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The Derivation of $MoOCl_3(PrCN)_2$ and $Mo_2Cl_9(PrCN)_4 \cdot 4H_2O$ from $MoCl_4(PrCN)_2$

C. A. McAULIFFE

Departments of Chemistry of Auburn University, Auburn, Ala. 36830, U.S.A. and University of Manchester Institute of Science and Technology, Manchester M60 1QD, U.K.

and A. WERFALLI

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD, U.K.

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There has been considerable interest in the chemistry of the metal nitrile complexes [1, 2] for two particular reasons, *viz.* the alkylcyanide is isoelectronic with molecular nitrogen and because these complexes can serve as convenient precursors for the production of a wide range of coordination compounds. It is for the latter reason that we are interested in $MoCl_4(PrCN)_2$ for, like the coordinated tetrahydrofuran in $MoOCl_3(THF)_2$ [3], the organic species is readily substituted on reaction of these soluble materials with a wide variety of ligands.

During our investigations of molybdenum(IV) coordination compounds [4, 5] we have frequently handled $MoCl_4(PrCN)_2$ and have noted some interesting features which we feel warrant the attention of workers in this area. The complexes $MoCl_4(RCN)_2$ (R = Me, Et, Pr) are conveniently prepared by reacting $MoCl_5$ with an excess of the appropriate alkyl cyanide [6], and some characterisation data has been reported [6, 7].

We note that $MoCl_4(PrCN)_2$ appears to hydrolyse rapidly in moist air, changing from dark brown to green and finally to a black oily substance with the loss of hydrogen chloride. A sample of $MoCl_4(PrCN)_2$ sealed under dry dinitrogen showed no change in colour even after one year, but a second sample sealed under moist air showed interesting colour changes, the surface of the solid becoming black and oily but the interior changed from brown to emerald green. Storing $MoCl_4(PrCN)_2$ under dry air shows also the change to emerald green. These simple tests indicate that $MoCl_4(PrCN)_2$ absorbs moisture to give a black oil, but dry air gives a green oxidation product. E.p.r. spectra shows only a trace of molybdenum(V) in the sample stored under dinitrogen, an appreciable amount in the black oil/emerald green mixture and that the emerald green compound alone is genuine molybdenum(V).

The reaction of $MoCl_4(PrCN)_2$ in dry toluene with molecular oxygen results in the formation of the emerald green solid, elemental analysis of which indicates the formula $MoOCl_3(PrCN)_2$ (Found: C, 26.7; H, 4.7; Cl, 29.3; Mo, 28.9%. Calculated; C, 26.9; H, 4.7; Cl, 29.8; Mo, 27.0%). This extremely moisture sensitive complex exhibits ν(CN) at 2280 cm^{-1} and ν(Mo=O) at 983 cm^{-1}. The room temperature magnetic moment, $\mu_{eff} = 1.70$ BM, is very close to the spin-only value calculated for molybdenum(V), d^1, 1.73 BM. The e.p.r. spectrum at room temperature indicates the presence of only one species, $g = 1.949$, $A = 55$ G. The physical properties of $MoOCl_3(PrCN)_2$ prepared in this way are in close agreement with those reported by Edwards [8] who obtained this complex by direct reaction of $MoOCl_3$ with PrCN.

The extreme sensitivity to moisture and oxidation of $MoCl_4(PrCN)_2$ may be guaged from the fact that stirring this complex for 4 days in what we had believed to be dry toluene and under dinitrogen caused the colour to slowly change to red-brown. Analysis of this material indicates that it has the empirical formula $Mo_2Cl_9(PrCN)_4 \cdot 4H_2O$ (Found: C, 22.5; H, 4.2; N, 6.6; Cl, 36.9%. Calculated: C, 22.4; H, 4.2; N, 6.5; Cl, 37.1%).

The infrared spectrum of $Mo_2Cl_9(PrCN)_4 \cdot 4H_2O$ exhibits a broad band between 3500–3200 cm^{-1} and a medium band *ca.* 1600 cm^{-1} which are absent in the spectrum of the $MoCl_4(PrCN)_2$ complex. These bands are assigned to lattice water [9]. The ν(CN) band is present in the same position as in the spectrum of $MoCl_4(PrCN)_2$.

Solid $Mo_2Cl_9(PrCN)_4 \cdot 4H_2O$ is readily soluble in dry nitromethane, in contrast to $MoCl_4(PrCN)_2$, which is very sparingly soluble in this solvent. In nitromethane $Mo_2Cl_9(PrCN) \cdot 4H_2O$ behaves as a 1:1 electrolyte [10], $\Lambda = 80$ ohm^{-1} cm^2 mol^{-1}, and thus we tentatively formulate this complex as $[MoCl_4(PrCN)]^+[MoCl_5(PrCN)_2]^- \cdot 4H_2O$. The e.p.r. spectrum in dichloromethane at room temperature indicates the presence of an appreciable amount of molybdenum(V) species relative to the $MoCl_4(PrCN)_2$ starting material.

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