SOME NEW NICKEL AND COPPER 
N,N-DETHYLDITHIOCARBAMATES

BY

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In preceding papers \(^1\)-\(^3\) the oxidation of \(N,N\)-dialkyl dithiocarbamate \((R_2\text{d}tc)\) complexes of Ni(II) and Cu(I) by Cl\(_2\) or Br\(_2\), yielding Ni(IV) \((R_2\text{d}tc)_3^{+}\text{I}^3_\text{−}\), Cu(III)\(X_2(R_2\text{d}tc)\) and \((\text{Cu}_{2(II)}X_6)^{2−}(R_2\text{d}tc)_2^{2+}\ldots\text{X} = \text{Cl},\text{ Br}\), was reported. The successful preparation of complexes with the metals in an unusually high oxidation state (Ni(IV) and Cu(III)) is due to the stabilizing effect of the dithiocarbamato ligand. This effect should be described in terms of stable oxidized forms of the ligand as has been done for the cis-1,2-dithiolato ligand \(^4\). Therefore, the high oxidation numbers are of a formal significance only as the actual oxidation state of the metal will be lower. This report deals with the oxidation of the \(N,N\)-diethyl dithiocarbamates \((\text{Et}_2\text{d}tc)\) of Ni(II), Cu(II) and Cu(I) by I\(_2\), yielding Ni(IV)\((\text{Et}_2\text{d}tc)_3^{+}\text{I}^3_\text{−}\) and Cu\((\text{Et}_2\text{d}tc)_2^{+}\text{I}^3_\text{−}\), respectively. Furthermore, the detection (by ESR) is reported of Ni(III)\((\text{S}_2\text{COEt})_2(\text{Et}_2\text{d}tc)\) and Cu(II)\(X_2(\text{Et}_2\text{d}tc)^{−}\ldots\text{X} = \text{Cl},\text{ Br}\).

Oxidation of Ni\((\text{Et}_2\text{d}tc)_2\) with I\(_2\) in chloroform as solvent results in the formation of the diamagnetic compound Ni\((\text{Et}_2\text{d}tc)_3\text{I}_3\). The IR and electronic spectra of this new product are, with neglect of the absorption bands due to \(I^3_−\), identical with those of Ni(IV)\((\text{Et}_2\text{d}tc)_3^{+}\text{I}^3_\text{−}\ldots\text{X} = \text{Cl},\text{ Br}\). These data combined with the fact that Ni\((\text{Et}_2\text{d}tc)_3\text{I}_3\) appears to be a 1:1 electrolyte in nitrobenzene clearly indicate the composition Ni(IV)-(Et\(_2\text{d}tc)_3^{+}\text{I}^3_\text{−}\).

The existence of both Ni(IV)\((R_2\text{d}tc)_3^{+}\) and Ni(II)\((\text{S}_2\text{COR})_3^{−}\text{15}\) \((\text{S}_2\text{COR} = \text{O-alkylxanthate})\) prompted the investigation of the preparation of a Ni(III) complex in which the metal is ligated by both types of ligands.

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Starting from the diamagnetic Ni(S₂COEt)₂ a red-brown reaction product is immediately formed upon oxidation with N,N',N'-tetraethylthiuram disulfide (Et₄tds) in a chloroform–ethanol (1:1) solution⁶; its ESR spectrum consists of one line and has an isotropic g-value of 2.106 at 20°. However, at room temperature the red-brown reaction product is rapidly converted into Ni(Et₂dtc)₂. No increase of the conductivity was observed during the reaction process. The combined data suggest a composition Ni(III)(S₂COEt)₂(Et₂dtc) for the red-brown complex. Unfortunately, this complex has not been isolated so far.

Oxidation of Cu(I)(Et₂dtc) and Cu(II)(Et₂dtc)₂ with I₂ in CHCl₃ or CS₂ yields the diamagnetic compound Cu(Et₂dtc)₂I₃. Its far IR spectrum (700–200 cm⁻¹) resembles strongly that of Au(Et₂dtc)⁺ and that of Ni-(Et₂dtc)₂. As the metals in Au(Bu₂dtc)⁺ and Ni(Et₂dtc)₂ have a planar four-coordination of the M—S₄ type⁷,⁸, such a coordination may be expected for Cu in Cu(Et₂dtc)₂I₃ too. Conductivity studies, carried out in nitrobenzene, showed this compound to be a 1:1 electrolyte. So it should be formulated as Cu(Et₂dtc)₂⁺I₃⁻. This composition agrees with the results of a polarographic study on Cu(Et₂dtc)₂ and Cu(Et₂dtc)₂I₃. For Cu(Et₂dtc)₂ a reversible one electron oxidation is observed at a half wave potential (E₁/₂) of 0.66 V (in CH₂Cl₂, using a rotating platinum electrode versus a Ag/AgI electrode). The same E₁/₂ is observed for the reduction of Cu(Et₂dtc)₂I₃. The existence of Cu(Et₂dtc)₂⁺I₃⁻ proves that dithiocarbamate complexes can undergo one electron transfer reactions (though on a small scale) like the metal 1,2-dithiolates⁴,¹⁰.

Of much interest are the Cu—S stretch frequencies, being 357 and 398 cm⁻¹ for Cu(Et₂dtc)₂ and Cu(Et₂dtc)₂⁺I₃⁻, respectively (measured in CsI discs). The IR data suggest a striking strengthening of the Cu—S bond upon oxidation of Cu(II) to Cu(III). This strengthening can be satisfactorily explained on the basis of a molecular orbital scheme set up from an ESR spectroscopic study of Cu(Et₂dtc)₂¹¹. This study pointed out that the unpaired electron is situated in an antibonding σ orbital, which is composed mainly of copper and sulfur orbitals. Therefore, removal of this electron will increase the strength of the Cu—S bond by means of a better σ bonding between these atoms.

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⁶ This observation was also made by R. G. Fischer and J. P. Fackler, personal communication.
⁹ J. G. M. van der Linden and H. G. J. van der Roer, to be published.
In contrast with a recent publication\textsuperscript{12} we did not succeed in preparing Cu(III)I\textsubscript{2}(Et\textsubscript{2}dtc).

In order to complete our knowledge about CuX(R\textsubscript{2}dtc)\textsuperscript{1} \ldots X = Cl, Br we did react chloride ions with CuCl(Et\textsubscript{2}dtc) in CHCl\textsubscript{3}. This solution gives an ESR spectrum which is illustrated in Fig. 1. The four major lines are due to interaction of the spin of the unpaired electron with the nuclear spin of copper (I\textsubscript{Cu} = \frac{3}{2}). The hyperfine splitting structure over the major line at high field can be very well explained considering interaction with the nuclear spins of two equivalent chlorine atoms (I\textsubscript{Cl} = \frac{3}{2}). At room temperature the isotropic g-value is 2.072, a\textsubscript{Cu} = 74 gauss and a\textsubscript{Cl} = 8 gauss. Two complex ions are considered for giving this signal: either CuCl\textsubscript{2}(Et\textsubscript{2}dtc)\textsuperscript{−} or CuCl\textsubscript{2}(Et\textsubscript{2}dtc)\textsubscript{2}\textsuperscript{2−}. The latter ion could be ruled out because addition of chloride ions to a solution of Cu(Et\textsubscript{2}dtc)\textsubscript{2} did not affect the original signal of Cu(Et\textsubscript{2}dtc)\textsubscript{2}.

Addition of bromide ions to a solution of CuBr(Et\textsubscript{2}dtc) in CHCl\textsubscript{3} gives an ESR spectrum which consists of 13 nearly equidistant lines. The quality of this spectrum is, however, very bad. The same spectrum can be obtained much better on addition of bromide ions to a solution of Cu(III)Br\textsubscript{2}(Et\textsubscript{2}dtc) in CHCl\textsubscript{3} (Fig. 2). It can be ascribed to CuBr\textsubscript{2−}(Et\textsubscript{2}dtc)\textsuperscript{−}, g = 2.065, a\textsubscript{Cu} = 2a\textsubscript{Br} = 80 gauss. The reduction by Br\textsuperscript{−}, which we assume to occur in the latter reaction, is also observed in the reaction of CuBr\textsubscript{2} with Br\textsuperscript{−} to CuBr\textsubscript{2−}\textsuperscript{13}. The poor quality of the spectrum of the reaction mixture of Br\textsuperscript{−} and CuBr(Et\textsubscript{2}dtc) is possibly due to such a reduction process.

Fig. 2

The existence of CuX₂(Et₂dtc)⁰⁻¹ forms another example of dithiocarbamate complexes which are related by one electron steps. The polarographic behaviour of these compounds is the subject of further investigations.

Acknowledgement

The investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization of Pure Research. The author wishes to thank Prof. J. J. Steggerda for his continuous interest and Dr. H. van Willigen and Dr. J. A. M. van Broekhoven for their assistance in the ESR study.

(Received September 24th, 1970)