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Moisture Affected Disproportionation Reaction of a Ni(III) Complex to a Ni(II)–Ni(IV) Mixed-Valence Complex

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Recently we reported that apparently tervalent nickel complexes with diamines, linear-tetramines and N_4-macrocycles are classified into two types; (1) intrinsic d^7 Ni(III) complexes, and (2), halogen-bridged one-dimensional Ni(II)–Ni(IV) mixed-valence complexes [1–3]. In addition, some Ni(III) complexes were found to be disproportionated to Ni(II)–Ni(IV) mixed-valence complexes by treatment with 70% $HClO_4$. The structures and electronic states of these complexes of two types are of interest from various viewpoints since the common oxidation number for Ni is +2 [4–9].

Previously $Ni(en)_2Cl_3$ (en = ethylenediamine) was revealed to be a Ni(III) complex formulated as $[Ni^{III}Cl_2(en)_2]Cl$ on the basis of the magnetic moment (1.90 BM) and ESR spectrum of a powde sample ($g_\perp > g_\parallel$) [1]. In this study the ESR spectrum of this compound in a DMSO solution at liquid nitrogen temperature shows very clear axial symmetry with the parallel feature split into seven almost equally spaced lines (28 G) of relative intensity *ca.* 1:2:3:4:3:2:1, due to two axial chloro atoms indicating that this is *trans*-dichloro hexacoordinate $[NiCl_2(en)_2]Cl$ with one unpaired electron in the d_{z^2} orbital (Fig. 1).

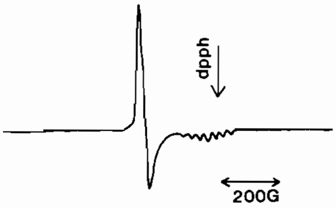

Fig. 1. The ESR spectrum of $[Ni^{III}Cl_2(en)_2]Cl$ in a DMSO solution at liquid nitrogen temperature.

We found that the powder sample of $[NiCl_2(en)_2]$-Cl gradually changed its yellow-brown color to almost black on exposure to moisture for a few months. The elemental analysis of the resultant black complex is consistent with that of the initial yellow-brown Ni(III) complex or $Ni(en)_2Cl_3$. However, the magnetic moment of the black complex decreased to 0.76 BM and the ESR signal was not clearly observed. The electronic spectra of both complexes in Nujol mull are shown in Fig. 2. The black complex showed a very strong absorption at around 15000 cm^{-1}. On the basis of the elemental analysis, magnetic moment and electronic spectrum, the black complex is considered to be a Ni(II)–Ni(IV) mixed-valence complex. Hence, the very strong absorption around 15000 cm^{-1} would be assigned to an intervalence charge transfer transition from Ni(II) to Ni(IV). The authenticity of the mixed-valence state is also evidenced by the electrical conductivity. As shown in Fig. 3, the temperature dependence of the electrical conductivity is well-expressed by the semiconducting character with the thermal activation energy ΔE as $\sigma(T) = \sigma_0 \exp(-\Delta E/kT)$, where σ_0, k and T are pre-exponential factor independent of temperature, Boltzmann's constant and absolute temperature, respectively. The conductivity data ($\sigma_{300} = 6 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$, $\Delta E = 0.51$ eV) are comparable to those of Ni(II)–Ni(IV) mixed-valence complexes so far reported [1–3]. It is thus definitely concluded that the black

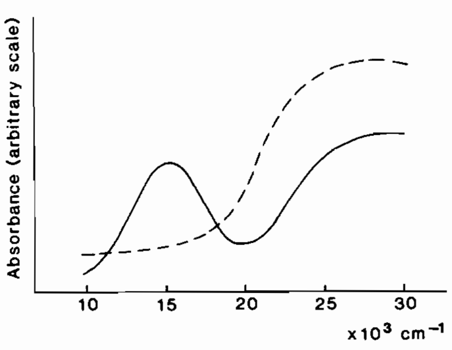

Fig. 2. Electronic spectra of $[Ni^{III}Cl_2(en)_2]Cl$ (– – –) and resultant black complex (——).

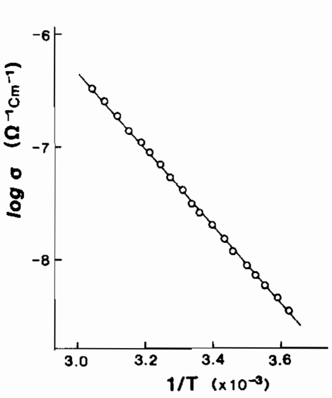

Fig. 3. Temperature dependence of the electrical conductivity of $[Ni^{II}(en)_2][Ni^{IV}Cl_2(en)_2]Cl_4$.

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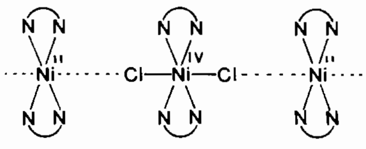
compound is a Ni(II)–Ni(IV) mixed-valence complex formulated as $[Ni^{II}(en)_2][Ni^{IV}Cl_2(en)_2]Cl_4$. As depicted below, square planar Ni(II) and hexacoordinate Ni(IV) units are alternately arranged with chloro-bridges, constructing a linear chain structure as in well-characterized Pt(II)–Pt(IV) and Pd(II)–Pd(IV) mixed-valence complexes [10–18].



Appropriate levels of moisture for such disproportionation reactions are needed, and excess moisture simply decomposes the Ni(III) complex to Ni(II) species.

If the Ni(III) complex is beforehand exposed to moisture for a day, then pressed at about 400 kg/cm^2 for several hours and then exposed the moisture, the disproportionation reaction proceeds in only a few days and the resultant compound is the same as that only by moisture. The high pressure probably plays a role in allowing discrete Ni(III) molecules to approach each other.

As reported before [1, 2], similar disproportionation reaction occurred in 70% $HClO_4$. The 70% $HClO_4$ solution disproportionates some of the Ni(III) complexes with diamines and linear tetramines, whereas moisture alone suffices for $[NiCl_2(en)_2]Cl$.

Further investigations for the elucidation of the mechanism are now in progress.

Experimental

The $[NiCl_2(en)_2]Cl$ complex was prepared according to the reported method [1]. The ESR spectrum was measured with a Varian spetrometer using an X-band at liquid nitrogen temperature. The magnetic moment was obtained by using Faraday method at room temperature. The electronic spectra in Nujol mull were obtained on a Hitachi 340 spectrometer. The electrical conductivity measurement was carried out on a pellet by the two-probe dc method over the temperature range of 0 °C to 60 °C.

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