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Mesitylcopper: Tetrameric and Pentameric

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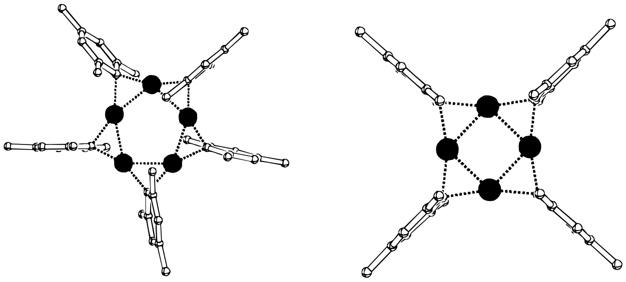
Summary: New phases containing tetrameric and pentameric mesitylcopper have been isolated from ether solvents and characterized with single-crystal X-ray diffraction. Mesitylcopper crystallized from toluene, which is a widely used reagent, has been found to contain one lattice solvent molecule. On the basis of these findings and cryoscopic molecular weight determinations, an equilibrium between a tetramer and pentamer in both etheral and aromatic solutions is proposed.

Mesitylcopper, a highly useful reagent for the synthesis of a variety of copper(I) compounds,[1] is known to be pentameric (see Chart 1) in the solid state when crystallized from toluene.[2] However, evidence has been presented suggesting a lower degree of aggregation in solution.[3] Furthermore, recent crystal structures of the homoleptic compounds (2,4,6-triisopropylphenyl)copper[4] and *o*-vinylphenylcopper,[5] feature tetrameric square-planar clusters (see Chart 1). Phenylcopper(I) has been isolated as the dimethylsulfide solvate with a square-planar tetrameric copper(I) core[6] which resembles the tetranuclear complex between mesitylcopper and tetrahydrothiophene.[3] In dimethyl sulfide (DMS) solution, however, phenylcopper would appear to be an equilibrium mixture of $(CuPh)_3$ and $(CuPh)_4$.[7] Arylcopper compounds that have functionalities with coordinating heteroatoms frequently exhibit the familiar tetrameric square-planar structure.[8] In order to further investigate the apparently very delicate balance between aggregation number 4 and 5 for mesitylcopper, we decided to primarily use ether solvents, which lie in between toluene and DMS in donor ability and are important solvents for preparative purposes.

Chart 1



The synthesis of mesitylcopper in THF is straightforward,[9] and large amounts of microcrystalline material are easily prepared. However, in our hands it was only possible to isolate X-ray quality crystals from THF solutions of mesitylcopper after adding diethyl ether. Structure determination using X-ray crystallography[10] revealed that mesitylcopper (**1**) which is crystallized from a THF/ether solution exhibits a square-planar tetramer with four THF molecules occupying the empty spaces between the mesityl ligands (see Figure 1). Interestingly, none of the THF molecules are actually coordinated, as opposed to the case in the DMS and tetrahydrothiophene (THT) solvates, which means that homoleptic mesitylcopper now is known as both a tetramer and a pentamer in the solid state. The mean Cu−Cu distance in **1** is 2.42 Å and, consequently, indicative of a bonding Cu−Cu interaction.[11] The C_{ipso} atoms in **1** are, within experimental errors, coplanar with the square-planar core formed by the four copper atoms. This is in contrast to the other two structurally charactreized homoleptic square-planar tetramers, *viz.* (2,4,6-triisopropylphenyl)copper[4] and *o*-vinylphenylcopper,[5] where the C_{ipso} atoms alternate 0.4 Å above and beneath the copper plane. We have recently determined the crystal structure of pentamethylphenylcopper,[12] which exhibits the same planar eight-membered ring as in **1**. It, thus, seems as if

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[3] Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067.

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[8] van Koten, G.; James, S. L.; Jastrzebeski, J. T. B. H. *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 3, pp 57−133.

[9] *Preparation of $[CuMes]_4$·4THF (**1**):* All operations were carried out under argon using standard Schlenk techniques. Solvents (dioxane, tetrahydrofuran, diethyl ether, toluene) were distilled under argon from sodium/benzophenone shortly prior to use. Mesityl bromide (5.5 g, 28 mmol) was added slowly to a slight excess of magnesium (0.70 g, 29 mmol) in 50 mL of THF. The solution was stirred for 12 h, whereafter it was centrifuged and the brownish supernatant was withdrawn and added to purified CuCl (3.0 g, 30 mmol) at −30 °C. The reaction solution was then slowly allowed to warm to ambient temperature, yielding a yellow solution and a white precipitate. Dioxane (20 mL) was added, stirring was continued for 2 h, and the solution was then centrifuged. The supernatant was evaporated to dryness under reduced pressure, dissolved in 50 mL of toluene, and centrifuged. The supernatant was evaporated to dryness under reduced pressure and crystals of **1** were grown from THF/diethyl ether (1:1 v:v) at −20 °C.

[10] $Cu_2O_2C_{26}H_{38}$ (**1**): monoclinic, $P2_1/n$, No. 14, $a = 12.720(6)$ Å, $b = 8.451(6)$ Å, $c = 24.338(6)$ Å, $\beta = 102.41(3)°$, $V = 2555(2)$ Å^3, $Z = 4$, $T = -100$ °C, $D_{calc} = 1.325$ g cm^{-3}. Refinement on F^2, using SHELXL, for 3121 reflections ($5 < 2\theta < 50°$) and 277 parameters gave $R1 = 0.051$ and $R_w = 0.135$ for $I > 2.0\sigma(I)$. Cu, O, and C were refined with anisotropic thermal displacement parameters, and the hydrogen atoms were included in calculated positions and allowed to ride on their respective carbon atom during refinement. The maximum and minimum values in the final difference map were 0.67 and −0.44 e/Å^3, respectively. The THF molecules exhibit some ring spinning causing the oxygen positions to be somewhat ambigous.

[11] (a) Mehrotra, P. M.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 2187. (b) Merz, K. M., Jr.; Hoffmann, R. *Inorg. Chem.* **1988**, *27*, 2120. (c) Subramanian, L.; Hoffmann, R. *Inorg. Chem.* **1992**, *31*, 1021. (d) Cui, C. X.; Kertesz, M. *Inorg. Chem.* **1990**, *29*, 2568. (e) Avdeef, A.; Fackler, J. P., Jr. *Inorg. Chem.* **1978**, *17*, 2182. (f) Lee, S. W.; Trogler, W. C. *Inorg. Chem.* **1990**, *29*, 1659. (g) Burdett, J. K.; Eisenstein, O. *Inorg. Chem.* **1992**, *31*, 1758. (h) Soloveichik, G. L.; Eisenstein, O.; Poulton, J. T.; Streib, W. E.; Huffmann, J. C.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3306. (i) Håkansson, M.; Örtendahl; M.; Jagner, S.; Sigalas, M. P.; Eisenstein, O. *Inorg. Chem.* **1993**, *32*, 2018. (j) Belanzoni, P.; Rosi, M.; Sgamelotti, A.; Baerends, E. J.; Floriani, C. *Chem. Phys. Lett.* **1996**, *257*, 41.

[12] Eriksson, H.; Håkansson, M.; Jagner, S. Manuscript in preparation.

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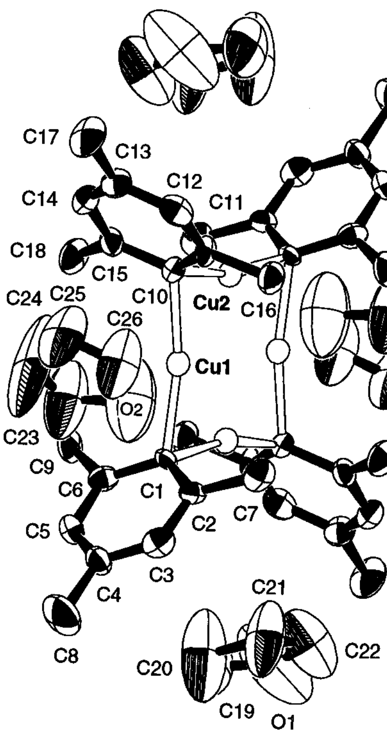

Figure 1. ORTEP drawing of **1**. Selected interatomic distances (Å) and angles (deg): Cu(1)−Cu(2) = 2.414(2), Cu(1)−Cu(2a) = 2.432(2), Cu(1)−C(1) = 1.990(9), Cu(1)−C(10) = 1.995(10), Cu(2)−C(10) = 1.986(10), Cu(2)−C(1a) = 1.999(9), C(1)−C(2) = 1.420(13), C(2)−C(3) = 1.394(13), C(3)−C(4) = 1.378(14), C(2)−C(7) = 1.529(13), C(1)−Cu(1)−C(10) = 164.0(4), C(1)−Cu(1)−Cu(2) = 143.5(3), C(10)−Cu(1)−C(1a) = 165.7(4), Cu(1)−Cu(2)−Cu(1a) = 89.10(6). Symmetry code: a = $-x + 1$, $-y + 1$, $-z$.

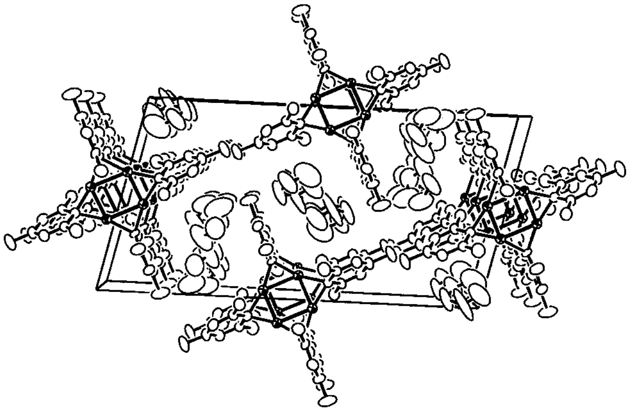

Figure 2. View along the *b*-axis showing how channels occupied by solvent molecules are formed in **1**. The intermolecular distance between two stacked copper squares is 8.5 Å.

absence of puckering in the eight-membered central ring is characteristic of arylcopper compounds with symmetrical aryl groups like mesityl or pentamethylphenyl.

The crystal packing pattern in **1** is displayed in Figure 2 and shows how channels are formed from the positioning of the tetramers. The channels are filled with four THF molecules for every tetramer, *i.e.*, one per Cu. Although the previously reported (2,4,6-triisopropylphenyl)copper[4] and *o*-vinylphenylcopper[5] have no cocrystallized solvent, we decided to perform a refinement of the pentameric mesitylcopper phase previously reported[2] and were able to locate one toluene molecule for every pentamer in the crystal lattice.[13] Pentameric mesitylcopper crystallized from toluene should, thus, be formulated as [$Cu_5(Mes)_5$]·toluene (**2**), which is of importance taking into account the widespread use of [$Cu_5(Mes)_5$]·toluene as a precursor.

When a freshly prepared THF/ether solution of mesitylcopper was stored at −80 °C, a previously unknown phase crystallized. A single-crystal X-ray determination, using low-temperature handling techniques,[14] showed that this phase, [$Cu_5(Mes)_5$]·*x*THF (**3**), contains a pentameric cluster with several disordered noncoordinating solvent molecules in the crystal lattice.[15] Unfortunately, a detailed geometric analysis of this molecule is not meaningful since the disorder is also present in some of the mesityl groups. On prolonged standing at −20 °C under THF/ether, the pentameric phase was completely transformed into the tetrameric phase, leading us to believe that the solution is dominated by an equilibrium between pentamers and tetramers. Previously reported NMR studies in various solutions support the assumption of two equilibrating species.[3] Also, recent DFT calculations show that the tetramer and pentamer are very close in energy.[11j]

In order to determine the degree of association in solution, a molecular weight determination in benzene by cryoscopy was performed. We excluded the interference of the crystal lattice toluene in [$Cu_5(Mes)_5$]·toluene by recrystallizing from benzene and drying under vaccum while keeping track of the weight. Using cryoscopic measurements on benzene solutions (equilibrated for 24 h) of different concentrations, we determined the aggregation number to be 4.16, while no concentration dependence was found. An equilibrium between pentamers and tetramers, thus, seems to be the obvious explanation.

While trying to dissolve the disorder in the pentameric THF phase by obtaining high-quality data, we are also pursuing mesitylcopper species occurring in solutions of Grignard composition in order to determine the effects of magnesium halide complexes on the association degree of mesitylcopper.

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Supporting Information Available: Text giving the details of the cryoscopic measurements, tables of crystal data and structure refinement, atomic coordinates, interatomic distances and angles, and anisotropic thermal parameters for **1**−**3**, and ORTEP diagrams of **2** and **3** (28 pages). Ordering information is given on any current masthead page.

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[13] $Cu_5C_{52}H_{63}$ (**2**): monoclinic, $P2_1/n$, No. 14, $a = 15.992(6)$ Å, $b = 15.819(6)$ Å, $c = 18.930(7)$ Å, $\beta = 96.902(10)°$, $V = 4754(3)$ Å^3, $Z = 4$, $T = -120$ °C, $D_{calc} = 1.405$ g cm^{-3}. Refinement on F^2 for 8370 reflections ($5 < 2\theta < 50°$) and 479 parameters gave $R1 = 0.055$ and $R_w = 0.151$ for $I > 2.0\sigma(I)$. Cu and C were refined with anisotropic thermal displacement parameters, and the hydrogen atoms were included in calculated positions and allowed to ride on their respective carbon atom during refinement. The maximum and minimum values in the final difference map were 1.76 and −0.73 e/Å^3, respectively.

[14] Håkansson, M. *Inorg. Synth.*, in press.

[15] [$Cu_5(Mes)_5$]·*x*THF (**3**): monoclinic, $P2_1/n$, No. 14, $a = 15.067(8)$ Å, $b = 20.70(9)$ Å, $c = 19.076(9)$ Å, $\beta = 96.30(1)°$, $V = 5936(5)$ Å^3, $Z = 4$, $T = -140$ °C, $D_{calc} = 1.233$ g cm^{-3}. Refinement on F^2 for 1219 reflections ($5 < 2\theta < 30°$) and 306 parameters gave $R1 = 0.067$ and $R_w = 0.162$ for $I > 2.0\sigma(I)$. Cu was refined with anisotropic thermal displacement parameters and carbon with isotropic thermal parameters. Due to poorly diffracting and quickly decomposing crystals, data collection had to stop at $2\theta = 30°$, which gave a low reflection/parameter ratio. This and disordered solvent molecules are probably contributing factors to the difficulties in obtaining a satisfactory structural model after refinement. The maximum and minimum values in the final difference map were 0.35 and −0.46 e/Å^3, respectively.