Inorganica Chimica Acta, 28 (1978) L165–L166
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The Structures of two Aryldiazenido-Complexes of Molybdenum of the Type [Mo(N_2Ar)(S_2CNMe_2)$_3$]

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Received April 4, 1978

We have recently prepared a series of organodiazenido-complexes of molybdenum of the general formula [Mo(N_2R)(S_2CNMe_2)$_3$] [1] and have studied their fluxionality by ^{1}H n.m.r. spectroscopy [2] and their redox properties [3]. We found that where R is a substituted aryl group C_6H_4X, the fluxionality and redox behaviour could be related to the Hammett σ function indicating an inductive release of electrons by S to Mo, although formally a mesomeric release is more plausible. We also found that the redox behaviour of [MO{N_2-3-$C_6H_4(NO_2)$}(S_2CNMe_2)$_3$], alone of all the complexes we investigated, is anomalous, its oxidation potential being *ca.* 0.1V too low. We therefore decided to determine the molecular structures of both [Mo(N_2PH)(S_2CNMe_2)$_2$]·CH_2Cl_2 (A) and the *m*-nitro-derivative (B) to discover whether their structures could give an insight into this anomaly.

Crystals of (A) and (B) suitable for an X-ray analysis were grown from dichloromethane and are monoclinic. For (A), a = 13.056(1), b = 13.366(1) and c = 15.350(1) Å; β = 93.80(1)°; z = 4; space group $P2_1/n$; 2849 independent reflections. In the case of (B), a = 32.442(8), b = 17.670(4), c = 17.867(3) Å; β = 99.03(1)°; z = 8; space group $C2/c$; 3898 independent reflections [Mo-Kα four-circle diffractometry: $2\theta \leqslant 50°$; $I_{obs} > 3\sigma(I_{obs})$; intensities corrected for Lorentz and polarisation effects and for absorption] formed the basis of the X-ray structure analysis. The positional parameters of all the non-hydrogen atoms were determined by Patterson and difference Fourier synthesis and refined with the anisotropic thermal parameters by full-matrix least-squares methods.

For (A), the positions of all hydrogen atoms were found from a difference synthesis and their contributions were included in the structure factor calculations and their positions refined. Refinement converged to R = 0.036 (weighted R = 0.038). The molecular structure is shown in the Figure.

For (B) positions of hydrogen atoms have not been included in the structure factor calculations. Refinement converged to R = 0.053 (weighted R = 0.066). The two molecules of [MO{N_2-3-$C_6H_4(NO_2)$}(S_2CNMe_2)$_3$] in the asymmetric unit are essentially chemically equivalent and the molecular structure is also shown in the Figure. The bond lengths and angles quoted are the average values. The carbon and oxygen atoms of the solvent CH_2Cl_2 and H_2O molecules are at special positions (0, y, ¼).

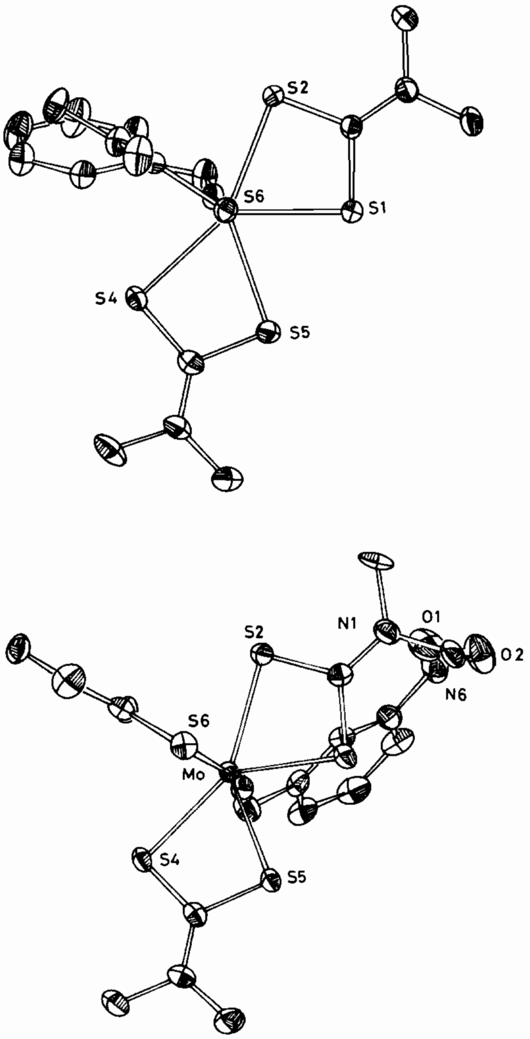
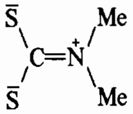


Figure. Structures of (a) [Mo(N_2Ph)(S_2CNMe_2)$_3$] (A) and (b) [Mo{N_2-3-$C_6H_4(NO_2)$}(S_2CNMe_2)$_3$] (B) viewed from comparable positions. Some important bond lengths and angles are Mo–S_{axial}, (A) 2.411(1), (B) 2.574(2); Mo–$S_{equatorial}$ (mean value), (A) 2.514, (B) 2.515; Mo–N, (A) 1.781 (4), (B) 1.770(6); N–N, (A) 1.233(6); (B) 1.262(9); N–C(Ph), (A) 1.417(7), (B) 1.410(10); O1··· N1, (B) 3.257(12) A; Mo–$\hat{N}$–N, (A) 171.5(4)°, (B) 170.6(6)°; N–$\hat{N}$–C, (A) 120.5(5)°, (B) 117.9(7)°.

Both molecules possess the seven-coordinate pentagonal bipyramidal structure expected for such complexes, with two dithiocarbamato-ligands (dtc) in the pentagonal plane and the third spanning an axial and an equatorial position (see Figure). The distortions from the ideal bipyramid due to the narrow bite of the dtc are as expected, and the $Mo–S_{(apical)}$ bond length is longer than the $Mo–S_{(equatorial)}$, which is always found when a multiply-bonded group occupies an apical position [4]. The aryldiazenido-ligands, singly-bent, occupy the remaining axial position and the other important bond lengths and angles, as shown in the Figure, are not unusual. However, the detailed geometry is unexpected.

The phenyl ring of (A) [Fig. (a)] takes up a position roughly in the plane of the dtc spanning between an equatorial position and an apex so that steric repulsions are minimised. It is twisted out of the plane containing the $N–N–C_{aryl}$ atoms by 6.1°, so that through conjugation from the phenyl ring to Mo is not maximised. This is consistent with the correlation of σ_p of X (X = Me, OMe, Cl, *etc.*) with the redox potential of $[Mo(N_2\text{-}4\text{-}C_6H_4X)(dtc)_3]$ (dtc = S_2CNMe_2) [3]. A similar geometrical effect has been noted in $[RhCl(N_2Ph)\{PhP(CH_2CH_2CH_2PPh_2)_2\}]^+$, although there the twist is 9.6° and the N_2Ph group is doubly bent [5]. There is no indication of close contacts between the phenyl rings and the dtc.

The phenyl rings in the independent molecules of (B) are also twisted out of the $Mo–N–N–C_{aryl}$ planes in this case by 4.4 and 6.5°. However, the rings are rotated by *ca.* 110° about the Mo–N–N axis away from the apparent position of minimum repulsion occupied in (A). This suggests that delocalisation in the Mo–N–N system has little influence on the overall geometry. The consequence is that the nitro-group has one of its oxygens within contact distance [3.257(12)Å] of one of the equatorial dtc nitrogens. The nitro-oxygen dtc-methyl-carbon distances are 3.23(2), 3.48(2), 3.55(2), and 3.90(2) Å. The main force of this interaction is electrostatic, since the oxygen of the nitro-group is well known to be negatively charged and the nitrogen of the dtc is strongly positive owing to predominance of the canonical form (I) [6]. Thus, the nitro-group influences the molecular properties through the polarisation of the dtc to increase the negative charge at the ligating sulphur atoms and thence the molybdenum. This accounts for the anomalous redox potential of $[Mo(N_2\text{-}3\text{-}C_6H_4NO_2)(dtc)_3]$. The ^1H n.m.r. spectra of the complexes $[Mo(N_2C_6H_4X)(dtc)_3]$ in the methyl region are very dependent upon the solvent used [2]. The structure we have observed for (B) indicates how interaction with a solvent such as nitrobenzene occurs and that it is sufficiently strong to effect significantly the physical and chemical properties of dithiocarbamato-complexes.



(I)

Acknowledgments

We acknowledge the support of the S.R.C. (to G.A.W. and A.R.P.S.) and the award of a Travelling Scholarship by the University of Melbourne (to G.A.W.).

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