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.

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(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

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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 $K_4[Pt_2(pop)_4]\cdot 2H_2O$.

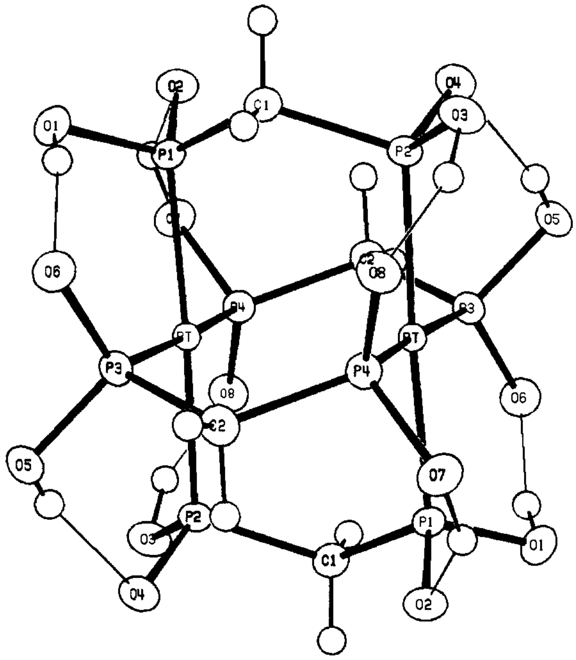

Figure 1. ORTEP diagram of $K_4[Pt_2(P_2CH_4O_4)_4]\cdot 6H_2O$. Pt—Pt 2.980 (0); Pt–P 2.328 (1) [5]; P–C, 1.820 (3) [5]; P═O, 1.530 (2) [1]; P—O, 1.608 (2) [5]; O–H··O, 2.578 (3) [24] Å. Pt–Pt–P, 91.77 (2) [119]°; Pt–P–C, 111.58 (9) [131]°; P–C–P, 117.1 (1)° and 119.3 (1)°; P–Pt–P, 89.95 (2) [36]°.

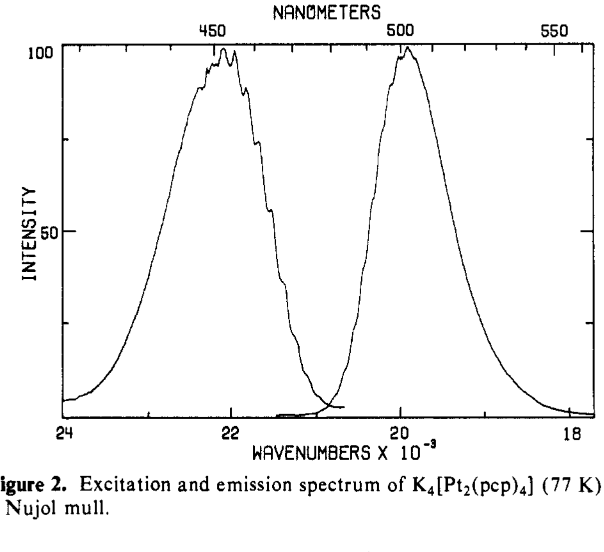

Figure 2. Excitation and emission spectrum of $K_4[Pt_2(pcp)_4]$ (77 K) in a Nujol mull.

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

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(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.

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glass tube which was flushed with nitrogen and sealed with a septum (eq 1). The yellow crystals of $K_4[Pt_2(pcp)_4]\cdot 6H_2O$ which

$$2K_2PtCl_4 + 4K_2pcp \rightarrow K_4[Pt_2(pcp)_4] + 8KCl \qquad (1)$$

form can be separated, and then additional product can be obtained from the supernatant liquid by addition of ethanol. Solution (D_2O) characterization by NMR spectroscopy gives the following: $\delta(^1H)$ 2.89 ($\omega_{1/2}$ = 20 Hz), $\delta(^{31}P)$ 97.0; $\delta(^{195}Pt)$ 5037 (^1J(Pt–P) = 2490, ^2J(Pt–P) = 7 Hz). An X-ray crystal structure of the complex shows that $Pt_2(pcp)_4^{4-}$ has a "lantern"-type structure with four bridging P-bonded $CH_2(P(O)(OH))_2^{2-}$ ligands (Figure 1). The Pt··Pt separation of 2.980 (0) Å is slightly longer than that found in $Pt_2(pop)_4^{4-}$ (2.925 (1) Å)[5] and the long P—O and short P=O bonds are linked by hydrogen (O—H··O) bonds.[6]

The complex shows absorption bands at 382 nm (ϵ 2.9×10^4 M^{-1} cm^{-1}) and 470 nm (ϵ 142 M^{-1} cm^{-1}) and a phosphorescence at 510 nm (Figure 2).[7] No fluorescence corresponding to the 403-nm emission band of $Pt_2(pop)_4^{4-}$ has yet been observed (Table I). The ambient-temperature triplet lifetime of $Pt_2(pcp)_4^{4-}$ in aqueous solution (0.055 μs) is much shorter than that found for $Pt_2(pop)_4^{4-}$ (9.5 μs). Both the radiative rate constant (k_r) and ϕ_{isc} (>0.9) are similar to $Pt_2(pop)_4^{4-}$; however, the nonradiative rate constant (k_{nr}) is 300 times faster. At 295 K we calculate $k_r = 4 \times 10^4$ s^{-1} and $k_{nr} = 2 \times 10^7$ s^{-1}. On lowering the temperature the lifetime and intensity both increase due to a decrease in k_{nr} (E_a = 2100 ± 100 cm^{-1} over the range 295–160 K). At 77 K the lifetime is 10 μs for both compounds. Replacing all the pcp bridging ligands with pcp-d_2 (pcp-d_2 = $CD_2(P(O)(OH))_2^{2-}$)[4] results in only a small (10%) increase in this triplet lifetime; hence vibrational coupling between ν(C–H) and the triplet excited state is not the only reason for the shortened lifetime in $Pt_2(pcp)_4^{4-}$.[8] Possibly the triplet is quenched by transfer to other closely spaced d levels in the manifold.

The methylene bridge in pcp causes $Pt_2(pcp)_4^{4-}$ to be less acidic than $Pt_2(pop)_4^{4-}$. For $Pt_2(pop)_4^{4-}$ we find $pK_{a1} = 3.0$ and $pK_{a2} = 8.0$, whereas with $Pt_2(pcp)_4^{4-}$ we find $pK_{a1} = 8.0$ and $pK_{b1} = 11.0$.[9] The complex $Pt_2(pop)_4^{4-}$ is unstable in solutions above pH 7.5, but $Pt_2(pcp)_4^{4-}$ is stable for ~30 min at pH 11. Halogens (X_2) add across the axial positions to give $Pt_2(pcp)_4X_2^{4-}$ (λ_{max} = 262 nm, Cl; 324 nm, Br; 352, 438 mm, I).[10] Aqueous solutions of $Pt_2(pcp)_4^{4-}$ show an irreversible wave at 0.70 V (vs. Ag/AgCl) corresponding to the oxidation to $Pt_2(pcp)_4^{3-}$.

Acknowledgment. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. We thank R. Schmehl and K. R. Mann for helpful discussions.

Supplementary Material Available: Tables of bond distances and angles, atom coordinates, hydrogen atom coordinates and isotropic thermal parameters, and anisotropic thermal parameters (5 pages); table of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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(5) Filomena dos Remedios Pinto, M. A.; Sadler, P. J.; Neidle, S.; Sanderson, M. R.; Subbiah, A.; Kuroda, R. J. *J. Chem. Soc., Chem. Commun.* **1980**, 13–15. Marsh, R. E.; Herbstein, F. H. *Acta Crystallogr., Sect. B* **1983**, *B39*, 280–287.

(6) Monoclinic, space group $P2_1/n$, a = 12.708 (1) Å, b = 12.429 (1) Å, c = 9.555 (2) Å, β = 93.57 (2)°, Z = 2, ρ_{calcd} = 2.696 g/cm^3. Full-matrix refinement of 214 variables (anisotropic for Pt, K, P, O, and C; isotropic for ligand H atoms) gave R = 0.021 for 4442 reflections with $I > 3\sigma(I)$. The H atoms on the water molecules were not refined. Numbers in square brackets are root-mean-square deviations from the mean.

(7) A simplified MO model (Mann, K. R.; Gordon, J. G., II; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 3553–3555) predicts that a longer Pt···Pt separation will cause a shift in this $d^*\sigma \rightarrow p\sigma$ transition to shorter wavelengths. Clearly small changes in the equatorial ligation cannot be ignored when estimating this energy separation.

(8) Kropp, J. L.; Windsor, M. W. *J. Chem. Phys.* **1965**, *42*, 1599–1608.

(9) Bryan, S. A. Ph.D. Thesis, Washington State University, 1985. We define pK_{a1} and pK_{a2} for the removal respectively of the first and second protons from the 4– anion and pK_{b1} for the addition of the first proton to this 4– anion.

(10) The Pt(III)–Pt(III) distance in $K_4[Pt_2(pcp)_4Cl_2]\cdot 8H_2O$ is 2.750 (0) Å. Triclinic, space group $P\bar{1}$, a = 9.179 (2) Å, b = 9.788 (3) Å, c = 10.625 (2) Å, α = 68.83 (2)°, Z = 1, ρ_{calcd} = 2.571 g/cm^3.

Intermolecular $^1H\{^1H\}$ Nuclear Overhauser Effects in Diastereomeric Complexes: Support for a Chromatographically Derived Chiral Recognition Model

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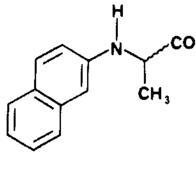
Enantiomers of *N*-(3,5-dinitrobenzoyl) amino acid amides show facile separation upon chiral stationary phases (CSPs) derived from *N*-(2-naphthyl) amino acids.[1] Herein, the validity of a chiral recognition model proposed to account for the observed separations is tested by a series of $^1H\{^1H\}$ nuclear Overhauser experiments (NOE) on the diastereomeric complexes resulting from either enantiomer of methyl *N*-(2-naphthyl)alaninate (**1**), a soluble analogue of the aforementioned CSP, and (*S*)-*N*-(3,5-dinitrobenzoyl)leucine *n*-propylamide (**2**).



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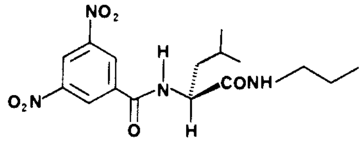

(s)-2

Figure 1 illustrates the interactions asserted to occur during chromatography as applied to the *S* enantiomers of **1** and **2**. Three bonding interactions were proposed: a π-donor–acceptor complex between the dinitrobenzoyl ring of **2** and the naphthyl ring of **1**, a hydrogen bond between the dinitrobenzoyl amide proton of **2** and the carbonyl of **1**, and a second weaker hydrogen bond between the amino proton of **1** and the C-terminal carbonyl of **2**. Both **1** and **2** are shown in the conformations which approximate those expected to be most stable in solution. A change in relative configurations results in the loss of at least one of the bonding interactions. Hence, the origin and sense of the chiral recognition is clear.

Samples 0.043 M in each component in $CDCl_3$ were freeze–thaw degassed and sealed under vacuum. The *S–S* mixture is a dark orange whereas the *R–S* sample is much lighter in color owing to a much lower degree of π-donor–acceptor interaction. Chemical shift changes noted in the mixtures (relative to the uncomplexed species) for amino proton H8 of **1** ($\Delta\delta_{S-S}$ = +1.3 ppm; $\Delta\delta_{R-S}$ = +0.2 ppm) indicate that hydrogen bonding between H8 and the C-terminal carbonyl of **2** is also more extensive in the *S–S* complex. However, there is little difference in the induced shifts of the dinitrobenzoyl N*H* between the *S–S* and *R–S* mixtures ($\Delta\delta_{S-S}$ = +0.28 ppm vs. $\Delta\delta_{R-S}$ = +0.31 ppm).

During each NOE experiment, decoupler power level was set as high as possible without saturating nearby resonances.[2] Because of the varying power levels, the comparison of absolute enhancement values between experiments is not warranted, and these values are provided only for comparison within a single experiment. When comparison is made, the compared values were

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(1) Pirkle, W. H.; Pochapsky, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 352–354.

(2) These NOE experiments were performed on a Varian XL-200 FT NMR 200-MHz spectrometer. The decoupler, set to the desired frequency, was turned on for 10 s prior to acquisition. A 90° pulse was applied, preceded by a short (0.05 s) switching time, and the free induction decay acquired with the decoupler off. Reference spectra were obtained in the same fashion with the decoupler frequency set to irradiate an empty region of the spectrum. Four transients were acquired with the decoupler on-resonance, followed by four reference transients. Typically, 160–200 transients were acquired per experiment. NOE enhancements were identified by inspection of a different spectrum obtained by the subtraction of the reference from the enhanced FID. Percent enhancements, based on the signal intensity of the reference spectrum, were calculated from integrations of the transformed spectra.

(3) Neuhaus, D. *J. Magn. Reson.* **1983**, *53*, 109.

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