Oxidation of Ni^{II} to Ni^{III} with Nitrosyl Tetrafluoroborate

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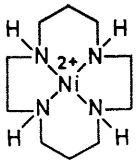
Summary A new method is reported for preparing some Ni^{III} amine complexes by oxidation of the parent Ni^{II} complex with nitrosyl tetrafluoroborate in acetonitrile solution.

A RECENT compilation of reported Ni^{III} complexes indicates that a variety of preparative methods have been successful in oxidizing Ni^{II} to Ni^{III} in at least a few cases.[1] Many of these procedures lead to complex mixtures of products and low yields of Ni^{III} complexes. We have recently discovered a clean oxidative method based on nitrosyl tetrafluoroborate which yields Ni^{III} complexes of certain ligands. Others have used this reagent to oxidize elemental metals suspended in acetonitrile or ethyl acetate with evolution of NO gas.[2-4] In each case the product complex contained the metal in a common oxidation state and with a normal co-ordination number. Hathaway and Underhill first utilized this method to prepare acetonitrile complexes of Ni^{II}, Co^{II}, Fe^{II}, and Cu^{II} from the respective pure metals.[2,3] Wayland extended the reaction to include palladium.[4] In no instances were unusual oxidation states reported.

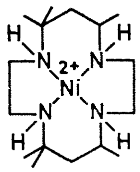
We have found that a number of Ni^{II} complexes react with $NOBF_4$ when dissolved in acetonitrile and that, in certain cases, Ni^{III} complexes may be obtained from the reaction mixtures in high yields. In acetonitrile solutions complexes (I)[5] and (II)[6] react rapidly with 1 equiv. of $NOBF_4$ with a concomitant change in the solution colour from yellow to dark green and with evolution of NO. The addition of 2—3 equiv. of tetra-alkylammonium perchlorate followed by evaporation of the solution to a small volume yields green crystalline materials with the composition $Ni(L)(NCCH_3)_2(ClO_4)_3$. Complex (I′) appears to be stable indefinitely in the solid state and is only slowly decomposed in aqueous solution. Complex (II′) is stable only for short periods of time in the solid state and is decomposed instantly in water. Acetonitrile is not removed from either complex *in vacuo*. Magnetic-susceptibility measurements indicate that each complex has one unpaired electron with $\mu_{eff} = 2{\cdot}13$ BM for (I′) and 2·15BM for (II′). The i.r. spectra of these complexes show absorptions for N–H and C≡N stretching modes. No i.r. absorptions are present for C=N bonds and this indicates that oxidation of the ligand has not occurred.[7] The solid-state spectra of these complexes consist of three bands at about 645, 410, and 320 nm. The low-energy band is somewhat broad, and may contain two components. The assignment of these bands is uncertain although there are similarities with the spectra for NiF_6^{3-} whose spectrum has recently been treated by crystal-field theory.[8] Complex (II′) has properties identical with those reported for a nickel(III) complex prepared by an electrochemical oxidation.[9]

Nitrosyl tetrafluoroborate reacts with a number of other amine complexes in acetonitrile. Complex (III) gives a green solution like those just described. A nickel(III) complex containing this ligand has also been prepared by electrochemical methods.[9] Nickel(II) complexes with tetramine ligands such as (IV) and (V) also react with $NOBF_4$ to give transient green colours which rapidly decay. Products from these reactions have not yet been isolated.

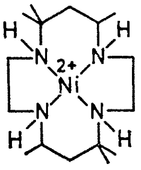
This reagent also appears to provide a clean route to bis-acetonitrile derivatives of certain Co^{III} complexes by oxidation of the parent Co^{II} compounds in acetonitrile. These are useful intermediates for preparing a number of substitution products.



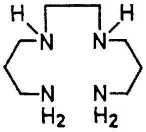
(I)



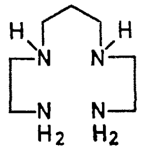
(II)



(III)



(IV)



(V)

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