Electronic Structure of 5,7,12,14-Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-2,4,6,9,11,13-hexaenato–nickel(II) Cation Radical, the Central Member of a Ligand-based Electron-transfer Series

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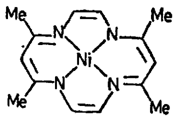
Summary The e.s.r. spectra of the title complex and four deuteriated derivatives exhibit well resolved hyperfine splittings which have been analysed in terms of a ${}^2B_{1u}$ ground state with extensive ligand delocalization of the odd electron.

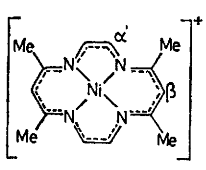
Electron-transfer reactions of metal complexes involve, in a limiting sense, changes in oxidation state of the metal or ligand system. Those approaching or fulfilling the latter description are far less common, being primarily confined to dithiolene-type complexes[1] and metalloporphyrins,[2] and are best demonstrated by observation of ligand nuclei hyperfine splittings in the e.s.r. spectrum of a member of the redox couple.

The central member (title compound) of the previously established[3] reversible electron transfer series (I) $\rightleftharpoons$ (II) $\rightleftharpoons$ (III) exhibits an apparent monomer–dimer equilibrium in non-aqueous media. At sufficiently low concentrations (*ca.* 5×10^{-4}M) in MeCN–CHCl$_3$ a highly resolved e.s.r. spectrum of the spin-doublet monomer cation (II) is observable (Figure). The spectrum is independent of anion (BF$_4^-$, CF$_3$SO$_3^-$) and contains over 80 hyperfine components separated by a nearly constant spacing of *ca.* 0·41 G, indicating an extensively delocalized π-electron and coupling constants which are near-integral multiples of this spacing. The cation (II) was found to undergo selective deuteriation. Treatment with MeCN–D$_2$O (pH *ca.* 2) at 25 °C affords the β-dideuterio species [^{2}H$_2$]-(II); in the same medium at 80 °C β- and α'-H–D exchange occurs yielding [^{2}H$_6$]-(II). The latter readily back-exchanges β-D at 25 °C in MeCN–H$_2$O (pH *ca.* 2) producing [^{2}H$_4$]-(II). Direct synthesis[4] of 5,7,12,14-tetramethyl[^{2}H$_{12}$]-1,4,8,11-

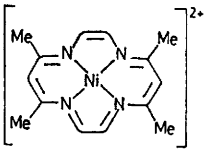
tetra-azacyclotetradeca-4,6,11,13-tetraene utilizing CD_3-$COCH_2COCD_3$, insertion of Ni^{II}, and oxidative dehydrogenation with $Ph_3C^+BF_4^-$ affords [$^2H_{12}$]-(II). Reduction of these cations with $NaBH_4$ in EtOH gives the corresponding deuteriated derivatives of diamagnetic (I) whose ^1H n.m.r. spectra indicate $>$ *ca.* 95% deuteriation in all cases. E.s.r. spectra of the four deuteriated species of (II) reveal distinctly different hyperfine patterns indicating coupling by all ligand protons.



(I)



(II)



(III)

Computer analysis of the spectra of (II) and its deuteriated derivatives has led to accurate spectral simulations based on the following coupling constants: a_N 2·08, $a_{\beta H}$ 4·53, $a_{\alpha H}$ 2·87, a_{Me} 0·81 G, and a_D 0·154 a_H. The computed spectrum of (II) is shown in the Figure. HMO calculations on the tetra-azaannulene-type ligands previously proposed[3] for (I)—(III) indicate the electron configuration $\cdots (2b_{2g})^2(3b_{1u})^1(2a_u)^0$ for the ligand system of (II) over a reasonable range of parameters. Spin densities estimated from the preceding *a*-values using $a = Q\rho_C$ (Q_{CMe} *ca.* 30, Q_{CH} *ca.* -23 G) accord far better with the spin density pattern expected for the $3b_{1u}$ than for the $2b_{2g}$ and $2a_u$ MO's from HMO and McLachlan[5] calculations. In particular, the latter orbital has a node through β-C whereas experimentally the largest C-$p\pi$ spin density (*ca.* $|0{\cdot}20|$) is found at these positions. Of the metal valence orbitals the $3b_{1u}$ ligand MO can mix only with the vacant $4p_z$ under the D_{2h} symmetry of (II) indicated by spectral simulation, a restriction not inconsistent with the extensive delocalization observed. Consequently, (II) approaches the formalism Ni^{II}–L$^{\cdot-}$ (15-π), providing strong support for the indicated description of (I)—(III) as a Ni^{II} ligand-based (14—16π) electron-transfer series. Finally, the formalism for (II) is similar to that for certain D_{4h} metal(II) porphyrin cation radicals[2] whose two closely spaced highest occupied MO's allow either no metal interaction (a_{1u}) or mixing with p_z only (a_{2u}).

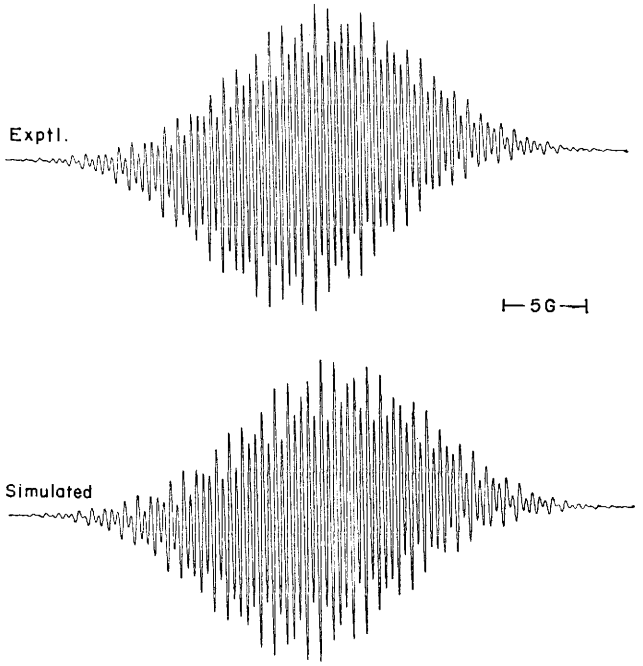


FIGURE. Experimental and calculated e.s.r. spectra of (II) in MeCN–CH_2Cl_2 solution at *ca.* 25 °C. The spectrum is centred at $g = 2{\cdot}001$.

This research was supported by grants from the National Science Foundation and the National Institutes of Health. We thank G. N. LaMar for the McLachlan calculations.

(*Received*, 31*st December* 1974; *Com.* 1578.)

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