perexchange mechanism is operative through the bridging terephthalato dianion between two copper centers separated by a distance of 11.25 Å. Of the two possible superexchange pathways, σ- and π-exchanges, the π-pathway appears to provide the dominant antiferromagnetic interaction in **2** (t_{2g}^3-configurated Mn(IV) centers).

The results described in the present paper show that tris(dimethylglyoximato)metalate(II) dianions are capable of coordinating as a bridging ligand to give rise to various kinds of trinuclear complexes. These materials are ideally suited for the study of intramolecular magnetic-exchange interactions.

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Supplementary Material Available: Listings of atomic coordinates and isotropic thermal parameters (Table SI), bond lengths and angles (Tables SII and SIII), anisotropic thermal parameters (Table SIV), and hydrogen atom parameters (Table SV) (9 pages); a listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

Lehrstuhl für Anorganische Chemie I
Ruhr-Universität
Postfach 102148
D-4630 Bochum, Germany
Phalguni Chaudhuri*
Manuela Winter
Frank Birkelbach

Institut für Physikalische Chemie
Technische Hochschule
D-6100 Darmstadt, Germany
Peter Fleischhauer
Wolfgang Haase

Allgemeine Anorganische und Analytische Chemie
Universität-Gesamthochschule
D-4790 Paderborn, Germany
Ulrich Flörke
Hans-Jürgen Haupt

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Synthesis and Characterization of (β-Diketonato)copper(I) Alkyne Complexes: Structural Characterization of (Hexafluoroacetylacetonato)(diphenylacetylene)copper(I)

The synthesis of copper compounds for the chemical vapor deposition (CVD) of copper is receiving much research attention. Among the requirements of copper compounds for this purpose are high volatility, to achieve high deposition rates, and the presence of a facile decomposition mechanism, to facilitate deposition of pure copper films.[1] In the past it has proven difficult to satisfy all these requirements simultaneously. Copper(II) bis(β-diketonates) exhibit high vapor pressures,[2] but their thermal decomposition results in formation of pure films only at a substrate temperature of 350 °C.[3] At higher temperatures significant carbon and oxygen contamination has been observed, while, below this temperature, no deposition is observed. On the other hand, copper(I) compounds such as copper(I) *tert*-butoxide[4] and cyclopentadienylcopper(I) Lewis base compounds[5-7] have lower volatility but have led to the deposition of purer copper films over a lower and wider temperature range. More recently the deposition of copper films from copper(I) β-diketonate compounds, (β-diketonate)CuL_n, where L = $\mathrm{PMe_3}$, vinyltrimethylsilane, and 1,5-cyclooctadiene (1,5-COD) and n = 1, have been described.[1,8-13] These species exhibit interesting structural chemistry. The monophosphine adducts such as (β-diketonate)Cu($\mathrm{PMe_3}$) are monomeric with an approximately trigonal-planar copper(I) coordination environment,[11] while (β-diketonate)Cu(1,5-COD) has been described as "3 + 1" coordinate with an asymmetrically bound 1,5-COD ligand.[12] Their volatility is close to that of the copper(II) bis(β-diketonate) compounds, and a thermally induced disproportionation mechanism (eq 1) has resulted in the deposition

$$2(\beta\text{-diketonate})\mathrm{Cu^{I}L}_n \rightarrow \mathrm{Cu^{0}} + \mathrm{Cu^{II}}(\beta\text{-diketonate})_2 + 2n\mathrm{L} \qquad (1)$$

of pure copper films.[1,8-13] In addition, selective deposition of copper from these species onto various substrates has been observed as a function of the nature of the substrate, the deposition temperature, and the nature of the β-diketonate ligand.[1,9] At present, there is no fundamental understanding of the factors which affect selective deposition of copper from such precursors, although a number of studies have addressed the reactions of β-diketones with metal surfaces.[14] The first step in such a study is to device a series of compounds in which the steric and electronic demands of both the β-diketonate and Lewis base ligands can be subtly varied in a systematic fashion and which deposit pure copper via thermally induced disproportionation. Here we report the synthesis spectroscopic and structural characterization of a new series of compounds, (β-diketonato)copper(I) alkyne, which are volatile, monomeric, and capable of systematic substitution and undergo thermally induced disproportionation reactions to produce pure copper films.

The (β-diketonato)copper(I) alkyne complexes, where alkyne = bis(trimethylsilyl)acetylene (BTMSA), diphenylacetylene (DPA), and 2-butyne and where β-diketonate = hexafluoroacetylacetonate (hfac), were prepared by the addition of Na(β-diketonate) to a mixture of CuCl and the corresponding alkyne in diethyl ether solution according to the reaction shown in eq 2.[15] Similar methods have been used to prepare cyclo-

$$\mathrm{CuCl} + \text{excess alkyne} + \mathrm{Na(hfac)} \rightarrow (\mathrm{hfac})\mathrm{Cu(alkyne)} + \mathrm{NaCl} \qquad (2)$$

pentadienylcopper(I) alkyne complexes, and dimeric (alkyne)-copper(I) chloride complexes have previously been isolated.[16] The

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[15] A typical experimental procedure is presented here together with spectroscopic and analytical data for three representative compounds. A solution containing an excess (about 1.5 equiv) of alkyne in 50 mL of $\mathrm{Et_2O}$ was transferred to a cold (0° C) slurry solution of CuCl in 50 mL of $\mathrm{Et_2O}$, and the solution mixture was stirred for 30 min to make the alkyne adduct of CuCl. Addition of a solution of Na(β-diketonate) (1.2 equiv) in $\mathrm{Et_2O}$ into the reaction flask resulted in immediate formation of a yellow solution, which was continuously stirred for 5 h. Removal of volatile species in vacuo gave a pale yellow solid. The pure product (β-diketonate)Cu(alkyne) was obtained by extraction and recrystallization with pentane in approximately 30–60% yield depending on the alkyne. The yields and properties are summarized as follows: (hfac)Cu(2-butyne), 33% yield, pale yellow solid, sublimed at room temperature; (hfac)Cu(BTMSA), 62% yield, yellow solid, sublimed at room temperature; (hfac)Cu(DPA), 35% yield, pale yellow solid, sublimes >70 °C. Spectroscopic characterization data are available as supplementary material.

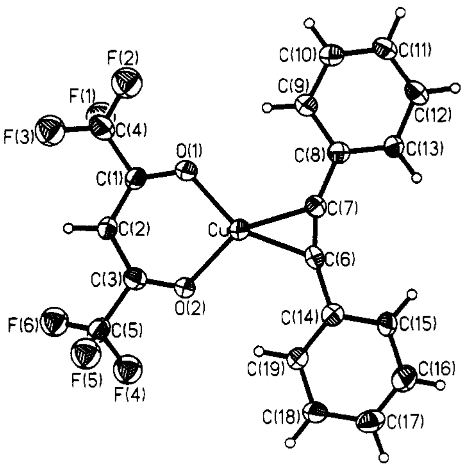

Figure 1. ORTEP plot (50% probability ellipsoids) of the molecular structure of (hfac)Cu(diphenylacetylene), showing the monomeric nature of the compound and the trigonal-planar geometry around copper(I). Relevant bond lengths (Å) include Cu–O(1) = 1.969 (6), Cu–O(2) = 1.954 (6), Cu–C(6) = 1.959 (8), Cu–C(7) = 1.956 (8), and C(6)–C(7) = 1.246 (13), and relevant bond angles (deg) include O(1)–Cu–O(2) = 93.8 (2), C(6)–Cu–C(7) = 37.1 (4), Cu–C(6)–C(14) = 128.2 (6), Cu–C(7)–C(8) = 129.8 (7), C(6)–C(7)–C(8) = 158.4 (8), and C(7)–C(6)–C(14) = 160.4 (8).

title compounds were characterized by NMR, IR, and mass spectroscopies and by elemental analyses.[15] In toluene-d_8 solution, (hfac)Cu(2-butyne) undergoes exchange with 1 equiv of added hfacH. This exchange is slow on the ^{1}H NMR time scale at room temperature as determined by observation of two distinct, but exchange-broadened, β-diketone and β-diketonate methine protons. This exchange process has an activation barrier of 14.4 (5) kcal/mol (T_c = 306 K). Addition of 2-butyne, 1 and 3 equiv, to (hfac)Cu(2-butyne) resulted in rapid exchange between free and coordinated alkyne at room temperature as determined by ^{1}H NMR spectroscopy. The 2-butyne methyl peak exhibited substantial broadening at −90 °C although the low-temperature-limiting spectrum could not be reached. From these observations, it would appear that the activation barrier for exchange between free and coordinated alkyne is likely to be lower than that for hfacH/hfac exchange.

These species are very volatile and can be sublimed at room temperature onto a cold finger at −78 °C. CVD experiments have been carried out in a cold-wall reactor, and the deposition of pure copper films has been demonstrated. For (hfac)Cu(2-butyne), an activation energy of 23 (2) kcal/mol for CVD of copper was observed in the surface reaction limited regime over the substrate temperature range 150–200 °C at 50 mTorr.[17] Interestingly, this value is quite different from that reported for (hfac)Cu(vinyltrimethylsilane).[13]

As a result of the high volatility of the title compounds, it seems likely that they exhibit a low degree of oligomerization. Mass spectral data for the title compounds are consistent with a monomeric molecular formula.[15] However, while many examples of copper(I) alkyne complexes have been characterized, few are monomeric.[16,18–22,26] To investigate this aspect further, we have structurally characterized one example of the title compounds, (hfac)Cu(diphenylacetylene), in the solid state by single-crystal X-ray diffraction.[23] An ORTEP plot is shown in Figure 1, emphasizing the coordination geometry about copper. The compound (hfac)Cu(diphenylacetylene) is monomeric in the solid state, and the copper center possesses an approximately trigonal-planar coordination environment where the alkyne ligand is considered to occupy one coordination site. The dihedral angle between the planes defined by *O*–*C*(CF_3)–*C*(H)–*C*(CF_3)–*O*–*Cu* and (Ph)*C*–*C*(Ph)–*Cu* is 2.2°. The reason for the coplanarity of the two ligands is not clear at this stage. The copper–oxygen distances, the O–Cu–O bite angle of 93.8°, and other angles and distances of the hfac ligand are similar to those observed for other examples of structurally characterized copper(I) hfac complexes.[8–12,24] The coordinated alkyne ligand exhibits a short C–C bond distance (1.246 (13) Å), similar to that of free alkynes (1.20 Å),[25] a large C–C–Ph deformation angle of 158°, and long Cu–C bond distances. All these features are consistent with poor back-donation from copper to the alkyne ligand.

Further experiments are in progress to determine the influence of the alkyne and β-diketonate ligand substituents on solution exchange processes and the mechanism of thermally induced disproportionation.

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Supplementary Material Available: Tables of crystal data, data collection parameters, and solution and refinement data, bond lengths and angles, non-hydrogen and hydrogen atom coordinates, and anisotropic displacement coefficients, figures showing ORTEP structures, and text giving spectroscopic characterization data for (hfac)Cu(2-butyne), (hfac)Cu(BTMSA), and (hfac)Cu(DPA) (13 pages); a table of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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(23) Crystals of (hfac)Cu(diphenylacetylene) were grown from toluene solution at −30 °C. The crystal used for the X-ray study was 0.138 × 0.322 × 0.644 mm and was sealed in a glass capillary under a nitrogen atmosphere. Crystal data: empirical formula $C_{19}H_{11}CuF_6O_2$, triclinic space group $P\bar{1}$, a = 8.619 (3) Å, b = 10.230 (3) Å, c = 11.720 (3) Å, α = 66.63 (2)°, β = 81.04 (2)°, γ = 81.44 (2)°, and Z = 2. A total of 3286 independant reflections were measured in the range $2 < 2\theta < 50°$ on a Siemens R3m/V diffractometer at 293 K using a graphite-monochromated Mo Kα radiation, λ = 0.71073 Å, with $+/-2\theta$ scan mode, $2\theta_{max}$ = 50°. The structure was solved by direct methods using SHELXTL PLUS and was refined by full-matrix least-squares techniques. Initially, all non-hydrogen atoms were refined anisotropically and the *F*'s were disordered. In the next cycle, each fluorine was refined over two sites. Then all non-hydrogen atoms were refined anisotropically except for the disordered *F*'s, which had fixed occupancies. Hydrogen atoms were refined using a riding model with fixed isotropic U set to 1.25U(equiv) of the parent atom. The final agreement factors were R = 0.096 and R_w = 0.147 for 2374 reflections having $F > 3.0\sigma(F)$.

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(27) Department of Chemistry.

(28) Department of Chemical Engineering.

Departments of Chemistry and
Chemical Engineering and Center
for Micro-Engineered Ceramics
University of New Mexico
Albuquerque, New Mexico 87131

K.-M. Chi[27]
H. K. Shin[27]
M. J. Hampden-Smith*[,27]
T. T. Kodas*[,28]
E. N. Duesler[27]

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