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Reaction of a Hydroxylamido(N,O) Ligand to a Side-on Coordinated Oximato Ligand. Preparation of $[Mo(NO)\{ONC(CH_3)_2\}(NCS)_4]^{2-}$

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The high concentration of Mo in sea water [1] (higher than that of any other transition metal) and the observation of Egami [2] that a variety of amino acids are formed from formaldehyde and hydroxylamine (relevant starting materials according to the investigations of Oró [3]) in a 'modified sea medium' enriched with MoO_4^{2-}, indicate the possible importance of complexes of this bio-metal as catalysts in prebiotic processes. Substances dissolved in the earth's primeval atmosphere are regarded as the initial materials for the development of life [4]. Recent investigations demonstrate [5] that complexes with $\{MoNO\}^4$ configuration are formed in neutral or acidic molybdate solutions in the presence of hydroxylamine and other ligands. However, solutions containing these complexes with hydroxylamido-ligands react with formaldehyde to form HCN [6], which is generally considered to be one of the more important precursors of biological materials on the primitive earth. The importance of complexes with $\{MoNO\}^n$ configuration (n = 4,5,6) for the chemistry of the lower valence states of Mo in aqueous medium as well as the great formation tendency and stability of those with n = 4 were already mentioned by us [7].

We report here a relevant reaction of the hydroxylamido ligand in an $\{MoNO\}^4$ complex with acetone to form a side-on coordinated and until now, not much characterized oximato ligand [8].

Results and Discussion

$[(C_6H_5)_4P]_2[Mo(NO)\{ONC(CH_3)_2\}(NCS)_4]$ (1) is formed by the reaction of $[(C_6H_5)_4P]_2[Mo(NO)(ONH_2)(NCS)_4]$ (2) [9] with acetone (see Experimental section) and has been characterized by an X-ray structure analysis (Syntex $P2_1$; Mo-K_α; space group $P\bar{1}$; $a = 9.456(4)$, $b = 14.021(6)$, $c = 21.361(10)$ Å, $\alpha = 87.09(4)$, $\beta = 76.60(3)$, $\gamma = 81.62(3)°$; $Z = 2$; $\rho_c = 1.35$ g cm^{-3}; 5469 observed reflections; $R_w = 0.077$).

Reactions of the hydroxylamido ligand have pratically not been studied. The ligands in the complex anion form a distorted pentagonal-bipyramid (Fig. 1). Until now, relatively few nitrosyl complexes with this geometry are known [10]. The bond distances and the interbond angles in the MoNO group are comparable to those in other complexes with $\{MoNO\}^4$ configuration [5]. The Mo–N bond distance of the axial NCS group is longer (2.192 Å) than those in equatorial positions (average: 2.114 Å), which is due to the *trans*-effect of the nitrosyl ligand. (1) is interesting, particularly because until now, very few complexes with a side-on bonded oximato ligand were known [8]. The geometrical data and the nature of its coordination are given in Figure 1. The C–N and N–O bonds could roughly be viewed as double and single bonds, respectively. (For the relation to the corresponding compound with the isomeric carboxamido ligard [11], see [12]).

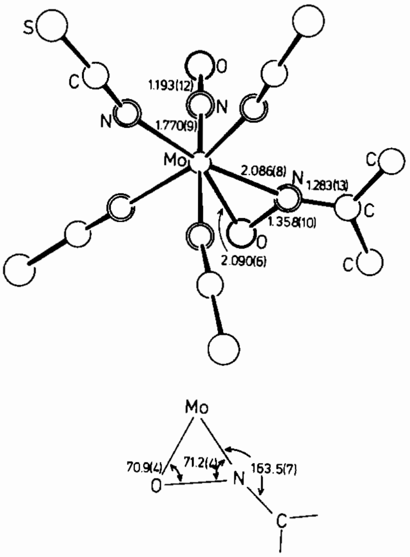

Fig. 1. Molecular structure of $[Mo(NO)\{ONC(CH_3)_2\}(NCS)_4]^{2-}$.

A possible prebiotic relevance of the reaction follows from the fact that $\{MoNO\}^4$ complexes containing hydroxylamido ligands react with formaldehyde in aqueous solution to form HCN [6]. Perhaps, the generated formoximato ligand decomposes to yield HCN and H_2O.

Experimental

Preparation of $[(C_6H_5)_4P]_2[Mo(NO)\{ONH_2\}(NCS)_4]$

A solution of 2.4 g (10 mmol) $Na_2MoO_4 \cdot 2H_2O$ and 9.7 g (100 mmol) KSCN in 40 ml H_2O, to which 2.1 g (30 mmol) $NH_2OH \cdot HCl$ was added with stirring, was heated to 80 °C for about 1 h. After acidification

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with 0.5 ml concentrated hydrochloric acid, an aqueous solution (50 ml) of 7.5 g (20 mmol) $[(C_6H_5)_4P]Cl$ was added. The yellow precipitate was filtered, washed with water and methanol and dried over $CaCl_2$. After extracting the dry product with CH_2Cl_2 the solvent was evaporated. The yellow glass-like residue was recrystallised from $CHCl_3$. (Yield: 3.6 g).

Preparation of $[(C_6H_5)_4P]_2[Mo(NO)\{ONC(CH_3)_2\}(NCS)_4]$

A solution of 2.2 g (2 mmol) $[(C_6H_5)_4P]_2[Mo(NO)(ONH_2)(NCS)_4]$ in 20 ml acetone was refluxed for 1 h. After evaporation of half of the solvent as much 1:1 mixture of ether and ethanol was added, as was needed to initiate precipitation. The yellow crystalline compound precipitated after some hours. (Yield: 1.5 g).

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