Table I. Comparison of Carbon-13 Shifts and Intensities of Two Identical Samples One of Which Contained Paramagnetic Additive (~0.01 *M*)

	Spectrum of control sample			Spectrum of treated sample		
Assignments	Memory address no.	δ_{CS_2}, ppm	Ht, mm	Memory address no.	δ_{CS_2}, ppm	Ht, mm
Tetramethylsilane	1939	193.1	20	1938	192.9	26
Hexamethyldisiloxane	1920	191.0	63	1920	191.0	76
Methylene	1555	151.6	135	1555	151.6	91
Methyl ester	1458	141.2	68	1458	141.2	66
Chloroform	1218	115.3	72	1217	115.1	189
Aromatic, para	759	65.7	113	759	65.7	109
Aromatic, ortho	745	64.2	168	745	64.2	231
Aromatic, meta	738	63.5	246	738	63.5	242
Aromatic, substituted	691	58.4	28	691	58.4	111
Carbonyl	345	21.1	58	346	21.2	109
Noise			5			5

that the cmr spectrum would have 2.44 Hz per address, and assuming that the ^{13}C peaks would not be more broadened than the ^1H peaks.

Samples were prepared consisting of 654 ± 1 mg of methyl phenylacetate, 300 ± 1 mg of hexafluorobenzene, 159 ± 1 mg of hexamethyldisiloxane, 80 ± 2 mg of tetramethylsilane, and 1.00 ml of spectroquality chloroform. To one of these, 7 mg of iron tris-(pentane-2,5-dionate) was added. The samples were run at probe temperature (45° inside sample) in 10-mm tubes on a Bruker HX-90 spectrometer with a 15-in. magnet, pulse unit, broad-band ^1H decoupler, and fluorine lock. In ~13 min 2048 pulses of 20-μsec duration were given, with 0.4096-sec scanning time and no additional rest time between pulses. The range of 5000 Hz was covered by the 2048 addresses of the transformed spectrum. All other adjustments of the spectrometer and accessories were also kept constant.

Table I lists the spectral data. It shows that: (1) shifts are constant within one memory address absolute; (2) the height of CO, substituted aromatic, and $CHCl_3$ carbon increases dramatically; (3) the height of methylene carbon decreases to about the level of the above ones; (4) no noticeable broadening occurs; (5) a medium effect rather than specific association operates, as the reagent is unbiased toward the COO carbon *vs.* the less coordinating environment of the substituted aromatic carbon.

Further work is to be directed toward determining the best compromise between degree of enhancement of the intensity of weak carbons, loss of NOE enhancement, peak broadening, relaxing efficiency, inertness, and removability of additive, etc.

The results so far are of great practical benefit, since *the weakest, most easily missed peaks are enhanced* by adding only a trace of additive. This tool allows (1) shorter accumulation time (machine time) for a given amount of sample or (2) a smaller absolute amount of or more dilute sample, and (3) indirect benefits, *e.g.*, easier retention of spectrometer lock, since either pulsing time is reduced, or more lock compound (a bad solvent for large molecules) can be employed when the substrate concentration is lower.

The preferred strategy for retaining the diagnostic value of high contrast involves (1) pulsing the untreated sample just enough time to see the intense peaks, then (2) adding the agent and pulsing to locate every carbon. The two together may take less time and offer more and more certain structural information than running the conventional PFT cmr alone to satisfactory signal-to-noise ratios.

The value of equalized intensities for tackling mixtures of unknowns and for quantitative analysis is evident.

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A Photochemical Reaction Induced by Infrared Radiation. The Kinetics of Planar-Octahedral Interconversion in a Nickel(II) Complex

Sir:

Photochemical reactions induced by infrared radiation are rather rare on account of (i) the low energy per quantum in comparison with that normally required to bring about chemical change and (ii) the efficient degradation of vibrational energy into translational energy, particularly in the liquid phase. However, if the irradiation power is high, as in a neodymium Q-switched laser (1.06 μm), and the detection system sufficiently sensitive, it is sometimes possible to observe chemical change in systems having a sufficiently low energy requirement. A recently reported example[1] is the ionic dissociation of *vibrationally* excited water, $H_2O^* \rightarrow H^+ + OH^-$, the reverse recombination being detected conductometrically (τ = 42 μsec at 296°K). We now report an example of a photochemical reaction initiated by 1.06-μm radiation involving the formation of an *electronically* excited species in the primary step.

The species concerned is the blue octahedral complex formed between nickel(II), 1,4,8,11-tetraazaundecane (2,3,2-tet), and water. In aqueous solution this exists mainly as the trans configuration in equilibrium[2] with the yellow, unhydrated, square-planar configuration (λ_{max} 440 nm).

$$\mathrm{Ni(2,3,2\text{-}tet)(H_2O)_2^{2+} \rightleftharpoons Ni(2,3,2\text{-}tet)^{2+} + 2H_2O} \qquad (1)$$

A 0.1 *M* solution of the complex chloride was irradiated at 23° with a 2-J (incident energy), 30 nsec, Q-switched pulse of 1.06-μm radiation from a neo-

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(1) D. M. Goodall and R. C. Greenhow, *Chem. Phys. Lett.*, **9**, 583 (1971).

(2) R. G. Wilkins, R. Yelin, D. W. Margerum, and D. C. Weatherburn, *J. Amer. Chem. Soc.*, **91**, 4326 (1969).

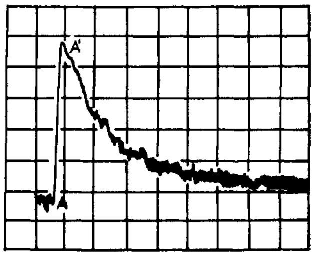

Figure 1. Absorbance change at 440 nm as a function of time in 0.1 *M* Ni(2,3,2-tet)$^{2+}$ at 23°: initial absorbance (*A*) 0.41; vertical scale, 1% absorbance change/division; horizontal scale, 0.2 μsec/division.

dymium laser[3] and the concentration of the square-planar form was monitored by the absorption at 440 nm; the result is shown in Figure 1. There was a rapid 5% rise (AA') in the concentration of the square-planar species followed by a return almost to the original level, with a relaxation time of about 0.3 μsec. The difference in the equilibrium absorbance before and after irradiation is due to the slight temperature rise in the system (~0.15°).

The relaxation time was independent of the concentration over the range 0.05–0.2 *M* but varied (0.3–0.09 μsec) with temperature (12–58°). The effect was observed at other monitoring wavelengths within the 440-nm band of the square-planar form and also when D_2O was used as solvent. D_2O is transparent at 1.06 μm whereas H_2O is not; this shows that the effect does not occur through absorption by the solvent. No absorbance changes were observed for nickel(II) chloride solutions in the absence of 2,3,2-tet; effects such as cavitation can therefore be ruled out as a possible cause of the observed transients. Since the complex absorbs at the laser wavelength ($\epsilon_{1.06}$ ~2.0 M^{-1} cm^{-1}), the absorption being attributed to the electronic transition ($^3T_{2g} \leftarrow {}^3A_{2g}$) of the trans-octahedral form,[4,5] we conclude that the observed effect in Figure 1 is due to a photochemical displacement of equilibrium 1 followed by rapid restoration of equilibrium (*i.e.*, chemical relaxation).

The interpretation of the relaxation time τ depends on the assumed mechanism for the configurational change. It is likely that this proceeds in two stages (L denotes 2,3,2-tet)

$$\mathrm{NiL^{2+} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NiL(H_2O)^{2+}} \qquad (2)$$

$$\mathrm{NiL(H_2O)^{2+} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NiL(H_2O)_2{}^{2+}} \qquad (3)$$

as proposed for the octahedral–tetrahedral interconversion in cobalt(II) complexes.[6] $\mathrm{NiL(H_2O)_2{}^{2+}}$ is a high-spin species whereas $\mathrm{NiL^{2+}}$ is a low-spin species.[2,4,5] Considerations of the stereochemistry and the extent of d-orbital perturbation expected to be caused by the water ligand[7] indicate that the pentacoordinated intermediate is also likely to be a high-spin species, so that step 2, involving a change of spin, is likely to be rate controlling.[8] On the basis of this mechanism and making the steady-state approximation for $\mathrm{NiL(H_2O)^{2+}}$, the following expression for the relaxation time τ may be derived[6]

$$\tau^{-1} = k_1[\mathrm{H_2O}] + k_{-1}k_{-2}/k_2[\mathrm{H_2O}] \qquad (4)$$

$$= k_1[\mathrm{H_2O}](1 + K) \qquad (5)$$

where $K = [\mathrm{NiL^{2+}}]/[\mathrm{NiL(H_2O)_2{}^{2+}}]$. Using the values[9] $K = 0.16$, $[\mathrm{H_2O}] = 55\ M$, $\tau = 0.28$ μsec, all at 23°, the value of k_1 at 23° is $(5.6 \pm 0.3) \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$. The activation parameters associated with k_1 were calculated from a least-squares plot of ln (k_1/T) *vs.* $1/T$: $\Delta H^{\ddagger} = 20 \pm 2$ kJ mol^{-1}; $\Delta S^{\ddagger} = -48.6 \pm 5$ J mol^{-1} K^{-1}; the errors quoted are twice the standard deviations. We have also observed similar effects in aqueous solutions of the Ni(II) complex with triethylenetetramine (trien), a homolog of 2,3,2-tet. The relaxation times were about a factor of 2 slower than in the 2,3,2-tet system.

Finally it may be noted that the transition, $^3T_{2g} \leftarrow {}^3A_{2g}$, which we believe to be responsible for the absorption of the laser radiation, is symmetry forbidden. It is therefore observable only on account of the simultaneous excitation of a molecular vibration of the correct symmetry, a point which may be relevant to a discussion of the photophysical processes involved in the rearrangement of the excited octahedral species, with the expulsion of two H_2O ligands, to the square-planar form. The enthalpy change[9] for equilibrium 1, 20 kJ mol^{-1}, confirms that the energy required to bring about photodissociation of the water molecules is less than that available at the laser wavelength (113 kJ mol^{-1}).

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[3] M. Farrell, K. J. Ivin, R. Jamison, and J. J. McGarvey, manuscript in preparation.

[4] C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 399 (1957).

[5] B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc. A*, 1331 (1966).

[6] R. D. Farina and J. H. Swinehart, *J. Amer. Chem. Soc.*, **91**, 568 (1969).

[7] E. K. Barefield, D. H. Busch, and S. M. Nelson, *Quart. Rev., Chem. Soc.*, 22, 483 (1968).

[8] We acknowledge valuable discussions with Dr. S. M. Nelson on this point.

[9] *K* values were estimated from spectral measurements using a value of 61 M^{-1} cm^{-1} for the extinction coefficient of $\mathrm{NiL^{2+}}$ at 440 nm, measured in aqueous solution saturated with $\mathrm{NaClO_4}$.[4] A value of $\Delta H° = 20 \pm 1$ kJ mol^{-1} for equilibrium 1 was calculated from the temperature variation of *K*.

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Nuclear Magnetic Resonance Paramagnetic Shift Reagents. The Use of Internal Protons as Standards for Structural Determinations. A Method for Determination of Complexation Equilibrium Constants

Sir:

Rare-earth paramagnetic and diamagnetic nmr shift reagents[1,2] have recently received widespread attention. Structural assignments have generally been made[1-3]

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[1] C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

[2] J. K. M. Sanders and D. H. Williams, *ibid.*, **93**, 641 (1971).

[3] H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958); G. N. La Mar, W. DeW. Horrocks, Jr., and L. C. Allen, *ibid.*, **41**, 2126 (1964); G. N. La Mar, *ibid.*, **43**, 1085 (1965); B. R. McGarvey, *ibid.*, **53**, 86 (1970); R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, **2**, 286 (1970); the exact form is unimportant to the present discussion.