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Reaction of Copper(II) tetrafluoroborate with Cobalt(III) and Manganese(III) dithiocarbamates

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In our general study of the solution chemistry of transition metal dithiocarbamates, we have already shown a peculiar behaviour of copper(II) resulting in a disproportionation into copper(III) and copper(I) [1]. We report here the reactions of copper(II) tetrafluoroborate with several cobalt(III) and manganese(III) dithiocarbamates.

Reaction with Cobalt(III) Tris Dithiocarbamates

Six CoL_3 compounds have been prepared, in CH_2Cl_2, by reacting cobalt(II) perchlorate hexahydrate with the corresponding dithiocarbamate sodium salt with a 1/3 metal/ligand ratio [2]. Recrystallisation was done in CH_2Cl_2 or $CHCl_3$. The metal, carbon, hydrogen and nitrogen contents were checked: the compounds are: $Co(Me_2dtc)_3$, $Co(Et_2dtc)_3$, $Co(Bz_2dtc)_3$, $Co(MePhdtc)_3$, H_2O, $Co(pyrrdtc)_3$, $CHCl_3$ and $Co(Mepipdtc)_3$, $3H_2O$ where the ligand abbreviations have their usual meaning and where pyrrdtc means pyrrolidine dithiocarbamate and Mepipdtc N-methyl piperazine dithiocarbamate.

Only the compounds with L = Et_2dtc and MePhdtc were soluble enough to undertake a solution study in a mixture of dichloromethane and acetone (80–20%). The acetone was necessary to solubilize $Cu(BF_4)_2$. The continuous variations method shows a sharp break at 0.33 (Fig. 1) indicating a reaction between 2 moles of CoL_3 and 1 mole of $Cu(BF_4)_2$. Therefore we suggest the following reaction:

$$2CoL_3 + Cu(BF_4)_2 \longrightarrow [Co_2L_5]BF_4 + CuLBF_4$$

Such dinuclear cobalt complexes were first reported by Hendrickson *et al.* [3, 4]. We have isolated and characterized the analogous dark-green diamagnetic solids for the six ligands when using a cobalt/copper ratio of 2/1 in support of the proposed reaction. The paramagnetic $CuLBF_4$ solids are difficult to obtain and were only isolated for L = Et_2dtc and pyrrdtc.

Reaction with Manganese(III) Tris Dithiocarbamates

The MnL_3 compounds with L = Et_2dtc, Bz_2dtc, MePhdtc and pyrrdtc have been prepared as cobalt(III) tris dithiocarbamates [2]. Two breaks in the optical density mole fraction plots (Job's method) are obtained: one at 0.6, stable in time (at least 24 hours), and another one between 0.3 and 0.5, unstable in time and depending on L. The break at 0.6 is in agreement with the reaction of 2 MnL_3 with 3 $Cu(BF_4)_2$. One of the reaction products is a copper(III) compound CuL_2BF_4 which has been analytically characterized for each ligand. All of the above compounds are diamagnetic. Practically all the copper and dithiocarbamate ligands are recovered in the copper(III) complex. The fact that the second break is not stable can be attributed to the formation of a manganese(II) product which is spontaneously oxidised into Mn(III) in the presence of dithiocarbamate in a non deaerated solvent [5–7]; this compound is then able to reoxidise new amounts of $Cu(BF_4)_2$.

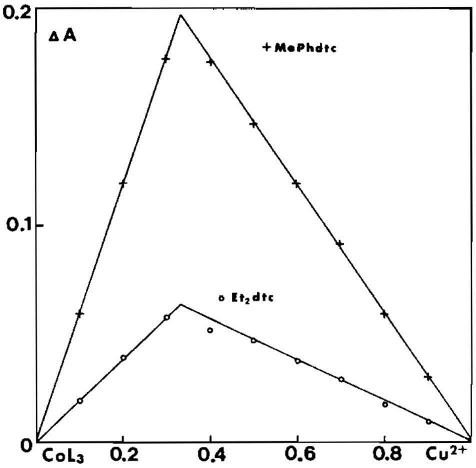

Fig. 1. Continuous variations method for the CoL_3-$Cu(BF_4)_2 \cdot 6H_2O$ system. Concentration 10^{-3} *M*; cell width 1 cm; Wavelengths 625 nm, L = Et_2dtc; 600 nm, L = MePhdtc.

Conclusion

A very different behaviour is observed between Co(III) tris dtc and Mn(III) tris dtc when reacted with copper(II) tetrafluoroborate.

In the first case, the high affinity of copper(II) for dtc ligands is able to withdraw a bidentate ligand from an octahedral stable cobalt(III) complex, inducing therefore the formation of the dinuclear compound. This reaction is a much easier way to prepare $Co_2L_5{}^+BF_4{}^-$ than the one described previously [3].

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In the second case, the d^4 Mn(III) tris dtc is a good oxidising agent toward copper(II) giving a copper(III) complex.

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