stage we are not commiting ourselves to an acceptance of any particular viewpoint—we merely demonstrate that the generally accepted significance of ρ values is quite contrary to the Hammond postulate and note that in general such interpretation of *linear* free energy relationships is by definition incompatible with structure–reactivity correlations invoking variable transition states.[18]

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[18] See, *e.g.*, remarks on the Brønsted equation: F. G. Bordwell and W. J. Boyle, *J. Amer. Chem. Soc.*, **94**, 3910 (1972).

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Nuclear Magnetic Relaxation Rates of Thallium(I)-205 in Aqueous Solution with Respect to Complexing of Molecular Oxygen

Sir:

The nmr relaxation rates of spin half ($^1/_2$) nuclei have not been widely investigated. Information is available for hydrogen, fluorine-19, carbon-13, and silicon-29.[1-3] Recently, a study of spin-lattice relaxation rates of ^{205}Tl, in the presence of the enzyme pyruvate kinase, has been reported in an attempt to indicate the binding site of the monovalent metal activator.[4,5] The only other study of ^{205}Tl(I) spin relaxation was aimed at the nature of bonding in aqueous solution between paramagnetic $Fe(CN)_6^{3-}$ and free Tl(I) ion.[6] A study of ^{205}Tl(I) nuclear spin relaxation is reported here for the aqueous ion and selected results are listed in Table I. No dependence of R_1 on the Tl(I) concentration is observed between 0.03 and 3.5 *M* and furthermore the anion dependence of R_1 is also negligible for the ions acetate, fluoride, sulfate, and nitrate. The most striking feature of the data is the sensitivity of R_1 and R_2 to dissolved oxygen, which at atmospheric partial pressure has a solubility of 4.8×10^{-6} mole fraction in pure water at 25°.[7] The relaxation times of ^{205}Tl(I) solutions cited by Reuben and Kayne[5,6] are included in Table I and clearly reflect the presence of dissolved oxygen. The conclusions of these authors, regarding distances between monovalent and bivalent binding sites estimated from relaxation rates of ^{205}Tl(I), are quite suspect since both R_1 and R_2 are strongly dependent on oxygen concentration.

The results in this study indicate a relaxation mechanism, in oxygenated solutions, which is dominated by electron-nuclear dipole–dipole interaction. A contact hyperfine interaction seems unlikely because R_2 is not appreciably greater than R_1.[8] The dipole–dipole mechanism is very short range with an r^{-6} dependence, so oxygen must penetrate the loose solvation sphere[9] of Tl(I) to form a weak "complex" through interaction with the thallous ion, *via* the (6s) "lone pair" electrons. Work is in progress to discover the nature of this metal ion–molecular oxygen complex. The rapid reversibility and reproducibility of the relaxation data with oxygen pressure are a strong argument in favor of an ion–molecule complex. It is known that ^{23}Na(I) and ^{7}Li(I) in aqueous solution do not relax appreciably faster with molecular oxygen in solution.[10,11] The effect is almost two orders of magnitude smaller. The relaxation rate of ^{19}F in aqueous fluoride ion is affected, to about the same extent as ^{205}Tl(I) in this study, by addition of aqueous Cu(II) which forms a paramagnetic complex CuF^+.[12,13] Cu(II) and ferricyanide also enhance the relaxation rate of ^{205}Tl(I) (see Table I). The preferential increase in R_2 indicates a significant hyperfine transverse relaxation which is not completely averaged by exchange.

Table I. Relaxation Rates of Aqueous Solutions of Tl^+

Solute	Solvent	Concn, mol l.$^{-1}$	R_1,[a] sec^{-1}	R_2,[b] sec^{-1}
$TlNO_3$	$H_2O(N_2)$[c]	0.0803	0.54	0.83
	H_2O(air)[d]		8.3	9.6
	$H_2O(O_2)$[e]		38.0	
	f	*f*	5.8[f]	17.5[f]
	$D_2O(N_2)$[c]	0.0839	0.44	0.8
	D_2O(air)[d]		8.3	*g*
	$D_2O(O_2)$[e]		41.0	*g*
	$H_2O(N_2)$[c] 8×10^{-5} *M* $Fe(CN)_6^{3-}$	0.080	15.3	13
	$H_2O(N_2)$[c] 7×10^{-3} *M* Cu^{2+}	0.15	9.9	19

[a] $R_1 = 1/T_1$, the longitudinal relaxation rate, measured from plots of log of free-induction decay amplitude *vs.* pulse spacing (ref 13), from standard 180 to 90° pulse sequences. Estimated precision ±4%. [b] $R_2 = 1/T_2$, the transverse relaxation rate, measured from standard Carr-Purcell spin-echo sequences (ref 13). Estimated precision ±8%. A Fabritek (Nicolet) 1074 signal averager was used to enhance repetitive signals in both R_1 and R_2 measurements. Probe temperature 26.0°. [c] The sample was thoroughly purged with N_2, and less than 10^{-6} mol of $N_2H_4 \cdot H_2O$ was added to reduce any remaining O_2. [d] The sample was saturated with air. [e] The sample was saturated with O_2 at 1 atm. [f] From Table IV of ref 5. The sample consisted of 0.10 *M* $TlNO_3$ and 0.05 *M* cacodylate buffer. [g] Measurements of R_2 in D_2O in the presence of dissolved oxygen indicate that the relaxation rate is independent of the isotopic composition of the solvent. The enhancement of the relaxation rate follows that in H_2O.

The relaxation mechanism in the absence of oxygen or paramagnetic substances is somewhat problematical because in uncontaminated water the relaxation times of ^{205}Tl are almost independent of isotope substitution of deuterium in the water. The relaxation mechanism, if dominated by nuclear dipole–dipole coupling (correlation times for tumbling assumed equal), should give R_1 and R_2 approximately in the ratio $\gamma_H^2/\gamma_D^2 \simeq 42$ when H_2O is changed to D_2O as solvent. An order of magnitude calculation for the dipole–dipole contribu-

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tion in the case of ^{23}Na(I) in aqueous solution gives $R_1 \simeq 10^{-2}$ sec^{-1}. In ^{205}Tl solutions the experimental relaxation rate is much faster than this, but if the larger size of this ion is taken into account, an even smaller relaxation rate would be expected.

The accelerated relaxation rate of ^{205}Tl(I) in a pure aqueous solution is similar to an effect that has been reported for ^{129}Xe in liquid xenon.[14] The explanation in the case of ^{129}Xe is a fluctuating local magnetic field associated with rotating distorted spherical orbitals during Xe/Xe collisions. This has been called a "transient spin-rotation relaxation."[15] If Tl(I)/Tl(I) encounters in solution are very frequent and also give a random local magnetic field, it is possible that this mechanism contributes to relaxation of ^{205}Tl(I) in aqueous solution. A scalar interaction of the "first kind," discussed by Abragam,[16] between ^{205}Tl(I) and ^{203}Tl(I) is another possible mechanism. This unusual relaxation pathway for aqueous solutions would render the relaxation rates of ^{205}Tl(I) and ^{203}Tl(I) equal. Measurements of the relaxation rates of ^{203}Tl(I) (spin $^1/_2$, 30% abundant) give values equal to those for ^{205}Tl(I) reported in Table I within experimental error.

In all relaxation mechanisms, R_1 is dependent on rotational and translational correlation times in the liquid which can be empirically treated in terms of the macroscopic viscosity. An interesting feature of the tabulated values of R_1 is that the ratios for $R_1(D_2O)/R_1(H_2O)$ are the same as the ratios of the macroscopic viscosities of pure D_2O and H_2O at 25°. This infers that the relaxation mechanism is the same in H_2O and D_2O.

The results reported here point out the need for scrupulous care in purifying materials and preparing samples to avoid molecular oxygen and other paramagnetic impurities. Work is proceeding to determine the nature of the oxygen complex using both nmr and other techniques.

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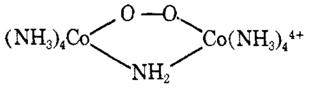
A Novel Compound with a Planar Fe–S–S–Fe Bridge and Its Possible Relation to Ferredoxins[1]

Sir:

In exploring iron–sulfur chemistry which may have a bearing on structure and function in the ferredoxin class of proteins,[2] we have synthesized a compound, [CpFe(SC_2H_5)S]$_2$ (Cp = cyclopentadienyl), whose X-ray crystal structure, shown in Figure 1, reveals a novel feature: a planar Fe–S–S–Fe bridge (see Table I). The ethyl sulfide ligands also bridge the two iron atoms, while the π-cyclopentadienyl groups complete the roughly octahedral iron coordination spheres. The iron–iron separation, 3.31 Å, is nonbonding.[3] Other distances and angles, given in Table II, are unexceptional. While a M–S–S–M bridge is unprecedented, there are several analogous *peroxide* and *superoxide* bridges in binuclear cobalt(III) complexes,[4] *e.g.*



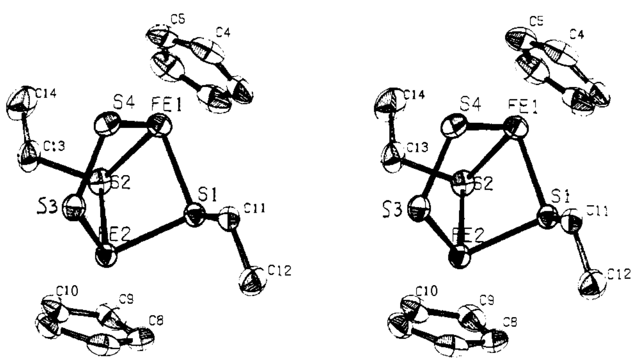


Figure 1. ORTEP stereodrawing of [CpFe(SC_2H_5)S]$_2$ showing the anisotropic thermal ellipsoids.

Table I. Least-Squares Plane of the Fe–S–S–Fe Bridge

$0.6879X + 0.5451Y - 0.4793Z = 7.7909$			
Atom	Dev, Å	Atom	Dev, Å
Fe(1)	+0.003	S(3)	+0.012
Fe(2)	−0.003	S(4)	−0.014

Table II. Interatomic Distances (Å) and Angles (deg)[a]

	Distances		
Fe(1)–Fe(2)	3.307 (3)	Fe(2)–S(2)	2.285 (5)
Fe(1)–S(1)	2.273 (5)	Fe(2)–S(3)	2.129 (5)
Fe(1)–S(4)	2.129 (5)	Fe(2)–S(1)	2.275 (5)
Fe(1)–S(2)	2.289 (5)	S(3)–S(4)	2.023 (7)
	Angles		
S(1)–Fe(1)–S(2)	76.44 (5)	S(1)–Fe(2)–S(2)	76.50 (5)
S(1)–Fe(1)–S(4)	94.31 (5)	S(1)–Fe(2)–S(3)	93.98 (5)
S(2)–Fe(1)–S(4)	93.43 (5)	S(2)–Fe(2)–S(3)	94.17 (5)
Fe(1)–S(1)–Fe(2)	93.28 (5)	Fe(1)–S(4)–S(3)	107.76 (6)
Fe(1)–S(2)–Fe(2)	92.62 (5)	Fe(2)–S(3)–S(4)	107.33 (6)

[a] Standard deviations in parentheses refer to the least significant digit.

Moreover, a similar structure involving Fe(III) atoms has been suggested for the oxy form of the oxygen binding protein hemerythrin.[5,6]

The nmr spectrum of [CpFe(SC_2H_5)S]$_2$ shows a *sharp* cyclopentadienyl resonance at τ 5.27 (compare τ 5.68 for diamagnetic [Cp(CO)Fe(SCH_3)]$_2$[7]). Susceptibility measurements on a Gouy balance confirm that the

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