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SOME NEW NICKEL AND COPPER *N,N*-DIETHYLDITHIOCARBAMATES

BY

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In preceding papers¹⁻³ the oxidation of *N,N*-dialkyldithiocarbamate (R_2dtc) complexes of Ni(II) and Cu(I) by Cl_2 or Br_2 , yielding Ni(IV) (R_2dtc)₃⁺ X^- , Cu(III) $X_2(R_2dtc)$ and $(Cu_2(II)X_6)^{2-}(R_2dtc)_2^{2+} \dots X = Cl, Br$, 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 dithiocarbamate 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 ligand⁴. 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*-diethyldithiocarbamates (Et_2dtc) of Ni(II), Cu(II) and Cu(I) by I_2 , yielding Ni(IV)(Et_2dtc)₃⁺ I_3^- and Cu(Et_2dtc)₂⁺ I_3^- , respectively. Furthermore, the detection (by ESR) is reported of Ni(III)(S_2COEt)₂(Et_2dtc) and Cu(II) $X_2(Et_2dtc)^- \dots X = Cl, Br$.

Oxidation of Ni(Et_2dtc)₂ with I_2 in chloroform as solvent results in the formation of the diamagnetic compound Ni(Et_2dtc)₃ 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)(Et_2dtc)₃⁺ $X^- \dots X = Cl, Br$. These data combined with the fact that Ni(Et_2dtc)₃ I_3 appears to be a 1:1 electrolyte in nitrobenzene clearly indicate the composition Ni(IV)-(Et_2dtc)₃⁺ I_3^- .

The existence of both Ni(IV)(R_2dtc)₃⁺ and Ni(II)(S_2COR)₃⁻¹⁵ ($S_2COR = O$ -alkylxanthate) prompted the investigation of the preparation of a Ni(III) complex in which the metal is ligated by both types of ligands.

¹ H. C. Brinkhoff, J. A. Cras, J. J. Steggerda and J. Willemse, Rec. Trav. Chim., **88**, 633 (1969).

² P. T. Beurskens, J. A. Cras and J. J. Steggerda, Inorg. Chem., **7**, 810 (1968).

³ J. Willemse and J. J. Steggerda, Chem. Comm., 1123 (1969).

⁴ G. N. Schrauzer, Transition Metal Chem., **4**, 299 (1968).

⁵ D. Coucouvanis and J. P. Fackler, Inorg. Chem., **6**, 2047 (1967).

Starting from the diamagnetic $\text{Ni}(\text{S}_2\text{COEt})_2$ a red-brown reaction product is immediately formed upon oxidation with N,N,N',N' -tetraethylthiuram disulfide (Et_4tds) 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 $\text{Ni}(\text{Et}_2\text{dtc})_2$. No increase of the conductivity was observed during the reaction process. The combined data suggest a composition $\text{Ni}(\text{III})(\text{S}_2\text{COEt})_2(\text{Et}_2\text{dtc})$ for the red-brown complex. Unfortunately, this complex has not been isolated so far.

Oxidation of $\text{Cu}(\text{I})(\text{Et}_2\text{dtc})$ and $\text{Cu}(\text{II})(\text{Et}_2\text{dtc})_2$ with I_2 in CHCl_3 or CS_2 yields the diamagnetic compound $\text{Cu}(\text{Et}_2\text{dtc})_2\text{I}_3$. Its far IR spectrum ($700\text{--}200\text{ cm}^{-1}$) resembles strongly that of $\text{Au}(\text{Et}_2\text{dtc})_2^+$ and that of $\text{Ni}(\text{Et}_2\text{dtc})_2$. As the metals in $\text{Au}(\text{Bu}_2\text{dtc})_2^+$ and $\text{Ni}(\text{Et}_2\text{dtc})_2$ have a planar four-coordination of the M—S_4 type^{7,8}, such a coordination may be expected for Cu in $\text{Cu}(\text{Et}_2\text{dtc})_2\text{I}_3$ too. Conductivity studies, carried out in nitrobenzene, showed this compound to be a 1:1 electrolyte. So it should be formulated as $\text{Cu}(\text{Et}_2\text{dtc})_2^+\text{I}_3^-$. This composition agrees with the results of a polarographic study on $\text{Cu}(\text{Et}_2\text{dtc})_2$ and $\text{Cu}(\text{Et}_2\text{dtc})_2\text{I}_3$. For $\text{Cu}(\text{Et}_2\text{dtc})_2$ ⁹ a reversible one electron oxidation is observed at a half wave potential ($E_{1/2}$) of 0.66 V (in CH_2Cl_2 , using a rotating platinum electrode *versus* a Ag/AgI electrode). The same $E_{1/2}$ is observed for the reduction of $\text{Cu}(\text{Et}_2\text{dtc})_2\text{I}_3$. The existence of $\text{Cu}(\text{Et}_2\text{dtc})_2^{0,+1}$ proves that dithiocarbamate complexes can undergo one electron transfer reactions (though on a small scale) like the metal 1,2-dithiolates^{4,10}.

Of much interest are the Cu—S stretch frequencies, being 357 and 398 cm^{-1} for $\text{Cu}(\text{Et}_2\text{dtc})_2$ and $\text{Cu}(\text{Et}_2\text{dtc})_2^+\text{I}_3^-$, respectively (measured in CsI discs). The IR data suggest a striking strengthening of the Cu—S bond upon oxidation of $\text{Cu}(\text{II})$ to $\text{Cu}(\text{III})$. This strengthening can be satisfactorily explained on the basis of a molecular orbital scheme set up from an ESR spectroscopic study of $\text{Cu}(\text{Et}_2\text{dtc})_2$ ¹¹. 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.

⁶ This observation was also made by R. G. Fischer and J. P. Fackler, personal communication.

⁷ P. T. Beurskens, H. J. A. Blaauw, J. A. Cras and J. J. Steggerda, *Inorg. Chem.*, **7**, 805 (1968).

⁸ M. Bonamico, G. Dessy, C. Mariani and L. Zambonelli, *Acta Cryst.*, **19**, 898 (1965).

⁹ J. G. M. van der Linden and H. G. J. van der Roer, to be published.

¹⁰ J. A. McCleverty, *Progress Inorg. Chem.*, **10**, 49 (1968).

¹¹ M. J. Weeks and J. P. Fackler, *Inorg. Chem.*, **7**, 2548 (1968).

In contrast with a recent publication¹² we did not succeed in preparing $\text{Cu(III)I}_2(\text{Et}_2\text{dtc})$.

In order to complete our knowledge about $\text{CuX(R}_2\text{dtc)}^1 \dots \text{X} = \text{Cl, Br}$ we did react chloride ions with $\text{CuCl(Et}_2\text{dtc)}$ in CHCl_3 . This solution gives an ESR spectrum which is illustrated in Fig. 1. The four major

Fig. 1

lines are due to interaction of the spin of the unpaired electron with the nuclear spin of copper ($I_{\text{Cu}} = \frac{3}{2}$). 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 ($I_{\text{Cl}} = \frac{3}{2}$). At room temperature the isotropic g -value is 2.072, $a_{\text{Cu}} = 74$ gauss and $a_{\text{Cl}} = 8$ gauss. Two complex ions are considered for giving this signal: either $\text{CuCl}_2(\text{Et}_2\text{dtc})^-$ or $\text{CuCl}_2(\text{Et}_2\text{dtc})_2^{2-}$. The latter ion could be ruled out because addition of chloride ions to a solution of $\text{Cu(Et}_2\text{dtc})_2$ did not affect the original signal of $\text{Cu(Et}_2\text{dtc})_2$.

Addition of bromide ions to a solution of $\text{CuBr(Et}_2\text{dtc)}$ in CHCl_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 $\text{Cu(III)Br}_2(\text{Et}_2\text{dtc})$ in CHCl_3 (Fig. 2). It can be ascribed to $\text{CuBr}_2(\text{Et}_2\text{dtc})^-$, $g = 2.065$, $a_{\text{Cu}} = 2a_{\text{Br}} = 80$ gauss. The reduction by Br^- , which we assume to occur in the latter reaction, is also observed in the reaction of CuBr_2 with Br^- to CuBr_2^{-13} . The poor quality of the spectrum of the reaction mixture of Br^- and $\text{CuBr(Et}_2\text{dtc)}$ is possibly due to such a reduction process.

¹² Y. Nigo, I. Masuda and K. Shinra, Chem. Comm., 76 (1970).

¹³ J. J. Lingane and F. C. Anson, Anal. Chem., 28, 1871 (1956).

Fig. 2

The existence of $\text{CuX}_2(\text{Et}_2\text{dtc})^{0,-1}$ 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.

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