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Abstract
Three nickel(II) pentaazamacrocycles bearing pendant alkyl tails have been synthesized, and the crystal structure of one (bearing an octyl tail) is reported. The redox potentials of the complexes, for oxidation of the nickel(II) centre, is 0.72 V (versus S.H.E.) in all cases, indicating that the pendant alkyl tails have no effect on the redox site. The kinetics of oxidation of the complexes by peroxodisulfate, S2O82- and by aqua(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-1-acetato)nickel(III), [Ni(hmca)(OH2)]2+ have been studied. Oxidation by S2O82- occurs by ion-pairing of the reactants, followed by electron transfer with concomitant peroxo bond fissure. Oxidation by [Ni(hmca)(OH2)]2+ occurs by an outer sphere electron transfer process. Redox kinetics at the nickel centre provides a probe for supramolecular interactions at the pendant tails in such complexes.

Abbreviations: hmca = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-1-acetato tacn = 1,4,7-triazacyclononane

Introduction
There is a rich chemistry centred on the reactivity of macrocycles [1], with a variety of donor atoms that complex to metal ions. In recent years there has been a great deal of interest in the functionalization of macrocycles, producing pendant-arm complexes [2]. The synthesis and chemistry of polyazamacrocycles bearing pendant arms has been reviewed [3]. Pendant-arm macrocyclic complexes as biological models has also been reviewed [4]. Azamacrocycles having one alkyl pendant-arm can be incorporated into liquid membranes [5]. Catalytic activity in solution can be greatly affected by the ability of a reagent to aggregate in solution, forming structured assemblies such as micelles, vesicles and lipid bilayers. This ability is dependent on the reagent having certain structural and electronic characteristics, such as a charged hydrophilic “headgroup” and a long hydrophobic “tail” [6]. Hexaazamacrocycles containing six attached long aliphatic tails have been prepared, and have been shown to form a tubular mesophase (liquid crystal) by stacking the macrocyclic units [7]. Amphiphilic ferrocene-containing micelles have been shown to be disrupted by oxidation to the Fe(III) state, but re-micellize on reduction back to Fe(II) [8]. More recently, there has been a significant interest aroused in the ability of amphiphilic complexes to exhibit liquid crystal behaviour [9]. While many of the systems were of penta- or octahedral coordination, improved liquid crystal behaviour is found for systems with square planar geometry, since structural anisotropy of the ligand is not compromised.

Polyazamacrocycles have been long known to stabilize unusual oxidation states in transition metals [10] and much work has been published on electron transfer kinetics, particularly for the nickel(II/III) system [11]. In spite of the interest in the redox kinetics of transition metal macrocycles, there have to date been no kinetic studies of redox reactions involving amphiphilic macrocyclic complexes. In this work we have synthesized several nickel(II) pentaazamacrocycles bearing pendant alkyl “tails” ([NiL4]2+, [NiL8]2+ and [NiL12]2+, where the superscripts refer to the length of the carbon chain in the alkyl “tails” and in one case we have characterized the complex crystallographically. We have examined their oxidation kinetics by the peroxodisulfate anion and by the octahedral cationic nickel(III) complex of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-1-acetic acid, [Ni(hmca)(OH2)]2+ (where the pendant acetic acid is deprotonated and coordinated to the nickel(III) centre). The mechanisms of these oxidations are discussed, and the potential for such redox centres to be used as probes for supramolecular interactions is suggested.

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Experimental

Materials

Potassium peroxodisulfate (BDH) was recrystallized twice from cold distilled water prior to use. The [Ni(hmca)(OH$_2$)](ClO$_4$)$_2$ complex was prepared as reported previously [12]. The nickel(III) form was prepared in situ by oxidation with a stoichiometric deficiency of Co(III)(aq). Stock solutions of the latter were prepared by electrochemical oxidation of cobalt(II) perchlorate solutions in perchloric acid. Cobalt(III) solutions were analysed by titration (for perchloric acid concentration) and by UV/visible spectrophotometry (for Co(III), molar absorptivity = 35.3 dm$^3$ mol$^{-1}$ cm$^{-1}$) [13]. All other reagents and solvents were of Analar grade and were used as received. All solutions were prepared using distilled, deionized water.

Synthesis of the [NiL$^{4,8,12}$](ClO$_4$)$_2$ complexes

The general “padlock” method of Suh and Kang was followed, where a template condensation of a polyamine and a primary amine with formaldehyde was carried out in the presence of nickel(II) [14]. Stoichiometric amounts of nickel(II) chloride hexahydrate (1 equivalent), 1,4,8,11-tetraazadecane (1 equivalent) and the appropriate alkyl amine (carbon chain 4 to 12) (1 equivalent) in methanol solvent were refluxed with aqueous formaldehyde (2 equivalents) for 24 h. Addition of excess perchloric acid to the individual cooled, filtered reaction mixtures resulted in precipitation of the yellow products, which were filtered, washed thoroughly with methanol, diethyl ether and air-dried. The complexes were characterized by elemental analysis, infrared spectroscopy, and for the octyl-complex, [NiL$^8$(ClO$_4$)$_2$], by X-ray crystallography. Analytical data are reported in Table 1.

Caution! Compounds containing perchlorate anions must be regarded as potentially explosive and should be handled with caution.

Crystallography

X-ray quality crystals were obtained by the diffusion method using acetonitrile/diethyl ether. The X-ray structure determination was performed on a Mercury CCD area detector coupled with a Rigaku AFC8 diffractometer, using graphite monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å). The orange plate crystal was mounted on a glass fibre. Full tabulations of atomic coordinates; all bond lengths and angles (with anisotropic displacement parameters); hydrogen coordinates (with isotropic displacement parameters); and observed and calculated structure factors have been deposited as supplementary material.

Electrospray mass spectrometry

The mass spectrometry measurements were obtained on a VG quadrupole mass spectrometer with an atmospheric pressure electrospray source. Samples, in distilled water, were introduced into the source at a flow rate of 5 mL min$^{-1}$.

Cyclic voltammetry

Cyclic voltammograms were measured using a Princeton Applied Research model 482 fast-scanning electrochemical apparatus, in aqueous 0.10 M trifluoromethanesulphonic acid, under an argon atmosphere. A 1 mm diameter Pt disk working electrode, a platinum wire counter electrode and a Ag/AgCl (sat. KCl) reference electrode were used.

Kinetics

All kinetic experiments were carried out in aqueous media, using deionized, doubly-distilled water. For the oxidations involving the nickel(III) macrocycle [Ni(hmca)(OH$_2$)]$^{2+}$ as oxidant, kinetic measurements were made using a Hi Tech SF61-DX2 stopped flow spectrometer, thermostatted to ±0.1 °C with a Lauda model RM6 refrigerated recirculating water bath. Pseudo-first-order conditions were maintained, using an excess of the appropriate nickel(II) amphilphile macrocycle. A constant ionic strength of 0.100 M (NaClO$_4$/HClO$_4$) was maintained for all experiments. Perchlorate was used as an inert, non-coordinating ion. The ionic strength was limited since the perchlorate salts of