calculated with the two larger basis sets is probably fairly accurate for $SF_3{\equiv}CH$, and the remaining qualitative changes, particularly the changes in dipole direction on fluorination, should reflect reality. A positive value for the dipole moment corresponds to carbon positive with respect to sulfur. A rough estimate of the basis-set effect may be obtained by noting that for $SF_3{\equiv}CH$ the calculation with d functions on only the sulfur atom drew excessive electron density to the sulfur atom (as compared with the calculations with the larger, more balanced basis sets) to an extent that made the dipole moment too positive by about 1 D. A similar situation may be expected for the computed dipole moments of $SH_3{\equiv}CH$, $SF_3{\equiv}CF$, and $SF_3{\equiv}C{-}CF_3$.

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Registry No. $SH_3{\equiv}CH$, 91759-11-4; $SF_3{\equiv}CH$, 91759-12-5; $SF_3{\equiv}CF$, 91759-13-6; $SF_3{\equiv}C{-}CF_3$, 88476-03-3.

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^{13}C CP/MAS NMR and Crystallographic Investigations of the Structure and Solid-State Transformations of Lead(II) Acetate Trihydrate

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Lead(II) acetate trihydrate undergoes solid-state transformations at room temperature, resulting in anomalous and variable peaks in the ^{13}C cross-polarization magic-angle-spinning (CP/MAS) NMR spectra of powder samples of this compound. Isotropic chemical shift differences of up to 12 ppm are observed for the carboxyl carbons as a result of these rearrangements; 2 ppm differences are observed for the methyl carbons. We have demonstrated the usefulness of ^{13}C CP/MAS NMR studies in conjunction with X-ray crystallographic analysis for monitoring solid-state reactions and providing a structural basis for some of the observed spectral features. The ^{13}C CP/MAS NMR spectrum of lead(II) acetate trihydrate changes from a single sharp resonance at 51 ppm (relative to benzene) for the carboxyl carbon and at −103 ppm for the methyl group, to patterns having several lines in the carboxyl region and two lines in the methyl region. X-ray crystal structure analysis of lead(II) acetate shows that there are two crystallographically nonequivalent acetate groups per molecule that differ in their intermolecular interactions; however, these chemical differences are not sufficient to yield resolvable isotropic chemical shifts for the carboxyl or methyl groups. Crystal data: $PbC_4O_7H_{12}$, $a = 15.803$ (2) Å, $b = 7.269$ (2) Å, $c = 9.049$ (2) Å, $\beta = 109.55$ (3)°; monoclinic, $C2/m$, $Z = 4$, 1526 unique reflections, collected on an automatic diffractometer, 1124 with $I > 3\sigma(I)$ used for structure solution; Patterson and Fourier syntheses used for structure solution; full-matrix least-squares refinement to $R = 0.043$. The lead atom is nine-coordinate with two bidentate acetate groups, three coordinated water molecules, and two bridging bonds to oxygens on neighboring acetate groups. Intramolecular Pb–O distances range from 2.446 (8) to 3.11 (1) Å.

Introduction

During our investigations of ^{13}C chemical shielding anisotropies in a series of metal acetates, we have found that, unlike other acetates we have studied, lead(II) acetate and calcium(II) acetate give multiple CP/MAS isotropic lines instead of the expected single line for each of the chemically distinct carbon atoms.[1] Although both lead acetate and calcium acetate yielded apparently simple powder line shapes in the static sample, we did not analyze them for chemical shielding tensors in our previous work because of the presence of more than one CP/MAS line. Crystallographic anomalies are often cited in the literature as the probable cause of anomalous peaks in solid-state high-resolution NMR spectra, but only rarely have actual correlations between spectral patterns and crystal structure features been made. Crystal effects that can lead to extra peaks or peaks with unexpected or varying intensities include loss of molecular point group symmetry in the crystal space group,[2] the presence of more than one molecule in an asymmetric unit,[3] occurrence of different conformers in the solid state compared to solution,[4] and interactions with neighboring quadrupolar nuclei such as ^{14}N, ^{2}H, ^{35}Cl, ^{63}Cu, etc.[5] The coexistence of multiple solid-state phases due to impurities, amorphous regions, polymorphism, or cocrystallization[6] and the occurrence of solid-state phase transformations[6,7] can also cause anomalous spectral features. The fact that such anomalies are observed indicates the sensitivity of ^{13}C CP/MAS NMR to changes in the chemical environment of particular functional groups in the solid state. In this study we report the crystal structure and CP/MAS ^{13}C NMR spectra of $Pb(O_2C_2H_3)_2{\cdot}3H_2O$. The NMR spectra show multiple lines for the carboxyl and methyl portions of the spectrum that are not due to the specific packing pattern of $Pb(O_2C_2H_3)_2{\cdot}3H_2O$ but that arise from chemical changes in the solid state associated with the loss of volatile components (water and acetic acid). The study illustrates the ease with which solid-state reactions may be followed with ^{13}C CP/MAS NMR.

Experimental Section

Commercial samples were obtained as follows: calcium acetate hydrate, technical grade (MCB); lead(II) acetate trihydrate, AG grade (Mallinckrodt); lead subacetate, ACS grade (Aldrich); lead carbonate,

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0020-1669/84/1323-3580$01.50/0

Table I. Positional Parameters and Their Estimated Standard Deviations for $Pb(O_2C_2H_3)_2 \cdot 3H_2O$ (Oxygens from Water Molecules Indicated by w)

atom	x	y	z	B_{av}, Å^2
Pb1	0.16804 (3)	0.000	0.41321 (6)	2.12
O1	0.3031 (5)	0.149 (1)	0.6264 (8)	3.07
O3	0.2835 (6)	0.000	0.2884 (11)	2.80
O4	0.1516 (7)	0.000	0.1024 (14)	4.42
O5(w)	0.0871 (5)	0.231 (1)	0.6015 (9)	4.80
O6(w)	0.0343 (8)	0.000	−0.2118 (14)	4.87
C1	0.343 (1)	0.000	0.679 (1)	2.16
C2	0.436 (1)	0.000	0.785 (2)	3.79
C3	0.233 (1)	0.000	0.143 (2)	3.34
C4	0.281 (1)	0.000	0.020 (2)	5.76

reagent grade (Merck). Recrystallizations were done as described in the text. All NMR measurements were made on a home-built spectrometer described previously[1] operating at 14.195 and 56.44 MHz for ^{13}C and ^{1}H, respectively. ^{13}C cross-polarization magic-angle-spinning spectra were obtained by employing a single-contact Hartman–Hahn match with ^{1}H rf field of at least 10 G; typically several thousand free-induction decays were signal averaged to improve signal to noise ratio. Infrared spectra were run on a Perkin-Elmer 297 grating spectrphotometer.

X-ray Analysis

A brilliant colorless rod-shaped crystal, 0.26 × 0.10 × 0.10 mm, was obtained by recrystallization from water. After about 0.5 h in the air, some opaque white domains had become apparent on the crystal faces. The crystal was immediately sealed in a capillary, and no further decomposition was visible for the remainder of the data collection. The lattice parameters were determined, at room temperature, on an Enraf-Nonius CAD-4 diffractometer using 18 reflections in the θ range 10–25° (Mo Kα radiation, $\lambda = 0.7107$ Å, graphite monochromator) to give $a = 15.803$ (2) Å, $b = 7.269$ (2) Å, $c = 9.049$ (2) Å, $\beta = 109.55$ (3)°, $Z = 4$, $V = 979$ Å^3, $\rho = 2.41$ g cm^{-3}. From systematic extinctions (hkl) ($h + k$ odd), the space group was determined to be $C2$ or $C2/m$. The structure was solved in $C2/m$. A total of 1603 reflections were collected in the θ range 0–30°, in the hkl octant ($h_{max} = 22$, $k_{max} = 10$, $l_{max} = 12$). A total of 1526 unique reflections were obtained, of which 1124 were observed at the $I > 3\sigma(I)$ significance level. Three reflections used as intensity standards showed no significant loss in intensity during data collection. Empirical absorption corrections were made with relative transmission factors ranging from 1.00 to 0.82.[8] The absorption coefficient was 169 cm^{-1}, and $F(000) = 652$. The structure was solved from Patterson and Fourier syntheses and refined with full-matrix least-squares refinement on F's, using the programs available in the Enraf-Nonius Structure Determination Package.[9] Refinement of the non-hydrogen atoms with anisotropic temperature factors converged with $R = 0.043$, $R_w = 0.051$ ($w = 1/\sigma^2(F_o)$, where $\sigma(F_o)$ is calculated from $\sigma^2(I) = \sigma^2(I)_{counting} + (0.3I)^2$). A difference Fourier map revealed several peaks of intensity >1.0 e/A^3, but their positional parameters did not correspond to expected hydrogen positions. Hydrogen atoms were not included in the final refinements. The largest parameter shift in the final least-squares cycle was 0.03 time its esd. The esd in an observation of unit weight is 1.38. Positional parameters are given in Table I. Thermal parameters and structure factor tables are available as supplementary material.

Results

Optical Microscopy and Infrared Analysis of Phase Changes. When freshly recrystallized lead acetate crystals or powder are exposed to the atmosphere, they begin to turn opaque and white within about 0.5 h. After 24 h, optical microscopy shows that the crystals have turned completely opaque and that this polycrystalline character extends throughout the bulk of the crystal. Single crystals retain their morphology but are easily crumbled by gentle pressure. When one large single crystal is heated over a low Bunsen burner flame, the (100) faces turn completely opaque,[10] while the other faces remain clear. When a single crystal is exposed to infrared radiation, however, the crystal face which is directly exposed to the radiation turns opaque immediately. Infrared analysis of Nujol mulls of the opaque solid showed that their spectra matched standard spectra of lead subacetate,[11] $Pb(O_2C_2H_3)_2 \cdot 2Pb(OH)_2$. It was not possible to obtain an infrared spectrum of $Pb(O_2C_2H_3)_2 \cdot 3H_2O$ since it rearranges in the infrared beam.[12]

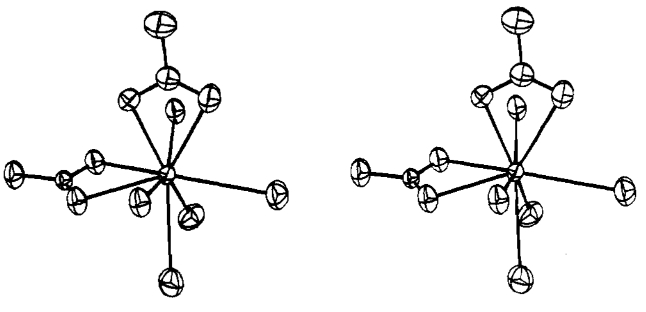

Figure 1. ORTEP stereoview of the Pb environment in $Pb(O_2C_2H_3)_2 \cdot 3H_2O$. The nine-coordinate central lead atom has two bidentate acetate groups, three coordinated water molecules, and two O1 oxygen atoms that form bridging bonds to neighboring lead atoms. The thermal ellipsoids are drawn at a probability level of 50%.

Table II. Selected Intra- and Intermolecular Bond Lengths (Å) and Angles (deg) and Estimated Standard Deviations for $Pb(O_2C_2H_3)_2 \cdot 3H_2O^a$

	Distances		
Pb–O1	2.59 (1)	C1–O2	1.46 (2)
Pb–O1′	2.64 (1)	C3–O3	1.29 (1)
Pb–O3	2.45 (1)	C3–O4	1.22 (1)
Pb–O4	2.74 (1)	C3–C4	1.53 (1)
Pb–O5	2.97 (1)	O4–O6′	2.83 (2)
Pb–O6	3.11 (1)	O5–O6′	2.70 (2)
C1–O1	1.26 (1)	O5–O3′	2.76 (1)
	Angles		
O1–Pb–O1′	63.8 (2)	O1–C1–O1′	118 (1)
O1–Pb–O1″	49.6 (3)	O3–C3–O4	112.2 (8)
O3–Pb–O4	49.8 (3)	Pb–O3–O5′	114.2 (4)
O5–Pb–O5′	68.8 (4)	Pb–O4–O6′	147.0 (5)
O5–Pb–O6	77.3 (4)	O5–O6–O5″	76.7 (6)

[a] Single prime superscripts indicate intermolecular bonds; double primes indicate atoms related by a mirror operation to the corresponding nonprimed atom.

Fresh $Pb(O_2C_2H_3)_2 \cdot 3H_2O$ can be stored in a tightly capped vial for several weeks without visible signs of deterioration. When it is placed in a vacuum desiccator, it turns opaque and white almost immediately. Similarly, heating a powder sample on a hot plate to about 100 °C results in a rapid change to opaque white crystals and a noticeable odor of acetic acid.

Molecular and Crystal Structures of $Pb(O_2C_2H_3)_2 \cdot 3H_2O$. The molecular structure of lead(II) acetate trihydrate, as determined from this X-ray crystal structure analysis, shows that there are three coordinated water molecules and two bidentate acetate groups present. The acetate group, O3–C3–O4, lies in a mirror plane that bisects the O1–C1–O1′

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(10) Crystal morphology assigned by matching our crystal planes to those assigned by optical goniometry and reported by: Groth, P. "Elementen der Physikalischen und Chemischen Krystallographie"; R. Oldenbourg; München, Berlin, 1921; p 139.

(11) Sadtler Spectrum No. 63400K, Sadtler Research Laboratories, Standard Infrared Grating Spectra, Bio-Rad Laboratories Researchers, Editors & Publishers, 1983.

(12) An IR spectrum of lead(II) acetate trihydrate is reported as such in the literature;[13] however, that spectrum is most likely due to lead subacetate also since it matches the Sadtler reference for lead subacetate.[11]

(13) Sawyer, D. T.; Paulsen, P. J. *J. Am. Chem. Soc.* **1959**, *81*, 818.

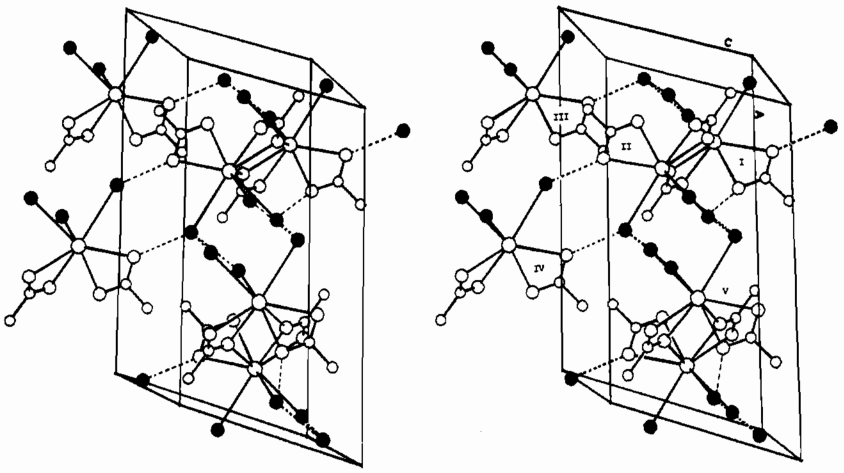


Figure 2. [010] ORTEP stereoview of the unit cell of $Pb(O_2C_2H_3)_2·3H_2O$. Intermolecular hydrogen bonds are shown by dotted lines, and water oxygen atoms are shaded. Inversion-related molecules I and II are associated into chains via intermolecular Pb···O1 contacts between I (*x*, *y*, *z*) and II ($^1/_2 - x$, $^1/_2 - y$, $1 - z$). These chains are further linked by hydrogen bonds from O4 on molecule II to O6 on molecule IV ($^1/_2 + x$, $^1/_2 - y$, $1 + z$) and from the same O6 to O5 and O5′ on V ($^1/_2 + x$, $^1/_2 - y$, *z*).

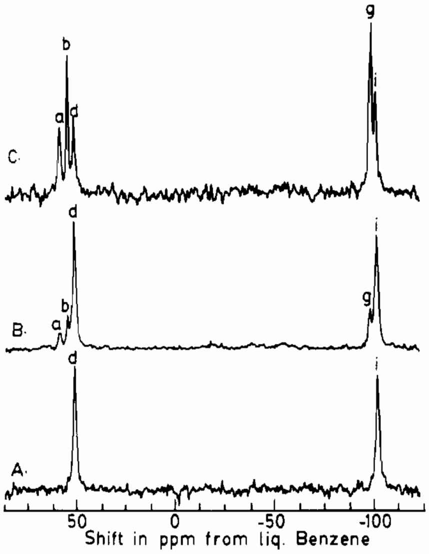
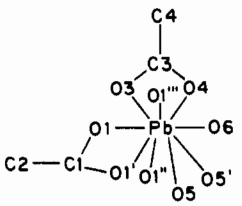


Figure 3. ^{13}C CP/MAS NMR spectra of reacting lead(II) acetate trihydrate (14.2 MHz): (A) freshly recrystallized crystals of $Pb(O_2C_2H_3)_2·3H_2O$ packed into the spinner without grinding and run immediately; (B) sample A run 12 h later; (C) sample A after about 24 h. ^{13}C signal of liquid benzene is at 128.5 ppm with respect to Me_4Si.

group, and the O1 and O1′ oxygen atoms bridge to neighboring lead atoms. The resulting structure contains nine-coordinate lead atoms, shown in Figure 1 and



(the labeling scheme used in the above diagram has mirror related atoms indicated by a prime; multiple primes indicate bridging atoms from neighboring acetate groups). Selected bond lengths and angles are given in Table II.

The packing pattern of $Pb(O_2C_2H_3)_2·3H_2O$ is shown in a stereoview in Figure 2. An important feature of this pattern is the bridging of acetate groups via O1″···Pb···O1‴ contacts between neighboring inversion-related molecules. These interactions lead to a chain of lead acetate units extending along [010]. The Pb···O1″ chelating distance is 2.637 (7) Å, only 0.15 Å longer than the internal Pb···O1 ligand distance. O3 and O4 oxygens of the other acetate group do not bridge but are both involved in hydrogen-bond interactions established by O···O intermolecular contacts less than 3.0 Å, shown in Table II. O3 on molecule I is bonded to water oxygens O5 and O5′ on II, while O4 is hydrogen bonded to the water oxygen O6, linking molecules II and IV.

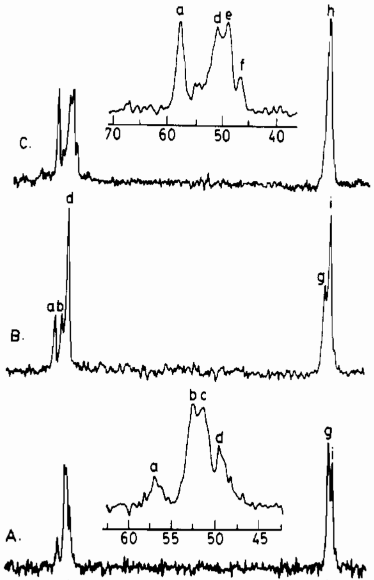


Figure 4. ^{13}C CP/MAS NMR spectra of products of lead(II) acetate trihydrate reactions: (A) $Pb(O_2C_2H_3)_2·3H_2O$ dried in a vacuum desiccator for about 24 h; (B) commercial lead(II) acetate trihydrate; (C) commercial anhydrous lead subacetate, $Pb(OH)_2·2Pb(O_2C_2H_3)_2$. Expanded displays of the carboxyl regions of A and C are shown as insets.

^{13}C CP/MAS NMR. Freshly recrystallized lead(II) acetate trihydrate gives the simple two-line ^{13}C CP/MAS NMR spectrum shown in Figure 3A. This spectrum was obtained from a sample of small freshly grown single crystals of II packed, without grinding, into a spinner with a small hole in the cap. Spectra were accumulated on this sample over a 24-h period during which new resonances appear at the expense of the two original lines as shown in Figure 3. When fresh crystals are dried at room temperature in a vacuum desiccator or heated to about 100 °C, the spectrum shown in Figure 4A

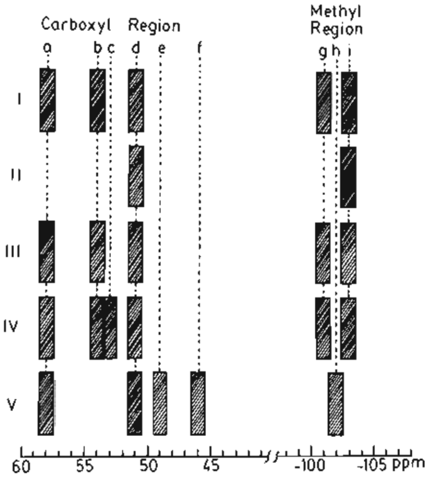


Figure 5. Summary of ^{13}C CP/MAS spectral features: I, commercial lead acetate trihydrate; II, fresh single crystals of lead acetate trihydrate; III, sample II 24 h after sample preparation; IV, crystals of fresh lead acetate trihydrate after drying in vacuo for about 24 h or heating to 100 °C for a few minutes; V, commercially available anhydrous lead subacetate. Shaded blocks are drawn to represent accurate line positions but not intensities.

is observed. The chemical shift variations that result from their solid-state transformations are summarized in Figure 5, in which a three-line pattern (a, b, d) in the carboxyl region (45–60 ppm) and a two-line pattern (g, i) in the methyl region (−100 to −105 ppm) occur in those samples of lead acetate that have been exposed to air more than 12 h, exposed to a vacuum, or exposed to high temperatures (I, III, IV). Of these lines, d and i are due to residual lead(II) acetate trihydrate that remains in the samples in varying amounts. IV is the only sample that exhibits a unique resonance, C, at 53 ppm. This sample is also the only one that requires a pulse sequence with a recycle time greater than 1 s (10 s needed) for satisfactory data accumulation.

Since the IR spectrum of II indicated that lead subacetate, V, formed readily when II was exposed to IR radiation, we obtained the NMR spectrum of V for comparison, shown in Figure 4C. In this spectrum the methyl carbon line, h, is now slightly broadened and occurs between the methyl lines, g and i, of the other samples. The NMR spectrum in the carboxyl region of V is distinctly different from that found for the other samples. In particular, there are two new lines, e and f, and a marked decrease in intensity of lines b and c.

Discussion

The crystal structure of II shows that there is only one molecule per asymmetric unit but two crystallographically nonequivalent acetate groups per molecule. The O1–C1–O1′ acetate group bridges via O1···Pb intermolecular bonds such that these bridging bond lengths are 2.637 (7) Å while the intramolecular bidentate O1···Pb bonds are 2.586 (6) Å. The other acetate group, containing, O3–C3–O4, is also bidentate but has no bridging bonds to neighboring lead atoms. Instead, O3 and O4 both are involved in hydrogen-bond interactions: O3 is hydrogen bonded to O5 and O5′ water molecules on an inversion-related molecule and O4 is hydrogen bonded to the O6 water molecule related by a glide operation. The O–C and C–C bond lengths compare favorably with similar bonds in other acetate structures,[14] and the intramolecular geometry of the two different acetate groups is nearly identical. The molecular geometry and the intermolecular bonding patterns of $Pb(O_2C_2H_3)_2{\cdot}3H_2O$ are very similar to those of $Cd(O_2C_2H_3)_2{\cdot}2H_2O$.[14a] In both compounds the acetate groups are bidentate and lie in planes that are at right angles to each other. One acetate group in the cadmium compound participates in two hydrogen bonds (one to each of its oxygen atoms), and the other acetate group has one oxygen that bridges to a neighboring cadmium and one oxygen that participates in a hydrogen bond.

Lead(II) acetate trihydrate could, in principle, give a ^{13}C CP/MAS spectrum with two lines each for the carboxyl and methyl groups since there are two chemically different acetate groups present in its structure. Correlating the structural differences with the solid-state isotropic chemical shifts observed in their ^{13}C CP/MAS spectra is, however, not straightforward. While the spectrum in Figure 3A shows only one sharp line in the carboxyl and methyl regions for fresh lead acetate, two carboxyl lines ($\Delta\sigma = 2$ ppm) and a single methyl line are observed in ^{13}C CP/MAS spectrum of structurally similar cadmium acetate.[15] In order to determine the structural basis for these spectral differences, further analysis is needed such as single-crystal and slow-spinning CP/MAS techniques for determining chemical shift anisotropies.[16] The usefulness of these tools for making structural correlations with high-resolution solid-state spectral features has been demonstrated recently for calcium formate.[17]

The ^{13}C CP/MAS NMR spectrum of lead(II) acetate trihydrate shows further anomalies, since multiple lines appear in the spectrum of freshly recrystallized II after approximately a 30-min exposure to air. II is reported to react with carbon dioxide to form lead carbonate under conditions of extended exposure to air or in a highly concentrated carbon dioxide atmosphere at elevated temperatures.[18] We have no evidence that our samples form lead carbonate. The IR spectrum of reacted II is distinctly different from that of lead carbonate, and the reaction products are all water soluble. ^{13}C CP/MAS NMR spectra of lead carbonate corroborate this conclusion since only a single resonance is observed at 38 ppm (relative to liquid benzene), far removed form the acetate carboxyl resonances of I–V.

The solid-state reactions of $Pb(O_2C_2H_3)_2{\cdot}3H_2O$ that cause the changes in the solid-state carbon spectra involve, at least in part, the loss of volatile components. Thermogravimetric analyses show that this compound begins to lose water at 44 °C and is completely anhydrous at 100 °C.[19] This observation holds for powders or single crystals of II for which the (100) crystal faces preferentially turn opaque upon heating. This observation is consistent with the packing pattern shown in Figure 2, in which the (100) planes contain all the water oxygens, thus providing a reasonable pathway for water to escape from the crystal with minimum disruption of the structure.

The reactions of powdered samples of II can be correlated with the observed chemical shifts presented in Figure 5. Sample II has only two peaks, d and i, but as it reacts to form III, peaks a, b, and g appear. These three peaks are also present in IV, suggesting that they are characteristic of a partially dehydrated form of II. IV contains an additional line,

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(14) (a) Harrison, W.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1958**, 957. (b) Hsa, L. Y.; Nordman, C. E. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 690. (c) Galigne, J. L.; Mouvet, M.; Falgueirettes, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr., Cryst. Chem.* **1970**, *B26*, 368.

(15) In a detailed single-crystal and CP/MAS NMR study of cadmium acetate dihydrate we have found that the two crystallographically nonequivalent carboxyl carbons have shift anisotropies of 120.8 and 117.5 ppm., respectively: Ganapathy, S.; Bryant, R. G.; Chacko, V. P.; Etter, M. C., unpublished work.

(16) Veeman, W. S. *Philos. Trans. R. Soc. London, Ser. A* **1981**, *A299*, 629.

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(19) Duval, C.; Wadier, C. *Anal. Chim. Acta* **1960**, *23*, 257.

c, which could be due to anhydrous lead(II) acetate since this sample is the only one that has been heated and is the only one in which this peak occurs. Other possible chemical products that could arise by air oxidation, dehydration, as well as reaction with carbon dioxide include various hydrates, solvates, basic acetates, and basic carbonates. The NMR spectrum of lead subacetate (V) indicates that V is not one of the major products of room-temperature or thermal decomposition of II, although IR spectra clearly show that V is the major product formed by exposure of II to infrared radiation. Chemical identification of the products that yield peaks a, b, and g is still uncertain, and the analysis is complicated by the presence of mixed solid-state phases in these samples.

The fact that solids undergo reactions and phase transformations, which are either unique or occur unexpectedly in the solid state, presents a general problem for solid-state NMR analysis. For example, ^{13}C CP/MAS NMR spectrum of calcium acetate has four lines in the carboxyl region, which have been attributed to the presence of four nonequivalent acetate groups in the asymmetric unit of the crystal.[3] Since the crystal structure has not yet been reported, this may be a reasonable assumption. However, we have found that a spectrum run in our lab of commercial calcium acetate hydrate matches the published spectrum of supposedly anhydrous calcium acetate, leading us to question the actual composition and stability of calcium acetate solids. We have not analyzed the solid-state chemistry of calcium acetate in detail but note that the ^{13}C CP/MAS spectrum in both the carboxyl and methyl regions is a sensitive function of sample history.

In summary, we have shown that ^{13}C CP/MAS NMR is an efficient means for characterizing solid-state reactions. When used in conjunction with X-ray crystallographic studies, correlations are possible between structural details and the chemical shift. The crystal structure of lead(II) acetate shows that at most one could expect two methyl carbon lines and two carbonyl carbon lines in the NMR spectrum. The presence of more lines in old samples indicates the presence of other phases; the presence of only one line for each group shows that the structural differences in the solid state are not sufficient to allow resolution of the crystallographically inequivalent sites. Changes that take place in the ^{13}C CP/MAS NMR spectrum of II as solid-state dehydration and subsequent phase transformations take place are readily monitored by following the changes in intensity of lead(II) acetate trihydrate lines relative to new product lines that appear.[20]

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Registry No. $Pb(O_2C_2H_3)_2 \cdot 3H_2O$, 92011-13-7.

Supplementary Material Available: Listings of thermal parameters for all atoms and observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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(20) Upon completion of this manuscript, it was brought to our attention that the crystal structure of II had been recently published.[21] The structural features presented are essentially the same as described in the present paper, but the use of an automatic diffractometer and a crystal mounting technique which prevented crystal decomposition made the precision of the crystallographic results presented here significantly greater than those reported in ref 21.

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Synthesis, Spectroscopic Properties, and X-ray Structure of [1,7-Bis(5-methylimidazol-4-yl)-2,6-dithiaheptane]dichlorocopper(II): A Compound with Unusually Long Copper(II)-Thioether Bonds

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The synthesis, X-ray structure determination, and spectroscopic properties of (1,7-bis(5-methylimidazol-4-yl)-2,6-dithiaheptane)dichlorocopper(II) are described. The compound $CuC_{13}H_{20}N_4S_2Cl_2$ crystallizes in the orthorhombic space group *Pbca* with $a = 12.927$ (3) Å, $b = 18.933$ (5) Å, $c = 14.469$ (2) Å, $V = 3541$ (2) Å^3, $d_{\text{obsd}} = 1.62$ g/cm^3, and $d_{\text{calcd}} = 1.616$ (1) g/cm^3 for $Z = 8$. The structure was solved by heavy-atom and direct methods. Least-squares refinements and Fourier methods resulted in a $R_w = 0.022$ for 1641 reflections with $I > 2\sigma(I)$. The copper(II) ion has a compressed octahedral coordination geometry, with the two imidazole nitrogen atoms along the main axis at 1.949 (2) and 1.955 (2) Å and both chloride ions and the two thioether sulfur atoms at longer distances in the equatorial plane, [Cu-Cl = 2.395 (1), 2.457 (1) Å, Cu-S = 2.886 (1), 2.970 (1) Å]. This structure shows that long equatorial Cu(II)-S(thioether) bonding, like in type I copper proteins, is also possible in more simple coordination compounds. The ESR and electronic spectra are discussed on the basis of this geometry and agree with a d_{z^2} ground state.

Introduction

The copper sites in some type I proteins are now fairly well-known, both by spectral and crystallographical studies.[2-4] The copper ion appears to be unusually coordinated in a distorted-tetrahedral geometry, with the sulfur- and nitrogen-containing residues of the amino acids cysteine, methionine, and histidine forming the CuN_2S_2 chromophore.[3,5]

The use of chelating ligands with built-in thioether and imidazole groups as model compounds for type I copper proteins may shed more light on their interesting structural, spectral, and electrochemical properties and their mutual dependencies. Several closely related compounds containing

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