Reference

1 C. Preti and G. Tosi, *Z. Anorg. allg. Chem.*, *419*, 185 (1976), and references therein quoted.

Chemical and Electrochemical Generation of Nickel-(III) Poly-aza Macrocyclic Complexes in Aqueous and non-Aqueous Solutions

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It is a property of tetra-aza macrocycles to stabilize unusually high oxidation states of transition metals, which are not accessible to the simple solvocation. A well known example is that of Ni(III), for which extended preparative and electrochemical studies have been reported [1]. We have addressed our attention to the formation of Ni(III) complexes with saturated unsubstituted poly-aza macrocycles of increasing denticity (n = 4, 5, 6) and of varying cavity size. The dark green solutions of the Ni(III) complexes can be prepared through chemical (with $NOBF_4$) or electrochemical (at the platinum anode) oxidation of the corresponding Ni(II) species. The authenticity of the +3 state is demonstrated by the ESR spectra, which are those expected for a low-spin d^7 chromophore in an octahedral environment. The relative solution stability of the Ni(III) species can be expressed by the $E_{1/2}$ value associated to the electrochemically reversible redox change, determined through conventional voltammetric techniques. Most studies have been carried out in acetonitrile, due to the high resistance to the oxidation of this solvent, which allows the attainment also of extremely strong oxidizing species.

For a complete series of 12- to 16-membered tetra-aza macrocycles, the easiest Ni(II)/Ni(III) oxidation process occurs with the symmetric 14-membered system ($E_{1/2}$ = 0.702 V, *vs.* Ag/Ag^+ 0.01 *M*, CH_3CN 0.1 *M* Et_4NBF_4), whereas progressive expansion or contraction of the ligand cavity produces a dramatic increase of the oxidation potential (to 1.12 V). This oxidation selectivity disappears with the introduction of a fifth nitrogen atom in the ligand framework: for a novel series of 15- to 17-membered penta-aza macrocycles, the easiest oxidation occurs with the smallest term ($E_{1/2}$ = 0.732 V), but progressive enlarging of the ligand aperture causes only a moderate increase of $E_{1/2}$ (to 0.817 V). Insertion of a further nitrogen atom, to form the 18-membered cyclic hexamine, makes the attainment of the +3 state somewhat more difficult ($E_{1/2}$ = 0.905 V).

Whereas it is generally believed that the production of Ni(III) polyamine complexes requires strictly anhydrous conditions, relatively stable Ni(III) species can be obtained also in water. Reversible CV profiles are obtained at the carbon paste electrode and the sequence of the $E_{1/2}$ values parallels that found in acetonitrile. However, due to the lower oxidation limit of the water as solvent, only the less oxidizing Ni(III) complexes can be electrochemically or chemically prepared (included that with the open-chain tetramine, 2.3.2-tet).

Reference

1 a) F. V. LoVecchio, E. S. Gore and D. H. Busch, *J. Amer. Chem. Soc.*, *96*, 3109 (1974); b) L. Sabatini and L. Fabbrizzi, *Inorg. Chem.*, *18*, 438 (1979).

π Interaction in Mixed Ligand Complexes

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The study of Cu·dipy·L–L systems, where L–L is a ligand coordinating through two oxygen atoms and has a delocalized π-electron cloud, has shown that $K^{Cu\cdot dipy}_{Cu\cdot dipy\cdot L–L} > K^{Cu}_{Cu\cdot L–L}$ [1, 2]. This is because in $Cu(dipy)^{2+}$, Cu(II) has more class 'A' character and hence has greater affinity for the oxygen atoms in the secondary ligand. Further, in case of π-bonding ligands it can be seen that there is a better match between the π-orbitals of Cu·dipy and L–L rather than in Cu·L–L [3]. In other words the π-delocalization between dipyridyl and the secondary ligand is stabilized through the metal ion. The effect is more pronounced in the case of ligands coordinating through oxygen atoms (O–O) because of the additional pair of electrons on the oxygen atoms.

In order to further confirm this fact, the study of the formation constants of complexes of the type Cu·A·L, where A = dipyridyl, *o*-phenanthroline, 2,2′-pyridyl benzimidazoline, 2,2′-pyridyl imidazoline and L = acetoacetanilidide, acetoacet-*o*-anisidide, acetoacet-*o*-toluidide, benzoatoacetanilide have been carried out.

Though the β-ketoanilides have higher K^H values, they form less stable complexes than β-diketones [4]. This shows that π-delocalization is less in metal β