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Copper(III) and Nickel(III) Diethyldithiocarbamates. An Example of Copper(II) Disproportionation

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Despite the fact that solid dithiocarbamate metal complexes are well described in the literature [1–3], their oxidation reactions with chemical reagents have practically not been studied in solution though the electrochemical oxidation and reduction of nickel(II) and copper(II) have been detailed [4, 5]. We report here studies on oxidation of copper(II) and nickel(II) diethyldithiocarbamates with curpric and ferric salts in acetone or methylene chloride.

Experimental

Bis(diethyldithiocarbamates) of copper(II) and nickel(II) were prepared from metallic perchlorate or nitrate and sodium diethyldithiocarbamate in water, extracted and recrystallized in methylene chloride as previously described [1, 2]. Electronic spectra were recorded with a Beckman 5240 spectrophotometer. Magnetic susceptibilities were determined with a Curie–Cheneveau balance (T = 20 °C) using $CuSO_4 \cdot 5H_2O$ as calibrant.

Results and Discussion

Copper Compounds

The addition in either solvent of copper salts, $Cu(BF_4)_2 \cdot 6H_2O$ or $Cu(ClO_4)_2 \cdot 6H_2O$, to brown solutions of $Cu(Et_2dtc)_2$ yields green solutions.

With $Cu(BF_4)_2$ a green diamagnetic Cu(III) compound, $Cu(Et_2dtc)_2BF_4$ (Calcd for $C_{10}H_{20}BN_2F_4S_4Cu$: C, 26.88; H, 4.51; N, 6.27; Cu, 14.2. Found: C, 27.07; H, 4.49; N, 6.23; Cu, 14.5) was isolated after elimination of a crude brownish product. The break at 0.33 in the optical density mol–fraction plots (Job's method) (Fig. 1) and the 0.74 value of the ratio $[Cu(Et_2dtc)_2^+]/[Cu(Et_2dtc)_2]_{initial}$, calculated from the optical density at the break support the following reaction stoichiometry:

$$4Cu(Et_2dtc)_2 + 2Cu^{2+} \longrightarrow 3Cu(Et_2dtc)_2^+ + \text{'X'}$$

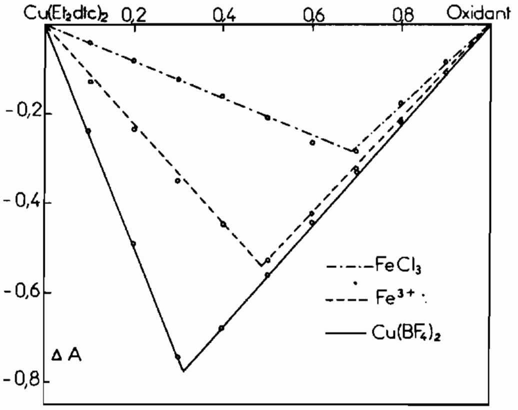

Fig. 1. Continuous variations method for bis(diethyldithiocarbamato)copper(II) and different oxidizing reagent solutions. Concentration 2 m*M*; cell width 0.5 cm; wavelength 500 nm.

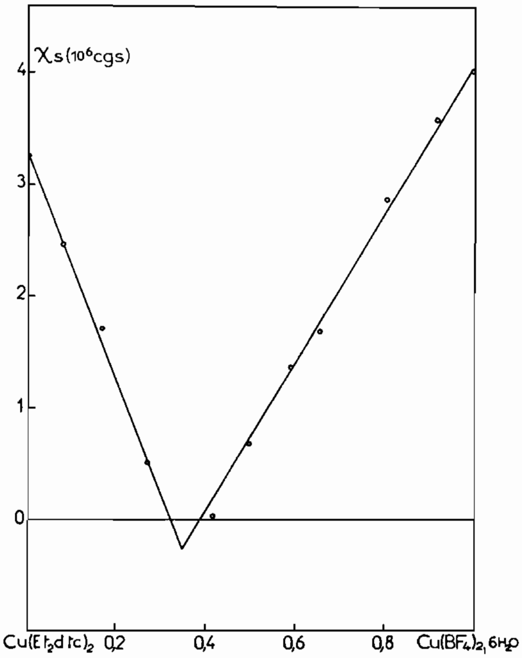

Fig. 2. Specific magnetic susceptibilities for the $Cu(Et_2dtc)_2$–$Cu(BF_4)_2 \cdot 6H_2O$ system *vs.* the mol fraction of $Cu(BF_4)_2 \cdot 6H_2O$.

The stoichiometry for the $Cu(Et_2dtc)_2$–$Cu(BF_4)_2$ reaction has been confirmed magnetically by an adaptation of Job's method (Fig. 2). The different mixtures were evaporated and the magnetism of the remaining solid product measured. The negative minimum at 0.33 indicates diamagnetic products, *i.e.* a low spin Cu(III) and a Cu(I) complex. This 'X' species can be formulated as '$Cu_3(Et_2dtc)_2BF_4$', a compound previously indicated [6].

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Analyses of the brownish product are in agreement with this formula. The reaction must then be written in the form of a very unusual copper(II) disproportionation:

$$4Cu^{II}(Et_2dtc)_2 + 2Cu^{II}(BF_4)_2 \longrightarrow 3Cu^{III}(Et_2dtc)_2BF_4 + Cu^{I}_3(Et_2dtc)_2BF_4$$

and not $CuR_2 + Cu^{2+} \rightarrow 2CuR^+$ as published by Regenass *et al.* [7].

When the oxidant is a ferric salt, the breaks in optical density *vs.* mol fraction plots (Fig. 1) depend on the nature of the salt and the reactions can be written for the perchlorate:

$$Cu(Et_2dtc)_2 + Fe^{3+} \longrightarrow Cu(Et_2dtc)_2^+ + Fe^{2+}$$

and for the chloride:

$$Cu(Et_2dtc)_2 + 2FeCl_3 \longrightarrow [Cu(Et_2dtc)_2][FeCl_4] + FeCl_2$$

Nickel Compounds

The oxidation of the dark green $Ni(Et_2dtc)_2$ solution by ferric salts, $(Fe(ClO_4)_3 \cdot 6H_2O$ or $FeCl_3$, gives a brown solution. The continuous variations method, studied in a 80%–20% CH_2Cl_2–acetone mixture, gives similar results to those obtained before on $Cu(Et_2dtc)_2$, with breaks respectively at 0.50 and 0.67 with $Fe(ClO_4)_3$ and $FeCl_3$.

The reactions are:

$$Ni(Et_2dtc)_2 + Fe^{3+} \longrightarrow Ni(Et_2dtc)_2^+ + Fe^{2+}$$

$$Ni(Et_2dtc)_2 + 2FeCl_3 \longrightarrow [Ni(Et_2dtc)_2][FeCl_4] + FeCl_2$$

in agreement with previous results [3]. It may also be noted that in pure acetone, the Ni(III) complex is not stable and slowly oxidises the solvent.

When the oxidizing reagent is a copper(II) salt, the reaction is more complicated but shows again a copper(II) disproportionation: addition of $Cu(ClO_4)_2$ in a $Ni(Et_2dtc)_2$ acetone solution gives at first a brown then a green colour. The electronic spectra are characteristic respectively for $Cu^{II}(Et_2dtc)_2$ and $Cu^{III}(Et_2dtc)_2^+$ and the breaks at 0.5 and 0.6 on Job's curves (Fig. 3) agree with an exchange between Ni^{2+} and Cu^{2+} cations followed by the oxidation of $Cu(Et_2dtc)_2$, described before.

The two steps are:

$$4Ni(Et_2dtc)_2 + 4Cu^{2+} \xrightarrow{ClO_4^-} 4Cu(Et_2dtc)_2 + 4Ni^{2+}$$

$$\underline{4Cu(Et_2dtc)_2 + 2Cu^{2+} \xrightarrow{ClO_4^-} 3Cu(Et_2dtc)_2^+ + \text{‘}Cu_3(Et_2dtc)_2ClO_4\text{’}}$$

$$4Ni(Et_2dtc)_2 + 6Cu^{2+} \xrightarrow{ClO_4^-} 3Cu(Et_2dtc)_2^+ + \text{‘}Cu_3(Et_2dtc)_2ClO_4\text{’} + 4Ni^{2+}$$

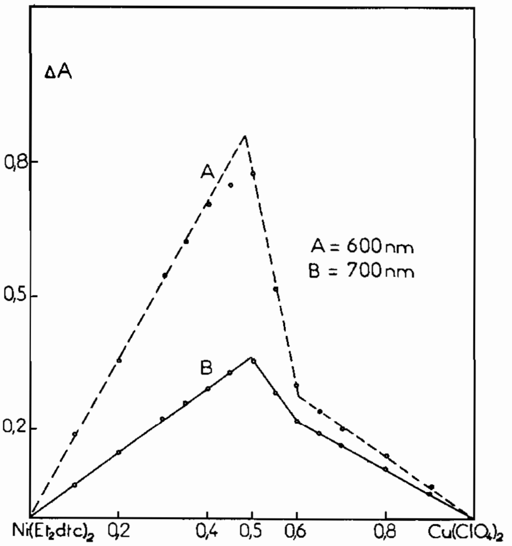

Fig. 3. Continuous variations method for the $Ni(Et_2dtc)_2$–$Cu(ClO_4) \cdot 6H_2O$ system. Concentration 2 m*M*; cell width 1 cm; wavelengths (A) 600 nm, (B) 700 nm.

Conclusion

This study has shown that oxidation of Cu(II) and Ni(II) diethyldithiocarbamates by chemical reagents goes through a common monoelectronic process, but a very unusual disproportionation of copper(II) in to copper(III) and copper(I) has been proved; the formation of a very stable copper(I) complex, probably a cluster, may be the driving force for this reaction.

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