

crystal structures and their magnetic properties. Structural factors leading to one-dimensional ferrimagnetic behavior on the one hand and to interchain ferromagnetic interaction on the other hand are better and better understood. The control of these structural factors during the synthetic process remains however a very difficult task. The crystal engineering in molecular chemistry still is in its infancy.

Acknowledgment. We would like to express our deepest gratitude to the Société Nationale Elf Aquitaine which has financially supported this work and offered a research grant to K.N. We are also grateful to J. P. Renard for his help with the low-field

SQUID magnetic measurements.

Supplementary Material Available: Tables SI-SIX, listing data collection and refinement information, anisotropic thermal parameters for the non-hydrogen atoms, coordinates for the hydrogen atoms, the hydrogen bond data, and the least-squares mean planes for both MnCu(Cl₄obbz)(H₂O)₅ and MnCu(Br₄obbz)(H₂O)₃·2.5H₂O, and Figure S1, showing a stereoview of packing of molecules within the crystal lattice of MnCu(Cl₄obbz)(H₂O)₅ (15 pages); tables of calculated and observed structure factors for MnCu(Cl₄obbz)(H₂O)₅ and MnCu(Br₄obbz)(H₂O)₃·2.5H₂O (27 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Solid-State NMR Studies of Magneto-Structural Correlations in Anhydrous Copper(II) Carboxylates

Gordon C. Campbell,[†] Joseph H. Reibenspies, and James F. Haw*

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Magneto-structural correlations are probed in a series of anhydrous copper(II) carboxylates via solid-state NMR spectroscopic techniques. Temperature-dependent ¹³C cross-polarization magic-angle-spinning (CP/MAS) results are presented for copper(II) propionate (Cu₂(C₂H₃CO₂)₄), copper(II) isobutyrate (Cu₂(C₃H₇CO₂)₄), and copper(II) isovalerate (Cu₂(C₄H₉CO₂)₄). Observed contact shifts are related to magnetic information and used to calculate singlet-triplet energy level separations ($-2J$), diamagnetic chemical shifts (δ_{dia}), and electron-nucleus hyperfine coupling constants (A). As structural information is manifest in NMR signal multiplicity, this report also includes an X-ray crystal structure determination of Cu₂(C₄H₉CO₂)₄. The compound crystallized in the triclinic space group $P\bar{1}$ (No. 2), with $a = 5.1910$ (13) Å, $b = 10.840$ (2) Å, $c = 11.063$ (2) Å, $\alpha = 83.120$ (15)°, $\beta = 86.92$ (2)°, $\gamma = 85.60$ (2)°, $Z = 1$, and $V = 615.6$ (2) Å³. Full-matrix least-squares refinement on F^2 yielded the final R value of 0.0654 for 1571 unique observed reflections.

Introduction

Copper(II) carboxylates, Cu₂(RCO₂)₄L_{*n*} with $n = 0$ or $n = 2$, have been the focus of research attention since the early part of the twentieth century.¹ Interest in the magneto-structural correlations² in these (and related) materials spans fields ranging from chemistry to biology and physics. Although once somewhat controversial, the mechanism of antiferromagnetic coupling between dimeric copper centers is now generally thought to involve the electronic orbitals of the bridging carboxylate ligands in what is termed the superexchange pathway.³ Recently,⁴ two of us reported the role that solid-state nuclear magnetic resonance (NMR) spectroscopy can play in the development of a better understanding of the properties of these compounds. We were able to quantitatively refine earlier qualitative reports⁵ and gain new insights into the relationship between structure and magnetism in a representative copper(II) carboxylate.

Variable-temperature⁶ (VT) ¹³C cross-polarization magic-angle-spinning (CP/MAS) NMR spectroscopy⁷ has, we feel, provided the most convincing experimental evidence yet reported for magnetic superexchange between metal centers in these solids. Paramagnetic contact shifts were observed for all ¹³C resonances corresponding to sites along the carboxylate bridges in anhydrous copper(II) *n*-butyrate (R = C₃H₇, $n = 0$). In addition to being directly related to the presence of unpaired electron density at these nuclei,⁸ the temperature dependence of the shifts allowed the determination of electron-nucleus hyperfine coupling constants (A), singlet-triplet energy level separations ($-2J$, from the spin Hamiltonian $H = -2JS_1 \cdot S_2$), and diamagnetic chemical shifts (δ_{dia}). Signs and relative magnitudes of A values were shown to be related to mechanisms of magnetic superexchange coupling and structurally significant in a sense completely analogous to the Karplus relationship,⁹ which is well-known in solution-state

Table I. Crystallographic Data for Anhydrous Copper(II) Isovalerate

mol formula	C ₂₀ H ₃₆ O ₈ Cu ₂	space group	$P\bar{1}$
fw	531.6	T	193 K
a	5.1910 (13) Å	λ	0.7107 Å
b	10.840 (2) Å	ρ_{obsd}	1.46 g cm ⁻³
c	11.063 (2) Å	ρ_{calcd}	1.434 g cm ⁻³
α	83.120 (15)°	μ	1.769 mm ⁻¹
β	86.92 (2)°	rel transm factors:	0.9714-0.9928
γ	85.60 (2)°	$R(F_o^2)$	0.065
V	615.6 (2) Å ³	$R_w(F_o^2)$	0.063
Z	1		

NMR spectroscopy. The reliability of $-2J$ values determined via NMR techniques is in principle superior to that from corresponding bulk measurements due to the relative insensitivity of NMR spectra to the presence of small amounts of paramagnetic impurities. Potential complications could arise, however, from

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* To whom correspondence should be addressed.

[†] Present address: Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$)^a for Anhydrous Copper(II) Isovalerate

atom	x	y	z	<i>U</i> (eq)
Cu(1)	2109 (2)	466 (1)	-459 (1)	25 (1)
O(1)	-1521 (9)	-1620 (5)	-753 (5)	38 (2)
O(2)	2101 (9)	-779 (5)	-1571 (4)	35 (2)
C(1)	392 (15)	-1551 (7)	-1514 (7)	34 (3)
C(2)	572 (17)	-2459 (7)	-2444 (7)	49 (3)
C(3)	549 (14)	-3805 (7)	-1900 (7)	40 (3)
C(4)	469 (18)	-4670 (8)	-2873 (9)	64 (4)
C(5)	2766 (19)	-4178 (10)	-1094 (10)	85 (5)
O(3)	87 (8)	-1604 (5)	1554 (4)	31 (2)
O(4)	3723 (8)	-801 (4)	809 (4)	28 (2)
C(6)	2459 (12)	-1539 (6)	1546 (6)	25 (2)
C(7)	3948 (12)	-2378 (6)	2513 (6)	29 (2)
C(8)	4631 (16)	-1650 (9)	3558 (8)	55 (3)
C(9)	2465 (20)	-922 (9)	4083 (9)	69 (4)
C(10)	5908 (17)	-2606 (9)	4523 (8)	69 (4)

^aEquivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

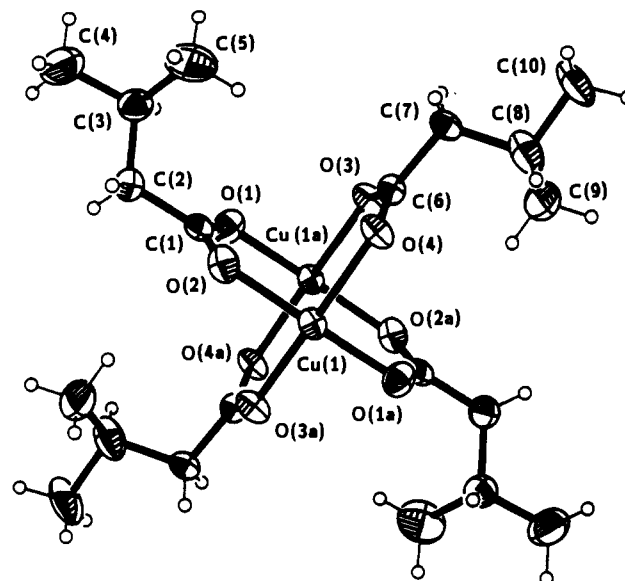
broad NMR lines with an attendant uncertainty in temperature-dependent shifts.

This contribution illustrates the generality of the NMR method through its application to other anhydrous ($n = 0$) copper(II) carboxylates. Magnetic and structural information regarding the propionate ($R = C_2H_5$, prop), isobutyrate ($R = C_3H_7$, *i*-but), and isovalerate ($R = C_4H_9$, *i*-val) will be presented. We find in general a number of magnetic and structural similarities between the compounds discussed in this contribution and copper(II) *n*-butyrate.⁴ In one or two cases, however, the temperature-dependent NMR properties were complicated by molecular motions that prevented us from estimating magnetic properties. A further purpose of this contribution is to report the X-ray crystal structure of $Cu_2(i\text{-val})_4$.

Experimental Section

Compound Preparation and NMR Methods. Anhydrous copper(II) carboxylates were prepared by using standard literature methods¹⁰ and packed into Kel-F MAS NMR rotors. Spectroscopic studies were performed on approximately 0.3 g of powder. All variable-temperature ¹³C CP/MAS NMR spectra were obtained at 25.02 MHz on a Chemagnetics M-100S spectrometer with a 1-ms cross-polarization contact time and a pulse delay of 1 s. Magic-angle-spinning frequencies typically ranged between 4 kHz at ambient temperatures and 2.5 kHz at 77 K. A total of 400 transients were collected at each temperature and multiplied by an exponential weighting function of 50 Hz before transforming. Spectral assignments were facilitated by the interrupted decoupling experiment.¹¹ Statistical analyses of the temperature-dependent chemical shift data were done with the NLIN program of the SAS (Statistical Analysis Service) package.

Crystallographic Data Collection and Structure Determination. Single crystals of $Cu_2(i\text{-val})_4$ were grown from isovaleric acid solution. The details of the data collection and structure determination are summarized in Table I. A more complete report is included as supplementary material (Table SI). A blue plate crystal [0.04 mm (001 → 001) × 0.18 mm (010 → 010) × 0.21 mm (100 → 100)] was mounted on a glass fiber and cooled to 193 (1) K in a N₂ cold stream. Data were collected on a Nicolet R3m/V X-ray diffractometer and worked up by routine procedures. A face-indexed numerical absorption correction was applied ($T_{\min} = 0.9714$, $T_{\max} = 0.9928$), and the structure was solved by direct methods using the SHELXTL-Plus program library.¹² The combination of intensity statistics with solid-state NMR data (vide infra) allowed unambiguous space group (*P*1) determination. Extinction corrections were not applied, and hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08. Final atomic positional parameters and equivalent isotropic displacement parameters are given in Table II. A plot of the structure of anhydrous copper(II) isovalerate is presented in Figure 1, with bond distances and angles given in Table III. Anisotropic thermal parameters (Table SII), calculated hydrogen atom coordinates (Table SIII), and a listing of observed and calculated structure factors

**Figure 1.** Thermal ellipsoid (50%) and atom-labeling projection of anhydrous copper(II) isovalerate.**Table III.** Bond Lengths (Å) and Angles (deg) in Anhydrous Copper(II) Isovalerate

Cu(1)-O(2)	1.932 (5)	Cu(1)-O(4)	2.010 (4)
Cu(1)-Cu(1A)	2.588 (2)	Cu(1)-O(1A)	1.939 (6)
Cu(1)-O(3A)	1.966 (4)	Cu(1)-O(4A)	2.227 (4)
O(1)-C(1)	1.268 (9)	O(1)-Cu(1A)	1.939 (6)
O(2)-C(1)	1.260 (9)	C(1)-C(2)	1.502 (11)
C(2)-C(3)	1.511 (10)	C(3)-C(4)	1.513 (13)
C(3)-C(5)	1.495 (13)	O(3)-C(6)	1.238 (8)
O(3)-Cu(1A)	1.966 (4)	O(4)-C(6)	1.265 (8)
O(4)-Cu(1B)	2.227 (4)	C(6)-C(7)	1.523 (9)
C(7)-C(8)	1.546 (12)	C(8)-C(9)	1.458 (13)
C(8)-C(10)	1.536 (12)		
O(2)-Cu(1)-O(4)	90.6 (2)	O(2)-Cu(1)-Cu(1A)	84.5 (1)
O(4)-Cu(1)-Cu(1A)	82.4 (1)	O(2)-Cu(1)-O(1A)	169.9 (2)
O(4)-Cu(1)-O(1A)	89.3 (2)	Cu(1A)-Cu(1)-O(1A)	85.5 (2)
O(2)-Cu(1)-O(3A)	89.4 (2)	O(4)-Cu(1)-O(3A)	169.2 (2)
Cu(1A)-Cu(1)-O(3A)	86.9 (1)	O(1A)-Cu(1)-O(3A)	88.7 (2)
O(2)-Cu(1)-O(4A)	95.1 (2)	O(4)-Cu(1)-O(4A)	79.2 (2)
Cu(1A)-Cu(1)-O(4A)	161.7 (1)	O(1A)-Cu(1)-O(4A)	94.8 (2)
O(3A)-Cu(1)-O(4A)	111.5 (2)	C(1)-O(1)-Cu(1A)	121.2 (5)
Cu(1)-O(2)-C(1)	122.8 (5)	O(1)-C(1)-O(2)	126.0 (7)
O(1)-C(1)-C(2)	116.2 (7)	O(2)-C(1)-C(2)	117.8 (7)
C(1)-C(2)-C(3)	113.9 (6)	C(2)-C(3)-C(4)	111.7 (7)
C(2)-C(3)-C(5)	111.7 (7)	C(4)-C(3)-C(5)	111.4 (7)
C(6)-O(3)-Cu(1A)	121.9 (4)	Cu(1)-O(4)-C(6)	124.1 (4)
Cu(1)-O(4)-Cu(1B)	100.8 (2)	C(6)-O(4)-Cu(1B)	135.1 (4)
O(3)-C(6)-O(4)	124.6 (6)	O(3)-C(6)-C(7)	117.7 (6)
O(4)-C(6)-C(7)	117.7 (5)	C(6)-C(7)-C(8)	111.4 (6)
C(7)-C(8)-C(9)	115.0 (7)	C(7)-C(8)-C(10)	106.7 (7)
C(9)-C(8)-C(10)	111.7 (7)		

are available as supplementary material.

Results

¹³C CP/MAS NMR Spectroscopy. Before the presentation of NMR and X-ray results, it is appropriate to discuss our reasons for investigating these anhydrous ($n = 0$) materials rather than their better known solvated counterparts ($n = 2$). Numerous attempts to obtain CP/MAS NMR spectra of the solvated materials in this work have met with failure at temperatures as low as ca. 130 K due to excessive ¹³C line widths (see, however, ref 5d). The question of line broadening due to inhomogeneous (anisotropic bulk magnetic susceptibility, ABMS) versus homogeneous (relaxation) effects in paramagnetic solids has been addressed by Ganapathy and Bryant.¹³ They propose that ABMS effects can be assessed by cogrinding the compound of interest with a material characterized by isotropic BMS (e.g., adamantane,

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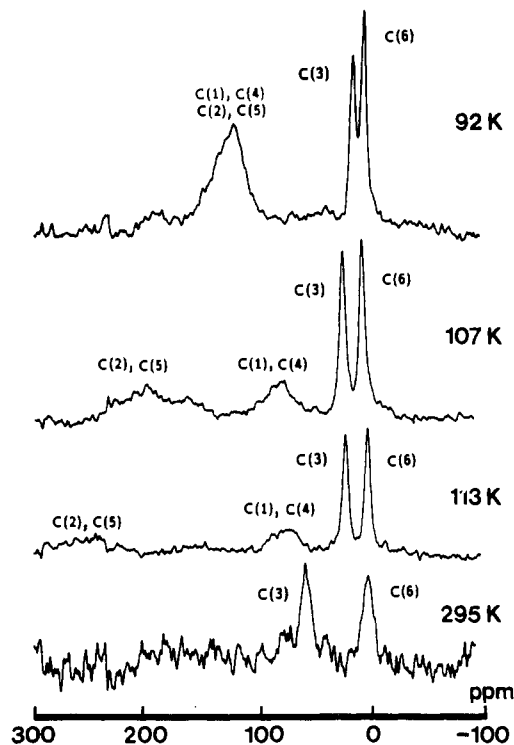


Figure 2. Variable-temperature ^{13}C CP/MAS NMR spectra of anhydrous copper(II) propionate. Signal assignments and their structural implications are discussed in the text.

$\text{C}_{10}\text{H}_{16}$). The absence of line broadening in the ^{13}C resonances of the latter medium indicates insignificant ABMS (from an NMR point of view) in the paramagnetic solid. We performed Ganapathy and Bryant's experiment for solvated analogues of all the copper(II) carboxylates discussed in this contribution. In each case, line broadening of ^{13}C adamantane resonances was not observed in the coground mixtures. While this could indicate the importance of electron relaxation effects in the determination of NMR line widths, the issue is somewhat clouded by the overall similarity in the ESR spectra of copper(II) carboxylates, regardless of their extent of solvation.^{2c}

Our understanding of the dominant line-broadening influences in the solvated carboxylates is thus somewhat incomplete, but we are still able to determine magnetic and structural properties of the unsolvated carboxylates. Paramagnetic chemical shift and line width behavior for copper(II) carboxylates can be most meaningfully discussed relative to the appropriate critical temperatures, T_c 's, defined as those temperatures above which the susceptibility of these materials decreases with increasing T . NMR spectra are characterized by temperature-dependent chemical shifts and line widths that, below T_c , increase in magnitude with increasing T and (to a first approximation) decreasing distance from the metal centers. This behavior is illustrated in Figures 2–4, which show the ^{13}C CP/MAS NMR spectra at representative temperatures for the propionate, isobutyrate, and isovalerate, respectively. T_c 's for copper(II) carboxylates are generally in the vicinity of ambient temperature.¹⁴

Signal assignments for $\text{Cu}_2(\text{prop})_4$ (Figure 2) conform to the precedent established in the literature crystal structure report for this compound.¹⁵ For example, C(3) and C(6) refer to methyl carbon resonances on crystallographically inequivalent alkyl chains (vide infra). Explicit functional group representations are used to assign the $\text{Cu}_2(i\text{-but})_4$ spectra in Figure 3, as the crystal structure for this material is currently unreported. Finally, $\text{Cu}_2(i\text{-val})_4$ signal assignments (Figure 4) use the numbering scheme established in Figure 1 from our X-ray crystal structure

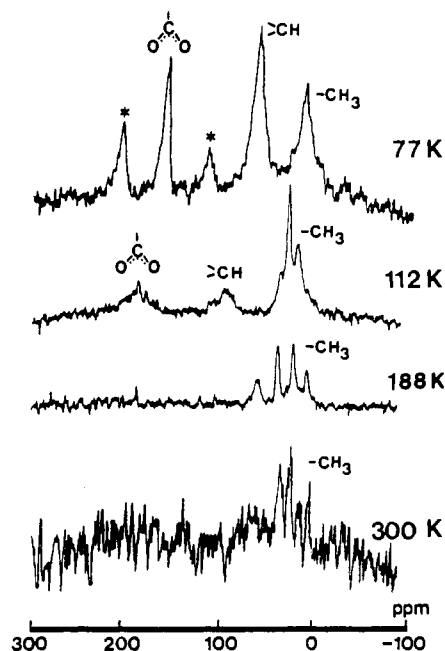


Figure 3. Variable-temperature ^{13}C CP/MAS NMR spectra of anhydrous copper(II) isobutyrate. Signal assignments are as indicated, and asterisks denote spinning sidebands.

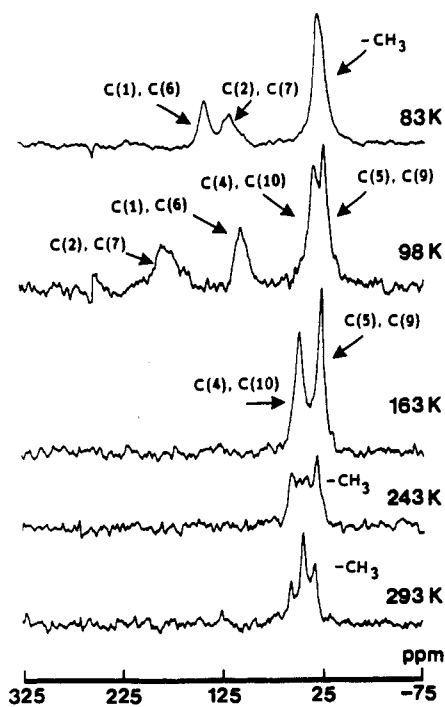


Figure 4. Variable-temperature ^{13}C CP/MAS NMR spectra of anhydrous copper(II) isovalerate. Signal assignments are based on the numbering scheme established in Figure 1. The signal intensity in the 83 K spectrum is reduced by a factor of 8 for this presentation.

determination. It is significant to note that in each stack plot there are temperatures at which two or more methyl carbon resonances are resolvable. These correspond to the presence of crystallographically inequivalent methyl carbon sites in the unit cells of these compounds. Similar inequivalencies are sometimes observed in solid-state NMR spectra of diamagnetic organic and organometallic compounds.¹⁶ Note that methyl carbon resonances in Figure 2 have been assigned to specific crystallographic sites—the

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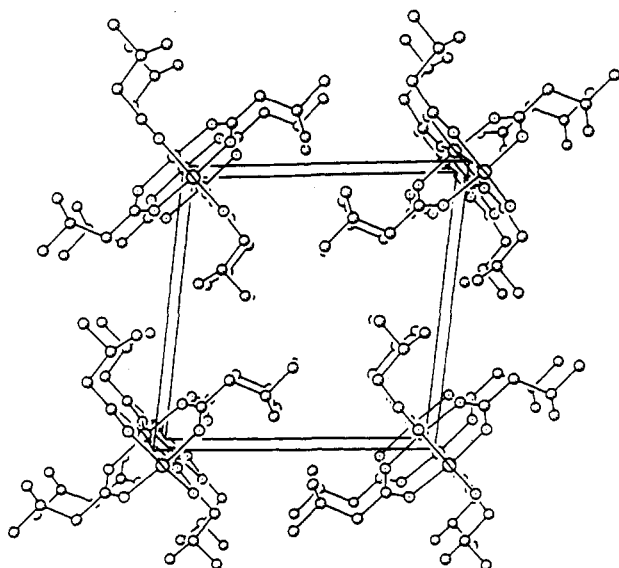


Figure 5. Packing diagram of anhydrous copper(II) isovalerate viewed down the b axis. Atoms are represented as balls, while bonds are shown as solid lines.

rationale for this will be presented in the Discussion.

Crystal Structure of $\text{Cu}_2(i\text{-val})_4$. This report includes the X-ray crystallographic structure determination of anhydrous copper(II) isovalerate. The structure (Figure 1, Tables I and II) is typical of that found for a variety of anhydrous copper(II) carboxylates.¹⁷ The copper-copper distance is 2.588 (2) Å, and dinuclear metal centers are bridged by four isovalerate ligands. The extended polymeric structure consists of chains of dimeric units. Figure 5 is a drawing of the unit cell of $\text{Cu}_2(i\text{-val})_4$ based on our measurement. The presence of an inversion center (space group $P\bar{1}$) renders pairs of bridging isovalerate ligands structurally equivalent.

Discussion

NMR Signal Multiplicity and Compound Structure. The crystal structure of $\text{Cu}_2(\text{prop})_4$ was reported in the literature by Simonov and Malinovskii in 1970.¹⁵ They found the unit cell of this compound to be triclinic with space group $P\bar{1}$ and a copper-copper distance of 2.578 (4) Å. The structure of the propionate is thus completely analogous to that of the isovalerate and n -butyrate.⁴ The room-temperature CP/MAS NMR spectrum of the propionate (Figure 2, bottom) contains two resolvable ^{13}C signals. Both survive the interrupted decoupling experiment¹¹ and are therefore assigned to methyl carbons (C(3), C(6)).

As we showed before with copper(II) n -butyrate,⁴ solid-state NMR spectroscopy can resolve signals from ^{13}C sites along crystallographically inequivalent carboxylate bridges in these compounds. The resolution of two methyl carbon signals is useful in structural studies, as it suggests the presence of an inversion center in the unit cell. This eliminates the need to solve the crystal structure in the noncentrosymmetric space group $P1$. Such an interpretation assumes no coincidental overlap of methyl carbon resonances—a likely situation at some temperature over the entire range accessible to VT CP/MAS NMR spectroscopy, given the relatively large temperature-dependent chemical shifts and modest line widths characteristic of anhydrous copper(II) carboxylates (vide infra). In this example, the solid-state NMR structural information was, of course, not used to aid in the crystal structure determination. It does, however, serve to illustrate the potential for other applications in the determination of X-ray crystal structures where ambiguities exist.

Such is the case for the structure of copper(II) n -butyrate discussed in ref 4 and also that of the isovalerate presented herein. From the symmetry of the unit cell drawing in Figure 5, one would

expect four nonequivalent methyl groups in $\text{Cu}_2(i\text{-val})_4$. The room-temperature ^{13}C CP/MAS NMR spectrum (Figure 4, bottom), however, contains only three signals. Since all are relatively upfield and survive 50 μs of interrupted decoupling,¹¹ it is reasonable to assign these resonances to methyl groups. Note that the approximate relative intensities are 1:2:1. Cooling the sample to 243 K results in the appearance of a fourth methyl signal along with a redistribution of relative intensities (about 1:1:1:1). Only the most and least shielded resonances have chemical shifts that are understandable in terms of exchange coupling between copper centers.⁴ The temperature-dependent behavior exhibited by the other methyl signal(s) is perhaps consistent with a dynamic process by which exchange occurs between two crystallographically inequivalent methyl sites at ambient temperature. If so, then it is only when the sample is cooled to temperatures sufficient to retard the relevant motion that expected signal multiplicity and relative intensities are observed. Below 243 K, methyl carbon resonance positions are dictated by increasingly important contributions from the temperature-dependent magnetic properties to be discussed below.

Probing the relationship between ^{13}C CP/MAS NMR signal multiplicity and compound structure is more difficult, yet perhaps more informative, for copper(II) isobutyrate than for any of the other materials discussed thus far. Numerous attempts were made to obtain single crystals of the isobutyrate that were suitable for crystallographic structure determination—all were unsuccessful. Fortunately, powdered samples are perfectly adequate for characterization by solid-state NMR techniques. The CP/MAS spectra presented in Figure 3, in fact, represent the most structural information yet published for copper(II) isobutyrate.

Note that in Figure 3 the 300 K CP/MAS NMR spectrum contains several signals—the ambiguity concerning exactly how many are present is clarified by 188 K where four resonances are clearly distinguishable. All of these peaks survive interrupted decoupling¹¹ and may thus be assigned to methyl carbons on the isobutyrate bridges. It therefore seems reasonable to expect that the structure of copper(II) isobutyrate may be analogous to that of the isovalerate discussed above. The similarity between temperature-dependent spectral parameters for these two branched compounds lends further credence to this hypothesis.¹⁸

It is worth mentioning that, although we expect to be able to resolve two ^{13}C CP/MAS resonances for each carbon type in these compounds, the distinction is only apparent in the methyl spectral region. With reference to the unit cell of $\text{Cu}_2(i\text{-val})_4$ as a representative case (Figure 5), structural inequivalence between carboxylate bridges is most pronounced at the methyl carbon sites. This is reflected in the NMR spectra. Relatively broad NMR line widths for the resonances due to carbons closer to the metal centers combine with these less inequivalent positions in the unit cell to prevent observation of the expected multiplicities for non methyl carbon signals.

Temperature-Dependent Shifts and Magneto-Structural Correlations. In attempting to describe the variation in ^{13}C resonance positions with temperature for these coupled d^9 systems, both contact⁸ and dipolar (pseudocontact)²⁰ contributions must be considered. Expressions can be developed that incorporate a term to account for the thermal distribution of electronic spins between the ground ($S = 0$) and excited ($S = 1$) states.²¹ Reference 4

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(18) An additional similarity between the NMR spectral results for the isobutyrate and isovalerate concerns their behavior toward the interrupted decoupling experiment. For copper(II) isobutyrate, the methyl carbon resonances that persist below about 98 K do not survive 50 μs of interrupted decoupling. The same is true of the more downfield methyl carbon resonance in the spectra of copper(II) isovalerate below about 150 K and the more upfield methyl signal below 110 K. Since similar observations were made for diamagnetic model compounds, this behavior is probably characteristic of methyl group motion that is not so slow as to make resonances unobservable (ca. 48 kHz)¹⁹ yet is slow enough that efficient (i.e., uninterrupted) proton decoupling is required for detection of ^{13}C signals. We are unaware of a previous report of this phenomenon in the literature.

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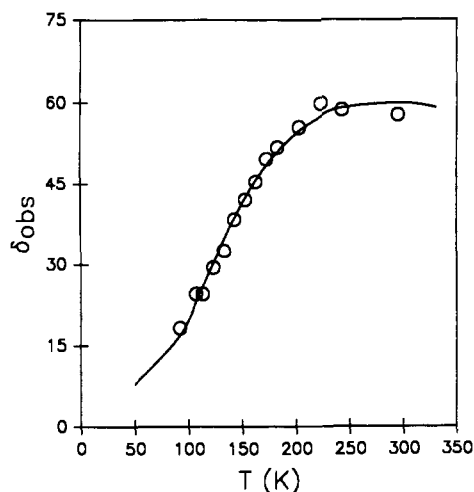


Figure 6. Plot of the downfield methyl carbon (C(3)) chemical shift vs absolute temperature for anhydrous copper(II) propionate. Circles are the experimental points, and the solid curve is the theoretical fit.

presents additional background and the relevant equations. For contact shifts, the observed NMR frequency (H_{obs}) is given by

$$H_{\text{obs}} = H_{\text{dia}} + \frac{2g\beta H_0 A}{(\gamma_c/2\pi)kT}(3 + e^{2J/kt})^{-1}$$

where H_{dia} is the frequency that the same nucleus would have in an equivalent diamagnetic environment, T is the absolute temperature, and the other terms have their usual meanings.

Equation 2 of ref 4 is the corresponding expression for the dipolar contribution to the observed shifts. As was the case with copper(II) *n*-butyrate,⁴ the dipolar contribution to the observed shifts for the propionate and isovalerate may be estimated from structural and magnetic parameters. Once again, the dipolar influences are found to be very minor and can be neglected. Due to the similarity between the NMR results for these compounds and those for the isobutyrate (vide supra), we feel justified in assuming that dipolar contributions to observed shifts for copper(II) isobutyrate are likewise negligible. $-2J$, H_{dia} , and A values can thus be estimated by using a nonlinear least-squares procedure to fit the VT CP/MAS NMR data to the contact shift equation presented above.

Figure 6 is a graphical depiction of the variation of observed chemical shift with absolute temperature. This illustrates the behavior found for the more downfield methyl carbon resonance in $\text{Cu}_2(\text{prop})_4$ and is very similar to data obtained for methyl resonances in the isobutyrate and isovalerate (plots not shown). Corresponding plots of chemical shift versus temperature can be made for other resolvable ^{13}C signals. In all cases, these plots resemble those found for the thermal variation of magnetic susceptibility in copper(II) carboxylates.¹⁰ Both parameters increase with temperature up to T_c ; beyond this they decrease due to increased randomization of unpaired electron orientation.

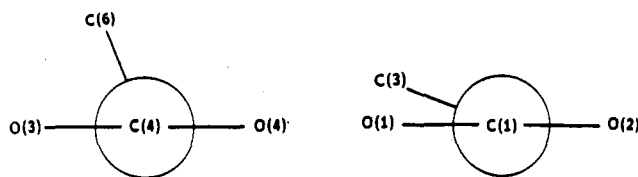
In copper(II) propionate, methylene and carboxylate carbon resonances are not observable over a sufficiently wide temperature range to yield similar plots. Also, the more upfield methyl carbon resonance shifts only slightly with changes in temperature between 300 and 77 K. The temperature-dependent chemical shift data presented in Figure 6 were thus the only propionate results that could be fit to the equation for the estimation of $-2J$, H_{dia} , and A . The singlet-triplet energy level separation ($-2J$) was calculated as $-314 \pm 4 \text{ cm}^{-1}$. This result agrees quite well with the value of -315 cm^{-1} determined previously by using variable-temperature bulk magnetic susceptibility measurements.¹⁰ The estimated diamagnetic chemical shift (9 ppm) was also typical of that expected for methyl carbons in ^{13}C spectra. Finally, the electron-

nucleus hyperfine coupling constant (A) was calculated as $0.467 \pm 0.01 \text{ MHz}$. A consideration of values for longer chain copper(II) carboxylates⁴ suggests that this value is reasonable for a nuclear site two bonds removed from a carboxylate carbon.

As already mentioned, the temperature dependence of the upfield methyl carbon (C(6)) resonance position could not be analyzed through the statistical procedure, since it changed only slightly with temperature. This is because the A value for this crystallographic site is evidently much less than 0.467 MHz , and therefore the extent of unpaired electron delocalization at C(6) is reduced relative to that found at the other methyl group. At this point, one might envision some sort of dihedral angle analysis similar to that used for copper(II) *n*-butyrate⁴ to assign the methyl resonances to particular carbon centers in the unit cell of the propionate.

This type of treatment, however, is somewhat more tenuous in the current example than it was for copper(II) *n*-butyrate. Karplus curves relating the magnitudes of coupling constants to dihedral angles are generally based upon a three-bond separation. In copper(II) propionate, there are only two intervening carbon-carbon bonds—a fact which might seem to restrict a structural analysis of A values for this compound. Both theory²² and experiment⁴ suggest, however, that unpaired electron density in copper(II) carboxylates is delocalized throughout the ligands with the oxygen atoms playing a primary role in the exchange coupling.

With this in mind, projections can be drawn as viewed from the site between the copper ions in individual dimers. The result is the establishment of three-bond O-C-C angles. Consider the result for the copper(II) propionate structural data presented in ref 15.



C(1) and C(4) are carboxylate carbons, while the methyl group carbons are designated C(3) and C(6). It is now reasonable to discuss dihedral angles in a manner equivalent to that used in ref 4 for copper(II) *n*-butyrate. The only difference is that in the present case two angles, therefore two A values (assumed additive), must be considered for each crystallographically inequivalent carboxylate bridge. The projection on the left has $\theta_{\text{O}(3)\text{-C}(6)}$ equal to 68° with $\theta_{\text{O}(4)\text{-C}(6)}$ its supplement. Both angles correspond to minimum coupling constants,⁹ so the net A value is expected to be small. Contrast this with the situation illustrated on the right, where both three-bond O-C-C angles (20° and 160°) are expected to generate maximum coupling constants.⁹ The resultant A value is expected to be relatively larger. It is therefore reasonable to assign the resonance designated C(3) in Figure 2 to the methyl group showing pronounced changes in chemical shift with changing temperatures.

Statistical analyses of the temperature-dependent chemical shifts for the isobutyrate and isovalerate were performed in a manner analogous to that outlined above. The results for anhydrous copper(II) isobutyrate are collected in Table IV. The overall similarity in signs and relative magnitudes between these parameters and those reported for the corresponding straight-chain compound⁴ is striking. Results presented in Table IV suggest that $-2J \approx -310 \text{ cm}^{-1}$ is a reasonable value for the singlet-triplet energy level separation. We were unable to find a $-2J$ value from variable-temperature magnetic susceptibility measurements for comparison with this result. One other distinction between the magnetic properties of copper(II) isobutyrate and those reported for either the *n*-butyrate or propionate pertains to the signs of methyl carbon A values. The most upfield methyl signal in Figure 3 is characterized by a negative electron-nucleus hyperfine cou-

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Table IV. Calculated Magnetic and Electronic Parameters for Anhydrous Copper(II) Isobutyrate^a

	carbon	
	carboxylate	methine
$-2J$, cm ⁻¹	-310 ^b	-310 ^b
A , MHz	-1.93 ± 0.07	3.23 ± 0.08
$\delta_{\text{dia,calc}}$	184 ^b	34 ^b
$\delta_{\text{dia,expt}}$ ^c	184	34

	methyl carbon ^d			
	1	2	3	4
$-2J$, cm ⁻¹	-309 ± 6	-296 ± 8	-310 ^b	-318 ± 5
A , MHz	0.467 ± 0.02	0.135 ± 0.01	0.0775 ± 0.02	-0.225 ± 0.07
$\delta_{\text{dia,calc}}$	9 ± 3	18 ± 1	9 ± 2	22 ± 1
$\delta_{\text{dia,expt}}$ ^c	19	19	19	19

^aUncertainties are expressed as one standard deviation. All chemical shifts are in ppm. ^bConstrained parameter. ^cSolution-state ¹³C chemical shifts of isobutyric acid. ^dHigher numbers indicate increased shielding.

Table V. Calculated Magnetic and Electronic Parameters for Anhydrous Copper(II) Isovalerate^a

	carbon			
	C(1), C(6)	C(2), C(7)	CH ₃ ^b	CH ₃ ^c
$-2J$, cm ⁻¹	-305 ^d	-305 ^d	-305 ± 3	-305 ^d
A , MHz	-2.88 ± 0.2	4.41 ± 0.2	0.201 ± 0.004	0.0480 ± 0.01
$\delta_{\text{dia,calc}}$	188 ± 4	48 ^d	26 ± 0.6	18 ± 1
$\delta_{\text{dia,expt}}$ ^e	184	48	25	25

^aUncertainties are expressed as one standard deviation. All chemical shifts are in ppm. ^bDownfield methyl carbon signal. ^cUpfield methyl carbon signal. ^dConstrained parameter. ^e¹³C chemical shifts of sodium isovalerate, a diamagnetic model compound.

pling constant (i.e., the resonance appears upfield of its diamagnetic value in Figure 3 at room temperature). A consideration of Karplus curves for three-bond coupling constants in carboxylate compounds²³ suggests that this observation is reasonable and related to the dihedral angle between the orbital containing unpaired electron density and this methyl site.

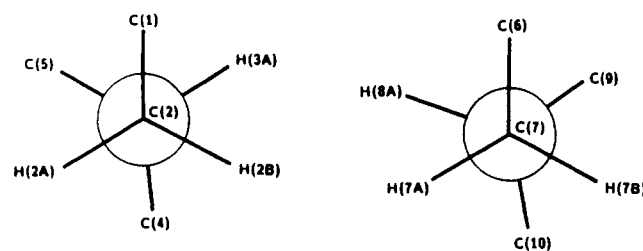
In addressing the magnetic properties of anhydrous copper(II) isovalerate, we find potentially 10 resonances that could be subjected to analysis through the contact shift equation (five ¹³C sites along each of two crystallographically inequivalent carboxylate bridges). Two practical considerations, however, limit the number of available signals. First, notice that Figure 4 does not contain any signal(s) attributable to methine carbons. This is probably a result of the complex nature of the upfield portions of the spectra presented in Figure 4. Model compound chemical shift data suggest that the methine carbon resonance is probably a contributor to some of the upfield spectral intensity below about 180 K.⁴ The expected (relatively small) hyperfine coupling constant for this site combined with the presence of several methyl resonances in the appropriate spectral region obscures the observability of methine signals. Also, chemical exchange between two of the methyl groups at ambient temperature (vide supra) prevents a description of their temperature-dependent resonance positions with the equation.

The result is that only carboxylate, methylene, and two of the methyl carbon signals are amenable to statistical analysis. The results for these ¹³C sites are reported along with their standard deviations in Table V. The limited temperature range over which carboxylate and methylene signals were observable dictated the constraint of several parameters in the analyses. Table V reports the result of a two-parameter fit for the carboxylate signal ($-2J$ constrained to -305 cm⁻¹) and a one-parameter fit for the methylene resonance ($-2J \equiv -305$ cm⁻¹ and $\delta_{\text{dia}} \equiv 48$ ppm). These defined parameters were obtained from the statistics of the downfield methyl carbon resonance and the diamagnetic chemical

shifts in sodium isovalerate, respectively. $-2J$ also had to be constrained to -305 cm⁻¹ for the fit of the upfield methyl data—not an unexpected requirement, considering the relatively small hyperfine coupling constant for this site.

The $-2J$ value calculated from the downfield methyl carbon data is consistent with what would be expected for this compound, although there is no reported literature value for comparison. Diamagnetic chemical shifts, where estimated, were in agreement with those found for the diamagnetic model compound and isovaleric acid solution. Electron-nucleus hyperfine coupling constants (A values) were estimated for each carbon site exhibiting temperature-dependent shifts describable by the equation. The results are consistent with those found for copper(II) *n*-butyrate⁴ and indicate that unpaired electron density is delocalized in σ orbitals between the methylene and methyl carbons.²⁴ Also, spin polarization by unpaired electron density in lone-pair oxygen orbitals may be invoked to account for the negative A value observed at C(1) and C(6).²⁵

Estimated A values for methyl carbon sites may again be related to the angular structure of the superexchange pathway. Newman projections



drawn on the basis of the X-ray crystal structure determination serve to illustrate the pronounced angular differences between the two inequivalent isovalerate bridges. Maximum hyperfine coupling constants are expected for methyl carbons C(4) and C(10), and relatively smaller A 's should be characteristic of methyl sites designated C(5) and C(9). The downfield methyl resonance in Figure 4 is assignable to methyl carbon(s) C(4) and/or C(10), while the more upfield signal is due to carbon(s) C(5) and/or C(9). More exact assignment of ¹³C CP/MAS NMR methyl carbon resonances to specific crystallographic locations is impossible due to the chemical exchange already discussed.

Conclusion

Variable-temperature ¹³C CP/MAS NMR studies of three anhydrous copper(II) carboxylates have been presented that establish the generality of the approach⁴ for the determination of magnetic and structural properties. Singlet-triplet energy level separations ($-2J$), electron-nucleus hyperfine coupling constants (A), and diamagnetic chemical shifts (δ_{dia}) are available from an appropriate analysis of the temperature dependence of the ¹³C chemical shifts. Although attempts at similar investigations of solvated copper(II) carboxylates were unsuccessful, the method should be useful in the study of a variety of metal dimers and clusters whose ¹³C CP/MAS NMR resonances are not excessively broad.

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Supplementary Material Available: Table SI, detailing the structural determination, and Tables SII and SIII, listing thermal parameters and calculated H atom coordinates (2 pages); a listing of calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

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