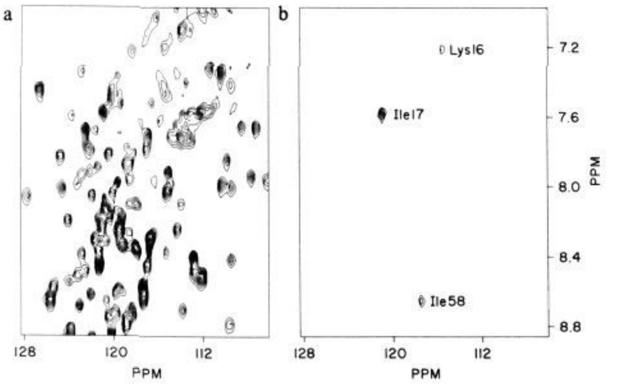

Figure 1. (a) Part of the 2DFE control spectrum of 2 mM fully labeled T4 lysozyme and (b) its corresponding difference spectrum with weak 0.8-s proton preirradiation at 5.45 ppm. The control and on-resonance spectra each took 4 h. The resolution was 10 Hz/point for protons and 15.6 Hz/point for nitrogen. A total of 240 t_1 values were used, with a maximum t_1 of 60 ms. NOEs were 4–15% with a signal-to-noise ratio between 2:1 and 6:1.

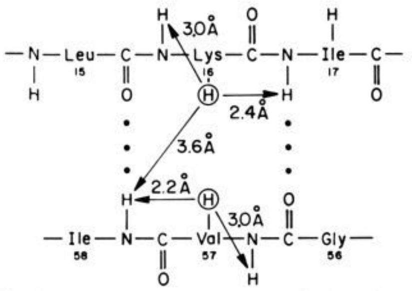

Figure 2. The β sheet region of T4 lysozyme indicating the connectivities observed when the Cα protons of lysine 16 and valine 57 are saturated.

that they have previously been classified by amino acid species through use of selective labels.

Fully and specifically labeled T4 lysozyme samples in 90% H_2O were prepared as described previously.[3] Spectra were recorded at 24 °C at 500 MHz. We perform an automated series of experiments consisting of a single 2D control (Figure 1a) with off-resonance preirradiation, followed by several other 2DFE's for which preirradiation is set at different CαH frequencies.

In one example, on-resonance preirradiation of uniformly labeled protein was set to 5.45 ppm because a single Cα proton resonance is found at this frequency, and three NOE peaks were found (Figure 1b). Previous 2DFE experiments with ^{15}N lysine specifically labeled protein showed that the peak at 7.23 ppm came from a lysine, but the amino acid classes of the other two resonances were ambiguous due to chemical shift degeneracy in the 2DFE spectrum of fully labeled T4 lysozyme.[1c,d] The assignment of these two peaks to isoleucine was established by repeating ST2DFE on a sample specifically labeled with only ^{15}N isoleucine.

The atomic model[2] indicates that spatial proximity of three such amino acids occurs only in a β sheet region of T4 lysozyme, consisting of lysine 16, isoleucine 17, and isoleucine 58 (Figure 2). Thus, the spectra in Figure 1 suggested that the Cα proton of lysine 16 at 5.45 ppm gives a 4% NOE to its own amide, a 15% NOE to the closest amide, isoleucine 17, and a 5% NOE to the isoleucine 58 amide proton.

Previously we had found a standard Cα–Cα proton NOESY connectivity between 5.45 ppm, assigned to CαH of lysine 16 above, and 5.23 ppm. ST2DFE with preirradiation at 5.23 ppm gave NOEs consistent with the connectivities in Figure 2 from CαH of valine 57. The valine 57 amide proton resonance is so close to that of the isoleucine 17 amide proton that it was necessary to confirm the assignment by repeating the experiment with a sample specifically labeled with ^{15}N valine. An edited HOHAHA[4] experiment also confirmed the lysine Cα assignment (not shown). Specifically labeled samples were absolutely required for these identifications.

The ST2DFE experiment is unexpectedly useful, and other applications will be described elsewhere. It is an alternative to a three-dimensional sequence, with NOESY-style preparation, but ST2DFE is as useful in certain cases because it is relatively simple.

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Registry No. Lysozyme, 9001-63-2.

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Lewis Basicity of the "Noncoordinating" Common Solvent 1,2-Dichloroethane: Strong RCl → Ag Bonding in AgOTeF$_5$(1,2-C$_2$H$_4$Cl$_2$)[†]

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A quest for reactive *soluble* metal ions naturally leads to solvents with low donor numbers,[2] such as aromatic hydrocarbons and halogenated hydrocarbons, which are generally considered noncoordinating.[3] Some examples of coordinated iodocarbons have been recently confirmed by X-ray diffraction,[4,5] and the possibility that even more weakly basic chlorocarbons might serve as ligands in cases of extreme coordinative unsaturation has been suggested by NMR and IR studies.[4a,6,7] The growing expectation that halocarbons will be found to have a rich coordination chemistry, possessing ligand strengths far weaker than other main group alkyls such as amines, phosphines, ethers, and sulfides, signals the beginning of a new chapter in inorganic chemistry. For example, soluble $MX_m(RCl)_n$ complexes would be the only practical starting materials for the preparation of metal complexes of very weak ligands (X^- = an ancillary anionic ligand, R = an alkyl or aryl group). Furthermore, some $MX_m(RCl)_n$ complexes might have very high catalytic activity, since they possess one of the key features of all homogeneous catalysts, "vacant" (i.e., weakly solvated) coordination sites.[8]

We report the structure of AgOTeF$_5$(1,2-C$_2$H$_4$Cl$_2$),[9,10] shown in Figure 1. This is the first structurally verified example of a chlorocarbon coordinated to a metal ion and further demonstrates that (1) chlorocarbons with more than one chlorine atom can

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[†] Dedicated to the memory of Professor Fred A. Snavely, a gifted teacher, coordination chemist, and friend.

[1] Alfred P. Sloan Research Fellow, 1987–1989.

[2] (a) Gutmann, V. *Coord. Chem. Rev.* **1976**, *18*, 225. (b) Gutmann, V. *Ibid.* **1967**, *2*, 239. (c) Gutmann, V. *Coordination Chemistry in Non-aqueous Solvents*; Springer Verlag: Wien-New York, 1969.

[3] Compare benzene (DN = 0.1) and 1,2-dichloroethane (DN = 0) with acetonitrile (DN = 14.1), acetone (DN = 17.0), and tetrahydrofuran (DN = 20.0).[2]

[4] (a) Crabtree, R. H.; Faller, J. W.; Mellea, M. F.; Quirk, J. M. *Organometallics* **1982**, *1*, 1361. (b) Burk, M. J.; Segmuller, B.; Crabtree, R. H. *Organometallics* **1987**, *6*, 2241.

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[9] For AgOTeF$_5$(1,2-C$_2$H$_4$Cl$_2$): orthorhombic, *Pbca*, $a = 13.371$ (5) Å, $b = 8.192$ (2) Å, $c = 32.720$ (9) Å, $V = 3584$ Å^3, $Z = 16$, $T = -120$ °C, $\rho_{calcd} = 3.30$ g cm^{-3}, $F(000) = 3232$. Nicolet R3m diffractometer, $\theta/2\theta$ scans, $4° < 2\theta < 50°$; $+h,+k,+l$; 2709 reflections with $|F_o| > 2.5\sigma|F_o|$. Lorentz and polarization corrections; empirical absorption correction, μ(Mo Kα) = 61.2 cm^{-1}, $T = 0.054 - 0.086$. Weighted least-squares refinement on F with neutral atom scattering factors and anomalous dispersion, anisotropic thermal parameters for non-H atoms, 217 parameters, H atoms in idealized positions; $R = 0.052$, $R_w = 0.057$, GOF = 2.11, slope of normal probability plot = 1.48.

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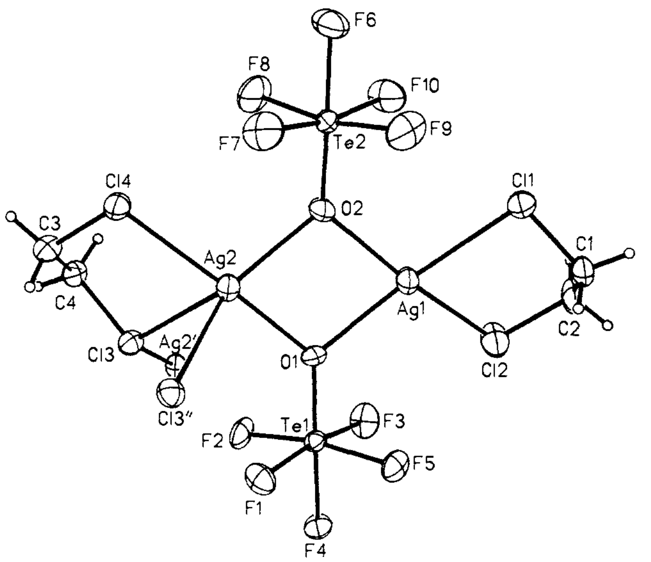

Figure 1. Drawing of the $[AgOTeF_5(1,2\text{-}C_2H_4Cl_2)]_2$ molecule (50% probability ellipsoids), also showing the intermolecular Ag-Cl bonds; Ag2' belongs to a molecule below the plane of the page, while Cl3'' belongs to a molecule above that plane. Relevant bond distances (Å) and angles (deg): Ag1-Cl1 = 2.705 (3), Ag1-Cl2 = 2.640 (3), Ag2-Cl3 = 2.914 (3), Ag2-Cl3'' = 3.000 (3), Ag2-Cl4 = 2.626 (3), ave. C-Cl = 1.80 (1), ave. Ag-O = 2.34 (1), ave. O-Ag-O = 78.9 (3), ave. Te-O = 1.78 (1), ave. Te-F = 1.85 (1), Cl1-Ag1-Cl2 = 78.0 (1), Cl3-Ag2-Cl4 = 75.9 (1), Cl3-Ag2-Cl3'' = 88.3 (1), Cl4-Ag2-Cl3'' = 91.2 (1).

function as polydentate ligands and (2) a chlorocarbon chlorine atom can bridge two metal ions. It has been accepted that there is no such thing as a completely noncoordinating anion;[11,12] with the coordinating ability of chlorocarbons now confirmed it is becoming apparent that there may be no such thing as a completely noncoordinating solvent.

The compound $AgOTeF_5$[10] is extraordinarily soluble in dichloromethane and 1,2-dichloroethane, forming >2.5 M solutions (cf. $AgClO_4$[10] and $AgBF_4$,[13] which form <0.001 M and ~0.010 M solutions, respectively, in dichloromethane). Clearly, some property of the $OTeF_5^-$ oxyanion renders metal ions in MX_m compounds very electron poor and open to coordination by extremely weak donors. Room temperature ^{13}C NMR spectra of solutions of $AgOTeF_5$ do not show separate resonances for free and bound chlorocarbon molecules, an observation we tentatively interpret as suggesting rapid exchange of free and bound solvent molecules. We have isolated very moisture-sensitive efflorescent crystals of $AgOTeF_5(CH_2Cl_2)$ and $AgOTeF_5(1,2\text{-}C_2H_4Cl_2)$ from saturated chlorocarbon solutions of $AgOTeF_5$. The structure of $AgOTeF_5(CH_2Cl_2)$ has not been satisfactorily solved, since crystals of this compound are twinned (see Supplementary Material).

The structure of $AgOTeF_5(1,2\text{-}C_2H_4Cl_2)$ is shown in Figure 1.[9] The structural parameters of the Ag_2O_2 core are similar to those in the related molecule $[AgOTeF_5(tol)_2]_2$ (tol = toluene).[10] The most interesting and significant feature of this structure is the disposition of the 1,2-dichloroethane molecules, which are strongly coordinated in bidentate fashion to the Ag^+ ions. One chlorine atom, Cl3, bridges two Ag2 atoms in adjacent dimeric molecules, forming linear chains.[14] Considering that the chlorine atom ligands do not bear a negative charge, the three Ag–Cl bonds to nonbridging chlorine atoms are quite short (av 2.657 (5) Å): cf. 2.512 (1) Å in Ag(diphos)Cl[15] and 2.408 (8) and 2.724 (8) Å in $Ag_2Pt_2Cl_4(C_6F_5)_4$.[16] The bridging Ag–Cl bond distances of 2.914 (3) and 3.000 (3) Å also fall well within the sum of van der Waals radii for Ag and Cl atoms, which is 3.5 Å.[17] The five-membered chelate rings adopt the normal puckered conformation:[18] each dimer contains one chelate ring of δ configuration and one of λ configuration.

The dimeric molecules are also linked by two weak intermolecular Ag···F interactions per Ag^+ ion (secondary bonds[19]). Thus, Ag1 is six-coordinate, while Ag2 is seven-coordinate. The Ag2···F distances (av 2.95 (1) Å) are longer than the Ag1···F distances (av 2.82 (1) Å), probably as a consequence of the greater amount of silver-chlorine bonding that Ag2 possesses. The closest intramolecular Ag···F distances are greater than 3.5 Å and are nonbonding since the sum of van der Waals radii for Ag and F atoms is 3.2 Å.[17] The four Ag···F bonding contacts are slightly longer than those in $AgSbF_6$ (2.62 Å)[20] and $[Ag_2(CH_2O)_6^{2+}][Ag^+][AsF_6^-]_3$ (2.60, 2.66 Å).[21]

Vibrational spectroscopic data are in harmony with the observed strong bonding between the Ag^+ ion and the chlorocarbon chlorine atoms. It has been shown that ν(TeO) is a measure of the strength of the interaction between the teflate oxygen atom and a metal ion, and therefore an indirect measure of the basicity of the ancillary ligands in a complex.[10,22,23] The ν(TeO) stretching frequency (average of the mutually exclusive IR and Raman bands from solid-state spectra) for $AgOTeF_5(CH_2Cl_2)$ is 831 cm^{-1}. This can be compared with 837 cm^{-1} for $[AgOTeF_5(CH_3CN)_2]_2$,[10] 828 cm^{-1} for $[AgOTeF_5(tol)_2]_2$,[10] and 800 cm^{-1} for $AgOTeF_5$.[24] Thus, the ligand strength of a chlorocarbon chlorine atom may not be very different from that of toluene for silver(I).

We have prepared other $M(OTeF_5)_x$ compounds that are very soluble in dichloromethane and 1,2-dichloroethane, including $Hg(OTeF_5)_2$ and $Ni(OTeF_5)_2$.[25] The coordination chemistry of these and other chlorocarbons and even more weakly basic fluorocarbon solvents is under active investigation in this laboratory.

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Supplementary Material Available: Drawings of the linear chain structure of $AgOTeF_5(1,2\text{-}C_2H_4Cl_2)$, the unit cell packing, the Ag^+ ion coordination spheres, and the chelate ring conformations,

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tables of positional and thermal parameters, bond distances and angles, and hydrogen atom positional and thermal parameters, and information concerning diffraction experiments with twinned crystals of $AgOTeF_5(CH_2Cl_2)$ (10 pages); table of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

The $Al(^2P)\{SiH_4\}$ Complex and the Photoreversible Oxidative-Addition/Reductive-Elimination Reaction: $Al(^2P)\{SiH_4\} \rightleftarrows H_3SiAlH$

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Weakly bound complexes between CH_4 and metal atoms in their *ground electronic states* (GS) have proven to be difficult species to detect and characterize by either gas-phase or matrix-isolation techniques.[1] One would anticipate that the longer, weaker SiH bonds of SiH_4 and the existence of low-lying empty 3d-orbitals would open up favorable electronic/structural channels for enhanced interactions with GS metal atoms compared to its lighter congener CH_4. In this communication we report spectroscopic and ab initio quantum chemical details for the $Al(^2P)\{SiH_4\}$ complex which support this view as well as information on the photoreversible oxidative-addition/reductive-elimination reaction:

$$Al(^2P)\{SiH_4\} \rightleftarrows H_3SiAlH$$

On depositing Al atoms into progressively doped SiH_4/Ar mixtures at 12 K, passing from neat Ar to neat SiH_4, one notes in the optical spectrum a smooth transformation from narrow Al atom $^2S \leftarrow {}^2P$ (340 nm), $^2D \leftarrow {}^2P$ (293, 288, 280 nm) excitations to a situation displaying broad, structured absorptions around 450–350 and 280–245 nm (Figure 1A–D). The substitution of SiH_4 for SiD_4 caused significant narrowing of these two broad features on the order of ~475 and ~150 cm^{-1} for the low- and high-energy absorptions, respectively (silane:argon = 1:10, Figure 1C), implicating a silane complex as the species responsible for the Al/SiH_4 optical spectrum.

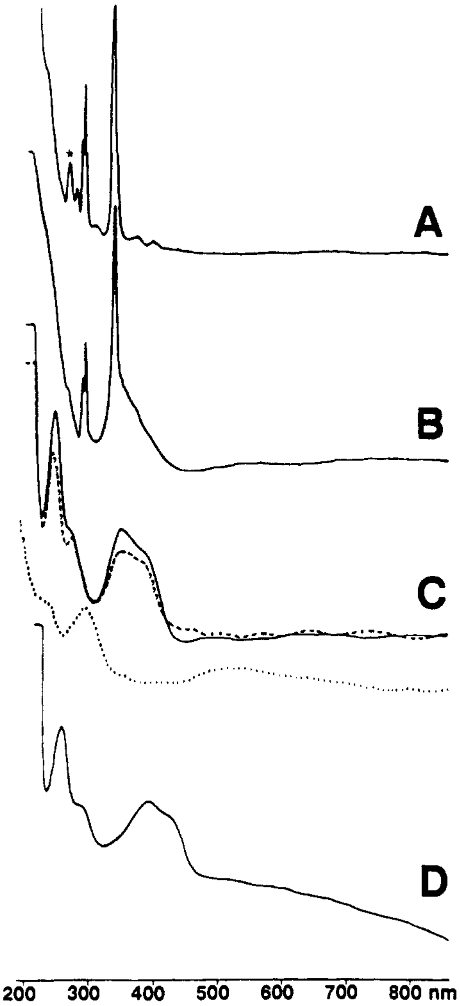
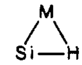


Figure 1. UV–vis spectra (12 K, ~6 μg total metal; ~1:10^4 dilution in host). * indicates band due to Al_2: (A) Al/Ar deposition spectrum. (B) Al/(1:100 SiH_4/Ar) deposition spectrum. (C) (—) Al/(1:10 SiH_4/Ar) deposition spectrum, (– – –) Al/(1:10 SiD_4/Ar) deposition spectrum, (···) Al/(1:10 SiH_4/Ar) after photolysis at 400 nm (20 nm fwhm) for 11 min. (D) Al/SiH_4 deposition spectrum.

The corresponding EPR spectra of Al/SiH_4 and Al/SiD_4 strongly support this view. In brief, the axial $Al(^2P)$ hyperfine sextet observed in solid Ar at 12 K (^{27}Al, $I = {}^5/_2$, natural abundance 100%, Figure 2A) on progressively doping with increased concentrations of SiH_4, is replaced by the dramatically distinct EPR spectra depicted in Figure 2 (parts B, C-i, and D). Since the differences exhibited within this group are very small relative to the change observed upon initial doping (silane:argon = 1:100, Figure 2 (parts A to B)), it is reasonable to postulate a 1:1 stoichiometry for the proposed $Al(^2P)\{SiH_4\}$ complex assuming that a statistical dispersion of the SiH_4 in Ar exists upon matrix formation. The participation of SiH_4 in the species responsible for these EPR spectra is demonstrated by the narrowing of the observed Al hyperfine lines in Al/SiD_4 matrices; $\beta_N^D/\beta_N^H = 0.307$ (Figure 2C-ii) consistent with the optical results described above.

In concert with the EPR spectral diagnostics, spin Hamiltonians including axial and orthorhombic magnetogyric tensors, ^{27}Al hyperfine and $^1H/^2H$ superhyperfine tensors, were employed to computer-model the EPR transitions of the different C_{3v}, C_{2v}, and C_s $Al(^2P)\{SiH_4\}$ geometries in attempts to simulate the experimental spectra. Excellent best-fit simulations[2] (omitting contributions from paramagnetic ^{29}Si; $I = {}^1/_2$, natural abundance 4.7%) could be obtained for each of these $Al\{SiH_4\}$ interaction schemes (i.e., Figure 2C-i) including in the spectra the presence of superimposed trace amounts of isolated SiH_3 radicals: $g_\parallel = 2.004$, $g_\perp = 2.006$, $A_\parallel = 17$ MHz, and $A_\perp = 23$ MHz (cf. ref 3). Preliminary ab initio quantum chemical calculations[4] favor the C_s geometry similar to the three-center bonding schemes in known hydrosilyl complexes of certain Cr- and Mn-containing organometallic compounds determined by



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