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Synthesis and Characterisation of a New $Cu(O_2CNAllyl_2)_2$ Carbamato Complex and an Unusual Polymeric Cu^I Complex $[Cu^I_4Cl_4(NHAllyl_2)_4]_n$: New Insights into Metal Carbamato Chemistry

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Transition-metal *N*,*N*-dialkylcarbamato complexes represent an interesting class of compounds that can be conveniently used as precursors for the controlled formation of inorganic compounds, typically oxides. They can also be used as convenient precursors for chemical grafting of metal oxides on oxide surfaces as well as for the synthesis of inorganic–organic hybrid materials. In this last case, the presence of double bonds on the complex would enable its covalent embedding into a polymer matrix through reaction with suitable monomers. To this aim, we addressed the synthesis of an allyl-functionalised copper carbamato complex. During the synthesis of the *N*,*N*-diallylcarbamato complex $Cu(O_2CNAllyl_2)_2$ (Cu**1**), the formation of the crystalline and unusual polymeric Cu^I complex $[Cu^I_4Cl_4(NHAllyl_2)_4]_n$ (Cu**2**) was observed. The new compound was characterised by X-ray single crystal diffraction and FTIR, ^1H and ^{13}C NMR spectroscopic analysis. In an attempt to investigate the redox mechanism and the equilibria leading to the formation of the observed unusual Cu^I polymeric complex, gas chromatography coupled with mass spectrometry (GC–MS) experiments were carried out, which allowed us to identify 3,4-dimethylpyrrole as the oxidation product of the reaction, leading to the reduction of Cu^{II} to Cu^I.

Introduction

The use of well-established and characterised classes of organometallic compounds and metal complexes as precursors for the preparation of nanostructured materials has been recognised as an effective strategy to master the bottom-up approach to nanosystems and to afford a fine modulation of their chemical composition and microstructure. In this field, several different classes of molecular precursors have been rediscovered and used for surface functionalisation,[1] preparation of nanocomposites[2] and highly controlled thin-film formation.[3] Among them, transition-metal *N*,*N*-dialkylcarbamato complexes[4] are an interesting class of compounds that have found increasing applications as precursors for inorganic compounds, typically oxides, and also for chemical grafting onto oxide surfaces.

The *carbamato* group is a monoanionic ligand with general formula $O_2CNR_2^{(-)}$ (R = H, alkyl, aryl). The "metal carbamates" are formulated as $[M(O_2CNR_2)_n]_m$, where n and m are the oxidation number of the central atom M and the nuclearity of the system, respectively. These compounds are thermodynamically unstable, and the ligand is a potential site of attack for electrophiles on nucleophilic oxygen and nitrogen atoms. For instance, attack by water can result in the formation of hydroxido-, oxido-, or carbonato groups. An excess amount of water causes the complete hydrolysis of the carbamato groups. In contrast, when the amount of water is carefully controlled, μ-oxido–carbamato clusters are usually obtained. A substantial contribution to the reaction driving force is the formation of carbon dioxide and the corresponding secondary amine.

Calderazzo et al.[4,5] synthesised a large variety of different *N*,*N*-dialkylcarbamato complexes based on different transition and lanthanide metals. By exploiting the described reactivity, metal carbamates have also been used as inorganic precursors for chemical grafting reactions onto silica matrices[4,6] and on silica–zirconia.[7] The functionalisation of these complexes with moieties that allow their use as precursors for further reaction, for example, functionalisation of surfaces, is currently an intensively investigated field.

It should be pointed out that, as far as copper *N*,*N*-dialkylcarbamato complexes are concerned, up to now only three structures are known and characterised by X-ray sin-

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gle crystal diffraction: the dinuclear species $Cu_2(O_2CNEt_2)_4(NHEt_2)_2$,[8] the planar mononuclear *trans*-$Cu(O_2CNBz_2)_2(NHBz_2)_2$[9] and the μ-oxido–octanuclear species $Cu_8O_2(O_2CN\mathit{i}Pr_2)_{12}$.[8]

In the present study, we prepared $Cu(O_2CNAllyl_2)_2$ (Cu**1**) which, to the best of our knowledge, has not yet been synthesised. During the synthesis of Cu**1**, formation of the unusual polymeric Cu^I complex $[Cu^I_4Cl_4(NHAllyl_2)_4]_n$ (Cu**2**) was observed as a byproduct, which was characterised by X-ray single crystal diffraction and FTIR, ^1H and ^{13}C NMR spectroscopic analysis.

Among the transition metals, copper compounds are intensively investigated for their interesting chemical and magnetic behaviour. In this context, the functionalisation of the copper complex with allyl groups is aimed to allow its use in further synthetic steps, for instance, its incorporation into an organic matrix through reaction with suitable monomers.

Results and Discussion

Synthesis and Characterisation of $Cu(O_2CNAllyl_2)_2$ (Cu1)

The formation of the desired compound Cu**1** by reaction of anhydrous $CuCl_2$ with a diallylamine solution saturated with CO_2 was expected to proceed as depicted in Scheme 1. This well-established $MCl_n/CO_2/R_2NH$ route, proposed by Calderazzo et al.[4,5] is based on the in situ preparation of the carbamato ligand by treating an excess amount of amine with CO_2 (first two equilibria). A simple ligand substitution, where the chloride ligands are substituted by the carbamato groups, leads to the metal carbamato. The formation of Cu**1** was confirmed by IR spectroscopy, elemental analysis and testing of its reactivity.

$$\begin{array}{rcl}
2\ NHAll_2 + 2\ CO_2 & \rightleftharpoons & 2\ All_2NC(O)OH \\
2\ NHAll_2 + 2\ All_2NC(O)OH & \rightleftharpoons & 2\ [All_2NH_2^+][O_2CNAll_2^-\ ] \\
CuCl_2 + 2\ [All_2NH_2^+][O_2CNAll_2^-\ ] & \longrightarrow & Cu(O_2CNAll_2)_2 + 2\ [All_2NH_2]Cl \\
\hline
CuCl_2 + 4\ NHAll_2 + 2\ CO_2 & \longrightarrow & Cu(O_2CNAll_2)_2 + 2\ [All_2NH_2]Cl
\end{array}$$

Scheme 1. In situ formation of diallylcarbamato ligand following the $MCl_n/CO_2/R_2NH$ route.

In the vibrational spectrum of the complex (Figure 1), the absence of the N–H vibration and the presence of the typical bands at 1602, 1577, 1395 cm^{-1} for the C(O)O group coordinated to Cu confirm the formation of the metal carbamato.

The stretching vibrations at 3079 cm^{-1}, ascribed to =C–H, and at 1649 cm^{-1}, ascribed to the C=C moiety of the diallylamine, were also detected. Furthermore, the blue heptane solution of Cu^{II} quickly reacts with water to give CO_2 and diallylamine, as evidenced by IR analysis of the vapours released by the reaction and collected in a cold trap.

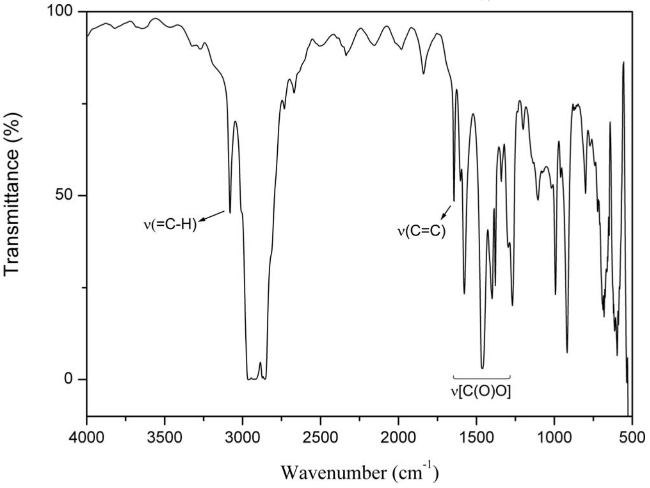


Figure 1. Infrared spectrum of Cu**1** recorded in nujol.

Synthesis and Characterisation of $[Cu^I_4Cl_4(NHAllyl_2)_4]_n$ (Cu2)

Further analysis revealed that the white precipitate obtained during the formation of Cu**1** is not the diallylammonium chloride salt as expected from Scheme 1. The coproduct was identified as the coordination polymer $[Cu^I_4Cl_4(NHAllyl_2)_4]_n$ (Cu**2**) and fully characterised by single-crystal X-ray diffractometry, FTIR and NMR spectroscopy and elemental analysis.

Description of the Structures

The crystal structure of Cu**2** (Figure 2) consists of 1D helical polymeric chain running perpendicular to the crystallographic 2_1 axis with a pitch of 11.16 Å. A similar type of helical polymer, containing the repeating tetranuclear unit $[Cu_4Cl_4(triallylamine)_4]_\infty$, has also been reported by Hakansson et al.[10] The only difference between the two polymers is the pitch of the helix, which differs by ca. 0.4 Å. In both cases, the helix winds perpendicular to a crystallographic twofold screw axis.

The immediate coordination sphere of the Cu ions consists of the allyl group, the two chlorine atoms and the nitrogen atom of the ligand. The coordination geometry of the Cu atoms can be described as a distorted tetrahedron, as can be judged from the values of the angles: Cl–Cu–Cl, Cl–Cu–N, C*–Cu–N: in the range 90–105, 99–108 and 122–125°, respectively (C* is the midpoint of the allylic double bond; Figure 3). Relevant bond lengths are listed in Table 1.

The asymmetric unit that corresponds to one turn of the helix contains two $Cu(\mu\text{-}Cl)_2Cu$ units in a bent conformation. The Cu–Cl bonds are significantly different with the shorter and longer bonds in the range 2.2949(9)–2.344(1) and 2.535(1)–2.696(1) Å, respectively.

The four diallylamine molecules in the asymmetric unit all act as bidentate ligands through the amine nitrogen atom and the C=C bonds of one of the allyl groups. Two

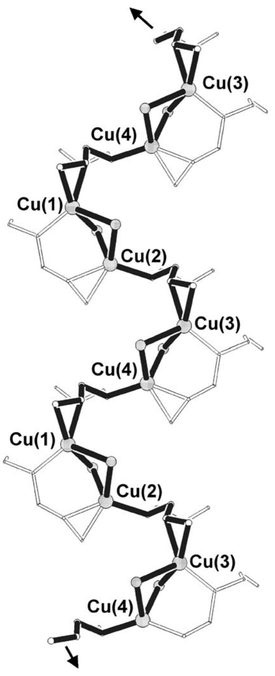


Figure 2. A view of the helical coordination polymer Cu**2**.

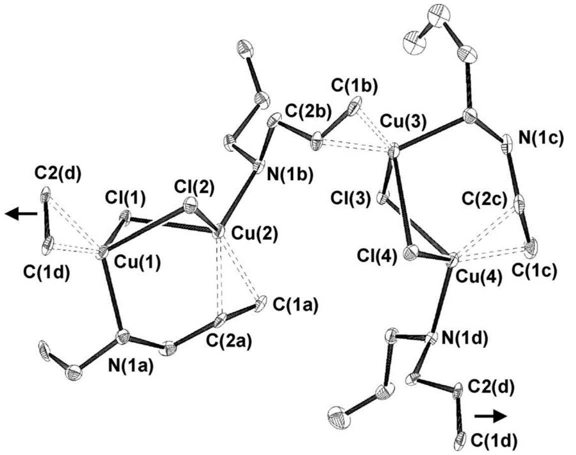


Figure 3. ORTEP drawing of asymmetric unit in compound Cu**2**, showing the crystallographic numbering. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths (Å) for Cu**2**.

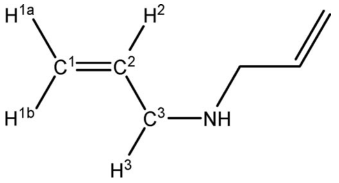
Cu(1)–N(1A)	2.045(3)	Cu(3)–N(1C)	2.046(3)
Cu(1)–Cl(1)	2.295(9)	Cu(3)–Cl(3)	2.311(1)
Cu(1)–Cl(2)	2.686(1)	Cu(3)–Cl(4)	2.697(1)
Cu(1)–C(1D)	2.047(3)	Cu(3)–C(1B)	2.051(4)
Cu(1)–C(2D)	2.095(4)	Cu(3)–C(2B)	2.094(4)
Cu(2)–N(1B)	2.045(4)	Cu(4)–N(1D)	2.053(3)
Cu(2)–Cl(1)	2.541(1)	Cu(4)–Cl(3)	2.536(1)
Cu(2)–Cl(2)	2.344(1)	Cu(4)–Cl(4)	2.321(1)
Cu(2)–C(1A)	2.062(4)	Cu(4)–C(1C)	2.057(4)
Cu(2)–C(2A)	2.103(4)	Cu(4)–C(2C)	2.099(4)

of the ligands form intracyclic bridges, whereas the other two bridge the neighbouring CuCl$_2$Cu units, thus forming a helix (the two nonbonding distances between the "··CuCl$_2$Cu··" units are 4.681(1) and 4.686(2) Å). Upon coordination to the Cu centre, a lengthening of the C=C bond is observed with distances in the range 1.36–1.37 Å.

Other examples of copper(I) chloride complexes with diallylamine are known, but the diallylamine acts as a tridentate ligand, thus yielding polymeric species that are structurally different.[11]

NMR Spectroscopic Analysis

The assignments are according to the labelling scheme reported in Scheme 2.



Scheme 2. Assignments labelling for diallylamine in Cu**2**.

The noticeable resonance narrowness (half linewidth ca. 0.4 Hz) observed in the ^{1}H NMR spectra of CD$_2$Cl$_2$ solutions of Cu**2** confirms the diamagnetic nature of the complex (and then the Cu^I oxidation state) for the metal atom, especially if a comparison is made with the large linewidth usually observed in the NMR spectra of Cu^{II} complexes.[12] At 298 K, the resonances of the allyl protons H^{1a}, H^{1b} and H^2 appear as the ABC part of an ABCX spin system at δ = 5.98, 5.42 and 5.26, respectively. The signal of the allyl CH$_2$ protons is observed as a moderately broad singlet at δ = 3.49 ppm. The ^{13}C resonances are observed at δ = 128.00 (C^2), 124.91 (C^1) and 48.02 (C^3). The marked upfield shift, $\Delta\delta$ [$\Delta\delta = \delta(\text{complex}) - \delta(\text{free})$], observed for resonances of C^1 and C^3 ($\Delta\delta$ = –8.77 and –3.74 ppm, respectively) together with the downfield shift observed for the resonance of C^2 ($\Delta\delta$ = +9.15 ppm) and the generally low downfield shift values observed for the all ^{1}H resonances confirm the coordination of the metal to the allyl π-electron system. At 298 K, the resonance of the NH proton is too broad to be observed; however, a pronounced narrowing together with a stepwise downfield shift is observed upon lowering the temperature to 183 K. In the same temperature interval, no substantial changes in the spectral line shape or chemical shift values were observed, and the maximum chemical shift difference between 183 and 298 K was 0.5 ppm for the ^{13}C nuclei and 0.1 ppm for the vinyl ^{1}H nuclei. Thus, we conclude that the different kinds of Cu-bonded allyl moieties observed in the crystal structure must exchange in solution at a rate sufficiently high to give rise, at least in the ^{1}H and ^{13}C NMR spectra, to a unique averaged set of signals.

FTIR Spectroscopic Analysis

The isolated compound was thoroughly characterised also by IR spectroscopy, and the collected spectrum is in agreement with the crystal structure. The spectrum of the crystalline compound is the same as the spectrum of the white precipitate isolated by filtration. Both solids show the same behaviour when exposed to air: they change colour quickly from white to green, thus evidencing oxidation of Cu^I to Cu^{II}.

As can be seen in Figure 4, the most interesting region is in the wavenumber range 1650–1550 cm^{-1} (see inset), where the C=C stretching of the allyl moieties occurs. Because, as evidenced by X-ray analysis, half of the double bonds are coordinated to Cu^I, a shift to lower wavenumber values could be expected. Actually, a shift of about 70 cm^{-1} was observed, and the band occurs at 1581 cm^{-1} (1643 cm^{-1} in the free diallylamine). This decrease may be due to the decrease in the double bond character of the allyl moiety as a consequence of the bond with Cu, and it is in agreement with both the bond length obtained by X-ray single crystal determination and with the values reported in literature for Cu^I complexes with vinyl monomers such as methacrylates, styrene and 1-octene.[13]

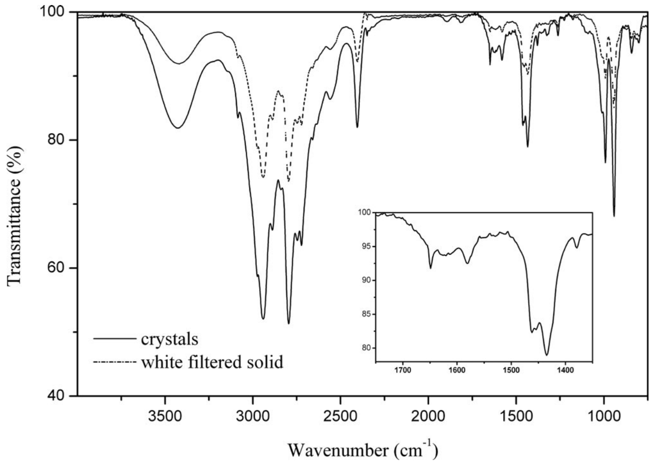


Figure 4. Infrared spectrum of Cu**2**; the inset shows the region 1750–1350 cm^{-1} magnified.

Hypothesis for the Mechanism of Formation of Cu2

Formation of compound Cu**2** seems to invalidate Scheme 1. No diallylammonium chloride was detected and a relevant significant part of Cu^{II} is reduced to Cu^I.

In an attempt to investigate the redox mechanism and the equilibria leading to the formation of the observed unusual Cu^I polymeric complex, gas chromatography coupled with mass spectrometry (GC–MS) experiments were carried out, which allowed us to identify the oxidation product of the reaction leading to the reduction of Cu^{II} to Cu^I. The formation of 3,4-dimethylpyrrole was observed, which was recognised as the product of diallylamine oxidation. Identification of the chromatographic peak at 4.4 min such as 3,4-dimethylpyrrole was confirmed by comparison of fragmentation patterns from experimental one (see Figure 5) to instrument library and reference spectra.[14]

This finding suggests that the reducing species is correlated to the diallylamine, which then undergoes cyclisation to give the detected pyrrole derivative. In the literature, the formation of pyrrole derivatives through ring-closing metathesis through in situ oxidative aromatisation of diallylamine in the presence of metal catalysts (typically ruthenium-based Grubbs catalyst) are reported.[15]

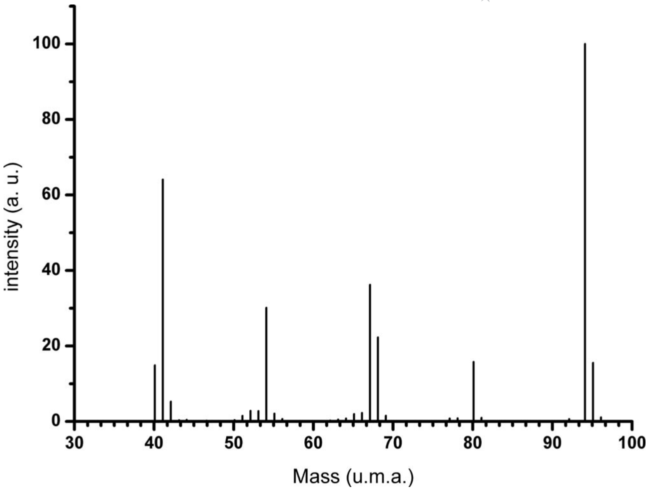


Figure 5. Fragmentation spectrum of peak at 4.4 min.

Moreover, it should be noted that the observed reaction requires the formation of diallylcarbamatodiallylammonium salt (second equilibrium, Scheme 1), as in the reaction of anhydrous $CuCl_2$ with diallylamine in heptane suspension and in the absence of CO_2, the formation of Cu**2** was not detected. Photoinitiated cyclopolymerisation of diallylammonium chloride and derivatives, through a radical intramolecular cyclisation and then a radical intermolecular propagation, were thoroughly described experimentally[16] and theoretically investigated.[17]

This cyclopolymerisability of the diallylammonium salt suggests that the formation of the diallylammonium chloride, as a byproduct in the synthesis of copper carbamato Cu**1**, is a key step towards polymeric complex Cu**2**. Compared with a simple radical polymerisation, this reaction seems to be driven from copper to a controlled intramolecular reaction, disclosing the possibility to develop a new method to prepare pyrroles substituted at the 3- and 4-carbon atoms. Hence, Scheme 1 does not satisfactorily describes the formation of compounds Cu**1** and Cu**2**, as further steps have to be included to explain the formation of the 3,4-dimethylpyrrole and the presence of Cu^I species. For the time being, on the basis of the experimental data available, we are not able to propose a well-advised reaction mechanism for the redox reaction.

In the literature, the described ring-closing metathesis is reported to occur at moderately high temperatures (60 °C) in the presence of ruthenium organometallic species[17] (Grubbs catalysts) or under special conditions (microwave irradiation[18]). Because the number of carbon atoms remains the same in the reactant and in the product, whereas in the reaction reported in the literature this decreases from six carbon atoms in the dilallylamine to four carbon atoms in the final pyrrole, we can exclude the metathesis mechanism.

In our case, none of the mentioned conditions were available; thus, it can be postulated that the reaction occurs through a slightly different mechanism, still likely to involve the formation of a radical, as reported in the cyclopolymerisation reactions of diallylammonium salts. However, the mechanism has to be investigated in more detail, and the study of the reactions in solution by time-resolved spectroscopic (IR, UV, Raman, NMR) methods will be the topic of a further contribution.

Conclusions

In this work, we described the synthesis and characterisation of the two allyl-functionalised copper complexes. In particular, during the synthesis of the *N*,*N*-diallylcarbamato complex $Cu(O_2CNAllyl_2)_2$ (Cu**1**), the formation of the crystalline and unusual polymeric Cu^I complex $[Cu^I_4Cl_4(NHAllyl_2)_4]_n$ (Cu**2**) was observed as a byproduct. The new compound was characterised by X-ray single-crystal diffraction and FTIR, ^1H NMR and ^{13}C NMR spectroscopic analysis. Although GC–MS experiments revealed 3,4-dimethylpyrrole to be the oxidation product of the reaction leading to the reduction of Cu^{II} to Cu^I, the mechanism leading to the formation of this novel compound remains unknown, although it likely involves the formation of a radical, as reported in the cyclopolymerisation reactions of diallylammonium salts.

Experimental Section

General Comments: All preparations were carried out in standard Schlenk tubes under an argon atmosphere, unless otherwise stated. Diallylamine ($NHAllyl_2$) and heptane (Aldrich) were distilled from the appropriate drying agent under an argon atmosphere. $CuCl_2·H_2O$ (99.8% purity, Aldrich), was dried before use by heating at 140 °C in vacuo for 3 d. CO_2 (99.99% purity, Air Liquide) and used as received. Elemental analyses were performed at the Microanalysis Laboratory of the Department of Chemistry of the University of Padova by using a Frisons EA 1108 instrument.

NMR Spectroscopy: ^1H and ^{13}C NMR spectra were obtained as CD_2Cl_2 solutions with a Bruker DMX-400 Avance spectrometer operating at 400.13 and 100.61 MHz, respectively. The chemical shift values (ppm) are given in δ units with reference to internal Me_4Si for both ^1H and ^{13}C. The assignments are according to the labelling scheme reported in Scheme 2. Suitable integral values for the proton spectra were obtained by a prescan delay of 10 s to ensure complete relaxation for all the resonances. The proton assignments were performed by standard chemical shift correlations as well as by 2D correlation spectroscopy (COSY), total correlation spectroscopy (TOCSY) and nuclear Overhauser enhancement spectroscopy (NOESY) experiments. The ^{13}C chemical shift values were obtained through 2D-heteronuclear correlation experiments, heteronuclear multiple quantum correlation (HMQC), with a bilinear rotation-decoupling (BIRD) sequence[19] and quadrature along F1 achieved by using the time-proportional receiver phase incrementation (TPPI) method[20] for the H-bonded carbon atoms and heteronuclear multiple bond correlation (HMBC)[21] for the other ^{13}C nuclei.

FTIR Spectroscopy: FTIR experiments were performed with a Nexus 870 FTIR (Nicolet), operating in the transmission range 400–4000 cm^{-1}, collecting 32 scans with a spectral resolution of 4 cm^{-1}. The measurements were recorded by dispersing the complexes in nujol for ***Cu*1** and in anhydrous KBr for Cu**2**.

GC-MS: The copper *N*,*N*-diallylcarbamato solution was analysed with an Agilent 6850 series gas chromatograph system equipped with a capillary column (HP-5, length 30 m, i.d. 0.25 mm, film 0.25 µm) coupled with an Agilent 5973Network mass selective detector. Helium carrier gas was set at a flow rate of 1.0 $mL\,min^{-1}$, and separation of components was obtained by following an oven temperature program: 40 °C for 5 min increased to 250 °C at a rate of 15 $°C\,min^{-1}$. The ionisation source, electron impact, was set at 230 °C with an electron energy of 70 eV and an emission of 35 µA. Aliquots of 1 µL were injected into the GC–MS system under split mode with a split ratio of 50:1 and injector set at 250 °C.

Crystallography: A crystal suitable for X-ray diffraction was mounted on a Bruker SMART diffractometer, equipped with a CCD detector, and cooled by using a cold nitrogen stream, to 120 K. The space group was determined from the systematic absences, whereas the cell constants were refined at the end of the data collection with the data reduction software SAINT.[22] Data were collected by using ω scans ($2< \theta_{max} <24°$). Experimental conditions, crystallographic and other relevant data are listed in the Supporting Information. The collected intensities were corrected for Lorentz and polarisation factors and empirically for absorption by using the SADABS program.[23] The structures were solved by direct methods and refined by full-matrix least-squares on F^2[24] by using anisotropic displacement parameters for all nondisordered atoms. One of four independent ligands was found to be disordered over two positions (with occupancies of 66 and 34% respectively) and refined isotropically. The hydrogen atoms bonded to nitrogen atoms were located from a difference Fourier map; their positions were refined, whereas the displacement parameters were constrained to be 1.2 times the equivalent B factors of the bonded atoms. The remaining hydrogen atoms, in their calculated positions, were refined by using a riding model [$B(H) = aB(C_{bonded})(Å^2)$, and $a = 1.2$]. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[25] All calculations were carried out by using the SHELX,[24] WINGX[26] and ORTEP[26] programs. CCDC-746597 (for Cu**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $Cu(O_2CNAllyl_2)_2$ (Cu1) and $[Cu^I_4Cl_4(NHAllyl_2)_4]_n$ (Cu2): A solution of $NHAllyl_2$ (7 mL, 56.8 mmol) in heptane (25 mL) was saturated with CO_2 at atmospheric pressure. $CuCl_2$ (1.50 g, 11.2 mmol) was then added, and the suspension was stirred for 24 h. An intense blue-violet solution and a colourless precipitate were obtained (4.80 g, 55% yield based on Cu mol). The white precipitate was identified by FTIR as Cu**2** ($Cu_4Cl_4C_{24}H_{44}N$). The filtered solution was allowed to stand for 3 h at room temperature. During this time, the formation of copper-containing colourless needle-like crystals (Cu**2**), suitable for a single-crystal X-ray analysis, was observed. This latter product was separated by filtration and washed once with heptane (30 mL). FTIR: $\tilde{\nu}$ = 3085 [m, ν_s(=C–H)], 2940 [s, $\nu_{as}(CH_3)$, $\nu_{as}(CH_2)$], 2796 [s, $\nu_s(CH_3)$, $\nu_s(CH_2)$], 1643 [m, ν_s(C=C)], 1378 [m, $\delta(CH_3)$], 1581 [m, ν_s(C=C) coordinated to Cu^+], 1442 [m, $\delta(CH_2)$] cm^{-1}. ^1H NMR (CD_2Cl_2, 298 K): δ = 5.88 (m, 1 H, H^{1a}), 5.42 (m, 1 H, H^{1b}), 5.26 (m, 1 H, H^2), 3.49 (s, 2 H, CH_2) ppm. The NH proton signal is too broad to be detected at 298 K; the values of δ = 8.0, 8.1, 9.5 and 9.6 ppm are observed at T = 273, 233, 203 and 183 K, respectively, due to the line narrowing upon decreasing the solution temperature. ^{13}C NMR (CD$_2$Cl$_2$, 298 K): δ = 128.00 (C^2), 124.91 (C^1), 48.02 (C^3) ppm.

Cu1 was obtained from the filtrate after removal of the solvent in vacuo (1.35 g, 33% yield based on Cu mol). FTIR (heptane): $\tilde{\nu}$ = 3079 [m, ν_s(=C–H)], 2960 [s, ν_{as}(CH$_3$), ν_{as}(CH$_2$)], 2860 [s, ν_s(CH$_3$), ν_s(CH$_2$)], 1460 [m, δ(CH$_2$)], 1643 [m, ν_s(C=C)], 1378 [m, δ(CH$_3$)], 1602, 1577, 1395 [C(O)O group] cm^{-1}. CuO$_4$C$_{16}$H$_{20}$N$_2$ (367.89) calcd. C 48.9, H 5.9, Cu 18.5, N 8.2; found C 47.4, H 6.6, Cu, 18.8; N 9.2.

Supporting Information (see also the footnote on the first page of this article): NMR spectra, crystallographic and refinement details for Cu**2**.

Acknowledgments

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