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Crystal and molecular structures of *syn* and *anti* isomers of $[MoO(\mu\text{-}NAr)(S_2CNR_2)]_2$ (R = Et, Pr; Ar = Ph, *p*-tolyl)

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Abstract

Crystallographic studies have been carried out on four complexes of the type, $[MoO(\mu\text{-}NAr)(S_2CNR_2)]_2$ (R = Et, Pr; Ar = Ph, *p*-tol). Each contains a binuclear molybdenum(V) centre bridged by two imido ligands, with each molybdenum atom also carrying terminal dithiocarbamate and oxo moieties. *Syn* and *anti* structural types are seen which result in significant differences within the Mo_2N_2 core; that in the *anti* structures being planar, while fold angles of 151.1° and 164.6° are observed in the *syn* complexes.
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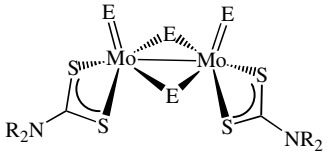
Keywords: Molybdenum; Imido; Oxo; Isomerism; Dithiocarbamate; Syn; Anti

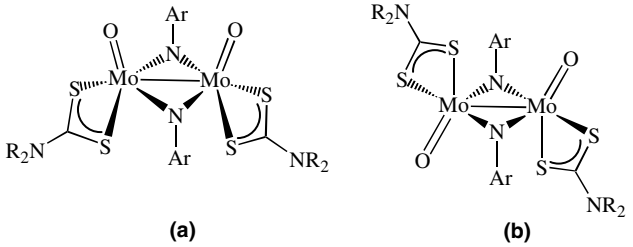
1. Introduction

Dithiocarbamate supported molybdenum(V) dimers of the type, $[MoE(\mu\text{-}E)(S_2CNR_2)]_2$ (E = O, S, NR′), are very common [1–24] being widely studied primarily in connection with a view to the biological importance of molybdenum. As a result a large number of crystal structures have been performed [13–27]. All show two distorted square pyramidal molybdenum(V) centres, which invariably adopt a *syn* conformation.



syn

During our work on the chemistry of molybdenum imido complexes, we have prepared and characterised a number of complexes of the type, $[MoO(\mu\text{-}NAr)(S_2CNR_2)]_2$; being easily generated as one of the products of the thermolysis $[MoO_2(S_2CNR_2)_2]$ with aryl isocyanates in toluene [25–27]. When we initially carried out this work, we assumed that the complexes contained a *syn* conformation, and failed to fully appreciate the appearance of minor peaks in the ^1H NMR spectra of these complexes. These were present after chromatographic work-up, but absent after a later recrystallisation step. More recently we have inadvertently discovered that, while the major products are the expected *syn* isomers, these minor components are in fact the previously unknown *anti* isomers.



1 R = Et, Ar = Ph
2 R = Et, Ar = p-tol
3 R = Pr, Ar = p-tol

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2. Results and discussion

Close inspection of the ^{1}H NMR spectra of samples of [MoO(μ-NPh)(S_2CNEt_2)]$_2$ (**1**), generated from the thermolysis of [MoO_2(S_2CNEt_2)$_2$] and one equivalent of phenylisocyanate in toluene followed by chromatographic purification, shows the existence of two isomeric species in ca. 8:1 (**1a**:**1b**). Precise ratios depend to some extent upon the sample history and preparation, primarily a result of the differing solubilities of the two components. We had previously observed this, but since the minor component was absent after the standard recrystallisation step (from dichloromethane–methanol mixtures) we had not deemed it worthy of note. However, upon recrystallisation of (**1**) from chloroform solution we noted the formation of small numbers of well-formed orange crystals of (**1b**) that differed significantly in appearance from the yellow needles of (**1a**) resulting from dichloromethane–methanol mixtures. Further, unlike the yellow material these orange crystals were not very soluble in chloroform, and when we were able to redissolve them it was apparent that they were the minor component of the original sample. In order then to fully characterise the components of the original mixture we sought to generate X-ray quality crystals of both. Crystallisation of the mixture from toluene afforded yellow crystals of (**1a**). While we were able to collect crystallographic data for (**1a**) · C_7H_8 (Fig. 1) and (**1b**) · $CHCl_3$ (Fig. 2). These results clearly established the mixture as being that of the *syn* and *anti*-[MoO(μ-NPh)(S_2CNEt_2)]$_2$, although neither data set was of particularly good quality. That for (**1b**) suffered due to loss of intensity as a result of chloroform loss during the collection, while in (**1a**) the co-crystallised toluene could only be refined isotropically.

Hence, in order to establish the precise nature of the structural differences in these *syn* and *anti* isomers, the analogous *para*-tolyl complexes [MoO(μ-*N*-*p*-tol)(S_2CNR_2)]$_2$ (R = Et, Pr) (**2**–**3**) were prepared (**2a**:**2b** ca. 12:1 and **3a**:**3b** ca. 3.5:1) and good quality crystals of both *syn*-[MoO(μ-*N*-*p*-tol)(S_2CNPr_2)]$_2$ (**3a**) and *anti*-[MoO(μ-*N*-*p*-tol)(S_2CNEt_2)]$_2$ (**2b**) were generated upon recrystallisation from dichloromethane–methanol mixtures. These results are displayed in Figs. 3 and 4, respectively. In (**2b**), there are two half molecules in the asymmetric unit. They do not differ significantly and only one of them is shown in Fig. 4, however, throughout the discussion values for both will be given. A comparison of molybdenum–molybdenum bond lengths and Mo_2E_2 fold angles for all four complexes together with those for related dithiocarbamate species are given in Table 1.

The *syn* and *anti* isomers are similar in many respects but differ in a number of ways. Bond lengths do not vary to any significant effect between the two structural types. Molybdenum–molybdenum bonds of 2.629–2.685 Å are similar to those found in related imido-bridged dimeric molybdenum(V) complexes (Table 1), while molybdenum–oxygen bonds of 1.684–1.703 Å are also as expected. The bridging imido ligands are approximately symmetrically bound to each molybdenum centre.

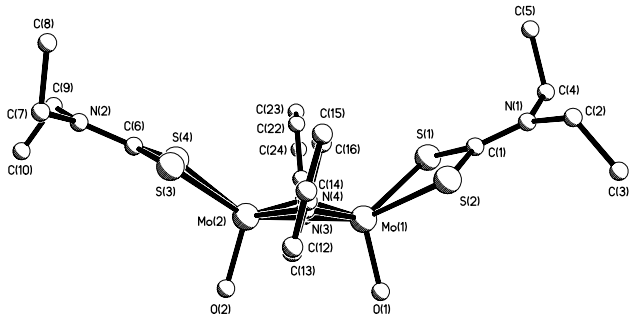

Fig. 1. Molecular structure of *syn*-[MoO(μ-NPh)(S_2CNEt_2)]$_2$ (**1a**) with selected bond lengths (Å) and angles (°); Mo(1)–Mo(2) 2.645(2), Mo(1)–O(1) 1.703(10), Mo(2)–O(2) 1.683(13), Mo(1)–S(1) 2.481(6), Mo(1)–S(2) 2.481(6), Mo(2)–S(3) 2.487(5), Mo(2)–S(4) 2.486(6), Mo(1)–N(3) 1.989(13), Mo(1)–N(4) 1.92(2), Mo(2)–N(3) 1.95(2), Mo(2)–N(4) 1.955(13), Mo(1)–N(3)–Mo(2) 84.4(6), Mo(1)–N(4)–Mo(2) 85.9(5), N(3)–Mo(1)–N(4) 91.7(6), N(3)–Mo(2)–N(4) 92.1(6), Mo(1)–Mo(2)–O(2) 104.8(5), Mo(2)–Mo(2)–O(1) 104.8(5), S(1)–Mo(1)–S(2) 71.2(2), S(3)–Mo(2)–S(4) 70.7(2).

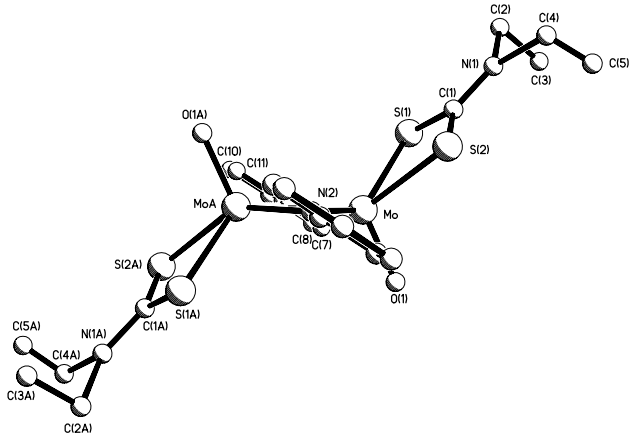

Fig. 2. Molecular structure of *anti*-[MoO(μ-NPh)(S_2CNEt_2)]$_2$ (**1b**) with selected bond lengths (Å) and angles (°); Mo–MoA 2.685(2), Mo–O(1) 1.696(11), Mo–S(1) 2.450(6), Mo–S(2) 2.485(6), Mo–N(2) 1.981(10), Mo–N(2A) 1.922(11), Mo–N(2)–MoA 86.9(4), N(2)–Mo–N(2A) 93.1(4), MoA–Mo–O(1) 116.4(5), S(1)–Mo–S(2) 70.39(19).

The most obvious difference between *syn* and *anti* isomers is the conformation of the central Mo_2N_2 core; being flat in the latter and folded in the former. All examples of crystallographically characterised *syn* complexes of this type have a puckered Mo_2E_2 core, fold angles varying between 145° and 155° (Table 1). Both *syn* isomers characterised here exhibit similar behaviour, although fold angles of 155.1 (**1a**) and 164.6 (**3a**) are greater than might have been anticipated. The latter is especially noteworthy, being some 9° flatter than all previous examples, including the isomeric *syn*-[MoO(*N*-*o*-

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