



Tri- ($M = \text{Cu}^{\text{II}}$) and hexanuclear ($M = \text{Ni}^{\text{II}}, \text{Co}^{\text{II}}$) heterometallic coordination compounds with ferrocene monocarboxylate ligands: Solid-state structures and thermogravimetric, electrochemical and magnetic properties



Karoline Müller^a, Marcus Korb^a, Changhyun Koo^b, Rüdiger Klingeler^{b,c}, Dominique Miesel^a, Alexander Hildebrandt^a, Tobias Rüffer^{a,*}, Heinrich Lang^a

^a Technische Universität Chemnitz, Faculty of Natural Science, Institute of Chemistry, Inorganic Chemistry, D-09107 Chemnitz, Germany

^b Kirchhoff Institute of Physics, Heidelberg University, D-69120 Heidelberg, Germany

^c Center for Advanced Materials (CAM), Heidelberg University, Heidelberg, Germany

ARTICLE INFO

Article history:

Received 2 May 2017

Accepted 14 September 2017

Available online 23 September 2017

Keywords:

Molecular structure

Electrochemical studies

Single crystal X-ray diffraction

Thermogravimetry

Magnetic susceptibility

ABSTRACT

The synthesis and characterization of the hexanuclear $[\text{M}_2(\kappa\text{O}-\text{O}_2\text{Cfc})_2(\mu-\text{O}_2\text{Cfc})_2(\mu-\text{H}_2\text{O})(\kappa^2\text{N},\text{N}'\text{-tmeda})_2]$ ($M^{\text{II}} = \text{Ni}$, **5**; Co , **6**; Fc = ferrocenyl, $(\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{Fe}$; $\text{tmeda} = \text{N},\text{N},\text{N}',\text{N}'\text{-tetramethylethylenediamine}$) and the trinuclear $[\text{Cu}(\kappa^2\text{N},\text{N}'\text{-tmeda})(\kappa^2\text{O},\text{O}'\text{-O}_2\text{Cfc})_2]$ (**7**) coordination compounds are described. Compounds **5–7** were prepared by the consecutive reaction of ferrocene carboxylic acid (FcCO_2H ; **1**) with $[\text{tBu}_4\text{N}]\text{OH}$ followed by treatment of *in situ* formed $[\text{tBu}_4\text{N}][\text{FcCO}_2]$ with the metal salts $[\text{M}(\text{tmeda})(\text{NO}_3)_2]$ ($M = \text{Ni}$, **2**; Co , **3**; Cu , **4**). The structures of **5–7** in the solid state were determined by single crystal X-ray diffraction analysis. Isostructural **5** and **6** crystallise in the triclinic $P\bar{1}$ (**5**) and in the monoclinic space group $P2_1/n$ (**6**). The two $M^{\text{II}}(\text{tmeda})$ entities of **5** and **6** with $M^{\text{II}} = \text{Ni}$, Co , respectively, are *syn*, *syn*-bridged by two FcCO_2^- functionalities and one μ -bridging water molecule. Additionally, two FcCO_2^- ligands are κO -coordinated to each M^{II} ion to form octahedral MN_2O_4 coordination setups. A related MN_2O_4 coordination setup is observed for **7** as well, whereby the Cu^{II} ion is coordinated by two O_2Cfc and one tmeda ligand. Electrochemical investigations reveal that all individual Fc units of **5–7** are oxidized separately. Thermogravimetric analysis showed that **5** and **6** start to decompose at 110 and 125 °C and thus at significantly lower temperatures compared to **7** (200 °C). The mass residues obtained after decomposition are composed of Fe_2O_3 , FeNi_3 and $\text{Fe}_{0.64}\text{Ni} = \text{Ni}_{0.36}$ (**5**), Fe and Co_3O_4 (**6**) and Cu_2O and CuFeO_2 (**7**), as determined by powder X-ray diffraction analysis (PXRD). Thermal susceptibility measurements of **5** and **6** determined a weak antiferromagnetic coupling in **5** and **6** with $J = 1.1$ K and $J = 1.9$ K, respectively.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The discovery, that the electrical resistance of a magnetic device is tunable by modifying its magnetic texture, thus of the giant magneto-resistance (GMR) effect [1–4], manifested the beginning of the field of magneto-electronics or, in other words, of *Spintronics*. As comprehensively reviewed by Sanvito [5], the use of organic molecules for the construction of GMR devices gave rise to the new field *Molecular Spintronics*. Basically, “... The general idea behind spintronics is that of detecting the response of spins to an external stimulus ...” [5], whereby the “organic molecule” could be even a

single molecule magnet. Following this idea we became interested in the possible interplay between complexes displaying both inter-valence charge/transfer properties and single molecule magnetic properties. Our group reported frequently on the synthesis and electrochemical properties of novel charge-transfer compounds, considering especially ferrocenyl-containing coordination compounds [6–10].

Previously, we have reported the electrochemical and magnetic properties of the isostructural hexanuclear coordination compounds $[\text{M}_2(\text{O}_2\text{CfcCO}_2)_2(\text{H}_2\text{O})(\text{tmeda})_2]$ ($M = \text{Ni}$, **8**; $M = \text{Co}$, **9**). We demonstrated, that the two ferrocenyl units of both **8** and **9** were oxidized at significant different redox potentials and that **8** exhibits a small ferromagnetic ($\theta = 1.6$ K) and **9** an antiferromagnetic Weiss temperature ($\theta = -14.5$ K) [11]. Furthermore, and in the

* Corresponding author.

E-mail address: tobias.rueffer@chemie.tu-chemnitz.de (T. Rüffer).

search for Ni^{II}-containing coordination compounds which decompose to pure metallic nickel we recently reported on [Ni₂(κO-O₂CH)₂(μ-O₂CH)₂(μ-H₂O)(κ²N,N'-tmeda)₂] (**10**) [12]. The structure of **10** is closely related to the one of **8** and **9**, and we were surprised that **10** exhibits a weak intramolecular antiferromagnetic coupling ($J = -7.8$ K) together with an easy plane magnetic anisotropy.

In order to narrow further to materials in which the spins response to an external stimuli we aimed to replace the two O₂-CFCO₂ ligands of **8** and **9** by four FcCO₂ ligands as in [M₂(κO-O₂-CFC)₂(μ-O₂CFC)₂(μ-H₂O)(κ²N,N'-tmeda)₂] (M^{II} = Ni, **5**; Co, **6**). Here we report on the synthesis and solid state structures of **5** and **6** together with [Cu(κ²N,N'-tmeda)(κ²O,O'-O₂CFC)₂] (**7**). Furthermore, we describe the thermal and electrochemical properties of **5–7** and the results of susceptibility studies of **5** and **6**.

2. Experimental

2.1. Materials and measurements

All reactions were carried out under an atmosphere of argon unless otherwise stated. Starting materials Fc(CO₂H) (**1**) and [M(tmeda)(NO₃)₂] (M = Ni (**2**), Co (**3**), Cu (**4**)) were prepared by published procedures [11,13]. Pyridine was dried with KOH, distilled under argon atmosphere and stored over molecular sieve 4 Å. Acetonitrile was purified by distillation from P₄O₁₀. Diethyl ether and dichloromethane were dried using a MBraun MP SPS-800 system (double column solvent filtration, working pressure 0.5 bar). The melting points were determined using a Gallenkamp MFB 595 010M melting point apparatus. The elemental analyses were measured with a Thermo FlashEA 1112 Series instrument. IR spectra were measured using KBr pellets in the range of 400–4000 cm⁻¹ with a Nicolet IR 200 spectrometer from Thermo Electron Corporation. For each spectrum 16 scans were measured at a resolution of 2 cm⁻¹. High-resolution mass spectra were recorded with a Bruker Daltonik microTOF-QII spectrometer. Thermal gravimetric measurements combined DSC measurements were performed with a Mettler Toledo TGA/DSC1 1600 System equipped with a MX1 balance. Powder X-ray diffraction (PXRD) studies were performed with a STOE-STADI-P diffractometer with Cu K_{α1} = 1.540 Å in the range of 20–90° for 2θ. Electrochemical measurements were performed on 1.0 mmol·L⁻¹ solutions of **5–7** in dichloromethane in a dried, argon-pulled cell at 25 °C with a Radiometer Voltalab PGZ 100 electrochemical workstation interfaced with a personal computer. [¹⁸Bu₄N][B(C₆F₅)₄] (0.1 mol·L⁻¹) was used as supporting electrolyte.

Spectroelectrochemical UV-Vis/NIR measurements of 1.0 mmol L⁻¹ solution of **6** in anhydrous acetonitrile containing 0.1 mol L⁻¹ of [¹⁸Bu₄N][B(C₆F₅)₄] as the supporting electrolyte were performed in an OTTE (= Optically Transparent Thin-Layer Electrochemical) [14] cell with a Varian Cary 5000 spectrophotometer at 25 °C.

The static magnetic susceptibility $\chi(T) = M(T)/B$ of **5** and **6** was measured by means of a Quantum Design MPMX XL-5 SQUID magnetometer. The measurements were done in the temperature range of $T = 2–300$ K and at $B = 5$ T and 1 T, respectively. In order to account for the contribution of the ligands, the temperature independent diamagnetic susceptibility of the coordination compounds as calculated by means of Pascal's constants has been subtracted from the experimental data [15].

2.1.1. Crystallographic studies

All data were collected with an Oxford Gemini S diffractometer. All structures were solved by direct methods using SHELXS-2013 and refined by full-matrix least-square procedures on F^2 using SHELXL-2013 [16]. All non-hydrogen atoms were refined anisotropically.

All C-bonded hydrogen atoms were refined using a riding model. For further details cf. Table S1 and additional explanation (SI).

2.2. Synthesis of [Ni₂(O₂CFC)₄(H₂O)(tmeda)₂] (**5**)

FcCO₂H (**1**) (150 mg, 0.652 mmol) was suspended in acetonitrile (20 mL) and [¹⁸Bu₄N]OH (0.42 mL, 0.652 mmol, 40% in water) was added in a single portion at ambient temperature. After stirring this solution for 20 min, a solution of [Ni(tmeda)(NO₃)₂] (**2**) (97 mg, 0.326 mmol) in acetonitrile (10 mL) was added drop-wise. After stirring for 2 h the solution volume was reduced to 5 mL and stored over night at 5 °C. The obtained precipitate was filtered off and washed with cold acetonitrile (2 × 3 mL) and diethyl ether (2 × 3 mL). The solid was recrystallized in a mixture of acetonitrile and diethyl ether (ratio 3:5, v/v) and stored at 5 °C. After one week crystals suitable for crystallographic studies were obtained, filtered off, washed with cold diethyl ether (2 × 3 mL) and were dried in vacuum. Yield: 0.143 mg (68% of **5** based on **1**). *Comment:* Crystals selected under an optical microscope for crystallographic characterisation were observed to become quickly brittle, which indicates loss of packing solvent molecules. Note that crystallographic characterisation revealed a composition of [(**5**)₂(MeCN)₃(Et₂O)] (**5'**). The elemental analysis of **5** dried in vacuum confirmed the loss of the packaging solvent molecules (*Anal. Calc.* for C₅₆H₇₂N₄O₉Ni₂Fe₄ (1285.96 g/mol, **5**·%): C, 52.30; H, 5.64; N, 4.36. Found: C, 51.98; H, 5.85; N, 4.34.), while material that was stored on air produced an elemental analysis which refers to **5** with an incorporation of one molecule of H₂O per molecule of **5**. M.p.: 175 °C. *Anal. Calc.* for C₅₆H₇₄N₄O₁₀Ni₂Fe₄ (1303.97 g/mol, **5**·H₂O; %): C, 51.58; H, 5.72; N, 4.30. Found: C, 51.46; H, 5.80; N, 4.46. IR (KBr, cm⁻¹): 3096 (w), 3018 (w), 2903–2840 (m), 2794 (w), 2055 (w, br), 1617 (s), 1534 (w, br), 1473 (s), 1388 (s), 1359 (s), 1348 (m, sh), 1287 (w), 1187 (w), 1106 (w), 1024 (m), 957 (w), 802 (m), 773 (s). ESI-MS: $m/z = 403.0732$ [M – Ni(tmeda)(O₂CFC)₃]⁺; 1035.1187 [M – O₂CFC]⁺. Fig. S1 (SI) gives the IR spectra of **5** and **5**·H₂O and Fig. S4 (SI) the ESI-MS spectrum of **5**.

2.3. Synthesis of [Co₂(O₂CFC)₄(H₂O)(tmeda)₂] (**6**)

Compound **6** was prepared according to the procedure reported for **5**. FcCO₂H (**1**) (150 mg, 0.652 mmol) was reacted with [¹⁸Bu₄N]OH (0.42 mL, 0.652 mmol; 40% in water) and [Co(tmeda)(NO₃)₂] (**3**) (94 mg, 0.33 mmol) in acetonitrile. After stirring for 2 h at ambient temperature the volume was reduced to 5 mL and stored over night at 5 °C. The formed precipitate was filtered and washed with acetonitrile (2 × 3 mL) and diethyl ether (2 × 3 mL). Crystals were obtained out of a mixture of acetonitrile and diethyl ether (ratio 3:5, v/v) containing **6** after partial evaporation of diethyl ether. Yield: 0.125 mg (60% for **1**). M.p.: 195 °C (decomp.). *Anal. Calc.* for C₅₆H₇₂N₄O₉Co₂Fe₄ (1286.44 g/mol; %): C, 52.28; H, 5.64; N, 4.36. Found: C, 52.37; H, 5.74; N, 4.25. IR (KBr, cm⁻¹): 3090 (w), 3012 (w), 2974 (w), 2907 – 2839 (m), 2788 (w), 2048 (w, br), 1612 (s), 1532 (w, br), 1472 (s), 1388 (s), 1359 (m), 1347 (m), 1283 (w), 1158 (w), 1106 (w), 1015 (m), 951 (w), 799 (m), 767 (m), 560 (m). ESI-MS: $m/z = 404.0660$ [M – Co(tmeda)(O₂CFC)₃]⁺; 1037.1144 [M – O₂CFC]⁺. Fig. S1 (SI) gives the IR spectrum of **6** and Fig. S5 (SI) gives the ESI-MS spectrum of **6**.

2.4. Synthesis of [(tmeda)Cu(O₂CFC)₂] (**7**)

Compound **7** was prepared according to the procedure reported for **5**. FcCO₂H (**1**) (150 mg, 0.652 mmol) was reacted with [¹⁸Bu₄N]OH (0.42 mL, 0.652 mmol, 40% in water) and [Cu(tmeda)(NO₃)₂] (**4**) (99 mg, 0.326 mmol) in acetonitrile. After stirring the reaction mixture for 1 h at ambient temperature, the precipitated solid was filtered and washed with diethyl ether (3 × 10 mL). Single

Download English Version:

<https://daneshyari.com/en/article/5153932>

Download Persian Version:

<https://daneshyari.com/article/5153932>

[Daneshyari.com](https://daneshyari.com)