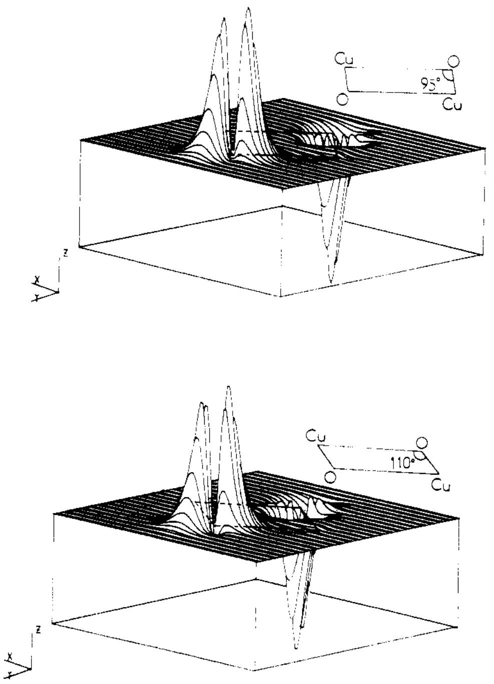

Figure 3. Overlap density $\rho^{(xy,x^2-y^2)}$ for two values of the bridging angle. $\rho^{(xy,x^2-y^2)}$ exhibits two positive lobes around one of the bridges and two negative lobes around the other bridge, of which the extrema are weakly sensitive to the variations of θ.

pointed out that D^{ex} in a bibridged copper(II) dimer was related to J, in the $Cu^{II}VO^{II}$ complex with the same bridging ligands.[7–15]

To approach in a more quantitative way the influence of θ on the magnitude of the zero field splitting within the triplet state, we explicitly calculated $j^{(xy,x^2-y^2,xy,x^2-y^2)}$ from ${\phi_A}^{(xy)}$ and ${\phi_B}^{(x^2-y^2)}$ as obtained from the EH method.[16] The result is shown in Figure 4. $j^{(xy,x^2-y^2,xy,x^2-y^2)}$ has a maximum for θ close to 95°. On the same Figure 4 we plotted the variation of $j^{(xy,xy,xy,xy)}$ which is proportional to the ferromagnetic component of the S–T splitting. Since D^{ex} is expected to depend only on $j^{(xy,x^2-y^2,xy,x^2-y^2)}$, its angular behavior should be parallel to that of the latter. In fact, the experimental data[7–9] available so far show that the D^{ex} dependence vs. the Cu···Cu separation d is not so dramatic for small values of d but becomes more marked as d increases. Since the variation of d is parallel to that of θ, it seems that the present results are in fairly good agreement with the experimental data.

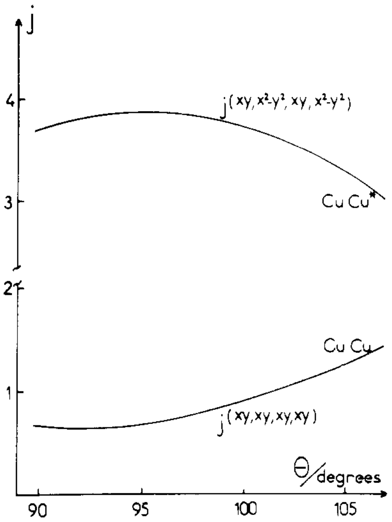

Figure 4. Variations of $j^{(xy,xy,xy,xy)}$ and $j^{(xy,x^2-y^2,xy,x^2-y^2)}$ vs. the bridging angle. The EH method exaggerates the delocalization of the metal orbitals toward the nearest neighbors, so that the unit of j should be considered as arbitrary.

To conclude this work, we want again to emphasize that the topological approach we propose cannot replace an ab initio calculation with large basis set and extended CI of the type of those that recently appeared in the field of the coupled systems.[17–19] However, these calculations only dealt with the isotropic interaction characterized by J. This work is to our knowledge one of the first attempts to interpret the variation of the anisotropic interaction in a series of related compounds. Moreover, a sophisticated calculation, even when it reproduces the experimental data in a satisfying way, has the form of a black box. We think that our approach owing to its conceptual simplicity may be more appealing for the experimentalists looking to understand the EPR spectra of coupled complexes.

Acknowledgment. This work is supported by NATO Research Grant No. 0271/83.

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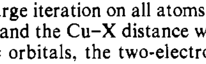
(16) For each θ value, the ${\phi_A}^{(xy)}$ and ${\phi_B}^{(x^2-y^2)}$ orbitals were determined as in ref 11 on the model monomeric fragment



The calculations were performed according to the Forticon 8 version of the EH method with charge iteration on all atoms. The parametrization is the same as in ref 11, and the Cu–X distance was taken equal to 1.92 Å. From the magnetic orbitals, the two-electron-exchange integrals were explicitly calculated from: "Table of Molecular Integrals"; Kotani, M., Amemiya, A., Ishiguro, E., Eds; Mazuren: Tokyo, 1963.

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Contribution from the Department of Chemistry,
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Magnetic Properties and Crystal Structure of a Linear-Chain Copper(II) Compound with Bridging Acetate and Oxamidate Ligands

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The magnetic properties of linear-chain compounds have been actively investigated,[2–4] particular attention being devoted to alternating chains. In order to synthesize complexes that have these structural (and hopefully magnetic) properties, several strategies are possible. One is that of reacting metal ions with two different potentially bridging ligands to yield structures of type **1**.

L′–M–L–M–L′–M–

1

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(1) (a) ISSECC, CNR. (b) University of Florence. (c) University of Modena.

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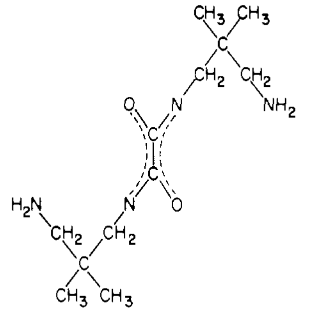
0020-1669/86/1325-1063$01.50/0

Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement

formula	$C_8H_{15}N_2O_3Cu$
fw	250.7
space group	$P2_1/n$
a, Å	6.633 (5)
b, Å	21.146 (7)
c, Å	7.698 (4)
β, deg	100.1 (2)
V, A^3	1062.93
Z	4
D_{calcd}, g cm^{-3}	1.57
cryst size, mm	0.10 × 0.23 × 0.20
μ(Mo Kα), cm^{-1}	19.6
transmission factor	0.82–0.69
scan type	ω–2θ
scan width ($\Delta(2\theta)$), deg	$1.0 + 0.3 \tan\theta$
scan speed, deg min^{-1}	3.0
2θ limits, deg	5–52
data collecn range	$\pm h,k,l$
no. of unique data $F_o^2 > 3.0\sigma(F_o^2)$	1493
R_{merg}[a]	0.025
no. of variables	127
R	0.033
R_w	0.037

[a] $R_{merg} = [\sum N_i \sum_{j=1}^{N_i} (\bar{F}_j - F_j)^2 / \sum (N_i - 1) \sum_{j=1}^{N_i} (F_j)^2]^{1/2}$, where N_i is the number of equivalent reflections in a given set, F_i is one member of the set, and $\bar{F}_j$ is the mean.

In the course of a study of the mechanism of exchange between copper ions bridged by oxalate, oxamate, and oxamidate ligands[5,6] we obtained a mononuclear copper intermediate with *N,N'*-bis(2-(aminomethyl)-2-methylpropyl)oxamidate (**2**, amoxa), which,



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by reaction with copper acetate hydrate, yielded a polynuclear complex of formula $Cu_2(amoxa)(CH_3COO)_2$, in which the copper ions are bridged by both oxamidate and acetate ligands. We wish to report here the X-ray crystal structure of $Cu_2(amoxa)(CH_3COO)_2$ together with a description of its magnetic properties.

Experimental Section

Ligand and Complex Preparation. The ligand *N,N'*-bis(2-(aminomethyl)-2-methylpropyl)oxamidate, amoxa, was obtained by reacting 0.1 mol of diethyl oxalate in 14 mL of absolute ethanol with 0.2 mol of neopentanediamine in 25 mL of the same solvent at 0 °C. The mixture was refluxed for 30 min. A 0.1-mol amount of copper sulfate hydrate and 0.2 mol of NaOH in a minimum amount of water were added sequentially to the above solution. The resulting solution was refluxed on a water bath for 60 min. After filtration and evaporation fuchsin-colored crystals were collected, which gave a satisfactory analysis for Cu(amoxa). Anal. Calcd for $CuC_{12}N_4H_{24}O_2$: N, 17.51; C, 45.06; H, 7.60. Found: N, 17.38; C, 45.12; H, 7.56. The compound was characterized only through the IR spectra, which suggested an N_4 coordination around the copper ion.

Equimolar amounts of copper acetate hydrate and Cu(amoxa) were mixed in a minimum amount of water. After a few days blue crystals were collected, which gave a satisfactory analysis for $Cu_2(amoxa)(CH_3COO)_2$. Anal. Calcd for $Cu_2C_{16}N_4H_{30}O_6$: N, 11.17; C, 38.32; H, 6.03. Found: N, 11.14; C, 38.12; H, 6.03.

Table II. Positional Parameters for Non-Hydrogen Atoms of $Cu_2(amoxa)(CH_2COO)_2$[a,b]

atom	x	y	z
Cu	5914 (1)	5300	−3071 (1)
N_1	6599 (5)	6081 (1)	−4328 (4)
N_2	5355 (4)	5729 (1)	−978 (4)
O_1	2990 (4)	5219 (1)	−5190 (3)
O_2	5439 (4)	4514 (1)	−1759 (3)
O_3	1010 (4)	5971 (1)	−4417 (4)
C_1	4969 (5)	5343 (2)	245 (5)
C_2	5869 (6)	6689 (2)	−3740 (5)
C_3	6480 (6)	6812 (2)	−1756 (5)
C_4	5981 (8)	7506 (2)	−1421 (6)
C_5	8780 (7)	6697 (2)	−1163 (6)
C_6	5222 (7)	6410 (2)	−677 (5)
C_7	1420 (5)	5590 (2)	−5508 (5)
C_8	71 (6)	5534 (3)	−7303 (6)

[a] Standard deviations in the last significant digits greater than 5×10^{-6} are in parentheses. [b] Coordinates multiplied by 10^4.

Table III. Selected Bond Distances (Å) and Angles (deg) of $Cu_2(amoxa)(CH_3COO)_2$

Cu–N_1	2.01 (1)	Cu–N_2	1.94 (2)
Cu–O_1	2.31 (7)	Cu–O_2	1.998 (8)
Cu–O_1'	1.97 (2)	N_2–C_1	1.30 (1)
N_2–C_6	1.464 (5)	C_2–C_3	1.53 (2)
C_3–C_4	1.536 (6)	C_3–C_5	1.53 (2)
C_3–C_6	1.53 (2)	C_2–N_1	1.473 (9)
C_7–C_8	1.51 (4)	C_7–O_1	1.29 (2)
C_7–O_3	1.23 (1)		
N_1–Cu–N_2	96.2 (1)	N_1–Cu–O_1	87.3 (1)
N_1–Cu–O_2	176.0 (3)	N_1–Cu–O_1'	89.4 (1)
N_2–Cu–O_1	111.2 (1)	N_2–Cu–O_2	84.2 (1)
N_2–Cu–O_1'	166.8 (1)	O_1–Cu–O_2	96.2 (1)
O_1–Cu–O_1'	80.9 (1)	O_2–Cu–O_1'	89.4 (1)
Cu–N_2–C_1	113.3 (2)	C_1–N_2–C_6	118.4 (3)
Cu–N_2–C_6	128.1 (3)	N_2–C_6–C_3	114.0 (3)
C_2–C_3–C_4	107.6 (3)	C_2–C_3–C_5	110.2 (3)
C_2–C_3–C_6	111.8 (3)	C_4–C_3–C_5	109.5 (3)
N_1–C_2–C_3	114.3 (3)	Cu–N_1–C_2	117.1 (2)
Cu–O_1–C_7	129.6 (3)	O_1–C_7–O_3	122.4 (2)
O_1–C_7–C_8	116.9 (3)	O_3–C_7–C_8	120.6 (3)
Cu–O_1–Cu'	99.0 (1)		

X-ray Structure Determination. Diffraction data for $Cu_2(amoxa)(CH_3COO)_2$ were collected at room temperature on a Philips PW 1100 automated diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The crystals were shaped as irregular prisms. Details on crystal data, intensity collection, and refinement are reported in Table I. Lattice constants were obtained by a least-squares fit of 22 reflections in the range $8° \leq 2\theta \leq 20°$. Stationary background counts were taken at each end of the scan for a time equal to half the scan time. The intensities of three standard reflections measured every 90 min showed no systematic variation. The principal computer programs used in the crystallographic calculations are listed in Ref 7. Data were processed with use of a p value of 0.03 in the calculation of $\sigma(I)$'s.[8] Corrections for Lorentz and polarization effects,[7a] as well as for absorption,[7b] were applied. The space group $P2_1/n$ was identified by the systematic absences $h0l$ ($h + l = 2n$) and $0k0$ ($k = 2n$). Direct methods (MULTAN) were used to solve the structure, by locating the copper atoms. Carbon, nitrogen, and oxygen atoms were located by Fourier and difference Fourier synthesis. The structure was then refined by full-matrix least-squares techniques and difference Fourier maps. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w = 0.96/(\sigma^2(F_o) + 10^{-3}F_o^2)$. All the atoms were assigned anisotropic thermal parameters. Hydrogen atoms were introduced in calculated positions (C–H = 0.95

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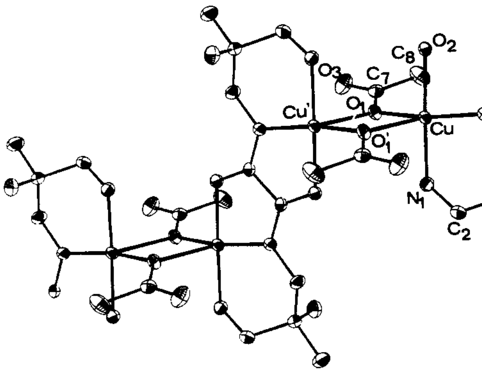

Figure 1. ORTEP view of the asymmetric unit and of three symmetry-related units of $Cu_2(amoxa)(CH_3COO)_2$.

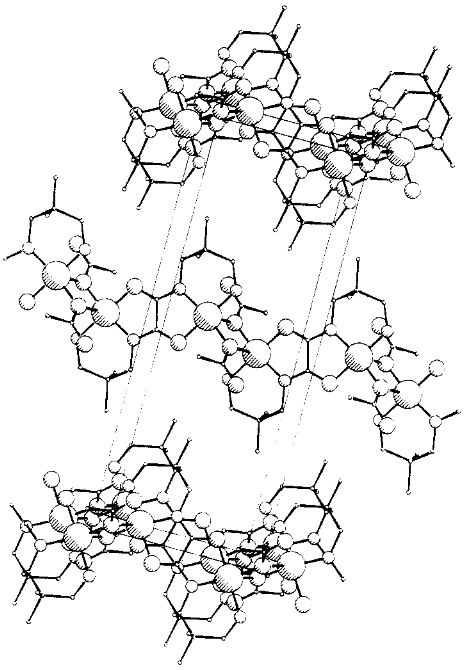

Figure 2. A schematic view of the unit cell of $Cu_2(amoxa)(CH_3COO)_2$ along the *a* axis.

Å; N-H = 0.95 Å) and their contributions were included in F_c. Each hydrogen atom was assigned an isotropic temperature factor ca. 20% higher than the isotropic factor of the corresponding C or N atom. The scattering factors for the neutral atoms were taken from ref 9, and the anomalous dispersion correction term for Cu was from ref 10. The final values of the discrepancy indices, defined as $R = \sum(|F_o| - |F_c|)^2/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$, were $R = 0.033$ and $R_w = 0.037$. The highest peak in the last difference Fourier map calculated at the end of the refinement was less than 0.6 e $Å^{-3}$.

The final atomic positional parameters for non-hydrogen atoms are listed in Table II. Thermal parameters and positional parameters of the hydrogen atoms are listed in Tables SI and SII, respectively.[11] A listing of the observed and calculated structure factors is available.

Results and Discussion

Description of the Structure. The crystal structure of $Cu_2(amoxa)(CH_3COO)_2$ consists of zigzag chains of copper atoms bridged by amoxa and acetate groups. Selected bond distances and angles are shown in Table III. A view of the asymmetric unit and of three symmetry-related units is shown in Figure 1. In Figure 2 a schematic view of the unit cell is shown.

The coordination environment around the copper ions, which are related by an inversion center lying on the amoxa ligand, can be described as a distorted square pyramid. The equatorial plane is defined by the oxygen (O_2) and nitrogen (N_2) of the amide, the amine nitrogen (N_1), and an oxygen atom of an acetate group (O_1'). The best least-squares plane for these atoms has its normal with direction cosines in the *abc** reference frame 0.8724, −0.0047, 0.4888. The mean displacement of the four atoms from this plane is 0.066 (2) Å. The N_2–Cu–O_1' and N_1–Cu–O_2 angles are 166.8 (1) and 176.0 (3)°, respectively. The axial coordination site is occupied by another oxygen atom (O_1) of an acetate group which is equatorially bound to the neighboring copper atom (Cu′). Each copper atom is displaced out of the equatorial plane toward the axial oxygen by 0.13 Å. The acetate group is, therefore, acting as a monodentate ligand, bridging two different copper atoms. A similar coordination behavior of the acetate ion was reported previously for a copper dimer[12,13] and for a polynuclear molybdenum complex.[14] The two oxygen–copper bonds are markedly different from each other, the equatorial being 1.998 (8) Å and the axial 2.31 (7) Å. As compared to the previously reported[13] $[Cu(L)(CH_3COO)_2]\cdot H_2O\cdot C_2H_5OH$ (LH = *N*-(1,1-dimethyl-2-hydroxyethyl)salicylaldimine), the present compound has slightly longer equatorial (1.998 (8) vs. 1.952 (1) Å) and slightly shorter axial (2.31 (7) vs. 2.446 (2) Å) bond distances. The copper–copper distance for the ions separated by the amoxa ligand is 5.24 (5) Å while that for the ions bridged by acetate is 3.261 (1) Å.

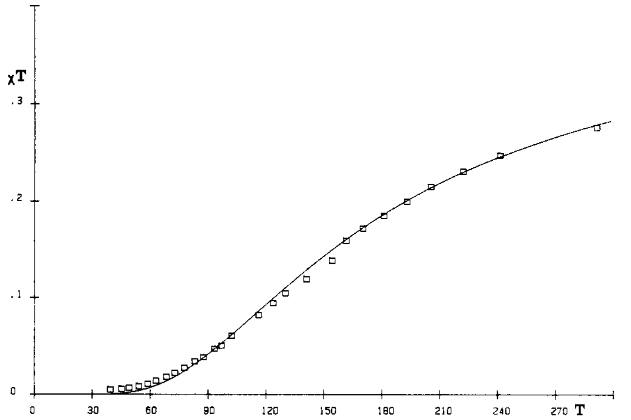

Figure 3. Temperature dependence of the magnetic susceptibilty of $Cu_2(amoxa)(CH_3COO)_2$ in the range 30–300 K. The curve was calculated as described in the text. χT is expressed in cm^{-1} mol K and *T* in K.

Magnetic and EPR Data. The temperature dependence of the magnetic susceptibility per copper atom of $Cu_2(amoxa)(CH_3COO)_2$ in the form χT vs. *T* is shown in Figure 3. The smooth decrease of χT with *T* in the range 300–30 K is indicative that an antiferromagnetic interaction larger than 300 K is operative between the copper atoms. As one looks at the structure of the complex, two different exchange pathways are possible, one through the amoxa and the other through the acetate ligand. Oxamidate ligands are known to be very effective in transmitting the exchange interaction between copper ions when both the sets of oxygen and nitrogen donors occupy equatorial coordination sites in the metal ion environment.[5,15] The comparison with similar dinuclear complexes suggests that for the observed geometry the interaction through the amoxa ligand can be larger than 400 cm^{-1}. On the other hand, the acetate bridge is such that the magnetic orbitals on the two neighboring copper ions are parallel to each other on two different planes. Under these conditions the magnetic coupling between the two ions is expected to be very small.[16,17]

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Indeed, a very weak ferromagnetic coupling of -1.26 cm^{-1} was observed for $[Cu(L)(CH_3COO)_2]\cdot H_2O\cdot H_5OH$, which shows a similar geometry. Therefore, although the crystal structure suggests an alternating linear chain, it should be possible to interpret the data with a simple Bleaney–Bowers equation,[18] because the above considerations suggest that magneically the compound must behave as a chain of weakly interacting dimers. The curve calculated under this assumption fits satisfactorily the experimental points as shown in Figure 3, the systematic deviation of the curve at low temperature being probably due to the presence of a small amount of a paramagnetic impurity. The relative parameters are $g = 2.145$ (4) and $J = 431.7$ (6) cm^{-1} with the interaction Hamiltonian defined as $\mathcal{H} = J\mathbf{S}_1\mathbf{S}_2$. We attempted to fit the magnetic data in the hypothesis of an alternating chain, using the Duffy and Barr approach[19] in the development carried out by Hatfield et al.[20] The calculated values of the alternation parameter, α, were found very close to zero, as expected, and the fit did not improve significantly. Therefore, the magnetic data do not allow us to decide whether the description of the compound as an alternating chain is correct.

The EPR spectra recorded at room temperature show an asymmetric feature at $g = 2.08$ and no signal at half-field. This was checked by measuring the spectra at the maximum receiver gain setting of our instruments. The spectra do not change on lowering the temperature: they simply decrease in intensity but never show any hyperfine splitting.

The absence of any resolved hyperfine splitting, and of the $\Delta M = \pm 2$ transition, is indicative of a fast averaging of the triplet excitons; i.e., the spectra are a proof of the fact that the αJ value is much larger than either the fine or hyperfine splitting, whichever is the largest. Since in dimers bridged by oxamidate ligands D has been found[6] to be of the order of 0.01 cm^{-1}, even $\alpha J = 0.1$ cm^{-1} should be enough to yield exchange-narrowed spectra. Therefore, the EPR description of the magnetic properties of the present compound is that of an alternating chain. These results confirm that magnetic susceptibility and EPR spectra should be used together in order to take advantage of their complementarity.[21]

Registry No. **2**, 100113-54-0; Cu(amoxa), 100113-55-1; Cu_2(amoxa)$(CH_3COO)_2$, 100113-57-3; diethyl oxalate, 95-92-1; neopentanediamine, 7328-91-8.

Supplementary Material Available: X-ray crystallographic data for Cu_2(amoxa)$(CH_3COO)_2$ including tables of anisotropic temperature factors for non-hydrogen atoms, positional parameters for hydrogen atoms, and observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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Photochemistry of Copper(II)–Poly(acrylic acid) Complexes: Photogeneration and Photolysis of an Alkyl–Copper Intermediate

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The UV irradiation of complexes of copper(II) with carboxylic acids populate charge-transfer states that decay to an oxidized ligand and copper(I).[1-5] This behavior can be illustrated with $CuOCOCH_3^+$, which under 254-nm photolysis decomposes according to eq 1.[1,2] Recombination of the reactive products

$$CuOCOCH_3^+ \underset{\leftsquigarrow}{\xrightarrow{h\nu}} CT \longrightarrow [Cu^+, CH_3CO_2\cdot] \qquad (1)$$

following the rapid decarboxylation of the organic radical, eq 2–4,

$$[Cu^+,CH_3CO_2\cdot] \rightarrow CuOCOCH_3^+ \qquad (2)$$

$$[Cu^+,CH_3CO_2\cdot] \rightarrow [Cu^+,CH_3\cdot] + CO_2 \qquad (3)$$

$$[Cu^+,CH_3\cdot] \rightarrow CuCH_3^+ \qquad (4)$$

leads to metastable alkyl–copper intermediates, which exhibit strong optical absorptions in the near-UV, e.g. ca. 370 nm.[1-7]

The copper ion in the alkyl–copper intermediates can be regarded as ligated to the alkyl ligand by a covalent bond that favors an oxidation state much lower than 2+ for the metal. This suggests that some properties of the alkyl–copper species should approach those found in related copper(I) complexes, namely copper(I) hydrides, halides, and pseudohalides. Little is known, however, about the reactivity of the alkyl–copper intermediates under various conditions. In this regard, the investigation of the photochemistry of copper(II) ions complexes with polymeric carboxylic acids, e.g. poly(acrylic acids), serves the dual purpose of investigating the photochemistry of the polymeric complexes and the reactivity of alkyl–copper intermediates subject to interactions with a polyelectrolyte.

Experimental Section

Photochemical Procedures. Flash irradiations were carried out in an experimental setup described elsewhere.[8] For excitations, a Quanta Ray Nd Yag pumped dye laser was used as a source of 266-nm flashes with ca. 10 ns duration and ~20 mJ of energy. An average of at least 10 experiments, at each particlular wavelength, were used for the determination of transient spectra or the investigation of reaction kinetics. A fresh solution of photolyte, deaerated with streams of O_2-free nitrogen, was used for each irradiation. The ionic strength of these solutions was adjusted to 0.1 M with $NaClO_4$ and the acid concentration to pH 6.0 by titration with NaOH.

Titrations were followed with a combined reference–glass electrode and a high-impedance microvoltmeter. The complexation of copper(II) was established from determinations of Cu^{2+}(aq) ions with an electrode specific for copper ions and mathematical analyses of the equilibria reported for poly(acrylic acid)–copper(II) mixtures.[9] In the experiments reported below, the concentration of free copper(II) ions was less than 1% of the total copper(II) concentration, and the number of copper(II) ions per polyacrylic acid molecule was adjusted to values between one and eight.

Materials. Aldrich poly(acrylic acid) with an average formula weight of 5000, namely an average of 70 carboxylic groups per molecule, was purified by dialysis in a Spectra-Por dialysis tubing, fw cutoff 3000. The concentration of the resulting solution was estimated by titrating the acid with NaOH to neutral pH. Since the spectrum of polyacrylic acid in solutions with pH 6.0 exhibited an absorption band, $\lambda_{max} \sim 210$ nm, with an apparent extinction coefficient of 115 M^{-1} cm^{-1}, the optical density of the solutions was used for the verification of the acid concentration. Solutions of the copper–poly(acrylic acid) complexes were prepared by adding appropriate amounts of Analysis grade $Cu(ClO_4)_2$ to solutions containing a known concentration of poly(acrylic acid). Other materials were reagent grade and used without further purification.

Results

Flash photolysis of the Cu(II)–poly(acrylic acid) complexes produce transient spectra with maxima at 400 and 540 nm, Figure

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