Properties of (1,4,7,10,13-Penta-azacyclohexadecane)nickel(III) in Aqueous Solutions: A Pulse Radiolytic Study

Luigi Fabbrizzi *
Istituto di Chimica Generale ed Inorganica dell Universita di Pavia, 27100 Pavia, Italy
Hain Cohen *
Nuclear Research Centre Negev, Beer-Sheva, Israel
Dan Meyerstein
Chemistry Department, Ben-Gurion University of the Negev and Nuclear Research Centre Negev, Beer-Sheva, Israel

The oxidation of (1,4,7,10,13-penta-azacyclohexadecane)nickel(II) by OH˙ radicals in aqueous solutions was studied, and the properties of the resulting nickel(III) complex are compared with those of analogous complexes $[NiL]^{3+}$ where L is a tetra-azacyclotetradecane ligand. The difference in the properties is attributed to the fifth nitrogen donor atom which decreases the acidity of the central tervalent nickel.

We have been recently engaged in a study of factors affecting the chemical properties of tervalent nickel complexes with tetra-aza macrocyclic ligands in aqueous solutions.[1–6] Several common properties were observed for this class of complexes.

(*i*) All tervalent nickel complexes with water as the axial ligands have a strong absorption band around 300 nm and a weak band around 550 nm.[1,5–8]

(*ii*) The complexes have a p*K* of about 3.5 ± 0.5 which is due to one of the axially bound water molecules [1,3,5] [equation (1)]. For L = *meso*- (L^1) or *rac*-5,7,7,12,14,14-hexamethyl-

$$[NiL(H_2O)_2]^{3+} \rightleftharpoons [NiL(OH)]^{2+} + H_3O^+ \qquad (1)$$

1,4,8,11-tetra-azacyclotetradecane (L^2) and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (L^3) the results indicate that the nickel ion in $[NiL(OH)]^{2+}$ is five-co-ordinated,[5] whereas for 1,4,8,11-tetra-azacyclotetradecane (L^4) the alkaline form is $[NiL^4(OH)_2]^+$,[5] suggesting octahedral co-ordination.

(*iii*) Anions, *e.g.* SO_4^{2-}, HPO_4^{2-}, $H_2PO_4^-$, $C_6H_4(CO_2^-)_2$, and Cl^-, form complexes with $[NiL(H_2O)_2]^{3+}$ according to

$$[NiL(H_2O)_2]^{3+} + 2X^{n-} \rightleftharpoons [NiLX_2]^{(3-2n)+} \qquad (2)$$

equation (2). No mixed complexes of the type $[NiL(X)(OH)]^{(2-n)+}$ are observed at least for L = L^1.[3,5,6]

(*iv*) The tervalent nickel complexes of this type are short lived in neutral and slightly acidic aqueous solutions, $t_{\frac{1}{2}} \approx$ 1 min for L^1—L^4. In alkaline solutions the decomposition reaction becomes first order in $[OH^-]$[5] [equation (3)] where L′ indicates

$$[NiL(OH)]^{2+} + OH^- \longrightarrow [Ni^{II}L'] \qquad (3)$$

the ligand L modified by oxidation. Equation (3) is not balanced as clearly a second nickel complex has to be involved in the two-electron redox process.

It seemed of interest to study the effect of the insertion of a fifth nitrogen atom into the macrocyclic ligand framework on the properties of tervalent nickel in aqueous solutions. We chose to study the properties of the complex with 1,4,7,10,13-penta-azacyclohexadecane (L^5) as its redox potential in acetonitrile is similar to that of $[NiL^4]^{3+}$.[9]

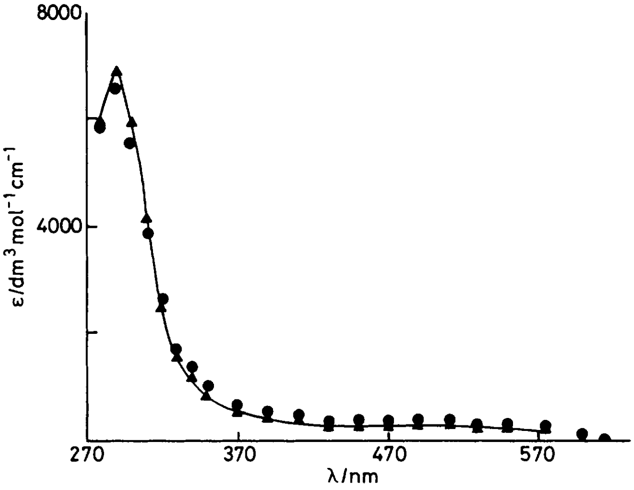

Figure. Absorption spectrum of $[NiL^5]^{3+}$ in neutral aqueous solutions. Solution composition: 5 × 10^{-5} mol dm^{-3} $[NiL^5][ClO_4]_2$, pH 6.0, N_2O-saturated. Pulse yielding 5 × 10^{-6} mol dm^{-3} of free radicals. ●, 32 μs after the pulse; ▲, 2 ms after the pulse

Experimental

The complex $[NiL^5][ClO_4]_2$ was identical with that used in the electrochemical study.[9] The pulse radiolytic experiments were carried out at the electron linear accelerator of the Hebrew University of Jerusalem. The procedures used for solution preparation, irradiation, kinetic and spectrophotometric data analysis were identical with those described earlier in detail.[3]

Results and Discussion

Nitrous oxide (N_2O)-saturated solutions containing 0.5 × 10^{-4}—2 × 10^{-4} mol dm^{-3} $[NiL]^{2+}$ in the range 3.0 ≤ pH ≤ 11.0 were irradiated. Under these conditions over 90% of the free radicals formed are hydroxyl radicals, the rest being hydrogen atoms. The formation of an unstable intermediate with a strong absorption band at $\lambda_{\text{max.}} = 290 \pm 5$ nm ($\varepsilon_{\text{max.}} = 6\,900 \pm 700$ dm^3 mol^{-1} cm^{-1}), Figure, was observed under these conditions. The reaction observed can be expressed as in equation (4). The same product is formed by oxidation

$$[\text{NiL}^5]^{2+} + \text{OH}\cdot \longrightarrow [\text{NiL}^5]^{3+}; \quad k = (5 \pm 2) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (4)$$

with $Br_2^{\cdot -}$ (N_2O-saturated solutions containing 0.01 mol dm^{-3} NaBr), however the corresponding rate constant is $\leqslant 5 \times 10^7$ dm^3 mol^{-1} s^{-1}, *i.e.* this reaction is considerably slower than that reported for the tetra-aza macrocyclic complexes of nickel studied so far.[1,7,8,10] (For all the latter the rate of reaction approaches the diffusion-controlled limit.) The oxidation of all nickel complexes by $Br_2^{\cdot -}$ was shown to occur *via* the inner-sphere mechanism.[1,10] The lower rate observed for the reaction $Br_2^{\cdot -} + [NiL^5]^{2+}$ is attributed to the fact that the nickel in the complex has a high-spin electronic configuration and therefore has an octahedral co-ordination sphere. The approach of $Br_2^{\cdot -}$ to the central nickel is thus hindered relative to the low-spin planar tetra-aza macrocyclic complexes.*

Reaction (4) is followed by a first-order reaction with $k = (6 \pm 2) \times 10^3$ s^{-1} which causes a very slight change in the absorption spectrum of the product, Figure. Similar processes were observed for the tetra-aza macrocyclic nickel(III) complexes and were attributed to intramolecular rearrangement of the $Ni^{III}L$ complex formed in reaction (4).[1,3,5] The exact nature of these rearrangement reactions was not elucidated in this study or those cited. It clearly involves a change in the configuration of the inner sphere of the nickel, probably in the configuration of one or more of the five- and six-membered rings formed by the ligand and the central cation.

The kinetics of decomposition of $[NiL^5]^{3+}$ were followed and found to obey a second-order rate law with $k = (5.1 \pm 1.0) \times 10^4$ dm^3 mol^{-1} s^{-1}, the rate of reaction being independent of pH in the range studied ($3.0 \leqslant \text{pH} \leqslant 11.5$). The rate of decomposition and the absorption coefficient at 300 nm were not affected by the addition of 0.13 mol dm^{-3} Na_2SO_4 or 1×10^{-4} mol dm^{-3} $FeSO_4$ to solutions at pH 3.3. The latter observation indicates that $k \leqslant 1 \times 10^3$ dm^3 mol^{-1} s^{-1} for $[NiL^5]^{3+} + Fe^{2+}$. The reaction $[NiL^5]^{3+} + O_2$ at pH 3.5 was studied and a rate constant of $(2 \pm 1) \times 10^3$ dm^3 mol^{-1} s^{-1} was determined.

The identification of the product of reaction (4) as $[NiL^5]^{3+}$ is based on the following reasoning.

(*a*) The absorption peak of the transient at 290 nm and its absorption coefficient are similar to those reported for other $Ni^{III}L$ complexes.[1-8,10]

(*b*) The rate of reaction of the transient with oxygen is orders of magnitude lower than that of aliphatic radicals, free or ligated to nickel(II),[10] the other possible product of reaction (4). Similar rates of reaction with oxygen were reported for other tervalent nickel complexes,[10,11] although not for tetra-aza macrocyclic ligands. However, the rate of reaction of $[NiL^5]^{3+}$ with Fe^{2+}(aq) is lower than that reported for tervalent nickel complexes with tetra-aza macrocyclic ligands.[10]

The difference in the chemical properties of $[NiL^5]^{3+}$ and of $[NiL]^{3+}$ ($L = L^1$—L^4) seems to be due to the σ-donating properties of the fifth nitrogen atom of the ligand. Thus one could argue as follows.

(*i*) The higher electron density on the central nickel due to the fifth ligating nitrogen is expected to raise pK_1, as observed.† The fact that the results indicate that $pK_1 > 12.5$ suggests furthermore that $[NiL^5]^{3+}$ is five-co-ordinated in analogy with $[NiL(OH)]^{2+}$ ($L = L^1$—L^3) as it is difficult to envisage a water molecule bound to Ni^{III} with such a high p*K*.‡

(*ii*) The fact that 0.13 mol dm^{-3} sulphate ions do not affect the stability or absorption spectrum of $[NiL^5]^{3+}$ suggests that the stability constant for ligation of sulphate to this complex is low, in agreement with observations for $[NiL^1(OH)]^{2+}$.[3,6]

(*iii*) The fact that reaction (3) is not observed for $[NiL^5]^{3+}$ up to pH $\leqslant 11.5$, although it is the major reaction for $Ni^{III}L$ ($L = L^1$—L^4) at pH > 8.5,[5] indicates that the p*K* for the loss of the $\overset{|}{\underset{|}{\text{M-N-H}}}$ proton is higher by at least three pH units in the present system. This conclusion is also in agreement with the suggestion that the fifth nitrogen donor atom decreases the acidity of the central nickel complex.

In conclusion, all the experimental observations are in agreement with the suggestion that the central nickel in $[NiL^5]^{3+}$ is five-co-ordinated and that it is less acidic than that in other $[NiL]^{3+}$ complexes. We cannot rule out the possibility that at very high alkalinity $[NiL^5(OH)]^{2+}$, a six-co-ordinated species, might be formed.

Acknowledgements

This work was supported in part by a grant from the U.S.-Israel Binational Science Foundation (B.S.F.), Jerusalem.

References

1 M. Jaacobi, D. Meyerstein, and J. Lilie, *Inorg. Chem.*, 1979, **18**, 429.

2 E. Zeigerson, G. Ginzburg, N. Schwarts, Z. Luz, and D. Meyerstein, *J. Chem. Soc., Chem. Commun.*, 1979, 241.

3 H. Cohen, L. J. Kirschenbaum, E. Zeigerson, M. Jaacobi, E. Fuchs, G. Ginzburg, and D. Meyerstein, *Inorg. Chem.*, 1979, **18**, 2763.

4 E. Zeigerson, G. Ginzburg, L. J. Kirschenbaum, and D. Meyerstein, *J. Electroanal. Chem. Interfacial Electrochem.*, 1981, **127**, 113.

5 E. Zeigerson, G. Ginzburg, J. Becker, L. J. Kirschenbaum, H. Cohen, and D. Meyerstein, *Inorg. Chem.*, 1981, **20**, 3988.

6 E. Zeigerson, I. Bar, J. Bernstein, L. J. Kirschenbaum, and D. Meyerstein, *Inorg. Chem.*, 1982, **21**, 73.

7 P. Marathamuthu, L. K. Patterson, and G. Ferraudi, *Inorg. Chem.*, 1978, **17**, 3157.

8 K. D. Whitburn and G. S. Laurence, *J. Chem. Soc., Dalton Trans.*, 1979, 139.

9 L. Fabbrizzi, *J. Chem. Soc., Chem. Commun.*, 1979, 1063.

10 P. Morliere and L. K. Patterson, *Inorg. Chem.*, 1981, **20**, 1458; 1982, **21**, 1833, 1837.

11 J. Lati and D. Meyerstein, *Int. J. Radiat. Phys. Chem.*, 1975, **7**, 611; E. Fuchs, H. Cohen, K. Wieghardt, J. Koresh, and D. Meyerstein, unpublished work.

12 A. Bencini, L. Fabbrizzi, and A. Poggi, *Inorg. Chem.*, 1981, **20**, 2544.

Received 16*th December* 1982; *Paper* 2/2097

---

* Morliere and Patterson[10] have offered a similar explanation for the oxidation of a series of analogous tetra-aza macrocyclic nickel complexes with different degrees of unsaturation of the ligand. However, the effect was considerably less pronounced in their system.

† The fact that the kinetics of decomposition are pH independent up to pH 11.5 indicates that $pK_1 \gg 12.5$, as the alkaline form in all analogous complexes decomposes *via* a fast first-order process.[5] This conclusion is also corroborated by the fact that the absorption spectrum is pH independent.

‡ It should be noted that in acetonitrile $[NiL^5]^{3+}$ is octahedral with a solvent molecule occupying the sixth co-ordination site.[12] Thus the results suggest a different behaviour in these two solvents. Alternatively, one would have to argue that the spectrum of $[NiL^5(OH)]^{2+}$ and its kinetics of decomposition are identical, within experimental error, to those of $[NiL^5]^{3+}$.