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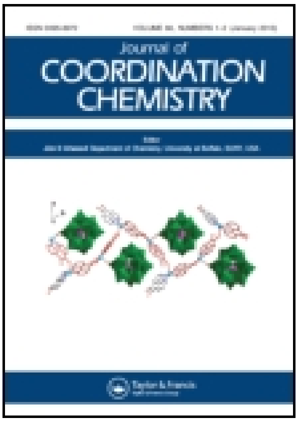

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SHORT COMMUNICATION

Ferrocenyl *β*-diketonato-based Cu(II)-oxo clusters with Cu_7 and Cu_{10} cores

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Crystallization of $[Cu(\beta\text{-diketonate})(PPh_3)_2]$ (**1a**, *β*-diketonate=1-ferrocenyl-butane-1,3-dionato (= *fb*); **1b**, = 1,3-diferrocenyl-propane-1,3-dionato (= *dfp*)) from ethanol, layered with a mixture of pentane/diethyl ether of ratio 1 : 1 (v/v) in air, afforded Cu(II)-oxo clusters $[Cu_{10}(fb)_8(O)_4(tmdd)_2]\cdot1.5Et_2O$ (**2**) and $[Cu_7(dfp)_6(O)_2(OH)_2(tmdd)]\cdot2Et_2O$ (**3**), respectively, in minor yield (*tmdd* = $1\kappa^2C$, $3\kappa^2C$-tetramethyldisiloxane-1,3-diolato). These clusters were obtained in somewhat better yield when $HOSiMe_2OSiMe_2OH$ was added to the crystallization mixtures. The molecular structures of **2** and **3** in the solid state are reported.

Keywords: Copper; Cluster; X-ray analysis

Transition metal *β*-diketonates are an intensively studied family of complexes, because a high number of *β*-diketones are commercially available and the appropriate metal complexes are easily accessible by standard synthetic methodologies [1–7]. For example, Cu(I) and Cu(II) *β*-diketonates received intense research activity, since they can successfully be used as precursors in Chemical Vapor Deposition and Atomic Layer Deposition processes for the deposition of pure, dense, conformal, and conductive copper or copper oxide thin layers on different substrates [1, 8–19]. We are also interested in the electrochemistry of ferrocenyl-based copper(I) and copper(II) *β*-diketonates [20–22]. In the course of these studies, we noticed that copper(II)-oxo clusters† $[Cu_{10}(fb)_8(O)_4(tmdd)_2]\cdot1.5Et_2O$ (**2**) and $[Cu_7(dfp)_6(O)_2(OH)_2(tmdd)]\cdot2Et_2O$ (**3**) (*tmdd* = $1\kappa^2C,3\kappa^2C$-tetramethyldisiloxane-1,3-diolato; *fb* = 1-ferrocenyl-butane-1,3-dionato; *dfp* = 1,3-diferrocenyl-propane-1,3-dionato) were accessible by air decomposition of pentane and diethyl ether (ratio 1 : 1, v/v) layered ethanol solutions containing **1a** or **1b** at ambient temperature, whereby red crystals were formed in minor yield (*ca.* 3%). The copper(II)-oxo clusters were formed by a

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†In the context of this report the terminus "copper(II)–oxo clusters" refers to all multinuclear copper (II) complexes with at least one *μ*-O atom, independent whether the O atom corresponds to an O_2^- or an RO^-, respectively (R = any residue).

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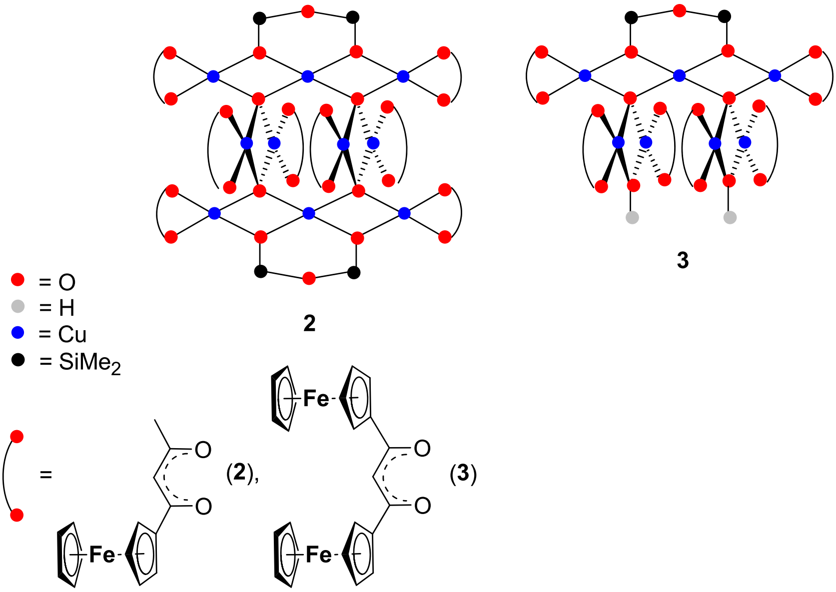
redox-induced self-assembly of the Cu(I) β-diketonates and were stabilized by *tmdd* ligands, liberated from the silicon grease used (silicone paste Baysilone, highly viscous) [23]. Better yields (*ca.* 10%) have been obtained when crystallization was done in the presence of $HOSiMe_2OSiMe_2OH$ [24].

The structures of **2** and **3** in the solid state were determined by single crystal X-ray structure analysis [25]. Scheme 1 illustrates the schematic structures of **2** and **3**, whereas figure 1 shows the molecular structures of the two clusters in the solid state.

The copper(II)-oxo cluster **2** possesses no symmetry, while for **3** crystallographically induced C_2 symmetry has C_2 axes going through O10 and Cu3. For both **2** and **3**, the β-diketonato ligands are coordinated in the $\kappa^2O^1O^3$ fashion to external Cu(II) Cu1, Cu3, Cu4 and Cu6 – Cu10 of **2**, and Cu1, Cu2, Cu4, Cu1A, Cu2A and Cu4A of **3** (figure 1). This indicates that {Cu(*fb*)} and {Cu(*dfp*} of **1a** and **1b** prevailed during their redox-induced transformation into **2** and **3**, respectively. For **3**, the internal Cu3 and the Cu4 and Cu4A are coordinated by a μ_3-*tmdd* ligand, forming a trinuclear {Cu_3(*fb*)$_2$(*tmdd*)} entity (entity **I**). Furthermore, the {Cu(*fp*} fragments comprising Cu1 and Cu2 or Cu1A and Cu2A are connected by μ-hydroxo ligands comprising O7 and O7A, respectively, forming binuclear {Cu_2(*fb*)$_2$(OH)} entities (2 × entity **II-OH**). The Cu/O atoms of entity **I** (Cu3, Cu4, O5, O6, O9 and symmetry generated ones) form a less planar plane (*rmsd* = 0.479 Å, *hdp* observed for O5A with 0.731(11) Å), whereas the Cu/O atoms of entity **II-OH** (Cu1, Cu2, O1-O4, O7) are nearly planar (*rmsd* = 0.140 Å, *hdp* observed for O2 with 0.234(4) Å) [26]. Building block **II-OH** is nearly perpendicular towards entity **I**, as the interplanar angle is 87.0(1)°. The two **II-OH** moieties are connected to entity **I** by μ_4-O^{2-} O8 and O8A.

The molecular structure of **2** is closely related to that of **3**. Two crystallographically different trinuclear {Cu_3(*dfb*)$_2$(*tmdd*)}entities (entity **IIIA** comprising Cu1–Cu3 and moiety



Scheme 1. Chemical structure of **2** (octakis(*fb*)-$1\kappa^2O^1,O^3;3\kappa^2O^1,O^3;4\kappa^2O^1,O^3;5\kappa^2O^1,O^3;\ 6\kappa^2O^1,O^3;7\kappa^2O^1,O^3;8\kappa^2O^1,O^3;10\kappa^2O^1,O^3$-bis($\mu_3$-tmdd-$1{:}2\kappa O^1,2{:}3\kappa O^3;8{:}9\kappa O^1,9{:}10\kappa O^3$)-tetrakis($\mu_4$-oxo) $1{:}2{:}4{:}\ 5\kappa^3O;2{:}3{:}6{:}7\kappa^3O;4{:}5{:}8{:}9\kappa^3O;6{:}7{:}9{:}10\kappa^3O$-dodecacopper, left) and **3** (hexakis(dfp)-$1\kappa^2O^1,O^3;\ 3\kappa^2O^1,O^3;\ 4\kappa^2O^1,O^3;5\kappa^2O^1,O^3;6\kappa^2O^1,O^3$($\mu_3$-tmdd-$1{:}2\kappa O^1,2{:}3\kappa O^3$)-bis($\mu_4$-oxo)$1{:}2{:}4{:}5\kappa^2O;2{:}3{:}6{:}7\kappa^2O$-bis ($\mu$-hydroxo)-$4{:}5\kappa O;6{:}7\kappa O$-heptacopper, right).

IIIB comprising Cu4–Cu6) and two binuclear $\{Cu_2(\mathit{dfb})_2(O)\}$ building blocks (entity **IVA-O** comprising Cu7, Cu8 and group **IVB-O** comprising Cu9, Cu10) are observed. The oxygens O18/O20 of **IVA-O/IVB-O** act as μ_4-O^{2-} anions, connecting **IIIB**, as μ_4-O^{2-}O17 and O19 bind the binuclear $\{Cu_2(\mathit{dfb})_2(O)\}$ moieties to the upper trinuclear $\{Cu_3(\mathit{dfb})_2(\mathit{tmdd})\}$ entity **IIIA** [27].

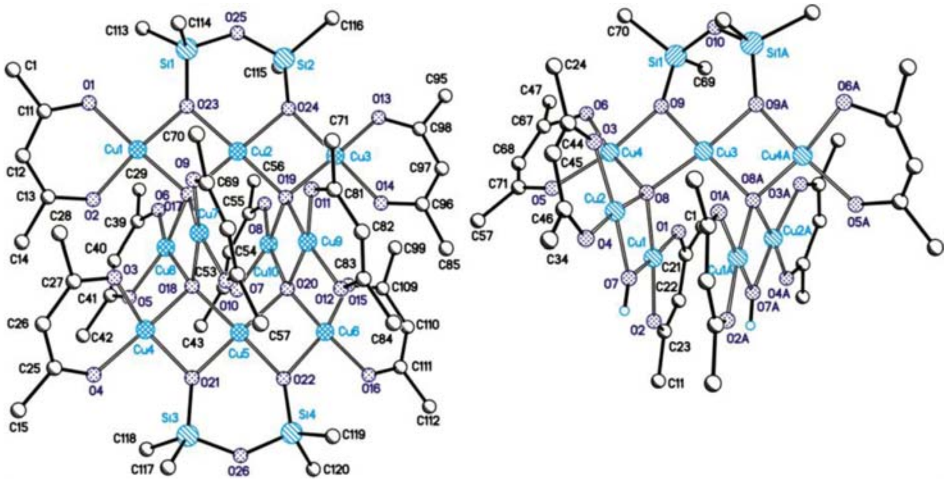
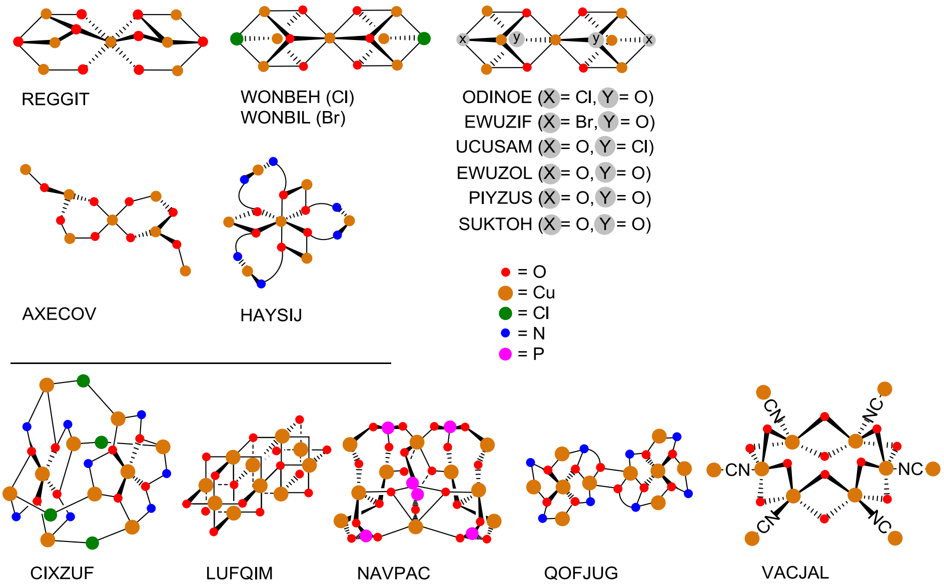


Figure 1. Molecular structure of **2** (left) and **3** (right) in the solid state. For all ferrocenyl groups, only the pivot atom is shown. All C–bonded hydrogens and packing solvent are omitted. Of disordered units, only one atomic position is displayed. Symmetry code for **3**:$-x+{}^3/_2$, y, $-z+½$.



Scheme 2. Principal chemical structures of described hepta-nuclear (above) and deca-nuclear copper(II)-oxo clusters (below). CSD ref codes are given for identification (REGGIT [28]; WONBEH, WONBIL [29]; ODINOE [30]; EWUZIF, EWUZOL [31]; UCUSAM [32]; PIYZUS [33]; SUKTOH [34]; AXECOV [35]; HAYSIJ [36]; CIXZUF [37]; LUFQIM [38]; NAVPAC [39]; QOFJUG [40], VACJAL [41]).

Besides the different substitution of the β-diketonato ligands of **2** and **3**, the most striking difference of both copper(II)-oxo clusters is the observation of different binuclear entities (**2**: **IVA-O/IVB-O** *versus* **3** : 2 × **II-OH**). The presence of μ-hydroxo in **3** in contrast to μ_4-O^{2-} in **2** emphasizes the self-assembly process of both compounds. Obviously, traces of water are required which might be responsible for a condensation reaction of preformed $\{Cu_3(\beta\text{-diketonato})_2(tmdd)(H_2O)_2\}$ and $\{Cu_2(\beta\text{-diketonato})_2(H_2O)_4\}$ fragments. The hypothetic condensation of self-assembly process stops then in case of the more bulky *fb* ligands at the formation of heptanuclear **3**, whereas with the less sterically demanding *dfb* decanuclear **2** can be formed.

The bis(μ_4-oxo)1:2:4:5κ^2O;2:3:6:7κ^2O core of **2** and the tetrakis(μ_4-oxo)1:2:4:5κ^3O;2:3:6:7κ^3O;4:5:8:9κ^3O;6:7:9:10κ^3O core of **3** are both unprecedented when compared to other hepta- and decanuclear copper(II)-oxo clusters, respectively (Scheme 2). Furthermore, to the best of our knowledge, although (hetero)multinuclear M-oxo clusters comprising the denoted fragments of **2** and **3**, respectively, are described, their exclusive formation has not been observed (M = 3d transition metal in neutral or any charged state).

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[24] Compounds **2** and **3**, respectively, did crystallize from ethanol solutions layered with a mixture of pentane/diethyl ether of ratio 1 : 1 (v/v). After the crystallization went to end, both complexes could be smoothly isolated. Further, amorphous material did precipitate as well. Elemental analysis of those amorphous materials gave always varying compositions, and the NMR characterization gave no reliable results due to the presence of paramagnetic impurities. Thus, the nature of the remaining material is unclear so far.

[25] Crystal structure analysis: Data collections were performed at 100 K with Cu K_α ($\lambda = 1.54184$ Å) for **3** and with Mo K_α radiation ($\lambda = 0.71073$ Å) for **2** with an Oxford Gemini S diffractometer. Of 39114/61152 collected 9990/24166 reflections were independent ($R_{int} = 0.0872/0.0337$) for **3/2**, respectively. Both structures were solved by direct methods and refined by full-matrix least-squares on F^2 with the SHELXTL-97 program package [42]. For **3**, the two ferrocenyl fragments comprising Fe5/C47–C56 and Fe6/C57–C66 and the atoms O5/O6/C71 were refined, disordered with split occupancies of 0.49/0.51, 0.50/0.50 and 0.52/0.48, respectively. For **2**, the methyl and ferrocenyl substituents of one *fb* ligand (C95 and C85–C94/Fe7) and one Et_2O molecule were refined, disordered with split occupancies of 0.73/0.27 and 0.54/0.46, respectively. A further Et_2O molecule was refined with an occupation factor of 0.5. Crystal data for $C_{150}H_{148}Cu_7Fe_{12}O_{21}Si_2$ (**3**): $M = 3457.84$ g mol^{-1}, monoclinic, *P2/n*, $a = 18.5088(3)$, $b = 15.0688(2)$, $c = 25.0369(3)$ Å, $\beta = 102.874(1)$, $V = 6807.39(16)$ Å^3, $Z = 2$, $D_c = 1.687$ g cm^{-3}, $\mu = 11.758$ mm^{-1}, $R_1 = 01368$ (all data), $wR_2 = 0.1268$ (all data) and goodness-of-fit on F_2 is 0.874. Crystal data for $C_{252}H2_{86}Cu_{20}Fe_{16}O_{55}Si_8$ (2): $M = 6583.93$ g mol^{-1}, triclinic, P^{-1}, $a = 15.4764(8)$, $b = 17.4332(10)$, $c = 28.2358(14)$ Å, $\alpha = 96.937(4)$, $\beta = 90.083(4)$, $c = 112.707(5)$, $V = 6966.6(6)$ Å^3, $Z = 1$, $D_c = 1.569$ g cm^{-3}, $\mu = 2.394$ mm^{-1}, $R_1 = 0.0849$ (all data), $wR_2 = 0.1648$ (all data) and goodness-of-fit on F_2 is 1.189. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 901760 (**2**), 901761 (**3**)). Bond lengths, bond and torsion angles of **2** and **3** are given in tables 1–4 in the Supplementary material.

[26] *rmsd* = root mean square deviation from planarity. *hdp* = highest deviation from planarity.

[27] *Calculated mean planes*. **IIIA**: *rmsd* = 0.303 Å, *hdp* = 0.475(3) Å for O2. **IIIB**: *rmsd* = 0.291 Å, *hdp* = 0.483 (3) Å for O15. **IVA-O**: *rmsd* = 0.404 Å, *hdp* = 0.708(3) Å for O5. **IVB-O**: *rmsd* = 0.897 Å, *hdp* = 1.414(3) Å for O8. *Interplanar angles*. **IIIA:IIIB** = 19.2(1). **IIIA:IVA-O** = 77.22(6). **IIIB** : **IVB-O** = 82.41(7). **IIIA** : **IVB-O** = 86.58(7). **IIIB** : **IVA-O** = 83.67(6). **IVA-O** : **IVB-O** = 48.5(1).

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