X-Ray Crystal Structure of a Molybdenum Complex with Both End-on Hydrazido(2—)- and Side-on Hydrazido(1—)-ligands

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Summary The bis[hydrazido(2—)]-complex [Mo(NNMePh)$_2$(S$_2$CNMe$_2$)$_2$] reacts with 1 equiv. of HCl to give [Mo(NNMePh)(NHNMePh)(S$_2$CNME$_2$)$_2$]$^+$, isolated as the tetraphenylborate salt, an *X*-ray crystal structure determination of which shows that the complex is seven-co-ordinate, displaying both end-on hydrazido-(2—)- and side-on hydrazido(1—)-co-ordination; the N–N distance in the hydrazido (2—)-ligand of 1·29 Å is close to that observed in the bis[hydrazido(2—)]-precursor, and the hydrazido(1—)-ligand is asymmetrically side-on bound with metal–nitrogen distances of 2·07 and 2·18 Å and an N–N distance of 1·39 Å.

The protonation of co-ordinated dinitrogen to ammonia has been shown to involve hydrazido(2—)-intermediates,[1] which may also be involved in the conversion of dinitrogen into ammonia by the enzyme nitrogenase.[2] However, the mechanism of the degradation of the hydrazido(2—) species to ammonia is a matter of speculation. As part of our investigation of the protonation of hydrazido(2—)-complexes we here report the preparation and structure of an unusual 7-co-ordinate complex containing both end-on hydrazido(2—)- and side-on hydrazido(1—)-ligands.

The bis[hydrazido(2—)]-complex [Mo(NNMePh)$_2$(S$_2$CNMe$_2$)$_2$] (**1**)[3] reacted with 1 equiv. of trimethylsilyl chloride in methanol to give the cationic species [Mo(NHNMePh)(NNMePh)(S$_2$CNMe$_2$)$_2$]$^+$ (**2**) isolated as a brown-red crystalline tetraphenylborate salt. Addition of an excess of acid gave [MoCl$_2$(NNMePh)(S$_2$CNMe$_2$)$_2$] and quantitatively liberated the hydrazine PhMeNNH$_2$, identified by g.l.c. Analogously, alkylation of (**1**) with trimethyloxonium tetrafluoroborate produced [Mo(NMeNMePh)(NNMePh)(S$_2$CNMe$_2$)$_2$]$^+$ again isolated as the tetraphenylborate salt. The ^{1}H n.m.r. spectrum at room temperature of (**2**) is complex in the dithiocarbamate and hydrazide alkyl region indicating that the proton is apparently localized on the hydrazido(1—)-ligand.

Crystal data: (**2**), monoclinic, space group $P2_1/c$, a = 16·102(3), b = 15·669(5), c = 18·752(2) Å, β = 112·23(1)°, U = 4380·0 Å^3, Z = 4. The solution of the structure was based on 3060 symmetry-independent reflections with $I_{\text{obs.}} > 2{\cdot}58\sigma(I_{\text{obs.}})$ (Mo-K_α radiation, λ = 0·71069 Å). The positions of the molybdenum and four sulphur atoms were revealed by means of a statistical *E*-synthesis using the method of symbolic addition. The remaining non-hydrogen atoms were located on the subsequent difference

Fourier map, and all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located on the final Fourier map and were included in the least-squares

$[Mo(NNMePh)_2(S_2CNMe_2)_2]$
(1)

$[Mo(NHNMePh)(NNMePh)(S_2CNMe_2)_2][BPh_4]$
(2)

calculations as fixed contributions. The final value for the conventional discrepancy index, *R*, was 0·051.†

The cation exhibits severely distorted pentagonal bipyramidal geometry with the equatorial plane defined by the sulphur donors of one dithiocarbamate group, S(1) and S(2), the nitrogens of the phenylmethylhydrazido(1—)-ligand which is 'side-on' bound to the molybdenum and a sulphur, S(4), from the remaining dithiocarbamate group. The axial positions are occupied by S(3) from the dithiocarbamate ligand which spans the equatorial plane and the axial sites and by the nitrogen N(3) of the 'end-on' bound hydrazido(2—)-ligand (Figure).

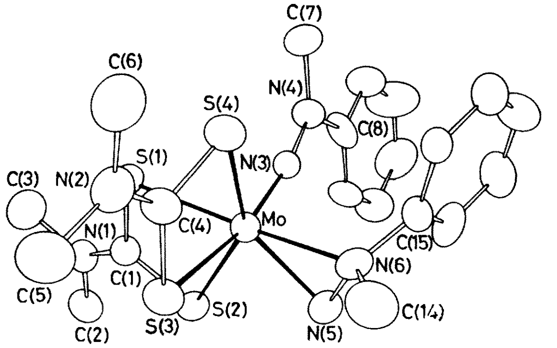
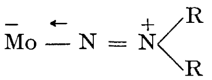


FIGURE. ORTEP representation of the structure of $[Mo(NNMePh)(NHNMePh)(S_2CNMe_2)_2]^+$ showing the atom labelling scheme. Relevant bond lengths (Å) and angles (°) are: Mo–S(1), **2·513(3)**; Mo–S(2), **2·480(3)**; Mo–S(3), **2·565(4)**; Mo–S(4), **2·495(3)**; Mo–N(3), **1·752(10)**; Mo–N(5), **2·069(8)**; Mo–N(6), **2·175(9)**; N(3)–N(4), **1·285(14)**; N(5)–N(6), **1·388(12)**; ∠S(1)–Mo–S(2), **69·7(1)**; S(3)–Mo–S(4), **69·3(1)**; S(3)–Mo–N(3), **164·3(3)**; N(5)–Mo–N(6), **38·1(3)**; Mo–N(3)–N(4), **169·6(7)**.

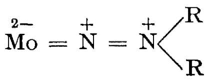
The Mo–N distances to the hydrazido(1—)-group are not equivalent, the distance of 2·069(8) Å to N(5) being significantly shorter than the Mo–N(6) distance of 2·175(9) Å. A similar trend has been observed for the only other example of *dihapto*-hydrazido(1—)-ligation, $[(\eta^5\text{-}C_5H_5)_2W(H_2NNPh)]^+$, where the W–N distances are 2·037 Å to the three-co-ordinate nitrogen and 2·161 Å to the four-co-ordinate nitrogen.[4]

The short Mo–N(3) distance [1·75(1) Å] for the terminally bound hydrazido(2—)-ligand is consistent with significant multiple bond character, as is the essentially linear Mo–N(3)–N(4) angle of 169·6°, a value well within the range reported for hydrazido(2—)-species.[3,5–8]

The N–N distances for the hydrazido(1—)- and hydrazido(2—)-ligands are 1·37 and 1·29 Å, respectively. The N(3)–N(4) distance of 1·29(1) Å suggests significant delocalization within the Mo-hydrazido(2—)-group as previously discussed,[8] that is, a formalism in which the hydrazido(2—)-group behaves as a four-electron donor (A) or (B).[9] On the other hand, the N(5)–N(6) distance of 1·37(1) Å corresponds to a typical N–N single bond, the hydrazido(1—)-ligand thus behaving formally as a three-electron donor.



(A)



(B)

The geometry of the dithiocarbamate ligands is in general unexceptional. The significantly longer Mo–S(3) distance of 2·565 Å, compared to the 2·496 Å average for the equatorial Mo–S bonds, is consistent with the anticipated lengthening due to occupation of the axial site and a consequence of the strong *trans*-influence associated with the multiply bonded hydrazido(2—)-ligand. The major source of distortion to regular pentagonal bypyramidal geometry arises from the constraints on the ligand 'bite' angle of the axial–equatorial dithiocarbamate ligand, resulting in an S(3)–Mo–S(4) angle of 69° rather than the 90° angle anticipated for idealized pentagonal bipyramidal geometry.

The above structure suggests that when a hydrazido(2—)-ligand on an open-shell metal centre is protonated at the nitrogen adjacent to the metal a three-membered ring structure will be generated. It is not yet clear whether the *dihapto*-bonding is retained through the next protonation stage, and the crystal structures and protonation of several other species believed to contain hydrazido(1—)-ligands are under investigation to try to resolve this question.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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