The fact that this novel coordination mode lowers the N-N rotational barrier is understandable based on $d\pi(Os) \rightarrow \pi^*$ back donation to the N-bound nitrosamine ligand. Previously reported reactions between electrophiles (E^+), including metal ions, and nitrosamines have yielded predominantly O-bound products.[13] They have increased N-N rotational barriers relative to the uncomplexed nitrosamines.[14] Nitrosamines can also be protonated at the amino nitrogen.[14] The complexes reported here appear to be the first examples of nitrosamine complexes having the $[R_2N\text{-}N(E)=O]^+$ structure. We have been unable to obtain crystals suitable for X-ray diffraction.

A plausible mechanism for nitrosamine formation by eq 1 is shown in Scheme I. It is based upon results of earlier studies on the six-electron oxidation of **1** and its Ru analogue to the metal-nitro complexes.[3,15,16] The first step involves oxidation to Os(III), followed by loss of a second electron and two protons to give an osmium(IV)-imido intermediate. Before it can undergo further oxidation, the imido complex must be trapped by nucleophilic attack by the secondary amine to form an osmium(II)-hydrazine complex. A related reaction has been reported for the ruthenium analogue, which in aqueous solution undergoes nucleophilic attack by water to give the corresponding hydroxylamine complex (reaction 2).[15] At the potential of the elec-

$$[(tpy)(bpy)Ru^{IV}{=}NH]^{2+} + H_2O \longrightarrow [(tpy)(bpy)Ru^{II}(NH_2OH)]^{2+} \quad (2)$$

trolysis, the hydrazine complex, once formed, must be further oxidized, first to the diazenido complex and then by two more electrons coupled with water addition to form the nitrosamine product.

Both **2** and **3** form as products of an independent route which utilizes the electrophilic properties of the osmium nitrosyl complex, **4**, as a starting point (reaction 3).[17] When excess amine was

$$[(tpy)(bpy)Os^{II}NO]^{3+} + 2R_2NH \longrightarrow [(tpy)(bpy)Os^{II}(\overset{O}{\overset{\|}{N}}\text{-}NR_2)]^{2+} + R_2NH_2^+ \quad (3)$$

4

added to a suspension of **4** as its PF_6^- salt in dichloromethane, the solid dissolved, and the color of the solution changed from pale yellow to deep orange/brown. After a water wash and concentration of the dichloromethane solution, the product was precipitated by adding the dichloromethane solution to hexane. ^1H NMR analysis of the product dissolved in acetonitrile-d_3 revealed that it consisted of a small amount of bound nitrosamine complex (<10%) mixed with the corresponding nitro complex and other unidentified products. We have not yet found a satisfactory way to purify the nitrosamine products obtained by this route. Similar products were obtained when $[(tpy)(bpy)Ru^{II}(NO)]^{3+}$ was allowed to react with the secondary amines.

Warning! Most *N*-nitroso compounds are potent carcinogens[18] which must be handled, stored, and discarded with due respect for the possible hazards involved.

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One-Dimensional Nuclear Overhauser Effect with Two-Dimensional Heteronuclear Multiple Quantum Coherence Detection: Proton-Proton Nitrogen-15 Correlation in T4 Lysozyme

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We have been working for some time on identification of as many proton and nitrogen resonances as reasonably possible in T4 lysozyme, with emphasis on the use of ^{15}N labeled samples and a variety of isotope-edited NMR techniques.[1] The X-ray structure of this 18.7 KD protein is already well known,[2] and our objective is to use these identifications for physical studies. Here we present one method which has allowed us to assign or help assign several resonances in the protein. The method is identical with one-dimensional nuclear Overhauser effect (NOE), except that a sensitive two-dimensional isotope-edited detection scheme is used which provides the extra resolution of a 2D experiment and the capability to edit spectra by selective isotope labeling.

One-dimensional NOE spectra are obtained as the difference between a control spectrum with off-resonance preirradiation that leaves all spins unperturbed and a spectrum for which the preirradiation frequency is coincident with a spin resonance. We extended this scheme to two-dimensional detection by replacing the 1D observe pulse with a version of proton-detected multiple quantum coherence detection[3a] which we call two dimensional forbidden echo or 2DFE.[1a] The NOE version is called saturation transfer 2DFE or ST2DFE.

The 2DFE map of uniformly ^{15}N enriched T4 lysozyme gives distinct peaks for many ^{15}NH amide and other groups (Figure 1a). Over 140 peaks have previously been classified by amino acid species by using selectively labeled samples,[1] and over 30 had been specifically identified by mutational substitution and by various edited NOE and double-label experiments.[1,3c] The ST2DFE experiment as applied here connects Cα proton frequencies with one or more of these amide peaks and is sometimes sufficient for identification of pairs of 2DFE amide peaks provided

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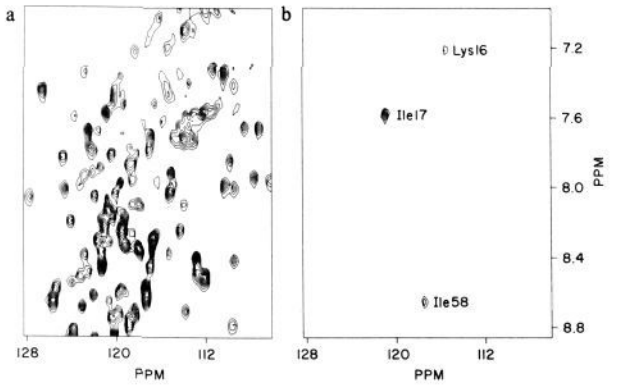

Figure 1. (a) Part of the 2DFE control spectrum of 2 mM fully labeled T4 lysozyme and (b) its corresponding difference spectrum with weak 0.8-s proton preirradiation at 5.45 ppm. The control and on-resonance spectra each took 4 h. The resolution was 10 Hz/point for protons and 15.6 Hz/point for nitrogen. 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.

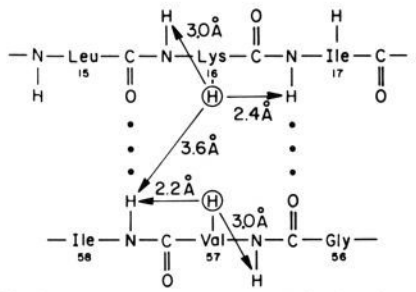

Figure 2. The β sheet region of T4 lysozyme indicating the connectivities observed when the Cα protons of lysine 16 and valine 57 are saturated.

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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Lewis Basicity of the "Noncoordinating" Common Solvent 1,2-Dichloroethane: Strong RCl → Ag Bonding in $AgOTeF_5(1,2\text{-}C_2H_4Cl_2)$†

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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 $AgOTeF_5(1,2\text{-}C_2H_4Cl_2)$,[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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(9) For $AgOTeF_5(1,2\text{-}C_2H_4Cl_2)$: 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, ρ_{calcd} = 3.30 g cm^{-3}, $F(000)$ = 3232. Nicolet R3m diffractometer, $\theta/2\theta$ scans, 4° < 2θ < 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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