centered radical in the Hofmann–Löffler reaction.[13] In this latter case, the initially formed tricoordinate nitrogen radical cation analogous to **3** reacts to give a species such as **2** while the corresponding reaction for the neutral radical, which would be similar to **6** → **5**, is not observed. Thus, combining information from the two systems, it is clear that the preponderant radicals are of type **2** for the radical cation and of type **6** for the neutral radical irrespective of whether one starts from carbon-centered or nitrogen-centered radicals. This strongly suggests a thermodynamic basis for the difference in reactivity, radicals such as **2** and **6** being more stable than their respective isomers **3** and **5**.

In fact, thermochemical data for prototype reactions were used by one of us some 25 years ago to predict that a nitrogen-centered radical cation should be more reactive than its counterpart neutral radical in hydrogen atom abstraction, the argument being that a stronger N–H bond is formed in the former case.[14,15] A corollary is that for the reverse process of hydrogen atom transfer from nitrogen, the reaction of the neutral radical should be favored over that of the radical cation, and this case is clearly exemplified here by the facility of **5** → **6** in comparison with **2** → **3**.[16,17] Since the above prediction depends only on the relative heats of reaction, the origin of the reactivity difference can be kinetic or thermodynamic. Clearly the reaction selectivity will in general be greatest when thermodynamics controls the outcome, such that an endothermic hydrogen transfer to the radical becomes exothermic for the radical cation, and vice versa for the reverse process.[18] These simple principles are nicely illustrated by the present results and those previously obtained in studies of the Hofmann–Löffler reaction.[13]

Acknowledgment. We thank Professor Stephen F. Nelsen for his interest in the problem and for communicating the results of his computations on the reactions of interest. We are also indebted to a referee who encouraged us to expand our discussion to include a more explicit consideration of the information gained from the Hofmann–Löffler reaction. This research has been supported by the Division of Chemical Sciences, U.S. Department of Energy (Report DOE/ER/02968-163).

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(13) The Hofmann–Löffler reaction has an extensive bibliography. Some leading references to the history, mechanism, and synthetic utility of this reaction are: (a) Wolff, M. E. *Chem. Rev.* **1963**, *63*, 55. (b) Wawzonek, S.; Thelen, P. H. *J. Am. Chem. Soc.* **1950**, *72*, 2118. (c) Wawzonek, S.; Nelson, Jr., M. F.; Thelen, P. J. *J. Am. Chem. Soc.* **1951**, *73*, 2806. (d) Corey, E. J.; Hertler, W. R. *J. Am. Chem. Soc.* **1960**, *82*, 1657. (e) Neale, R. S.; Walsh, M. R. *J. Am. Chem. Soc.* **1965**, *87*, 1255. (f) Neale, R. S. *Synthesis* **1971**, *1*. (g) Deno, N. C. In *Methods in Free Radical Chemistry*; Huyser, E. S., Ed.; Marcel Dekker: New York, 1972; Vol. 3, Chapter 3, pp 135–154. (h) Chow, Y. L.; Danen, W. C.; Nelsen, S. F.; Rosenblatt, D. H. *Chem. Rev.* **1978**, *78*, 243–274. (i) Green, M. M.; Moldowan, J. M.; Armstrong, M. W.; Thompson, T. L.; Sprague, K. J.; Hass, A. J.; Artus, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 849.

(14) Williams, F. *J. Am. Chem. Soc.* **1962**, *84*, 2895.

(15) By means of a simple thermochemical cycle, the difference between the $-\Delta H$ values for **3** → **2** and **6** → **5** can also be related to the difference between the proton affinities or basicities of **5** and **6**. Another useful relation obtained by coupling these reactions together is that, at equilibrium,

$$\log_{10} \frac{[\mathbf{2}][\mathbf{6}]}{[\mathbf{3}][\mathbf{5}]} = \mathrm{p}K_a(\mathbf{2}) - \mathrm{p}K_a(\mathbf{3})$$

(16) Computations by Nelsen using the AM1 program show that the reaction

$$\mathbf{3} + \mathbf{5} \rightarrow \mathbf{2} + \mathbf{6}$$

is exothermic by 20.6 kcal mol^{-1}, in agreement with the principle of our discussion here and elsewhere:[14] Nelsen, S. F., private communication.

(17) Neale and Walsh[13e] have criticized our earlier brief consideration[14] of the Hofmann–Löffler reaction by stating that contrary to our thesis, the basicity of Bu_2N may be greater than that of the parent amine Bu_2NH, since there is evidence that the basicity of the anilino radical C_6H_5NH exceeds that of aniline (Land, E. J.; Porter, G. *J. Chem. Soc.* **1961**, 3540). We believe that this comparison is inappropriate and emphasize that our considerations are not applicable to delocalized radicals. Curiously, Neale and Walsh also seem to doubt the validity of this comparison in footnote 13 of their paper. More recently, it has been shown that the basicity of Me_2NH exceeds that of Me_2N (Fessenden, R. W.; Neta, P. *J. Phys. Chem.* **1972**, *76*, 2857), and this is in fact the general rule for localized nitrogen-centered radicals.[13h]

(18) For simplicity, we assume that the contribution of entropy changes, which should be minimal for hydrogen-transfer reactions of the type considered here, through $T\Delta S$ to the position of thermodynamic equilibrium can be neglected in comparison with ΔH.

Isolation and Characterization of Vinylidene from the Dehydrogenation of Ethylidyne on the Ru(001) p(2×2)O Surface

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Although the structure and bonding of a variety of adsorbed species on transition-metal surfaces have been compared to those of similar ligands in homogeneous metal compounds, the chemical reactions which these two entities undergo have not been related. This connection represents the logical and necessary next step in relating the organometallic chemistry of homogeneous compounds with that of extended surfaces, i.e., the relationship between homogeneous catalysis by organometallic compounds and heterogeneous catalysis by metallic surfaces. It has been found that ethylene reacts with $Os_3(CO)_{12}$ to form a μ-vinylidene complex, $H_2Os_3(CO)_9(CCH_2)$, which can be hydrogenated to a μ-ethylidyne complex, $H_3Os_3(CO)_9(CCH_3)$.[1-3] Similarly, ethylene adsorbed on the hexagonal Ru(001),[4] Pt(111),[5] Pt(100),[6,7] Pd(111),[9] and Rh(111)[10] surfaces at room temperature forms ethylidyne, which dehydrogenates at higher surface temperatures. However, vinylidene has been neither isolated nor unambiguously identified as an intermediate in either the formation or the decomposition of adsorbed ethylidyne.[11] This paper reports the first conclusive spectroscopic identification of adsorbed vinylidene, which was observed following the annealing of adsorbed ethylidyne on the Ru(001) p(2×2)O surface.[12]

The high-resolution electron energy loss spectroscopic (EELS) measurements were carried out in an ultrahigh vacuum system that has been described in detail previously.[14] The p(2×2) oxygen overlayer on the Ru(001) surface, which is depicted in Figure 1a, corresponds to a fractional surface coverage of atomic oxygen of 0.25. The existence of this ordered overlayer was confirmed by EEL spectra which exhibit a $\nu_\perp$(Ru–O) mode at 535 cm^{-1} and a phonon mode characteristic of the ordered overlayer at 250 cm^{-1}.[15]

Exposure of the Ru(001) p(2×2)O surface to ethylene at temperatures below 240 K results in the adsorption of π-bonded molecular ethylene.[13,16] Upon annealing to 250 K, the π-bonded

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[†] AT&T Bell Laboratories Predoctoral Fellow.

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(7) The Pt(100) surface reconstructs to a slightly buckled, close-packed (5×20) superstructure.[8]

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(11) Indeed, *no intermediate* has been observed in the reaction of molecularly adsorbed ethylene to ethylidyne. Likewise, no intermediate in the decomposition of adsorbed ethylidyne has been observed heretofore in which carbon–carbon bonding is preserved.

(12) The ethylidyne is a stable intermediate in the dehydrogenation of π-bonded, molecular ethylene on the Ru(001) surface on which an ordered p(2×2) overlayer of oxygen adatoms is present.[13]

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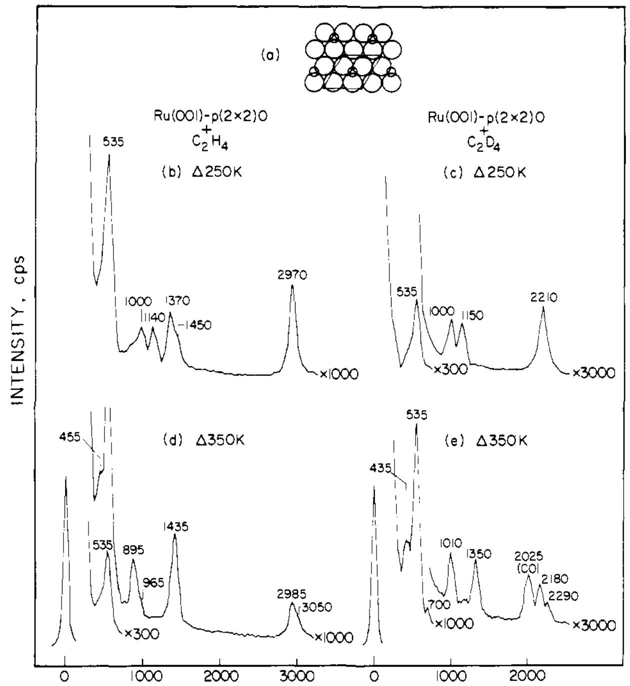

Figure 1. (a) Unit cell and basis of the p(2×2) ordered oxygen overlayer on the Ru(001) surface. The EEL spectra that result from 2-langmuir, exposures of (b),(d) C_2H_4 and (c),(e) C_2D_4 on the Ru(001) p(2×2)O surface at 80 K and heated to (b),(c) 250 and (d),(e) 350 K. The intense peak at 535 cm^{-1} in all spectra is due to the $\nu_\perp$(Ru—O) mode of the p(2×2)O oxygen overlayer. The peak at 2025 cm^{-1} in spectrum (e) is due to the ν(C≡O) mode of a small amount ($\theta_{co} < 0.01$) of coadsorbed carbon monoxide.

Table I. Comparison of Vibrational Frequencies (in cm^{-1}) of Vinylidene on the Ru(001) p(2×2)O Surface with $Os_3H_2(CO)_9(CCH_2)$

mode	CCH_2 on Ru(001) p(2×2)O	CCD_2 on Ru(001) p(2×2)O	$Os_3H_2(CO)_9(CCH_2)$ (3)
ν(RuC)	455	435	255–311
$\tau(CH_2)$ or $\tau(CD_2)$	nr^a	nr^a	808
$\omega(CH_2)$ or $\omega(CD_2)$	895	700	959
$\rho(CH_2)$ or $\rho(CD_2)$	965	nr^a	1048
$\delta(CH_2)$ or $\delta(CD_2)$	1435	1010	1328
ν(CC)	1435	1350	1467
$\nu_s(CH_2)$ or $\nu_s(CD_2)$	2985	2180	2990
$\nu_a(CH_2)$ or $\nu_a(CD_2)$	3050	2290	3052

^{a}nr = not resolved.

ethylene reacts to form chemisorbed ethylidyne with the desorption of hydrogen. The ethylidyne is identified by intense ν(CC) and $\delta_s(CH_3)$ modes at 1140 and 1370 cm^{-1} (1150 and 1000 cm^{-1} for CCD_3) which are evident in the EEL spectra of Figure 1b,c.[17]

Upon heating to approximately 350 K, the ethylidyne reacts quantitatively to form vinylidene with simultaneous evolution of hydrogen. The EEL spectra of adsorbed vinylidene are shown in Figure 1d,e. The intense feature at 1435 cm^{-1} in Figure 1d is due to the overlapping ν(CC) and $\delta(CH_2)$ modes of CCH_2. The $\delta(CD_2)$ mode shifts to 1010 cm^{-1} in the deuterated spectrum (Figure 1e), permitting the observation of the ν(CC) mode of CCD_2 at 1350 cm^{-1}. The modes of the adsorbed vinylidene are assigned and compared to those of vinylidene in $H_2Os_3(CO)_9(CCH_2)$ in Table I. The excellent agreement between the vibrational frequencies of the vinylidene ligand and the adsorbed vinylidene suggests that the bonding of the two is quite similar. An X-ray crystallographic structural determination of the triosmium cluster has shown that the CCH_2 ligand is bridge-bonded to two osmium atoms, that the carbon–carbon bond length of 1.38 Å is only slightly elongated from that of gaseous ethylene (1.34 Å), and that there is π-electron donation from the carbon–carbon double bond to the third osmium atom.[1-3] The carbon–carbon bond length of the vinylidene ligand suggests that the carbon atoms are nearly sp^2-hybridized, and due to the good agreement between the ν(CC) modes of the vinylidene ligand and the adsorbed vinylidene, the carbon atoms of the latter are also expected to be nearly sp^2-hybridized. The frequency of the ν(CC) mode of the adsorbed CCH_2 is lowered from that of CH_2CBr_2 (1593 cm^{-1})[18] and that of the μ-vinylidene ligand in $Cp_2Mn_2(CO)_4(CCH_2)$ (1542 cm^{-1})[19] due to π-electron donation from the carbon–carbon bond of the vinylidene to the ruthenium surface upon which the p(2×2) oxygen overlayer is present. This π-electron donation implies that the adsorbed vinylidene is tilted with respect to the surface normal, as is observed in $H_2Os_3(CO)_9(CCH_2)$.

Annealing the adsorbed vinylidene to 400 K initiates decomposition to methylidyne (identified by EELS) and surface carbon with simultaneous evolution of hydrogen, and the methylidyne decomposes above 500 K, creating additional surface carbon and evolving hydrogen.[13] Hydrogen thermal desorption spectra are also consistent with this decomposition mechanism. These spectra show that half of the total amount of hydrogen desorbs below 350 K, indicating that the species present on the surface at this temperature has a stoichiometry of C_2H_2. Another quarter of the hydrogen desorbs in a peak centered at 400 K, in accordance with the decomposition of vinylidene to methylidyne. The final quarter of the hydrogen desorbs between 500 and 700 K as the methylidyne decomposes.

In contrast to the formation of vinylidene from ethylidyne[20] and the subsequent decomposition of vinylidene to methylidyne on the Ru(001) p(2×2)O surface, ethylidyne decomposes completely near 355 K to carbon and hydrogen on the Ru(001) surface.[4,21] The fact that methylidyne is a stable intermediate in the decomposition of ethylidyne on the Ru(001) p(2×2)O surface, while it is not on the Ru(001) surface, implicates the existence of different mechanisms of the decomposition reactions on the two surfaces. On Ru(001), sp^3 hybridization and σ-bonding to the surface are favored, whereas on Ru(001) p(2×2)O sp^2 hybridization and π-donation to the surface are favored, as judged, for example, by the di-σ-bonded and π-bonded molecularly adsorbed ethylene that is observed on the respective surfaces. Hence, the π-bonded vinylidene that was isolated on the Ru(001) p(2×2)O surface is unlikely to be an (unstable) intermediate in ethylidyne decomposition on Ru(001), although a different, more nearly sp^3-hybridized vinylidene may well be involved.[22]

To summarize, adsorbed vinylidene has been isolated following the decomposition of ethylidyne on the Ru(001) p(2×2)O surface at 350 K. The bonding of the adsorbed vinylidene is analogous to that of the vinylidene ligand in $H_2Os_3(CO)_9(CCH_2)$, with very nearly sp^2-hybridized carbon atoms and tilting of the vinylidene with respect to the surface normal due to π-electron donation from the carbon–carbon double bond to the surface. Indeed, the formation of vinylidene from adsorbed ethylidyne is analogous to the reverse of the hydrogenation reaction of $H_2Os_3(CO)_9(CCH_2)$ to $H_3Os_3(CO)_9(CCH_3)$. The decomposition of ethylidyne to vinylidene on the Ru(001) p(2×2)O surface differs from the decomposition mechanism of ethylidyne on the Ru(001) surface due to electronic perturbations of the ruthenium surface by the

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(16) The nature of this chemisorption bond is very different from that of the di-σ-adsorbed ethylene on the clean Ru(001) surface.[4]

(17) A detailed discussion of the assignment of all the observed vibrational modes of adsorbed ethylidyne has been presented elsewhere.[4]

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(20) The observation of ethylidyne decomposition to vinylidene, but not the reverse reaction, is a consequence of the negligible coverage of hydrogen on the surface at the temperatures at which vinylidene is stable. The recombinative desorption of hydrogen occurs below 220 K on the Ru(001) p(2×2)O surface.

(21) On the Ru(001) surface, ethylene also reacts to form acetylide (CC-H), which decomposes to methylidyne at 360 K. The methylidyne dehydrogenates between 500 and 700 K.[4]

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ordered oxygen overlayer. These perturbations are also manifest in the observed π-bonding of molecular ethylene at 200 K, as opposed to the di-σ-bonded molecular ethylene that is observed on the Ru(001) surface.

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Superhyperfine Coupling between Metal Ions at the Active Site of *S*-Adenosylmethionine Synthetase

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S-Adenosyl-L-methionine synthetase (ATP:L-methionine *S*-adenosyltransferase) is one of numerous enzymes which require monovalent cations for significant catalytic activity.[1-3] Although *S*-adenosyl-L-methionine (AdoMet) synthetase from *Escherichia coli* has been shown to bind a single monovalent cation on each of the four identical subunits,[3] it had not been determined whether this cation binds at the active site. Like many other monovalent cation activated enzymes for which the physiological cation activator is probably K^+, the Tl^+ ion activates to ~80% of the level of K^+ and binds to the enzyme with higher affinity than other monovalent cation activators.[3,4] In a continuation of our EPR studies using the VO^{2+} ion to probe the structure of the divalent metal ion binding site at the active site of AdoMet synthetase,[5] we have observed superhyperfine coupling between the nuclear spin of the Tl^+ ion and the electron spin of VO^{2+}. The results reported herein demonstrate that the monovalent cation activator binds at the active site and suggest the formation of a metal ion cluster at the active site of *S*-adenosylmethionine synthetase.

S-Adenosylmethionine synthetase was purified to homogeneity from the *E. coli* strain DM25pK8[3,6] and was prepared for EPR spectroscopy as described.[5] All samples were prepared in D_2O solutions of 50 mM Hepes/$(CH_3)_4N$ buffer (Hepes = 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid), pH meter reading 7.6 (uncorrected for deuterium effect on the pH electrode), since narrower spectral lines are obtained in D_2O.[5] EPR spectra were recorded on a computer-interfaced Varian E-109 spectrometer operating at 9.14 GHz. Spectra were recorded in solution at 1 °C, and were generally the average of 4–10 scans. Spectra were analyzed by computer simulation, using the program QPOW of Belford and co-workers.[7] The reported *g* values and hyperfine coupling constants are apparent values since the rigid limit values are partially averaged due to slow rotation of the macromolecular complex. Uncertainties in the reported hyperfine coupling constants are estimated to be ±1 MHz and uncertainties in *g* values to be ±0.003.

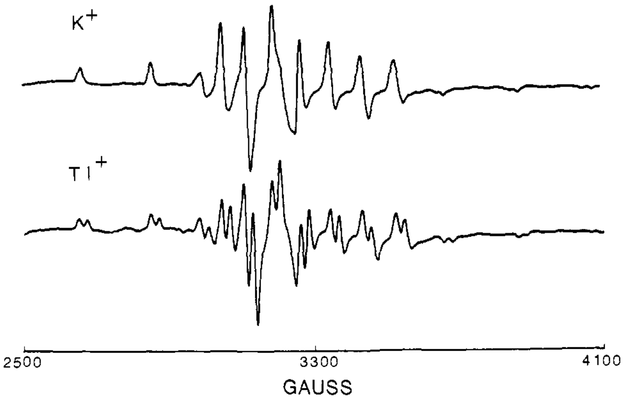

Figure 1. EPR spectra of VO^{2+} complexes of *S*-adenosylmethionine synthetase. Solutions contained 1.0 mM AdoMet synthetase active sites, 1.0 mM $VOSO_4$, 5.0 mM methionine, 1.0 mM AMPPNP, and either 50 mM KNO_3 or 2 mM $TlNO_3$.

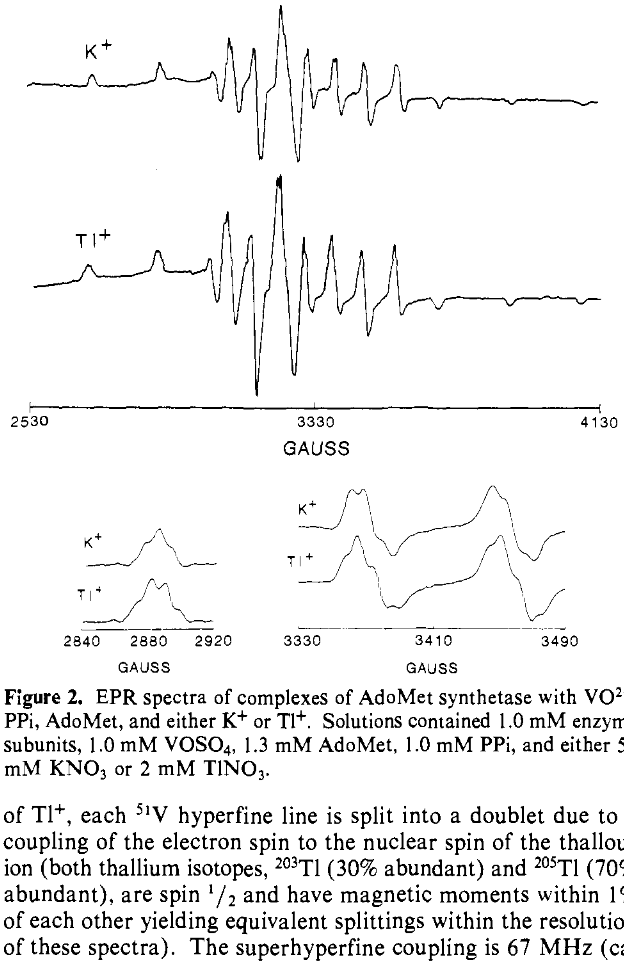

Figure 2. EPR spectra of complexes of AdoMet synthetase with VO^{2+}, PPi, AdoMet, and either K^+ or Tl^+. Solutions contained 1.0 mM enzyme subunits, 1.0 mM $VOSO_4$, 1.3 mM AdoMet, 1.0 mM PPi, and either 50 mM KNO_3 or 2 mM $TlNO_3$.

Figure 1 compares EPR spectra for complexes of *S*-adenosylmethionine synthetase with VO^{2+}, methionine, and the ATP analogue 5′-adenylylimidodiphosphate (AMPPNP) in the presence of K^+ and Tl^+. The spectra, which are essentially rigid-limit powder spectra due to the slow rotation of the 168 000-dalton protein complex, show that the *g* values and ^{51}V hyperfine coupling constants for the axially symmetric spectra are identical for the two monovalent cations ($g_\parallel = 1.923$, $g_\perp = 1.975$; $A(^{51}V)_\parallel = 540$ MHz, $A(^{51}V)_\perp = 208$ MHz). However, in the presence of Tl^+, each ^{51}V hyperfine line is split into a doublet due to a coupling of the electron spin to the nuclear spin of the thallous ion (both thallium isotopes, ^{203}Tl (30% abundant) and ^{205}Tl (70% abundant), are spin $^1/_2$ and have magnetic moments within 1% of each other yielding equivalent splittings within the resolution of these spectra). The superhyperfine coupling is 67 MHz (ca. 23 G) for both the parallel and perpendicular orientations of the complex in the magnetic field. Since the coupling is isotropic, it arises from delocalization of the unpaired electron spin into the Tl^+ orbitals. The superhyperfine coupling constant is equivalent to 0.16% of the unpaired electron spin density being located in a thallium 6s orbital.[8] The maximal anisotropy of the interaction is 3 MHz, which would have been undetectable at these line widths; in a point dipole approximation,[8] a 3-MHz anisotropy would reflect a distance of 3.6 Å between V(IV) and Tl^+, yielding a lower limit for the separation of the ions.

The other complexes of AdoMet synthetase with VO^{2+} and substrates were examined for coupling to the Tl^+ ion. The addition of Mg(II) to the above complex (which allows catalysis to occur

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