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COMMUNICATION

SYNTHESIS AND STRUCTURAL CHARACTERISATION OF THE DIMERIC TETRAIMIDO COMPLEX [Mo(N-*o*-tolyl)(η^2-S_2CNEt_2)(μ-N-*o*-tolyl)]$_2$

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Abstract—Thermolysis of a slight excess of *o*-tolylisocyanate with either [$MoO_2(\eta^2$-$S_2CNEt_2)_2$] or [$MoO(\eta^2$-$S_2CNEt_2)(\mu$-$O)]_2$ afforded the tetraimido complex [Mo(N-*o*-tolyl)(η^2-S_2CNEt_2)(μ-N-*o*-tolyl)]$_2$ characterised by X-ray crystallography in the solid state and which exists as a mixture of interconverting rotomers in solution due to restricted rotation about the nitrogen–carbon bond of the imido ligands.

During the past decade there has been a resurgence of interest in the chemistry of complexes containing the imido ligand, and π-donor ligands in general, being triggered in part by the publication of an excellent book on the subject.[1] Of dimeric complexes of this type, the most studied are those based around the $[Mo_2X_2(\mu\text{-}X)_2]^{2+}$ (X = O, S, NR) core, the remaining ligands being typically monoanionic chelates such as dithiocarbamate (S_2CNR_2) and dithiophosphinate ($S_2P(OR)_2$), or the cyclopentadienyl (C_5R_5) ligand. Within this core, it has proved possible to synthesise complexes containing many different combinations of π-donor ligands via ligand exchange reactions. For example all the oxo-sulfido complexes of the type [$Mo_2(O)_{4-n}(S)_n(\eta^2$-$S_2CNR_2)_2$] ($n = 0^2$; 1^3; 2^4; 3^5; $4^{6,7}$) have been prepared[8] and crystallographically characterised. Surprisingly then the analogous tetraimido complexes [Mo(NR)(η^2-S_2CNEt_2)(μ-NR)]$_2$ remain virtually unknown.[9] We have previously shown that an excellent route to cyclopentadienyl stabilised tetraimido complexes [Mo(NR)(η^5-C_5H_4Me)(μ-NR)]$_2$ is via the substitution of the oxo ligands in [MoO(η^5-C_5H_4Me)(μ-O)]$_2$ upon reaction with arylisocyanates.[10] Herein we describe the synthesis and structural characterisation of the first dithiocarbamate stabilised tetraimido complex, namely [Mo(N-*o*-tolyl)(η^2-S_2CNEt_2)(μ-N-*o*-tolyl)]$_2$ (**1**).

Thermolysis of a toluene solution of [MoO(η^2-S_2CNEt_2)(μ-O)]$_2$ and a slight excess of *o*-tolylisocyanate afforded, after chromatography, complex **1** in 90% yield as an orange air-stable crystalline solid,† and in a similar manner **1** was formed in 34% yield from the monomeric molybdenum(VI) complex [$MoO_2(\eta^2$-$S_2CNEt_2)_2$]. While the former reaction simply represents the well-known substitution of oxo for imido ligands, in the latter, reduction of the molybdenum centre occurs together with π-donor exchange. We have observed

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† Complex **1** was characterised by elemental analyses and IR and NMR spectra. *Selected data*: ^{1}H NMR (d_8-toluene) (383 K) δ7.25 (br, 2H, Ph), 7.20 (d, $J = 7.2$ Hz, 2H, Ph), 7.15 (t, $J = 7.5$ Hz, 2H, Ph), 6.92 (d, $J = 8.3$ Hz, 2H, Ph), 6.88 (d, $J = 8.8$ Hz, 2H, Ph), 6.75 (d, $J = 6.7$ Hz, 2H, Ph), 6.57 (m, 4H, Ph), 3.28 (q, $J = 7.0$ Hz, 8H, CH_2), 2.42 (s, 6H, Me), 2.31 (s, 6H, Me), 0.75 (t, $J = 7.0$ Hz, 12H, CH_2CH_3); (233 K) δ8.15–6.65 (m, Ph), 2.98 (m, CH_2), 2.75 (s, Me), 2.70 (s, Me), 2.66 (s, Me), 2.55 (s, Me), 2.46 (s, Me), 2.36 (s, Me), 0.62 (t, $J = 6.8$ Hz, CH_2CH_3), 0.56 (t, $J = 7.0$ Hz, CH_2CH_3); IR (KBr) 1515s, 1472m, 1455m, 1437m, 1321m, 1272s, 1263s, 1204w, 1150w, 1113w, 1076w, 992w, 756s, 718w cm^{-1}. Found: C, 49.7; H, 5.2; N, 9.1; S, 14.2. Calc. for $Mo_2C_{38}H_{48}S_4N_6$: C, 50.2; H, 5.3; N, 9.1; S, 14.1.

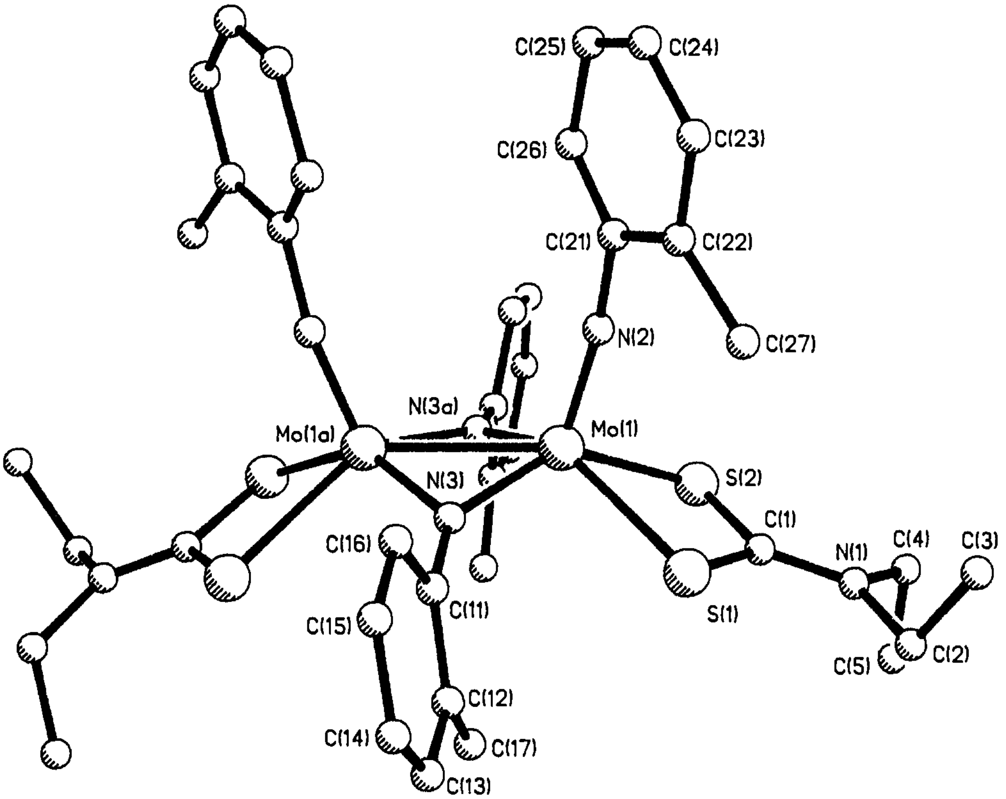

Fig. 1. Molecular structure of **1**. Selected bond lengths (Å) and angles (°); Mo(1)—Mo(1A) 2.633(1), Mo(1)—S(1) 2.481(1), Mo(1)—S(2) 2.493(1), Mo(1)—N(2) 1.741(3), Mo(1)—N(3) 1.958(4), Mo(1)—N(3A) 1.978(4), Mo(1)—N(2)—C(21) 167.9(3), Mo(1A)—Mo(1)—N(2) 108.7(1), Mo(1)—N(3)—Mo(1A) 83.9(1), Mo(1)—N(3)—C(11) 139.3(2), Mo(1A)—N(3)—C(11) 136.7(2).

this previously[11] and have identified tetraethyl thiuram disulfide, $Et_2NC(S)S—S(S)CNEt_2$, as the oxidised species.[12]

Single crystals of **1** were grown upon diffusion of methanol into a saturated dichloromethane solution, and the results of the crystallographic study are shown in Fig. 1 and its caption.[†] The molecule shows the expected geometry for complexes of this type, namely a *cis* arrangement of the terminal ligands and a puckered Mo_2X_2 core. Crystallographically only half of the molecule is unique, being related to the second half by a C_2 rotation axis that bisects the molybdenum–molybdenum vector and the bridging imido nitrogens. The metal–metal bond length of 2.633(1) Å is slightly longer than in the analogous tetraoxo complex [2.580(1) Å],[2] but is much shorter than that found in the tetrasulfido complex [2.817(2) Å].[7] The elongation of the molybdenum–molybdenum vector when spanned by sulfido moieties has previously been noted.[4] The terminal imido ligands are approximately linear at nitrogen [Mo(1)—N(2)—C(21) 167.9(3)°], while the molybdenum–nitrogen bond length [Mo(1)—N(2) 1.741(3) Å] is within the expected range for the imido ligand to be acting as a four-electron donor.[1,13] The bridging imido moieties span the metal–metal vector approximately symmetrically [Mo(1)—N(3) 1.958(3); Mo(1a)—N(3) 1.978(4) Å], while the coordination geometry about the bridging nitrogen is trigonal planar, indicating that it also acts as a four-electron donor ligand. The dihedral angle within the Mo_2N_2 core of 151.8° compares well with analogous tetraoxo, tetrasulfido

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[†] *Crystal data for* $Mo_2S_4N_6C_{38}H_{48}$: $M = 909.04$, monoclinic space group, $C2/c$, $a = 20.639(3)$, $b = 10.810(1)$, $c = 20.425(3)$ Å, $\beta = 113.21(1)°$, $U = 4188.1$ Å^3, $Z = 4$, $T = 292$ K, $D_c = 1.44$ g cm^{-3}, $F(000) = 1864$, $\lambda = 0.71073$ Å, $\mu(Mo\text{-}K_\alpha) = 8.09$ cm^{-1} Intensity data were collected on a crystal of dimensions $0.80 \times 0.40 \times 0.40$ mm mounted on a Nicolet R3mV diffractometer, by the ω-2θ scan technique ($5 \leqslant 2\theta \leqslant 50°$). From 5871 measured data, 3179 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 0.035 and 0.039.

and mixed oxo-sulfido complexes (148–153°). A further noteworthy feature of the solid-state structure of **1** is the disorder of the methyl groups over the ortho sites of the aryl rings being on C(12) and C(22) [60% occupancy] (shown) and C(16) and C(26) [40% occupancy].

Complexes containing the $[Mo_2(NR)_2(\mu\text{-}NR)_2]^{2+}$ have previously been prepared with cyclopentadienyl ligands completing the coordination environment, and only one such complex, namely $[Mo(NPh)(\eta^5\text{-}C_5H_4Me)(\mu\text{-}NPh)]_2$, has been crystallographically characterised.[10] It differs from **1** in that both terminal and bridging imido ligands act as three-electron donors and the molecule adopts a *trans*-planar core geometry. A further difference between the latter and **1** is the orientation of the aryl ring with respect to the Mo_2N_2 core, being approximately perpendicular in **1** but parallel in the cyclopentadienyl complex. This may be a result of orbital requirements, however, a steric interpretation appears more likely. Thus in **1**, if the aryl rings of the bridging imido ligand were to rotate by 90° then unfavourable steric interactions between the methyl substituent and the dithiocarbamate ligands would be envisaged.

In solution **1** exists as a number of interconverting rotomers. This is clearly shown by the ^1H NMR spectrum, the region between $\delta 2.8$–2.3 where the methyl substituents are observed being particularly informative. Thus at $-40°C$ in d_8-toluene, six sharp resonances are seen in this region of relative integrated intensities; $\delta 2.75(2)$, 2.70(9), 2.66(9), 2.55(1), 2.46(1), 2.36(2), suggesting that there is one major rotomer at this temperature and (at least) two minor rotomers. Warming results in a gradual collapse of the these signals and at 110°C the spectrum simplifies and two sharp singlets of equal intensity are observed at $\delta 2.42$ and 2.31. A comparison of the chemical shifts with the mixed oxo-imido complex $[MoO(\eta^2\text{-}S_2CNEt_2)(\mu\text{-}N\text{-}o\text{-}tolyl)]_2$ suggests that the signal to lower field is that associated with the bridging imido moiety.[12] In light of the solid-state structure of **1**, it is tempting to assign the major rotomer at low temperature to that shown in Fig. 1, however, a number of others are possible and it is difficult to differentiate between them. That signals assigned to both bridging and terminal imido moieties vary over the temperature range studied indicates that in each there is restricted rotation about the nitrogen–carbon bond. This is probably seen in a range of arylimido complexes but is generally difficult to monitor. Thus the *o*-methyl substituent acts as a good probe for the process.

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