Formation and Decomposition Study of Electrochemically-generated Nickel(III)–nota Complexes in Aqueous Solution (nota^{3-} = 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetate)

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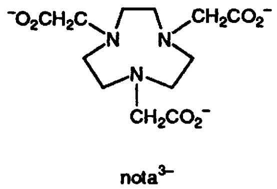
Electrochemical oxidation of the nickel(II) complex of the macrocyclic ligand 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetate (nota^{3-}) in aqueous solution yields the nickel(III) complex, which undergoes fast base-promoted chemical decomposition. This decomposition process was studied by cyclic voltammetry, ESR and electronic spectroscopy, and gave first-order kinetics relative to the nickel(III) complex. This is compatible with intramolecular reduction of the metal centre by the ligand, followed by rapid decomposition of the radical species formed. The ligand fragmentation process was analysed by proton NMR spectroscopy of the electrolysed solution of the complex.

The chemistry of metal complexes in less common oxidation states has been the subject of increasing interest in inorganic chemistry, due to the important role that these compounds play in catalytic and biological processes. Specifically, nickel-(I) and -(III) complexes have received considerable attention since it was recognized that nickel in those oxidations states participates in the catalytic cycles of several enzymes.[1]

Previous work from our laboratory focused on factors that control the availability of nickel-(I) and -(III) oxidation states with pseudo-macrocyclic Schiff-base ligands.[2] Polyazacycloalkanes are part of another family of ligands that allow the formation of several metal complexes in various oxidation states, whose stability may be varied over a substantial range through structural modifications of the macrocyclic framework.[3,4b] In particular triazamacrocycles and *N*-functionalized derivatives have been extensively investigated,[3,5] leading to the isolation of rather stable trivalent nickel complexes.[5–7] The stabilization of Ni^{III} is attributed to the full octahedral coordination with a minimum steric demand afforded by these ligands.[6b,8] One of these stable nickel(III) complexes was obtained after chemical oxidation of the nickel(II) complex of 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetate (nota^{3-}).[7] The isolated [Ni^{III}(nota)] reveals a crystal structure with a six-coordinate centre around nickel, resulting from a distorted octahedral geometry generated by a N_3O_3 donor set.

Just before the isolation of this complex, the electrochemical behaviour of Na[Ni^{II}(nota)] in aqueous 0.05 mol dm^{-3} KCl was studied by Wieghardt *et al.*,[9] showing a reversible one-electron transfer process, that was attributed to the oxidation of Ni^{II} to Ni^{III}. Formation of [Ni^{III}(nota)] in 0.05 mol dm^{-3} KCl aqueous solution by oxidation of the corresponding nickel(II) complex by pulse-radiolytic techniques was reported and it was claimed that these species are stable in deaerated solution for at least 24 h at 25 °C.[9] However, since then, no further characterization of this new species formed in solution has been performed.

More recently Fabbrizzi *et al.*[8b] have shown in their electrochemical studies, with Na[Ni^{II}(nota)], that the ligand (with an electric charge of 3−) favours access to this unusually high oxidation state due to a very favourable entropy term, that reflects a substantial increase of translational entropy associated with the release of water molecules from the hydration sphere of the complex during the [Ni^{II}(nota)]$^{-}$–[Ni^{III}(nota)] oxidation process. This fact was employed to explain the surprisingly low oxidation potential obtained in the present system, as compared with other ligands with similar or higher ligand-field intensities.[8b]



nota^{3-}

The above considerations prompted us to investigate the reactivity in aqueous solution of the nickel(III) complex with the nota^{3-} ligand, which was characterized by cyclic voltammetry together with electronic, ESR and NMR spectroscopies.

Experimental

Synthesis.—The ligand 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetate (nota^{3-}) and the corresponding nickel(II) complex were prepared according to procedures described in the literature.[8,9] Controlled-potential electrolysis of [Ni^{II}(nota)]$^{-}$ (5×10^{-3} mol dm^{-3}, 0.1 mol dm^{-3} $NaClO_4$) was carried out at 0 °C under nitrogen, using platinum foil as working and counter electrodes, and a Ag–AgCl (1 mol dm^{-3} NaCl) reference electrode.

Physical Measurements.—Cyclic voltammetry experiments were performed at 25 °C with a potentiostat/galvanostat PAR 273A using a three-electrode cell with platinum as working and counter electrodes and a Ag–AgCl (1 mol dm^{-3} NaCl) reference electrode; the supporting electrolyte was 0.1 mol dm^{-3} $NaClO_4$ (**CAUTION**: perchlorates are hazardous and may explode).

The ESR spectra were obtained with a Varian E-109 X-band spectrometer (9 GHz) equipped with a variable-temperature accessory and were recorded at 273 and 77 K. The spectra were calibrated with diphenylpicrylhydrazyl (dpph) and the magnetic field was calibrated using Mn^{2+} in MgO. Concentrations of the electrochemically generated nickel(III) complex were monitored by quantitative ESR spectroscopy: The Ni^{III} concentrations were evaluated by double integration, including baseline and Aasa and Vanngard corrections,[10] using aqueous copper(II) nitrate solutions as concentration standards.

Proton NMR spectra were obtained with a Varian Unity 500 spectrometer operating at 499.92 MHz. Probe temperature was accurate to ± 0.5 °C. Proton shifts were referenced to $SiMe_4$.

Electronic spectra were recorded at 273 K with a Shimadzu UV-3101PC spectrophotometer. Decomposition reactions of the electrochemically generated nickel(III) complex in acidic solutions (pH $\leqslant$ 2) were monitored by electronic spectroscopy at λ = 315 nm and 273 K.

Results and Discussion

Electrochemical Studies.—Oxidation of Na[Ni^{II}(nota)] was studied by cyclic voltammetry in aqueous solutions. Cyclic voltammograms (Fig. 1) are identical to those previously reported[8b,9] and exhibit, in the pH range 1–10, one anodic and the corresponding cathodic wave with $E_{\frac{1}{2}}$ = + 940 mV (*vs.* Ag–AgCl); however in more strongly alkaline solutions the cathodic peak can no longer be observed, thus indicating that an irreversible process has taken place.

The results obtained at several pH values and at a scan rate of 50 mV s^{-1} are summarized in Table 1. In acidic solutions (pH < 4) a process that resembles a reversible one-electron transfer reaction must be operative, since at 50 mV s^{-1} the anodic–cathodic peak separation lies between 70 and 80 mV and is practically independent of scan rate in the range used (500–20 mV s^{-1}). Additional support for electrochemical reversibility can be gained by noting (*a*) the linear dependence between i_p and $v^{\frac{1}{2}}$ (5 points; with *R* ranging from 0.999 to 0.997), and (*b*) that the ratio i_{pc}/i_{pa} is equal to unity and is independent of scan rate.[11]

At pH higher than 4, a different behaviour is observed and the claim for chemical and electrochemical reversibility cannot easily be supported, despite the linear dependence between i_p and $v^{\frac{1}{2}}$ (5 points; with *R* ranging from 0.999 to 0.995), as: (*a*) ΔE is scan-rate dependent and increases with pH, and (*b*) i_{pc}/i_{pa} only approaches unity for scan rates higher than 100 mV s^{-1}.[11] The observation that this latter ratio is smaller than unity can be taken to suggest that a fast chemical reaction must follow the electron-transfer process and that the oxidized species has reduction paths different from that associated with electron transfer involving the nickel centre.

Electrolysis of [Ni^{II}(nota)]$^-$.—In aqueous solution electrolysis performed at + 1000 mV (*vs.* Ag–AgCl) produces a change in solution colour from violet to yellow-brown implying the formation of new species in solution. The ESR spectra of these latter solutions recorded at 273 K show a single signal centred at g = 2.10, indicative of a metal-centred oxidation process. The electrolysed acidic aqueous solutions become ESR silent in about 3 min at room temperature and in about 15 min at 273 K. An increase in pH produces a faster decay, especially at pH values higher than 6, thus implying faster decomposition rates of the oxidized species under more basic conditions.

When the pH of electrolysed acidic solutions is raised by addition of NaOH to a value higher than 10, the decomposition, even at 273 K, is practically immediate. These observations are surprising since our results are, apparently, in contrast with those reported in the literature,[7,9] where a stable nickel(III) species was claimed to be found with this ligand. However our results are similar to those previously found for decomposition of nickel(III) tetra- and tri-aza macrocyclic complexes.[12] These latter complexes usually show a remarkable stability in acetonitrile and in strongly acidic solutions, but decompose rapidly in the presence of basic solvents.[4]

We also found that during exhaustive electrolysis the concentration of the nickel(III) species reaches a maximum and then starts to decrease, thus implying the involvement of the nickel(III) complex in further reactions on the electrolysis timescale. The concentration of nickel(III) was monitored by quantitative ESR and the maximum concentration of nickel(III) centres in strongly acidic solution (pH 2) was obtained after 20–30 min of electrolysis and was *ca.* 15% of total nickel.

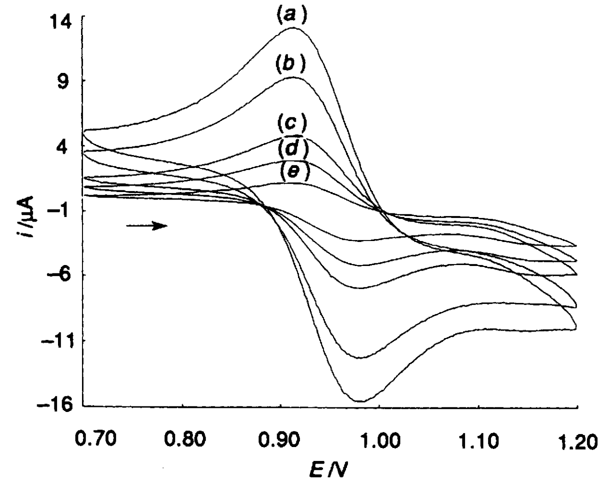


Fig. 1 Variable-scan rate voltammograms at 298 K of [Ni(nota)]$^-$ in aqueous solution (pH $\approx$ 2; 0.1 mol dm^{-3} $NaClO_4$); peak potentials *vs.* Ag–AgCl (1 mol dm^{-3} NaCl); scan rate (mV s^{-1}): (*a*) 500, (*b*) 250, (*c*) 100, (*d*) 50 and (*e*) 20

Table 1 Electrochemical data for Na[Ni(nota)] in aqueous solutions at different pH values and kinetic data for its decomposition in aqueous solution[a]

pH	E_{pa}	E_{pc}	ΔE	$E_{p1/2}$	i_{pc}/i_{pa}	k_{obs}/s^{-1}
1[b]	975	905	70	940	0.97	0.0040
2	974	896	78	935	0.98	0.0056
4	977	895	82	936	0.95	—
6[c]	986	890	96	938	0.91	—
8[c]	994	882	112	938	0.86	—
10[c]	999	880	119	940	0.70	—
12	1010	—	—	910[d]	—	—

[a] All potentials in mV and reported *versus* Ag–AgCl (1 mol dm^{-3} NaCl). Solute concentration $\approx 3 \times 10^{-3}$ mol dm^{-3}, 0.1 mol dm^{-3} $NaClO_4$; scan rate 50 mV s^{-1}; $\Delta E = E_{pa} - E_{pc}$; $E_{p1/2} = (E_{pa} + E_{pc})/2$; and E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. [b] In 0.1 mol dm^{-3} $HClO_4$. [c] The ratio was observed to change with scan rate, from 0.70 at 20 mV s^{-1} to 1.05 at 500 mV s^{-1}. [d] The value reported, $E_{\frac{1}{2}}^{ox}$, is the potential at half height.

After exhaustive oxidation of Na[Ni^{II}(nota)], the voltammetric waves corresponding to this species are no longer detected, indicating that decomposition leads to destruction of the initial complex. However these electrolysed solutions show: (*a*) new cyclic voltammetric waves for a process that resembles a reversible one-electron process with $E_{\frac{1}{2}}$ = + 1130 mV at 50 mV s^{-1} (*vs.* Ag–AgCl) and (*b*) electronic spectra having three bands similar to those of non-oxidized solutions, but with intensities and maxima different from those of the initial solution. These results suggest the formation of a new species during decomposition of [Ni^{III}(nota)].

Spectral Characterization of Nickel(III) *Species.*—Electronic spectra obtained after electrolysis (20 min) of aqueous solutions 5×10^{-3} mol dm^{-3} in Na[Ni^{II}(nota)] at pH 2 exhibit, in the range 1000–300 nm, bands at 620, 495 (sh), 415 (sh) and 315 nm, which are due to the nickel(III) complex formed upon oxidation (Fig. 2), as they are absent from the original non-oxidized solution; the spectra of similar solutions in the range pH 1–6 are practically indistinguishable from those at pH 2. Coupling quantitative ESR and spectroscopic data it was possible to estimate ε values for the bands at 620 and 315 nm which are $\approx$ 100 and $\approx$ 7000 dm^3 mol^{-1} cm^{-1}, respectively. The electronic spectra are similar to those observed for the low-spin nickel(III)

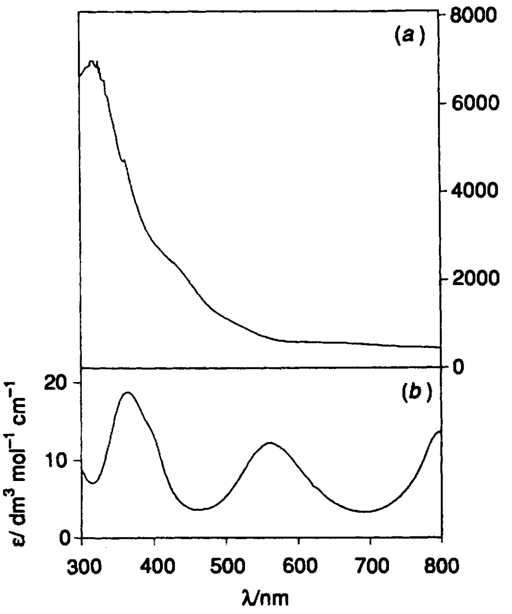


Fig. 2 Electronic spectra of (*a*) [Ni^{III}(nota)] and (*b*) [Ni^{II}(nota)]$^-$ in aqueous solutions at pH 2

complex [Ni([9]aneN_3)$_2$]$^{3+}$ ([9]aneN_3 = 1,4,7-triazacyclononane)[12c] for which two bands were observed in the same wavelength range, one at λ = 562 nm (ε = 42 dm^3 mol^{-1} cm^{-1}) and the other at λ = 310 (ε = 9800); the bands (shoulders) at 495 and 415 nm are probably masked in the latter complex by the very intense one at 310 nm.

Frozen-solution ESR spectra of electrolytically synthesized nickel complexes (Fig. 3) show *g* tensor anisotropy and are typical of low-spin d^7 ($S = \frac{1}{2}$) nickel(III) complexes, in a distorted octahedral environment.[6,8,13] The observed ESR spectrum shows a three-*g* pattern indicative of rhombic stereochemistry. The ESR parameters are interpreted and derived as usual[6,8,13] and for the present case the following values are obtained: g_1 = 2.154, g_2 = 2.099 and g_3 = 2.033. In the g_3 component coupling to one nitrogen atom (^{14}N, I = 1) is observed with a value of 1.8 mT, implying axial elongation[6,8] and suggesting that the unpaired electron lies in an orbital that is mainly d_{z^2} in character, which corresponds to a $^2A_1$ ground state for the metal centre. Low-spin d^7 nickel(III) complexes [Ni([9]aneN_3)$_2$] and [Ni([10]aneN_3)$_2$]$^{3+}$ ([10]aneN_3 = 1,4,7-triazacyclodecane) exhibit *g* values[6,8] similar to those obtained in the present work, indicating similar distortions from the ideal octahedral geometry in both cases.

The crystal structures of complexes of nota^{3-} with Ni^{II}, Ni^{III}, Cr^{III}, Co^{II} and Mn^{II} reveal six-co-ordinate centres, with three nitrogen and three oxygen atoms occupying facial positions, respectively, of a distorted octahedron.[7,9] However for the corresponding copper(II) and iron(III) complexes the X-ray data indicate a distorted-prismatic environment rather than octahedral, generated by the N_3O_3 donor set.[7,9] The ESR data obtained in aqueous solutions for the Ni^{III}(nota) complex provide evidence that the distorted octahedral geometry around nickel is maintained upon oxidation, which is thus favoured relative to the distorted prismatic stereochemistry.

Decomposition Studies.—Analysis of the electronic data for the nickel-(II) and -(III) species shows that the strong band at 315 nm is due to Ni^{III} and that no other species present in solution contribute significantly to absorption at this wavelength thus making it possible to follow the kinetic decomposition of nickel(III) complexes by monitoring spectrophotometrically the absorbance at this wavelength. However, as the pH decreases slightly during decomposition, reasonable kinetic data can only be obtained if the concentration of H^+ is held constant. No buffer solution was used in order to avoid introducing further pathways in the decomposition mechanism, and consequently a large excess of H^+ or OH^- was needed to keep the pH constant; we have thus only obtained kinetic data for strongly acidic solutions (pH < 2). At these pH values decomposition of electrochemically generated [Ni^{III}(nota)] follows a first-order dependence on concentration of Ni^{III} (Fig. 4) and the calculated rate constants k_{obs} are presented in Table 1; the values were obtained using data recorded during at least four half-lives of nickel(III) species (400 data points). The values now reported present further experimental support to the belief that decomposition rates increase with pH, as raising the pH from 1 to 2 produces a *ca.* 40% increase in the decomposition rate constant.

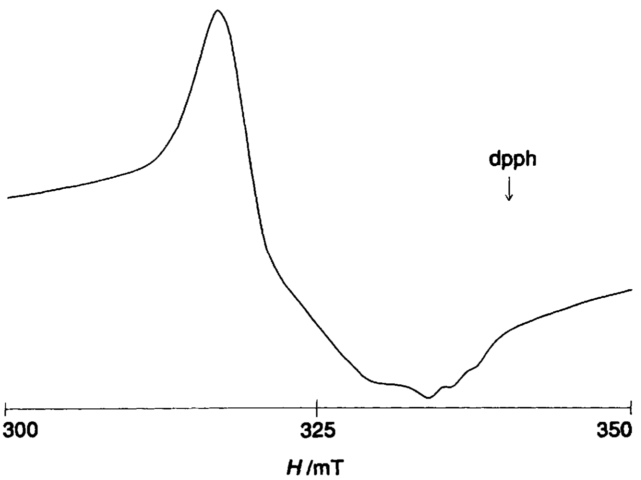


Fig. 3 Frozen-aqueous solution X-band ESR spectrum at 77 K of electrochemically oxidized solution of Na[Ni(nota)]

For nickel(III) complexes with tetra-,[12a] tri-aza[12c] and porphyrinic[14] macrocyclic ligands and with Schiff-base pseudomacrocyclic ligands,[15] the first path in their decomposition mechanism was claimed to be a reduction at the metal centre as result of a intramolecular electron-transfer mechanism from the ligand, thus leading to formation of radical species. These radicals are involved in further reactions and the final products are largely dependent on the equatorial ligands and on the solvent. However, where decomposition rates follow a first-order dependence on the nickel(III) complex, formation of radical species is believed to be the rate-limiting step, followed by rapid formation of decomposition products resulting from ligand fragmentation in accordance with the following scheme [equations (1) and (2)].[12,14,15]

$$[Ni^{III}L] \longrightarrow [Ni^{II}L^{\bullet}] \qquad (1)$$

$$[Ni^{II}L^{\bullet}] \longrightarrow \text{products} \qquad (2)$$

Our results seem to be in accordance with this general mechanism, as (*a*) the monomolecular path observed for decomposition of our complex in acidic aqueous solution suggests a decay of the probable radical species formed without further reaction with the Ni^{II}– or Ni^{III}–nota^{3-} complexes present in solution, and (*b*) the detected proton NMR spectra of the new species formed during decomposition can only be interpreted in terms of fragmentation of nota^{3-}.

We tried to characterize the ligand decomposition products by comparing the proton NMR spectra of the initial [Ni^{II}(nota)]$^-$ solution with that of the same solution 5 h after electrolysis at 293 K and pH 2. The proton spectrum of [Ni^{II}(nota)]$^-$ [Fig. 5(*a*)] shows four signals, spread over a very wide chemical shift range (δ +31, +17, +12 and −80). These (mainly) contact and pseudocontact shifted resonances of the nota ligand are typical of a distorted-octahedral paramagnetic (S = 1) nickel(II) complex.[9,16] However, the proton spectrum

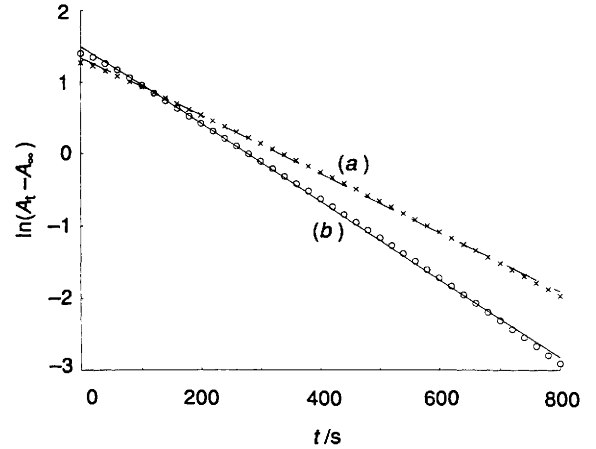


Fig. 4 First-order plots for decomposition of [Ni^{III}(nota)] at pH 1 (*a*) and 2 (*b*); 273 K, absorbances obtained at λ = 315 nm

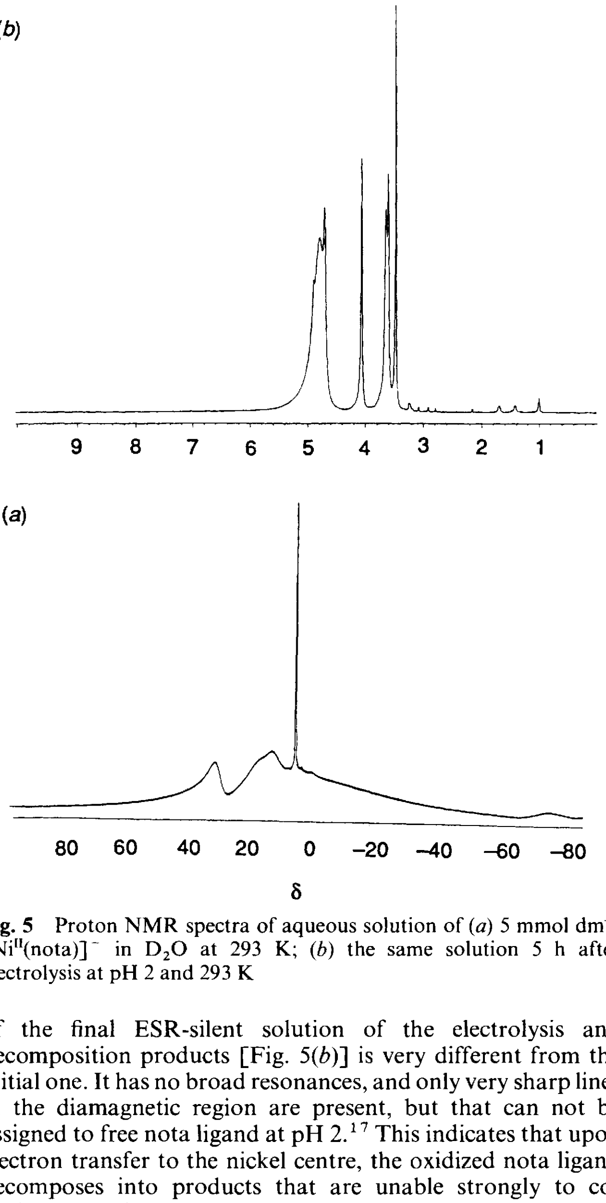


Fig. 5 Proton NMR spectra of aqueous solution of (*a*) 5 mmol dm^{-3} [Ni^{II}(nota)]$^-$ in D_2O at 293 K; (*b*) the same solution 5 h after electrolysis at pH 2 and 293 K

of the final ESR-silent solution of the electrolysis and decomposition products [Fig. 5(*b*)] is very different from the initial one. It has no broad resonances, and only very sharp lines in the diamagnetic region are present, but that can not be assigned to free nota ligand at pH 2.[17] This indicates that upon electron transfer to the nickel centre, the oxidized nota ligand decomposes into products that are unable strongly to co-ordinate the nickel(II) cation, a situation that can be contrasted to what happens with N_2O_2 Schiff-base ligands for which the ligand structure is preserved.[15] This implies that nota decomposition can originate several fragments of low denticity thus implying ring opening, probably by nucleophilic attack on a methylene ring carbon by OH^-/H_2O.[12]

Conclusion

The main conclusion resulting from this study relates to the fast decomposition of the [Ni^{III}(nota)] complex generated by electrochemical oxidation, a result that must be contrasted with those of ref. 5 where lifetimes higher than 24 h for this complex have been reported. A half-life of 173 s was observed in the present study for [Ni^{III}(nota)] in strong acidic aqueous solutions (pH 1), and much faster decomposition rates took place at higher pH values: in all cases the decomposition mechanism seems to involve ring opening and fragmentation.

Acknowledgements

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References

1 *The Bioinorganic Chemistry of Nickel*, ed. J. R. Lancaster, VCH, New York, 1988.
2 B. de Castro and C. Freire, *Inorg. Chem.*, 1990, **29**, 5113; M. Carrondo, B. de Castro, A. Coelho, D. Domingues, C. Freire and J. Morais, *Inorg. Chim. Acta*, 1993, **205**, 157.
3 P. Bernhardt and G. Lawrence, *Coord. Chem. Rev.*, 1990, **104**, 297.
4 (*a*) D. Busch, *Acc. Chem. Res.*, 1978, **11**, 392; (*b*) F. Lovecchio, E. Gore and D. Busch, *J. Am. Chem. Soc.*, 1974, **96**, 3109; (*c*) D. Pillsbury and D. Busch, *Inorg. Chem.*, 1980, **19**, 3148.
5 K. Wieghardt, W. Wolfgang, B. Nuber, J. Weiss, A. Ozarowski, H. Stratemeier and D. Reinen, *Inorg. Chem.*, 1986, **25**, 1650; K. Wieghardt, W. Schmidt, W. Herrmann and H. Kuppers, *Inorg. Chem.*, 1983, **22**, 2953; K. Wieghardt, E. Schoffmann, B. Nuber and J. Weiss, *Inorg. Chem.*, 1986, **25**, 4877.
6 (*a*) A. McAuley and S. Chandrasekhar, *Inorg. Chem.*, 1992, **31**, 480; (*b*) A. McAuley and S. Chandrasekhar, *Inorg. Chem.*, 1992, **31**, 2234; (*c*) A. McAuley and C. Xu, *Inorg. Chem.*, 1988, **27**, 1204.
7 M. van der Merwe, J. Boyens and R. Hancock, *Inorg. Chem.*, 1983, **22**, 3489.
8 (*a*) A. Buttafava, L. Fabbrizzi, A. Perotti, A. Poggi, G. Poli and B. Seghi, *Inorg. Chem.*, 1986, **25**, 1456; (*b*) L. Fabbrizzi, M. Mariani, B. Seghi and F. Zanchi, *Inorg. Chem.*, 1989, **28**, 3362.
9 K. Wieghardt, U. Bossek, P. Chaudhuri, W. Herrmann, B. Menke and J. Weiss, *Inorg. Chem.*, 1982, **21**, 4308.
10 V. Aasa and T. Vanngard, *J. Magn. Reson.*, 1975, **19**, 308.
11 A. Bard and L. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, Wiley, New York, 1980.
12 (*a*) N. Jubran, D. Meyerstein, J. Koresh and H. Cohen, *J. Chem. Soc., Dalton Trans.*, 1986, 2509; (*b*) E. Zeigerson, I. Bar, J. Bernstein, L. Kirschenbaum and D. Meyerstein, *Inorg. Chem.*, 1982, **21**, 73; (*c*) M. Jaacobi, D. Meyerstein and J. Lilie, *Inorg. Chem.*, 1979, **18**, 429; (*d*) B. Sonnberger, P. Huhn, A. Waberburger and F. Wasgestian, *Inorg. Chim. Acta*, 1992, **196**, 65.
13 A. Chakravorty, S. Bhattacharya and R. Mukherjee, *Inorg. Chem.*, 1986, **25**, 3448.
14 K. M. Kadish, *Prog. Inorg. Chem.*, 1986, **34**, 435; K. M. Kadish, M. Franzen, B. C. Han, C. Araulo-McAdams and D. Sazou, *J. Am. Chem. Soc.*, 1991, **113**, 512; A. M. Stolzenberg and M. T. Stershic, *J. Am. Chem. Soc.*, 1988, **110**, 6391; *Inorg. Chem.*, 1988, **27**, 1614.
15 B. de Castro, C. Freire and E. Pereira, *J. Chem. Soc., Dalton Trans.*, 1994, 571 and refs. therein.
16 I. Bertini and C. Luchinat, *NMR of Paramagnetic Molecules in Biological Systems*, Benjamin-Cummings, Menlo Park, 1986.
17 C. F. G. C. Geraldes, A. D. Sherry, M. P. M. Marques, M. C. Alpoim and S. Cortes, *J. Chem. Soc., Perkin Trans. 2*, 1991, 137.

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