Inorganica Chimica Acta, 36 (1979) L391–L393
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Nickel(III) Complexes with Cyclic and Non-cyclic Tetramines

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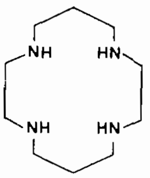
Received May 4, 1979

It is a feature of tetra-aza macrocycles, such as *1*, *2* and *3*, to favour the oxidation of the encircled metal ion to unusually high states.



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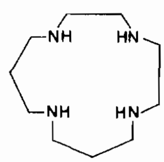

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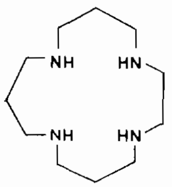

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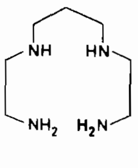

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A well known example is that of nickel(II), which is easily oxidized to +3 state both chemically (by using NO$^+$ [1], S$_2$O$_8^{2-}$ [2], HNO$_3$ [2]) and electrochemically (at the platinum electrode, in acetonitrile) [3–5]. The authenticity of the Ni(III) state has been proved through ESR experiments, as the spectra are consistent with those of a d^7, low-spin, chromophore in an octahedral environment (NiL(CH$_3$CN)$_2^{3+}$) [5].

Some authors [3] have claimed that a closed ligand framework is the required condition to obtain unusually high oxidation states, such as Ni(III), which are therefore inaccessible in presence of the open-chain analogues of macrocycles, such as *4*.

This conclusion implies meaningful consequences from a bioinorganic point of view: in fact, many physiologically important 3d metal ions, whose activity is strictly connected with a +2 to +3 easily reversible change, are merged in highly specific closed environments (porphyrins, corrins) and operate in a cyclic rather than in a non-cyclic coordinative framework.

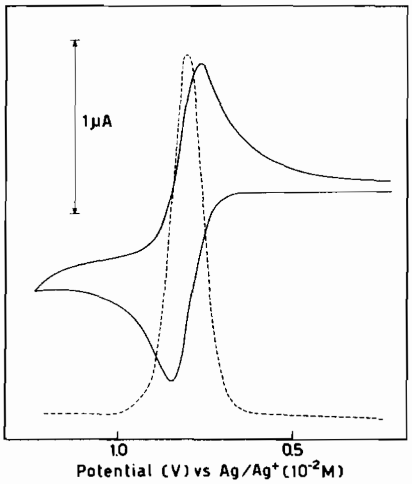

Fig. 1. Voltammograms at the platinum electrode of a 10^{-3} *M* solution of Ni(2.3.2-tet)(ClO$_4$)$_2$ 0.1 *M* Bu$_4$NClO$_4$, at 25 °C: (———) CV, 50 mV s^{-1}; (------) AC, 2 mV s^{-1}.

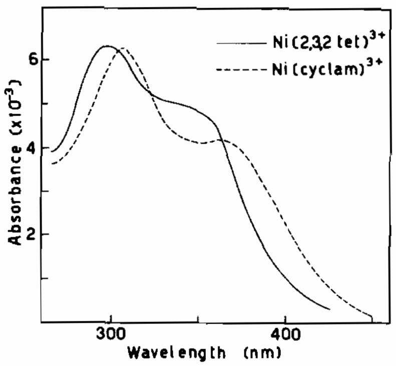

Fig. 2. UV spectra of solutions (CH$_3$CN, 0.1 *M* Et$_4$NBF$_4$) of Ni(2.3.2.-tet)$^{3+}$ and Ni(cyclam)$^{3+}$ anodically generated in controlled potential electrolysis experiment, at the platinum gauze.

In the course of systematic studies of the redox properties of nickel(II) complexes with poly-aza ligands, we have found that the complexes with the open-chain tetramine 2.3.2-tet (*4*) undergo a reversible one-electron oxidation at the platinum electrode in acetonitrile. The simplicity and reversible nature of the oxidation process is confirmed by the usual electrochemical tests: i) the ratio of the anodic and cathodic peak currents in CV voltammograms (Fig. 1) is unity and i_P is proportional to the square root of the potential scan speed; ii) the response of the AC experiment is a symmetric peak and the width of the half-peak is 90 mV; iii) current/potential curves obtained with non-stationary electrodes (rotating or vibrating wires) are typically S-shaped, the ($E_{3/4} - E_{1/4}$) difference being 60 mV. The stoichiometry of the electron transfer has been coulometrically confirmed. Furthermore, exhaustive electrolysis at the fixed oxidation potential produced a solution of an intense green colour, which is typical for Ni(macrocycle)(CH$_3$CN)$_2^{3+}$ complexes. The UV spectrum is

TABLE I. Oxidation Potentials of Nickel(II) Tetramine Complexes in Acetonitrile 0.1 *M* Bu_4NClO_4, at 25 °C.[a]

Complex	Mixture	High-spin	Low-spin
$Ni(cyclam)^{2+}$	0.702^b	0.71^c	0.68^c
$Ni(2.3.2\text{-}tet)^{2+}$	0.793^d	0.80^e	0.72^e

[a] E(V) *vs.* $Ag/AgNO_3$, 0.01 *M*; 0.1 *M* Bu_4NClO_4; measured at the platinum electrode, ±0.005 V; ±0.01 for potentials corrected to high- and low-spin species. [b] 78% high-spin; 22% low-spin. [c] Calculated through ΔG^0 (high-spin = low-spin) = 0.66 kcal mol^{-1} (see ref. 7). [d] 95% high-spin; 5% low-spin. [e] Calculated through ΔG^0 (high-spin = low-spin) = 1.74 kcal mol^{-1}.

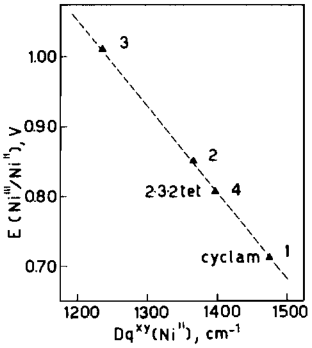

Fig. 3. Correlation of the electrode potential of the Ni(III)/Ni(II) couple with the $Dq^{xy}(Ni^{II})$ for high-spin tetramine complexes. Dq^{xy} values, obtained from chloride complexes, at 77 K, are taken from references 10, 11 (*1* and *3*), 7(*2*) and 11(*4*).

that expected for a $Ni(tetramine)(CH_3CN)_2^{3+}$ chromophore [3] and is analogous to that of $Ni(cyclam)(CH_3CN)_2^{3+}$ (see Fig. 2; cyclam = *1*); $Ni(2.3.2\text{-}tet)^{3+}$ lasts for several hours in anhydrous acetonitrile, but quickly decomposes when exposed to moisture, a behavior generally observed for $Ni(macrocycle)^{3+}$ complexes [6].

The oxidation of $Ni(2.3.2\text{-}tet)^{2+}$ occurs at a potential 100 mV higher than that observed for $Ni(cyclam)^{2+}$, the latter being the complex with tetra-aza macrocycles which is most easily oxidized [5, 7]. However, the comparison is not strictly correct as the above complexes exist in acetonitrile solution as a mixture of two species in equilibrium: a high-spin, octahedral $NiL(CH_3CN)_2^{2+}$ species and a low-spin, square NiL^{2+} species. The distributions vary with the ligand (2.3.2-tet: low-spin, 5%; high-spin, 95%; cyclam: low-spin, 22%; high-spin, 78%). From the appropriate combination of ΔG^0 value for the high-spin/low-spin equilibrium and the measured potential (which refers to the mixture), the oxidation potentials for each species of different spin multiplicity are calculated (see Table I).

Both high- and low-spin complexes of cyclam are oxidized more easily (at less positive potentials) than the corresponding complexes with 2.3.2-tet; this energy gain, which is greater in the case of high-spin species (9 kJ mol^{-1}; 4 kJ mol^{-1} for the low-spin complexes), could be defined as a novel *macrocyclic effect*, in analogy with kinetic and thermodynamic properties of tetra-aza macrocyclic complexes (extreme inertness [8] and high solution stability [9] with respect to complexes with open-chain homologues).

From a qualitative point of view, the magnitude of the oxidation potential can be related to the energy of the metal orbital from which the electron is abstracted. For the complexes under consideration, having a tetragonal geometry with the amine donor atoms in the equatorial sites, for stronger in-plane interactions, which induce a higher energy of the redox orbital ($x^2 - y^2$, for the high-spin; xy, for the low-spin nickel(II) ion), the lower oxidation potentials are expected. Perhaps significantly, for presently available high-spin Ni(II) complexes of tetramine a very good inverse correlation exists between the electrode potential and the strength of the in-plane Ni–N interactions, expressed as $10Dq^{xy}$ (Fig. 3). The open-chain complex $Ni(2.3.2\text{-}tet)(CH_3CN)_2^{2+}$ is not so easily oxidized as the cyclam complex, however it is oxidized more easily than the other two macrocyclic complexes *2* and *3*.

This can be attributed to the stronger in-plane coordinative bonds.

Concerning the low-spin species, the energy of the unique band in the visible region can be an approximate estimate of the in-plane bond strength [12, 13]. $Ni(2.3.2\text{-}tet)^{2+}$ absorbs at a frequency slightly lower than $Ni(cyclam)^{2+}$ (22420 and 22470 cm^{-1}, respectively) and is oxidized at a slightly higher electrode potential. However, its oxidation is remarkably favoured with respect to the other 14-membered tetra-aza macrocycle *2* (E^0 = 0.81 V) [7], which exhibits lower Ni–N interactions (ν_{max} = 21600 cm^{-1}).

If one considers the oxidation potentials of Ni(II) complexes with saturated and unsaturated, substituted and unsubstituted tetra-aza macrocycles, electrochemically investigated up to date (more than 30), oxidation of the open-chain complex $Ni(2.3.2\text{-}tet)^{2+}$ is less easy than that of $Ni(cyclam)^{2+}$, but it is favoured with respect to all the other macrocyclic complexes (potentials up to +1.30 V *vs.* Ag/Ag^+ 10^{-2} *M*) [5, 14]. From these considerations it results that accessibility to the Ni(III) state, expressed by the magnitude of the electrode potential, is not related to the cyclic nature of the ligand, as claimed by some authors [3], but only depends upon the energy of Ni–N interactions, *i.e.* on the capability of the ligand to meet the electronic and stereochemical requirements of the metal ion (to dispose donor atoms at the corners of a square, at the right distances).

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