Journal of

The Chemical Society,

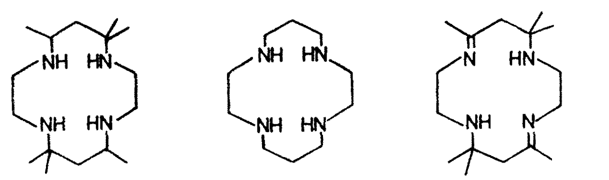
Chemical Communications

NUMBER 6/1979 15 MARCH

Electrochemical Preparation of Stable Nickel(III) Complexes with Tetradentate Macrocyclic Ligands in Aqueous Solutions

By ESTHER ZEIGERSON and GREGORY GINZBURG
(*Chemistry Department, Ben-Gurion University of the Negev, Beer-Sheva, Israel*)
NAOMI SCHWARTZ and ZEEV LUZ
(*The Weizmann Institute of Science, Rehovot, Israel*)
and DAN MEYERSTEIN*
(*Chemistry Department, Ben-Gurion University of the Negev, and Nuclear Research Centre Negev, Beer-Sheva, Israel*)

Summary Stable solutions of Ni^{III} complexes of the 14-membered macrocyclic ligands (I), (II), and (III) were obtained by electrochemical oxidation on gold and platinum electrodes of the corresponding Ni^{II} complexes in mild acidic aqueous solutions in the presence of sulphate; the Ni^{III} complexes formed represent a new kind of strong, easily accessible, single-electron, oxidizing agent with E° *ca.* 1 V *vs.* standard hydrogen electrode (S.H.E.) in aqueous media.



[14] ane N_4 (I) cyclam (II) [14] 4,11 diene N_4 (III)

NICKEL(II) complexes with macrocyclic ligands are known to be stable in aprotic solvents and have been extensively investigated.[1] In water and other solvents more basic than acetonitrile they undergo rapid decomposition, which is slowed down in highly acidic solutions.[2] The preparation of Ni^{III} complexes by chemical oxidation in the presence of concentrated acids has been described.[3] Oxidation of Ni^{II} complexes by hydroxyl free radicals in neutral and slightly acidic aqueous solutions yields intermediates with half-lives of seconds, characterized as Ni^{III} complexes.[4,5] We report here that the addition of polyvalent anions, *e.g.* SO_4^{2-}, as axial ligands stabilizes tervalent nickel complexes in mildly acidic aqueous solutions.

The perchlorate salts of Ni^{II} complexes of the ligands (I), (II), and (III), (hereafter called complexes A, B, and C) were synthesized and characterized according to published procedures.[5,6] The oxidized products were prepared by controlled-potential electrolysis, using a Pt-screen working electrode, at potentials *ca.* 100 mV above the anodic peak potential as measured by a three-electrode potentiostatic circuit (Figure 1). All solutions contained 1 M sodium sulphate supporting electrolyte, at pH $\leqslant 4$. Potentials are reported *vs.* an Ag–AgCl in 3 M KCl reference electrode. When solutions containing complexes A, B, or C are electrolysed under the above conditions the solutions in the anodic compartment changed colour. We here report data proving that these coloured solutions contain the relatively stable tervalent nickel complexes, $Ni^{III}LSO_4^+$, which can be used as powerful, one-electron oxidizing agents under mild conditions.

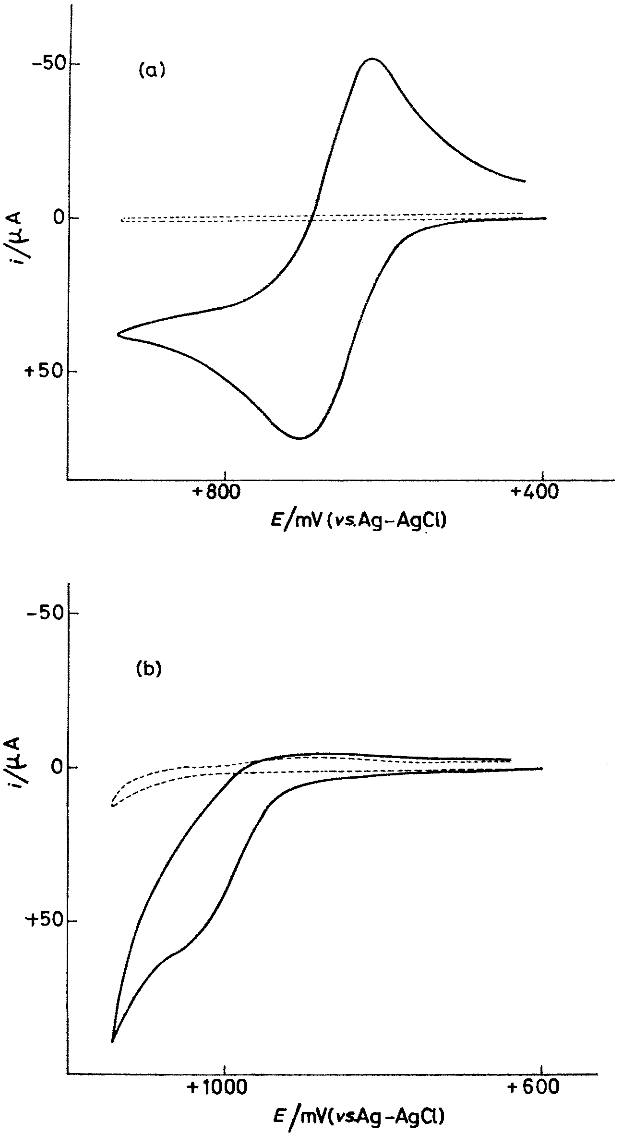


FIGURE 1. Linear potential sweep voltammetry on a gold electrode of $1{\cdot}2\ cm^2$ area at a scan rate of $11{\cdot}2\ mV\ s^{-1}$. (a) $1{\cdot}0 \times 10^{-3}$ M solution of complex A in $0{\cdot}5$ M Na_2SO_4 supporting electrolyte, pH 1·6. (b) $0{\cdot}36 \times 10^{-3}$ M solution of complex A in $NaClO_4$ supporting electrolyte, pH 1·6. Dotted lines: supporting electrolyte.

Cyclic voltammograms obtained for complex A in sulphate and perchlorate as supporting electrolytes are shown in Figure 1. The absence of the reduction peak in the case of perchlorate indicates that the primary oxidized product decomposes during the cycle and demonstrates the importance of the SO_4^{2-} ions in stabilizing the oxidation product, assuming that perchlorate does not promote decomposition. Furthermore, a higher potential is required for the oxidation in perchlorate solution. Similar results were obtained also for the complexes B and C. Data concerning the redox potential, stability, u.v.–visible, and e.s.r. spectra of the three oxidation products are summarised in the Table. Figure 2 shows the u.v.–

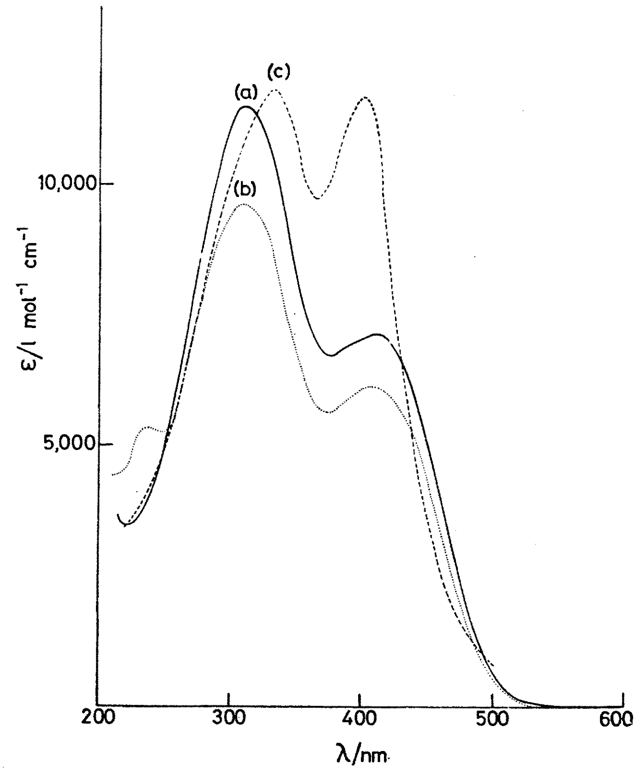


FIGURE 2. Electronic absorption spectrum of the oxidation product of complex A measured by a Cary 17 spectrophotometer. (a) Immediately after preparation in aqueous $0{\cdot}5$ M Na_2SO_4 solution at pH 1·6. (b) 3·5 months after preparation, solution as in (a). (c) In acetonitrile, from ref. 1a.

visible absorption spectrum of the Ni^{III} complex A obtained in aqueous sulphate solution, and, for comparison, that in acetonitrile. The oxidation products do not absorb at 550 nm, even when the pH is raised or when *in situ* spectroelectrochemical observations at pH 10 are performed. Thus the spectrum of the oxidized product differs from that of the unstable intermediate obtained by dissolving solid $Ni^{III}L(ClO_4)_3$[2] or by oxidizing $Ni^{II}L^{2+}$ by hydroxyl free radicals.[4] The e.s.r. results are summarized in the Table and Figure 3. At room temperature in acidic (pH $\leqslant 4$) sulphate solution all three compounds showed a single e.s.r. peak at g *ca.* 2·16 with a width of *ca.* 30 G.

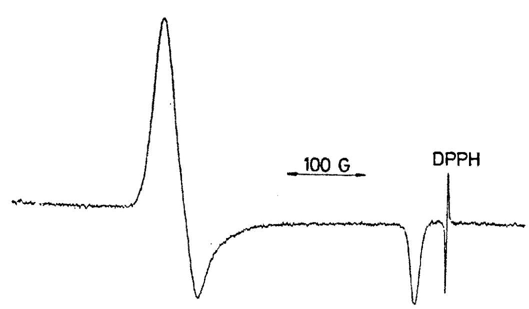


FIGURE 3. X-Band e.s.r. spectrum of a frozen solution (liquid air temperature) of the oxidation product ($0{\cdot}5 \times 10^{-3}$ M) of complex A measured by an X-band Varian E-12 e.s.r. spectrometer. DPPH = diphenylpicrylhydrazyl.

Table. Characterization of the electrochemically oxidized products (in aqueous 0·5 M Na_2SO_4 solutions at pH 1·6)

Complex	Redox potential[a] /mV	Half-life	E.s.r. spectrum: Solution g	Line-width[b]	Frozen sample $g_{\parallel}$	$g_{\perp}$	Electronic spectrum λ/nm (ε/l mol⁻¹ cm⁻¹)	Solution colour
A	640	> year	2·172	32	2·028	2·238	410 (7 × 10^3) 310 (11 × 10^3)	Olive green
B	490	*ca.* 5 days	2·163	27	2·026	2·232	370 sh (6 × 10^3) 295 (11 × 10^3)	Bright green
C	930	*ca.* 1 day	2·166	30	2·021	2·232	320 (12 × 10^3) 262 (7 × 10^3)	Light green

[a] *vs.* Ag–AgCl. [b] Peak to peak separation of the derivative spectrum (Gauss).

In frozen solution, (liquid air temperature) the spectra were typical of an axially symmetric g-tensor with $g_{\parallel} = 2{\cdot}03$ and $g_{\perp} = 2{\cdot}23$. These results are characteristic of Ni^{III} tetragonal complexes of the tetra-aza macrocyclic ligands with the unpaired electron in the d_{z^2} orbital, thus providing direct and unequivocal evidence of the oxidation state of the electrochemically generated products.

The Ni^{III} complexes of ligands (I) and (II) are the first Ni^{III} complexes with fully saturated ligands which are stable in mild, acidic, aqueous solutions.[7] The complexes are identified as $Ni^{III}LSO_4^+$ owing to the role of SO_4^{2-} in stabilizing the Ni^{III} complexes. Furthermore in an independent pulse radiolytic study[8] it was shown that $Ni^{III}L^{3+}$ (for complex A) reacts with SO_4^{2-} according to equation (1). The $Ni^{III}LSO_4^+$ complex thus formed has

$$Ni^{III}L^{3+} + SO_4^{2-} \rightleftharpoons Ni^{III}LSO_4^+ \qquad (1)$$

identical properties to that formed electrochemically.

$Ni^{III}LSO_4^+$, for L = (I), oxidizes quantitatively I^- to I_3^-, Fe^{2+}_{aq} to Fe^{3+}_{aq} and decomposes hydrogen peroxide. The above results, in conjunction with the redox potentials reported in the Table, prove that these easily accessible tervalent nickel complexes can be used as powerful, single-electron oxidizing agents under conditions where few oxidants are available.[9]

Furthermore preliminary studies indicate that phosphate ions also stabilize the $Ni^{III}L^{3+}$ complexes. Thus it seems that stabilization of $Ni^{III}L^{3+}$ complexes can be achieved by the inclusion of an anion, at its highest oxidation state, in the inner sphere of the complex.

We thank Prof. D. H. Busch of the Ohio State University for a sample of Ni^{II} complex A, for comparison, and the Alberto and Kathleen Casali Fellowship Foundation Association for partial support.

(*Received*, 13*th July* 1978; *Com.* 750.)

[1] (a) D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, 1969, **8**, 1611; (b) F. V. Lovecchio, E. S. Gore, and D. H. Busch, *J. Amer. Chem. Soc.*, 1974, **96**, 3109; A. Desideri and J. B. Raynor, *J.C.S. Dalton*, 1977, 2051.
[2] E. K. Barefield and M. T. Mocella, *J. Amer. Chem. Soc.*, 1975, **97**, 4238.
[3] N. P. Curtis and D. F. Cook, *Chem. Comm.*, 1967, 962; E. S. Gore and D. H. Busch, *Inorg. Chem.*, 1973, **12**, 1.
[4] G. Ferraudi and L. Patterson, *J.C.S. Chem. Comm.*, 1977, 755.
[5] M. Jaacobi, D. Meyerstein, and J. Lillie, *Inorg. Chem.*, in the press.
[6] L. G. Warner and D. H. Busch, *J. Amer. Chem. Soc.*, 1969, **91**, 4092; B. Bosnich, M. L. Tobe, and G. A. Webb, *Inorg. Chem.*, 1965, **4**, 1109.
[7] F. P. Bossu and D. W. Margerum, *Inorg. Chem.*, 1977, **16**, 1210; C. F. Wells and D. Fox, *J.C.S. Dalton*, 1977, 1498, 1502.
[8] H. Cohen, L. J. Kirschenbaum, E. Zeigerson, M. Jaacobi, E. Fuchs, G. Ginzburg, and D. Meyerstein, to be published.
[9] G. Charlot, A. Callumeaw, and M. J. C. Marchon, 'Selected Constants, Oxidation Reduction Potentials of Inorganic Substances in Aqueous Solutions,' Butterworths, London, 1971.