

An Air-stable d⁹ Nickel(I) Catenate: Stabilisation of Monovalent Nickel by Interlocked Macrocyclic Ligands

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The catenand cat-30 forms a d⁹ nickel(I) complex by electroreduction of the nickel(II) precursor, Ni(cat-30)²⁺; owing to the particular arrangement of the co-ordinating subunits and to the special topology of the ligand, the nickel(I) complex displays exceptional redox stability.

Examples of nickel(I) complexes with nitrogen ligands are mainly restricted to tetra-aza macrocyclic compounds.¹⁻³ These complexes have a very high reducing power,¹⁻⁴ unless the macrocyclic ligand is N and C methylated.⁵ Quinquedentate macrocyclic ligands^{6,7} or their open-chain analogues⁸ have also led to six- or seven-co-ordinate d⁹ nickel(I) complexes. The Ni^I oxidation state is expected to be preferred by ligands selectively appropriate to a tetrahedral geometry. Such an arrangement strongly disfavours the +2 oxidation state, since the affinity of Ni^{II} for such hypothetical ligands is too low, precluding preparation and characterization of their corresponding complexes. We have recently synthesized the first member of a new class of ligands: the catenands.⁹ Such molecules consist of two interlocked co-ordinating rings, each cycle containing a 2,9-diphenyl-1,10-phenanthroline fragment as complexing subunit. The catenand cat-30 (two interlocked 30-membered rings; see Figure 1) is almost ideally adapted to tetrahedral geometries and forms highly stable copper(I) complexes.⁹⁻¹¹ We now report that a nickel(I) complex (catenate) formed with this same ligand can readily be made by electrochemical reduction of its Ni^{II} analogue and displays very unusual redox properties. For comparison, acyclic

nickel(I) complexes have also been studied; the ligands used and Ni(cat-30)ⁿ⁺ (*n* = 1 or 2) are represented Figure 1.

Cat-30 reacts slowly (2 days; room temperature) with a large excess of Ni(NO₃)₂ · 6H₂O in CH₂Cl₂-MeOH (1/1). After work-up and recrystallization (CH₂Cl₂-C₆H₆), a yellow crystalline solid is obtained (yield: 70%). A good elemental analysis (C, H, N) was obtained as well as a contact shifted ¹H n.m.r. spectrum (CH₂Cl₂, room temperature) consistent with the paramagnetic d⁸ complex Ni^{II}(cat-30)²⁺. By contrast, the use of dmp or dap (see Figure 1) instead of the catenand leads to no isolable complex, demonstrating the importance of the topological catenand effect. However, Ni(dap)₂²⁺ and, to a lesser extent, Ni(dmp)₂²⁺, are sufficiently stable in CH₂Cl₂ and MeCN solutions to be studied by electrochemical methods. The electrochemical properties of the three nickel complexes are shown in Table 1, the corresponding cyclic voltammograms being represented in Figure 2.

The Ni^{II}/Ni^I couple is reversible for the three complexes. For the nickel catenate, the second electron transfer is also reversible and occurs at -1.13 V vs. Ag/Ag₃I₄⁻ in CH₂Cl₂.†

† Ca. -1.42 V vs. saturated calomel electrode.

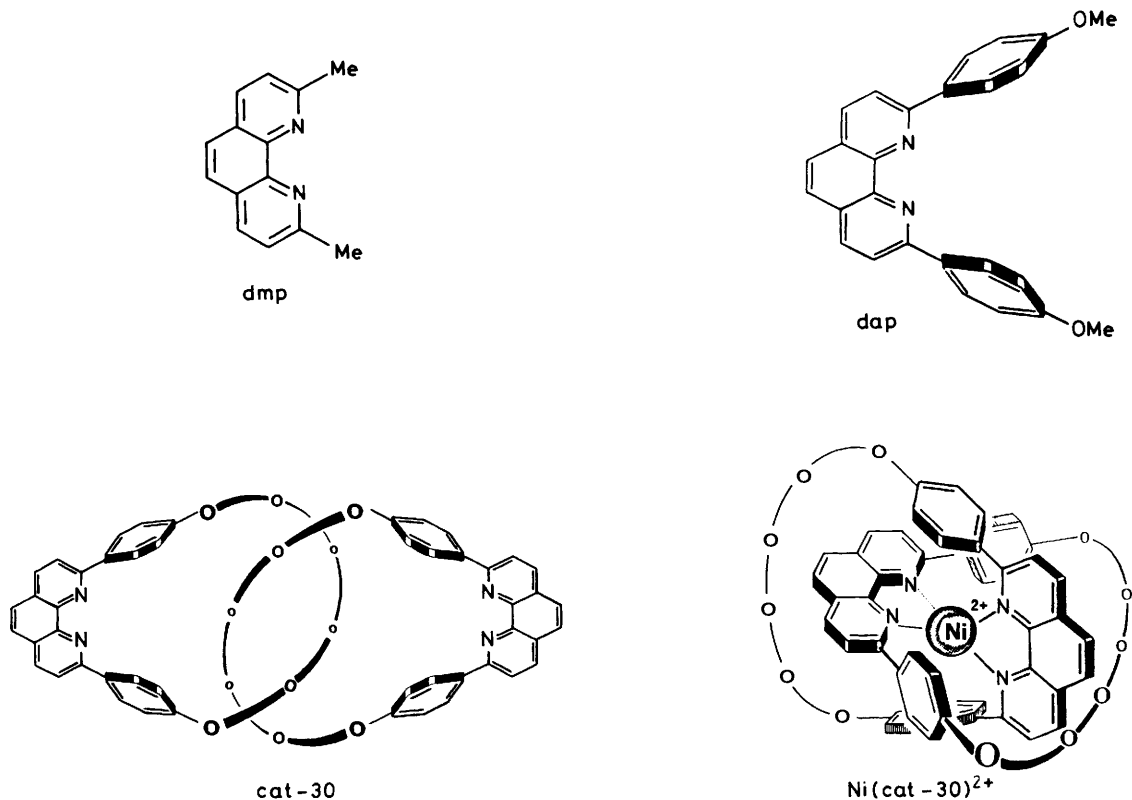


Figure 1

Coulometric measurements unambiguously show the Ni(cat-30)²⁺ or Ni(dap)₂²⁺ reductions to be one-electron processes.

Controlled potential electrolysis of either Ni(cat-30)²⁺ or the dap complex in CH₂Cl₂ at -0.3 V vs. Ag/Ag₃I₄⁻ (Pt wire) yields a deep blue-green solution of nickel(I), whereas the reduced dmp species decomposes as soon as it is formed.‡ Spectroelectrochemical measurements show that Ni(cat-30)²⁺ is quantitatively converted into Ni(cat-30)⁺. The electronic spectrum of the dap-nickel(I) complex is superimposable on that of Ni(cat-30)⁺: it contains a broad band centred at 645 nm (ϵ 2400 mol⁻¹ l cm⁻¹).

E.s.r. studies of Ni(cat-30)⁺ and its dap equivalent have been performed on electrochemically generated species. Both spectra are identical and display characteristic features of d⁹ nickel(I) complexes: they comprise several anisotropic lines whose corresponding *g* values are indicated in Table 1. These e.s.r. data are in good agreement with those previously obtained for other Ni^I species.^{3,6-8} It is striking that such easily reducible nickel(II) complexes, involving di-imine ligands, lead to d⁹ species by reduction and not to nickel(II) stabilized radical anions, as previously observed for unsaturated macrocyclic complexes.^{3,12} Such a behaviour stresses the important contribution of the tetrahedral arrangement in stabilizing Ni^I. This geometrical effect is also estimated in comparing the complexes formed with dmp and dap; whereas the nickel(I) complex of the only slightly hindering dmp ligand could not be accumulated in solution, Ni(dap)₂²⁺ is perfectly stable under argon. The two dap fragments fit in together while complexing Ni^I, creating thus a highly rigid and encaging

‡ The nickel(I) catenate is so stable that it can easily be obtained chemically from a Ni(cat-30)²⁺ solution containing a weak reducing agent (an alcohol, ascorbic acid, etc.).

Table 1. Electrochemical and e.s.r. data.

| Complex | E° ^a (Ni ^{III} /Ni ^I) | <i>g</i> values of the nickel(I) complexes ^b |
|------------------------------------|---|--|
| Ni(dmp) ₂ ⁿ⁺ | -0.100 | — |
| Ni(dap) ₂ ⁿ⁺ | +0.105 | <i>g</i> ₁ = 2.388 <i>g</i> ₂ = 2.143 |
| Ni(cat-30) ⁿ⁺ | +0.105 | <i>g</i> ₃ = 2.071 |

^a At room temperature, in CH₂Cl₂, Buⁿ₄NClO₄ (0.1 M), V vs. Ag/Ag₃I₄⁻ reference electrode; scan rate: 50 mV s⁻¹; Pt button; the peak to peak separation is $\Delta E_p \sim 60-70$ mV. For the ferricenium⁺-ferrocene couple, the redox potential is $E^{\circ} = +0.655$ V vs. Ag/Ag₃I₄⁻. ^b Measured in frozen CH₂Cl₂ solution (77 K).

assembly. This particular topography has already been taken advantage of in stabilizing the charge-transfer excited states of a copper(I) complex.¹³ The relatively low reactivity of Ni(dap)₂²⁺ and the inertness of Ni(cat-30)⁺ with respect to their reoxidation by O₂ are also remarkable. We have measured the corresponding bimolecular rate constant, *k*(O₂), in CH₂Cl₂ at 20 °C, by monitoring the visible spectrum of the reduced complex in the presence of a known concentration of O₂: for Ni(dap)₂²⁺, *k*(O₂) ~ 2 mol⁻¹ l s⁻¹ whereas Ni(cat-30)⁺ can hardly be reoxidized, even in O₂-saturated CH₂Cl₂ solution for days [*k*(O₂) $\sim 10^{-5}$ mol⁻¹ l s⁻¹]. Although Ni(dap)₂²⁺ solutions are reoxidized by air in minutes, even this complex displays unusual low reactivity with O₂; one of the most stable Ni^I complexes ever reported with nitrogen donors reacts with O₂ several orders of magnitude faster than does Ni(dap)₂⁺.⁵

The comparison between the topographically similar species Ni(dap)₂²⁺ and Ni(cat-30)⁺ provides a direct measure of

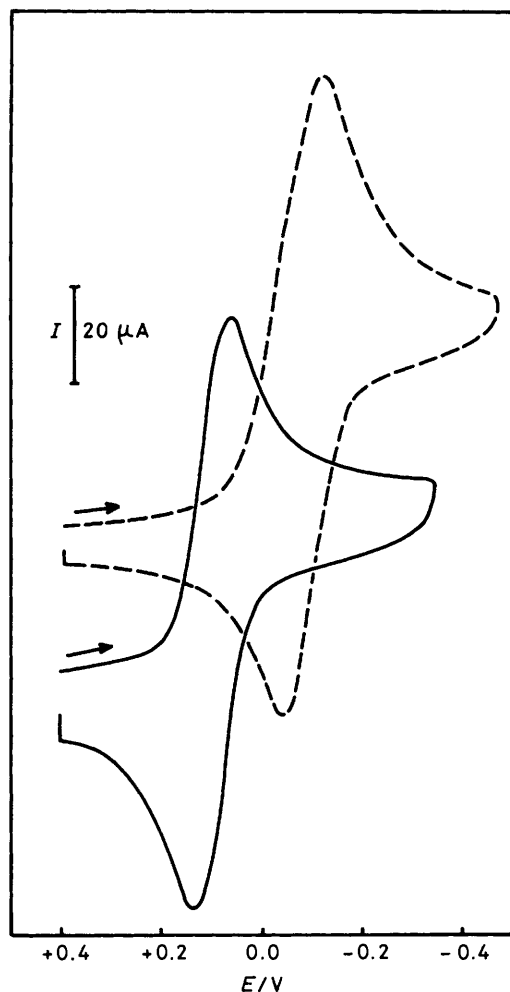


Figure 2. Cyclic voltammograms of Ni(dmp)_2^{2+} (---) and Ni(cat-30)^{2+} (—) in CH_2Cl_2 ; experimental conditions: see footnote a, Table 1.

the catenand effect; the reaction with O_2 is more than 10^5 times slower for Ni(cat-30)^+ than for its acyclic analogue Ni(dap)_2^+ , in spite of the strictly identical electrochemical properties of both compounds. This large factor is of purely topological origin (interlocking of the two rings). In conclusion, the present results show that the conjunction of topographical and topological properties allows exceptional stabilization of low-valent transition metals like d^9 nickel(I).

We thank the CNRS for financial support; J. J. André and M. Bernard are also gratefully acknowledged for e.s.r. measurements.

Received, 1st March 1985; Com. 275

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