Reaction of Oxygen with a Nickel(I) Cyclic Amine Complex

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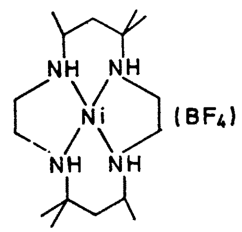
Summary An unusual reaction of O_2 with a Ni^I cyclic amine complex is reported.

The preparation and isolation of cyclic amine Ni^I complexes have been described previously.[1] An example is the compound (I). Stable complexes of univalent nickel containing only σ-donor ligands are rare and may exhibit unusual chemistry. Most Ni^I complexes are stabilized by ligands capable of dative π-bonding such as CN^- and PR_3.

The Ni^I cyclic amine complexes have an unpaired electron and in many respects behave as radicals. We have studied the reaction of (I) with O_2 in some detail using polarographic and spectral methods. The reaction is complex and is accompanied by two colour changes. The initial colour change is from pale green to bright blue and occurs before a full equivalent of O_2 has been added. A charge-transfer band appears in the visible spectrum at 595 nm. A change from blue to brown occurs when an excess of O_2 is present.



(I)

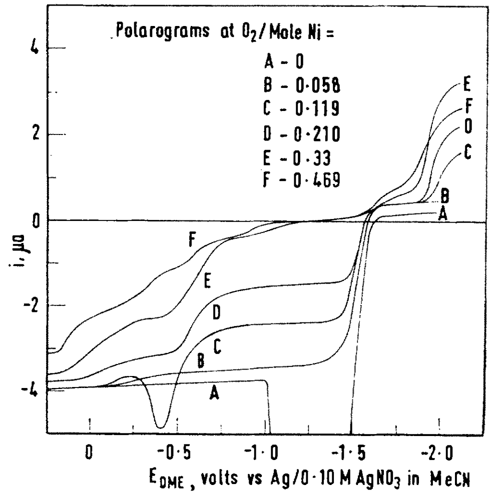


Figure 1. *Titration of* (I) *with* O_2 *in* MeCN.

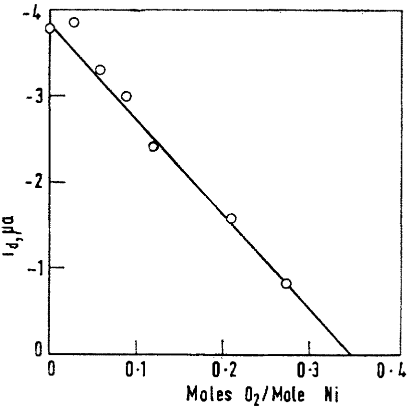


Figure 2. *Titration of* (I) *with* O_2 *in* MeCN; *decrease in* i_d *of* NiL^+ *wave.*

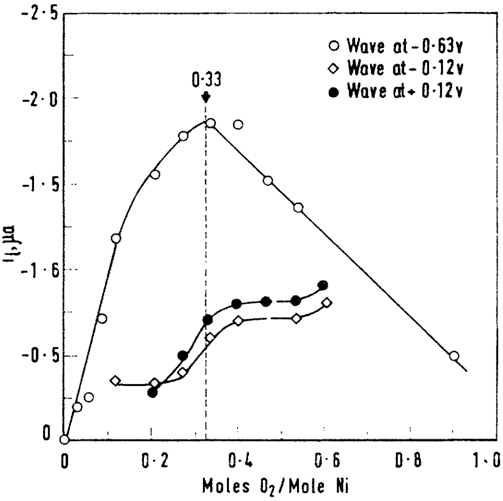


Figure 3. *Titration of* (I) *with* O_2 *in* MeCN; *variation of limiting currents of polarographic waves due to products formed.*

The reaction was followed in acetonitrile by polarography and spectrophotometry. Figure 1 shows the change in the polarographic pattern as O_2 is added to a solution of (I). The anodic wave at $-1{\cdot}5$ v due to $NiL^+ - e \rightarrow NiL^{+2}$ decreases as three new anodic waves and a cathodic wave due to products grow. The dependence of the limiting currents of the waves on the amount of O_2 added is seen in Figures 2 and 3. The wave due to NiL^+ has completely disappeared at 0·33 mole-equivalent O_2 and the waves due to products show either a maximum or an inflection at this point. Similar behaviour was observed by following spectral changes in the u.v. and visible regions, an example of which is shown in Figure 4. Thus the critical reaction between NiL^+ and O_2, accompanied by a green to blue colour change, occurs according to the unusual stoicheiometry,

$$NiL^+ + 1/3\ O_2 \longrightarrow \text{products}$$

A 3 : 1 complex is not the product of this stage of the reaction. When carried out at higher concentrations a pale purple solid rapidly precipitates, (II). Elemental analyses of the material were consistent with a 1 : 1 complex, $O_2NiL(BF_4)$. The compound is paramagnetic and does not give up O_2 under vacuum. When the filtrate from which the above compound precipitated was stripped to dryness, a blue solid, (III), was obtained which contained only a small amount of oxygen. Elemental analyses and i.r. spectra indicated that (III) was a Ni–cyclic amine complex containing a molecule of acetonitrile. Neither $NiL(BF_4)$ nor $NiL(BF_4)_2$ co-ordinates acetonitrile.

The i.r. spectrum of the oxygen complex was complicated, but nonetheless some general conclusions could be drawn. No evidence was found for the existence of a band attributable to an oxygen–oxygen stretching vibration in the region 800—900 cm^{-1} where one would expect a peroxy-group $\overline{\text{O–M–O}}$ to absorb.[2] The existence of a superoxide form of oxygen is still possible but unverifiable as the strong absorption of the BF_4^- anion seems to obscure the 1000—1100 cm^{-1} region where one would expect ν_{O-O} to occur for this form. A band of moderate intensity at 3606 cm^{-1} is found for $^{16}O_2NiL(BF_4)$ indicating the presence of an OH bond in the complex. Numerous small differences between the spectra of $NiL(BF_4)$ and $O_2NiL(BF_4)$ indicate that the macrocyclic ring is somewhat altered upon complexing with oxygen. Differences in visible and u.v. spectra also indicate changes in the macrocyclic ring of (III) with respect to $NiL(BF_4)$ and $NiL(BF_4)_2$.

An excess of oxygen definitely causes attack on the cyclic amine ligand. The brown products obtained on bubbling air through an acetonitrile solution of (I) were treated with CN^- in aqueous EtOH to remove nickel as $Ni(CN)_4^{-2}$. The original cyclic amine (42%) was recovered unchanged. Most of the remaining material was recovered as a yellowish-brown, very soluble organic solid which was not identified. The C and H content was similar to that of cyclic amine·$2H_2O$ but the N content was considerably higher. A band characteristic of $-C{\equiv}N$ was found in the i.r. spectrum. Potentiometric titration of the material in acetonitrile with perchloric acid gave a two-break curve characteristic of strong basic groups. The cyclic amine also gave two breaks, but one of them occurred in a different potential range from that of the unknown. This indicates that one of the amine groups was altered.

While the present results are not sufficient to unravel the complex oxidation reaction, they do point to some conclusions. The initial step probably involves co-ordination of O_2 by (I) to produce a species which attacks the co-ordinated ligand of another two molecules of (I). This could account for the complete disappearance of (I) after only 1/3 mole-equivalent O_2 are added. It is also consistent with the formation of (III), a product with an altered macrocyclic ring and containing little oxygen. The paramagnetic precipitate containing oxygen, (II), which forms during this stage of the reaction is probably an intermediate which can react further when more O_2 is added. The presence of an OH band in the i.r. spectrum indicates that the species may contain an O_2H radical. Addition of an excess of oxygen causes further attack on co-ordinated ligand. The fact that a large portion of the ligand can be recovered unchanged would seem to indicate that the initial oxygen species does not attack the ligand of the complex in which it is co-ordinated.

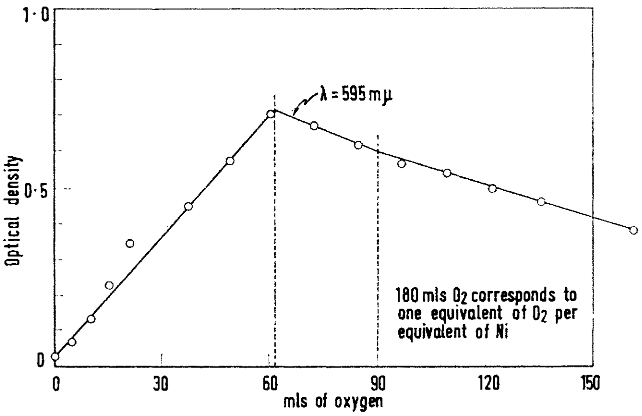


FIGURE 4. *Titration of* (I) *with* O_2 *in* MeCN; *spectral changes as a function of* O_2 *added.*

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[1] D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, 1969, **8**, 1611.

[2] W. P. Griffiths, *J. Chem. Soc.*, 1964, 5248.