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Stabilization of Monovalent Nickel in Aqueous Solutions by Complexation with the β-Isomer of C-5,12-Racemic-1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11-tetraazacyclotetradecane

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Abstract

The monovalent nickel complex formed by the reduction of the β-isomer of the complex of C-5,12-racemic-1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11-tetraazacyclotetradecane nickel(II), NiL_1^{2+} in 0.1 M HCO_2Na, pH 7.6, has a half-life longer than 90 h. The redox potential of the couple NiL_1^{+}/NiL_1^{2+} is −0.94 V *vs.* Ag/AgCl. The absorption spectrum of NiL_1^{+} consists of a band with $\lambda_{max} = 335$ nm and $\epsilon_{max} = 2200\ M^{-1}\ cm^{-1}$. For the analogous complex with C-5,12-racemic-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, L_2, the half-life time of NiL_2^{+} is less than 1 min and the redox potential is −1.44 V *vs.* Ag/AgCl. These results are similar to those reported earlier for the analogous nickel complexes with the *meso*-isomers of the ligands. The results thus indicate that both the kinetic and thermodynamic stabilization of monovalent nickel by N-methylation of tetraazamacrocyclic ligands is not significantly affected by the configuration of the ligand.

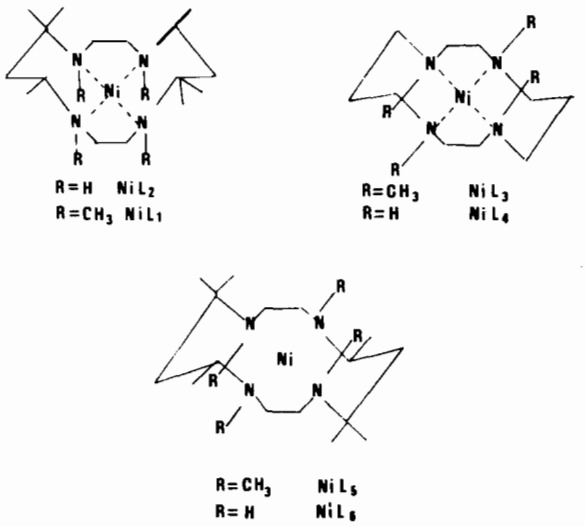
Introduction

In a recent study [1] we have shown that the N-methylation of the divalent nickel complexes in the *trans* **III** configuration [2] (see Scheme 1), with 1,4,8,11-tetraazacyclotetradecane, L_4, and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, L_6, facilitates the reduction of the central nickel cation and kinetically stabilizes the monovalent nickel complex in aqueous solutions [1]. The increase of the redox potential upon N-methylation was attributed to a slight increase in the cavity size of the ligand and to the more hydrophobic nature of the N-methylated complex [1, 3]. The kinetic stabilization of the monovalent nickel complexes by the N-methylation was attributed to the hindering, or slowing down, of the ligand loss reaction by N-methylation [1]. It

$$NiL^{+} + 2H_3O^{+} \longrightarrow Ni^{+}_{aq} + LH_2^{2+}$$

seemed of interest to check whether the configuration of the ligand has a major role on these effects.

The divalent nickel complex with C-5,12-racemic-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, L_2, is known to exist in two isomeric forms, α and β [4]. The latter, which has the *trans* **I** configuration [2], is more stable in neutral and alkaline solutions [4]. In this isomer the nickel is also relatively exposed [4], see Scheme 1. We decided, therefore, to check what effects the N-methylation of this isomer has on the properties of its monovalent nickel complex.



Scheme 1.

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Experimental

The complex $NiL_2(ClO_4)_2$ was prepared by mixing the free ligand with $Ni(CH_3CO_2)_2$ in methanol at 60 °C, addition of $NaClO_4$, cooling down and filtration. The precipitate was recrystallized from 0.01 M $HClO_4$. The orange crystals thus obtained have an IR spectrum in KBr with absorptions at 3195 cm^{-1}, attributed to the N–H stretching, and a broad band at 1110 cm^{-1} and a narrow one at 625 cm^{-1} both due to the perchlorate. The visible absorption spectrum in aqueous solutions has $\lambda_{max} = 453$ nm, $\epsilon_{max} = 105$ M^{-1} cm^{-1}. The NMR spectrum in CF_3CO_2H consists of a doublet at 1.23 ppm, six protons, attributed to the methyls bound to the assymetric carbon; a singlet at 1.33 ppm, six protons, attributed to the equatorial methyls of the $C(CH_3)_2$ groups; a singlet at 2.36 ppm, six protons, attributed to the axials methyls of the $C(CH_3)_2$ groups. Additional peaks between 1.7–2.0 ppm are due to the methylenic groups of the five-membered rings and between 1.4–1.7 ppm to the methylenic groups of the six-membered rings. The visible, IR and NMR data are in accord with the reports in the literature [4].

The complex $NiL_1(ClO_4)_2$ was prepared by a procedure analogous to that introduced by Wagner and Barefield for analogous complexes [5]. In a three-neck flask fitted with a condenser, 5 g of $NiL_2(ClO_4)_2$ were dissolved in 50 ml Me_2SO under nitrogen. After 15 min of stirring 10 g of powdered KOH was added; the colour changed from yellow to deep blue. After an additional 15 min of stirring, 10 ml CH_3I were added. The solution warmed up as a result and changed its colour to green. After slow cooling the solution became pink–violet. (In some cases this change in colour occurred only after prolonged cooling in the refrigerator). Addition of a 1:3 mixture of ethanol:ether resulted in the precipitation of NiL_1I_2. After filtration the precipitate was dissolved in hot water saturated with $NaClO_4$ or KPF_6; cooling resulted in the precipitation of $NiL_1(ClO_4)_2$ or $NiL_1(PF_6)_2$, respectively, which were recrystallized from hot water, yield *ca.* 70%. *Anal.* Calc. for $NiL_1(PF_6)_2$: C, 34.85; H, 6.43; N, 8.12. Found: C, 34.56; H, 5.90; N, 7.72%. The complex has no absorption at 3195 cm^{-1} indicating that all the N–H groups were indeed methylated. The visible spectrum of $NiL_1(PF_6)_2$ in aqueous solutions consists of a band at 546 nm with $\epsilon = 190$ M^{-1} cm^{-1}. The NMR spectrum in CF_3CO_2H consists of a doublet at 1.16 ppm, six protons, attributed to the methyls bound to the asymmetric carbon (only half of the doublet is clear; the second half overlaps with the next peak). The singlet due to the equatorial methyls of the $C(CH_3)_2$ groups appeared at 1.18 ppm, six protons; the singlet of the axial methyls appeared at 2.78 ppm, six protons. There are two further singlets, six protons each, which are not observed for $NiL_2(ClO_4)_2$, at 2.81 and 3.24 ppm. These are attributed to the $N–CH_3$ groups; the position of these peaks is in accord with that reported for the $N–CH_3$ groups of $NiL_5(ClO_4)_2$ [6]. The shift in the peak of the equatorial methyls from 2.36 ppm for $NiL_2(ClO_4)_2$ to 2.78 ppm for $NiL_1(ClO_4)_2$ indicates that in the latter complex these methyls are nearer to the NiN_4 plane and are therefore more deshielded by the unisotropic field of the Ni^{2+} center. The results thus prove that indeed NiL_1^{2+} is a complex of Ni^{2+} with 5,12-rac-1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11-tetraazacyclotetradecane. Furthermore, the NMR data strongly support the conclusion that the complex has maintained the *trans* I configuration of the β isomer of NiL_2^{2+} which was used as a starting material.

All other materials were of A.R. grade and were used without further treatment. All solutions were prepared with use of heat-distilled water that was then passed through a Millipore water purification setup, the final resistance being >10 MΩ/cm.

The electrochemical, pulse radiolysis and spectroscopic measurements were identical to those previously described in detail [1].

Results and Discussion

In Fig. 1 are shown typical cyclic voltammograms of NiL_1^{2+} and NiL_2^{2+} in aqueous solutions. The results clearly indicate that the reduction of both complexes is electrochemically reversible. However, the oxidation wave for NiL_2 is considerably lower than the reduction wave, indicating that the life time of NiL_2^{+} is short, $t_{1/2} < 1$ min. On the other hand, the results indicate that NiL_1^{+} is stable on the time scale of the experiment. The cyclic voltammograms of NiL_1^{2+}

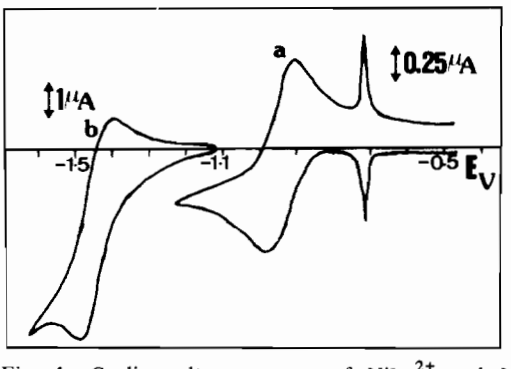

Fig. 1. Cyclic voltammograms of NiL_1^{2+} and NiL_2^{2+}. Metrohm E 410 hanging mercury dropping electrode served as a cathode, the auxiliary electrode was a Pt wire, and an Ag/AgCl electrode served as a reference electrode. (a) 57 mV/s, solution composition: 1.0×10^{-3} M NiL_1I_2, 1.0 M Na_2SO_4 at pH 6.0; (b) 44 mV/s, solution composition 5.0×10^{-3} M $NiL_2(ClO_4)_2$, 0.1 M $NaClO_4$, pH 6.0.

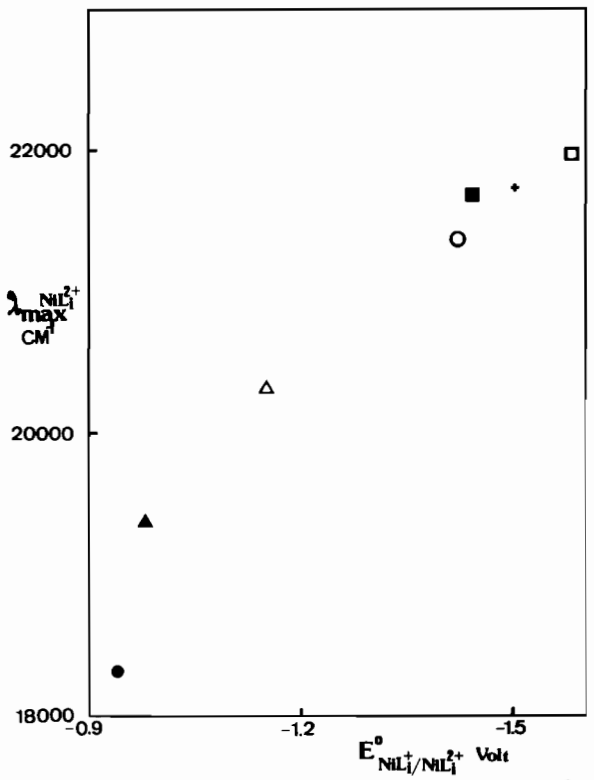

Fig. 2. Correlation between the redox potentials of NiL^{2+} complexes and the maxima of their visible absorption band. • NiL_1^{2+}; □ NiL_2^{2+}; △ NiL_3^{2+}; □ NiL_4^{2+}; ▲ NiL_5^{2+}; ○ NiL_6^{2+}; × NiL_7^{2+} (L_7 = 1,4,8,12-tetraazapentacyclodecane.). Data for NiL_3^{2+}, NiL_4^{2+}, NiL_5^{2+}, NiL_6^{2+} from ref. 2 and for NiL_7^{2+} from ref. 4.

are independent of time in contrast to those of NiL_5^{2+}.

The results clearly indicate that N-methylation shifts the redox potentials of NiL_2^{2+} to a less negative potential by 0.50 V in analogy to the effect of N-methylation on the redox potential of NiL_4^{2+} and NiL_6^{2+} [1]. The correlation of the redox potential of a series of NiL_1^{2+} complexes in aqueous solution with 10 *Dq* for these complexes as determined spectrophotometrically [7] is plotted in Fig. 2. The correlation clearly points out that the redox potential is shifted to less negative potentials with the decrease in the ligand field splitting caused by the ligand. This finding is in accord with earlier reports [1, 7]. It is of interest to note that the results seem to indicate that the ligand field splitting in NiL_1^{2+} is smaller than expected from the redox potential The effect of N-methylation on the relative ligand field splittings of NiL_2^{2+} and NiL_1^{2+} is in accord with expectations [5].

The results do not support the suggestion that the shift in the redox potential upon N-methylation is mainly due to either the increase in the ligand cavity or to the increase in the hydrophobic nature of the complex. Though X-ray crystallographic data are not available, it is difficult to believe that N-methylation of NiL_2^{2+} and NiL_6^{2+} will cause a similar increase in the cavity size. Furthermore, it is unreasonable to expect that the cavity size of L_1, L_3 and L_6 is considerably larger than that of 1,4,8,12-tetraazacyclopentadecane, as the results [3] would indicate if the cavity size were the major factor affecting the redox potential. Due to the different conformation of the ligand one expects a considerably higher solvation energy for NiL_1^{2+} and NiL_2^{2+} than for NiL_5^{2+} and NiL_6^{2+}. (This expectation is verified by the observation that the stability constant for the formation of NiL_1OH^+ and NiL_2OH^+ is considerably higher than for that of NiL_5OH^+ and NiL_6OH^+, respectively [8]).

One would therefore expect that the increased hydrophobic nature upon N-methylation would have a larger effect on the redox potential for the NiL_5^{2+}/NiL_6^{2+} couple than for the NiL_1^{2+}/NiL_2^{2+} couple. Therefore, one has to conclude that the shift of the redox potential to less negative potentials upon N-methylation is due to the fact that tertiary amines are weaker σ donor ligands than secondary amines.

Helium saturated solutions containing 1×10^{-3} M $NiL_1(ClO_4)_2$, 0.1 M HCO_2Na, at pH 7.6 were irradiated in a ^{60}Co-γ source by a dose of *ca.* 50 000 rad. Under these conditions the e_{aq}^- and CO_2^- radicals formed which reduced NiL_1^{2+} to NiL_1^+ [1]. The UV–Vis spectrum of NiL_1^+ thus formed was measured in a Carry 17 spectrophotometer. The spectrum consists of one absorption band with $\lambda_{max} = 335 \pm 3$ nm, $\epsilon_{max} = 2200 \pm 400$ M^{-1} cm^{-1}. (The molar absorption coefficient was measured by the pulse radiolysis technique, in analogy to that of the other monovalent nickel complexes [1, 3]. The absorption due to NiL_i^+ in this solution disappeared slowly; after 20 h *ca.* 86% of the absorption still remained. As the solution was kept in a spectrophotometric cell sealed with a glass joint, some of the disappearance might be due to oxygen penetration. We thus conclude that the half-life time of NiL_1^+ in neutral solutions is longer than 90 h.

The results thus indicate that the spectral properties of the divalent and monovalent nickel complexes, their redox potentials and the life times of the monovalent complexes are similar for the complexes in the *trans* **I** and *trans* **III** configuration. N-methylation lowers the ligand field splitting for both isomers and hinders the ligand loss reaction.

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References

1 N. Jubran, G. Ginzburg, H. Cohen and D. Meyerstein, *J. Chem. Soc., Chem. Commun.*, 517 (1982); N. Jubran, G. Ginzburg, H. Cohen, Y. Koresh and D. Meyerstein, *Inorg. Chem., 24,* 251 (1985).

2 B. Bosnich, C. K. Poon and M. L. Tobe, *Inorg. Chem., 4,* 1102 (1965).

3 N. Jubran, H. Cohen and D. Meyerstein, *Isr. J. Chem., 25,* 118 (1985).

4 L. G. Warner and D. H. Busch, *J. Am. Chem. Soc., 91,* 4092 (1969).

5 F. Wagner and E. K. Barefield, *Inorg. Chem., 15,* 408 (1976).

6 F. Wagner, M. T. Mocella, M. J. D'Aniello, A. H. J. Wang and E. K. Barefield, *J. Am. Chem. Soc., 96,* 2625 (1974).

7 F. V. Lovecchio, E. S. Gore and D. H. Busch, *J Am. Chem. Soc., 96,* 3109 (1974).

8 N. Jubran and D. Meyerstein, to be published.