nm.[8]

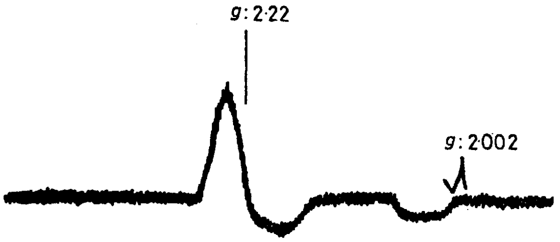


FIGURE 2. E.s.r. spectrum of the frozen solution of the intermediate generated by radiolysis of $\{Ni[14]dieneN_4\}^{2+}$ in N_2O-saturated solution.

We thank Drs. H. Paul and H. Levenon for assistance with the e.s.r. measurements, and the Division of Physical Research of the U.S. Energy Research and Development Administration for support.

(*Received*, 12*th July* 1977; *Com.* 716.)

---

[1] D. Meyerstein and J. Lati, *J. Radiation Phys. Chem.*, 1975, **7**, 611; J. Lati and D. Meyerstein, *Inorg. Chem.*, 1972, **11**, 2393.

[2] J. Lati, J. Koresh, and D. Meyerstein, *Chem. Phys. Letters*, 1975, **33**, 286.

[3] D. C. Olson and J. Vasileskis, *Inorg. Chem.*, 1969, **8**, 1611.

[4] N. F. Curtis and D. F. Cook, *Chem. Comm.*, 1967, 962, and references therein.

[5] V. L. Goedken and D. H. Busch, *Inorg. Chem.*, 1971, **10**, 2679.

[6] OH· radicals were generated by irradiation (10 MeV Linac electrons) of N_2O in aqueous solutions: J. H. O'Donnell and D. F. Sangster, 'Principles of Radiation Chemistry,' Elsevier, New York, 1976.

[7] F. K. Lovecchio, E. S. Gore, and D. H. Busch, *J. Amer. Chem. Soc.*, 1974, **96**, 3109; A. H. Maki, N. Edelstein, A. Davidson, and R. Holm, *ibid.*, **86**, 4580; A. Wolberg and J. Manassen, *Inorg. Chem.*, 1970, **9**, 2365.

[8] C. J. Ballhausen, 'Introduction to Ligand Field Theory,' McGraw Hill, New York, 1962; J. S. Griffith, 'The Theory of Transition Metal Ions,' Cambridge University Press, 1961; F. A. Cotton, 'Chemical Applications of Group Theory,' Wiley-Interscience, New York, 1963.