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Carbethoxydiazenido-complexes of Molybdenum and Tungsten and the Lengths of Molybdenum–Nitrogen Multiple Bonds

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A variety of organodiazenido-complexes [1] containing the ligands N_2R (R = alkyl [2], aryl [2], acyl [2], aroyl [2], and CH_2COOEt [3]) are now known. We here report the first examples of a new class of organodiazenido-complexes which offer the possibility of far-reaching preparative and physical studies. They contain the carbethoxydiazenido-group, N_2CO_2Et, and were obtained as follows.

The complexes $[M(N_2)_2(dppe)_2]$ [M = Mo or W; dppe = 1,2-bis(diphenylphosphino)ethane] react with ethyl chloroformate under irradiation in benzene solution to yield, after acidification, $[MCl(N_2HCO_2Et)(dppe)_2]^+$, which, upon base treatment, produce neutral $[MCl(N_2CO_2Et)(dppe)_2]$. The carbethoxydiazenido-complexes are characterised by strong, broad bands in the i.r. spectra (KBr discs) at 1632 (M = Mo) and 1613 (M = W) cm^{-1} [$\bar{\nu}$(C=O) and/or $\bar{\nu}$(N=N)] and further very strong, broad bands at 1382, 1202 (Mo) and 1366, 1216 (W) cm^{-1} (unassigned). The bands at *ca.* 1200 cm^{-1} apparently have counterparts on the spectra of acyldiazenidocomplexes [2]. In the ^{13}C n.m.r. spectra there are resonances at 161.938 (Mo) and 160.599 (W) p.p.m. downfield from tetramethylsilane (tms) which we assign to the carbonyl carbons.

The reaction of $[MoO_2(dtc)_2]$ (dtc = N,N-dimethyldithiocarbamate) with ethyl carbazate in MeOH yields $[Mo(N_2CO_2Et)(dtc)_3]$. This diazenido-complex has ν(CO) in its i.r. spectrum at 1669 cm^{-1} (br, s) and a further strong band at 1531 cm^{-1} [probably $\bar{\nu}$(N=N)]. The carbonyl resonance in the ^{13}C n.m.r. spectrum is difficult to identify with certainty due to lack of solubility, but probably occurs at 163.32 p.p.m. downfield from tms. We have obtained homologous products from other alkyl carbazates.

Crystals of $[Mo(N_2CO_2Et)(dtc)_3]$ were examined by X-ray diffraction methods and shown to be monoclinic, space group $P2_1/n$ with $a = 15.031(3)$, $b = 16.264(2)$, $c = 10.935(1)$Å, $\beta = 98.34(2)°$, $Z = 4$. From the 4648 independent reflections ($\theta < 20°$) measured on an Enraf-Nonius CAD4 diffractometer, with monochromated Mo-K_α radiation, the structure was determined by the heavy atom method. At the present state of refinement, R = 0.066 for the 4001 reflections which have net intensities greater than zero. There appears to be a molecule of solvent CH_2Cl_2 disordered in several orientations, and this has not yet been adequately resolved; refinement of the structure is therefore not complete.

The coordination about the molybdenum is essentially pentagonal bipyramidal, with 5 S-atoms in the equatorial plane and the remaining S-atom and an N-atom at the apices, a commonly found arrangement of 7-coordinate tris(dithiocarbamato)-complexes [4]. The dtc ligands are each essentially planar, and only the methyl carbon atom of the carbethoxydiazenido- group is out of the plane containing all the other skeletal atoms of that ligand. The Figure shows the general disposition of the atoms.

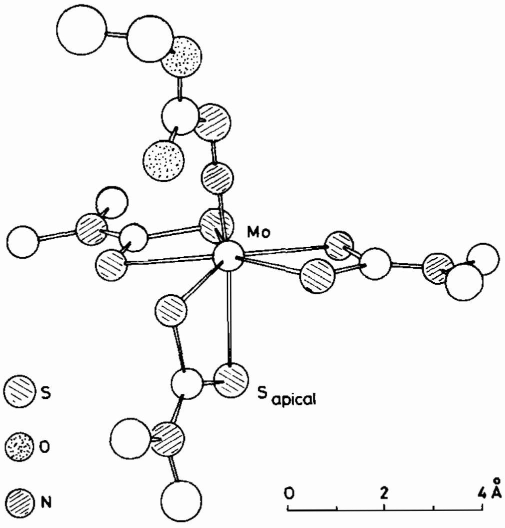

Figure. View of the molecule. The molybdenum and sulphur atoms and all but the ethyl C-atoms of the diazenido-ligand have been refiend anisotropically; boundaries of the vibration ellipsoids and of the spheres of the isotropic atoms are drawn at the 25% probability level.

The geometry and bond lengths differ very little from those of the complex $[Mo(N_2Ph)(dtc)_3]$ [5] although the Ph substituent, which exerts its electronic influence here mainly by an inductive effect [6], is very different from the CO_2Et group. Thus, in the present case, Mo–N, N–N and N–C (dtc) are 1.732(5), 1.274(7), and 1.382(10)Å, respectively.

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TABLE. Selected Mo–N Bond Lengths.

Complex	Formal Mo Oxidation State	Formal Mo–N Bond Order	M–N (Å)	Reference
[MoN $(S_2CNMe_2)_3$]	VI	3	1.618(14)	7
[Mo(N_2EtPh) $\{S_2CN(CH_2)_5\}_3]^+$	VI	2	1.715(16)	8
[MoI$(N_2HC_8H_{17})$ $(dppe)_2]^+$	IV	2	1.801(11)	9
[Mo$Cl_2(NC_6H_4$-4-Me) $(C_6H_5CON_2C_6H_4$-4-Me) (PMe_2Ph)]	II or IV or VI	2	1.726(9)	10
[Mo(N_2Ph) $(S_2CNMe_2)_3$]	IV	1	1.781(4)	5
[Mo$(N_2C_6H_4$-3-$NO_2)$ $(S_2CNMe_2)_3$]	IV	1	1.770(6)	5
[Mo(N_2CO_2Et) $(S_2CNMe_2)_3$]	IV	1	1.732(5)	This work
[Mo(NO) $(S_2CNBu^n{}_2)_3$]	III	1	1.731(8)	11
[Mo(NS) $(S_2CNMe_2)_3$]	III	1	1.74(1)	7
[MoCl(N_2COPh) $(dppe)_2$]	II	1	1.81	12

The corresponding values in the phenyl compound are 1.718(4), 1.233(6), and 1.417(7)Å. The distance Mo–S_{apical} [2.604(2)Å] is longer than Mo–$S_{equatorial}$ (in range 2.487–2.529Å). The corresponding distances in the phenyl compound are 2.611(1)Å and 2.479–2.532Å. The bond angles in the two compounds are also very similar: S_{apical}–$\widehat{Mo}$–N = 164.3(2) [163.5(1) in the phenyl compound], Mo–$\widehat{N}$–N = 178.9(5) [171.5(4)], and N–$\widehat{N}$–C = 117.0(6)° [120.5(5)°].

The relative insensitivity of the geometry and bond lengths to the substituents is surprising but it is nevertheless quite general. The Table shows a selection of Mo–N separations from a range of very different compounds. The almost linear Mo–N–A (A = N, O, S, or C) system is interpreted to indicate that all these Mo–N–A systems have delocalised multiple-bond character, independent of formal Mo–N bond order, which varies from 1 to 3, and molybdenum oxidation state. Evidently, the significance of minor variations in such bond lengths cannot be easily assessed, but the variation is not great whatever the formal bond order.

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