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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).

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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 $K^{Cu\cdot dipy}_{Cu\cdot dipy\cdot L\text{–}L} > K^{Cu}_{Cu\cdot L\text{–}L}$ [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 ketoanilide (Cu•L) rings. However, the ternary complexes Cu•A•L are very stable. Δ log$[K_{Cu \cdot A \cdot L}^{Cu \cdot A} - K_{Cu \cdot L}^{Cu}]$ is positive though in Cu•β-diketone complexes Δ log K is zero. This must be because of the lone pair of electron over the anilide nitrogen, which gets delocalized over the β-ketoanilide ring. Due to increased electron density in the ring, Cu dπ orbitals do not match in energy with the β-ketoanilide pπ-orbitals in the binary Cu•L complex. In the mixed ligand complex Cu• A• L, however, mutual stabilization due to π-delocalization is more pronounced and hence there is greater stabilization. The extent of stabilization of the mixed ligand complex should depend on the π-delocalization in Cu•A. The order of π-delocalization can be expected to be Cu•dipyridyl > Cu•*o*-phenanthroline > Cu•2,2′-pyridyl benzimidazoline > Cu•2,2′-pyridyl imidazoline. The formation constants of the mixed ligand complexes Cu•A•L are in the same order.

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Mixed Iron and Cobalt Acetylenic Carbonyl Derivatives

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Acetylenic derivatives of mixed metal carbonyl clusters have so far received little attention [1]. Confining to the case of mixed iron and cobalt species $HFeCo_3(CO)_9(C_2Ph_2)_2$ [1], $FeCo_3(CO)_{10}C_2Ph_2$ and $FeCO_3(CO)_8C_2Ph_2$ [2] have been reported, but not fully characterized. We have studied the reactions of aliphatic acetylenes with iron and cobalt carbonyls by reacting in acetone the alkyne either with a preformed iron and cobalt cluster, $HFeCo_3(CO)_{12}$, or with a mixture of $Fe(CO)_5$ and $Co_2(CO)_8$. The products are substantially the same from both reactions, but they are obtained in different yields. For the alkyne being 3-hexyne the following complexes have been obtained: $Co_4(CO)_{10}C_2Et_2$, $Co_2(CO)_6C_2Et_2$, $Co_2(CO)_6EtC_2COMe$, $Co_2(CO)_6EtC_2CHOHMe$, $FeCo_2(CO)_9C_2Et_2$, $FeCo(CO)_6EtC_2CHMe$. The known cobalt derivatives have been fully characterized by m.s., i.r., ^1H and ^{13}C-n.m.r. The activation of one of the methylene groups α to the triple bond has also been observed in the products of the reaction with 4-octyne. The results of the reactions of $HFeCo_3(CO)_{12}$ with 3-hexyne in various solvents suggest that water is the source of the oxygen.

The single crystal X-ray analysis of $FeCo_2(CO)_9C_2Et_2$ shows that the complex is made of an iron and cobalt triangle with three terminal CO's bonded to each metal atom. The organic ligand is σ bonded to each cobalt atom and π coordinated to the iron one, acting as a four electron donor. The binuclear iron and cobalt derivative is obtained in low yield from the above reactions, but the yield is increased to 50% by reacting $Fe(CO)_5$ with $Co_2(CO)_6EtC_2CHOHMe$. Similarly from the reaction of iron pentacarbonyl with $Co_2(CO)_6C_2(CH_2OH)_2$, $FeCo(CO)_6CH_2OHC_2CH_2$ is obtained: in this reaction also complete dehydroxylation of the ligand occurs with transfer of the ligand from cobalt to iron to give the known $Fe_2(CO)_6CH_2C_2CH_2$ complex [3]. On this evidence and on the basis of the spectroscopic data we suggest for the $FeCo(CO)_6RC_2CHR'$ derivatives a structure in which the ligand is σ bonded to the iron atom (*via* the carbon atom previously bearing the hydroxy group) and π coordinated to the iron and cobalt atoms.

The stereochemical non rigidity of the novel complexes and of $FeCo_3(CO)_{12}$ will be discussed and compared with that of other iron and cobalt mixed clusters [4].

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Solute–Solvent Interaction Studies of Some Cu(II) Complexes by EPR Technique

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Even though many workers have studied solute–solvent interactions of paramagnetic complexes in