Co-ordination of a 16-Membered Dioxopenta-amine Macrocycle to High-spin Nickel(II). *X*-Ray Study of Structural Requirements for a Mono-oxygenase Model

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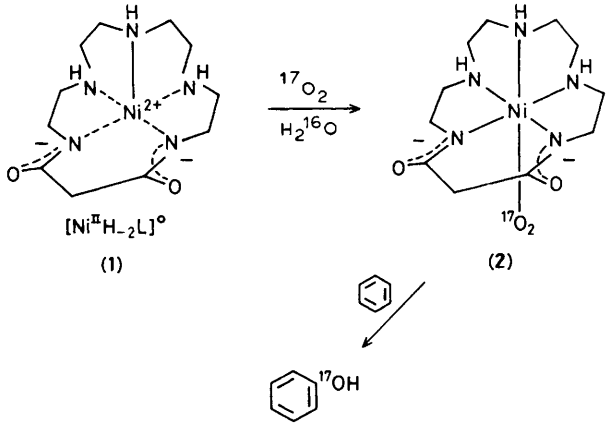
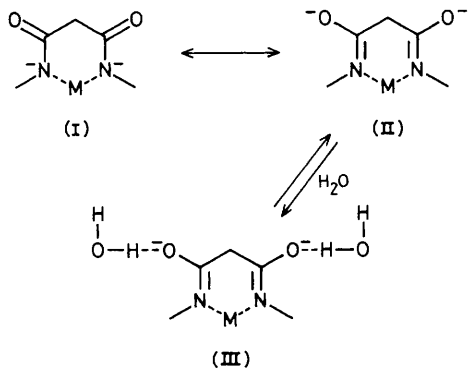
X-Ray crystal structure analysis of the nickel(II) 16-membered dioxopenta-amine macrocyclic complex (**1**) reveals that the constrained ligand configuration and the possible electron-sink properties of the deprotonated amide donors could be favourable for its interaction with O_2.

The nickel(II) complex (**1**) with a 16-membered macrocyclic dioxopenta-amine takes up O_2 in aqueous solution to form the 1:1 O_2 adduct (**2**). The O_2 thus activated can then directly attack benzene to yield phenol (Scheme 1).[1—3] The chemical features of this novel mono-oxygenase model complex have been identified in aqueous solution. The nickel(II) is in a high-spin state ($S = 1$) and is five-co-ordinated with the penta-amine unit, including the two deprotonated amide nitrogen atoms. The resulting complex shows an unusually low redox potential of +0.24 V *vs.* S.C.E. (standard calomel electrode) for $Ni^{III/II}$. The most puzzling fact is that the E value of (**1**) is more positive than the $M^{III/II}$ values of reported O_2 uptake systems such as hemoglobin (−0.07 V *vs.* S.C.E. at pH 7),[4] and yet (**1**) readily undergoes oxygenation to give (**2**) assuming formal Ni^{3+}–O_2^- bonding character.[3] Recently we have succeeded in isolating (**1**) in crystalline form and now report *X*-ray crystallographic results. Violet crystals of $Ni^{II}H_{-2}L{\cdot}H_2O$ were obtained by the reaction of $Ni^{II}(OH)_2$ with the free ligand in water, followed by slow evaporation of water under argon at room temperature. *Crystal data*: monoclinic, space group $P2_1/n$, $a = 8.670(1)$, $b = 11.896(2)$, $c = 14.054(3)$ Å, $\beta = 99.22(1)°$, $Z = 4$, $D_c = 1.52$ g cm^{-3}, Mo-K_α radiation. 2466 Structure factors with $F_0 > 3\sigma(F_0)$ were derived from 3285 intensities collected using a Syntex-R3 diffractometer. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares to an R value of 0.048 with anisotropic Ni, N, O, and C and isotropic H atoms.†



Scheme 1



Scheme 2

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

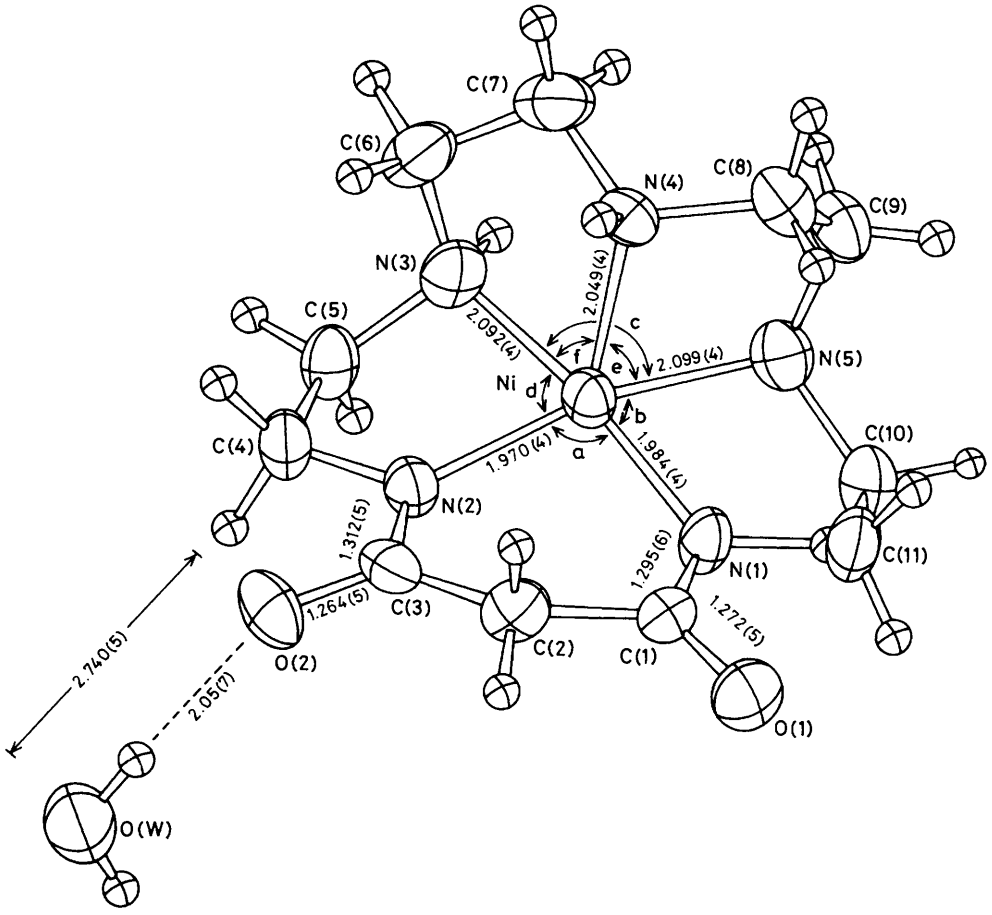


Figure 1. *X*-Ray crystal structure of (**1**), with distances in Å. Bond angles: a, 92.8(2); b, 82.5(2); c, 100.1(2); d, 82.1(2); e, 84.4(2); f, 84.4(2)°.

The structure of the complex (**1**) is shown in Figure 1. The Ni^{II} and four N donors including two trigonal (*i.e.* deprotonated) amide N atoms are nearly coplanar with the remaining N in an axial position, thus forming a square-pyramidal structure. An H_2O molecule hydrogen-bonds with each of two amide oxygens, bridging between separate molecules of the macrocycle–Ni complex. The average distances for equatorial Ni–N(amide) and Ni–N(amino) bonds, 1.978(4) and 2.095(4) Å, respectively, are in ranges similar to those in octahedral, high-spin Ni^{II} complexes with bis(H_{-1}GlyGly) (1.99—2.02 and 2.11—2.15 Å, respectively)[5] or with cyclam (1,4,8,11-tetra-azacyclotetradecane) (2.058 Å for Ni-amino bonding),[6] but are longer than those (1.84 and 1.92 Å) in the low-spin Ni^{II} complex with H_{-2}GlyGlyGly.[5] However, significant shortening is found in the axial Ni–N(4) bond distance, 2.049(4) Å, associated with a tilted axial bond angle, ∠ N(4)–Ni–N(3), of 84.4(2)°. Strain is also seen in the narrow bite of the five-membered chelate rings [*e.g.* N(1)–Ni–N(5) average 82.5(2)°] and in the wide opening of the angle N(3)–Ni–N(5), 100.3(2)°. Evidently, the 16-membered macrocyclic cavity is not of an ideal size for accommodation of a high-spin Ni^{II} in a square-pyramidal complex.

With deprotonation of the amide nitrogens, delocalization of the carbonyl double bonds leads to two resonance forms in a similar fashion to peptides (Scheme 2).[7] As a result, the C=O bond lengthens [average 1.268(6) Å. *vs.* 1.24 Å with free peptides[8]] while the OC–N bond length decreases [1.304(6) Å *vs.* 1.33 Å with free peptides[8]]. This notion is supported by the i.r. stretching frequency ν_{CO} (KBr) that occurs at 1570 cm^{-1} for (**1**), compared with 1660 cm^{-1} for the free ligand. Hydrogen bonding between the electron-rich amide oxygen and water molecules [2.736(6) and 2.740(5) Å; see form (III)] further enhances this trend. The reverse trend to favour the resonance form (I) would be expected if the metal ion were in a higher oxidation state.

The unique structural features of (**1**) which combine to give it O_2 uptake properties may be understood on the basis of the present studies. The strong donor ability of the deprotonated amide N atoms [as demonstrated by the shorter bond lengths for Ni–N(amide) than for Ni–N(amino)] stabilizes the Ni^{III} character of the O_2 adduct.[3] The strong compression from an axial N contributes more electrons to the Ni and also enhances the π-back donor ability of Ni to the O_2. Moreover, the square-pyramidal co-ordination of the macrocyclic ligand in (**1**) with a large, high-spin nickel(II) ion gives rise to appreciable strain, and, hence oxidation or oxygenation of the central metal ion with consequent shrinkage in size would relieve such strain. A shortened Ni^{III}–N(amino) bond distance of 1.97 Å was reported for $[Ni^{III}(cyclam)Cl_2]ClO_4$.[9]

Since O_2 is a good π-acceptor, its co-ordination would demand an increase in N → Ni π donation to help compensate for the Ni →O_2 π back bonding. Referring to Scheme 2, the

deprotonated amides possibly act as 'electron sinks' and can modify their π-donor characteristics towards the Ni ion *via* the sp^2 N donor form. A similar *cis*-effect has been reported in co-ordination of CO to iron–porphyrin complexes.[10]

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