An unusually stable octanuclear σ-mesityl-bridged μ_4-oxo-copper(I) complex encapsulated by a pyrazolate-based compartmental ligand scaffold†

Michael Stollenz, Christian Große and Franc Meyer*

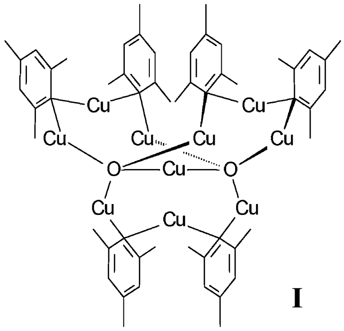
Received (in Cambridge, UK) 14th November 2007, Accepted 10th January 2008
First published as an Advance Article on the web 6th February 2008
DOI: 10.1039/b717571j

A new compartmental pyrazole-derived chelating ligand, four equivalents of mesitylcopper and stoichiometric amounts of dioxygen lead to the formation of a remarkably stable organometallic framework that can be described as a heteroleptic O-centered cuprate anion $[(\mathrm{MesCu^I})_4(\mu_4\text{-O})]^{2-}$ linked *via* σ-mesityl-bridges to two surrounding binuclear $\mathrm{Cu^I}$-pyrazolate clamps.

The activation of dioxygen, mediated by copper, is of outstanding interest for important synthetic applications, such as the catalytic oxidation of ethylene to ethylene glycol, the Wacker process, or the oxidative coupling of acetylenes and of biaryls.[1–4] Albeit several efforts were made to clarify the specific roles of copper in oxidatively induced C–C coupling reactions, most mechanisms are not fully understood so far.[2–4] Controlled oxygenation of well-defined σ-organo $\mathrm{Cu^I}$ compounds,[5] which serve as precursors in copper-mediated oxidative couplings, appears to be a promising approach to get some insight in the mechanistic details of such reactions. As shown earlier, however, mostly undefined copper complexes and biaryls are formed under usual conditions.[6] A milestone in this context is the controlled oxygenation of mesitylcopper—which is a powerful synthon for the preparation of unusual homocuprates,[7] homoleptic $\mathrm{Cu^I}$ alkoxides and phenoxides,[8] Schiff base macrocyclic complexes,[9] arylated B-, Sn-, as well as P-halides[10] and, as shown recently, luminescent cluster frameworks[11]—affording bimesityl and the highly sensitive complex $[\mathrm{Cu_{10}O_2(Mes)_6}]$ (**I**) that contains seven μ-O-bridged $\mathrm{Cu^I}$ centres, according to the X-ray structure elucidation.[12] Due to its extreme sensitivity, however, no further analytical and spectroscopic data could be obtained for this compound so far.

Herein, we now report on an exceptionally stable σ-organocomplex with a concealed $[(\mathrm{MesCu^I})_4(\mu_4\text{-O})]^{2-}$ heteroleptic cuprate core that is stabilised by two binucleating pyrazolate clamps, and its complete characterisation including an X-ray structure determination.

Multifunctional pyrazolate ligands with chelating side arms in the 3- and 5-positions of the heterocycle have been shown to offer versatile scaffolds for a wide range of homo- and heterobinuclear complexes, with applications in biomimetic chemistry and catalysis.[13] In the context of the present organometallic objectives we set out to further elaborate such ligands by introducing a phenyl group in the 4-position of the pyrazolate ring, in order to provide enhanced solubility in less polar solvents such as benzene and toluene. This modification makes the pyrazolate-based bridging ligands valuable tools for stabilising sensitive organometallic species that generally do not tolerate any polar coordinating or protic solvents. The new ligand **2**H, which was synthesised starting from 3,5-bis(hydroxymethyl)-4-phenyl-1*H*-pyrazole[14] as shown in Scheme 1, is predestinated (after deprotonation) to span two metal ions nested in its two tridentate binding sites. Since $\mathrm{Cu^I}$ tends to prefer four as its highest coordination number, **2** should be particularly suitable for insulating sensitive organocopper frameworks. In contrast to related pyrazolate ligands lacking the phenyl group, **2**H is indeed well soluble in benzene and toluene (compare ESI†).



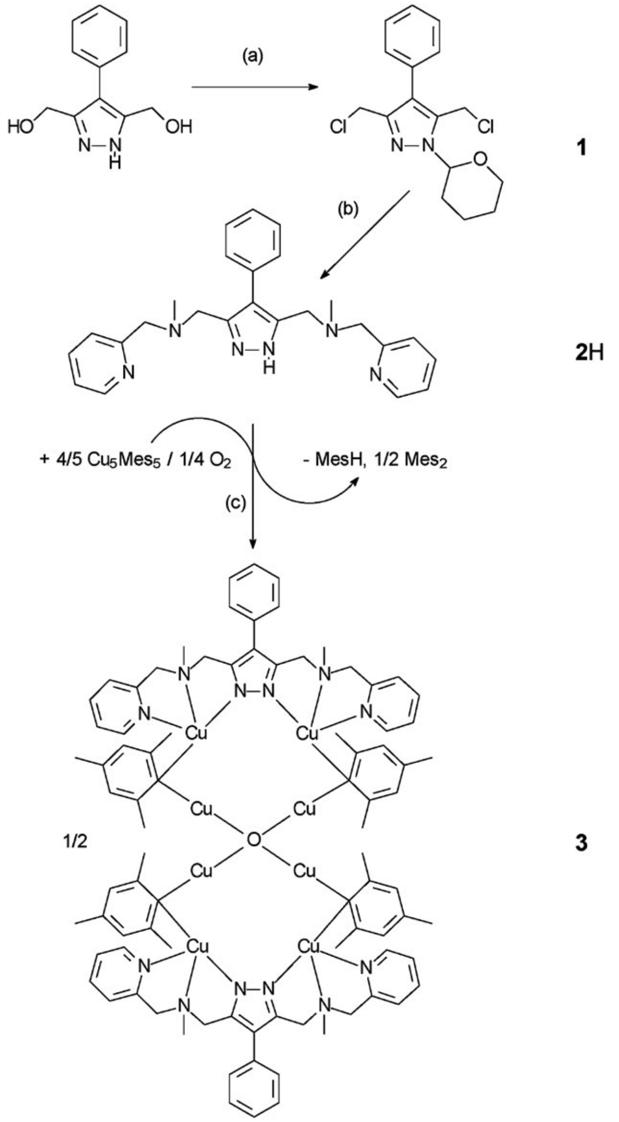
I

As previously demonstrated, chelating pyrazolate ligands usually afford binuclear complexes with M···M distances in the range 3.5–4.5 Å, depending on the chelate arms.[15] Mesitylcopper forms oligonuclear ring structures $[\mathrm{CuMes}]_n$ (n = 4, 5) where the interatomic Cu···Cu distances are governed by the geometric requirements of the $\mathrm{Cu_5}$ pentamer as well as the mesityl bridging ligands.[16] Intermetallic distances between the next but one neighbouring Cu atoms in the pentamer are around 4.04 Å. Therefore **2**H (after deprotonation) should provide the right premises to accommodate and stabilise a tailored "corner piece" of mesitylcopper such as fragments $[\mathrm{Cu}(\mu\text{-Mes})\mathrm{Cu}(\mu\text{-Mes})\mathrm{Cu}]^+$ or $[\mathrm{Cu}(\mu\text{-Mes})\mathrm{Cu}(\mu\text{-Mes})\mathrm{Cu}(\mu\text{-Mes})\mathrm{Cu}]^+$ by hosting the two terminal Cu ions.

Reactions of **2**H with CuMes were initially carried out in the molar ratio 1 : 4 at −78 °C, resulting in the formation of complex **3** which was isolated as yellow needles, albeit in poor yields.

Institut für Anorganische Chemie, Georg-August-Universität, Tammannstraße 4, D-37077 Göttingen, Germany. E-mail: franc.meyer@chemie.uni-goettingen.de; Fax: (+49)-551-393063; Tel: (+49)-551-393012

† Electronic supplementary information (ESI) available: Experimental procedures, spectral and analytical data for **1**–**3**, additional crystallographic details concerning **3**. See DOI: 10.1039/b717571j



Scheme 1 *Reaction conditions*: (a) (i) $SOCl_2$, RT, 24 h; (ii) DHP, CH_2Cl_2, RT, 24 h; (b) i) 2 eq. $PyCH_3(Me)NH–Na_2CO_3$, AN, reflux, 40 h; (ii) hydrolysis with HCl–EtOH; (c) toluene, −78 °C, 18 h, RT, 2 h.

Upon drying *in vacuo*, the colour of **3** immediately changes to beige, but this has no consequences for the spectroscopic and analytical data. The ESI-MS spectrum of **3** in THF shows a prominent peak for the fragment $[(\mathbf{2})Cu_2Mes + 1]^+$ at $m/z = 657$, supporting the presence of an organocopper species. Several lines of evidence suggested, however, that an oxygenated complex had been formed: firstly, the presence of dry oxygen increases the yield of **3** dramatically (to 87%). Secondly, bimesityl was found as a by-product, very likely originating from an oxidatively induced elimination (see ESI†). And finally the results of elemental analyses were inconsistent with the composition of the anticipated organometallic compound $[(\mathbf{2})Cu_2(\mu\text{-Mes})_2Cu_2(\mu\text{-Mes})]$, but indicated that some other element should also be present in **3**. The reaction was carried out repeatedly, but no product other than **3** could be isolated.

The ^1H NMR spectrum of **3** in D_6-benzene reflects a symmetric arrangement of the chelating ligand, since only one set of the expected proton signals is observed. In comparison with the free ligand **2**H, the singlet related to the CH_3 groups at $\delta = 1.71$ ppm, a CH_2-signal at $\delta = 2.97$ ppm, and the resonances of the pyridyl-rings at $\delta = 6.31$ and 6.89 ppm as well as the *o*-phenyl signal $\delta = 7.20–7.22$ ppm are shifted to higher field, whereas the protons closest to the pyridyl-N-donors are strongly downfield-shifted and appear at $\delta = 10.07$ ppm in the complex, confirming their coordination to the σ-organo-Cu^I core. Interestingly, the relative intensities of the singlets at $\delta = 2.25$, 2.60 and 6.83 ppm attributed to the σ-bound mesityl ligands suggested a 2 : 1 ratio with respect to the pyrazolate ligand, but not 3 : 1, as would be expected for a complex of the type $[(\mathbf{2})Cu_2(\mu\text{-Mes})_2Cu_2(\mu\text{-Mes})]$ (ESI†).‡ Hence, we concluded from the combined spectroscopic and analytical data that **3** should have the stoichiometric composition $[(\mathbf{2})Cu_4Mes_2O_{0.5}]_n$.

The molecular structure of **3** was finally elucidated by X-ray crystallography on single crystals that were obtained by slow diffusion of diethyl ether into a THF solution of the product at +4 °C (Fig. 1).§ **3** crystallises in the monoclinic space group $P2_1/c$ with two independent molecules in the asymmetric unit. These have only slightly different bond distances and angles (see ESI†), and those discussed here refer to one of the molecules that is shown in Fig. 1.

3 features a distorted pseudo-tetrahedral $(\mu_4\text{-O})Cu^I{}_4$ nucleus with tethered σ-mesityl-bridges that are linked to two binuclear Cu^I-pyrazolato scaffolds in the typical three-centre two-electron bonding mode. This gives rise to an overall octanuclear organometallic Cu^I framework. The O-bonded

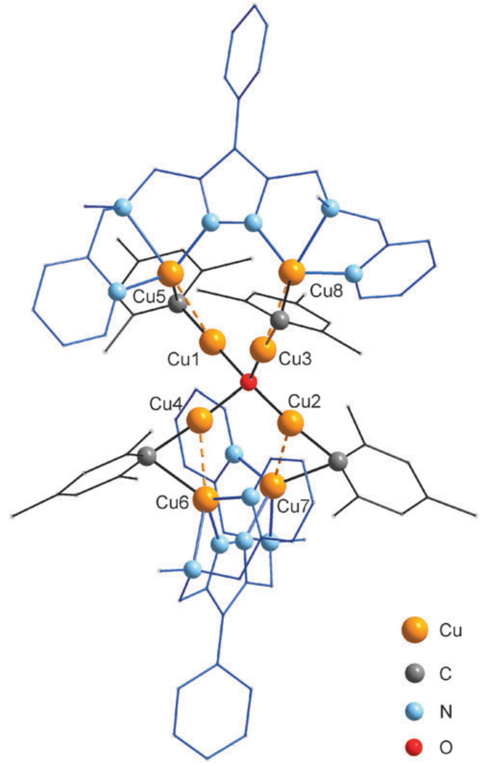


Fig. 1 Solid-state structure of one of the two independent molecules of **3**, determined by single-crystal X-ray diffraction analysis. Hydrogen atoms are omitted for clarity. Cu···Cu contacts are represented as dashed lines. A figure with the complete atom numbering is given in the ESI.†

copper atoms show nearly linear coordination (average of O–Cu–C_{ipso}-angles 175.3(3)°), whereas the copper ions hosted by the chelating pyrazolate ligands are found in a distorted tetrahedral environment. The distortion of the $(\mu_4\text{-O})Cu^I_4$ unit from an ideal tetrahedron is reflected by the Cu–O–Cu-angles that range from 94.75(19)° to 124.6(3)°. All Cu–O bonds (average length 1.851(5) Å) are quite short and similar to those of **I**, but significantly shorter than those of the well-known Cu^{II} complexes of type $[L_4Cu^{II}_4(\mu\text{-O})X_6]$ (L = monodentate ligand, X = halogen).[12,17] Drastic distortion of the {N_3C} coordination sphere of the peripheral Cu^I ions from tetrahedral is caused by the constraints of the binding pockets of **2**. An additional contribution might arise from closed-shell Cu···Cu-contacts that—if considered as such—would lead to a description of the Cu(5–8) environment as pseudo trigonal-bipyramidal.

The Cu–C bond lengths and Cu–C_{ipso}–Cu angles (average 73.5(2)°) as well as the Cu···Cu-separations (average 2.4286(14) Å) within the Cu(μ-Mes)Cu bridging units of **3** are in good agreement with the corresponding values determined for $[Cu_{10}O_2(Mes)_6]$ and parent $[CuMes]_5$, respectively.[12,16] However, bridging of the mesityl groups is rather asymmetric, since the Cu–C bonds to the central O-bound copper atoms (average 1.920(7) Å) are significantly shorter than those to the peripheral copper atoms hosted by the pyrazolate ligands (average 2.131(7) Å). As a consequence, the mesityl rings are leaning towards the outer copper centres (although without any π-contacts), which is evident from the relatively small Cu(5–8)–C_{ipso}–C_{para} angles that lie in the range 118–127°, clearly different from the angles Cu(1–4)–$C_{ipso}C_{para}$ (160–169°). Complex **3** can thus be viewed as a *hetero*leptic cuprate anion $[(MesCu^I)_4(\mu_4\text{-O})]^{2-}$ that is flanked and stabilised by two cations $[(\mathbf{2})Cu^I_2]^+$. This rare motif is distinct from most of the hitherto known organocopper(I) compounds. Only a few of those, like 8-(dimethylamino)-naphthylcopper(I), feature a *homo*leptic organocuprate as a structural theme.[18]

In the presence of air and moisture, **3** decomposes within a few hours to give a green powder. However, under argon, **3** can be stored at room temperature for several months. In contrast to $[Cu_{10}O_2(Mes)_6]$ (**I**), complex **3** can be dissolved without any significant decomposition in dry toluene, benzene or THF. Thereby a small amount of a brown precipitate might be formed, together with mesitylene (observed by NMR).

In conclusion, we have synthesised in high yield a novel σ-organo Cu^I-oxo complex that is unusually stable and bears remarkable cuprate-like structural features, unique in this context. Currently we are investigating the reactivity of **3** with regard to typical cuprate applications.

We thank Prof. Dr G. M. Sheldrick and Dr I. Dix for providing X-ray data collection facilities, and the Fonds der Chemischen Industrie for financial support.

Notes and references

‡ *Characterisation data for* **3**: elemental analysis calcd (%) for $C_{86}H_{98}N_{12}OCu_8$ (1824.15): C, 56.62; H, 5.42; N, 9.21; found: C, 56.41; H, 5.40; N, 9.39; m.p.: 100 °C (decomp.). ^1H NMR (500.13 MHz, C_6D_6): δ 1.71 (s, 6 H, N–CH_3), 2.15 (m, 9 H, signal of mesitylene, CH_3), 2.25 (s, 6 H, p-CH_3), 2.60 (s, 12 H, o-CH_3), 2.97 (s (broad), 4 H, CH_2), 3.49 (s, 4 H, CH_2), 6.31 (d, ^3J(H,H) = 7.6 Hz, pyridyl-C^3), 6.71–6.72 (m, 3 H, signal of mesitylene, CH), 6.77–6.80 (m, 2 H, pyridyl-C^5), 6.83 (s, 4 H, m-CH), 6.89 (dt, ^4J(H,H) = 1.7 Hz ^3J(H,H) = 7.6 Hz, 2 H, pyridyl-C^4), 7.09–7.12 (m, 1 H, p-Ph), 7.20–7.22 (m, 2 H, o-Ph), 7.27–7.30 (m, 2 H, m-Ph), 10.07 (d, ^3J(H,H) = 4.3 Hz, pyridyl-C^6). ^{13}C NMR (125.77 MHz, C_6D_6): δ 21.3 (CH_3, signal of mesitylene), 21.6 (CH_3, p-CH_3), 29.7 (CH_3, o-CH_3), 43.2 (CH_3, N–CH_3), 55.7, 61.1 (CH_2), 115.2 (C, pyrazole-$C^{3,4,5}$), 122.3 (CH, pyridyl-C^3), 123.1 (CH, pyridyl-C^5), 124.5 (CH, m-CH), 127.4 (CH, signal of mesitylene), 128.1 (CH (masked by benzene signal), m-, p-Ph), 129.0 (CH, o-Ph), 135.5 (C), 135.9 (CH, pyridyl-C^4), 137.0, 137.6 (C), 137.6 (C, signal of mesitylene), 144.6 (C), 152.4 (CH, pyridyl-C^6), 153.4, 157.9 (C). MS (ESI in THF): m/z (rel. intensity) = 657.0 (24) $[(\mathbf{1})Cu_2Mes + 1]^+$, 537.2 (100) $[(\mathbf{1})Cu_2]^+$.

§ *Crystal data for* **3**: $C_{86}H_{98}N_{12}OCu_8 \cdot 4.63C_4H_8O$, M = 2157.56, monoclinic, $P2_1/c$, a = 23.249(5), b = 32.447(7), c = 26.971(5) Å, β = 92.42(3)°, V = 20 328(7) Å^3, Z = 8, T = 100(2) K, 160 032 reflections measured (yellow needle, $2.13 \leq \theta \leq 59.85°$), 29 068 unique ($R_{(int)}$ = 0.0998), 2836 parameter. Data were collected on a Bruker three circle diffractometer with a SMART 6000 detector and Cu-Kα radiation (λ = 1.54178 Å) at low temperature. The structure was solved using direct methods and refined by full-matrix least-squares procedures against F^2. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were added using the riding model. Since all THF molecules are disordered and the THF oxygen could not be located, the solvent molecules were refined first as cyclopentane and later with THF-restrains from the PRODRG dungee server.[19] R_1 ($F_o > 4\sigma F_o$) = 0.0703, wR_2 = 0.1767, GoF = 1.365. CCDC 666842. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b717571j.

1 (*a*) N. Kitajima and Y. Moro-oka, *Chem. Rev.*, 1994, **94**, 737; (*b*) J. I. van der Vlugt and F. Meyer, *Top. Organomet. Chem.*, 2007, **22**, 191.

2 P. Siemsen, R. C. Livingston and F. Diederich, *Angew. Chem.*, 2000, **112**, 2740 (*Angew. Chem., Int. Ed.*, 2000, **39**, 2632).

3 G. van Koten, J. T. B. H. Jastrzebski and J. G. Noltes, *J. Org. Chem.*, 1977, **42**, 2047.

4 B. H. Lipshutz, K. Siegmann and E. Garcia, *Tetrahedron*, 1992, **48**, 2579.

5 J. T. B. H. Jastrzebski and G. van Koten, in *Modern Organocopper Chemistry*, ed. N. Krause, Wiley-VCH GmbH, Weinheim, 2002, ch. 1, pp. 1–44.

6 A. Camus and N. Marsich, *J. Organomet. Chem.*, 1972, **46**, 385.

7 R. P. Davies, S. Hornauer and A. J. P. White, *Chem. Commun.*, 2007, 304.

8 (*a*) M. J. McGeary, R. C. Wedlich, P. S. Coan, K. Folting and K. G. Caulton, *Polyhedron*, 1992, **11**, 2459; (*b*) M. Håkansson, C. Lopes and S. Jagner, *Organometallics*, 1998, **17**, 210.

9 J. M. Veauthier, E. Tomat, V. M. Lynch, J. L. Sessler, U. Mirsaidov and J. T. Markert, *Inorg. Chem.*, 2005, **44**, 6736.

10 F. Jäkle and I. Manners, *Organometallics*, 1999, **18**, 2628.

11 A. L. Keen, M. Doster, H. Han and S. A. Johnson, *Chem. Commun.*, 2006, 1221.

12 M. Håkansson, M. Örtendahl, S. Jagner, M. P. Sigalas and O. Eisenstein, *Inorg. Chem.*, 1993, **32**, 2018.

13 (*a*) F. Meyer, *Eur. J. Inorg. Chem.*, 2006, 3789; (*b*) G. Noël, J. C. Röder, S. Dechert, H. Pritzkow, L. Bolk, S. Mecking and F. Meyer, *Adv. Synth. Catal.*, 2006, **348**, 887; (*c*) A. Prokofieva, A. I. Prikhod'ko, E. A. Enyedy, E. Farkas, W. Maringgele, S. Demeshko, S. Dechert and F. Meyer, *Inorg. Chem.*, 2007, **46**, 4298.

14 A. Sachse, L. Penkova, G. Noël, S. Dechert, O. A. Varzatskii, I. O. Fritsky and F. Meyer, *Synthesis*, in press.

15 F. Meyer, K. Heinze, B. Nuber and L. Zsolnai, *J. Chem. Soc., Dalton Trans.*, 1998, 207.

16 (*a*) E. M. Meyer, S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *Organometallics*, 1989, **8**, 1067; (*b*) H. Eriksson and M. Håkansson, *Organometallics*, 1997, **16**, 4243.

17 (*a*) J. A. Bertrand, *Inorg. Chem.*, 1967, **6**, 495; (*b*) J. T. Guy, Jr, J. C. Cooper, R. D. Gilardi, J. L. Flippen-Anderson and C. F. George, Jr, *Inorg. Chem.*, 1988, **27**, 635.

18 (*a*) E. Wehman, G. van Koten, M. Knotter, H. Spelten, D. Heijdenrijk, A. N. S. Mak and C. H. Stam, *J. Organomet. Chem.*, 1987, **325**, 293; (*b*) M. D. Janssen, M. A. Corsten, A. L. Spek, D. M. Grove and G. van Koten, *Organometallics*, 1996, **15**, 2810.

19 A. W. Schüttelkopf and D. M. F. van Aalten, *Acta Crystallogr., Sect. D: Biol. Crytallogr.*, 2004, **60**, 1355.