Inorganica Chimica Acta
LETTER

Stabilization of nickel(III)-1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane by axial binding of anions in neutral aqueous solutions

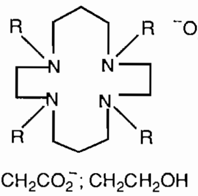
Israel Zilbermann, Avraham Meshulam, Haim Cohen and Dan Meyerstein*
Nuclear Research Centre Negev and Chemistry Department, Ben Gurion University of the Negev, Beer-Sheva (Israel)

(Received October 19, 1992; revised January 2, 1993)

Abstract

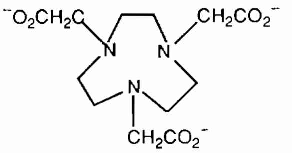
The title tervalent nickel complex, $Ni^{III}L^5aq$, is stabilized in neutral and slightly alkaline aqueous solutions in the presence of stabilizing anionic ligands via the formation of $Ni^{III}L^5X_2$ complexes, where $X = F^-$, SO_4^{2-}, HPO_4^{2-}, HCO_2^-, $C_6H_5CO_2^-$, $CH_3CO_2^-$ and $(CH_3)_3CCO_2^-$. These complexes can be used as new powerful single electron oxidizing reagents in this medium. Some of the properties of the $Ni^{III}L^5X_2$ complexes are described and discussed.

There is a growing interest in the use of transition metal complexes as catalysts in oxidation processes. One group of complexes which shows promising potential is that of the nickel complexes with saturated tetraazamacrocyclic ligands [1–6]. This, and the discovery of nickel enzymes in which tervalent nickel is plausibly involved [7], renewed the interest in the study of the properties of tervalent nickel complexes in aqueous solutions. It was found that a variety of tervalent nickel complexes with tetraazamacrocyclic ligands can be stabilized in acidic aqueous solutions, mainly by binding of anionic axial ligands [8]. However, the results indicated that these complexes are unstable in neutral solutions [8, 9]. To this rule there are two exceptions, i.e. those of $Ni^{III}L^1$ [10].

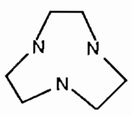


$R = CH_2CO_2^-$; CH_2CH_2OH

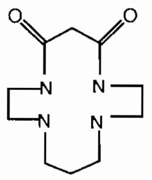
L^1



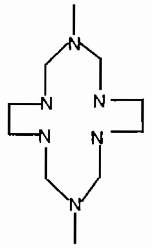
L^2



L^3



L^4



L^5

Few other tervalent nickel complexes are relatively stable in neutral aqueous solutions, i.e. those with edta [11–14], nta [12] and L^2 [15] in the absence of air, the complex NiL^3_2 [16–18], complexes with peptides and peptide-like ligands [9, 19] including those of L^4 [20–22] and its analogs and some complexes with thiol groups as the donating ligands [19]. Most of the latter have relatively low redox potentials and are therefore not good oxidizing agents.

There is a special interest in stabilizing in neutral solutions complexes of the type $Ni^{III}L^iX_2$, where X are monodentate ligands and L^i are tetradentate ligands, with a relatively high redox potential [23]. These complexes have the advantage that the following equilibria occur

$$Ni^{III}L^iX_2 \rightleftharpoons Ni^{III}L^iX_{aq} + X \qquad (1)$$

$$Ni^{III}L^iX_{aq} \rightleftharpoons Ni^{III}L^i_{aq} + X \qquad (2)$$

The complexes $Ni^{III}L^iX_{aq}$ and $Ni^{III}L^i_{aq}$ are considerably stronger oxidants, though short lived, and the central cation is accessible to the substrate. Thus they are expected to be oxidants with interesting properties and good catalysts for various oxidation processes, including electrocatalytic oxidations.

Recently the synthesis of the complex $NiL^{5\,2+}$ was reported [24]. It was shown that it has in aprotic media similar redox properties to those of $NiL^{1\,2+}$ where $R = H$ [24]. It was decided to study its redox properties in neutral aqueous solutions using the pulse radiolysis technique [25]. Some of the experiments surprisingly indicated that $[Ni^{III}L^5(HCO_2)_2]^+$ is relatively stable at pH 6.0 [25]. Therefore the study of the redox properties of NiL^5 in the presence of a variety of monodentate anionic ligands, using electrochemistry and spectrophotometry, was undertaken. The results reported herein indicate that indeed a variety of $Ni^{III}L^5X_2$ com-

---

*Author to whom correspondence should be addressed at the Ben Gurion University.

0020-1693/93/$6.00

plexes are relatively stable in neutral aqueous solutions though they are powerful oxidizing agents.

The redox potential of $NiL^{5\ 2+}$ in the presence of various anions was determined using cyclic voltammetry; a set of typical voltammograms is presented in Fig. 1, the results are summed up in Table 1. The redox potential in neutral solutions containing only $NaClO_4$ cannot be determined as the electrochemical process is irreversible due to the fast decomposition of $Ni^{III}L^5{}_{aq}$ under these conditions. Therefore this potential was determined at pH 2.2 where $NiL^5(H_2O)_2{}^{3+}$ has a long enough life time. From the dependence of the redox potential on [X], i.e. a slope of *c.* 120 mV of the plots of E versus log[X] (see Table 1), the detailed data are not presented, it is concluded that the complexes formed are $Ni^{III}L^5X_2$. From the redox potentials in the perchlorate containing solution and those in the presence of the stabilizing anions X the equilibria constants $K=[Ni^{III}L^5X_2]/[Ni^{III}L^5(H_2O)_2{}^{3+}][X]^2$ were calculated applying the Nernst equation. The results are given in Table 1. (The electrochemical results suggest that the concentrations of $Ni^{III}L^5X(H_2O)$ are negligible; clearly the equilibria constants for the formation of the latter complexes cannot be derived from the electrochemical data.)

The results lead to the following conclusions:

(i) A variety of anionic ligands stabilizes $Ni^{III}L^5$ in neutral aqueous solutions.

(ii) The stability constants of the complexes $Ni^{III}L^5X_2$ for X = oxo anions are similar.

(iii) The detailed relative thermodynamic stability of the $Ni^{III}L^5X_2$ complexes seems to be a complex function of the pK_a of HX, and the bulkiness of the substituents on the organic residues.

(iv) Divalent anions, $SO_4{}^{2-}$ and $HPO_4{}^{2-}$ (it should be pointed out that though at pH 6.0 $H_2PO_4{}^-$ is the major form present in solution one expects [23] that in the complex $HPO_4{}^{2-}$ is the ligand), are better stabilizing ligands, when their pK_as are taken into account.

The kinetics of decomposition of the $Ni^{III}L^5X_2$ complexes in aerated solutions (preliminary data indicate that deaeration has no effect) were studied spectrophotometrically in the wavelength range where only the $Ni^{III}L^5X_2$ complexes have an appreciable absorption coefficient. The kinetics obey first order rate laws. No product analysis and no detailed kinetic studies were performed. The data presented in Table 1 are only intended to point out the relative stabilities of the $Ni^{III}L^5X_2$ complexes and to point out that they are relatively long lived. According to the effect of [X] on the rate of decomposition the complexes can be divided into three groups:

1. When the concentration of X is increased by a factor of ten the rate of decomposition of $Ni^{III}L^5(C_6H_5CO_2)_2{}^+$, $Ni^{III}L^5(CH_3CO_2)_2{}^+$ and $Ni^{III}L^5F_2{}^+$ decreases by a factor of 27–39. These results indicate that the decomposition occurs mainly via $Ni^{III}L^5{}_{aq}$ though also the decomposition of $Ni^{III}L^5X_{aq}$ contributes to the processes observed.

2. When the concentration of X is increased by a factor of 10 the rate of decomposition of $Ni^{III}L^5(CHO_2)_2{}^+$, $Ni^{III}L^5(SO_4)_2{}^-$ and $Ni^{III}L^5(HPO_4)_2{}^-$ decreases by a factor of 7.2–9.4. These results indicate that these decompositions occur mainly via $Ni^{III}L^5X_{aq}$.

3. The rate of decomposition of $Ni^{III}L^5((CH_3)_3CCO_2)_2{}^+$ depends only slightly on $[(CH_3)_3$-

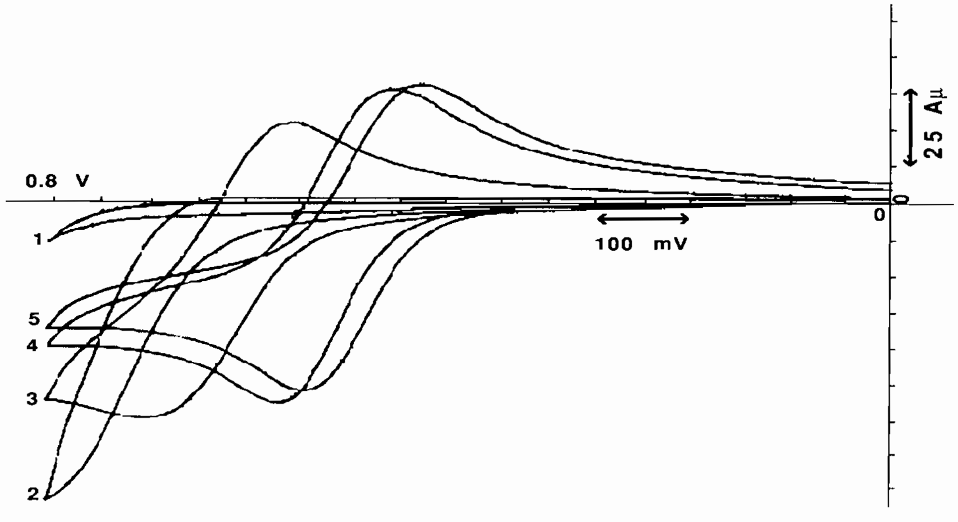


Fig. 1. Cyclic voltammograms: working electrode Au, reference SCE, scan rate 5 mV/s, pH 6.0. Ionic strength regulated with $NaClO_4$. 1: 0.15 M $NaClO_4$. 2: 5×10^{-4} M $NiL^5(ClO_4)_2$; 0.15 M $NaClO_4$, $I=0.15$. 3: 5×10^{-4} M $NiL^5(ClO_4)_2$; 0.005 M Na_2SO_4; $I=0.15$. 4: 5×10^{-4} M $NiL^5(ClO_4)_2$; 0.05 M Na_2SO_4; $I=0.15$. 5: 5×10^{-4} M $NiL^5(ClO_4)_2$; 0.40 M Na_2SO_4.

TABLE 1. Properties of $Ni^{III}L^5X_2$ complexes in neutral and slightly alkaline aqueous solutions[a]

X	[X] (M)	pH	Redox potential (V) vs. SCE[b]	Slope of E vs. log[X][b]	K (M^{-2})	λ_{max} (nm)	$t_{1/2}$[c]
H_2O		2.2	0.78				
$HCOO^-$	0.01	6.0	irr.				5.6 min
	0.1	6.0	0.58	0.11	6.5×10^6	282	41.2 min
	0.5	9.4	irr.				52 s
$C_6H_5COO^-$	0.01	6.0	0.59				1.8 h
	0.1	6.0	0.49	0.10	2.5×10^7	292	64 h
	0.1	9.0					3.9 min
CH_3COO^-	0.01	6.0	irr.				22.5 min
	0.1	6.0	0.54	0.13	6.7×10^6	284	14.5 h
	0.1	9.0	irr.				24.3 s
$(CH_3)_3CCOO^-$	0.01	6.0	0.58				16.7 h
	0.1	6.0	0.47	0.12	7.3×10^7	288	29.2 h
	0.1	9.6					9.4 min
SO_4^{2-}	0.01	6.0	0.64				58 min
	0.1*	6.0		0.12	1.4×10^7	286	7.0 h
	0.1*	9.0	irr.				4.7 min
$H_2PO_4^-$[d]	0.01	6.0	0.59				37 min
	0.1	6.0	0.49	0.10	2.3×10^7	276	5.8 h
	0.1*	9.0					22 min
F^-	0.01	6.0	irr.				4.1 min
	0.1	6.0	0.65	0.10	3.5×10^3	288	1.9 h
	0.1	9.0	irr.				50 s

[a] All experiments were carried out at a constant ionic strength, $I=0.15$ except* where $I>0.15$. [b] Accuracy ±0.01 V. [c] Half life for the decomposition of $Ni^{III}L^5X_2$. Errror limits are ±2% for $t_{1/2}<1$ h and ±10% for $t_{1/2}>1$ h. [d] At pH 6.0 $H_2PO_4^-$ is the major form of the free ligands but the complex present is $NiL^5(HPO)_2^-$. At pH 9.0 the free ligand is HPO_4^{2-}.

CCO_2^-] a result which indicates that $Ni^{III}L^5$-$((CH_3)_3CCO_2)_2^+$ is the major decomposing species.

The detailed mechanisms of decomposition including the nature of the final products are under study. It is hoped that this study will explain the reason for the different effect of [X] on the rage of decomposition of the $Ni^{III}L^5X_2$ complexes.

In conclusion the results point out that $Ni^{III}L^5$ can be stabilized at considerably higher pHs than commonly accepted for analogous complexes. The complexes formed are relatively strong single electron oxidizing agents. Their use in catalytic oxidation processes is being studied.

Acknowledgements

This study was supported in part by a grant from the Israel Academy of Sciences. D.M. thanks Mrs Irene Evens for her continuous interest and support.

References

1 Y. Uzan and D. Meyerstein, *Israel J. Chem., 27* (1986) 280.

2 J. F. Kinneary, J. S. Albert and C. J. Burrows, *J. Am. Chem. Soc., 110* (1988) 6124.

3 (a) H. Yoon and C. J. Burrows, *J. Am. Chem. Soc., 110* (1988) 4087; (b) T. R. Wagler, Y. Fang and C. J. Burrows, *J. Org. Chem., 54* (1989) 1584.

4 (a) H. Yoon, T. R. Wagler, K. J. O'Connor and C. J. Burrows, *J. Am. Chem. Soc., 112* (1990) 4568; (b) K. J. O'Connor, S. J. Wey and C. J. Burrows, *Tetrahedron Lett., 33* (1992) 1001.

5 X. Chen, S. E. Rokita and C. J. Burrows, *J. Am. Chem. Soc., 113* (1991) 5884.

6 (a) K. J. O'Connor and C. J. Burrows, *J. Org. Chem., 56* (1990) 1344; (b) X. Chen, C. J. Burrows and S. E. Rokita, *J. Am. Chem. Soc., 114* (1992) 322.

7 R. Cammack, *Adv. Inorg. Chem., 32* (1988) 297.

8 E. Zeigerson, G. Ginzburg, N. Schwartz, Z. Luz and D. Meyerstein, *J. Chem. Soc., Chem. Commun.,* (1979) 241.

9 A. G. Lappin and A. McAuley, *Adv. Inorg. Chem., 32* (1988) 241.

10 (a) R. W. Hay, M. P. Pujari, W. T. Moodie, S. Craig, D. T. Richens, A. Perotti and L. Ungaretti, *J. Chem. Soc., Dalton Trans.,* (1987) 2605; (b) E. Kimura, T. Koike, M. Yamaoka and M. Kodama, *J. Chem. Soc., Chem. Commun.,* (1985) 1341.

11 J. Lati and D. Meyerstein, *Int. J. Radiat. Phys. Chem.,* (1975) 7611.

12 J. Lati, J. Koresh and D. Meyerstein, *Chem. Phys. Lett., 33* (1975) 286.

13 E. Fuchs, G. Ginzburg, J. Lati and D. Meyerstein, *J. Electroanal. Chem., 73* (1976) 83.

14 J. Lati and D. Meyerstein, *J. Chem. Soc., Dalton Trans.,* (1978) 1105.

15 M. J. Van der Merwe, J. C. A. Boeyens and R. D. Hancock, *Inorg. Chem., 22* (1983) 3489.

16 K. Wieghardt, W. Schmidt, W. Hermann and H. J. Küppers, *Inorg. Chem., 22* (1983) 1953.

17 A. McAuley, P. R. Norman and O. Olubuyide, *Inorg. Chem., 23* (1984) 1939.

18 A. Buttafava, L. Fabrizzi, A. Perotti, A. Poggi, G. Poli and B. Seglu, *Inorg. Chem., 25* (1986) 1456.

19 (a) D. W. Margerum, in J. R. Lancaster (ed.), *The Bioinorganic Chemistry of Nickel,* VCH, Weinheim, 1988; (b) H. J. Kruger, G. Peng and G. R. H. Holm, *Inorg. Chem., 30* (1991) 734.

20 L. Fabrizzi and A. Poggi, *J. Chem. Soc., Chem. Commun.,* (1980) 646.

21 L. Fabrizzi, A. Perotti and A. Poggi, *Inorg. Chem., 22* (1983) 1411.

22 E. Kimura, T. Koike, R. Machida, R. Nagai and M. Kodama, *Inorg. Chem., 23* (1984) 4181.

23 (a) E. Zeigerson, I. Bar, J. Bernstein, L. J. Kirschenbaum and D. Meyerstein, *Inorg. Chem., 21* (1982) 73; (b) E. Zeigerson, G. Ginzburg, L. J. Kirschenbaum and D. Meyerstein, *J. Electroanal. Chem. Interfacial Electrochem., 127* (1981) 113; (c) N. Jubran, H. Cohen, Y. Koresh and D. Meyerstein, *J. Chem. Soc., Dalton Trans.,* (1986) 2509.

24 M. P. Suh and S. G. Kang, *Inorg. Chem., 27* (1988) 2544.

25 I. Zilbermann, H. Cohen and D. Meyerstein, to be published.