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The Preparation of Molybdenum Dialkyldithiocarbamates using Oxidative decarbonylation of Tricarbonyl(η^6-1,3,5-cycloheptatriene)molybdenum

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Introduction

A brief account [1] of the preparation of Mo(III) dialkyldithiocarbamates using the oxidative decarbonylation of tricarbonyl(η^6-1,3,5-cycloheptatriene)-molybdenum has been called in question by some workers [2, 3]. Indeed, one group doubts whether tris complexes can be prepared by this method, as in spite of considerable effort they only obtained Mo(IV) dithiocarbamates, the properties of which have been well established [4]. In this note, we describe in detail the preparation of Mo(III) diethyldithiocarbamate, and show how Mo(IV) diethyldithiocarbamate can be obtained by a simple variation of the preparative method. Thus, all of the previous results can be reconciled, and a dilemma resolved [5, 6].

Method

Mo(III) diethyldithiocarbamate was prepared by refluxing freshly sublimed tricarbonyl(η^6-1,3,5-cycloheptatriene)molybdenum (0.01 mol) with recrystallized tetraethylthiuram disulphide (0.015 mol) in 100 ml of dry freshly distilled toluene under nitrogen in daylight. After *ca.* fifteen minutes, the original pale brown solution was noticeably darker and a reddish brown solution soon resulted. The reaction was monitored using the carbonyl stretching region, until no carbonyl absorptions were apparent (*ca.* 4 hr). The volume was reduced under vacuum until a few crystals were obtained, filtered under nitrogen, and the filtrate agitated strongly with 500 ml dry deoxygenated hexane. The red brown product (A) was filtered off and dried (80% yield). *Anal.* Found: C, 33.24; H, 5.61; N, 7.61; S, 35.16; Mo, 17.8%: Calcd. C, 33.33; H, 5.59; N, 7.77; S, 35.53; Mo, 17.8%. The melting point is 110–116 °C (with decomposition).

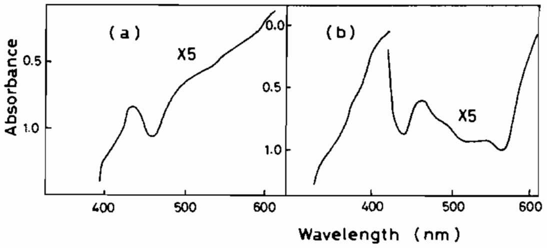

Fig. 1. U.V.–Visible spectra in benzene solution of (a) Mo(III) diethyldithiocarbamate 0.089 mM l^{-1}/10 mm cell, and (b) Mo(IV) diethyldithiocarbamate 0.093 mM l^{-1}/10 mm cell. X1 and X5 indicate normal and five fold absorption expansion respectively.

Molybdenum(IV) diethyldithiocarbamate (B) was prepared by a similar procedure except that the reaction flask was kept in the dark. In contrast to A, the tetrakis powder was recrystallized easily from dry deoxygenated acetone, yielding well-formed black crystals product B, in 60% yield, melting point 144–146 °C (with decomposition). *Anal.* Found: C, 34.62; H, 6.09; N, 7.36; S, 36.94; Mo, 13.5%; Calcd. C, 34.88; H, 5.81; N, 8.13; S, 37.21; Mo, 13.95%).

Discussion

Thus prepared, products A and B have characteristically different melting points. Although they are similar in colour in the powdered state, their UV/visible spectra in benzene solution are quite different, as shown in Fig. 1. Both products are stable for at least two months if stored under nitrogen.

References

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