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# Synthesis and characterization of the organocopper–copper halide complex $[CuMes^*\{Cu_2Br_2(SMe_2)_3\}]$ ($Mes^* = C_6H_2Bu^t{}_3$-2,4,6)

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Treatment of 3 equivalents of CuBr with LiMes* ($Mes^* = C_6H_2Bu^t{}_3$-2,4,6) in $Et_2O$ at *ca.* −78 °C afforded, upon treatment with $SMe_2$, the organocopper–copper halide complex $[CuMes^*\{Cu_2Br_2(SMe_2)_3\}]$ **1** which has the previously unobserved CuR : CuX ratio of 1 : 2; it is a very rare example of a structurally characterized CuR : CuX complex without chelating R groups.

Organocopper–copper halide aggregates are an important and growing class of organocopper compounds.[1] They are characterized by different organocopper to copper halide ratios. To date, well defined, aggregates with the CuR/CuX (R = alkyl or aryl; X = halide) ratios of 2 : 1,[2] 2 : 2,[2,3] 2 : 3,[4] 4 : 2[5] have been characterized. In many instances chelating aryl ligands such as $C_6H_4(CH_2NMe_2)$-2[6] have played a key role in stabilizing these complexes. During investigations of the reaction of LiMes* ($Mes^* = C_6H_2Bu^t{}_3$-2,4,6)[7] with copper bromide in diethyl ether solution, it was observed that most of the copper bromide appeared to have reacted when less than 0.5 equivalent of LiMes* was added. This observation suggested that an organocopper–copper halide, possibly of previously unobserved 1 : 2 stoichiometry, had formed. In this paper the synthesis and characterization of this new complex $[CuMes^*\{Cu_2Br_2(SMe_2)_3\}]$ **1** are now reported.

Compound **1** was synthesized† by the addition of LiMes* to CuBr in $Et_2O$ at *ca.* −78 °C. Warming to room temperature and the addition of dimethyl sulfide, followed by filtration and cooling in a −20 °C freezer, afforded colorless crystals of **1** in moderate yield. Proton NMR spectroscopy of **1** in $C_6D_6$ solution indicated a 3 : 1 ratio of $SMe_2$ to Mes* groups. The Cu–Mes* bonding was indicated by the appearance of an *ipso* carbon resonance at δ 167.50 in the $^{13}C$-$\{^1H\}$ NMR spectrum which is within the known range for *ipso* carbon shifts in arylcopper/arylcuprate solutions in $SMe_2$.[8] However, the exact structure of **1** was established by X-ray crystallography.† The illustration in Fig. 1 indicates that one CuMes* unit is associated with two copper bromides to form a very unusual six-membered ring composed of three coppers, two bromides and an *ipso* carbon from the Mes* group. The $Cu_3Br_2C$ array is almost planar (average deviation = 0.009 Å), but there are gross variations in the angles within the ring. There is an almost perpendicular angle of 88.2° between the plane of the Mes* ring and the $Cu_3Br_2C$ core. The ring distances are also quite variable; the shortest involve the C(1)–Cu(2)–Br(2) unit where Cu(2)–C(1) and Cu(2)–Br(2) bond lengths of 1.972(14) and 2.295(3) Å, respectively are observed. These may be compared to the much longer Cu(1)–C(1) and Cu(3)–Br(2) distances of 2.09(2) Å and 2.558(4) Å. These structural data as well as the near linear co-ordination at Cu(2) [C(1)–Cu(2)–Br(2) 170.6(4)°] suggest that the compound can be viewed as a contact ion pair composed of a $[BrCuMes^*]^-$ anion and a $[(Me_2S)_2Cu(\mu\text{-}Br)Cu(SMe_2)]^+$ cation. This view is further supported by the fact that the deviation of the Cu(2)–C(1) vector from the Mes* ring plane is 27.5° whereas the deviation for the Cu(1)–C(1) vector is 47.4°. In the anion, the Cu–C and Cu–Br bond lengths are just slightly longer than those observed in the solvent separated anion $[Cu(Br)\{CH(SiMe_3)_2\}]^-$ in which Cu–C = 1.920(0) Å and Cu–Br = 2.267(2) Å.[9] The longer distances in

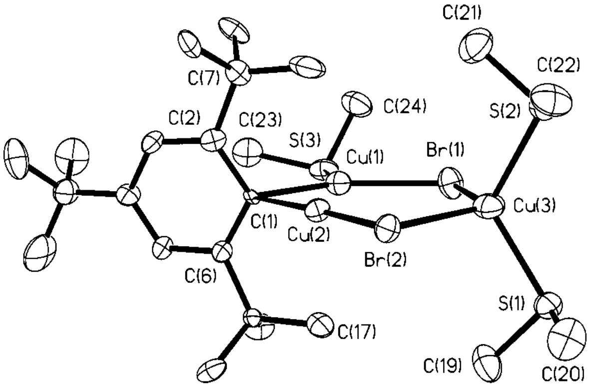

**Fig. 1** Computer generated drawing of **1** with H atoms not shown. Selected bond distances (Å) and angles (°): Cu(1)–C(1) 2.09(2), Cu(1)–S(3) 2.306(6), Cu(1)–Br(1) 2.420(4), Cu(2)–C(1) 1.972(14), Cu(2)–Br(2) 2.295(3), Cu(3)–Br(1) 2.510(3), Cu(3)–Br(2) 2.558(4), Cu(3)–S(1) 2.278(5), Cu(3)–S(2) 2.267(5); C(1)–Cu(1)–S(3) 111.5(4), C(1)–Cu(1)–Br(1) 142.6(4), S(3)–Cu(1)–Br(1) 105.7(2), Cu(1)–C(1)–Cu(2) 50.4(4), C(1)–Cu(2)–Br(2) 170.6(4), Cu(2)–Br(2)–Cu(3) 88.95(11), Br(1)–Cu(3)–Br(2) 113.8(2), Cu(1)–Br(1)–Cu(3) 110.6(2), S(1)–Cu(3)–S(2) 119.8(2), C(2)–C(1)–C(6) 115.5(13).

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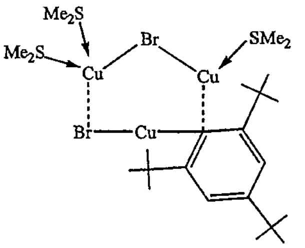
† Under anaerobic and anhydrous conditions LiMes* (0.504 g, 2 mmol) in $Et_2O$ (20 mL) was added to a well-stirred suspension of CuBr (0.86 g, 6 mmol) in $Et_2O$ (20 mL) with cooling in a dry ice bath. After *ca.* 1 h, the mixture was allowed to come to room temperature whereupon *ca.* 2 mL of $SMe_2$ was added. Stirring was continued for *ca.* 3 h and the pale yellow solution was filtered. The volume of the solution was reduced to *ca.* 10 mL and it was then stored in a −20 °C freezer for 24 h to afford the product **1** as colorless crystals. Yield 0.75 g, 0.96 mmol, 48%; mp 127 °C (decomp.). It has not been possible to obtain a satisfactory combustion analysis of **1** owing to desolvation of the crystals. However, atomic absorption spectroscopy indicates an approximate Cu : Br ratio of 3 : 2. $^1H$ NMR ($C_6D_6$, 25 °C): δ 7.59 (br s, 2 H, $m$-$C_6H_2$); 1.92 (br s, 18 H, $SMe_3$); 1.71 [s, 18 H, $o$-$C(CH_3)_3$]; 1.56 [s, 9 H, $p$-$C(CH_3)_2$]. $^{13}C$-$\{^1H\}$ NMR ($C_6D_6$, 25 °C): δ 167.50 ($i$-$C_6H_2$), 150.33 ($o$-$C_6H_3$); 120.37 ($p$-$C_6H_3$); 119.66 ($m$-$C_6H_3$); 38.53 [$o$-$C(CH_3)_3$], 35.09 [$p$-$C(CH_3)_3$]; 33.38 [$o$-$C(CH_3)_3$]; 30.65 [$p$-$C(CH_3)_3$]; 18.78 ($SMe_2$). The broad singlet obtained for the $SMe_2$ signal is probably due to rapid exchange of $SMe_2$ between the copper sites. Cooling the spectrum to −60 °C did not result in splitting of the signal.

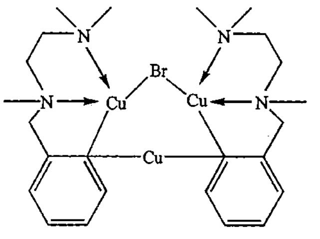
‡ Crystal data at 130 K with Mo-Kα (λ = 0.710 73) radiation for $C_{24}H_{47}Br_2Cu_3S_3$: $M = 782.24$, $a = 14.510(5)$, $b = 18.993(5)$, $c = 11.448(3)$ Å, $U = 3155(2)$ Å$^3$, orthorhombic, space group $Pca2_1$, $\mu = 4.747$ mm$^{-1}$, $Z = 4$, $R1 = 0.085$ for 2048 [$I > 2(\sigma)I$] data, $wR2 = 0.1874$ for all 3831 data, full-matrix least squares based on $F^2$. CCDC reference number 186/1079.

the anion of **1** can be attributed to the increased co-ordination numbers as a result of its association with the cation. The Cu–S distances observed in **1** lie in the middle of the currently known range [*ca.* 2.185(1)[10]–2.383(2) Å[11]] for SMe$_2$ complexes of organocopper species. The Cu(1)–S(3) bond length in **1** is 2.306(6) Å, which is longer than the 2.267(5) and 2.278(5) Å Cu–S distances observed for Cu(3). The longer Cu(1)–S(3) distance is surprising in view of the fact that the Cu(1) co-ordination number is lower than that of Cu(3). Part of the explanation may be that, since Cu(1) is also bound to the Mes* ligand, its environment may be more crowded which leads to a lengthened Cu–S bond.

The structural arrangement of **1** bears some resemblance to that of the chelated trimetallic species $Cu_3(Br)\{C_6H_4[CH_2N(Me)CH_2CH_2NMe_2]\text{-}2\}_2$ **2**.[2] In this molecule the anion has the formula $[Cu\{C_6H_4[CH_2N(Me)CH_2CH_2NMe_2]\}]^-$ with Cu–C distances that average 1.967(11) Å which is very similar to the Cu(2)–C(1) distance in **1**. Two further $Cu^+$ ions are complexed by the two N donors in each 'arm' of the ligand. These metals also interact with an *ipso* carbon on each aryl ring and have Cu–C distances that average 2.095(14) Å, which is identical to the Cu(1)–C(1) length in **1**. The structure is completed by a $Br^-$ ion which bridges the two amine complexed coppers to afford Cu–Br distances that average 2.435(8) Å. This length is very like the 2.420(4) Å seen for the Cu(1)–Br(1) bond in **1**. Longer bond lengths are seen for Cu(3) where distances of 2.510(3) and 2.558(4) Å were observed. This is probably a result of the higher co-ordination number at Cu(3).



**1**



**2**

The structure of **1** is also characterized by a relatively short Cu(1)···Cu(2) distance of 2.471(4) Å. This is longer than the corresponding average of 2.406(3) Å in **2**[2] but close to the 2.443(1) Å seen in the unusual dimer $[(Me_2S)_2Cu(\mu\text{-}C_6H_2Ph_3\text{-}2,4,6)CuC_6H_2Ph_3\text{-}2,4,6]$.[10] These Cu–Cu distances are indicative of a weak $d^{10}$–$d^{10}$ interaction between the metals.[12]

In summary, compound **1** represents the highest ratio (2:1) copper halide–organocopper complex that has been isolated to date. The structure of **1** provides further evidence that such complexes can be isolated in the absence of chelating ligands as well as underlining the importance of SMe$_2$ as ligand or solvent in organocopper chemistry.[13]

## Acknowledgements

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