

## Notes

### ON COBALT(II)N,N-DIETHYLDITHIOCARBAMATE

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A recent article by D'Ascenzo and Wendlandt [1] in this journal describes the preparation and thermal properties of an N,N-diethyldithiocarbamate ( $\text{Et}_2\text{dtc}$ ) complex of cobalt(II), namely  $\text{NaCo}(\text{Et}_2\text{dtc})_3$ . We were particularly interested in this complex since we have been trying for some time, so far without success, to synthesize diethyldithiocarbamate complexes of divalent first row transition metals (Cr–Zn(II) inclusive) of the type  $\text{M}(\text{Et}_2\text{dtc})_3^-$  with alkali metal or tetra-alkyl ammonium cations. We find this cobalt(II) complex even more significant in the light of a number of observations [2–4] that aqueous solutions of cobalt(II) are spontaneously oxidized to cobalt(III) in the presence of  $\text{NaEt}_2\text{dtc}$ , even when oxygen is rigorously excluded [5].

We therefore regarded the formulation of the product as  $\text{NaCo}(\text{Et}_2\text{dtc})_3$  with some scepticism and repeated the experimental procedure [1] for its preparation. From several different preparations we obtained the same dark green solid (m.p. 252–254°C) which we therefore assume to be identical with the product obtained by D'Ascenzo and Wendlandt [1]. This corresponds in all respects to the well known [6] complex of cobalt(III),  $\text{Co}(\text{Et}_2\text{dtc})_3$ . Thus, its solution (in methylene chloride) and reflectance spectrum which shows a band at  $15.500\text{ cm}^{-1}$  ( $\epsilon \sim 600$ ) and a shoulder at  $20.800\text{ cm}^{-1}$  is in good agreement with the published [4] spectrum of  $\text{Co}(\text{Et}_2\text{dtc})_3$ . The spectrum is also extremely similar to that of the complex  $\text{Co}(\text{S}_2\text{COC}_2\text{H}_5)_3$ , which can be made from cobalt(II) salts and potassium ethylxanthate [7]. The dithiocarbamate complex is strictly isomorphous with the black  $\text{Fe}(\text{Et}_2\text{dtc})_3$  [8]. Its mass spectrum (direct inlet, 220°C, 80 eV) shows very strong peaks at  $m/e$  503, which is the base peak and which corresponds to the molecular ion  $\text{Co}(\text{Et}_2\text{dtc})_3^+$ , and at 355 and 207 which correspond to the loss of one and two  $\text{Et}_2\text{dtc}$  units respectively, together with a large number of smaller peaks below  $m/e$  200. The metal analysis found by D'Ascenzo and Wendlandt of 11.3 is reasonably close to the value required for  $\text{Co}(\text{Et}_2\text{dtc})_3$  of 11.69% particularly if the compounds were not completely free of water, or possibly, contaminated with small amounts of sodium chloride.

We were also interested in the products listed as  $\text{Ni}(\text{Et}_2\text{dtc})_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Cu}(\text{Et}_2\text{dtc})_2 \cdot 1.5\text{H}_2\text{O}$ . In the course of our studies [9] on reactions between metal(II) bipyridyl and *o*-phenanthroline salts and  $\text{NaEt}_2\text{dtc}$  in aqueous solutions

we have observed on numerous occasions the formation of both  $\text{Ni}(\text{Et}_2\text{dtc})_2$  and  $\text{Cu}(\text{Et}_2\text{dtc})_2$ . These complexes can be dried under vacuum and are readily identified by X-ray powder diffraction and infrared methods. In no cases have we observed these products associated with water molecules.

Finally, the title of the paper [1] lists the metal dithiocarbamate complexes as "new volatile metal chelates". We would point out that Malatesta [10] noted the remarkable stability and volatility of dithiocarbamate complexes  $[\text{Ni}(\text{Et}_2\text{dtc})_2$  and  $\text{Co}(\text{Et}_2\text{dtc})_3]$  in 1940.

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