Non-selective Stabilization of Nickel(III) by Saturated Penta-aza Macrocycles of Varying Size

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Summary The nickel(II) complexes formed from the three novel penta-aza macrocycles (**1**), (**2**), and (**3**) are easily oxidised to the Ni^{III} species both chemically and electrochemically and the $E_{\frac{1}{2}}$ values for the Ni^{2+}/Ni^{3+} couple are only slightly dependent upon the macrocyclic ring size, in strong contrast with those found for tetra-aza systems.

ALTHOUGH Ni^{III} complexes are otherwise unusual, their complexes with tetra-aza-macrocycles have become familiar in co-ordination chemistry.[1] The relative stability of the Ni(macrocycle)$^{3+}$ species, expressed by the half-wave potential of the Ni^{2+}/Ni^{3+} couple in acetonitrile, is extremely sensitive to the size of the tetra-aza macrocyclic cavity and $E_{\frac{1}{2}}$ values for 12- to 16-membered systems vary over a substantial range (*ca.* 0·4 V; see Figure).†

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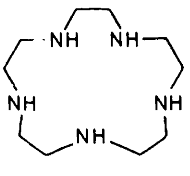
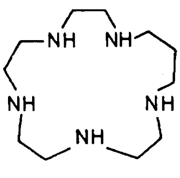
† All data refer to reversible or quasi-reversible processes at the platinum electrode in acetonitrile and 0·1 M Et_4NBF_4, and were taken from ref. 1c or measured in this work.



(1)



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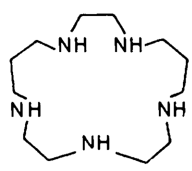

(3)

With the aim of evaluating to what extent the insertion of a fifth nitrogen atom in the ligand framework can influence the formation of $\mathrm{Ni^{III}}$ complexes, we have synthesized a novel series of saturated unsubstituted penta-aza macrocycles having 15 to 17 atoms in the ring, (**1**), (**2**), and (**3**).

The nickel(II) complexes of (**1**), (**2**), and (**3**), obtained as perchlorates, dissolve in acetonitrile as 2 : 1 electrolytes and show electronic spectra typical for high-spin distorted octahedral chromophores, in which the quinquedentate macrocycle is probably folded to span five co-ordination sites, the sixth one being occupied by a solvent molecule.

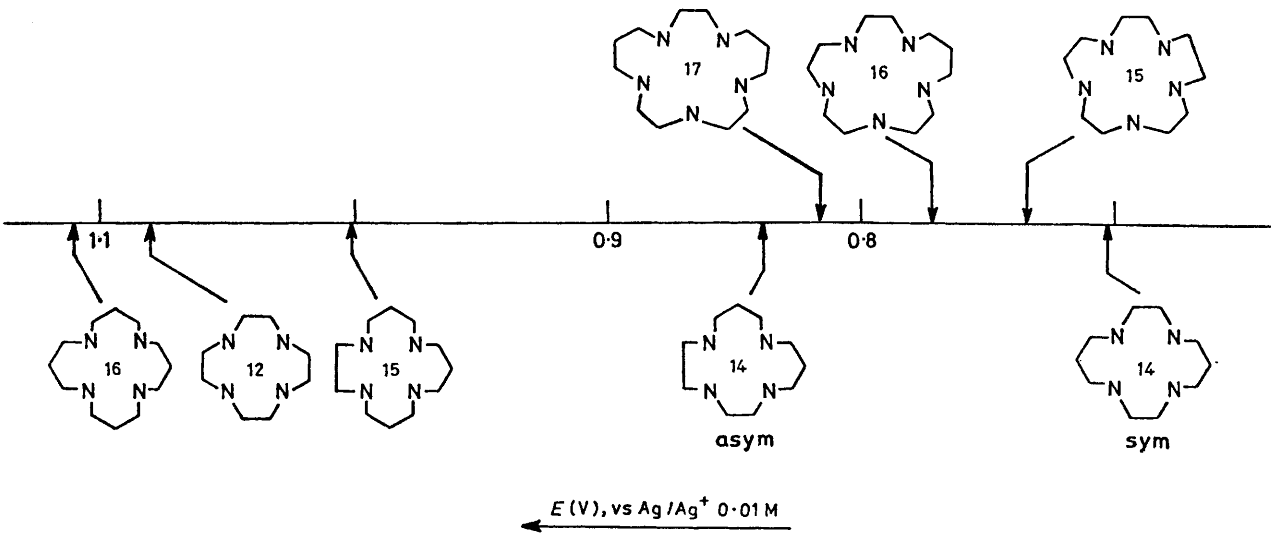

FIGURE. $E_{\frac{1}{2}}$ Values of $\mathrm{Ni^{2+}/Ni^{3+}}$ couples in penta-aza and tetra-aza macrocyclic complexes in acetonitrile solution, at 25 °C.

The energy of the lowest energy absorption band decreases along the series $\mathrm{Ni(\mathbf{1})^{2+}} > \mathrm{Ni(\mathbf{2})^{2+}} > \mathrm{Ni(\mathbf{3})^{2+}}$, indicating a progressive weakening of the Ni–N interactions with the enlarging of the ring size. All these complexes undergo a reversible one-electron oxidation process at a platinum electrode in acetonitrile containing 0·1 M $\mathrm{Et_4NBF_4}$. Cyclic voltammetric curves showed a peak potential separation of 60 mV and a peak current ratio of unity.[2] The one-electron stoicheiometry was ascertained by direct controlled potential coulometry. Green solutions of the nickel(III) complexes were obtained by bulk electrolysis; their e.s.r. spectra (at 77 K) show axial symmetry, with $g_{\perp} > g_{\parallel}$ and a value of $g_{\perp}$ considerably greater than 2 ($g_{\perp} = 2{\cdot}17$; $g_{\parallel} = 2{\cdot}03$). This is consistent with an octahedral low-spin d^7 system[3] and demonstrates the authenticity of the $\mathrm{Ni^{III}}$ oxidation state. The half-wave potentials for the three penta-aza macrocyclic complexes are surprisingly low [$\mathrm{Ni(\mathbf{1})^{2+/3+}}$: 0·737 V; $\mathrm{Ni(\mathbf{2})^{2+/3+}}$: 0·772 V; $\mathrm{Ni(\mathbf{3})^{2+/3+}}$: 0·817 V, *vs.* $\mathrm{Ag/AgNO_3}$ 0·01 M, 0·1 M $\mathrm{Et_4NBF_4}$, at 25 °C; ± 0·005 V], suggesting the possibility of synthesis of $\mathrm{Ni^{III}}$ species through chemical oxidation. In fact, $\mathrm{Ni^{III}}$ penta-aza macrocyclic complexes can be obtained by reaction with oxidizing agents such as $\mathrm{NOBF_4}$ (in MeCN) or $\mathrm{K_2S_2O_8}$ (in MeOH).

Comparison of $E_{\frac{1}{2}}$ values (see Figure) shows that formation of $\mathrm{Ni^{III}}$ complexes with penta-aza macrocycles is slightly more difficult than that of the 14-membered symmetric tetra-aza macrocyclic complex, but it occurs remarkably more easily than for all the other quadridentate systems. Furthermore, progressive enlarging of the 15-membered penta-aza size produces a small increase of the $E_{\frac{1}{2}}$ ($\mathrm{Ni^{2+}/Ni^{3+}}$) value, in complete contrast with that found for tetra-aza homologues, where the expansion or contraction of the 14-membered cavity causes dramatically large increases of $E_{\frac{1}{2}}$, making the oxidation process highly selective with respect to the strength of the oxidizing agent.

The present data demonstrate that insertion of a further nitrogen atom in a tetra-aza ligand framework, probably occupying an apical site of the co-ordination octahedron, can help the attainment of the $\mathrm{Ni^{III}}$ state and, in any case, releases the $\mathrm{Ni^{2+}/Ni^{3+}}$ redox process from heavy in-plane ring size effects. This situation is similar to that of some physiologically active metal ions, which are involved in electron transfer through +2/+3 redox changes. In fact, they are usually incorporated in co-planar tetra-aza macrocyclic systems, but they also experience the apical interaction of a fifth nitrogen atom, which comes from a flexible part of a protein.

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[1] (a) E. K. Barefield and D. H. Busch, *Chem. Comm.*, **1970**, 522; (b) F. V. LoVecchio, E. S. Gore, and D. H. Busch, *J. Amer. Chem. Soc.*, 1974, **96**, 3109; (c) L. Sabatini and L. Fabbrizzi, *Inorg. Chem.*, 1979, **18**, 438.

[2] As expected for one-electron reversible redox processes; see: R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **36**, 706.

[3] M. C. Rakowski, M. Rychek, and D. H. Busch, *Inorg. Chem.*, 1975, **14**, 1194.