

# Dicopper(I) oxalate complexes as molecular precursors for the deposition of copper compounds

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## Abstract

The synthesis, characterization, and thermal decomposition behavior of dicopper(I) oxalato complexes  $L_4Cu_2(C_2O_4)$  ( $L = CNtBu$  (**2a**),  $CNCMe_2CH_2tBu$  (**2b**),  $CNC_6H_3Me_2-2,6$  (**2c**)) is reported. **2c** can be prepared in a straightforward manner by the reaction of stoichiometric amounts of  $Cu_2O$  and oxalic acid with four equivalents of  $CNC_6H_3Me_2-2,6$ , while those complexes with aliphatic isocyanides are better prepared from a copper(I) oxalato complex with alkine capping ligands  $(Me_3SiC\equiv CSiMe_3)_2-Cu_2(C_2O_4)$  (**1**) via ligand exchange. Crystallographic and spectroscopic evidence for **2a–c** confirms the anticipated dinuclear structure with the oxalate in a  $\mu-1,2,3,4$  bridging mode and an essentially  $\sigma$ -character of the terminal isocyanides. In solid form the complexes are stable at room temperature and can be handled in air for some time. Their decomposition was studied by thermal gravimetric analysis coupled with mass spectrometry, and the degradation pathway was shown to depend on the type of isocyanide capping ligand. Decomposition of **2a,b** takes place between 150 and 200 °C to give  $CuCN$  in a clean process that involves isobutene elimination from the terminal ligands, with elimination of  $(CN)_2$  and conversion to elemental copper at higher temperatures. Heating of **2c** leads to  $CuO$  (and then to  $Cu_2O$ ) via release of the intact isocyanide,  $CO_2$ , and  $CO$  in a well-behaved thermal process around 200–280 °C.

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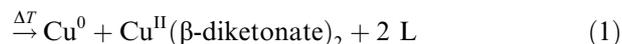
**Keywords:** Copper; Dinuclear complexes; Oxalate complexes; Precursor compounds; Thermal analysis

## 1. Introduction

Copper deposition has become an important and rapidly growing area in integrated circuit manufacturing, since copper is a favorable material for interconnect structures in microelectronic devices [1]. This has stimulated the search for molecular copper(I) and copper(II) complexes that may serve as sources for device quality copper via various deposition techniques [2,3]. In particular, chemical vapour deposition (CVD) has been studied intensively for the formation of copper thin films, and metal–organic  $Cu^I$  compounds of general formula

$LCu^I(\beta\text{-diketonate})$ , where the  $\beta$ -diketonate often is hexafluoroacetylacetonate (hfac) and  $L$  is a neutral Lewis-base such as a phosphine, alkyne, or alkene, have shown promising potential as copper CVD precursors [4,5]. Their deposition reaction involves disproportionation into  $Cu^{II}(\beta\text{-diketonate})_2$ , the free donor ligand  $L$ , and metallic copper according to Eq. (1), thus limiting the maximum yield of copper metal to 50%

$2 LCu^I(\beta\text{-diketonate})$

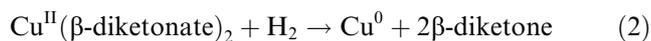


On the other hand,  $Cu^{II}$  precursors such as  $Cu^{II}(\text{hfac})_2$  may be used (Eq. (2)) [6], but in this case an external reducing agent such as  $H_2$  is required to get good quality thin films [3]. Furthermore, conversion to

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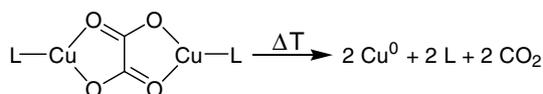
elemental copper is often inefficient, and in the absence of  $H_2$  large amounts of carbon or oxygen contaminants are found in the copper metal, due to uncontrolled ligand decomposition. Self-reducible  $Cu^{II}$  complexes with  $\beta$ -aminoalcoholate ligands have been proposed as alternative source reagents with an intrinsic decomposition pathway, giving ketone or imine fragments depending on the specific  $\beta$ -aminoalcoholate ligand used [7]



Despite considerable progress in copper CVD, however, drawbacks such as poor adhesion of the copper films onto the TiN diffusion barrier layer when using fluorine-containing copper precursors [8] have fired the search for new fluorine-free copper source reagents [3]. In addition, alternative precursor delivery methods are being developed in order to circumvent some general limitations of conventional CVD processes such as the requirement of high volatility of the metal compound. Recent approaches comprise, inter alia, spin coating [9] or aerosol-assisted CVD (AACVD) techniques [10] and, most recently, reductive copper deposition from supercritical carbon dioxide (chemical fluid deposition, CFD) [11,12]. Many organometallic complexes exhibit significant solubility in  $CO_2$ , and common  $Cu^{II}(\beta\text{-diketonate})_2$  complexes with either fluorinated or fluorine-free  $\beta$ -diketonate ligands have already been tested in CFD. Pyrolysis of copper oxalate hydrate under supercritical  $CO_2$  has most recently been reported to yield 1D copper nanowires [13].

Similarly, the controlled preparation of copper oxide films (which are known as p-type semiconductors) has received much attention in view of their applications in a wide range of technological fields such as electrochemical devices, solar cells, coatings, the synthesis of cuprate superconductors, and their importance in catalysis [14]. While conventionally prepared by, inter alia, electrodeposition, chemical or thermal oxidation, or chemical vapor deposition [15], careful regulation of conditions is required to obtain pure  $CuO$  or  $Cu_2O$  and alternative approaches are being sought, including those based on single-source precursors [16].

In a recent report, we described a series of novel dicopper(I) oxalate complexes stabilized by neutral Lewis bases L (L = alkyne, alkene) that are promising new candidates of self-reducing precursors for copper deposition [17]. While being reasonably air stable and highly soluble, these complexes incorporate the oxalate ligand as a built-in reducing equivalent that ensures a 100% yield of metallic copper upon thermal decomposition via an internal redox reaction (Scheme 1).



Scheme 1.

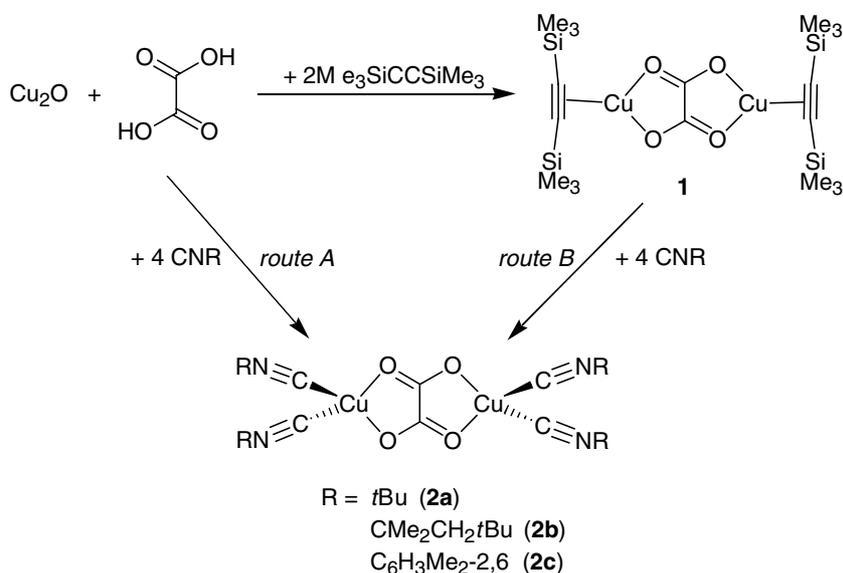
A obvious advantage of this clean and straightforward conversion is the formation of the reusable ligand L and non-toxic  $CO_2$  as sole byproducts. On the other hand, dicopper(I) oxalato complexes may also be anticipated to represent useful molecular precursors for the deposition of  $CuO$  or  $Cu_2O$  rather than elemental copper, if thermal degradation proceeds via other pathways with elimination of  $CO$  instead of  $CO_2$ , or a mixture of both. The prospect to switch between distinct decomposition pathways of such  $L_nCu_2(C_2O_4)$  systems by suitable variations of the capping ligands L is particularly attractive. The present contribution now describes the synthesis and structural characterization of a series of dicopper(I) oxalate complexes with isocyanide capping ligands, and preliminary results on their thermal behaviour with respect to copper and copper oxide deposition.

## 2. Results and discussion

### 2.1. Synthesis and spectroscopic characterization

In close analogy to the straightforward synthesis of complexes  $L_2Cu_2(C_2O_4)$  where the Lewis base L is an alkyne or alkene [17], initial attempts to prepare the sought-after complexes  $(RNC)_xCu_2(C_2O_4)$  were carried out by reacting  $Cu_2O$ , oxalic acid and the respective isonitrile RNC (R = *t*Bu,  $CMe_2CH_2tBu$ , cyclohexyl,  $C_6H_3Me_2-2,6$ ) at room temperature in  $CH_2Cl_2$  (route A, Scheme 2). However, this route only worked well for the aromatic isonitrile to give **2c** (R =  $C_6H_3Me_2-2,6$ ), while for aliphatic isonitriles (R = *t*Bu,  $CMe_2CH_2tBu$ , cyclohexyl) solutions of the reaction mixtures gradually turned blue, suggesting the unwanted formation of copper(II) species. In these experiments, the anticipated type **2** products could still be isolated, but yields are rather poor. In one case (R = cyclohexyl) pale blue crystals of the decomposition product **3** could be obtained in crystalline form, and **3** was identified as  $[Cu(CNR)_4]_2[Cu(C_2O_4)_2]$  by X-ray crystallography (see below). Gradual decomposition of type **2** complexes apparently involves some ligand dismutation.

We thus turned to a ligand exchange reaction starting from preformed  $(Me_3SiC\equiv CSiMe_3)_2Cu_2(C_2O_4)$  (**1**) [17] according to route B (Scheme 2). The reaction can be conveniently followed by IR spectroscopy, revealing efficient displacement of the  $Me_3SiC\equiv CSiMe_3$  capping ligands in **1** by the respective isonitriles to give **2a–c**. The colorless products **2a–c** are highly soluble in  $CH_2Cl_2$  or  $CHCl_3$  solutions and can be obtained in crystalline form upon cooling concentrated solutions in those solvents to  $-20^\circ C$ . Elemental analyses suggest the formula  $(RNC)_4Cu_2(C_2O_4)$  in all cases, indicating that two isonitrile capping ligands are bonded to each metal ion. While sensitive to oxygen in solution, the



Scheme 2. Synthesis of the complexes.

complexes are almost air stable as solids and can thus be handled in air for a short time.

IR spectra of the isolated materials display the characteristic strong  $\nu_{\text{as}}(\text{C}-\text{O})$  band of the oxalato ligand at around  $1620\text{ cm}^{-1}$ , corroborating its tetradentate bridging mode (Table 1). The  $\nu_{\text{as}}(\text{C}-\text{O})$  absorption is shifted by  $\sim 25\text{ cm}^{-1}$  to lower energy compared to the copper(I) oxalate complexes with alkyne and alkene capping ligands (e.g., **1**, Table 1) [17], presumably reflecting the less pronounced  $\text{Cu} \rightarrow \text{L}$  backbonding contribution for the isocyanides. A band appearing at  $1308\text{ cm}^{-1}$  in the IR spectra of all complexes **2a–c** is tentatively assigned to  $\nu_{\text{s}}(\text{C}-\text{O})$ . Two  $\nu(\text{N}\equiv\text{C})$  vibrations are observed for the isocyanide ligands, in accordance with a  $D_{2h}$  structure ( $B_{1u} + B_{2u}$ ). The  $\nu(\text{N}\equiv\text{C})$  stretches are shifted hypsochromically by  $\sim 30\text{ cm}^{-1}$  (**2a,b**) or  $\sim 20\text{ cm}^{-1}$  (**2c**) compared to the free isocyanides, in agreement with what is usually observed for terminally bound isocyanides that act as two-electron  $\sigma$ -donors towards copper(I) with only little  $\pi$ -backbonding [18–20]. Values for **2c** are close to those reported for  $[(p\text{-MeC}_6\text{H}_4\text{NC})_2\text{Cu}(\text{OPh})_2]$  ( $2145/2125\text{ cm}^{-1}$ ) [21], while values for **2a,b** are similar to those of  $[(\text{C}_6\text{H}_{11}\text{NC})_2\text{Cu}(\text{dmpnz})_2]$  ( $2165/2143\text{ cm}^{-1}$ ; dmpnz = 3,5-dimethyl-4-nitropyrazolato) [22].  $\nu(\text{N}\equiv\text{C})$  vibrations of all new complexes are very similar if mea-

sured either as KBr pellets or in  $\text{CH}_2\text{Cl}_2$ , indicating that structures in the solid state and in solution are the same. However, ESI mass spectra of  $\text{CHCl}_3$  solutions of the complexes do not show the expected molecular ion peaks but dominant signals for  $[\text{Cu}(\text{CNR})_2]^+$  and minor peaks characteristic for  $[\text{Cu}(\text{CNR})_3]^+$  and  $[\text{Cu}_3(\text{C}_2\text{O}_4)(\text{CNR})_3]^+$ .

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **2a–c** in  $\text{CDCl}_3$  consist of well-resolved single resonances for each of the organic groups of the coordinated isocyanides, reflecting the high symmetry of the molecules. The absence of any NMR signals for free isocyanide confirms that ligands do not dissociate in solution, in accordance with the IR spectral findings. In the  $^{13}\text{C}$  NMR spectra, resonances of the isocyanide-C are clearly shifted to higher field compared to the free isocyanides (Table 2), consistent with an essentially  $\sigma$ -donor character of the ligands [23].

The resonance of the oxalato carbon atoms appears at  $\sim 169\text{ ppm}$ , i.e., at somewhat higher field compared to the oxalato carbon signal of **1** ( $171.8\text{ ppm}$ ) and to all other copper(I) oxalate complexes with alkyne or alkene capping ligands [17]. This is consistent with the differences in  $\nu_{\text{as}}(\text{C}-\text{O})$  frequency discussed above.

Table 1  
Selected IR absorptions for complexes **2a–c**

Compound	$\nu(\text{N}\equiv\text{C})^{\text{a}}$	$\nu_{\text{as}}(\text{C}-\text{O})$
<b>1</b> [17]	–	1642
<b>2a</b>	2180/2151 (2136)	1617
<b>2b</b>	2172/2147 (2130)	1621
<b>2c</b>	2151/2128 (2121)	1622

<sup>a</sup> Values for the free isocyanides in parentheses.

Table 2  
Selected  $^{13}\text{C}$  NMR data for complexes **2a–c**

Compound	$^{13}\text{C}\{^1\text{H}\}$ NMR $\delta(\text{N}\equiv\text{C})$ (ppm) <sup>a</sup>	$^{13}\text{C}\{^1\text{H}\}$ NMR $\delta(\text{OCO})$ (ppm)
<b>1</b> [17]	–	171.8
<b>2a</b>	138.0 (152.5)	168.9
<b>2b</b>	139.8 (155.0)	168.9
<b>2c</b>	150.4 (167.6)	169.2

<sup>a</sup> Values for the free isocyanides in parentheses.

## 2.2. Solid state structures

While copper(II) oxalate and its complexes are well known, only few reports about copper(I) oxalate have been published. Apart from those  $L_2Cu_2(C_2O_4)$  complexes reported recently (with  $L$  = alkyne, alkene) [17], no structural data of copper(I) oxalate complexes are known. Complexes of type  $Cu_2(C_2O_4)(CNR)_2$  have been briefly mentioned in a patent, but no analytical data or structural information had been given [24]. In view of the present findings, it seems more likely that these complexes with isonitriles generally have the stoichiometry  $Cu_2(C_2O_4)(CNR)_4$ . To confirm the constitution of the new complexes as deduced from spectroscopy and to gain further insight into the structural details of copper(I) oxalate species, complexes **2a–c** and the partially oxidized product **3** were analyzed by X-ray crystallography. Molecular structures of **2a** and **2c** are depicted in Figs. 1 and 2 as examples. The other molecular structures are depicted in Figures S1 and S2 in the supporting material.

All copper(I)-complexes **2a–c** show a dinuclear structure with the oxalate in a  $\mu$ -1,2,3,4 bridging mode. Additionally each copper(I) atom is bound to two isonitrile ligands with almost linear  $Cu-C-N$  arrangement. The coordination environment for each metal atom is strongly distorted from tetrahedral due to, inter alia, the small bite angle imposed by the chelating oxalate. The  $Cu-O$  bond lengths in **2a–c** (2.081(2)–2.122(2) Å) are approximately 0.1 Å longer than those determined previously for  $[LCu]_2(\mu-C_2O_4)$  ( $L = Me_3SiC\equiv C-$

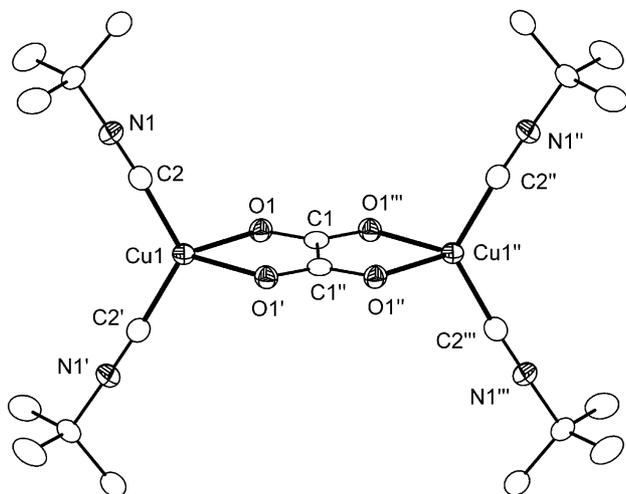


Fig. 1. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **2a**. For the sake of clarity all hydrogen atoms have been omitted. Selected atom distances (Å) and angles (°):  $Cu1-O1$  2.120(2),  $Cu1-C2$  1.902(4),  $O1-C1$  1.257(3),  $C1-C1''$  1.551(9),  $C2-N1$  1.164(5) and  $O1-Cu1-O1'$  78.9(1),  $C2-Cu1-C2'$  123.0(2),  $Cu1-C2-N1$  176.9(3),  $O1-C1-O1''$  125.9(4),  $O1-C1-C1''$  117.1(2). Symmetry transformations used to generate equivalent atoms: (')  $x, y, 1-z$ , (")  $1-y, 1-x, 1-z$ , ("" )  $1-y, 1-x, z$ .

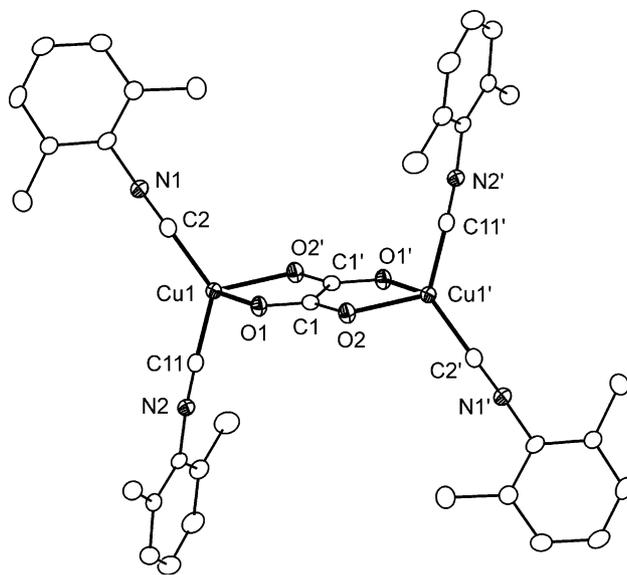


Fig. 2. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **2c**. For the sake of clarity all hydrogen atoms have been omitted. Selected atom distances (Å) and angles (°):  $Cu1-O1$  2.122(2),  $Cu1-O2'$  2.094(2),  $Cu1-C2$  1.874(4),  $Cu1-C11$  1.902(4),  $O1-C1$  1.249(4),  $O2-C1$  1.257(4),  $C1-C1'$  1.559(7),  $C2-N1$  1.163(5),  $C11-N2$  1.157(4) and  $O1-Cu1-O2'$  79.70(9),  $C2-Cu1-C11$  129.1(1),  $N1-C2-Cu1$  178.0(4),  $N2-C11-Cu1$  177.7(3),  $O1-C1-O2$  125.7(3),  $O1-C1-C1'$  117.9(3),  $O2-C1-C1'$  116.3(3). Symmetry transformation used to generate equivalent atoms: (')  $1-x, 1-y, 1-z$ .

$SiMe_3$ ,  $EtC\equiv CEt$ ) (1.987(1)–2.004(2) Å) [17] but comparable to those found in the bis( $\mu$ -phenoxo)dicopper(I) compound  $[(p-MeC_6H_4NC)_2Cu(\mu-OPh)]_2$  (2.066(4) and 2.083(4) Å) [21]. The  $Cu-C$  distances of about 1.9 Å are similar for **2a–c** and  $[(p-MeC_6H_4NC)_2Cu(\mu-OPh)]_2$  (1.905(7)/1.907(7) Å), but a little shorter than those of  $[(C_6H_{11}NC)_2Cu(dmpz)]_2$  (1.930(3)/1.937(4) Å) [22]. Even longer  $Cu-C$  bonds were determined for tetrakis(isonitrile) complexes of copper(I), such as  $[(MeNC)_4Cu]BF_4$  (1.94–2.00 Å) [25] or **3** (1.95(1)–1.98(2) Å; see below). Comparison of the  $NC$  bond lengths of the free isonitrile 2,4-Me-C<sub>6</sub>H<sub>4</sub>NC and the isonitrile complex **2c** shows no significant elongation or shortening (**2c**: 1.163(5) and 1.157(4) Å, 2,4-Me-C<sub>6</sub>H<sub>4</sub>NC: 1.160(3) and 1.161(2) Å) [26], while a somewhat smaller  $N\equiv C$  distance has been reported for  $[(p-MeC_6H_4NC)_2Cu(\mu-OPh)]_2$  [21]. In contrast to these findings a distinct lengthening of the  $C\equiv C$  bonds concomitant with alkyne bending was reported for the dicopper(I) oxalate  $[LCu]_2(\mu-C_2O_4)$  ( $L = Me_3SiC\equiv C-SiMe_3$ ) [17].

The unit cell of **3** consists of tetrahedral tetrakis(cyclohexylisonitrile)copper(I) cations and charge compensating bis(oxalato)cuprate(II) anions with square planar coordination of the copper(II) center (Figure S2). Geometric parameters of the cation are very similar to those reported previously for some  $[Cu(CNR)_4]^+$  ions [25,27].

### 2.3. Thermal behavior

Thermal gravimetric analysis and differential scanning calorimetry coupled to mass spectrometry (TGA/MS) was employed in order to evaluate the thermal stability of the copper(I) oxalate complexes **2a–c** and to investigate their decomposition behavior with increasing temperature. Several previous studies have dealt with the thermal decomposition of copper(II) oxalate and its derivatives: decomposition of  $\text{Cu}(\text{C}_2\text{O}_4) \cdot 0.25\text{H}_2\text{O}$  has been reported to proceed with release of  $\text{CO}_2$  and stepwise cation reduction ( $\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}^0$ ) [28], but it has also been observed that complexes  $\text{L}_n\text{Cu}(\text{C}_2\text{O}_4)$  (where L is  $\text{H}_2\text{O}$  or various N-ligands) thermally decompose without forming any isolable intermediate to give either  $\text{Cu}_2\text{O}$  or  $\text{CuO}$ , depending on L [29]. Molecular copper(I) oxalato complexes  $\text{L}_2\text{Cu}_2(\text{C}_2\text{O}_4)$  (L = alkyne, alkene) have recently been described as promising precursors for copper deposition, due to their clean conversion to elemental copper via an internal redox reaction according to Scheme 1 [17]. Since isonitrile ligands might be more strongly bound to Cu than alkenes and alkynes and might be more susceptible to ligand fragmentation, the release of  $\text{CO}$ ,  $\text{CO}_2$ , intact isonitrile CNR, or fragments of the latter could have been expected upon heating **2a–c**. It turns out that the thermal decomposition pattern of **2c** is different from those of **2a** and **2b**.

The TGA/DSC curves for **2a** and **2b** depicted in Fig. 3 clearly show major endothermic processes in the range 150–200 °C that are accompanied with a drastic weight loss. Mass spectrometric analyses reveal the release of  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{HCN}$  ( $m/z = 27$ ), and isobutene ( $m/z = 56$ ) during these processes. Minor amounts of  $\text{CN}t\text{Bu}$  are observed in the case of **2a**, while no intact  $\text{CNCMe}_2\text{CH}_2t\text{Bu}$  can be detected for **2b**. The remaining weight percentage at 200 °C of 33.5% (**2a**) or 23.3% (**2b**) is in excellent agreement with the theoretical value expected for  $\text{Cu}_2(\text{CN})_2$  (32.7% or 23.2%, respectively). IR spectra of TGA samples that have only been heated to 240 °C show the expected  $\text{C}\equiv\text{N}$  vibration for  $\text{CuCN}$  at  $2168\text{ cm}^{-1}$  [30,31], and the endothermic peak at  $\sim 472\text{ °C}$  in the DSC curves represents the characteristic melting point of  $\text{CuCN}$  [30]. Thermal decomposition of cupreous cyanide has been studied in quite some detail in the context of the preparation of cuprate superconductors, where  $\text{CuCN}$  was found to be a useful precursor for single-phase  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  [32]. The thermal behavior of **2a** and **2b** in the range 200–700 °C and the mass spectrometric detection of  $(\text{CN})_2$  ( $m/z = 52$ ) during continued heating is consistent with gradual decomposition of  $\text{CuCN}$  to yield elemental copper (theoretical weight values: 23.2% or 16.5% for **2a** and **2b**, respectively), which was reported to proceed via various cyclic  $\text{Cu}(\text{CN})_x$  intermediates. However, in the present case this process is already completed at  $\sim 620\text{ °C}$ , i.e., at a temperature much lower than

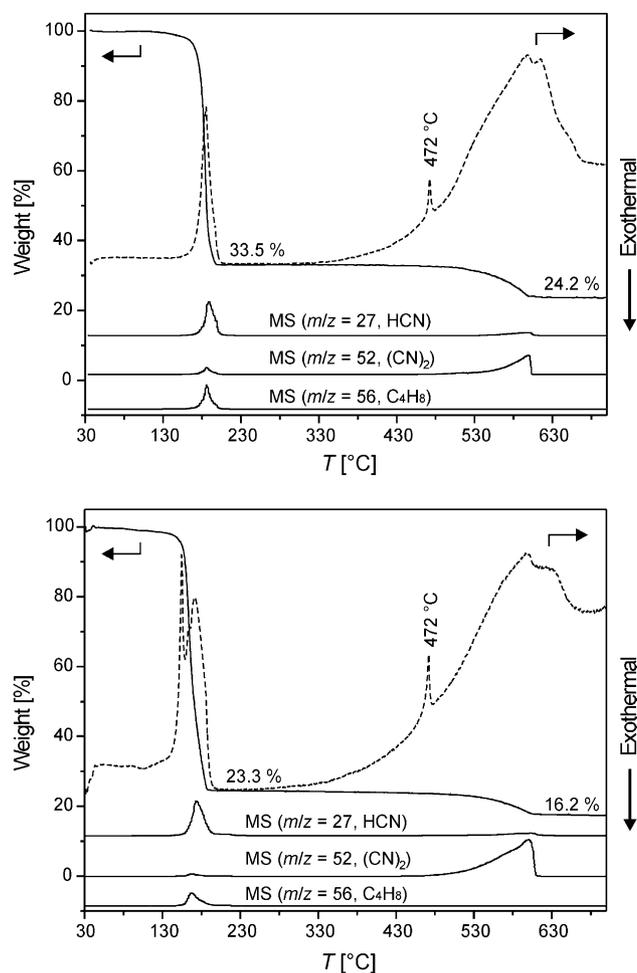


Fig. 3. TGA (solid) and DSC (broken) curves for **2a** (top) and **2b** (bottom), including selected MS traces; heating rate 5 °C/min.

$\sim 850\text{ °C}$  found for customary cupreous cyanide [30]. Formation of elemental copper as the final product is confirmed by an endothermic peak at  $1086\text{ °C}$  in the

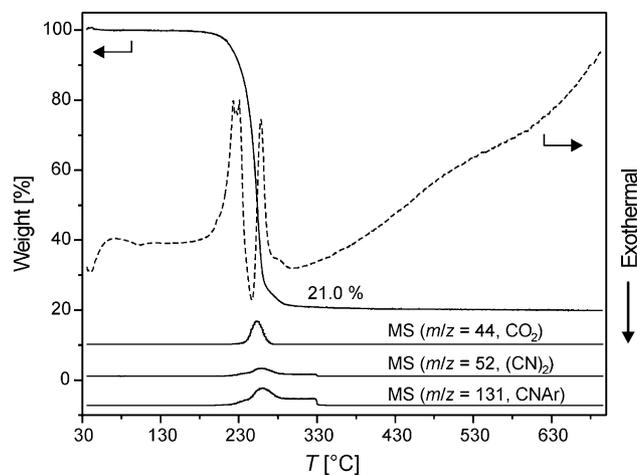


Fig. 4. TGA (solid) and DSC (broken) curves for **2c**, including selected MS traces; heating rate 5 °C/min.

DSC curves representing the melting point of the pure metal (not shown in Fig. 3).

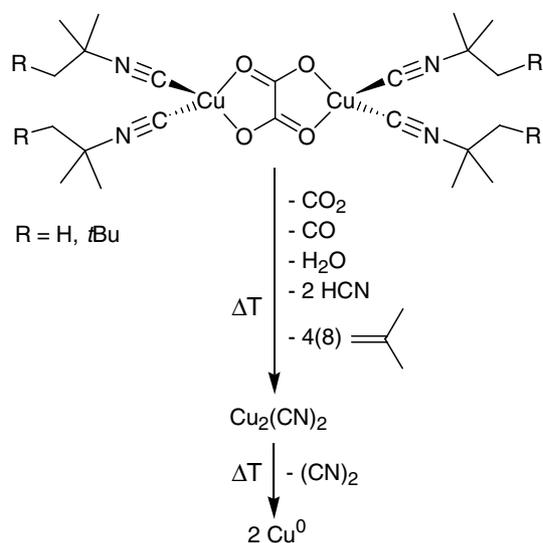
The TGA/DSC curves for **2c** are shown in Fig. 4. In the range 200–280 °C a series of endothermic processes take place, which according to mass spectrometric analyses of the volatile components correspond to the loss of CO and CO<sub>2</sub> (mainly around ~240 °C) and of the intact isonitrile (*m/z* = 131, mainly around ~260 °C). The remaining weight of ~21% at 310 K is quite consistent with the formation of CuO (expected: 21.5%), and minor additional weight loss upon continuous heating to 700 °C under N<sub>2</sub> might be due to gradual transformation into Cu<sub>2</sub>O (degradation of CuO to give Cu<sub>2</sub>O is most rapid above 800 °C and is completed around 1000 °C [33]). Cu<sub>2</sub>O has also been reported to form upon thermal decomposition of some dinuclear copper(I) complexes with perfluorinated carboxylates [Cu<sub>2</sub>{P(OMe)<sub>3</sub>}<sub>2</sub>(μ-R<sup>F</sup>COO)<sub>2</sub>] [34].

### 3. Conclusions

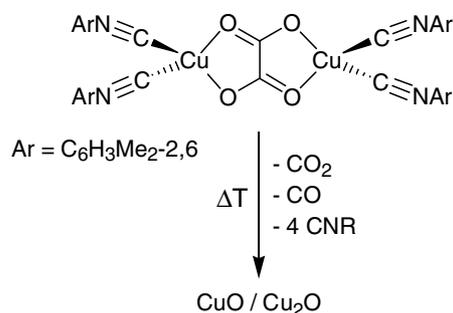
A series of new copper(I) oxalato complexes with isocyanide capping ligands has been prepared and fully characterized. X-ray crystal structures and spectroscopic data reveal further insight into (still rare) molecular copper(I) oxalato systems and confirm that the terminal isocyanides act as predominant σ-donors. Copper(I) oxalato complexes that bear neutral capping ligands have recently been considered as well defined and self-reducing molecular precursors for copper deposition, since they may potentially decompose with loss of the capping ligands and release of CO<sub>2</sub> to give a 100% yield of elemental copper via an internal redox reaction [17]. According to combined TGA/DSC-MS data, however, the present isocyanide complexes degrade in a more complex way, depending on the specific isocyanide. Thermal decomposition of **2a** and **2b** with aliphatic isocyanides that incorporate *t*Bu groups follows the sequence given in Scheme 3. Here, elimination of isobutene generates HCN, leading in a clean process to CuCN as the initial product. This decomposes further to elemental Cu, which is completed around 620 °C (see Fig. 3).

In contrast, isocyanide degradation is not a major process for **2c**, whose predominant decomposition pathway is sketched in Scheme 4. Generation of HCN is not favorable from the aromatic isocyanide ligand, which upon heating is mainly lost as the intact CNAr. In this case CuO (and Cu<sub>2</sub>O at higher temperatures) is formed.

The present findings once more underline the need of proper ligand choice in order to get to the desired product in a precursor-based deposition process. Whereas copper(I) oxalato complexes with alkene or alkyne capping ligands proved to be promising precursors for copper deposition [17], the isocyanide complexes described



Scheme 3. Major thermal decomposition pathway for **2a** and **2b**.



Scheme 4. Major thermal decomposition pathway for **2c**.

in this work are less suitable in this regard, but they lead to different copper compounds such as CuCN or CuO in distinct thermal decomposition pathways.

## 4. Experimental

### 4.1. General procedures and methods

All manipulations were carried out under an atmosphere of dry nitrogen by employing standard Schlenk techniques. Solvents were dried according to established procedures. **1** was synthesized according to the reported method [17], all other chemicals were used as purchased. Microanalyses: Analytisches Labor des Anorganisch-Chemischen Instituts der Universität Göttingen. – IR spectra: Digilab Excalibur, recorded as KBr pellets or in solution (NaCl cell). – Mass spectra: Finnigan MAT 95 (FAB-MS, matrix nitrobenzylalcohol) and Finnigan MAT LCQ (ESI-MS). – NMR spectra: Bruker Avance 500, measured at 300 K; residual proton signal of the solvent as internal chemical shift reference (CDCl<sub>3</sub>: δ<sub>H</sub> = 7.24, δ<sub>C</sub> = 77.0 ppm) – TGA/DSC-MS: Netzsch

STA 449C Jupiter QMS, using an open pan (Al<sub>2</sub>O<sub>3</sub>) which was purged with N<sub>2</sub>; heating rate 5 °C/min.

#### 4.2. Synthesis of the complexes

**Route A.** Cu<sub>2</sub>O (0.54 g, 3.7 mmol) is dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 ml) and oxalic acid (0.33 g, 2.6 mmol) and 2,6-dimethylphenylisocyanide (2.0 g, 15.2 mmol) are added. The reaction mixture is left stirring for 3 h at room temperature and any solid residue is then filtered off. The volume of the resulting clear solution is reduced to ~20 ml under reduced pressure and stored at –20 °C. Colorless crystals of the product **2c** gradually form. They are isolated by filtration, washed with small amounts of cold (–30 °C) CH<sub>2</sub>Cl<sub>2</sub>, and dried under vacuum. Analytical data are identical to those of **2c** obtained via route B.

**Route B.** **1** (1.0 g, 1.8 mmol) is dissolved in CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub> (50 ml) and four equivalents (7.2 mmol) of the respective isocyanide are added via a syringe at room temperature. After stirring for 2 h, the volume of the solution is reduced to ~20 ml under reduced pressure and stored at –20 °C. Colorless crystals of the product **2a–c** gradually form. They are isolated by filtration, washed with small amounts of cold (–30 °C) CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub>, and dried under vacuum. Non-optimized yields of crystalline material are in the range 25–45 %.

**Complex 2a.** <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.38 (s, 36H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 30.2 (CH<sub>3</sub>), 55.5

(C(CH<sub>3</sub>)<sub>3</sub>), 138.0 (C≡N), 168.9 (COO). IR (KBr): 2980 m, 2936 w, 2180 s, 2151 s, 1676 w, 1617 vs, 1402 w, 1370 w, 1308 w, 1199 m, 780 w. MS (ESI, CH<sub>2</sub>Cl<sub>2</sub>): *m/z* (%) = 526 (10) [Cu<sub>3</sub>(ox)(CN*t*Bu)<sub>3</sub>]<sup>+</sup>, 312 (27) [Cu(CN*t*Bu)<sub>3</sub>]<sup>+</sup>, 229 (100) [Cu(CN*t*Bu)<sub>2</sub>]<sup>+</sup>. Anal. calcd. for C<sub>22</sub>H<sub>36</sub>Cu<sub>2</sub>N<sub>4</sub>O<sub>4</sub> (547.64): C 48.25, H 6.63, N 10.23; Found: C 47.49, H 6.58, N 9.94.

**Complex 2b.** <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.01 (s, 36H, C(CH<sub>3</sub>)<sub>3</sub>), 1.43 (s, 24H, C(CH<sub>3</sub>)<sub>2</sub>), 1.56 (s, 8H, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 30.9 (CH<sub>3</sub>), 31.0 (CH<sub>3</sub>), 31.8 (C(CH<sub>3</sub>)<sub>3</sub>), 53.6 (CH<sub>2</sub>), 58.2 (C(CH<sub>3</sub>)<sub>2</sub>), 139.8 (C≡N), 168.9 (COO). IR (KBr): 2955 m, 2906 m, 2172 s, 2147 s, 1621 vs, 1474 m, 1397 w, 1370 m, 1308 m, 1217 m, 1132 w, 780 m, 756 w. MS (ESI, CHCl<sub>3</sub>): *m/z* (%) = 694 (4) [Cu<sub>3</sub>(ox)(CNC(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>*t*Bu)<sub>3</sub>]<sup>+</sup>, 480 (7) [Cu(CN(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>*t*Bu)<sub>3</sub>]<sup>+</sup>, 341 (100) [Cu(CN(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>*t*Bu)<sub>2</sub>]<sup>+</sup>. Anal. calcd. for C<sub>38</sub>H<sub>68</sub>Cu<sub>2</sub>N<sub>4</sub>O<sub>4</sub> (771.96): C 59.11, H 8.88, N 7.26; Found: C 58.47, H 8.60, N 7.23.

**Complex 2c.** <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 2.35 (s, 24H, CH<sub>3</sub>), 7.02 (d, *J* = 7.6 Hz, 8H, CH<sup>m</sup>), 7.15 (t, 7.6 Hz, 4H, CH<sup>p</sup>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 18.8 (CH<sub>3</sub>), 126.4, 127.8, 129.1, 135.3, 150.4 (C≡N), 169.2 (COO). IR (KBr): 3056 w, 2989 w, 2922 w, 2151 m, 2128 s, 1619 vs, 1472 w, 1308 m, 1274 w, 1163 w, 1036 w, 780 m, 721 w, 696 w, 494 m. MS (ESI, CHCl<sub>3</sub>): *m/z* (%) = 670 (45) [Cu<sub>3</sub>(ox)(CNC<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>]<sup>+</sup>, 325 (100) [Cu(CNC<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>]<sup>+</sup>. Anal. calcd. for C<sub>38</sub>H<sub>36</sub>Cu<sub>2</sub>N<sub>4</sub>O<sub>4</sub> (739.72): C 61.69, H 4.91, N 7.57; Found: C 61.47, H 4.92, N 7.64.

Table 3

Crystal data and refinement details for complexes **2a**, **2b**, **2c**, and **3**

	<b>2a</b>	<b>2b</b>	<b>2c</b>	<b>3</b>
Formula	C <sub>22</sub> H <sub>36</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>4</sub> , 2.25CH <sub>2</sub> Cl <sub>2</sub>	C <sub>38</sub> H <sub>68</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>4</sub> , 4CHCl <sub>3</sub>	C <sub>38</sub> H <sub>36</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>4</sub> , 3CHCl <sub>3</sub>	2C <sub>28</sub> H <sub>44</sub> CuN <sub>4</sub> <sup>+</sup> , C <sub>4</sub> CuO <sub>8</sub> <sup>2-</sup> , C <sub>7</sub> H <sub>8</sub>
<i>M<sub>r</sub></i>	741.71	1249.52	1097.89	1332.14
Crystal size (mm)	0.36 × 0.28 × 0.22	0.37 × 0.21 × 0.15	0.23 × 0.18 × 0.12	0.42 × 0.31 × 0.24
Crystal system	Tetragonal	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P4<sub>2</sub>/mmm</i> (no. 136)	<i>P2<sub>1</sub>/c</i> (no. 14)	<i>C2/c</i> (no. 15)	<i>C2/c</i> (no. 15)
<i>a</i> (Å)	11.3960(10)	12.5873(8)	18.7165(16)	47.304(2)
<i>b</i> (Å)	11.3960(10)	14.0048(7)	13.1684(8)	12.6338(4)
<i>c</i> (Å)	14.5846(15)	17.3091(12)	20.9320(17)	26.0673(10)
β (°)	90	91.582(5)	108.145(7)	117.601(3)
<i>V</i> (Å <sup>3</sup> )	1894.1(3)	3050.1(3)	4902.5(7)	13805.6(9)
ρ <sub>calcd.</sub> (g cm <sup>-3</sup> )	1.301	1.361	1.487	1.282
<i>Z</i>	2	2	4	8
<i>F</i> (000) (e)	764	1292	2224	5640
μ (Mo Kα) (mm <sup>-1</sup> )	1.471	1.261	1.401	0.973
<i>T</i> <sub>max</sub> / <i>T</i> <sub>min</sub>	0.7295/0.6411	0.8373/0.6188	0.8171/0.6887	0.7843/0.5963
<i>hkl</i> range	±13, ±13, –17 to 14	±14, –15 to 16, ±20	–21 to 22, –13 to 15, –23 to 24	±55, 14, ±30
θ range (°)	2.53–24.78	1.62–24.87	1.92–24.78	1.57–24.81
Measured reflections	7502	16431	13597	70083
Unique reflections ( <i>R</i> <sub>int</sub> )	909 (0.0447)	5250 (0.0416)	4195 (0.0523)	11826 (0.0677)
Observed reflections <i>I</i> > 2σ( <i>I</i> )	791	3988	3026	7659
Refined parameters	50	299	293	999
Goodness-of-fit	1.083	1.025	1.010	1.028
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0384, 0.1032	0.0313, 0.0703	0.0425, 0.0830	0.0860, 0.2115
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0456, 0.1066	0.0472, 0.0743	0.0698, 0.0900	0.1258, 0.2389
Residual electron density (e Å <sup>-3</sup> )	–0.406/0.196	–0.299/0.318	–0.473/0.534	–1.101/1.662

### 4.3. X-ray crystallography

X-ray data were collected on a STOE IPDS II diffractometer (graphite monochromated Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å) by use of  $\omega$  scans at  $-140$  °C (Table 3). The structures were solved by direct methods and refined on  $F^2$  using all reflections with SHELX-97 [35]. The unit cell of **2a** contains disordered CH<sub>2</sub>Cl<sub>2</sub>, for which no satisfactory model for the disorder was found. For further refinement the contribution of the missing solvent molecules (total electron count 190) was subtracted from the reflection data by the SQUEEZE [36] routine of the PLATON [37] program. Disordered solvent molecules were found in **2c** (CHCl<sub>3</sub>) and **3** (toluene) and were refined in the usual manner. In addition, six cyclohexyl isonitrile ligands (from a total of 12) in **3** are disordered about two positions. The respective occupancy factors were refined to 0.591(10)/0.409(10) (N3 to C37), 0.598(15)/0.402(15) (C42 to C47), 0.637(10)/0.363(10) (C52 to C57), and 0.522(12)/0.478(12) (C62 to C67). The atoms of the disordered toluene solvent in **3** were refined isotropically, all other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å<sup>2</sup>. Face-indexed absorption corrections were performed numerically with the program X-RED [38]. CCDC-263109 (**2a**), CCDC-263110 (**2b**), CCDC-263111 (**2c**), and CCDC-263112 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax (internat.): +44 1223/336 033; e-mail: deposit@ccdc.cam.ac.uk).

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2005.04.055](https://doi.org/10.1016/j.jorganchem.2005.04.055).

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