Oxidation of Nickel(II) and Copper(II) Complexes of *NN*-Diethyldithiocarbamate

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Summary On reaction of copper(II) and nickel(II) complexes of *NN*-diethyldithiocarbamate with Br_2 in CS_2 solution, the central metal ions of the complexes are oxidised to form compounds of formula $Cu^{III}(dtc)Br_2$ and $Ni^{IV}(dtc)_2Br_2$, respectively.

IT has been shown that the complex $Cu^{I}L$, where L is the *NN*-di-n-butyldithiocarbamate monoanion, reacts with Br_2 in CS_2 solution to give $Cu^{III}(L)Br_2$.[1] In a recent communication[2] it was reported that iron, cobalt, antimony, and copper complexes of *NN*-diethyldithiocarbamate (dtc) are oxidized by Cl_2 or Br_2 in $CHCl_3$ solution and form compounds containing an oxidized positive ion of dtc.

We found that $Cu^{II}(dtc)_2$ could be oxidized by Br_2 or I_2 in CS_2 solution to $Cu^{III}(dtc)Br_2$ or $Cu^{III}(dtc)I_2$. $Cu^{III}(dtc)Br_2$ was also formed by oxidizing $Cu^{I}(dtc)$ with Br_2. The Cu^{III} complex obtained was characterized by elemental analyses, i.r., and electronic spectra.

In the same way, $Ni^{II}(dtc)_2$ was converted into a complex with formula $Ni^{IV}(dtc)_2Br_2$. This is thought, on the basis of available data, to be a very rare example of a low-spin Ni^{IV} complex with a planar chelate structure.[3] The complex is soluble in organic solvents such as acetone, $CHCl_3$, or CH_3CN, and the solutions are stable. The complex is decomposed in aqueous solution, with almost quantitative precipitation of $Ni^{II}(dtc)_2$. Molecular-weight determination in $CHCl_3$ solution gave a value of 514, which corresponds closely to the above formula. $Ni^{IV}(dtc)_2Br_2$ is diamagnetic and the n.m.r. spectrum in $CDCl_3$ shows resonances at τ 8·6 (CH_3 : triplet) and 6·2 (CH_2 : quadruplet), with an integral ratio of 3 : 2. This n.m.r. feature is quite similar to that of $Ni^{II}(dtc)_2$ which shows two peaks at τ 8·6 (CH_3: triplet) and 6·1 (CH_2: quadruplet). Thus, the n.m.r. spectral data indicate that the (dtc) ligands are arranged in a planar and bidentate fashion in the complex.[4]

The electronic spectrum of $Ni^{IV}(dtc)_2Br_2$ in CH_2Cl_2 is characterized by intense absorption bands at 435 (log ϵ 3·9) and 500 nm (log ϵ 3·7). The i.r. spectrum of $Ni^{IV}(dtc)_2Br_2$ shows essentially the same pattern as that of $Ni^{II}(dtc)_2$ in the 1700—650 cm^{-1} region.

The ($C\overset{\cdots}{—}N$) frequency for $Ni^{IV}(dtc)_2Br_2$ is observed at 1530 cm^{-1}, compared with 1500 cm^{-1} for $Ni^{II}(dtc)_2$. This shift might be caused by a higher positive charge of the central metal ion in the Ni^{IV} complex.[5]

The polarographic behaviour of $Ni^{IV}(dtc)_2Br_2$, investigated in dimethylformamide solution, is significantly different from that of $Ni^{II}(dtc)_2$, and this provides the main evidence for the presence of Ni^{IV} in the complex.

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