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A Linear, Monomeric Copper(I) Acetate Derivative, $[Cu(phen)_2]_2[Cu(O_2CCH_3)_2]\cdot(O_2CCH_3)_2H$. An Effective Catalyst for the Decarboxylation of Carboxylic Acids

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The complex $[Cu(phen)_2]_2[Cu(O_2CCH_3)_2]\cdot(O_2CCH_3)_2H$, derived from the reaction of CuO_2CCH_3 with 1,10-phenanthroline in dichloromethane, has been characterized by X-ray crystallography at −80 °C. The crystals are monoclinic, space group *C*2/*c* with unit cell dimensions $a = 22.503$ (11) Å, $b = 14.066$ (6) Å, $c = 16.829$ (11) Å, $\beta = 112.44$ (4)°, $V = 4923$ (5) Å^3, $Z = 4$, and $R_F = 6.52\%$. The compound is shown to have the above stoichiometry, containing a unique, linear, mononuclear copper(I) acetate anion. The monodentate coordination of the acetates results in Cu2–O1 and Cu2–O1a distances (2.808 Å) which are significantly greater than those observed for the corresponding bonding interactions between Cu2–O2 and Cu2–O2a (1.821 (8) Å). The title complex was observed to be an extremely effective catalyst or catalyst precursor for the homogeneous decarboxylation of the carboxylic acids cyanoacetic and 9-fluorenecarboxylic acids.

Introduction

Derivatives of copper(I) have received extensive attention as decarboxylating reagents.[1] Specifically, Toussaint and co-workers have demonstrated that copper(I) oxide or copper(I) chloride acts catalytically to decarboxylate malonic and arylacetic acids in acetonitrile.[2-4] More pertinent to our efforts in carbon dioxide chemistry to define the mechanistic aspects of carboxylation/decarboxylation processes catalyzed by transition-metal complexes is the implication that some copper(I) carboxylates readily decarboxylate in the presence of amine and phosphine ligands (eq 1).[5-7]

$$\mathrm{NCCH_2CO_2Cu(P\text{-}}n\mathrm{\text{-}Bu_3)_{\mathit{x}} \rightleftharpoons NCCH_2Cu(P\text{-}}n\mathrm{\text{-}Bu_3)_{\mathit{x}} + CO_2} \qquad (1)$$

For these investigations fully characterized complexes are a prerequisite to conducting the studies. Therefore, we have undertaken the synthesis and structural characterization of species derived from the reaction of Cu^IO_2CR with chelating phosphine or amine ligands, where a copper(I) carboxylate complex containing the respective phosphine or amine ligand would be anticipated. We report herein the preparation and X-ray structural characterization of the resultant complex from the reaction of $Cu(O_2CCH_3)$ and 1,10-phenanthroline, $[Cu(phen)_2]_2[Cu(O_2CCH_3)_2]\cdot(O_2CCH_3)_2H$ (**1**), in which $[Cu(O_2CCH_3)_2]^-$ exists as a linear mononuclear structure between two $[Cu(phen)_2]^+$ units. A preliminary account of the use of **1** as a catalyst for the homogeneous decarboxylation of cyanoacetic and 9-fluorenecarboxylic acids is also presented.

Complex **1** was synthesized in an attempt to isolate the related species $(phen)CuO_2CCH_3$, which would presumably consist of a monomer with a bidentate acetate, similar to the structurally characterized $(PPh_3)_2CuO_2CCH_3$.[8] The synthesis of $(phen)CuO_2CCH_3$ was reported in 1975, with no definitive structural evidence.[9] A dimeric structure with bridging acetates (Scheme I, **2**) was suggested on the basis of the previously proposed structure of the 2,9-dimethyl-1,10-phenanthroline analog, $[Cu(O_2CCH_3)(2,9\text{-}Me_2phen)]$.[10] Furthermore, solution conductivity studies on this derivative indicated the presence of ions in solution. Hence, an equilibrium as shown in Scheme I was advocated.

Although **1** does not have the arrangement of ligands around the copper center originally suggested,[9,10] it does support the existence of a complex similar to that of **3** as in Scheme I. More importantly, complex **1** contains the first structurally defined example of a linear monomeric copper(I) acetate. The only other form of copper(I) acetate that has been structurally characterized is a planar polymeric chain.[11,12]

Experimental Section

Methods and Materials. All manipulations were carried out either in an argon drybox or on a double-manifold Schlenk vacuum line, using freshly distilled solvents. Reagent grade hexane was purified by distillation under nitrogen from sodium benzophenone ketyl. Dichloromethane was refluxed under nitrogen over phosphorous pentoxide and distilled prior to use. 1,10-Phenanthroline was purchased from Aldrich Chemical Co. CuO_2CCH_3 was prepared by the reduction of $Cu(O_2CCH_3)_2$ by copper foil with acetic acid/acetic anhydride in acetonitrile according to published procedures.[13] Infrared spectra were recorded on a Mattson 6021 spectrometer with DTGS and MCT detectors. GC–MS analysis was conducted on a Hewlett Packard 5890 Series II gas chromatograph coupled with a Hewlett Packard mass selective detector (30 m, 0.25 mm i.d. capillary column).

Synthesis of $[Cu(phen)_2]_2[Cu(O_2CCH_3)_2]\cdot(O_2CCH_3)_2H$ (1). A suspension of copper(I) acetate (0.67 g, 5.45 mmol) in CH_2Cl_2 (15 mL) was added to a solution of anhydrous 1,10-phenanthroline (0.98 g, 5.44 mmol) in CH_2Cl_2 (15 mL). The resulting red-brown solution was cooled to −78 °C while stirring under N_2 for 1 h. The solution was then filtered through Celite, and the solvent volume was reduced in vacuo to approximately 15 mL. A 30-mL volume of hexane was then added to precipitate a dark

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(1) Shepard, A. F.; Winslow, N. R.; Johnson, J. R. *J. Am. Chem. Soc.* **1930**, *52*, 2083. Leake, P. H. *Chem. Rev.* **1956**, *56*, 27 and references cited therein. Fieser, L. F.; Fieser, M. *Organic Chemistry*, 3rd ed.; D. C. Heath and Co.: Boston, MA, 1956; p 549. Cairncross, A.; Roland, J. R.; Henderson, R. M.; Sheppard, W. A. *J. Am. Chem. Soc.* **1970**, *92*, 3187.

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(8) Drew, M. G. B.; Othman, A. H. B. *Acta Crystallogr.* **1975**, 2695.

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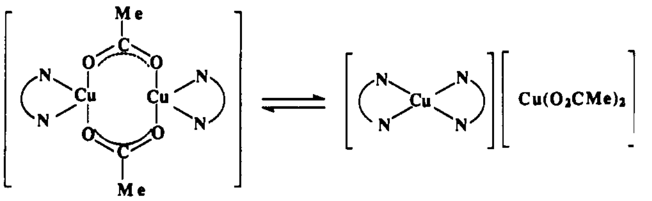
Scheme I



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3

Table I. Crystallographic Data for $C_{56}H_{45}N_8O_8Cu_3$

empirical formula	$C_{56}H_{45}N_8O_8Cu_3$	V, Å^3	4923 (5)
fw	1148.6	Z	4
space group	monoclinic, $C2/c$	D_{calcd}, g/cm^3	1.550
a, Å	22.503 (11)	μ (Mo Kα), mm^{-1}	1.351
b, Å	14.066 (6)	wavelength, Å	0.710 73
c, Å	16.829 (11)	R_F, %^{a}	6.52
β, deg	112.44 (4)	R_{wF}, %^{a}	5.60

^{a} $R_F = \sum|F_o - F_c|/\sum F_o$ and $R_{wF} = \{[\sum w(F_o - F_c)^2]/[\sum w(F_o)^2]\}^{1/2}$.

red-brown solid. The solid was filtered off and dried in vacuo. The powder is air sensitive, oxidizing to a green-blue solid upon extended exposure to air. Dark red crystals suitable for X-ray structure analysis were obtained by slow diffusion of diethyl ether into a concentrated dichloromethane solution of the compound at -20 °C. Anal. Calcd for (phen)CuO$_2$CCH$_3$ ($C_{14}H_{11}N_2O_2Cu$): C, 55.53; H, 3.66. Calcd for [Cu(phen)$_2$]$_2$[Cu(O$_2$CCH$_3$)$_2$]·(O$_2$CCH$_3$)$_2$H($C_{56}H_{45}N_8O_8Cu_3$): C, 58.56; H, 3.95. Found: C, 54.69; H, 3.58. IR (CH$_2$Cl$_2$): 1589 (s), 1387 (s) cm^{-1}.

Catalysis with 1. The title complex was found to homogeneously catalyze the decarboxylation of cyanoacetic and 9-fluorenecarboxylic acids. In a typical catalytic run, complex 1 (0.0087 mmol) and the carboxylic acid (0.177 mmol) were placed in separate 50-mL flasks and dissolved in 6.5 mL DME, respectively. Both solutions were equilibrated to the desired reaction temperature by employing a thermostated temperature bath (±0.1 °C). The carboxylic acid solution was then transferred to the flask containing the solution of complex 1 via cannula. The decarboxylation reaction was monitored to completion by observing the disappearance of the carboxylate stretch at 1750 cm^{-1} (cyanoacetic acid) and 1739 cm^{-1} (9-fluorenecarboxylic acid) in the infrared region. Quantitative analysis of the decarboxylated products (acetonitrile and fluorene) was conducted by GC-MS. The rate for the decarboxylation was determined from the slope of the line resulting from a plot of absorbance (1750 cm^{-1}) versus time (minutes). Activation parameters were determined by varying the temperature over the range 25–40 °C.

X-ray Crystallographic Study of 1. Crystal data and details of data collection are given in Table I. A dark red parallelepiped (0.24 mm × 0.30 mm × 0.42 mm) was mounted on a glass fiber with epoxy cement at room temperature and cooled to 193 K in a N$_2$ cold stream (Nicolet LT-2). Preliminary examination and data collection were performed on a Nicolet R3m/V X-ray diffractometer (oriented graphite monochromator; Mo Kα λ = 0.710 73 Å radiation). Cell parameters were calculated from the least-squares fitting of the setting angles for 20 reflections. ω scans for several intense reflections indicated acceptable crystal quality. Data were collected for $4.0° \leq 2\theta \leq 50.0°$ (θ–2θ scans, $-26 \leq h \leq 24$, $0 \leq k \leq 16$, $0 \leq l \leq 19$) at 193 K. Scan range, on ω, for the data collection was 1.20° plus Kα separation, with a variable scan rate of 2.00–14.65° min^{-1}. Three control reflections, collected every 97 reflections, showed no significant trends. Background measurements were obtained by stationary crystal and stationary counter techniques at the beginning and end of each scan for 0.50 of the total scan time.

Lorentz and polarization corrections were applied to 4742 reflections. A semiempirical absorption correction was applied (ellipsoid approximation; $\mu \times r = 0.10$; $T_{max} = 0.9127$, $T_{min} = 0.6951$). A total of 2049 unique reflections, with $|I| \geq 2.0\sigma(I)$, were used in further calculations. The structure was solved by Patterson Synthesis [SHELX, SHELXTL-PLUS program package, Sheldrick (1988)]. Full-matrix least-squares anisotropic refinement for all non-Hydrogen atoms [SHELXLS, SHELXTL-PLUS program package, Sheldrick (1988); number of least-squares parameters = 340; quantity minimized $\sum w(F_o - F_c)^2$; $w^{-1} = \sigma^2 F = gF^2$, $g = 0.000\ 10$] yielded $R = 0.065$, $R_w = 0.056$, and $S = 1.83$ at convergence (largest Δ/σ = 0.0021; mean Δ/σ = 0.0002; largest positive peak in the final Fourier difference map = 0.88 e Å^3; largest negative peak in the final Fourier difference map = −0.60 e Å^3). Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08 Å^3, except for the acidic hydrogen bound to O3 which was located in a difference Fourier map. The thermal parameter for the acidic hydrogen was fixed at 0.05 Å^3 and its coordinates were not refined. Neutral-atom scattering factors and anomalous scattering correction terms were taken from the *International Tables for X-ray Crystallography*.

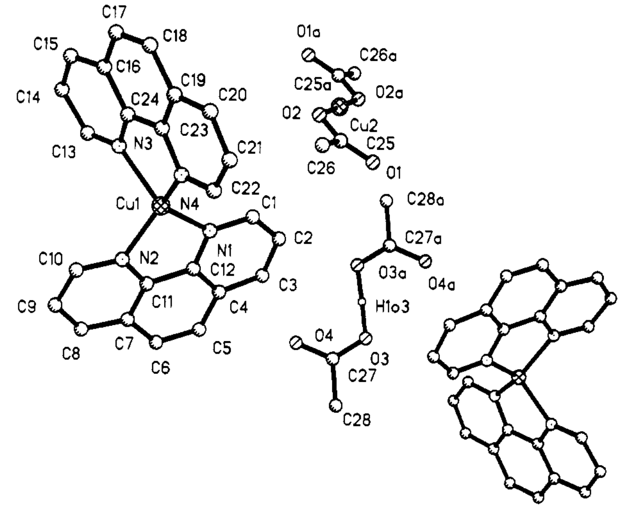

Figure 1. Ball-and-stick representation of crystals of 1.

The Cu2 atom was located on an inversion center, with the site occupation constrained to one-half. The site occupation for atom H103 was fixed to 50% occupation due to disorder. The model, corrected for variable site occupation, was used to refine the structure to convergence.

Results

Synthesis and Characterization of 1. The reaction of copper(I) acetate with 1,10-phenanthroline in dichloromethane, subsequent to solvent reduction and addition of hexane, has provided a red-brown powder in 85% yield. The powder is air sensitive, turning green-blue upon extended exposure to air. The infrared spectrum of the red-brown powder displayed two $\nu(CO_2)$ frequencies in dichloromethane at 1589 (s) and 1387 (s) cm^{-1}. Hence, the difference between the asymmetric $\nu(CO_2)$ and symmetric $\nu(CO)_2$ (Δ = 202 cm^{-1}) is greater than the difference observed in the free acetate ion (Δ = 164 cm^{-1}). This supports a unidentate mode of coordination for the acetate to the copper center.[14] These observations are similar to Nujol mull infrared data reported by Edwards and Richards for the correspondingly prepared complexes from copper (I) acetate and 1,10-phenanthroline ($\nu_{asym}(CO_2)$ 1574 and $\nu_{sym}(CO_2)$ 1380 cm^{-1}) or 2,2′-dipyridyl.[9]

Structural Characterization of 1. In order to define precisely the molecular structure of the complex, it has been subjected to a single-crystal X-ray diffraction investigation at −80 °C. Dark red crystals suitable for X-ray structure analysis were crystallized from dichloromethane/diethyl ether at −20 °C. Three crystalline forms were observed, with the red crystals constituting approximately 75% of the crystals formed. The other crystalline material appears to be copper(II) acetate (blue) and copper(I) acetate (white). A ball-and-stick view of the molecule is depicted in Figure 1, whereas, in Figure 2, a view of the copper(I) acetate anion is shown. The final atomic coordinates for all non-hydrogen atoms are provided in Table II. Bond lengths and bond angles are listed in Tables III and IV, respectively.

Catalytic Decarboxylation of Carboxylic Acids Using 1. Complex 1 was found to be an effective catalyst or catalyst precursor for the homogeneous decarboxylation of cyanoacetic acid and 9-fluorenecarboxylic acid (eqs 2 and 3). Figure 3

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(14) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986; pp 231–233.

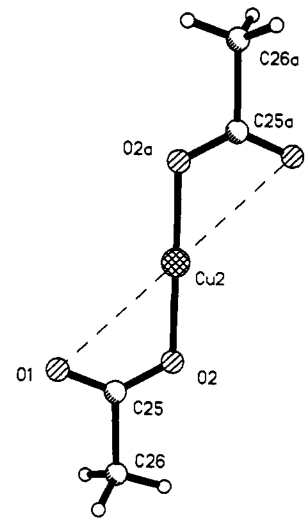


Figure 2. Ball-and-stick representation of the $Cu(O_2CCH_3)_2^-$ anion. The distal oxygen–copper distance (2.808 Å) is indicated by the dashed line.

Table II. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for $C_{56}H_{45}N_8O_8Cu_3$

	x	*y*	*z*	*U*(eq)[a,b]
Cu1	4673 (1)	2795 (1)	3845 (1)	49 (1)
Cu2	2500	2500	0	74 (1)
O1	1899 (4)	2807 (6)	1164 (5)	93 (4)
O2	2643 (3)	2011 (5)	1059 (5)	77 (4)
O3	2425 (3)	8080 (5)	465 (5)	72 (3)
O4	3438 (3)	7847 (5)	1362 (4)	61 (3)
N1	4193 (3)	3864 (5)	3015 (5)	39 (3)
N2	5289 (3)	3867 (5)	4408 (5)	37 (3)
N3	5213 (3)	1709 (5)	3684 (5)	40 (4)
N4	4191 (3)	1710 (5)	4122 (5)	38 (4)
C1	3642 (4)	3851 (7)	2332 (6)	50 (5)
C2	3376 (4)	4665 (7)	1856 (6)	54 (5)
C3	3679 (5)	5524 (7)	2098 (6)	52 (5)
C4	4259 (4)	5574 (6)	2832 (6)	42 (4)
C5	4611 (5)	6428 (6)	3143 (7)	49 (5)
C6	5187 (5)	6431 (6)	3811 (7)	54 (5)
C7	5453 (5)	5559 (6)	4255 (6)	40 (4)
C8	6054 (5)	5497 (7)	4913 (6)	54 (5)
C9	6264 (5)	4645 (7)	5302 (6)	50 (5)
C10	5876 (5)	3850 (6)	5035 (6)	55 (5)
C11	5092 (4)	4710 (6)	4013 (6)	33 (4)
C12	4498 (4)	4719 (6)	3267 (6)	36 (4)
C13	5742 (5)	1700 (7)	3523 (6)	46 (5)
C14	6051 (5)	866 (8)	3425 (6)	53 (5)
C15	5778 (5)	5 (7)	3471 (6)	45 (5)
C16	5224 (4)	−27 (7)	3649 (6)	34 (4)
C17	4920 (5)	−892 (7)	3709 (6)	45 (5)
C18	4393 (5)	−881 (6)	3887 (6)	43 (5)
C19	4112 (5)	−12 (6)	4041 (6)	35 (4)
C20	3573 (5)	24 (7)	4266 (6)	44 (5)
C21	3374 (5)	890 (8)	4413 (6)	50 (5)
C22	3690 (4)	1723 (7)	4342 (6)	42 (4)
C23	4406 (4)	850 (6)	3966 (5)	34 (4)
C24	4954 (4)	859 (6)	3768 (5)	33 (4)
C25	2309 (4)	2273 (8)	1392 (7)	39 (5)
C26	2433 (6)	1778 (7)	2282 (8)	89 (7)
C27	2892 (6)	8231 (6)	1161 (8)	51 (6)
C28	2827 (4)	8942 (7)	1770 (6)	67 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Estimated standard deviations are given in parentheses.

illustrates infrared spectra taken during the decarboxylation reaction of cyanoacetic acid, about 30 turnovers at 30 °C. The infrared band corresponding to the carboxylic acid function at 1750 cm⁻¹ was employed in measuring the rate of decarboxylation. Production of carbon dioxide was monitored by the band at 2338 cm⁻¹; concomitantly, the weak $\nu(C{\equiv}N)$ vibration for CH_3CN was noted at 2251 cm⁻¹. Quantitative assessment of

Table III. Selected Bond Lengths (Å)[a] for $C_{56}H_{45}N_8O_8Cu_3$

Cu1–N1	2.056 (7)	Cu1–N2	2.022 (7)
Cu1–N3	2.033 (8)	Cu1–N4	2.027 (8)
Cu2–O2	1.821 (8)	O2–C25	1.16 (1)
O1–C25	1.14 (1)	O4–C27	1.26 (1)
O3–C27	1.26 (1)		

[a] Estimated standard deviations are given in parentheses.

Table IV. Selected Bond Angles (deg)[a] for $C_{56}H_{45}N_8O_8Cu_3$

N1–Cu1–N2	82.0 (3)	N1–Cu1–N3	130.1 (3)
N2–Cu1–N3	106.5 (3)	N1–Cu1–N4	121.2 (3)
N2–Cu1–N4	141.7 (3)	N3–Cu1–N4	82.2 (3)
Cu1–N1–C1	130.7 (6)	Cu2–O2–C25	116.7 (7)
Cu1–N2–C10	130.4 (6)	Cu1–N1–C12	111.2 (5)
Cu1–N2–C11	112.8 (5)	Cu1–N2–C10	130.4 (6)
Cu1–N3–C13	131.9 (6)	Cu1–N3–C24	110.2 (7)
Cu1–N4–C23	111.3 (7)	Cu1–N4–C22	130.3 (6)
Cu2–C25–C26	153.4 (8)	O1–C25–O2	130.0 (1)
O2–C25–C26	114.0 (9)	O1–C25–C26	116.0 (1)
O3–C27–C28	119.0 (1)	O3–C27–O4	124.0 (1)
O4–C27–C28	116.6 (9)		

[a] Estimated standard deviations are given in parentheses.

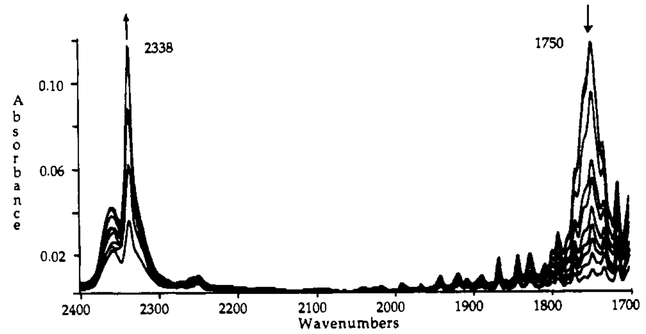
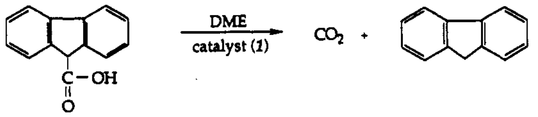


Figure 3. IR spectra taken over 24 min demonstrating the disappearance of $NCCH_2CO_2H$ ($\nu(CO_2)$ 1750 cm⁻¹) and appearance of CO_2 ($\nu(CO_2)$ 2338 cm⁻¹).

$$NCCH_2CO_2H \xrightarrow[\text{catalyst (1)}]{\text{DME}} CO_2 + CH_3CN \tag{2}$$



(3)

acetonitrile was established by GC–MS. Figure 4 depicts the kinetic plots for the decarboxylation of cyanoacetic acid in the presence of complex **1**. Similar catalytic activity was noted for an in situ prepared catalyst, i.e., a one-to-one mixture of copper(I) acetate and 1,10-phenanthroline. The robust nature of the catalyst is further illustrated in Figure 4, as well as the inhibiting effect of one of the products, CH_3CN. As expected, the substrate $NCCH_2CO_2H$ shows an inhibiting effect on the decarboxylation process due to nitrogen binding of the Cu(I) active site;[15] hence, it was necessary to pulse in the substrate in intervals of 90 equivalents in order to accomplish the 1500 turnovers indicated in Figure 4 in an efficient manner. Temperature-dependent rate data are provided in Table V, along with the derived activation parameter. Comparable rate data were determined for the decarboxylation of 9-fluorenecarboxylic acid, where at 30 °C cyanoacetic acid is decarboxylated in the presence of **1** 1.7 times faster than 9-fluorenecarboxylic acid.

Discussion

We have isolated in crystalline form and structurally characterized the air-sensitive product resulting from the reaction of

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(15) Darensbourg, D. J.; Longridge, E. M.; Atnip, E. V.; Reibenspies, J. H. *Inorg. Chem.* **1991**, *30*, 357.

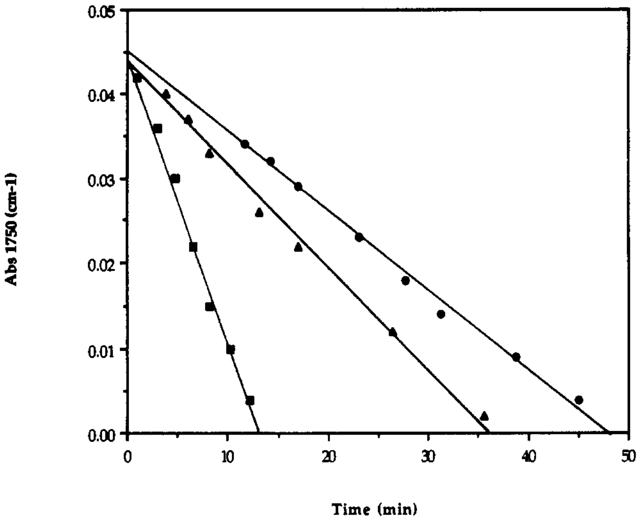


Figure 4. Plot of absorbance (1750 cm^{-1}) vs time (minutes) for three catalytic runs decarboxylating 20 equiv of $NCCH_2CO_2H$ at 30 °C in DME: (■) typical run; (▲) after first decarboxylation of 1500 equiv of $NCCH_2CO_2H$; (●) with 1500 equiv of CH_3CN added.

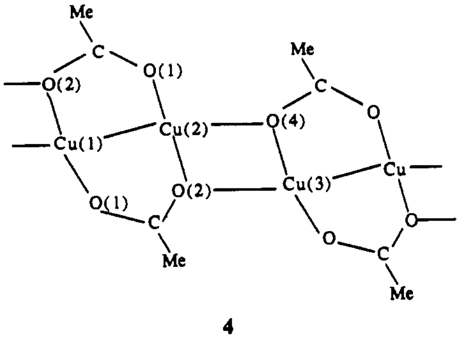
Table V. Temperature-Dependent Rate Data for the Decarboxylation of $NCCH_2CO_2H$ in DME[a,b]

temp, K	rate, 10^{-3} M s^{-1}	temp, K	rate, 10^{-3} M s^{-1}
298	0.615	308	1.59
303	1.04	313	2.76

[a] Concentration of complex **1** = 6.7×10^{-4} M; concentration of $NCCH_2CO_2H = 1.4 \times 10^{-2}$ M. [b] Energy of activation determined: 18.9 kcal/mol.

copper(I) acetate and 1,10-phenanthroline in dichloromethane. This complex possesses the same chemical and physical properties of the complex previously isolated,[9] but uncharacterized, from the slow reaction of a suspension of copper(I) acetate in benzene with 1,10-phenanthroline. Furthermore, infrared spectral data obtained in the diagnostic $\nu(CO_2)$ region indicate the solution and solid-state structures to be the same.

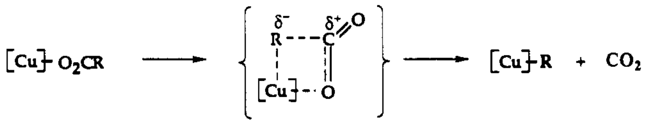
The molecular structure of **1** consists of discrete ions with the coordination geometry at copper being both four- and two-coordinate. In the linear copper(I) acetate anion only half of the ion is found in the asymmetric unit with copper(I) located on the inversion center. The remaining molecule is generated by the inherent symmetry (Figure 2). Copper(I) is two-coordinate with each acetate bound in a unidentate fashion to the metal. Consequently, the Cu2–O1 and Cu2–O1a distance (2.808 Å) is significantly greater than the corresponding bonding interaction observed between Cu2–O2 and Cu2–O2a (1.821 (8) Å). Additionally, these bond lengths are shorter than the analogous Cu–O bond distances (average Cu–O = 1.91 Å) of the polymeric chain form of $Cu(O_2CCH_3)$, species **4**.[11,12]



4

A hydrogen-bonded acetate pair is contained as well in the structure. Only one acetate group is found in the asymmetric unit; it lies close to a crystallographic inversion center and is hydrogen-bonded to its inverted image by a hydrogen atom located approximately midway between the pair of O3 atoms. The O3···O3a distance (2.37 (1) Å) is comparable to distances reported for hydrogen-bonded acetate pairs in molybdenum[16a] and cobalt[16b] complexes (2.44 (1) and 2.40 (4) Å, respectively). The acetate group has no affiliation with the copper atom and is similar to other hydrogen-bonded acetate pairs that have been characterized for a variety of metal species.[16] The N–Cu–N bond angles are acute with N1–Cu1–N2 and N3–Cu1–N4 equal to 82.0 (3) and 82.2 (3)°, respectively. The range of Cu–N distances observed is 2.022 (7)–2.056 (8) Å and is consistent with several examples of Cu^IL_2 complexes[17] and the previously characterized $Cu(phen)_2^+$ cation reported in the literature.[18]

Pertinent to the use of copper(I) derivatives as decarboxylating reagents, complex **1** was found to be an efficient catalyst or catalyst precursor for the decarboxylation of select carboxylic acids. In particular, cyanoacetic and 9-fluorenecarboxylic acids readily afford CO_2 and the corresponding hydrocarbons, CH_3CN and fluorene, in the presence of **1**. Furthermore, from a practical standpoint it is noteworthy that it is not necessary to isolate the very air-sensitive complex **1** prior to carrying out catalytic decarboxylation reactions. That is, an in situ prepared catalyst from the commercially available copper(I) acetate and 1,10-phenanthroline is equally effective. Since the carboxylates of both of the acids thus far investigated provide stabilized carbanions upon decarboxylation, at this stage of our studies a heterolytic decarboxylation mechanism is likely, proceeding via a transition state with carbonium character (**5**).[19]



5

Control experiments reveal that $Cu(phen)_2^+$ is not an effective catalyst for these decarboxylation processes. In addition the rate of the reaction was found to be sensitive to the nature of the bidentate nitrogen donor, e.g., 2,2′-dipyridyl provides a more active catalyst. Hence, it is likely that there are rapid ligand redistribution processes occurring[20] in the presence of carboxylic acids which yield active Cu(I) catalysts containing both the bidentate nitrogen donor ligand and the carboxylate functionality. A suggested possible species is of the type mentioned in the introduction, $(N{\sim}N)CuO_2CR$, which readily decarboxylates for electron-withdrawing R substituents. Consistent with this proposal, we find the structurally characterized $(Ph_3P)_2CuO_2CR$ derivative to decarboxylate both carboxylic acids examined here, albeit at a somewhat reduced rate.

Presently, studies are underway in our laboratories to define more precisely the mechanistic aspects of this important decarboxylation process, as well as the range of carboxylic acids and the influence of the ancillary ligands.

Concluding Remarks

To our knowledge, the determination of the molecular structure of complex **1** (Figure 1) represents the first structural charac-

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terization of a linear, monomeric copper(I) carboxylate. Nevertheless it is likely, on the basis of the similarity of their infrared spectra in the $\nu(CO_2)$ region, that other previously reported complexes derived from the reaction of copper(I) acetate with bidentate nitrogen donors have similar structures.[9,10] Finally, these copper(I) derivatives are extremely active and robust catalysts for the decarboxylation of select carboxylic acids.

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Supplementary Material Available: Tables of anisotropic displacement parameters, hydrogen atom coordinates and isotropic displacement parameters, and complete bond lengths and bond angles and an ORTEP drawing and a unit cell packing diagram for $[Cu(phen)_2]_2[Cu(O_2CCH_3)_2]\cdot(O_2CCH_3)_2H$ (6 pages). Ordering information is given on any current masthead page.