Ligand–Metal Interrelationships. I. The Tervalent Nickel Complex of 11,13-Dimethyl-1,4,7,10-tetraazacyclotrideca-10,13-diene. A Pulse Radiolytic Study

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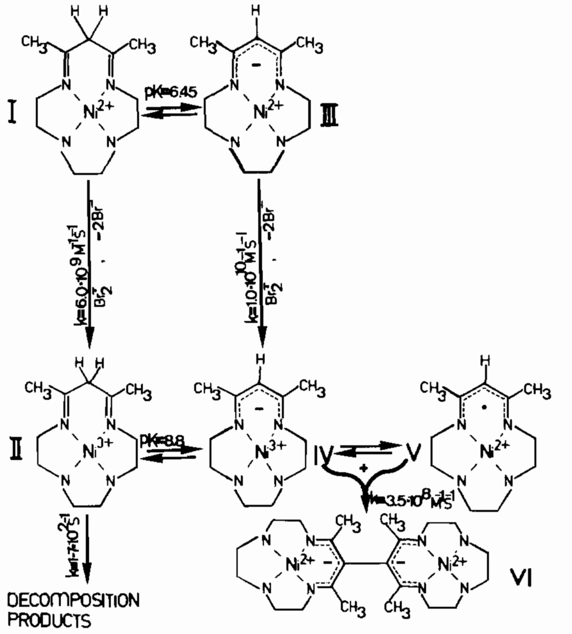
The ligand–metal interrelationships are doubtlessly profound phenomena in the chemistry of transition metal complexes. Parameters such as the core size in a given macrocycle [1], its charge [2] and its degree of unsaturation and conjugation [3] affect strongly the redox properties of the central metal and thus its capability to mimic coordination sites in natural proteins. Ligand to metal (or *vice versa*) electron transfer may serve as an important step in biological reactions such as porphyrin–chlorin transformations [4]. One example for such ligand to metal electron transfer is that of the dimerization of $Me_2(14)1,11$-diene N_4 cobalt(III) [5]. Deprotonation of this complex is followed by an immediate electron transfer from the anionic ligand to the tervalent cobalt and the resulting Co(II) π-radical complex dimerizes. The pK of the Co(III) complex (deprotonation at position 13) could only be estimated, the results indicating a dependence on the nature of the axial ligand. The kinetics of dimerization could not be measured using conventional techniques [5]. In a different case, the dimerization of a nickel complex was carried out by chemical [6] and electrochemical oxidation [8]. No oxidation of the metal was reported and the Ni(II) π-radical complex was suggested as the intermediate [7]. However, oxidation of analogous complexes, under somewhat different conditions, resulted in ligand dehydrogenation [8].

We shought to extend the knowledge of ligand–metal interrelationships prenomena *via* studying ligand to metal electron transfer processes in aqueous solutions. The research in progress includes the investigation of factors such as the size of the tetraaza macrocycle (*i.e.*, 13, 14 or 15), the introduction of a negative charge into the ligand and substituents on the ligand, on the chemical (pK and rate of dimerization) and physical (optical spectra) properties of these complexes. As complexes with uncommon oxidation states are unstable in aqueous media, we chose for this study the pulse radiolysis technique [9], which enables the study of very short lived intermediates. Here we present the results on the oxidation of 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,13-dienatonickel(II) diperchlorate, I, in aqueous solutions.

Oxidation of Br^- to Br_2^-† in the presence of I, at pH 3.6 is followed by two consequent reactions††. The first is the formation of the tervalent, nickel complex, II and obeys a pseudo-first order rate law, $k = 6.0 \times 10^9 M^{-1}sec^{-1}$.



Complex II is unstable and decomposes in a reaction which seems to be first order with a rate depending somewhat on the conditions, $1.0 \times 10^2 < k < 7.0 \times 10^2$ sec^{-1}. The detailed kinetics of this reaction will be reported separately. The optical spectrum of II is given in Fig. 1, for comparison the spectrum of I is also included. On the other hand, when the same reaction is carried out at pH 10.6, a different chemistry is observed. The first reaction yields the tervalent nickel complex IV, $k = 1.0 \times 10^{10} M^{-1}sec^{-1}$, while the second process, in alkaline media, obeys a pure sec-

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†The production of the Br_2^- free radicals is rapid enough to be completed before any reaction occurs. See for example M. S. Matheson, W. A. Mulac, J. L. Weeks, and J. Rabani, *J. Phys. Chem.*, *70*, 2092 (1966).

††The linear accelerator at the Hebrew University of Jerusalem was used. The pparaturs and procedures for data analysis were as described elsewhere [13]. Pulses yielding 2–10 $\times 10^{-6} M$ free radicals ware used. The optical path length was 12.5 cm. All experiments were performed at 22 ± 2 °C. Reproducibility of rate constant determination was whithin ±10%, and of σ ± 15%.

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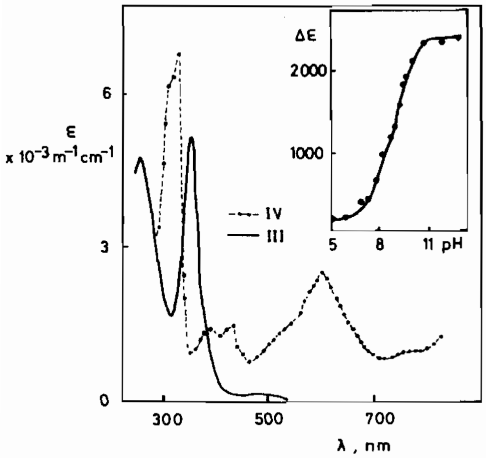
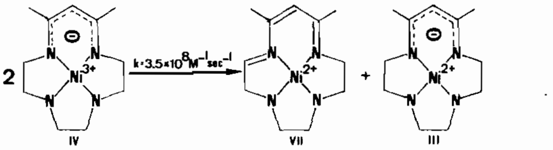


Fig. 1. Spectra of I and II at pH 3.6 spectrum of I measured by Carry 17 spectrophotometer. Spectrum of II measured by pulse-radiolysis solution composition: 0.1 M NaBr, N_2O saturated, concentration of I $2–20 \cdot 10^{-5} M$, pulse intensity 100–1000 rads respectively. The low concentration at $\lambda <$ 350 nm. The spectrum of II was calculated from $\epsilon_{II} - \epsilon_I$ and ϵ_I, the measured quantities.

ond order rate law, $k = 3.5 \times 10^8 M^{-1} sec^{-1}$. No significant changes were found for the second reaction kinetics in the pH region of 8.2–10.6 ($k = 3.9 \times 10^8 M^{-1} sec^{-1}$ at pH 8.2). An intramolecular electron transfer from the anionic ligand to the tervalent nickel to form a nickel(II) π-radical complex, V, which then dimerizes to give VI, provides the best internally self-consistent explanation for these data*



The tervalent nickel complexes II and IV are expected to have an octahedral coordination sphere due to their d^7 electronic configuration. Recently, the entropy change upon the oxidation of Ni(II) peptides to Ni(III) peptides in aqueous solutions was reported [11]. The results indeed indicated that the oxidation is accompanied by a transformation from planar to octahedral coordination [11]. We found that the properties of the oxidation product are independent of the nature of the oxidizing agent (I_2^-, Br_2^- or $OH^\cdot$) and on the anion present in solution, indicating that the axial ligands of IV are H_2O or OH^-. To clarify this point we checked the salt effect on the rate of the dimerization reaction at pH 10.6. We found that the rate is independent on μ in the range of $1.4 \times 10^{-3} M < \mu < 0.3 M$. This result indicates that IV is uncharged at pH 10.6 and therefore that two hydroxide ions are axially coordinated to the tervalent nickel. This observation is in agreement with the reported pK of water ligated to tervalent nickel, pK ~ 3.7 [13, 14].

The pK of II was established by measuring the pH dependence of the O.D. due to IV at 600 nm., under conditions where all the Br_2^- radicals oxidize I or III, and was found to be 8.8 ± 0.2 (Fig. 2)**. The high value of the pK of II as compared to that of I, (pK = 6.55 [12]) is probably due to the fact that whereas the divalent nickel complex is planar the tervalent one is octahedral with two hydroxides as axial ligands. The bound hydroxides increase the electron density on the central metal, as do axial ligands on cobalt(III) [5] and thus shift the pK in the unexpected direction.

The optical spectrum of IV is also of interest (Fig. 2). The absorption at 330 nm ($\epsilon = 6850 M^{-1} cm^{-1}$) is followed by an unusually strong absorption band

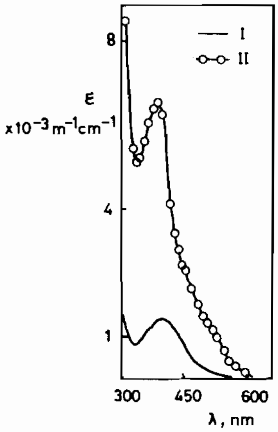


Fig. 2. Spectra of III and IV at pH 10.6. All other conditions as in Fig. 1. The accuracy in the range 350–420 nm is somewhat smaller due to the large changes in the absorption coefficients of III in this region. Insert $\Delta\epsilon$ observed at 600 nm as function of pH. Solutions in the pH range 5–9 contained also $1 \times 10^{-3} M$ phosphate buffer.

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*Though dimerization seems the most plausible pathway, other mechanisms can be envisaged, *e.g.* (Scheme 2), which leads to ligand oxidation as observed in the reaction of III with Br_2 in CH_3CN [7]. Only product analysis will enable the elucidation of the nature of the second order process. However, Br_2^- radicals are expected to react also with the products thus inhibiting preparative experiments [9]. It is possible that bromination at the γ position in analogous systems follows a mechanism of the type: $Ni(II)L^- + Br_2 \rightarrow Ni(III)L^- + Br_2^-$; $Ni(III)L^- \rightleftharpoons Ni(II)L^\cdot$; $Ni(II)L^\cdot + Br_2$ (or Br_2^-) $\rightarrow Ni(II)L'$, where L′ is the brominated ligand [12].

**It should be noted that at pH 7.8 where *ca.* 95% of Ni(II)L are in the form of III which upon oxidation is expected to yield IV, we observe 2μ sec after the pulse *ca.* 90% of II. Thus the results indicate that the equilibrium $IV + H_2O \rightleftharpoons II + OH^-$ is achieved very fast, though protonation on carbon atoms of this type is often relatively slow [10].

at 600 nm ($\epsilon = 2500\ M^{-1}\ cm^{-1}$), tentatively assigned as due to a charge transfer process. The absorption spectrum surprisingly continues into the near IR (*e.g.*, at 845 nm $\epsilon = 1250\ M^{-1}\ cm^{-1}$), which may indicate a delocalization of the π-electrons and the d-electrons (we could not, due to experimental limitations, extend the study to longer wave lengths). Thus the strong interaction between the ligand and the metal is source for the unusual optical spectrum in the visible region, as well as for the intramolecular electron transfer process observed.

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