Disproportionation of hydrazine by [$Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}Cl)(\mu\text{-}SMe)_3$] and formation of an $Mo_2(\mu\text{-}NH_2)$ amido bridge

Philippe Schollhammer,[a] François Y. Pétillon,*[a] Sylvie Poder-Guillou,[a] Jean Y. Saillard,[b] Jean Talarmin[a] and Kenneth W. Muir*[c]

[a] *URA CNRS 322, Chimie, Electrochimie Moléculaires et Chimie Analytique, Faculté des Sciences, Université de Bretagne Occidentale, BP 452, 29285 Brest-Cédex, France*

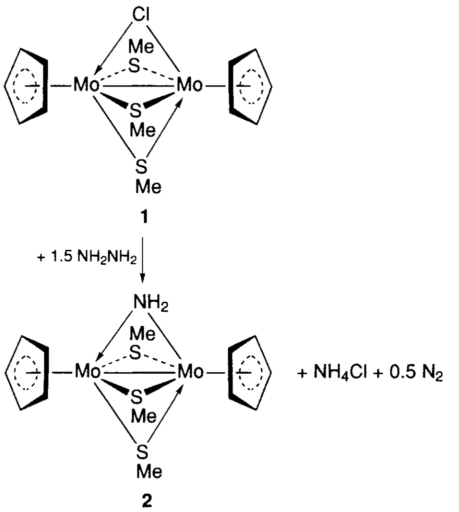
[b] *URA CNRS 1495, Laboratoire de Chimie du Solide et Inorganique Moléculaire, Université de Rennes I, 35042 Rennes Cedex, France*

[c] *Department of Chemistry, University of Glasgow, Glasgow, UK G12 8QQ*

Cleavage of the N–N bond of hydrazine by the dimolybdenum centre in [$Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}Cl)(\mu\text{-}SMe)_3$] 1 gives rise to the amido-bridged complex [$Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}NH_2)(\mu\text{-}SMe)_3$] 2.

The reactions of hydrazines with polymetallic systems can provide insight into the activation and the transformation of nitrogenous substrates by metalloenzymes.[1] In the case of nitrogenase, for example, it is now thought that hydrazido(2−) complexes are key intermediates in the reduction of N_2 to NH_3 and that the activation of N_2, hydrazine and other diazo compounds can occur at a single metal centre; however, both the role played by the molybdenum atoms of the enzyme in the reduction of dinitrogen and the nature of the site responsible for its binding and activation are not well defined.[1,2] These observations, coupled with evidence that catalytic activation of the N–N bond can be effected by various systems containing an {$M_2(\mu\text{-}SR)_n$} (M = Mo, W, Ru)[3] core, have led us to investigate the transformation of nitrogenous substrates by thiolato-bridged dimolybdenum systems. These systems were originally synthesised during our earlier studies of the chemistry of metal thiolates (M = Mo, V, W)[4] and they constitute convenient and simple models of a dimolybdenum site. Accordingly, we report here our preliminary results concerning the reaction of hydrazine with the complex [$Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}Cl)(\mu\text{-}SMe)_3$] 1,[4a] in which the disproportionation of NH_2NH_2 leads to the formation of the amido-bridged thiolato complex [$Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}NH_2)(\mu\text{-}SMe)_3$] 2, NH_4Cl and N_2.

Complex **1** reacted quantitatively with hydrazine at room temperature (or with moderate warming) to give **2** and NH_4Cl (Scheme 1).† **2** was characterised by IR and NMR spectroscopy.‡ The ^1H and ^{13}C NMR spectra of **2** exhibited one resonance for the cyclopentadienyl ligands and three for the SMe bridges, indicating that the molecule was symmetric and that the structure of the {$Mo_2(\mu\text{-}SMe)_3$} core was conserved during the conversion of **1** into **2**. Although the two protons of the amido bridge were not observed in the ^1H NMR spectrum of **2**, IR examination revealed two weak bands assignable to N–H vibrations at 3380 and 3280 cm^{-1}. These bands disappear on addition of D_2O to the complex, being replaced by two weak bands at 2580 and 2420 cm^{-1} which can be assigned to ν(N–D) vibrations.



Scheme 1

Complex **2** was isolated as red–brown crystals. An X-ray structure determination is consistent with the proposed formulation of **2** as a μ-amido compound (Fig. 1).§ In particular, it proved possible to locate and freely refine the two H atoms attached to N(1). The molecular structure of **2** is based on an $Mo_2(\mu\text{-}SMe)_3(\mu\text{-}N)$ core with a nearly linear ($\eta\text{-}C_5H_5$)Mo–Mo($\eta\text{-}C_5H_5$) group. The coordination geometry around each Mo atom can be described as a four-legged piano stool supplemented by a metal–metal bond. The Mo(1)–N and Mo(2)–N distances [2.152(3), 2.150(3) Å] and the acute Mo(1)–

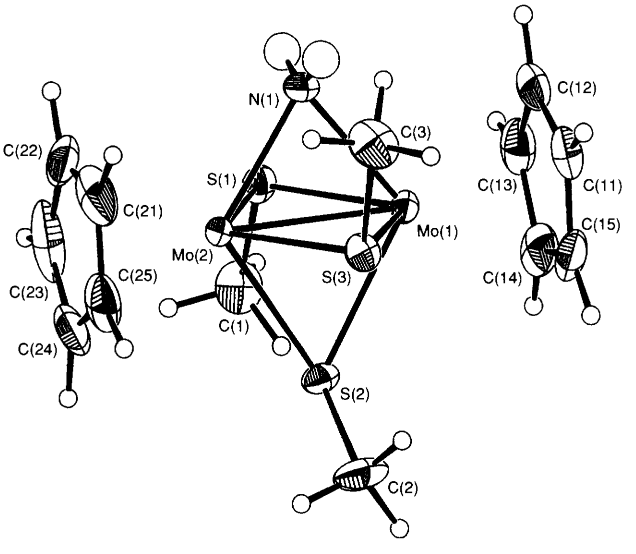


Fig. 1 The molecular structure of [$Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}NH_2)(\mu\text{-}SMe)_3$] **2** showing 30% displacement ellipsoids, except for methyl and cyclopentadienyl H-atoms which are shown as spheres of arbitrary size. The alternative sites with occupancy 0.139(2) for S(1), S(2), S(3) and N are not displayed. Selected distances (Å) and angles (°): Mo(1)–Mo(2) 2.5660(4), Mo(1)–N(1) 2.152(3), Mo(1)–S(1) 2.4818(9), Mo(1)–S(2) 2.4613(9), Mo(1)–S(3) 2.4505(9), Mo(2)–N(1) 2.150(3), Mo(2)–S(1) 2.4664(9), Mo(2)–S(2) 2.4481(8), Mo(2)–S(3) 2.4412(9), Mo–C(C_5H_5) 2.242(4)–2.335(3), Mo(2)–S(1)–Mo(1) 62.47(2), Mo(2)–S(2)–Mo(1) 63.02(2), Mo(2)–S(3)–Mo(1) 63.28(2), Mo(1)–N(1)–Mo(2) 73.25(10).

N–Mo(2) angle [73.3(1)°] suggest an order of unity for the Mo–N bonds. Normal electron counting rules require the presence of an Mo^{III}–Mo^{III} single bond in **2**. The Mo(1)–Mo(2) distance [2.566(1) Å] is typical for a tetra-bridged dimer of molybdenum(III).[6,7]

Extended Hückel molecular orbital calculations have been performed on the complex [$Mo_2(\eta$-$C_5H_5)_2(\mu$-$NH_2)(\mu$-$SMe)_3$].¶[8] The electron configuration of this compound, $\sigma^2\delta^{*2}\delta^2$, is similar to those reported previously for other quadruply bridged molybdenum(III) species [$Mo_2(\eta$-$C_5H_5)_2(\mu$-$X)_4$] (d^3–d^3) and is consistent with an Mo–Mo single bond.[7] These calculations also support our formulation of **2** as an amido, rather than a nitrido, species: a nitrido complex with the geometry found experimentally for **2** is Jahn–Teller unstable (HOMO–LUMO gap = 0.39 eV), while the corresponding μ-amido complex appears to be stable (HOMO–LUMO gap = 1.7 eV).

We are not yet able to describe clearly the mechanistic details of this reaction. The coordination of hydrazine is required for its further transformation. This step may be concomitant with opening of the chloro bridge. Later steps, leading to the release of NH_4Cl and N_2, could involve a diazene intermediate, as recently reported for the disproportionation of hydrazine by the dinuclear ruthenium complex [$Ru_2(\eta$-$C_5Me_5)_2(\mu$-$SR)_2$].[3c]

In conclusion, these results demonstrate that the dimolybdenum(III) system [$Mo_2(\eta$-$C_5H_5)_2(\mu$-$Cl)(\mu$-$SMe)_3$] provides a bimetallic site capable of cleaving the N–N bond of NH_2NH_2, a process which may parallel the activation and transformation of dinitrogen and related nitrogenous substrates by thiopolymetallic systems. Further experiments are under way with substituted hydrazines ($RNHNH_2$, $RNHNHR$ and R_2NNH_2) to define more exactly the mechanism of the formation of **2** and to extend the scope of this reaction.

We thank the CNRS, the EPSRC, Glasgow University and the University of Brest for financial support.

Footnotes

† *Experimental procedure*: NH_2NH_2 (48 μl, 1.5 mmol) was added to a solution of **1** (500 mg, 1 mmol) in thf (30 ml). The solution was stirred at room temp. or with moderate warming for 2 h, and changed from green to orange during this time. NH_4Cl (5.3 mg, 1 mmol) precipitated from solution and was separated by filtration. Evaporation of thf and washing of the residue with cold pentane afforded a brown powder of **2** (0.479 mg, 100%). C, H, N analysis for $C_{13}H_{21}NMo_2S_3$ **2**; Calc.: C, 32.7; H, 4.4; N, 2.9. Found C, 32.0; H, 4.4; N, 2.5%.

‡ *Selected spectroscopic data* for **2**: ^{1}H NMR ($CDCl_3$): δ 5.29 (s, 10 H, C_5H_5), 1.54 (s, 3 H, SCH_3), 1.53 (s, 3 H, SCH_3), 1.37 (s, 3 H, SCH_3); ^{13}C NMR ($CDCl_3$): δ 91.20 (C_5H_5), 12.55, 12.22, 9.65 (SCH_3).

§ *Crystal data* for **2**: $C_{13}H_{21}Mo_2NS_3$, M = 479.37, monoclinic, space group $P2_1/n$, a = 13.755(1), b = 8.132(1), c = 16.113(1) Å, β = 112.150(4)°, U = 1669.2(2) Å^3 [from setting angles of 25 reflections with $19.0 \leqslant \theta$(Mo-Kα) $\leqslant 25.6°$], Z = 4, D_c = 1.908 Mg m^{-3}, μ = 1.864 mm^{-1}, F(000) = 952.

Intensities of 4779 reflections with $2.5 \leqslant \theta$(Mo-Kα) $\leqslant 27°$ and $-2 \leqslant h \leqslant 17$. $-1 \leqslant k \leqslant 10$, $-20 \leqslant l \leqslant 19$ were measured at 20 °C from ω–2θ scans on an Enraf-Nonius CAD4 diffractometer with Mo-Kα X-rays, λ = 0.71073 Å, using a red–brown, block-shaped crystal of dimensions 0.20 × 0.20 × 0.20 mm. The mean intensity of three standard reflections showed no significant change during the experiment. Subsequent merging gave 3638 independent reflections [R_{int} = 0.025]. Refinement on F^2 of 194 parameters using 3638 observations converged ($\Delta/\sigma < 0.05$) at R_1 = 0.025, wR_2 = 0.062 for 3133 reflections with $I > 2\sigma(I)$ and R_1 = 0.033, wR_2 = 0.065 for all 3638 data, $|\Delta\rho| < 0.74$ e Å^{-3}, $w = 1/[\sigma^2(F_o^2) + (0.0326P)^2 + 1.28P]$ where $P = (F_o^2 + 2F_c^2)/3$.[5] Each bridging S and N atom is disordered over two sites with occupancies 0.861(2) and 0.139(2). A common isotropic U was refined for the four less occupied sites. Despite this disorder the H atoms bonded to major N(1) site were located in a difference map. Their positions were refined freely [N–H 0.84(4), 0.85(4) Å], as was a common U_{iso} = 0.040(8) Å^2. Riding methyl and cyclopentadienyl H atoms were included in the calculations. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/285.

¶ *Computational details*: all the MO calculations were of the extended Hückel type[9] using the weighted H_{ij} formula.[10]. The atomic parameters are taken from the literature.[11] Calculations were carried out with the CACAO package developed by Proserpio and Mealli.[12] The structure of **2** was idealised from the average experimental structure with the following distances (Å): Mo–Mo 2.56, Mo–S 2.459, Mo–N 2.16, Mo–C(C_5H_5) 2.287, C–C 1.387. Other bond distances used were: S–H 1.33, N–H 1.01.

References

1 M. Hidai and Y. Mizobe, *Chem. Rev.*, 1995, **95**, 1115.

2 R. R. Schrock, T. E. Glassman and M. G. Vale, *J. Am. Chem. Soc.*, 1991, **113**, 725; D. Sellmann, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 64.

3 (*a*) E. Block, G. Ofori-Okai, H. Kang and J. Zubieta, *J. Am. Chem. Soc.*, 1992, **114**, 758; (*b*) R. R. Schrock, T. E. Glassman, M. G. Vale and M. Kol, *J. Am. Chem. Soc.*, 1993, **115**, 1760; (*c*) K. D. Demadis and D. Coucouvanis, *Inorg. Chem.*, 1994, **33**, 4195; (*d*) S. Kuwata, Y. Mizobe and M. Hidai, *Inorg. Chem.*, 1994, **33**, 3619; (*e*) G. Ramachandraiah, *J. Am. Chem. Soc.*, 1994, **116**, 6733; (*f*) R. R. Eady and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1994, 2739; (*g*) K. D. Demadis and D. Coucouvanis, *Inorg. Chem.*, 1995, **34**, 3658; (*h*) R. A. Henderson, *J. Chem. Soc., Dalton Trans.*, 1995, 503; (*i*) T. A. Bazenova and A. E. Shilov, *Coord. Chem. Rev.*, 1995, **144**, 69; (*j*) K. D. Demadis, S. M. Malinak and D. Coucouvanis, *Inorg. Chem.*, 1996, **35**, 4038.

4 (*a*) M. B. Gomes de Lima, J. E. Guerchais, R. Mercier and F. Y. Pétillon, *Organometallics*, 1986, **5**, 1952; (*b*) P. Schollhammer, F. Y. Pétillon, R. Pichon, S. Poder-Guillou, J. Talarmin, K. W. Muir and Lj. Manojlovic-Muir, *Organometallics*, 1995, **14**, 2287; and references therein.

5 G. M. Sheldrick, SHELXL93, *A Program for Refining Crystal Structures*, University of Göttingen, Germany, 1993.

6 K. W. Muir, F. Y. Pétillon and P. Schollhammer, unpublished work.

7 D. L. Dubois, W. K. Miller and M. Rakowski Dubois, *J. Am. Chem. Soc.*, 1981, **103**, 3429; J. C. Green, M. L. H. Green, P. Mountford and M. J. Parkington, *J. Chem. Soc., Dalton Trans.*, 1990, 3407; W. Tremmel, R. Hoffmann and E. D. Jemmis, *Inorg. Chem.*, 1989, **28**, 1213.

8 F. Y. Pétillon, J. Y. Saillard and P. Schollhammer, unpublished work.

9 R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, 1962, **36**, 2179; R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397.

10 J. M. Ammeter, H. B. Bürgi, J. C. Thibeault and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 3686.

11 S. Alvarez, *Tables of Parameters for Extended Hückel Calculations*, Departamento de Quimica Inorganica, Universitat de Barcelona, Barcelona, Spain, 1989.

12 C. Mealli and D. Proserpio, *J. Chem. Educ.*, 1990, **67**, 399.

Received, 17th September 1996; Com. 6/06390J