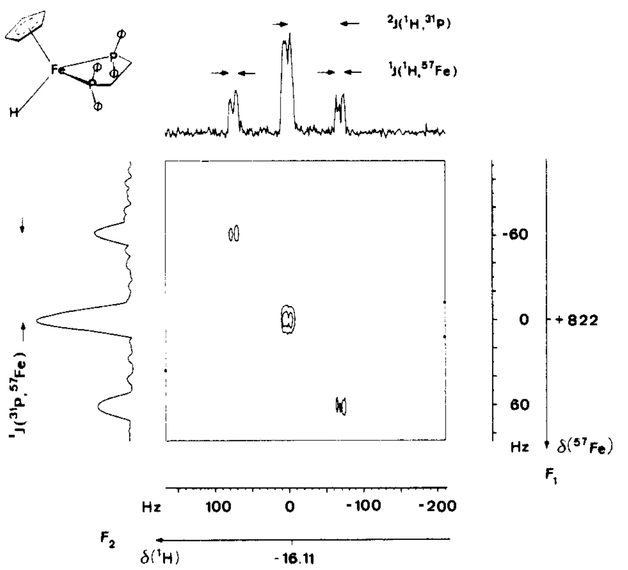

Figure 2. Reverse 2D $^1H\{^{57}Fe\}$ spectrum of **1** (5-mm sample, 8% solution in toluene-d_8) recorded at 295 K at 300.13 MHz using sequence 2a. The Fe carrier frequency was 9.725735 MHz; $^1/_2{}^1J$(Fe,H) was set to 0.0568 s; the repetition delay was 4 s. 112 transients were collected and 32 (16) experiments for 400 Hz spectral width were carried out. Note that due to the lower temperature $\delta(^{57}Fe)$ is 10 ppm smaller than in the $^{31}P\{^{57}Fe\}$ experiment.

measurements is determined by $T_1(^{31}P)$ rather than by $T_1(^{57}Fe)$, which may be significantly longer.

To the best of our knowledge no J(Fe,H) couplings have previously been reported. The ^1J(Fe,H) coupling of **1** was obtained by using sequence 1b. By irradiation of the exact ^{57}Fe frequency as known from the previously described 2D $^{31}P\{^{57}Fe\}$ experiments, the $(1/2J)$ period was varied until a clear up-down iron satellite response was observed. Subsequently an indirect 2D $^1H\{^{57}Fe\}$ measurement was performed (cf. Figure 2). $\delta(^{57}Fe)$ and ^1J(Fe,P) can be extracted from the projection of the contour plot onto the F_1 dimension. Besides $\delta(^1H)$ and ^2J(P,H) (71.2 Hz) the projection onto the F_2 dimension also contains ^1J(Fe,H) (9.3 Hz). In addition, the positions of the cross peaks indicate that ^1J(P,Fe) is of opposite sign relative to ^2J(P,H) since the lowest frequency proton peak is correlated with the highest frequency iron line (The phosphorus spins were not excited in this experiment).[14] All this information characterizing the environment of the iron nucleus of **1** could be obtained in one experiment of only 2-h duration using an 8% (w/w) solution of **1** in a 5-mm NMR tube inserted into a 10-mm probe, which is not the best choice for optimum sensitivity. This indirect 2D NMR technique should be suitable for many iron complexes because phosphorus compounds are frequently used ligands in iron chemistry and J(Fe,P) may become large. However, this procedure can also be applied even when small J(Fe,H)[15] couplings are present, enabling the ^{57}Fe NMR parameters to be detected with the sensitivity of the protons. We therefore conclude that the indirect observation of insensitive spin-$^1/_2$ nuclei is the most efficient technique and opens new horizons for the NMR investigation of low-γ nuclei, which exhibit a scalar coupling to a sensitive nucleus.

Supplementary Material Available: ^1H and ^{31}P NMR spectra showing $^2J(^1H,^{31}P)$, $^1J(^1H,^{57}Fe)$, and $^1J(^{31}P,^{57}Fe)$ (2 pages). Ordering information is given on any current masthead page.

---

(14) We are highly indebeted to a referee for drawing our attention to that point.

(15) In olefin-tungsten and -rhodium compounds ^2J(W,H) and ^2J(Rh,H) lie between 1 and 9 Hz. Corresponding indirect 2D $^1H\{^{183}W\}$ and $^1H\{^{103}Rh\}$ experiments for the rapid detection of ^{183}W and ^{103}Rh NMR parameters were found to be straightforward and posed no problems. It is likely that small ^2J(Fe,H) couplings are present in iron olefin complexes so that we feel optimistic that the 2D $^1H\{^{57}Fe\}$ technique can be applied to the large class of olefin iron compounds.

Variable-Temperature ^{13}C and ^{29}Si CPMAS NMR Studies of Poly(di-*n*-hexylsilane)

Gian C. Gobbi,† William W. Fleming,* R. Sooriyakumaran, and Robert D. Miller

K91/801, IBM Almaden Research Center
San Jose, California 95120-6099

Received April 1, 1986

Soluble high molecular weight substituted silane polymers are a new class of radiation-sensitive materials[1] which have demonstrated ceramic and lithographic applications.[2-4] Much of the recent scientific interest in these materials has centered around their unusual electronic spectra.[5,6] In this regard, substituted silane polymers all show an intense and molecular weight dependent absorption in the UV.[6] Recently, it has been shown that certain polysilanes are also thermochromic both in the solid state[7] and solution[8,9] state, a property which has tentatively been attributed to the formation of a trans backbone conformation at low temperatures. The present study was undertaken to investigate the dynamic characteristics of poly(di-*n*-hexylsilane) in the solid state by variable-temperature ^{13}C and ^{29}Si CPMAS NMR.[10-12]

Figure 1 shows the ^{29}Si and ^{13}C CPMAS NMR spectra of poly(di-*n*-hexylsilane). The ^{13}C peak assignments were based on comparisons to previously published spectra.[13,14] In addition, some assignments were confirmed by the synthesis of poly(di-*n*-hexylsilane-*1*-^{13}C) as part of a related study.[15] At 240 K, the ^{29}Si spectrum consists of a single peak. Between 304 and 310 K there is a sharp transition above which only a single high field peak is observed. It is assumed that at low temperatures the silicon backone exists predominantly in the all trans form.[7,16,17] Above the transition temperature of ca. 307 K the probability of gauche conformations is significant. Conformational mobility of the backbone results in a time-averaged resonance. This is consistent with recent empirical force field (EFF) calculations which suggest that the gauche conformer is less stable.[18] Figure 2 shows the all-trans content of the polymer as a function of temperature. This behavior mirrors thermal analysis data[7] and other temperature-dependent spectroscopic data.[17] The sharp transition at 305-310 K for the final 75% of the sample is particularly striking. The gradual decrease of about 25% of the all-trans fraction from 250 to 305 K is probably due to some local disorder, the molecular

---

† Present address: Dow Canada, Ltd., Sarnia, Ontario, Canada N7T 7M1.

(1) Miller, R. D.; Hofer, D.; McKean, D. R.; Willson, C. G.; West, R.; Trefonas, P. T., III ACS Symposium Series No. 266; American Chemical Society: Washington, DC, 1984; pp 293-310.

(2) Hofer, D. C.; Miller, R. D.; Willson, C. G. *SPIE Adv. Resist. Technol.* **1984**, *469*, 16.

(3) Hofer, D. C.; Miller, R. D.; Willson, C. G.; Neureuther, A. R. *SPIE Adv. Resist. Technol.* **1984**, *469*, 108.

(4) Yajima, S.; Liaw, C. F.; Omori, M.; Hayaski, J. *Chem. Lett.* **1976**, 435.

(5) Pitt, C. G.; Jones, L. L.; Ramsey, B. G. *J. Am. Chem. Soc.* **1967**, *89*, 5471.

(6) Trefonas, P., III; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 23 and references cited therein.

(7) Miller, R. D.; Hofer, D.; Rabolt, J.; Fickes, G. N. *J. Am. Chem. Soc.* **1985**, *107*, 2172.

(8) Harrah, L. A.; Zeigler, J. M. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, 23, 209.

(9) Trefonas, P., III; Damewood, J. R.; West, R.; Miller, R. D. *Organometallics* **1985**, *4*, 1318.

(10) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Pittman: London, 1983.

(11) Fyfe, C. A. *Solid State NMR for Chemists*; C. F. C. Press: Ontario, Canada, 1983.

(12) Duncan, T. M.; Dybowski, C. *Surf. Sci. Rep.* **1981**, *1*, 157-250.

(13) Zhang, X.-H.; West, R. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 159.

(14) Bremser, W.; Ernst, L.; Franke, B. *Carbon-13 NMR Spectral Data*; Verlag Chemie: New York, 1979.

(15) Fleming, W. W.; Gobbi, G. C.; Miller, R. D., manuscript in preparation.

(16) Extensive IR, Raman, and WAXD studies on streched films of poly(di-*n*-hexylsilane) indicate that the backbone conformation below 40 °C is most likely planar zig-zag: Rabolt, J.; Miller, R. D.; Farmer, B.; Kuzmany, H., manuscript submitted.

(17) Rabolt, J. F.; Hofer, D.; Miller, R. D.; Fickes, G. N. *Macromolecules* **1986**, *19*, 611-616.

(18) Damewood, J. R. *Macromolecules* **1985**, *18*, 1793.

0002-7863/86/1508-5624$01.50/0

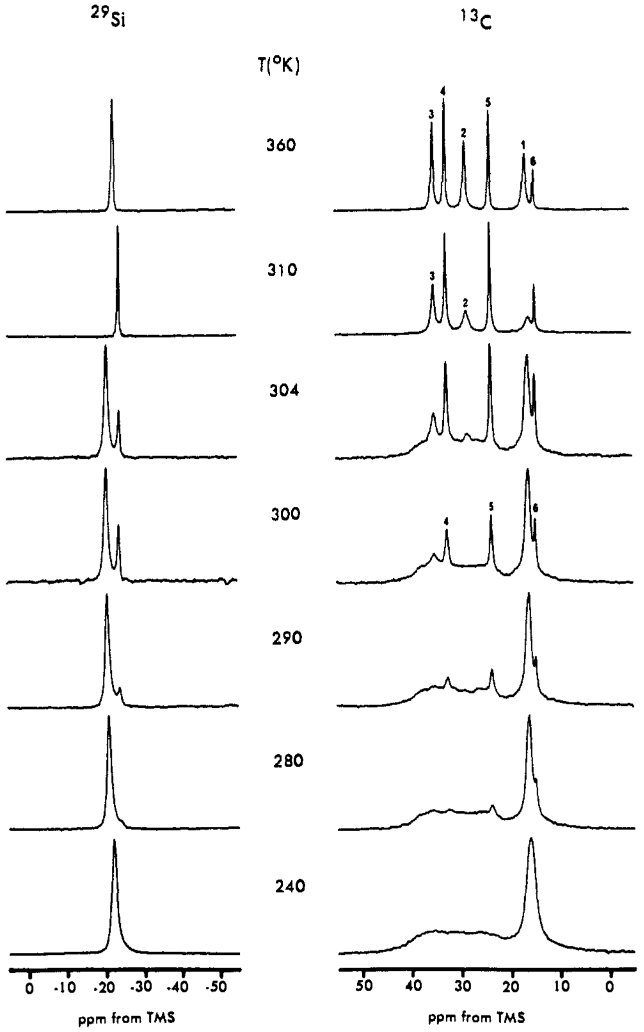

Figure 1. ^{29}Si and ^{13}C variable-temperature magic-angle-spinning spectra for poly(di-*n*-hexylsilane) from 240 to 360 K. Silicon and carbon contact times are 10 and 3 ms, respectively, and the matching and decoupling field was ca. 57 KHz. The ^{29}Si (39.5 MHz) chemical shifts for the spectrum at 300 K are −20.8 and −24.1 ppm relative to Me_4Si. The ^{13}C chemical shifts (50.3 MHz) at 360 K are 14.7, 16.5, 23.6, 28.6, 32.6, and 35.1 ppm relative to Me_4Si, where the peaks are numbered from the silane backbone. Spectra were acquired with an IBM Instruments WP-200 spectrometer equipped with a solid-state NMR accessory.

weight distribution, and chain end effects which are to be expected in high polymers.

The ^{13}C spectrum at 290 K consists of three sharp resonances and three broader resonances. Upon heating, the broad lines become sharp and well resolved while those lines which are already sharp at room temperature become only slightly narrower. At 300 K resonance 3 is composed of a broad and a narrower peak. At 304 K the relative intensity of the narrow resonance is larger than at 300 K. At 310 K, the temperature at which only the single high-field resonance is observed in the ^{29}Si spectrum, resonance 3 consists of only the single narrow peak. Although more difficult to see because of resonance overlap, resonance 2 at ca. 29 ppm similarly appears to be composed of a broad and a narrow peak with the narrow resonance increasing in relative intensity with increasing temperature. The sharper peaks in the ^{13}C spectra correlate with the presence of the high-field silicon resonance and the broad resonances correspond to the trans form. Surprisingly, the line width of resonance 1 does not seem to change appreciably with temperature although its intensity does change. The behavior of this resonance is clarified in Figure 3 which shows the presence of two peaks at 240 K of roughly equal intensity. The ability to resolve the peaks will be described elsewhere.[19] These spectra suggest that the C-1 carbon exists in two equally populated conformations in the low-temperature state. The broadness of the C-2 and C-3 signals below ca. 300 K and C-2 through C-5 below ca. 280 K is apparently due to a combination of motional broadening[20] effects and perhaps a contribution due to a distribution of chemical environments, which would be due to the effect of the two different C-1 conformations on the steric crowding and conformations of the rest of the aliphatic chain.

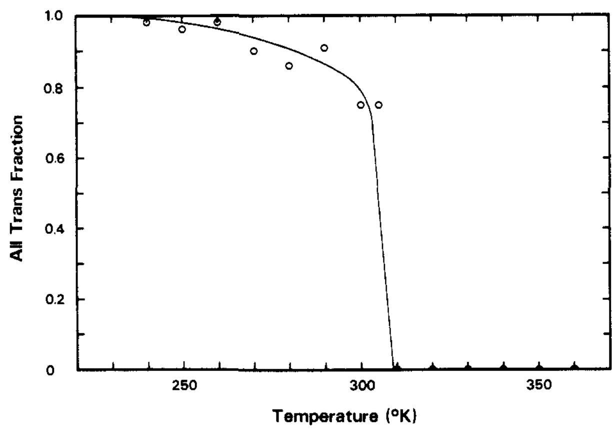

Figure 2. Normalized percentage of low-field (all trans) component vs. temperature as observed in the ^{29}Si NMR spectra. The data is based upon the first-order assumption that the all trans fraction is equal to twice the integral of the left half of the downfield (left) peak and that the rest of the total integral is due to other components such as gauche–trans and gauche–gauche conformations. Although the values may not be absolutely quantitative because of different cross-polarization efficiencies for the different components at different temperatures, the results are qualitatively close.

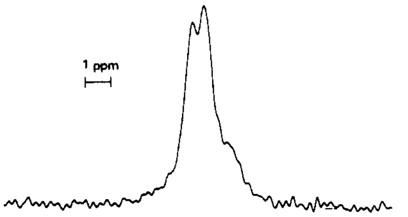

Figure 3. C-1 region of the ^{13}C $T_{1\rho}$ CPMAS spectrum at 240 K. The cross-polarization time was 2 ms and the τ value during which the decoupler is off and the carbon magnetization is spin-locked is 1 ms. The two peaks are of equal intensity and are spaced by 0.43 ppm. This pair of peaks like this was observed up to 300 K and are also of equal intensity at the other temperatures. The difference in the apparent peak heights is due to the presence of the part of the methyl resonance under the higher field peak. The spectrum was neither broadened nor resolution-enhanced.

In summary, variable-temperature ^{29}Si and ^{13}C CPMAS NMR confirm that poly(di-*n*-hexylsilane) is in a rigid form at temperatures below 310 K. It has been suggested[7,17] that the backbone rigidity is enforced be side-chain crystallization, and recent spectroscopic studies have confirmed that the backbone is predominantly planar zig-zag below the side-chain melting transition temperature. The ^{29}Si NMR confirms that the thermochromism of the UV spectrum is a result of backbone disordering above the transition temperature resulting in an increasing contributions from gauche conformations at elevated temperatures. At low temperatures the aliphatic side chains appear in a form in which the methylene adjacent to the backbone is present in two packing conformations of equal population. It is likely that these two rigid conformations exist in pairs along and/or across the silane backbone in order to permit packing of the molecules in their lowest energy form. In a similar fashion the C-2 and C-3 methylenes are also significantly crowded resulting in little motion compared to typical paraffins. As the temperature increases, the signals due to the three outermost carbons begin to narrow first

---

(19) Fleming, W. W., manuscript in preparation.

(20) Rothwell, W. P.; Waugh, J. S. *J. Chem. Phys.* **1981**, *74*, 2721.

because of their greater degree of freedom, followed by the remaining carbons which are constrained by the steric crowding. Thus, as the side chains beging to "melt", the outermost carbons undergo enhanced rotational motion first, followed by the carbons closer to the silicon backbone. Above the transition, the silane backbone is more disordered and highly mobile which permits the greater dynamic freedom of the side chains. It is possible that the high-temperature form is in a liquid-crystalline state with significant local motion but with long-range order. A detailed description of the variable-temperature spectra of polysilanes containing different side chains will be presented elsewhere.[21]

Acknowledgment. We acknowledge the useful discussions with J. R. Lyerla, C. S. Yannoni, and C. A. Fyfe during the inception and completion of this work. Financial assistance for G. C. Gobbi was provided by IBM Research and by the Natural Sciences and Engineering Research Council of Canada through a Postdoctoral Fellowship. R. D. Miller gratefully acknowledges the partial financial support from the Office of Naval Research and the National Science Foundation.

---

(21) Gobbi, G. C.; Fleming, W. W.; Miller, R. D., manuscript in preparation.

Synthesis, Structure, and Spectroscopy of the Diplatinum(II) Complex $Pt_2(pcp)_4^{4-}$, a $Pt_2(pop)_4^{4-}$ Analogue Having Methylenebis(phosphinic acid) Bridges

Christopher King,[1a] Roy A. Auerbach,[1a]
Frank R. Fronczek,[1b] and D. Max Roundhill*[1a]

Departments of Chemistry, Tulane University
New Orleans, Louisiana 70118
Louisiana State University
Baton Rouge, Louisiana 70803

Received May 5, 1986

The complex $Pt_2(pop)_4^{4-}$ (pop = $P_2O_5H_2^{2-}$) has attracted recent interest because of its photophysics and because of the emerging photochemistry of its triplet excited state.[2] This triplet state is sufficiently long-lived at ambient temperature in aqueous solution to be a potentially useful chemical reagent.[3] A limitation to the continued development of this chemistry is the lack of adaptability of the synthetic route for $Pt_2(pop)_4^{4-}$ to other metal ions and complexes, a restriction that is caused in part by the poor hydrolytic stability of pyrophosphorous acid, the precursor to the anionic pop ligand.

As an approach to circumvent these problems, we have synthesized the compound $CH_2(PH(O)(OH))_2$ ($pcpH_2$) by a route involving the hydrolysis of $CH_2(PCl_2)_2$.[4] We now report the synthesis and structure of the diplatinum(II) complex $K_4[Pt_2(pcp)_4]\cdot 6H_2O$ using this new ligand and then compare both the ground- and excited-state properties of the compound with those of $K_4[Pt_2(pop)_4]\cdot 2H_2O$.

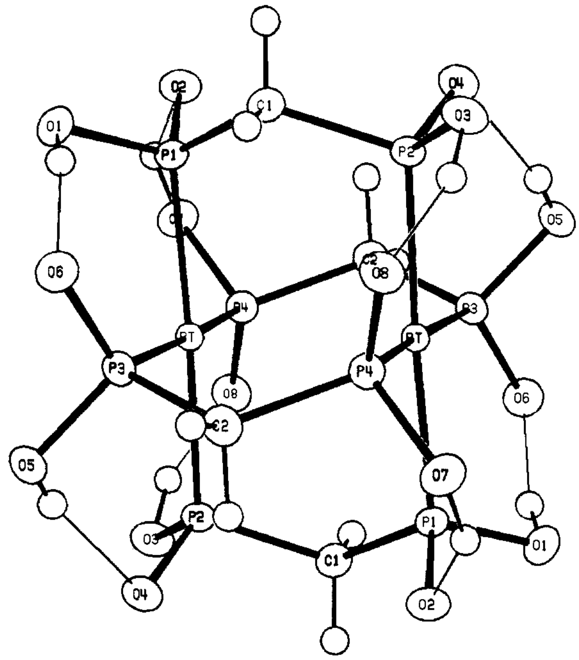

Figure 1. ORTEP diagram of $K_4[Pt_2(P_2CH_4O_4)_4]\cdot 6H_2O$. Pt—Pt 2.980 (0); Pt–P 2.328 (1) [5]; P–C, 1.820 (3) [5]; P═O, 1.530 (2) [1]; P—O, 1.608 (2) [5]; O–H··O, 2.578 (3) [24] Å. Pt–Pt–P, 91.77 (2) [119]°; Pt–P–C, 111.58 (9) [131]°; P–C–P, 117.1 (1)° and 119.3 (1)°; P–Pt–P, 89.95 (2) [36]°.

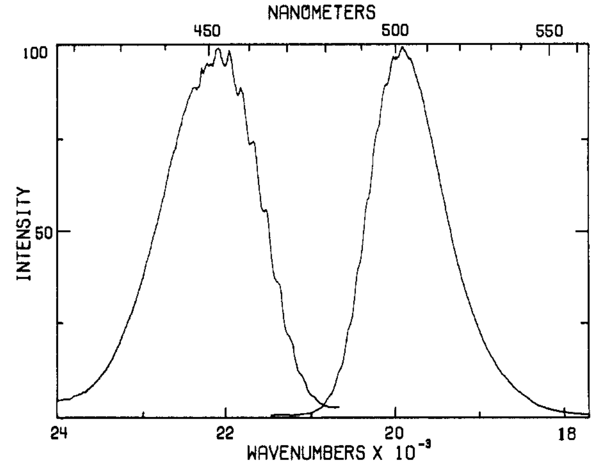

Figure 2. Excitation and emission spectrum of $K_4[Pt_2(pcp)_4]$ (77 K) in a Nujol mull.

Table I. Comparative Data for $Pt_2(pcp)_4^{4-}$ and $Pt_2(pop)_4^{4-}$

	$Pt_2(pcp)_4^{4-}$	$Pt_2(pop)_4^{4-\,a}$
d(Pt–Pt), Å	2.980 (0)	2.925 (1)
$\lambda_{max,absn}$, nm	382, 470	367, 452
ϵ_{max}, M^{-1} cm^{-1}	2.9×10^4, 142	3.5×10^4, 120
$\lambda_{max,emssn}$, nm	510	512
$\tau_{295\,K}$, μs	0.055	9.5
$\phi_{295\,K}$	0.0024 (3)	0.5
ν(Pt–Pt), cm^{-1}	113 (2)	115
ν(Pt–Pt)*, cm^{-1}	146 (2)	139, 155

[a] Taken from data in ref 2.

Potassium tetrachloroplatinate(II) (0.1 g), K_2pcp (0.21 g), and potassium acetate (0.3 mL of 1 M CH_3CO_2H adjusted to pH 5 with KOH) were heated for 72 h at 103 °C in an 8 mm × 40 mm

---

(1) (a) Tulane University. (b) Louisiana State University.

(2) Sperline, R. P.; Dickson, M. K.; Roundhills, D. M. *J. Chem. Soc., Chem. Commun.* **1977**, 62–63. Che, C. M.; Butler, L. G.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7796–7797. Markert, J. T.; Clements, D. P.; Corson, M. R.; Nagle, J. K. *Chem. Phys. Lett.* **1983**, *97*, 175–179. Nocera, D. G.; Maverick, A. W.; Winkler, J. R.; Che, C. M.; Gray, H. B. *ACS Symp. Ser.* **1983**, *No. 211*, 21–33. Bar, L.; Gliemann, G. *Chem. Phys. Lett.* **1984**, *108*, 14–17. Brummer, J. G.; Crosby, G. A. *Chem. Phys. Lett.* **1984**, *112*, 15–19. Fordyce, W. A.; Brummer, J. G.; Crosby, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 7061–7064. Parker, W. L.; Crosby, G. A. *Chem. Phys. Lett.* **1984**, *105*, 544–546. Shimizu, Y.; Tanaka, Y.; Azumi, T. *J. Phys. Chem.* **1984**, *88*, 2423–2425. Reisch, G. A.; Turner, W. A.; Corson, M. R.; Nagle, J. K. *Chem. Phys. Lett.* **1985**, *117*, 561–565. Heuer, W. B.; Totten, M. D.; Rodman, G. S.; Hebert, E. J.; Tracy, H. J.; Nagle, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 1163–1164. Shimizu, Y.; Tanaka, Y.; Azumi, T. *J. Phys. Chem.* **1985**, *89*, 1372–1374. Peterson, J. R.; Kalyanasundaram, K. *J. Phys. Chem.* **1985**, *89*, 2486–2492. Tanaka, Y.; Azumi, T. *Inorg. Chem.* **1986**, *25*, 247–248. Cho, K. C.; Che, C. M. *Chem. Phys. Lett.* **1986**, *124*, 313–316.

(3) Roundhill, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 4354–4356.

(4) King, C.; Roundhill, D. M. *Inorg. Chem.*, **1986**, *25*, 1290–1292.

0002-7863/86/1508-5626$01.50/0 © 1986 American Chemical Society