Inorg. Chem. **1984**, *23*, 3577-3580

Table IV. Comparison of Calculated[a] Quenching Constants Based on Scheme I with Experimental Values (Given in Parentheses)

	$k_q/10^9$ dm^3 mol^{-1} s^{-1}	
	$Fe(tfac)_3$	$Fe(hfac)_3$
benzophenone	4.3 ± 0.5 (3.5 ± 0.3)	7.5 ± 0.1 (7.5 ± 0.5)
triphenylene		7.9 ± 0.1 (7.9 ± 0.5)
phenanthrene	6.5 ± 0.2 (6.5 ± 0.4)	7.8 ± 0.1 (7.9 ± 0.5)
2-acetylnaphthalene	5.7 ± 0.4 (4.9 ± 0.4)	7.7 ± 0.1 (6.7 ± 0.4)
chrysene	6.4 ± 0.2 (6.1 ± 0.3)	7.8 ± 0.1 (7.9 ± 0.4)
coronene	6.5 ± 0.2 (6.4 ± 0.6)	7.8 ± 0.1 (7.8 ± 0.6)
1,2,3,4-dibenzanthracene	6.0 ± 0.4 (5.4 ± 0.3)	7.8 ± 0.1 (7.9 ± 0.4)
pyrene	5.8 ± 0.4 (6.3 ± 0.4)	7.8 ± 0.1 (7.8 ± 0.4)
acridine	$1.7\left\{\begin{matrix}+0.5\\-0.3\end{matrix}\right.$ (1.9 ± 0.1)	reacts
anthracene	3.9 ± 0.8 (4.5 ± 0.2)	7.5 ± 0.1 (7.8 ± 0.4)
perylene	3.3 ± 0.8 (3.8 ± 0.2)	7.3 ± 0.1 (7.9 ± 0.4)
pentacene	$0.9\left\{\begin{matrix}+0.8\\-0.5\end{matrix}\right.$ (0.8 ± 0.08)	6.4 ± 0.3 (5.1 ± 0.5)
β,β-carotene	$0.6\left\{\begin{matrix}+0.6\\-0.4\end{matrix}\right.$ (0.65 ± 0.04)	reacts

[a] Best fit values with $\kappa_{el} = 7.2 \times 10^{-3}$ and 16×10^{-3} for $Fe(tfac)_3$ and $Fe(hfac)_3$, respectively, $\Delta G_{el}^{\ddagger}(0) = 0.26$ eV for both quenchers, and energy-transfer parameters based on best fit of quenching data of $Fe(acac)_3$ (see Figure 2 and text). Range of values was calculated with the assumption of an uncertainty in $\Delta G_{el} = \pm 0.1$ eV.

The fits require κ_{el} values of 7.2×10^{-3} and 16×10^{-3}, respectively, and $\Delta G_{el}^{\ddagger}(0)$ values of 0.26 eV for both $Fe(tfac)_3$ and $Fe(hfac)_3$. There is considerable uncertainty about the value of $\Delta G_{el}^{\ddagger}(0)$ for $Fe(hfac)_3$ because most of the quenching constants for $Fe(hfac)_3$ have reached a plateau value of 7.9×10^9 dm^3 mol^{-1} s^{-1}. We have also fitted the experimental data to a scheme that eliminates spin restrictions for reversible electron transfer; i.e., reversible electron transfer is assumed possible for quartet, sextet, and octet exciplexes. The value of $\Delta G_{el}^{\ddagger}(0)$ does not change, but as one would expect when another channel is opened up for reverse electron transfer, the value of κ_{el} drops slightly to 5.4×10^{-3} for $Fe(tfac)_3$ and it was found that this fit is not as good as that from Scheme I. Thus, as well as being the simplest, Scheme I fits the experimental facts best. It is worth noting that all the different treatments give intrinsic barrier values of 0.26 ± 0.02 eV and the transmission coefficient values for the various approaches for quenching by $Fe(tfac)_3$ and $Fe(hfac)_3$ only vary in the range $(5.4-16) \times 10^{-3}$.

It is of interest to compare the best fit parameters of $\kappa_{el} = 0.016$ and $\Delta G_{el}^{\ddagger}(0) = 0.26$ eV obtained in this work for reversible electron-transfer quenching by $Fe(hfac)_3$ of triplet states after making due allowance for energy-transfer quenching as in Scheme I, which gives the predicted values in Table IV with the best fit values obtained for triplet-state quenching by $Cr(hfac)_3$ where competitive energy and electron transfer were occurring. The best fit values of the transmission coefficients are the same, but an intrinsic barrier of $\Delta G_{el}^{\ddagger}(0) = 0.16$ eV was obtained in the case of $Cr(hfac)_3$ where the Cr(II) produced is probably high spin.[10] According to outer-sphere electron-transfer theory, this difference would be attributed to higher intrinsic barrier for self-exchange in the Fe^{III}/Fe^{II} couple as opposed to the Cr^{III}/Cr^{II} couple, which can be interpreted in terms of the frequencies of critical promoting modes and the magnitude of the nuclear displacement associated with the individual vibrations. For a recent discussion see ref 35. It will be of interest to see whether this difference persists by comparison of reverse electron-transfer parameters for quenching by other ligands coordinated to Cr^{III} and Fe^{III} and to extend these studies to other central atoms. Such work is at present in progress.

Registry No. $Fe(tfac)_3$, 14526-22-8; $Fe(hfac)_3$, 17786-67-3; xanthone, 90-47-1; benzophenone, 119-61-9; triphenylene, 217-59-4; phenanthrene, 85-01-8; 2-acetylnaphthalene, 93-08-3; chrysene, 218-01-9; coronene, 191-07-1; 1,2,5,6-dibenzanthracene, 53-70-3; 1,2,3,4-dibenzanthracene, 215-58-7; pyrene, 129-00-0; acridine, 260-94-6; anthracene, 120-12-7; perylene, 198-55-0; methylene blue, 61-73-4; anthracene, 120-12-7; 2,3-benzanthracene, 92-24-0; pentacene, 135-48-8; β,β-carotene, 7235-40-7.

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The Nature of the $S\equiv C$ Triple Bond

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The structures of $SH_3\equiv CH$, $SF_3\equiv CH$, $SF_3\equiv CF$, and the staggered and eclipsed conformations of $SF_3\equiv C-CF_3$ have been fully optimized by ab initio Hartree–Fock gradient calculations using a 3-3-21 basis set with added polarization functions for S and a 4-21 basis for C and F. The SH_3 and SF_3 groups are essentially in an octahedral configuration with XSX angles between 91 and 93° in every case. The remaining three sulfur orbitals make up the $S\equiv C$ triple bond, which has a length of 1.41–1.45 Å, compared with a S=C double-bond length of 1.54 Å in $SF_4=CH_2$. Orbitals localized according to the Boys definition are used to assist in the interpretation of the geometric results. Tests are made with larger basis sets (d functions on all heavy atoms; d functions on all heavy atoms with two sets of d functions on S) to ensure basis set convergence in the computed angles in $SF_3\equiv CH$. Comparisons are made with geometries in other compounds.

Introduction

The hypervalent compounds of sulfur are currently attracting a great deal of attention both from preparative chemists and from theorists who are concerned with developing an understanding of the bonding involved. The known variety of such compounds has expanded in recent years as new compounds with multiple bonds to sulfur have been successfully synthesized. Especially interesting are the compounds with S=C double bonds, such as $SF_4=CH_2$,[1] and the even more recently prepared triply bonded compound $SF_3\equiv C-CF_3$.[2] The electronic and geometric structures of $SF_4=CH_2$ have been investigated previously[3] by ab initio gradient com-

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0020-1669/84/1323-3577$01.50/0

Table I. Structures of $SH_3{\equiv}CH$, $SF_3{\equiv}CH$, and $SF_3{\equiv}CF$[a]

	$SH_3{\equiv}CH$	$SF_3{\equiv}CH$	$SF_3{\equiv}CH$[b]	$SF_3{\equiv}CH$[c]	$SF_3{\equiv}CF$
$S_1{\equiv}C_5$	1.448_4	1.406_8	1.406_8	1.41_5	1.392_4
$S_1{-}X_2$	1.372_6	1.566_0	1.537_3	1.54_6	1.563_6
$C_5{-}Y_6$	1.043_5	1.045_5	1.055_7	1.05_6	1.326_2
$\angle C_5S_1X_2$	124.3_9	124.1_9	123.9_2	124	124.0_4
$\angle X_2S_1X_3$	91.2_3	91.5_1	91.8_9	$91._9$	91.7_2
μ	−2.23	1.52	0.42	0.54	−0.08
E	−433.177 19	−729.138 12	−729.275 29	−729.310 15	−827.693 10

[a] Bond lengths in angstroms, angles in degrees, dipole moment in debyes, and E in hartrees. See Figure 1 for labeling of atoms. Plane of symmetry assumed. Geometries optimized until residual forces are <0.004 in mdyn and Å units. Basis sets: 3-3-21 plus d functions (orbital exponent 0.8) on S, 4-21 on C and F except as noted. [b] *d* functions (exponent 0.8) on S, C, and F. [c] As in footnote *b* plus a second set of d functions (exponent 0.2) on S.

Table II. Structures of Two Conformations of $SF_3{\equiv}C{-}CF_3$[a]

	eclipsed	staggered
$S_1{\equiv}C_5$	1.404_4	1.404_3
$S_1{-}F_2$	1.551_7	1.551_9
$S_1{-}F_3$	1.551_6	1.551_8
$C_5{-}C_6$	1.434_9	1.435_0
$C_6{-}F_7$	1.360_0	1.360_0
$C_6{-}F_8$	1.360_0	1.360_0
$\angle S_1C_5C_6$	179.9_0	179.9_9
$\angle C_5S_1F_2$	123.3_3	123.3_7
$\angle C_5S_1F_3$	123.3_4	123.3_6
$\angle F_2S_1F_3$	92.6_9	92.6_5
$\angle F_3S_1F_4$	92.6_9	92.6_7
$\angle C_5C_6F_7$	111.9_0	111.8_9
$\angle C_5C_6F_8$	111.9_0	111.9_0
$\angle F_7C_6F_8$	106.9_4	106.9_4
$\angle F_8C_6F_9$	106.9_4	106.9_4
μ	−2.40	−2.40
E	−1063.947 17	−1063.947 11

[a] See footnote *a* in Table I.

putational techniques, and there has been a gas-phase electron diffraction study of its molecular structure.[4] The present paper is concerned with a series of compounds containing the S≡C triple bond.

Method of Computation

Our earlier paper[3] has demonstrated the high accuracy that can be achieved in ab initio gradient calculations of equilibrium geometries of molecules similar to those of interest here. Use of a 3-3-21 basis set[5] augmented by d functions for sulfur and the standard 4-21 basis set[6] for carbon, fluorine, and oxygen produced equilibrium bond *angles* within experimental error of those obtained by careful experiment for $SF_4{=}O$ and for $SF_4{=}CH_2$,[3] with computed bond *lengths* being nearly equally accurate. The accurate reproduction of bond *lengths* for these particular bonds represents a fortuitous but reproducible cancellation of errors arising from neglect of electron correlation and by use of a finite basis set of this particular size. The effect is well understood.[6-8] The present work evaluates the equilibrium structures of $SH_3{\equiv}CH$, $SF_3{\equiv}CH$, $SF_3{\equiv}CF$, and two conformations of $SF_3{\equiv}C{-}CF_3$ by using the program TEXAS,[9] the basis sets described above, and ab initio gradient methods that have been fully described previously.[3,6]

Results and Conclusions

The computed equilibrium structures are shown in Tables I and II, with the scheme used for numbering the atoms specified in Figure 1. The most striking result shown in the tables is that the structures of the SH_3 or SF_3 groups are basically similar in all of the compounds studied. In $SH_3{\equiv}CH$, $SF_3{\equiv}CH$, and $SF_3{\equiv}CF$, the XSX bond angles vary by only about $^1/_2$°, while in $SF_3{\equiv}C{-}CF_3$ they are about 1° larger. The geometry in every case is only very slightly distorted from the octahedral angle of 90°, with the sulfur atom retaining the octahedral configuration it exhibits, for example, in SF_6. Geometrically, three of the bonds have combined to form the S≡C linkage, leaving the remaining SF_3 moiety almost completely undisturbed. It is especially noteworthy that the behavior of this group is unchanged regardless of whether the substituents on the triply bonded sulfur and carbon atoms are H, F, or CF_3.

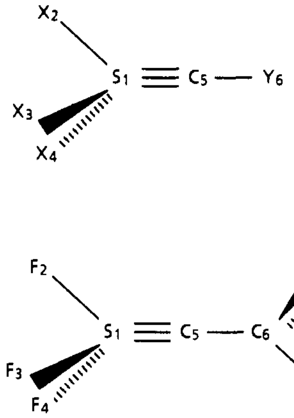

Figure 1. Labeling of the atoms in $SH_3{\equiv}CH$, $SF_3{\equiv}CH$, $SF_3{\equiv}CF$, and $SF_3{\equiv}C{-}CF_3$. In the eclipsed conformation of $SF_3{\equiv}C{-}CF_3$ (not shown), F_7 is in the symmetry plane.

Further evidence concerning this simple picture of the $SX_3{\equiv}$ group can be sought in the nature of the localized molecular orbitals. The canonical orbitals in the wave function obtained directly from the calculation on $SF_3{\equiv}CH$ were therefore transformed into a set of Boys localized orbitals.[10] Such orbitals give an approximation to the chemist's usual qualitative concepts of bonding pairs, lone pairs, etc. The three highest-energy occupied localized orbitals were found to correspond to the triple bond, with each one having a centroid of electron density located at 0.877 Å, or 62% of the distance from sulfur toward carbon, and 0.397 Å away from the S≡C axis. These three orbitals are oriented in such a way as to stagger the S–F bonds. This is in accord with the model of an octahedral orbital structure around sulfur with three of the electron pairs used to form the three components of the triple bond and the other three, essentially undisturbed, bonding to the fluorine or hydrogen atoms.

One of the three equivalent localized triple-bond orbitals of $SF_3{\equiv}CH$ is plotted in Figures 2 and 3. Figure 2 shows the electron density of this orbital in a plane containing the S and C atoms and the point of maximum electron density

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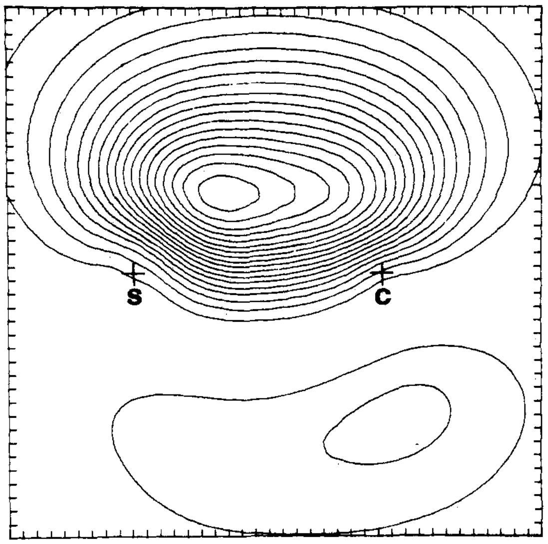

Figure 2. Electron density in one of three equivalent localized orbitals in $SF_3{\equiv}CH$ corresponding to a triple bond, plotted in a plane containing S and C atoms and the point of maximum electron orbital density. The plot measures 3 Å × 3 Å and the contour interval is 0.04 e bohr^{-3}.

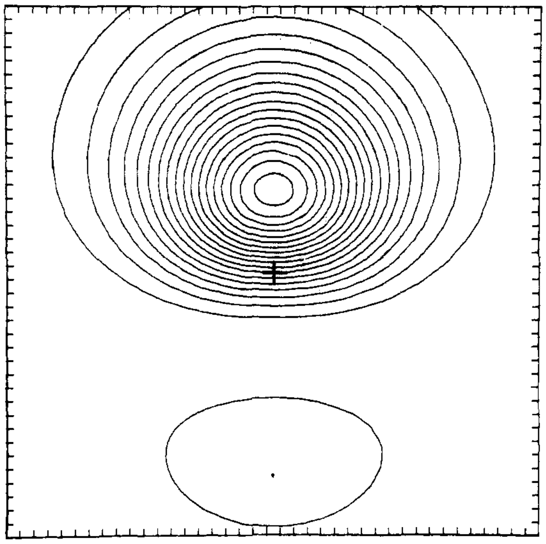

Figure 3. Electron density in same orbital as in Figure 2 (same scale), plotted in a plane perpendicular to the S≡C bond (intersection marked by +) and passing through the point of maximum orbital electron density.

of the orbital. The structure is that of a π bond strongly polarized in the direction of the more electronegative sulfur atom. Note that the point of maximum electron density is shifted toward sulfur compared with the point of center of charge of the orbital. Figure 3 shows the electron density of the same orbital in a plane perpendicular to the S≡C bond (denoted by the + in the diagram) and passing through the point of maximum orbital electron density. The other two identical orbitals (not shown) are centered symmetrically in the lower left and lower right of this presentation. The sum of the three orbitals, of course, gives an electron density that is cylindrically symmetric around the S≡C direction.

Examination of the localized orbitals corresponding to the triple bonds shows extensive contribution from the sulfur d orbitals, as would be expected. The participation of sulfur atomic orbitals in these molecular orbitals corresponds to a hybridization of approximately $s^{1.3}p^{5.2}d^{1.5}$, although this quantitative breakdown should not be taken too seriously considering the level of computation used, the limitations imposed by the Boys concept of orbital localization, and the inherent conceptual difficulty in giving quantitative meaning to the qualitative description of atomic hybridization. Nevertheless, it can be said that everything that can be noted in an examination of the localized orbitals reinforces the simple description of the nature of the $SX_3{\equiv}$ group given above.

In our earlier paper,[3] the structure around the sulfur atom in $SF_4{=}CH_2$ was discussed in terms of a trigonal bipyramid with the equatorial atoms grossly distorted from the trigonal FSF angle of 120° to the observed angle of 98°. It requires less distortion to consider the angles as enlarged by 8° from the octahedral angle. The four S–F bond distances are not equal, but the axial and equatorial lengths differ by only 0.02–0.03 Å rather than the 0.10 Å difference observed[11] in SF_4. Overall, the structure around sulfur in $SF_4{=}CH_2$ is qualitatively intermediate between trigonal bipyramid and octahedral. In the $SX_3{\equiv}$ compounds it is clearly octahedral.

Some further tests were made to ensure that the 91–92° XSX angles found were not an artifact of the level of computation used. It is well-known that inclusion of polarization functions in the sulfur atom basis set, as has been done in these calculations, is essential for proper description of the geometry around the sulfur atom. The question remains whether this alone is sufficient to give an accurate description of the geometry for the molecules studied here. As a test of the adequacy of the basis set used, the geometry optimization of $SF_3{\equiv}CH$ was repeated with use of (A) a set of d functions with the orbital exponent equal to 0.8 on carbon and fluorine as well as on sulfur and (B) that enlarged basis plus a second set of d functions with exponent 0.2 on sulfur. The results, shown in the fourth and fifth columns of Table I, show no significant change in the computed FSF angle. Clearly, the basis set used is adequate for proper angular description. The changes seen in computed bond lengths are compatible with expectations from many previous calculations involving similar basis set variations.[12]

The extremely short sulfur–carbon distance in all of the compounds studied demonstrates the true triple-bond character of the linkage in these substances. The S=C double-bond length varies from 1.611 Å in $S{=}CH_2$[13] down to 1.542 Å in $SF_4{=}CH_2$,[3] the latter being more comparable with the compounds investigated here. In the most closely analogous triple-bonded structure, $SF_3{\equiv}CH$, the triple bond is 0.135 Å shorter, both results being derived from calculations at the same level.

In $SF_3{\equiv}C{-}CF_3$, there is very little difference either in energy or in equilibrium geometry as the CF_3 group is rotated. The calculations show the staggered conformation to be more stable by only 35 cal mol^{-1}, but the significance of this small computed difference is questionable. The CF_3 group is very nearly tetrahedral with only 0.1° of tilt in the eclipsed conformation. The short C–C single-bond length of 1.435 Å shows the effect of the adjacent triple bond and is typical of that observed for an sp^3–sp C–C linkage. The corresponding value in $HC{\equiv}C{-}CH_3$ is 1.458 ± 0.005 Å,[14] and the same length is found within the very large experimental error in $HC{\equiv}C{-}CF_3$.[15,16]

Dipole moments calculated at this quantum-chemical level should not be taken too seriously since there is strong basis-set dependence as illustrated for $SF_3{\equiv}CH$. The 0.5 D value

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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 $SF_3{\equiv}C{-}CF_3$.

Acknowledgment. This work has been supported by Grant F-100 from the Robert A. Welch Foundation. The author is indebted to Professor Konrad Seppelt for calling his attention to these interesting compounds.

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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