



## Influence of the nature of organic components in dinuclear copper(II) pivalates on the composition of thermal decomposition products

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### ABSTRACT

Tetrabridged dinuclear complexes  $((2\text{-NH}_2)\text{C}_5\text{H}_4\text{N})_2\text{Cu}_2(\mu_2\text{-OOCMe}_3)_4$  (**2**-C<sub>6</sub>H<sub>6</sub>) and  $((3\text{-NH}_2)\text{C}_5\text{H}_4\text{N})_2\text{Cu}_2(\mu_2\text{-OOCMe}_3)_4$  (**3**) and the cocrystallization product  $((4\text{-NMe}_2)\text{C}_5\text{H}_4\text{N})_2\text{Cu}(\eta^2\text{-OOCMe}_3)_2 \cdot 2((4\text{-NMe}_2)\text{C}_5\text{H}_4\text{N})_2\text{Cu}_2(\mu_2\text{-OOCMe}_3)_4$  (**4**) were synthesized by the reaction of the polymer  $[\text{Cu}(\text{OOCMe}_3)_2]_n$  (**1**) with aminopyridine ligands (L) of different nature (Cu: L = 1:1) in C<sub>6</sub>H<sub>6</sub>. The solid-state thermal decomposition of these compounds was studied by differential scanning calorimetry and thermogravimetry, and their electrochemical behavior was investigated by cyclic voltammetry. All newly synthesized complexes were studied by X-ray diffraction, the magnetic properties of the complexes were investigated, and ESR measurements were performed.

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### 1. Introduction

In recent years, the use of metal complexes as molecular precursors for the preparation of nanosized metal particles [1,2] has attracted great interest because of the unique physical and catalytic properties [3–5] of such metallic materials. The solid-phase thermolysis of solutions of complex molecular precursors in suitable matrices [6–10] is used for the synthesis of metals as often as the gas-phase decomposition [1,11] or, for example, the sol-gel technologies [2]. However, the solid-state thermal decomposition of complexes containing metal cations in the absence of external reducing agents differs in that the organic components of precursors play an important role in this process. For instance, it is known that metals can easily be generated in the final step of thermal decomposition using complexes with ligands having strong reducing properties. This approach has recently been applied to the thermolysis of methylhydrazine 3d-metal complexes, which afforded metals or even alloys (in the case of the co-thermolysis of the complexes) [12] at rather low temperatures (below 400 °C). Presumably, these reactions proceed *via* the intramolecular reduction of metals with the involvement of ligands having reducing properties.

A rise of the temperature leads to a gradual elimination of organic fragments and the clustering of the metal core up to the formation of metal particles. Evidently, these processes essentially depend on the nature of metal ions in the precursors, as well as on the structural and electronic features of both the ligands having a reducing ability and the molecules as a whole.

As for the known type of carboxylate complexes, *viz.*, dinuclear tetrabridged d-block metal pivalates  $\text{LM}(\mu\text{-Piv})_4\text{ML}$ , where M = Mn(II) [13,14], Fe(II) [15], Co(II) [16–18], Ni(II) [19,20], or Cu(II) [21,22], it can be noted that the pivalate ligand (Piv = (CH<sub>3</sub>)<sub>3</sub>CCO<sub>2</sub><sup>−</sup>) is a potential reducing agent with respect to metal ions because it contains a large number of C–H bonds. However, it appeared that the nature of the metal ions, as well as the axial ligand, also play an important role. For example, the solid-phase thermolysis of dinuclear manganese and iron pivalates (M = Mn and Fe) did not afford metals in spite of the presence of strong reducing agents (aminopyridine ligands) as the ligands L [23]. On the other hand, the thermolysis of tetrabridged dinuclear complexes with nickel atoms sometimes afforded a metallic phase [24].

In the present study, we focused on the influence of the nature of the ligands L on the phase composition of thermolysis products and investigated the electrochemical behavior of a series of dinuclear copper pivalates  $\text{LCu}(\mu\text{-Piv})_4\text{CuL}$  (L is substituted pyridine). The results of this study allow the evaluation of the pathways of the transformations of these molecules in the course of thermal redox processes.

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## 2. Experimental

### 2.1. Synthesis

The synthetic operations were carried out under pure argon in oxygen-free solvents using the standard Schlenk technique. Starting copper pivalate **1** was synthesized according to a procedure described earlier [21]. The synthesis of new compounds was carried out with the use of trimethylacetic acid (Acros Organics), 2-aminopyridine, 3-aminopyridine, and 4-dimethylaminopyridine (Aldrich).

#### 2.1.1. $((2-NH_2)C_5H_4N)_2Cu_2(\mu-OOCMe_3)_4 \cdot C_6H_6$ (**2**· $C_6H_6$ )

Benzene (40 mL) was added to a mixture of polymer **1**  $[Cu(OOCMe_3)_2]_n$  (0.331 g, 1.169 mmol; per formula unit  $Cu(OOCMe_3)_2$ ) and 2-aminopyridine (0.109 g, 1.169 mmol), and the reaction mixture was stirred at 80 °C until the reagents were completely dissolved. The solution was concentrated to 15 mL and kept at room temperature for 24 h. Green crystals suitable for X-ray diffraction were gathered, washed with cold  $C_6H_6$ , and dried under a stream of argon. The solvate of compound **2** with one  $C_6H_6$  molecule was obtained in a yield of 0.477 g (96%). *Anal. Calc.* for  $C_{36}H_{54}Cu_2N_4O_8$ : C, 54.25; H, 6.82; N, 7.02. *Found*: C, 54.29; H, 6.91; N, 7.09%. IR (KBr)  $\nu/cm^{-1}$ : 3480 m, 3360 m, 3336 s, 3200 s, 2968 s, 2952 m, 2908 m, 2868 m, 1644 s, 1620 s, 1580 s, 1572 s, 1536 s, 1496 s, 1480 s, 1452 s, 1408 s, 1372 m, 1356 m, 1336 m, 1268 m, 1228 m, 1160 m, 1080 w, 1052 w, 1016 m, 952 w, 936 w, 896 m, 848 m, 804 m, 792 m, 776 s, 744 w, 680 m, 652 m, 620 m, 548 m, 516 m, 456 m, 400 w, 364 w, 356 w, 320 w.

#### 2.1.2. $((3-NH_2)C_5H_4N)_2Cu_2(\mu-OOCMe_3)_4$ (**3**)

Benzene (30 mL) was added to a mixture of polymer **1**  $[Cu(OOCMe_3)_2]_n$  (0.3 g, 1.129 mmol; per formula unit  $Cu(OOCMe_3)_2$ ) and 3-aminopyridine (0.105 g, 1.129 mmol), and the reaction mixture was stirred at 80 °C until the reagents were completely dissolved. The solution was concentrated to 15 mL and kept at room temperature for 24 h. Green crystals suitable for X-ray diffraction were gathered, washed with cold  $C_6H_6$ , and dried under a stream of argon. The yield of compound **3** was 0.390 g (96%). *Anal. Calc.* for  $C_{30}H_{48}Cu_2N_4O_8$ : C, 50.11; H, 6.72; N, 7.78. *Found*: C, 50.16; H, 6.80; N, 7.82%. IR (KBr)  $\nu/cm^{-1}$ : 3432 m, 3364 m, 3268 m, 2968 s, 2960 s, 2928 m, 2868 m, 1684 s, 1600 s, 1484 s, 1448 s, 1416 s, 1376 m, 1360 m, 1316 m, 1272 m, 1224 m, 1196 m, 1132 w, 1076 w, 1052 w, 1020 m, 936 w, 896 m, 856 m, 796 m, 788 s, 696 m, 644 m, 620 m, 548 m, 520 m, 440 m, 416 w, 392 w, 352 w, 316 w.

#### 2.1.3. Cocrystallization product $[((4-NMe_2)C_5H_4N)_2Cu_2(\mu-OOCMe_3)_4 \cdot 0.5Cu(\eta^2-OOCMe_3)_2((4-NMe_2)C_5H_4N)_2]$ (**4**)

Benzene (40 mL) was added to a mixture of polymer **1**  $[Cu(OOCMe_3)_2]_n$  (0.331 g, 1.169 mmol; per formula unit  $Cu(OOCMe_3)_2$ ) and 4-dimethylaminopyridine (0.143 g, 1.169 mmol), and the reaction mixture was stirred at 80 °C until the reagents were completely dissolved. The solution was concentrated to 15 mL and kept at ~5 °C for 24 h. Green crystals were gathered, washed with cold  $C_6H_6$ , and dried under a stream of argon. The yield of compound **4** was 0.493 g (96%). *Anal. Calc.* for  $C_{92}H_{150}Cu_5N_{12}O_{20}$ : C, 53.59; H, 7.33; N, 8.15. *Found*: C, 53.62; H, 7.36; N, 8.14%. IR (KBr)  $\nu/cm^{-1}$ : 3482 m, 3364 m, 3332 s, 2968 s, 2980 s, 2956 s, 2924 s, 2868 m, 2816 m, 1684 m, 1620 s, 1604 s, 1572 s, 1540 s, 1536 s, 1444 s, 1416 s, 1392 s, 1372 m, 1364 m, 1360 m, 1340 m, 1228 m, 1160 w, 1116 m, 1068 m, 1008 s, 980 w, 952 m, 936 w, 896 m, 888 m, 804 s, 788 m, 756 m, 680 m, 676 m, 616 m, 544 w, 524 m, 488 w, 432 m, 388 w, 352 w, 312 w.

Crystal suitable for X-ray diffraction was chosen from those precipitated from the benzene mother liquor.

### 2.2. Methods

Microanalyses were carried out on a Euro Vector Element CHN analyzer (Model EA 3000). The IR spectra were recorded on a Spectord M80 spectrometer in KBr pellets (4000–300  $cm^{-1}$ ). Magnetic measurements were performed on a Quantum Design MPMSXL SQUID magnetometer in the 2–300 K temperature range at a magnetic field strength of 5 kOe. The paramagnetic components of the magnetic susceptibility  $\chi$  were calculated taking into account the diamagnetic contribution estimated from the Pascal constants. The effective magnetic moment was calculated by the equation  $\mu_{eff} = (\frac{3k}{N_A\beta^2} \cdot \chi T)^{1/2} \approx (8\chi T)^{1/2}$  where  $N_A$ ,  $\beta$ , and  $k$  are Avogadro's number, the Bohr magneton, and the Boltzmann constant, respectively. The Q-band ESR spectra were recorded on a Bruker Elexsys E580 spectrometer (34 GHz) equipped with a standard EN 5107D2 resonator and an Oxford Instruments cryostat for cooling. All experiments were carried out with the use of polycrystalline samples, which were pre-dried with argon to remove the mother liquor (for approximately 1 min) and sealed in quartz tubes *in vacuo*. The calculations were performed using the EasySpin program package [25]. The thermal decomposition of compounds was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) on DSC-20 and TG-50 units of a Mettler TA-3000 thermoanalyzer. In all experiments, samples of the compounds were heated under dry argon at a constant rate of 5 deg/min. For each compound, two DSC experiments and three TG experiments were performed. The weight loss upon thermal degradation was determined directly on a TG-50 unit; the accuracy of weighing was  $\pm 2 \cdot 10^{-3}$  mg. The thermal decomposition was studied in steps by differential scanning calorimetry, which involved the division of the total temperature range into intervals. The size and number of these intervals were determined based on the overall patterns of weight loss upon decomposition. This approach allowed us to determine the weight loss in each temperature range and compare the results of DSC with the TG data. The results of these methods were in satisfactory agreement, which confirms the reliability of the experimental data. The accuracy of the determination of anomalous points and thermal effects in the DSC curves was  $\pm 1^\circ$  and  $\pm 0.5\%$ , respectively. The X-ray powder diffraction analysis of the decomposition products was carried out on a FR-552 monochromator chamber ( $CuK_{\alpha 1}$  radiation) using germanium as the internal standard (X-ray diffraction patterns were processed on an IZA-2 comparator with an accuracy of  $\pm 0.01$  mm) and with the use of the STOE Powder Diffraction System. The electrochemical oxidation and reduction potentials were measured with a digital IPC-Win potentiostat/galvanostat connected to a personal computer. The voltammograms were recorded in acetonitrile with 0.05 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> as a supporting electrolyte at 20 °C in 8 mL-electrochemical cell. Oxygen was removed from the solutions by purging with dry argon. Working electrode was a stationary platinum disk with a surface area of 0.049 cm<sup>2</sup>. A platinum plate was used as an auxiliary electrode, and a saturated silver chloride electrode was used as the reference electrode (the potential with respect to Fc/Fc<sup>+</sup> = –0.46 V in CH<sub>3</sub>CN). The measured potentials were corrected for ohmic losses. The number of electrons involved in each step of the electrochemical process was determined by the ferrocene reference method.

### 2.3. X-ray data collection

The X-ray data sets for complexes **2**· $C_6H_6$ , **3**, and **4** were collected according to a standard procedure [26] on a Bruker AXS SMART 1000 APEX II diffractometer equipped with a CCD detector

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