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A Novel Single Step Synthesis of Dinitrosylmolybdenum Derivatives directly from Molybdate(VI) in Aerobic and Aqueous Media

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During the past several years a large number of papers have appeared in the literature concerning the synthesis of the derivatives of dinitrosylmolybdenum moiety [1, 2]. Regarding synthetic approaches so far known, two broad based reactions which are followed are the oxidative reaction of nitrosyl salts on molybdenum hexacarbonyl or its carbonyl derivatives [1] and the reductive reaction of nitric oxide on molybdenum pentachloride [2]. Whichever of the above procedures used, the reaction is obviously carried out in dry oxygen free atmosphere.

Herein we report a novel, one-step generation of dinitrosylmolybdenum moiety characterised by isolating some of its known derivatives by reductive nitrosylation of molybdate(VI) by hydroxylamine in aqueous–aerobic conditions.

Results and Discussion

In strong alkaline medium, the use of hydroxylamine as a nitrosylating reagent is classically known [3] and recently its use as such has been demonstrated even in neutral and slightly acidic conditions [4]. In the context of the function of molybdenum as a redox catalyst in living processes [5] its reduction from hexavalent oxidation state by hydroxylamine to give $\{MoO\}^{3+}$ [6], $\{Mo(NO)\}^{3+}$ [4] and $\{Mo(NO)\}^{+}$ [7] in various pH conditions is noteworthy. The stoichiometric ratio molybdate(VI): hydroxylamine used to get optimum yield of $\{Mo(NO)\}^{n+}$ (n = 1 or 3) is 1:3 [4, 7]. However, when four equivalent of hydroxylamine is used instead of three in slightly basic (DMF) or acidic (pyridine in excess of acetic acid) media, the formation of $\{Mo(NO)_2\}^{2+}$ group is achieved.

To follow the course of reaction, 2,2′-dipyridyl in concentrated hydrochloric acid was used to trap the intermediate product formation with increasing reaction time. At 15 min reaction time the dipyridyl product thus isolated showed a strong i.r. band at 1695 cm^{-1} which is characteristic of coordinated nitric oxide in the $\{Mo(NO)\}^{3+}$ moiety [8]. After 30 min of reaction the isolated dipyridyl product showed two more peaks at 1760 and 1650 cm^{-1} and after 45 min of reaction the product showed the absence of the peak at 1695 cm^{-1} but retained the later two peaks. The appearence of the later two peaks suggests the formation of $\{Mo(NO)_2\}^{2+}$ moiety [1]. Though the dipyridyl products were always contaminated with oxomolybdenum(V) compound yet the formation of dinitrosyl-molybdenum moiety only after the mononitrosylation stage is clearly seen. This stepwise nitrosylation is very similar to that reported on molybdenum pentachloride with nitric oxide [2]. The facile conversion of the $\{Mo(NO)\}^{3+}$ into the $\{Mo(NO)_2\}^{2+}$ moiety either in the presence of excess of hydroxylamine or nitric oxide [2] can be explained by the formation of penta- and hexa-coordinated compounds of the $\{Mo(NO)\}^{3+}$ moiety [2, 8]. These compounds contain formally '14- and 16-electron configurations' respectively and hence tend to change to '18-electron configuration' with the formation of more stable dinitrosylmolybdenum derivatives.

Anker *et al.* [1f] have suggested that the methods used by Cotton and Johnson [1a, b] is stereospecific to give the *trans*-halo *cis*-ligand (L) isomer of $[Mo(NO)_2L_2X_2]$*. However, X-ray crystallograpy indicates *trans*-ligand *cis*-chloro arrangements for $Mo(NO)_2(C_6H_5)_3P_2Cl_2$ synthesized by this stereospecific method [9]. This compound shows two MoCl stretching vibrations at 346 and 318 cm^{-1} in the far-i.r. spectrum [1b] which can be attributed to the asymmetric and symmetric ν(Mo–Cl) for the *cis* attachment of the chloro groups in the compound. The compound $[Mo(NO)_2(C_5H_5N)_2Cl_2]$ prepared by our method shows only one ν(Mo–Cl) at 312 cm^{-1} suggesting *trans*-chloro attachments in this isomer.

Thus the present method of synthesis is a stereospecific one and can be operated using a simple set-up with reasonable time involvement. However, the yield is only 30% of the molybdate(VI) used and this remained insensitive even by carrying out all operations in an oxygen-free atmosphere. Some other representative derivatives prepared by this method are presented in the experimental section.

Experimental

Preparation of the Complexes

$[Mo(NO)_2(C_5H_5N)_2Cl_2]$

Ammonium heptamolybdate (1.0 g) and hydroxylamine hydrochloride (1.7 g) were taken in pyridine–

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*In $\{Mo(NO)_2\}^{2+}$ the attachment of the nitrosyl groups is *cis* (see ref. 1, 9).

glacial acetic acid mixture (7 ml: 10 ml) and slowly digested at 105 °C for an hour to get a greenish brown solution. 20 ml of concentrated hydrochloric acid was added into it to get a clear green solution which was poured into 250 ml of boiling water. The resulting solution was kept just below boiling for an hour and the green product thus formed was allowed to settle overnight. It was filtered off, washed with diluted hydrochloric acid and finally with water and air dried. The lemon green product (yield 0.44 g, 24%) melts at 296 °C (decomp.) (for the other stereoisomer lit. [1a] d.c. 150 °C). *Anal.* Found C 31.27, H 2.85, N 21.88, Cl 18.24; calc. for $C_{10}Cl_2H_{10}MoN_4O_2$: C 31.16, H 2.59, N 21.80, Cl 18.44. ν(NO) 1780s, ν(NO) 1665s.

[Mo(NO)₂(S₂CNEt₂)₂]

Ammonium heptamolybdate (1.0 g) and hydroxylamine hydrochloride (1.7 g) were heated in 10 ml of DMF at *ca.* 90 °C for an hour to get a green solution. It was cooled and a solution of sodium diethyldithiocarbamate trihydrate (2.0 g) in water (200 ml) was added with stirring (room temperature). A brown precipitate thus formed was allowed to settle for an hour, filtered off, washed with water and the diethyl ether soluble material was recrystallised from methanol. The golden-brown product (yield 1.0 g, 38%) melts at 126–127 °C (lit. [1d] m.p. 127–128 °C). *Anal.* Found: C 27.00, H 4.56, N 12.12; calc. for $C_{10}H_{20}MoN_4O_2S_4$: C 26.54, H 4.42, N 12.38. ν(NO) 1745s, ν(NO) 1630s.

[Mo(NO)₂(acac)₂]

Similarly, into the green solution in DMF, obtained as described above, a solution of acetylacetone (2 ml) in 15 ml methanolic KOH (1.3 g) was added and the resulting mixture was refluxed for an hour and poured into 250 ml of boiling water. On keeping at *ca.* 90 °C for 30 min the desired compound started separating as solid. The mixture was allowed to cool and the precipitate was filtered off, washed with water and air dried. The crude product was purified by column chromotography (silica gel) using benzene as eluent. The green product (yield 0.6 g, 30%) melts at 156 °C (lit. [1d] m.p. 146–147 °C). *Anal.* Found: C 34.75, H 3.87, N 8.00; calc. for $C_{10}H_{14}MoN_2O_6$: C 33.89, H 3.95, N 7.90. ν(NO) 1763s, ν(NO) 1645s; ^{1}H n.m.r. spectrum ($CDCl_3$): τ 4.40 (s, 2H, CH), 7.80 (s, 6H, CH_3), 8.02 (s, 6H, CH_3) (lit. [1d] identical values for i.r. stretchings and n.m.r. resonances). The elemental analyses were performed by Beller Microanalytical Laboratory, Göttingen, FRG. The infrared spectra were recorded in Nujol mulls using a PE 257 spectrometer and in the far-infrared using a PE 180 spectrometer with CsBr plates and polyethylene discs, respectively. The nmr spectra were recorded on a Varian Associates HA 100 spectrometer using TMS as standard (τ 10.00).

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