Table I. EPR Parameters of 4-Substituted-1-norbornyl Radicals[a]

Radical	Hyperfine splittings, G 4-Substituent	exo H_β	g-value
4	2.45[b]	$a_{\parallel} = 13.2$ $a_{\perp} = 8.1$	2.0026
5	13	$a_{\parallel} = 8$	2.0062
6	16	$a_{\parallel} = 10$	2.0116

[a] Values from a preliminary analysis, complete results will be reported at a later date. [b] From the solution data of ref 5.

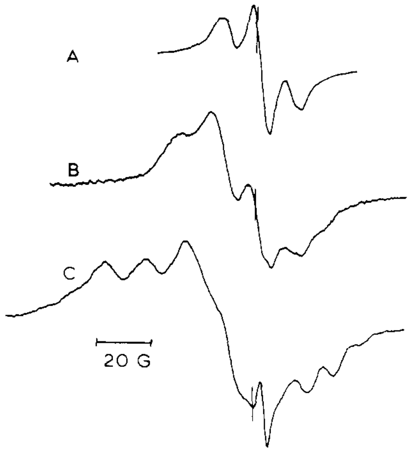
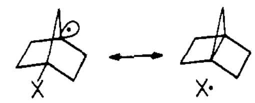


Figure 1. (A) EPR spectrum of **4** in argon at 12 K; (B) EPR spectrum of **5** in argon at 12 K; (C) EPR spectrum of **6** in argon at 12 K. Vertical bars indicate position of DPPH resonance; $g = 2.0037$.

retain a sizable anisotropy since a reasonable fit to the spectrum can be made with $a_{\parallel} = 13.2$ G and $a_{\perp} = 8.1$ G (Table I). The next largest hfsc in this radical is a long-range coupling of 2.45 G to the proton at the 4-position[5] which is not resolved in our spectrum.

Replacement of the 4-proton in the parent 1-norbornyl radical with either bromine or iodine results in sizable long-range halogen hyperfine coupling as evidenced by the EPR spectra of **5** and **6** shown in Figures 1B and 1C, respectively. Analysis of these spectra (Table I) reveals a bromine hfsc of 13 G (*g* value of 2.0062) for **5** and an iodine hfsc of 16 G (*g* value of 2,0116) for **6**. These hfsc and *g* values are much larger than one might expect from consideration of EPR data available for acyclic analogues of the 4-halo-1-norbornyl radicals. For example, the bromine hfsc of **5** is at least an order of magnitude larger than that of the γ-bromopropyl radical.[3] In fact, the hfsc and *g* values of **5** and **6** are among the largest reported for long-range halogen interaction and are comparable to those observed in radicals derived from 1-bromo- and 1-iodofluorenone oximes which have bromine hfsc of 10.4 G and iodine hfsc of 13.5 G with *g* values of 2.0068 and 2.0090, respectively[9] (cf. Table I).

The magnitudes of the hfsc and *g* values observed in the 4-halo-1-norbornyl radicals suggest the operation of a facile spin-delocalization mechanism in this system. The etiology of the 1,4-interaction in the norbornyl system has been investigated in theoretical studies by Hoffman and co-workers.[10] Their prediction of a predominantly "through-space" interaction in this system is supported by the results of Kawamura et al.[5] which suggests that the magnitude of the bridgehead proton hfsc in **4** may be adequately explained in terms of a direct "through-space" interaction. Such a mechanism, in valence-bond terminology, would take the form of a hyperconjugative interaction between the radical center and the C(4) to substituent bond. This interaction is represented pictorially below.



On this basis, it is perhaps not unreasonable to expect enhanced interaction (hence, larger hfsc and *g* values) as the 4-substituent is varied from hydrogen through bromine to iodine.

We are currently investigating possible chemical consequences of interactions of the type suggested by our data.

Acknowledgments. This work was supported in part by grants from the Research Foundation of the University of Connecticut and in part by Grant No. MPS 74-19380 from the National Science Foundation.

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Nonrigidity in Eight-Coordinate Tetrakis Chelates: the Stereochemical Integrity and Geometrical Isomerism of Tungsten (5-Methylpicolinato) (5,7-Dichloro-8-quinolinolato) Complexes

Sir:

All previous reports of eight-coordinate transition metal tetrakis chelates indicate nonrigidity on a nuclear magnetic resonance time scale at temperatures appreciably below room temperature.[1-8] In fact, Fay and his co-workers[1] have designated the tetrakis(*N*,*N*-dimethyldithiocarbamato)tantalum(V) cation as stereochemically rigid based on its nonequivalent proton magnetic resonance (^{1}H NMR) methyl resonances below −62 °C. We report here slow exchange limit ^{1}H NMR methyl signals at and above room temperature for the tetrakis eight-coordinate heterochelate tris(5-methylpicolinato)(5,7-dichloro-8-quinolinolato)tungsten(IV), abbreviated WP_3Q.

Furthermore, to our knowledge, geometrical isomers of an eight-coordinate transition metal complex in solution have not been obtained previously.[11,15] We wish to report the solution

Table I. Chromatographic and Spectral Properties of $W\overline{P}_nQ_{4-n}$ Series

Complex[a]	Elution order[b]	R_f $CHCl_3$	R_f $4CHCl_3$: $1CH_3COCH_3$ v/v	Low energy charge transfer transition[c] λ (nm)	$\bar{\nu}$ (cm^{-1})	ε (l. mol^{-1} cm^{-1})
WQ_4	1st	>0.9	>0.9	703	14 200	44 500
$W\overline{P}Q_3$	2nd	0.29	>0.9	675	14 800	38 100
α-$W\overline{P}_2Q_2$	3rd	0.11	0.83	648	15 400	27 000
β-$W\overline{P}_2Q_2$	4th	0.02	0.39	662	15 100	28 500
$W\overline{P}_3Q$	5th	0.01	0.32	623	16 000	22 200
$W\overline{P}_4$	6th	0.01	0.16	595	16 800	15 200

[a] The complexes are all diamagnetic with satisfactory analyses; cf. footnote 18. [b] Elution gradient from pure chloroform to chloroform/acetone solutions. [c] The spectra are for chloroform solutions except for the α and β isomers, which are for the $4CHCl_3$:$1CH_3COCH_3$ v/v eluting solvent.

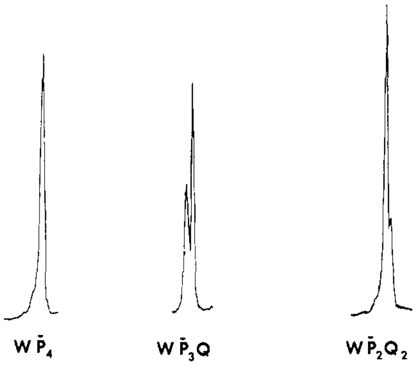

Figure 1. The methyl ^1H NMR resonances at 90 MHz for $W\overline{P}_4$, $W\overline{P}_3Q$, and $W\overline{P}_2Q_2$ at 35 °C in CD_2Cl_2.

evidence for two isomers of bis(5-methylpicolinato)bis(5,7-dichloro-8-quinolinolato)tungsten(IV),[18] abbreviated $W\overline{P}_2Q_2$. The isolated complexes give satisfactory analytical results for this formulation, both are diamagnetic as required for eight-coordination,[19] and both slowly isomerize to the same equilibrium mixture when redissolved. The two isomers have been designated α-$W\overline{P}_2Q_2$ and β-$W\overline{P}_2Q_2$.

We have developed synthetic methods for preparing a wide series of neutral molybdenum(IV) and tungsten(IV) tetrakis picolinato type species.[20] Previously, very inert d^2 tetrakis complexes of tungsten(IV) with 8-quinolinol derivatives had been synthesized in this laboratory[21,22] and their eight-coordinate nature proven via a single-crystal x-ray study.[23] Tetrakis(5-methylpicolinato)tungsten(IV)[18] exhibits only one methyl ^1H NMR signal at 2.44 ppm in CD_2Cl_2 (Figure 1),[24] which is consistent with a rigid dodecahedral $D_{2d}(mmmm)$, $S_4(gggg)$, or $D_2(gggg)$ stereoisomer;[17] an antiprismatic $C_4(llll)$, $D_2(llll)$, or $D_2(ssss)$ isomer; or an isomer or isomers of lower symmetry with unresolved methyl signals. Naturally, the single line is also consistent with a nonrigid structure. The substitution-inert nature of low-spin eight-coordinate d^2 complexes precludes rapid ligand exchange at room temperature.[25]

These syntheses have been extended to mixed ligand tetrakis heterochelates in order to determine whether the single resonances in the single ligand tetrakis homochelates are the result of nonrigid behavior or equivalent methyl groups in the ground state. The entire $W\overline{P}_xQ_y$ series, where $x + y = 4$, was prepared from a 2.5:2.5:1 mole ratio of $H\overline{P}$,[26] HQ, and $W(CO)_6$ in dry mesitylene heated under reflux conditions under nitrogen for 4 h.[27] The product mixture was separated on silica gel[28] with the chloroform eluent made progressively more polar with up to 30% acetone. A limiting slow-exchange ^1H NMR signal of intensity 2:1 has been observed for $W\overline{P}_3Q$[18] (Figure 1) from −50 to +55 °C.[29] This 2:1 resonance is consistent with the dodecahedral pseudo $D_{2d}(mmmm)$ isomer, which has been demonstrated for tetrakis(5-bromo-8-quinolinolato)tungsten(IV) in the solid state.[23] The actual symmetry of this new heterochelate complex cannot be higher than C_s if it has this common D_{2d} parentage. Other logical isomeric possibilities[30] for this complex all possess three nonequivalent methyl groups, which should have 1;1;1 ^1H NMR spectra, Naturally, if two of the methyl groups are very similar, their resonances may not be resolved, even at 90 MHz. Therefore, on a ^1H NMR time frame, the ligands of $W\overline{P}_3Q$ retain their relative stereochemical positions or "stereochemical integrity" without any appreciable broadening to at least 55 °C.[31]

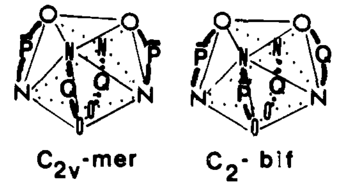

Figure 2. The two proposed $W\overline{P}_2Q_2$ isomers: meridonal (mer) and bifacial (bif).

During our isolation of the series of $W\overline{P}_xQ_y$ complexes, where $x + y = 4$, we noted a curious phenomenon. The third *and* fourth of the six bands obtained by liquid chromatography (or spots obtained by thin layer chromatography (Table I)) could be obtained by the reelution of either the third or the fourth band. The visible spectra of the two isomers in chloroform are slightly different. The α-$W\overline{P}_2Q_2$ isomer has maxima at 1.54 and 2.56 μm^{-1} with log ε values of 3.75 and 4.43, while the β-$W\overline{P}_2Q_2$ isomer has maxima at 1.51 and 2.70 μm^{-1} with log ε values of 3.68 and 4.45, respectively.[33] On aging in solution their spectra become indistinguishable and appear very similar to the original α-$W\overline{P}_2Q_2$ spectrum.

At 90 MHz two overlapping methyl ^1H NMR signals are observed (Figure 1) for the equilibrated $W\overline{P}_2Q_2$ complex at 2.41 and 2,37 ppm downfield from Me_4Si in CD_2Cl_2 with relative intensities of almost four to one. A thin layer chromatogram of the same solution yields two spots of similar relative absorption intensities, thus suggesting along with the visible spectral evidence that the α-$W\overline{P}_2Q_2$ isomer in equilibrated room temperature solutions is the dominant isomer. The ^1H NMR spectrum at 0 °C of the $W\overline{P}_2Q_2$ complex after equilibration in CD_2Cl_2 at 0 °C for 56 h shows a sharp decrease in the 2.37 ppm (β-$W\overline{P}_2Q_2$) methyl signal which slowly reappears on warming.

Two stereoisomers for the $W\overline{P}_2Q_2$ complex are logical assuming the $W\overline{P}_2Q_2$ species utilize the pseudo-$D_{2d}(mmmm)$ stereochemistry, which is consistent with the solid state structure of tetrakis(5-bromo-8-quinolinolato)tungsten(IV),[23] the $W\overline{P}_3Q$ methyl ^1H NMR signal intensities, and the lack of observable stereoisomers for other members of the $W\overline{P}_xQ_y$ series. The two isomers are labeled meridonal and bifacial in Figure 2.[34]

The visible spectra (Figure 2) give further evidence that the intermediate heterochelates retain the eight-coordinat geometry noted for the two homochelates at the ends of the series. The intense bands at the red end of the visible spectra are consistent with the metal to ligand charge-transfer designation determined for the tetrakis 8-quinolinol derivatives of tungsten(IV).[22] That is, the smaller aromatic picolinato ligands cause shifts to higher energies relative to the more highly conjugated quinolinolato ligands by about 0.06 μm^{-1} for each picolinato replacement.

Acknowledgments. Research supported by the U.S. Army Research Office and by the Materials Research Laboratory of the University of Massachusetts.

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(28) An E. Merck prepacked size B preparative "Silica gel 60" column was used.

(29) The 2:1 doublet is at 2.42 and 2.47 ppm at 35 °C in CD_2Cl_2.

(30) The only exceptions to this among the numerous dodecahedral and antiprismatic possibilities are a few which violate Orgel's rule; cf. footnote 31 and ref 23 and 32.

(31) These results do not prove a rigid stereochemistry exists for the WP_nQ_{4-n} series. Flexible or nonrigid metal centers can cycle through various polytopes without ligand scrambling.[10] (Figure 1 of ref 3 shows such a nonscrambling cycle including the C_{2v} hendecahedron, the D_{4d} antiprism, and the D_{2d} dodecahedron.) The ground states for all of the WP_nQ_{4-n} species are expected to have oxygen atoms at the dodecahedral A positions and nitrogen atoms at the B positions in accord with Orgel's rule.[23,32] Logical low energy paths involving antiprismatic and/or hendecahedral intermediates either lead back to the initial dodecahedron or to dodecahedra with some nitrogen and oxygen atoms exchanged from the low energy positions. Continual cycling to the same low energy dodecahedron can produce the observed stereochemical integrity. Details to be submitted for publication.

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(34) Theoretically, 11 WP_2Q_2 geometrical isomers exist which keep the nitrogens in the dodecahedral B positions and the oxygens in the dodecahedral A positions as anticipated from Orgel's rule. The remainining nine structures include four isomers derived from the parent C_2(*mmgg*) stereoisomer, three from D_2(*gggg*), and two from S_4(*gggg*).

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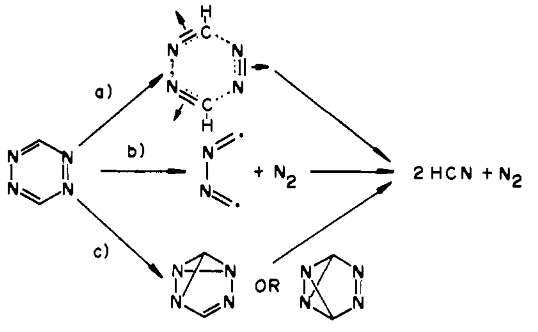
The Photochemical Decomposition of 1,4-s-Tetrazine-$^{15}N_2$

Sir:

Recently Hochstrasser and King[1] reported that *s*-tetrazine in mixed crystal systems undergoes isotopically selective photochemical decomposition from both the lowest n-π^* singlet and triplet state to yield, with near unit quantum efficiency,[2] stoichiometric quantities of nitrogen and hydrogen cyanide. No intermediate species were observed in this photolysis even when performed in organic crystals at 1.6 K.[1,3] These observations led us to investigate further the nature of this intriguing photochemical reaction. We wish to report here the preparation and state selective photochemical decomposition of the isotopic species 1,4-*s*-tetrazine-$^{15}N_2$. In addition, we draw attention to the potential of low temperature high resolution mixed crystal absorption spectroscopy as a novel nondestructive method for isotopic analysis.

Two general reaction pathways are immediately discernible for this photoinduced reaction, the primary distinction being the occurrence or nonoccurrence of bonding between the nitrogen atoms disposed 1,4 in the tetrazine molecule. For example, excitation as shown in eq 1, could lead either via a concerted (1a) or stepwise (1b or 1c) process to N_2 and HCN without the advent of a 1,4-nitrogen bonded intermediate. Alternatively, decomposition involving 1,4-bonding could proceed through such cyclic intermediates as triazacyclobutadiene (eq 2).[4] Refinement of the latter pathway allows for HCN extrusion to occur either prior to or after 1,4-nitrogen bonding. Ample precedent for eq 2 arises from the recent observation at room temperature of "Dewar" pyridine upon ir-



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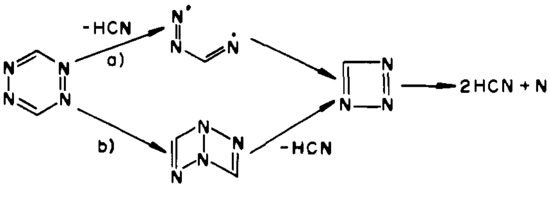

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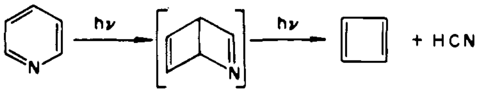

(3)