Synthesis and Structural Characterisation of Mixed Bimetal Compounds containing Molybdenum

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Reaction of $Mo(SBu^t)_4$ or $Mo(SBu^t)_2(CNBu^t)_4$ with $CuBr(CNBu^t)_3$ or '$Pd(CNBu^t)_2$' gives mixed d^4–d^{10} bimetal compounds; *X*-ray crystallographic studies have confirmed the presence of a highly delocalized MoS_2Cu core in two conformational isomers of $(Bu^tNC)_4Mo(\mu\text{-}SBu^t)_2CuBr$.

Our interest in Cu–Mo antagonism in ruminants[1] and the ongoing research in transition metal thiomolybdates[2] has led us to investigate the interaction of thiolatomolybdenum species with Cu compounds. Herein we report the synthesis, structural characterisation, and conformational equilibration of two new, d^4–d^{10} mixed bimetal compounds containing molybdenum.

Reaction of $Mo(SBu^t)_4$[3] with $CuBr(CNBu^t)_3$[4] in dry acetone under dinitrogen gave a crimson solution. After evaporation to dryness and washing with n-hexane, a crimson solid was

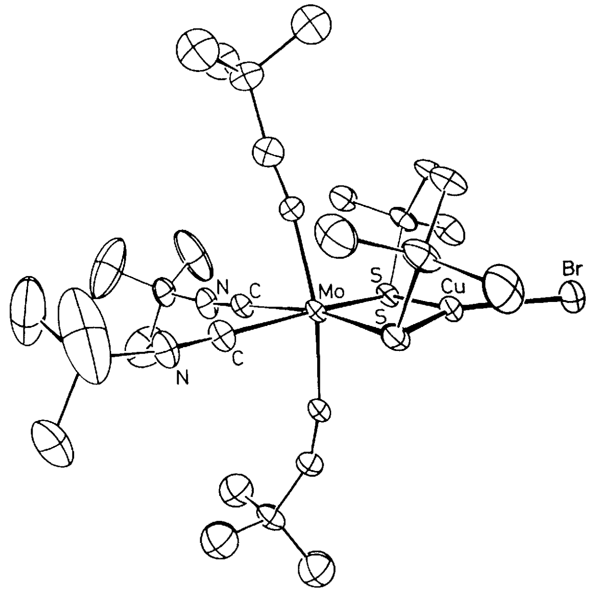

Figure 1. The Mo(CNBu^t)$_4$(μ-SBu^t)$_2$CuBr complex, (**1**). Selected intramolecular dimensions: Mo - - - Cu 2.615(2); Mo–S, 2.409(2); Cu–S, 2.233(3); Cu–Br, 2.314(2) Å; S–Mo–S, 105.0(1); S–Cu–S, 117.8(1); C(2)–Mo–C(2), 79.6(3); Mo–S–CMe$_3$, 120.4(3); Cu–S–CMe$_3$, 108.3(3); and Mo–S–Cu, 68.4(1)°.

obtained. Recrystallisation from a small amount of acetone gave (Bu^{t}NC)$_4$Mo(SBu^t)$_2$CuBr (**1**) in 60% yield. Alternatively, reaction of Mo(SBu^t)$_2$(CNBu^t)$_4$[5,6] with CuBr(CNBu^t)$_3$ in acetone gave (**1**) in 31% yield. A satisfactory elemental analysis was obtained. The complex is diamagnetic, and moderately stable to air and heat. The ^{1}H n.m.r. spectrum in chlorobenzene contained five signals assignable to the Bu^t groups of the isocyanide ligands, and two signals assignable to Bu^t groups of the thiolato ligands (because of the presence of two isomers; see later).

Crystal data for (**1**): $C_{28}H_{54}BrCuMoN_4S_2$, $M = 750.3$, orthorhombic, *Pnma*, $a = 21.994(2)$, $b = 16.411(3)$, $c = 10.605(1)$ Å, Cu-K_α, $\lambda = 1.54178$ Å, $U = 3838$ Å^3, $Z = 4$, $D_c = 1.301$ g cm^{-3}, and $\mu = 46.1$ cm^{-1}.

Crystallographic *m* symmetry is imposed upon the molecule. Refinement by full-matrix least-squares methods of F converged at agreement factors $R_1 = 0.08$ and $R_2 = 0.12$ using 2882 observations with $F^2 > 0$.† The compound (**1**) contains a MoS$_2$Cu core, formed by the known molecule Mo(SBu^t)$_2$(CNBu^t)$_4$[5] acting as a bidentate ligand to a CuBr moiety through bridging thiolato ligands, see Figure 1. The Bu^t substituents on the μ-thiolato ligands stand upright on the same side of the MoS$_2$Cu plane (*syn*-conformation). The molybdenum atom has a distorted octahedral geometry, arising from the d^4 electron configuration,[6] while the Cu atom has an almost ideal trigonal planar co-ordination.

Since Mo(SBu^t)$_2$(CNBu^t)$_4$ is extremely reactive to nucleophiles such as acetylenes,[7] we treated (**1**) with diphenylacetylene in refluxing acetone for 15 h. Work-up of the reaction mixture and recrystallisation from acetone–toluene gave crimson crystals (**2**), whose elemental analysis indicated a 1 : 1 acetylene adduct. However, the ^{1}H n.m.r. spectrum in [^{2}H$_6$]-acetone was almost identical with that of (**1**), and there was no i.r. absorption in the region 1900—1600 cm^{-1}.

Crystal data for (**2**): $C_{42}H_{64}BrCuMoN_4S_2$, $M = 928.5$, monoclinic, $P2_1$, $a = 11.702(2)$, $b = 20.134(4)$, $c = 10.455(4)$ Å, $\beta = 98.85(2)°$, Cu-K_α, $\lambda = 1.54178$ Å, $U = 2434$ Å^3, $Z = 2$, $D_c = 1.266$ g cm^{-3}, and $\mu = 48.2$ cm^{-1}.

Refinement by block-diagonal least-squares methods of F, using 3690 unique data with $F^2 > 0$, converged at $R_1 = 0.09$ and $R_2 = 0.10$.† No acetylene adduct has been formed. The crystals contain independent molecules of diphenylacetylene, and crystallisation of (**2**) from the less polar acetone–toluene mixture surprisingly gave the *anti*-isomer in this case (*i.e.* Bu^t groups on either side of the MoS$_2$Cu plane). There is close agreement in molecular dimensions between the two conformational isomers [*anti*-isomer: Mo - - - Cu, 2.628(2); Mo–S, 2.410(3) and 2.415(3); Cu–S, 2.234(3) and 2.244(3); Cu–Br, 2.317(2) Å; S–Mo–S, 105.0(1); Mo–S–Cu, 68.6(1) and 68.6(1)°] which differ in the disposition of the substituents on the μ-thiolato ligands. See Figure 1 for *syn*-isomer dimensions.

The *anti* $\rightleftharpoons$ *syn* conformational change was confirmed by the temperature dependence of the ^{1}H n.m.r. spectrum of (**1**). At room temperature in chlorobenzene the two isomers are present in a roughly 3 : 2 *anti* : *syn* ratio. Upon raising the temperature the two signals from the μ-SBu^t ligands coalesce at about 70 °C, as do those of the axial CNBu^t ligands. Above 70 °C only three signals remain, implying a rapid equilibration of *syn*- and *anti*-isomers.

The versatility of the bisthiolatomolybdenum fragment as a chelating ligand is further evident from its reaction with ‘Pd(CNBu^t)$_2$’.[8] Treatment of Mo(SBu^t)$_2$(CNBu^t)$_4$ with an equimolar amount of ‘Pd(CNBu^t)$_2$’ in toluene at ambient temperature overnight gave, after usual work-up, deep dull purple crystals (64%) of formula, (Bu^{t}NC)$_4$Mo(μ-SBu^t)$_2$Pd-(CNBu^t)·PhMe. The elemental analysis agreed well with the theoretical values. The molecular structure, isostructural to that of the *anti*-Mo–Cu complex, can be deduced on the basis of well defined i.r. (Nujol) [ν(N≡C), 2080, 2040, 1965, and 1940sh cm^{-1}, ν(Bu^t), 1221sh, 1207, and 1157 cm^{-1}] and ^{1}H n.m.r. spectra {δ ([^{2}H$_6$]acetone) 1.556 [s, SC(CH_3)$_3$], 1.497 [s, PdCNC(CH_3)$_3$], 1.414 [s, equatorial MoCNC(CH_3)$_3$], 1.250 [s, axial MoCNC(CH_3)$_3$]}.

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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.