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The Carbamido Moiety as Fixed and Side-on Bonded Ligand. X-Ray Crystal and Molecular Structure of $[(C_6H_5)_4P]_2[Mo(NO)(OCN(CH_3)_2)(NCS)_4]$

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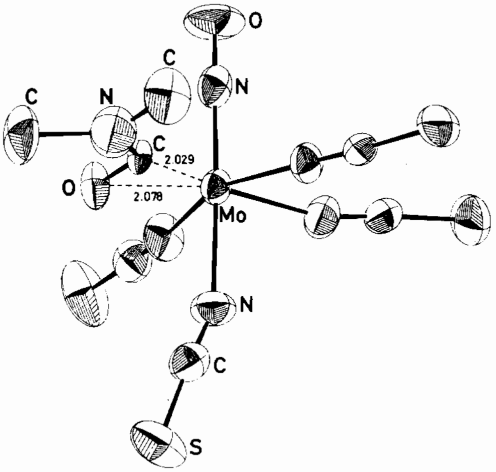

Figure. Molecular structure of $[Mo(NO)(OCN(CH_3)_2)(NCS)_4]^{2-}$ (without H-atoms). N–O 1.179(8); Mo–(NO) 1.767(6); C–S 1.648(8) (trans); C–N 1.128(9) (trans); Mo–N 2.188(6) (*trans*) (NCS group); C–S 1.627(7) (eq., av.); C–N 1.137(9) (eq., av.); Mo–N 2.114(6) (eq., av.) (NCS groups); C–O 1.322(7); C–N 1.240(10); N–C (av.) 1.553(17) A; OCN 123.96°(60)°; CNC (av.) 121.77°(69)°; $(CH_3)N(CH_3)$ 116.45(66)° (molybdenum–oxygen and –carbon distances, see figure).

The activation of molecules and the fixation of reactive and coordinatively unsaturated intermediates by transition metal complexes are actual problems of chemistry [1]. Results from this field are important for the homogeneous catalysis, the synthesis of organic compounds and for bioinorganic chemistry. Here it will be shown that the carbamido moiety $\{OCN(CH_3)_2\}$ can be fixed and can act as side-on bonded ligand in transition metal complexes.

$[(C_6H_5)_4P]_2[Mo(NO)(OCN(CH_3)_2)(NCS)_4]$ (ν-(NO) = 1676 cm^{-1} (nujol mull); ^{1}H NMR(CH_3): δ 2.27 and 2.19 ppm ($(CH_3)_4Si$, CD_2Cl_2)) which was thought according to the analysis [2] to contain the complex anion $[Mo(NO)(DMF)(NCS)_4]^{2-}$ was obtained using the method described [2] (in this paper [2] the preparation of several transition metal nitrosyl complexes was reported whereby the properties of the mentioned complex could not be understood). But because of the diamagnetism of the compound an unusual novel type of coordination with an 'activated DMF' had to be assumed which could only be explained by the crystal and molecular structure.

Crystals of $[(C_6H_5)_4P]_2[Mo(NO)(OCN(CH_3)_2)(NCS)_4]$ were examined by X-ray diffraction methods. Structural details may be seen from the Figure. ($C_{55}H_{46}N_6O_2P_2S_4Mo$, M = 1109.1, triclinic, space group $P\bar{1}$, a = 9.428(2), b = 13.973(2), c = 21.222(4) Å, α = 89.20(2), β = 77.72(1), γ = 81.66(1)° (λ = 0.7107 Å for Mo-K_α); U = 2702.2(8) Å^3, Z = 2, D_c = 1.36 g cm^{-3}, μ = 5.0 cm^{-1} for Mo-K_α). The structure was solved by the heavy atom method. Least squares refinements (with the phenyl carbon atoms refined independently) converged at R = 0.073 for 7525 independent reflections [$4.0° \leqslant 2\theta \leqslant 54°$; $I > 1.96\sigma(I)$] measured on a four-circle diffractometer with Mo-K_α radiation.

The ligands around molybdenum form a distorted pentagonal bipyramid. The outstanding feature is the side-on bonded carbamido moiety (CAD) (formed by carbon–hydrogen bond cleavage of DMF), which may be important for synthetic aspects as an activated species. This may be compared with another unusual feature of the Mo-complex $[Mo(SCNPr_2)(S_2CNPr_2)S]$ which contains beside the dithiocarbamate thiocarbamido ligands $\{R_2NCS\}$ (TCAD) [3]. The geometry of coordination of the thiocarboxamido and carboxamido ligands to molybdenum and comparable interatomic distances and bond angles within the ligands are practically equal. The carbon atom is very strongly bonded to molybdenum as in the TCAD complex. This can be interpreted according to the carbene character of the Mo–C bond [3]. The change of the CO and CN bond length in comparison to DMF [4] is as expected. TCAD ligands also occur in $[(CH_3)_2NCS)NiCN(CH_3)_2SCN(CH_3)_2S]^+$ and probably in a few carbonyl complexes like $[C_5H_5Mo(CO)_2(SCN(CH_3)_2)]$ [5].

The complex contains the moiety $\{Mo(NO)(OCN(CH_3)_2)\}^{2+}$ with the configuration $\{Mo(NO)(OCN(CH_3)_2)\}^4$, which explains the diamagnetism. As NO and CAD are not innocent ligands the discussion of oxidation states of the central atom is rather arbitrary (all other structural features as the N-coordination and the *trans*-effect should not be discussed here). The results of this note should be important for the understanding of the fixation of reactive and unsaturated ligands with a relevance to their use for synthetic chemistry.

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