Figure 7. ^{1}H NMR spectra (300 MHz) of $[Co_8S_6(SPh)_8]^{4-}$ (upper) and $[Co_8S_6(SPh)_8]^{5-}$ (lower) in CD_3CN solutions at $\sim$297 K. Signal assignments are indicated ($C^+ = n$-Pr_4N^+). The 5– cluster was generated in situ by the addition of a slight excess of a 0.4 M solution of $NaC_{12}H_8$ in THF-d_8 to a solution of the 4– cluster.

The cluster moment steadily increases with increasing temperature, to 3.82 μ_B at 292 K, indicating thermal access to higher spin state(s) in this temperature interval. Magnetic properties will be reported in more detail subsequently.

Summary. The unique cluster $[Co_8S_6(SPh)_8]^{4-}$ is readily prepared by the assembly reaction (1). It can be oxidized and

reduced to generate the three-member electron-transfer series (3). The reduced cluster $[Co_8S_6(SPh)_8]^{5-}$ is obtainable by means of reaction 2. The $[Co_8S_6]^{4+,3+}$ cluster cores closely approach cubic symmetry, being composed of concentric Co_8 cubes and S_6 octahedra. Spectroscopic and magnetic properties indicate antiferromagnetically coupled clusters, $S = 0$ (4–) and $^1/_2$ (5–) ground states, dominant hyperfine contact interactions in the ^{1}H NMR spectra, and, in solution, equivalent cobalt sites and thus complete delocalization of the odd spin of the 5– cluster (^{1}H NMR time scale). The cores have the same essential cubic topology as, but different oxidation states and much larger core volumes than, the Co_8S_6 clusters in the synthetic pentlandite Co_9S_8. Other than the various pentlandites, cubic M_8S_6 clusters have been found only in $K_6LiFe_{24}S_{26}Cl$, a synthetic compound structurally analogous to djerfisherite,[64] and bartonite, a potassium iron sulfide mineral.[65]

The clusters described here, as well as certain others cited at the outset, indicate that solubilized topological equivalents of metal sulfide clusters recognizable in extended lattices can be produced. It remains to be discovered to what extent structural and electronic features of discrete and bridged clusters are congruent. In this connection, a challenge in synthesis is the adjoining of discrete clusters into small aggregates, themselves discrete, by means of (largely) the same bridges that exist in the solid state.

Supplementary Material Available: Complete listings for (n-$Pr_4N)_4$-$[Co_8S_6(SPh)_8]$ and $(Et_4N)_5[Co_8S_6(SPh)_8]$ of atom coordinates, isotropic and anisotropic temperature factors, interatomic angles and distances, calculated hydrogen atom positions, and calculated and observed structure factors (102 pages). Ordering information is given on any current masthead page.

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A Further Example of a Dinuclear Copper(II) Complex Involving Monoatomic Acetate Bridges. Synthesis, Crystal Structure, and Spectroscopic and Magnetic Properties of Bis(μ-acetato)bis(7-amino-4-methyl-5-aza-3-hepten-2-onato(1–))dicopper(II)

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The synthesis, crystal structure, and spectroscopic and magnetic properties are reported for a dinuclear copper(II) complex, $[Cu(AE)CH_3COO]_2$, where AE is the anion of 7-amino-4-methyl-5-aza-3-hepten-2-one. This complex provides a further example of a somewhat unusual bridging mode since the two copper atoms are connected by a single atom bridge through one of the oxygen atoms of an acetate ligand. The compound crystallizes in the triclinic space group C_i^1-$P\bar{1}$ with 1 formula unit in a cell having the dimensions $a = 8.1362$ (8) Å, $b = 9.9886$ (8) Å, $c = 7.3448$ (11) Å, $\alpha = 92.42$ (1)°, $\beta = 96.48$ (1)°, and $\gamma = 69.76$ (1)°. Magnetic susceptibility measurements show a weak antiferromagnetic interaction. $\Delta M_s = 2$ transitions are observed in ESR spectra related to solid samples and frozen solutions (noncoordinating solvents) but spectral parameter values suggest a modification of the dimer structure on going from the solid to solutions.

Introduction

Acetate bridging between transition-metal atoms is well-known in complexes such as copper(II) acetate hydrate[1,2] and its analogues with other metal ions. This mode of bridging links adjacent

metal atoms via the two different oxygens of a carboxylate group to form a M–O–C–O–M bridge. Although it is an obvious a priori possibility that acetate be involved in monoatomic bridging, the occurrence of M–O–M bridges via one of the oxygen atoms of the acetate ligand has been firmly established in only four cases.[3–7]

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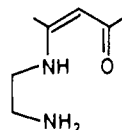
Figure 1. Struture of ligand (AEH).

Table I. Summary of Crystal and Intensity Collection Data

formula: $(C_{19}H_{16}N_2O_3Cu)_3$
fw: 527.1
$a = 8.1362$ (8) Å
$b = 9.9886$ (8) Å
$c = 7.3448$ (11) Å
$\alpha = 92.42$ (1)°
$\beta = 96.48$ (1)°
$\gamma = 69.76$ (1)°
$V = 556.5$ Å^3
$Z = 1$
$F(000) = 220$
$D_{measd} = 1.59$ g/cm^3 (measd by flotation in C_2Br_4/CH_3COCH_3)
$D_{calcd} = 1.573$ g/cm^3
space gp: C_i^1-$P\bar{1}$
radiation: Mo K$\bar{\alpha}$ from graphite monochromator
lin abs coeff (μ): 19.4 cm^{-1}
temp: 20 °C
receiving aperture: 4.0 × 4.0 mm
take-off angle: 3.45°
scan mode: ω-2θ
scan range: (0.90 + 0.35 tan θ)°
2θ limits: 60°

During the course of a general study of the novel tridentate ligand 7-amino-4-methyl-5-aza-3-heptene-2-one (Figure 1),[8–10] we succeeded in preparing a copper(II) complex containing a one-atom acetate bridging. The present report is concerned with the synthesis, properties, and crystal structure of bis(μ-acetato)bis(7-amino-4-methyl-5-aza-3-hepten-2-onato(1–))dicopper(II) with the aim of further characterizing this unusual type of bridge.

Experimental Section

Compound Preparation. To a 7 × 10^{-3} M solution of AEH[8] in methanol was first added triethylamine (2 mL) and, a few minutes later, the equivalent amount of copper ethanoate monohydrate (1.4 g) as a solid. The solid dissolved quickly upon stirring, giving a blue solution at room temperature. One hour later, the solution was filtered and evaporated, leaving a sticky product. Addition of acetone allowed a blue product to precipitate. Anal. Calcd for $(C_9H_{16}N_2O_3Cu)_2$: C, 40.99; H, 6.07; N, 10.63; Cu, 24.10. Found: C, 41.06; H, 6.29; N, 10.73; Cu, 24.06. Slow crytallization from a dichloromethane solution gave blue crystals suitable for X-ray diffraction study.

Physical Measurements. Infrared spectra of KBr disks were measured on a Perkin-Elmer 983 instrument. Electronic spectra were obtained with a Cary 14 spectrometer. EPR spectra were recorded at X- and Q-band frequencies with a Bruker 200 TT spectrometer operating at 9.4–9.5 and 34–34.5 GHz, respectively.

Magnetic susceptibility data were collected on powdered samples of the title compound with use of a Faraday type magnetometer fitted with a helium continuous-flow cryostat. Independence of the magnetic susceptibility vs. magnetic field was checked at each temperature. Mercury tetrakis(thiocyanato)cobaltate (susceptibility at 20 °C 16.44 × 10^{-6} cgsu) was used as a susceptibility standard. All data were corrected for diamagnetism (estimated at –114 × 10^{-6} cgsu for the title compound) and

Table II. Final Least-Squares Coordinates with Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c
Cu	0.54093 (2)	0.64987 (2)	0.48492 (2)
O(1)	0.3778 (2)	0.7338 (1)	0.6629 (2)
O(2)	0.6512 (2)	0.4851 (1)	0.6463 (2)
O(3)	0.8901 (2)	0.5459 (2)	0.6914 (3)
N(1)	0.4654 (2)	0.8193 (2)	0.3341 (2)
N(2)	0.6931 (2)	0.5550 (2)	0.2860 (2)
C(1)	0.5673 (2)	0.7999 (2)	0.1770 (2)
C(2)	0.6216 (3)	0.6438 (2)	0.1203 (2)
C(3)	0.2639 (2)	0.8610 (2)	0.6517 (2)
C(4)	0.2482 (2)	0.9617 (2)	0.5226 (2)
C(5)	0.3494 (2)	0.9432 (2)	0.3707 (2)
C(6)	0.1423 (2)	0.8976 (2)	0.8002 (3)
C(7)	0.3184 (2)	1.0727 (2)	0.2560 (3)
C(8)	0.8103 (2)	0.4639 (2)	0.7107 (2)
C(9)	0.8988 (3)	0.3271 (3) ·	0.8169 (3)
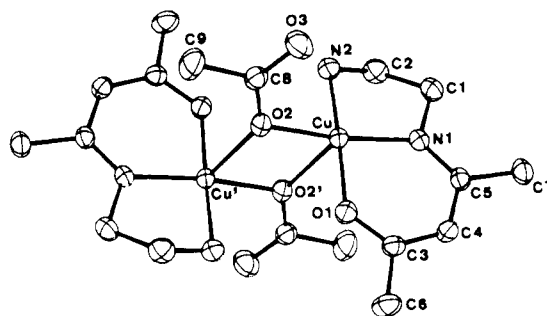
Figure 2. ORTEP plot of [Cu(AE)CH$_3$COO]$_2$ with the ellipsoids drawn at the 40% probability level.

TIP (taken as 60 × 10^{-6} cgsu/Cu atom).

Collection and Reduction of X-ray Data. Preliminary Weissenberg photographs failed to reveal any symmetry. Crystals belong to the triclinic system, space group $P1$ or $P\bar{1}$. The structure was successfully solved in the C_i^1-$P\bar{1}$ space group. The selected crystal was a dark blue parallelepiped with boundary planes {100}, {010}, and {001}. The distances from these faces to an arbitrary origin were 0.175, 0.088, and 0.225 mm, respectively. The crystal was sealed on a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer. Cell constants were obtained from the least-squares fit of the setting angles of 25 reflections. The summary of crystal and intensity collection data are given in Table I. A total of 3245 independent reflections were recorded out to 2θ(Mo) = 60° by procedures described elsewhere.[11] Intensity standards, recorded periodically, showed no fluctuations greater than 2%. Intensity data were corrected for Lorentz, polarization, and absorption (μ = 19.4 cm^{-1}, calculated[12] transmission range 0.50–0.73). A total of 2834 reflections having $F_o^2 > 4\sigma(F_o^2)$ were used in structure determination.

Structure Solution and Refinement. The structure was solved by the heavy-atom method and difference Fourier maps. The hydrogen atoms were localized and included in calculations in idealized positions (C–H = N–H = 0.95 Å). They are assigned an isotropic temperature factor equal to the equivalent isotropic temperature factor of the atom to which they are bonded. For all other atoms, ansiotropic thermal parameters were introduced.

The atomic scattering factors used were those prepared by Cromer and Waber[13] with anomalous dispersion effects.[14] Scattering factors for the hydrogen atoms were taken from Stewart et al.[15] The final full-matrix least-squares refinement converged to $R = 0.025$ and $R_w = 0.029$ with 2835 observations and 136 variables.[16] The weighting scheme used in

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Table III. Copper Atom Environment: Bond Lengths (Å) and Angles (deg)

Lengths			
Cu–O(1)	1.925 (1)	Cu–N(2)	2.012 (2)
Cu–N(1)	1.938 (1)	Cu–O(2)	1.955 (1)
Cu···O(2)'	2.490 (1)	Cu···O(3)	2.927 (2)[a]

Angles			
O(1)–Cu–N(1)	94.58 (6)	N(1)–Cu–N(2)	85.67 (6)
O(1)–Cu–N(2)	174.32 (5)	N(1)–Cu–O(2)	171.08 (5)
O(1)–Cu–O(2)	88.65 (6)	N(2)–Cu–O(2)	91.94 (6)
O(1)–Cu–O(2)'	89.47 (5)	N(2)–Cu–O(2)'	84.96 (6)
N(1)–Cu–O(2)'	103.65 (5)	O(2)–Cu–O(2)'	84.66 (5)
Cu–O(2)–Cu'	95.34 (5)		

[a] Long with respect to bonding.

the minimization of the function $\sum w(|F_o| - |F_c|)^2$ is defined as $w = [\sigma^2(F_o) + (0.026F_o)^2]^{-1}$. The error in an observation of unit weight[16] was 0.98. In the last cycle of refinement the shifts for all parameters were smaller than 0.01σ. A final difference Fourier map showed no excursion of electron density greater than 0.3 e/Å^3.

Calculations were carried out on a DPS8-70 computer using the SHELX-76 program package[17] and the ORTEP plotting program.[18]

Final fractional coordinates for non-hydrogen atoms are listed in Table II. Tables of anisotropic thermal parameters, hydrogen atom parameters, least-squares plane equations, and observed and calculated structure factors are available as supplementary material.

Results and Discussion

The reaction of pentane-2,4-dione with 1,2-diaminoethane generally yields the quadridentate Schiff base N,N'-ethylenebis(acetylacetone imine) (BAEH$_2$). However, if the reaction is carried out with a 1:1 ratio of reagents in carbon tetrachloride or chloroform and under dilute conditions, a single condensation product is obtained, 7-amino-4-methyl-5-aza-3-hepten-2-one (AEH). In spite of a moderate stability, AEH may be isolated with a fair degree of purity by vacuum distillation and used to complex metal ions.[8,10]

From the reaction with copper acetate in a 1:1 molar ratio the title complex may be obtained. According to the analytical data, it has to be formulated [Cu(AE)CH$_3$COO], but a dimeric structure was suggested by preliminary ESR data. This was definitively established by structural determination.

Description of the Structure. The complex consists of dimeric units that are well separated from each other. A view of the dimeric unit is given in Figure 2. The bridging Cu$_2$O$_2$ core is constrained to be planar by the presence of a crystallographic inversion center in the middle of the dimer. The relevant distances and angles are listed in Tables III and IV.

The geometry at each copper(II) ion is best described as a distorted (4 + 1) square-based pyramid. The basal plane consists of one oxygen and two nitrogen atoms from the AE ligand and a carboxylate oxygen while the apical site is occupied by one oxygen atom of another acetate anion that is basal to the second copper atom in the dimer. As expected, the axial bond is about 0.4 Å longer than the basal plane distances. The best least-squares basal plane calculated with the four atoms O(1), O(2), N(2), N(1) shows a tetrahedral distortion, the deviations from this plane as follows: O(1), 0.101 (1) Å; O(2), –0.100 (1) Å; N(1), –0.125 (2) Å; N(2), 0.157 (2) Å.

However, the copper atom is not far removed from this plane, the separation being 0.0306 (2) Å toward the bridging oxygen. It may be emphasized that the distance btween each metal atom and the related nonbridging carboxylate oxygen is long with respect to bonding (2.927 (2) Å). Furthermore, these oxygen atoms are non-hydrogen bonded to any solvent molecule as observed in previously reported complexes.[3–6] This unusual bonding mode results in a significant difference between the length of the two carboxylate CO bonds, 1.275 (2) and 1.229 (2) Å.

Table IV. Bond Lengths (Å), Angles (deg), and Closest Contacts (Å) between Two Molecules

Lengths			
N(1)–C(1)	1.464 (2)	C(5)–N(1)	1.309 (2)
C(1)–C(2)	1.519 (3)	C(3)–C(6)	1.504 (2)
C(2)–N(2)	1.477 (3)	C(5)–C(7)	1.505 (2)
O(1)–C(3)	1.287 (2)	O(2)–C(8)	1.275 (2)
C(3)–C(4)	1.376 (2)	C(8)–O(3)	1.229 (2)
C(4)–C(5)	1.429 (2)	C(8)–C(9)	1.509 (3)

Angles			
Cu–N(1)–C(1)	112.0 (1)	O(1)–C(3)–C(6)	114.0 (1)
N(1)–C(1)–C(2)	108.1 (1)	C(4)–C(3)–C(6)	119.6 (2)
C(1)–C(2)–N(2)	108.6 (1)	C(4)–C(5)–C(7)	117.1 (1)
C(2)–N(2)–Cu	107.0 (1)	N(1)–C(5)–C(7)	121.5 (2)
Cu–O(1)–C(3)	124.2 (1)	Cu–O(2)–C(8)	115.9 (1)
O(1)–C(3)–C(4)	126.4 (1)	Cu'–O(2)–C(8)	140.3 (1)
C(3)–C(4)–C(5)	126.7 (1)	O(2)–C(8)–O(3)	124.5 (2)
C(4)–C(5)–N(1)	121.5 (1)	O(2)–C(8)–C(9)	114.8 (2)
C(5)–N(1)–Cu	126.2 (1)	O(3)–C(8)–C(9)	120.7 (2)
C(1)–N(1)–C(5)	121.5 (1)		

Closest Contacts			
O(3)···N(2)	3.172 (2)	O(3)···O(3)	3.425 (4)

The distances related to nonbridging bonds, i.e. the Cu–N(1) and Cu–N(2) distances of 1.938 (1) and 2.012 (2) Å, respectively, and the Cu–O(1) distance of 1.925 (1) Å are within the range of values normally found for such bonds. More particularly, (they little differ from the values previously reported for N,N'-ethylenebis(acetylacetone iminato)copper(II) (CuBAE).[19] The acetylacetone ring is planar, with no atom deviating from the least-squares plane by more than 0.038 (2) Å, the copper atom being included in this plane. The five-membered ring defined by the copper atom and ethylenediamine is definitely nonplanar and has a gauche conformation as usually observed.

A relevant structural element is the quadrangle defined by the Cu–O–Cu–O core. The geometry of this bridging unit is compared (Table V) to those oberved for related dinuclear complexes involving monoatomic acetate bridges. Our dimer is characterized by a low value of the Cu–O–Cu bridging angle ($\phi = 95.34$ (5)°) whereas the out-of-plane ($R = 2.490$ (1) Å) and the in-plane Cu–O distances are similar to those reported for the other known complexes. This results in low values of the Cu–Cu separation and a ϕ/R quantity that would be expected to show a relationship with the exchange coupling constant within a series of closely related complexes (cf. ref 20 and references therein).

Spectroscopic Data. The solid-state infrared spectrum of [Cu(AE)CH$_3$COO]$_2$ displays many resemblances to those of CuBAE and [Cu(AE)Br]$_2$. However, attributions in the 1300–1600-cm^{-1} region are tedious due to the number of absorptions expected from both ligands (AE and CH$_3$COO$^-$). The most salient feature is a strong, broad band at 1597 cm^{-1} with a shoulder at 1615 cm^{-1}. This band is found in other complexes involving the CuAE entity[10] but with a lower intensity. The increased intensity observed in the present complex is likely due to overlapping of bands from CuAE with the antisymmetric stretching mode of the carboxylate group. This yields the following attributions: ν(CO) and ν(CC) at 1597 cm^{-1} for the AE moiety and ν_{as}(CO) at ca. 1615 cm^{-1} for CH$_3$CO$_2^-$. The strong absorption at 1512 cm^{-1} is attributed to ν(CN) (AE). These attributions are consistent with the values quoted for CuBAE,[21] i.e. ν(CO) and ν(CC) = 1592 cm^{-1} and ν(CN) = 1515 cm^{-1}, or for [Cu(AE)Br]$_2$,[10] i.e. ν(CO) = 1600 cm^{-1}, ν(CC) = 1570 cm^{-1}, and ν(CN) = 1515 cm^{-1}.

Owing to the nonsymmetric bonding mode of the carboxylate group, a large splitting (Δ) of the CO stretching frequencies is expected.[22] The symmetric role is observed at 1375 cm^{-1}, yielding a Δ value of ca. 240 cm^{-1}. Δ values of ca. 180 cm^{-1} are generally associated with classical carboxylate bridges (Cu–O–C–O–Cu).[23]

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Table V. Relevant Structural Parameters for Monoatomic Acetate-Bridged Complexes

	Cu-O, Å			Cu-O-Cu		
complex	in-plane	out-of-plane (R)	Cu-Cu, Å	(ϕ), deg	ϕ/R	ref
$[Cu(L)_2(CH_3COO)_2] \cdot 6H_2O^a$	1.986	2.424		102.45	42.3	5
$[Cu(L')CH_3COO]_2^b$	1.971	2.486	3.507	101.3	40.8	7
	1.981	2.540		102.9	40.5	
$[Cu(L'')CH_3COO]_2 \cdot H_2O \cdot C_2H_5OH^c$	1.952	2.446	3.445	102.6	39.0^e	4
	1.952	2.651		95.7		
$Cu_2(L''')(CH_3COO)_2 \cdot 2CH_3OH^d$	1.952	2.495	3.383	98.3	39.4	6
$[Cu(AE)CH_3COO]_2$	1.955	2.490	3.305	95.3	38.3	f

^{a} L = 1-methylimidazole. ^{b} L' = 7-amino-4,7-dimethyl-1-(o-hydroxyphenyl)-5-aza-3-hepten-2-onato(1–). ^{c} L'' = N-(1,1-dimethyl-2-hydroxyethyl)salicylaldiminato(1–). ^{d} L''' = dianion of N,N'-bis(2-((o-hydroxybenzhydrylidene)amino)ethyl)-1,2-ethanediamine. ^{e} Mean value. ^{f} This work.

Other absorptions in the spectrum (4000–600 cm^{-1}) are unremarkable and may be readily assigned, especially the two bands at 3285 and 3165 cm^{-1} attributed to the NH$_2$ group.

Identical electronic spectra are observed at room temperature in methanol and in dichloromethane. The occurrence of two absorption bands at 615 nm (ϵ = 130) and 420 nm (ϵ = 100) is consistent with a square-based structure. The charge-transfer bands are observed at 320 nm (ϵ = 19200) and 280 nm (ϵ = 13400).

Magnetic Properties. X- and Q-band spectra have been obtained for powdered samples and solutions at ambient and low temperatures.

The X-band spectrum of the powdered complex shows the features characteristic of a dinuclear system, with resonances corresponding to $\Delta M_S = \pm 1$ ($g_\| = 2.229$, $g_\perp = 2.064$) and $\Delta M_s = \pm 2$ ($H_{min} = 1505$ G) transitions. The "half-field" signal is not observed in Q-band spectra. The signals in the X- and Q-band spectra are devoid of any hyperfine structure. Pratically axial spectra with $g_\| > g_\perp$ are consistent with a distorted square-pyramidal configuration. The zero-field splitting parameter D may be approximated from the position of the half-field transition through the relationship $H_{min} = [(h\nu)^2 - {}^4/_3D^2]^{1/2}/2g\beta.^{24}$ The resultant value is $D \simeq 170.10^{-4}$ cm^{-1}.

At ambient temperature, solutions in CH$_2$Cl$_2$/C$_6$H$_5$CH$_3$ give isotropic spectra with a four-line pattern (g_0 = 2.105, $|A_0|$ = 99 × 10^{-4} cm^{-1}) indicative of a magnetically diluted mononuclear species. A seven-line pattern would be expected for a dimeric species.^{25} However, lowering the temperature to 100 K results in the observation of a triplet spectrum (Figure 3) characteristic of two interacting copper(II) ions. Due to the good quality of the spectrum, the various signals are assignable. The $\Delta M_S = \pm 1$ region (2300–3700 G) shows two pairs of zero-field split transitions that are indicative of a pratically axial symmetry. In the 2300–2900-G region, seven copper hyperfine lines are readily seen with an average spacing of 76 G. Three lines attributable to the second seven-line pattern resulting from zero-field splitting appear in the 3600–3800-G area. The remaining four lines are likely obscured by the strong signal at ca. 3550 G. These two patterns are attributed to the parallel signal. The two features are 3010 and 3543 G and are devoid of any hyperfine structure. They are attributed to the perpendicular component. The half-field transition appears as a seven-line pattern centered at 1560 G with an average spacing of 83 G. The overall appearance of this spectrum and more generally the limitation of the hyperfine pattern on the $\Delta M_S = \pm 2$ signal to seven lines point to a negligible rhombic component to zero-field splitting. The inequality of average copper hyperfine splittings between the $\Delta M_S = \pm 1$ and the $\Delta M_S = \pm 2$ signals would indicate a slight misalignment of the g and A tensors. Nevertheless, Wasserman's equations^{26} have been used in an attempt to fit the observed resonance field positions. The aforementioned
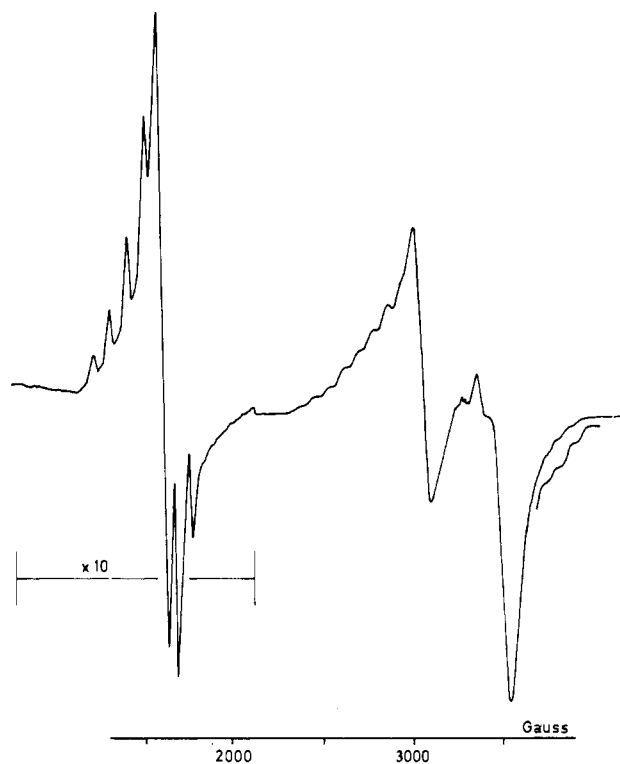
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Figure 3. X-Band EPR spectrum of all visible features of a frozen solution (dichloromethane/toluene ratio 4/1) of [Cu(AE)CH$_3$COO]$_2$ recorded at 100 K with a frequency of 9.407 GHz.

attribution leads to reasonable values of the parameters: i.e., $g_\|$ = 2.14$_2$, $g_\perp$ = 2.03$_8$, $|D|$ = 533 × 10^{-4} cm^{-1}. The overall agreement between observed (2620, 3037, 3543, 3658 G) and calculated (2630, 3020, 3556, 3648 G) magnetic fields for the $\Delta M_S = \pm 1$ transitions is reasonably good. Furthermore, inserting the D value of 533 × 10^{-4} cm^{-1} in the Kottis–Lefebvre's relationship (vide infra) yields the half-field resonance H_{min} = 1566 G in perfect agreement with the experimental value of 1560 G. At this stage it can be noted that the zero-field splitting related to frozen solutions is markedly larger than the value estimated for the powdered sample.

Addition of methanol to the solvent mixture (CH$_2$Cl$_2$/C$_6$H$_5$CH$_3$) results in the observations at 110 K of a characteristic doublet spectrum with $g_\|$ = 2.214, $g_\perp$ = 2.037, and $|A_\||$ = 202 × 10^{-4} cm^{-1}). Five lines are clearly resolved on the peerpendicular component, with a spacing of ca. 12 G suggesting interaction of the unpaired spin with two nitrogen nuclei.

From the whole set of data, one may conclude that coupled copper(II) dimers occur not only in the solid state, in agreement with the X-ray structure, but also in frozen solutions, provided noncoordinating solvents are used. However, at room temperature the bridges are not retained in solution even in noncoordinating solvent. Furthermore, it is suggested that the dimeric forms occurring in the solid and in frozen solutions are different. In this resepct, the difference in the $g_\|$ values (2.23, and 2.15) would

be consistent with a decrease of tetragonal distortion in going from the crystal to the glass.

In contrast with the observation of a half-field transition in the powder ESR spectrum, which implies the presence of an exchange interaction, the magnetic susceptibility data down to 10 K show only an extremely small interaction. The data obey the Curie–Weiss law, $\chi_A = C/(T - \Theta)$ with $C = 0.419$ and $\Theta = -1.46$ K.[27] From the very small negative value of Θ, it can be estimated that the compound is slightly antiferromagnetic. Least-squares fitting to the Bleany–Bowers equation yields $g = 2.10$ and $J = -0.50$ cm^{-1} (assuming the TIP = 60×10^{-6} cgsu).

As previously mentioned, four complexes are structurally related to our compound in that they have the copper atoms bridged through two coordinated oxygen atoms of the carboxylate anions. Their relevant structural features are quoted in Table V. To our knowledge, the magnetic properties of the 1-methylimidazole derivative have not yet been reported. $[Cu(L')CH_3COO]_2 \cdot H_2O \cdot C_2H_5OH$ (L' being the anion of N-(1,1-dimethyl-2-hydroxyethyl)salicylaldimine), which has two inequivalent Cu–O–Cu bridges, is characterized by a J value of +0.63 cm^{-1}.[4] In $Cu_2(L'')(CH_3COO)_2 \cdot 2CH_3OH$ (L'' being the dianion of N,N'-bis(2-((o-hydroxybenzhydrilene)amino)ethyl)-1,2-ethanediamine) the occurrence of 1,2-ethanediamine bridges together with acetate bridges prevents an unambiguous assignment of the coupling constants to the respective type of bridging ligands. However, the authors suggest that the value −1.50 cm^{-1} may be associated with the Cu_2O_2 unit.[6] Examination of these three sets of data provides no obvious correlation between the coupling constant and

any of the structural features. This is likely due to the restricted range of values exhibited by the structural parameters and coupling constants. Tentatively, we would suggest that, for most of the complexes reported in Table V, the structural parameters would lie in the vicinity of the crossover values from antiferromagnetic to ferromagnetic coupling. In this respect, it may be recalled that the hydroxide-bridged dimers show an angular dependence of J with a crossover at a Cu–O–Cu bridging angle of 97.6°.[28] Obviously, more examples are aimed at relating magnetic properties and structural features for this type of bridging.

Finally, the proper conclusions here is that $[Cu(AE)CH_3COO]_2$ is characterized by a small value of $|J|$. This results is not unexpected on the basis of the rationale proposed by Kahn and co-workers[29] and the actual geometry of the dimer. The two magnetic orbitals are essentially localized in parallel planes separated by 3.305 Å, and the resulting overlap density should be small. A co-square-planar geometry for the dimeric unit would result in a much more significant interaction. Systems of this type involving the AEH ligand are being studied.

Supplementary Material Available: Listings of structure factors, anisotropic thermal parameters, hydrogen parameters, and least-squares plane equations and a plot of the inverse of the atomic susceptibility χ_A^{-1} against temperature (18 pages). Ordering information is given on any current masthead page.

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(27) A plot of χ_A^{-1} vs. T is given in Figure 4 (supplementary material).

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Exchange Coupling in the Alternatingly Spaced Linear-Chain Compounds Lithium Copper(II) Trichloride Dihydrate, LiCuCl₃·2H₂O, and Isopropylammonium Copper(II) Trichloride, (C₃H₁₀N)CuCl₃

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New magnetic susceptibility data on lithium copper(II) trichloride dihydrate, LiCuCl₃·H₂O, and isopropylammonium copper(II) trichloride, (C₃H₁₀N)CuCl₃, exhibit maxima at 6.6 and 23 K, respectively. These maxima are indicative of antiferromagnetic exchange interactions. Interpretation of the magnetic susceptibility data by alternating Heisenberg linear-chain theory for $S = {}^1/_2$ ions yields $J = -3.7$ cm^{-1} and $\alpha = 0.89$ for LiCuCl₃·2H₂O using the EPR g value of 2.14 and $J = -13.7$ cm^{-1} and $\alpha = 0.35$ for (IPA) CuCl₃ using the EPR g value of 2.17.

Introduction

The theoretical problem of alternatingly spaced linear spin chains has been studied extensively[1–5] and reviewed recently.[5,6] Organic compounds with alternatingly spaced linear-chain structures have been known and studied for quite some time.[7] Exchange-coupled transition-metal compounds that are composed of alternatingly spaced linear chains have only recently received attention. The most thoroughly studied transition-metal compound

that exhibits alternating-chain magnetism is Cu(NO₃)₂·2.5H₂O.[6] However, the room-temperature X-ray crystal structure of Cu(NO₃)₂·2.5H₂O is ladderlike.[8]

Other transition-metal compounds[9–21] that exhibit alternat-

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