Double Sulfur–Carbon Bond Cleavage of a Dithiocarbamate Ligand at a Molybdenum(VI) Centre; Synthesis and X-Ray Structure of the Disulfur Complex [Mo(NPh)(S_2)(edtc)$_2$] (edtc = S_2CNEt_2)

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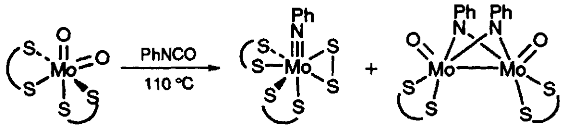
Reaction of 1 equiv. of PhNCO with [MoO_2(edtc)$_2$] leads to the isolation of [Mo(NPh)(S_2)(edtc)$_2$] formed as a result of oxo substitution and a double sulfur–carbon bond cleavage of the dithiocarbamate; a second product is dimeric [MoO(edtc)(μ-NPh)]$_2$.

The dithiocarbamate ligand finds widespread use in inorganic chemistry as a 3-electron donor moiety which can stabilise metal centres in a variety of oxidation states,[1] One of the major advantages of using this class of ligand is their relative inertness to a wide range of reaction conditions. Recently we have been interested in the synthesis of high valent molybdenum–imido species. We sought to synthesise such dithiocarbamate stabilised complexes *via* oxo substitution of the well known, and thermally stable, bisoxo complex [MoO_2(edtc)$_2$].[2] Arylisocyanates are well established as reagents which effect this transformation,[3] indeed we have recently shown that this transformation can occur at the dithiocarbamate stabilised molybdenum(VI) centre when the aryl group contains bulky substituents in the *ortho* positions.[4] Surprisingly, however, in the absence of such steric bulk, a second unprecedented double sulfur–carbon bond cleavage reaction of a dithiocarbamate ligand occurs together with the substitution process.

Heating a toluene solution of [MoO_2(edtc)$_2$] with 1 equiv. of PhNCO for 2 d did not give the anticipated yellow product, namely [MoO(NPh)(edtc)$_2$].[5] Rather the solution turned deep-green, and afforded after chromatography the imido–disulfide complex [Mo(NPh)(S_2)(edtc)$_2$] **1** in 35% yield.† The structure of **1** was elucidated by X-ray crystallography, the results of which are shown in Fig. 1.‡ As expected, molybdenum is bound to two dithiocarbamate ligands and a single linear phenylimido moiety [Mo(1)–N(3)–C(11) 165.2(3)°]. The imido ligand acts as a 4-electron donor to the molybdenum centre as evidenced by the short molybdenum–nitrogen distance [Mo(1)–N(3) 1.759(4) Å], and the relatively short elongated molybdenum–sulfur bond *trans* to it [Mo(1)–S(4) 2.605(1) Å].[4,5] Surprisingly, the coordination sphere about molybdenum is made up by a disulfur ligand, which lies *cis* to the imido moiety. It is bound approximately symmetrically to the molybdenum centre [Mo(1)–S(5) 2.398(2), Mo(1)–S(6) 2.431(2) Å], and thus the overall coordination geometry at molybdenum is that of a distorted pentagonal bipyramid. The sulfur–sulfur bond length of 2.033(2) Å is typical of such side-bound disulfur ligands.[6]

It appears strange that the major product of the reaction contains the units of three dithiocarbamate ligands, as opposed to two in the starting material. The origin of this extra dithiocarbamate became clearer with the isolation of the second, major reaction product, the molybdenum(V) dimer [MoO(edtc)(μ-NPh)]$_2$ **2** in 50% yield. Characterisation was made on the basis of spectroscopic and analytical data.† We assume that **2** contains a *trans* configuration of dithiocarbamate ligands as found in the related oxo bridged complex [MoO(edtc)(μ-O)]$_2$,[7] however our data does not unambigu-



1 **2**

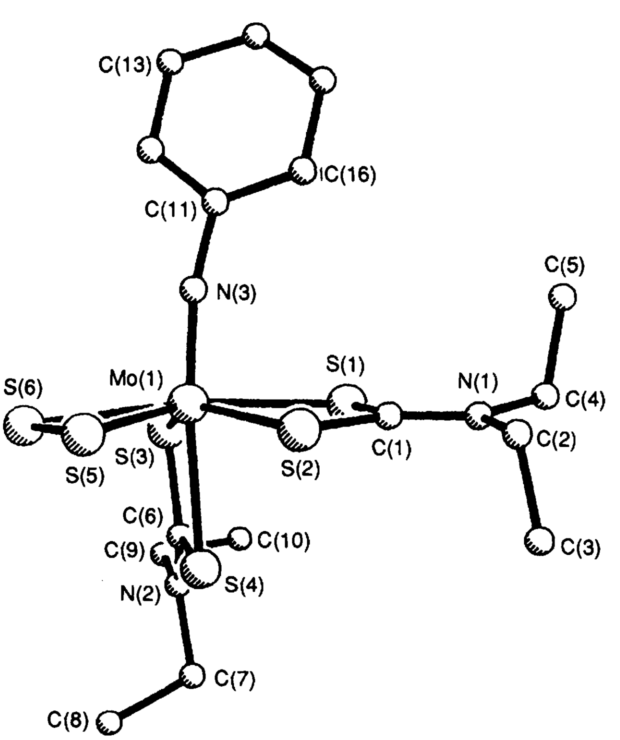


Fig. 1 Molecular structure of **1**. Important bond lengths (Å) and angles (°) include: Mo(1)–S(1) 2.544(1), Mo(1)–S(2) 2.487(1), Mo(1)–S(3) 2.511(1), Mo(1)–S(4) 2.605(1), Mo(1)–S(6) 2.431(2), Mo(1)–N(3) 1.759(4), S(5)–S(6) 2.033(2); S(5)–Mo(1)–S(6) 49.8(1), Mo(1)–N(3)–C(11) 165.2(3).

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† Complexes **1** and **2** were characterised by elemental analyses and IR and NMR (^{1}H and ^{13}C) spectra. Selected data (*J* values are given in Hz) for **1**: ^{1}H NMR ($CDCl_3$) δ 7.44 (t, 2 H, *J* 7.2, *m*-C_6H_5), 7.20 (d, 2 H, *J* 7.1, *o*-C_6H_5), 7.15 (t, 1 H, *J* 7.2, *p*-C_6H_5), 4.07–3.52 (m, 8 H, CH_2), 1.37 (t, 3 H, *J* 7.1, Me), 1.35 (t, 3 H, *J* 7.3, Me), 1.31 (t, 3 H, *J* 7.2, Me), 1.14 (t, 3 H, *J* 7.2, Me); IR ν/cm^{-1} (KBr) 1522s, 1497s, 1456m, 1435s, 1275s, 1206w, 1146m, 1092w, 1072m, 759m, 682m, 669m, 653m, 522w. **2**: ^{1}H NMR ($CDCl_3$) δ 7.43 (t, 4 H, *J* 7.1, *m*-C_6H_5), 7.31 (d, 4 H, *J* 7.0, *o*-C_6H_5), 7.17 (t, 2 H, *J* 7.1, *p*-C_6H_5), 3.86 (q, 8 H, *J* 7.0, CH_2), 1.30 (t, 12 H, *J* 7.0, Me); IR ν/cm^{-1} (KBr) 1585m, 1524vs, 1476s, 1457s, 1439s, 1381w, 1356w, 1278s, 1202m, 1151m, 1075m, 948s, 932s, 768m, 695m. Satisfactory elemental analyses were obtained for both **1** and **2**.

‡ *Crystal data* for **1**: $Mo_1S_6N_3C_{16}H_{25}$, $M = 547.69$, monoclinic, space group $P2_1/c$, $a = 10.436(2)$, $b = 9.963(2)$, $c = 23.406(7)$ Å, $\beta = 96.63(2)°$, $U = 2406.0(10)$ Å^3, $Z = 4$, $T = 292$ K, $D_c = 1.51$ g cm^{-3}, $F(000) = 1120$, $\lambda = 0.71073$ Å, μ(Mo-Kα) = 1040 cm^{-1}. Intensity data were collected on a crystal of dimensions 0.68 × 0.40 × 0.40 mm mounted on a Nicolet R3mV diffractometer, by the $\bar{\omega}$ scan technique ($5 \leqslant 2\theta \leqslant 50$). From 4761 measured data, 3268 with $I \geqslant 3\sigma(I)$ were considered observed. The structure was solved by direct methods and refined by full-matrix least-squares to R and R_w values of 0.039 and 0.041.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

ously confirm this. Complex **2** is formed as a result of both oxo substitution and dithiocarbamate loss. In separate experiments, heating either **1** or **2** in the presence or absence of phenylisocyanate did not result in the formation of the other.

While these transformations may initially appear to be novel, they have useful synthetic applications due to the abundant nature of the starting materials and the generality of the reaction. Thus, typically, reaction of 22 g of $[MoO_2(edtc)_2]^2$ yields approximately 8 g of **1** and 9 g of **2** in a simple one-pot synthesis. The reaction also proceeds in the presence of a range of both aryl and alkyl isocyanates. The latter is somewhat surprising since in many systems where arylisocyanates readily substitute oxo ligands, alkylisocyanates are ineffective. Since disulfur ligands have previously been generated from a number of sulfur containing sources, we considered that the abstraction of sulfur from the dithiocarbamate may not be selective, and the yield of **1** may increase if a second source of sulfur were present. Reaction of $[MoO_2(edtc)_2]$ with PhNCS, however, gave similar yields of both **1** and **2**. The dithiocarbamate cleavage reaction is also independent of the substituents on carbon. Thus, heating the methyldithiocarbamate complex $[MoO_2(mdtc)_2]$ in the presence of phenylisocyanate gave comparable yields of the methylsubstituted derivatives of **1** and **2**.

While the mode of formation of **1** is unclear, it apparently occurs as a result of a double sulfur–carbon bond cleavage reaction at the molybdenum(VI) centre. Such a process appears to be unprecedented, although the oxidative–addition of a single carbon–sulfur bond of a dithiocarbamate to yield sulfido–thiocarbamyl complexes has been reported in three instances.[8–10] Most notable in the context of our results is the formation of the binuclear complexes $[Mo_2(\mu\text{-}S)(\mu\text{-}RC_2R)(dtc)_3(\eta^2\text{-}SCNR'_2)]$ (dtc = dithiocarbamate) from the thermolysis of $[Mo(RC_2R)_2(dtc)_2]$ in the presence of phosphines.[8] In none of the above cases, however, does further sulfur–carbon bond cleavage of the thiocarbamyl ligand occur.

Since both **1** and **2** contain the imido functionality, we feel that the initial reaction may be that of oxo substitution to give the known mixed oxo/imido complex $[MoO(NPh)(edtc)_2]$.[5] Thermal loss of dithiocarbamate could then yield an unsaturated molybdenum(V) complex, which could dimerise to form **2**. Competitive with dithiocarbamate loss must be the attack of free dithiocarbamate on the molybdenum(VI) centre, followed by cleavage of the carbon–sulfur bonds affording **1**. We are currently exploring the mechanistic details of these transformations in more detail, and carrying out reactivity studies on **1** and **2**.

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