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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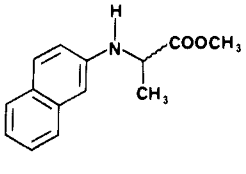
Enantiomers of *N*-(3,5-dinitrobenzoyl) amino acid amides show facile separation upon chiral stationary phases (CSPs) derived from *N*-(2-naphthyl) amino acids.[1] Herein, the validity of a chiral recognition model proposed to account for the observed separations is tested by a series of $^1H\{^1H\}$ 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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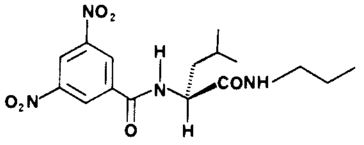

(s)-2

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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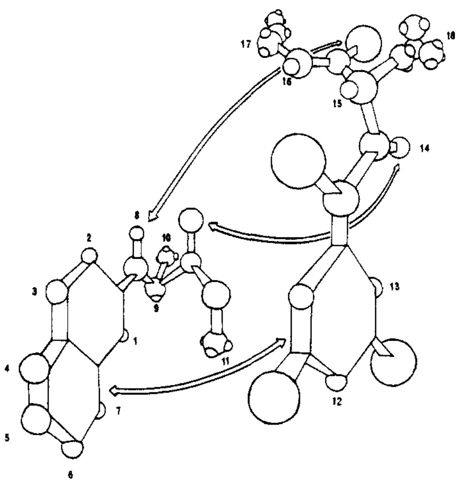

Figure 1. Chiral recognition between the *S* enantiomers of **1** and **2**. Three bonding interactions are shown: a van der Waals (π–π) interaction between the dinitrobenzoyl ring of **2** and the naphthyl ring of **1**, a hydrogen bond between the dinitrobenzamide proton of **2** and the carbonyl of **1**, and a second hydrogen bond between the amino proton of **1** and the C-terminal carbonyl of **2**.

obtained in the same experiment. When the target resonance is a multiplet, selective population-transfer suppression techniques were used.[3] A fairly large number of intermolecular NOEs are seen in the *S*–*S* mixture, indicating that, at the concentrations used, a large proportion of the material is present as the stable *S*–*S* complex and that this complex has a well-defined structure. Although the intermolecular enhancements are modest, they are reproducible and specific.[4] In contrast, only one intermolecular NOE was observed in the less stable *R*–*S* mixture.

The largest intermolecular effects are seen in the *S*–*S* complex for the aromatic ring protons of **1** and **2**. These protons normally have but inefficient relaxation processes available to them and give the most dramatic response to external enhancements of relaxation. Upon saturation of the overlapping H13 *o*-dinitrobenzoyl ring protons and the H14 dinitrobenzamide proton resonances, intermolecular NOEs are observed at H1 (4.8%), H2 (1.8%), and H7 (3.9%) of the naphthyl ring of **1**. The complementary effect on H13 (1.8%) is seen upon saturation of H1. Saturation of para proton H12 on the dinitrobenzoyl ring gives rise to specific effects in the naphthyl ring system at H5 (3.1%) and H6 (1.9%). Irradiation of the H5 multiplet gives rise to NOE enhancement of 1.5% at H12. Because the resonances of H6 and H7 occur in a crowded portion of the spectrum, these initially tentative NOE assignments were confirmed by intramolecular NOEs observed upon irradiation of H5 and H1, respectively. The resulting unambiguous assignments allow one to conclude that the two aromatic systems in the *S*–*S* complex are quite close, as expected for a π-donor–acceptor system.

Furthermore, saturation of the H17 methylene protons of the C-terminal amide group of **2** causes larger intermolecular NOEs at H2 (2.1%) than at H1 (0.5%), indicating that, on a time-average basis, H1 and H2 are near the *n*-propyl group of **2**, and the naphthyl rotamer placing H2 closest to the *n*-propyl group of **2** is preferentially populated. Additionally, intramolecular NOEs indicate that the naphthyl ring is oriented so as to place H1 syn to proton H9 on the chiral center of **1**, since saturation of the H9 resonance gives rise to a much larger effect at H1 (10.2%) than at H2 (1.9%). Saturation of amino proton resonance H8 produces NOEs at H1 (2.3%) and at H2 (5.4%). This intensity pattern suggests that H8 is anti to H9. Interestingly, saturation of H8 gives rise to a negative NOE (−9.5%) at H9, presumably because indirect NOEs from H1 and H2 predominate at H9. This also is consistent with the anti relationship of H8 and H9. For the *R*–*S* mixture, intramolecular NOEs indicate considerably less preference for the naphthyl rotamer depicted in Figure 1. Upon saturation of H9 in the *R*–*S* mixture, the H2 resonance is enhanced 4.8% as opposed to the H1 enhancement of 7.3%. Finally, saturation of the carbomethoxy proton resonance of **1** (H11), gives rise to an NOE at H13 (1.8%) of the dinitrobenzoyl ring of **2**.

In contrast, the *R*–*S* complex shows but one intermolecular NOE. An enhancement of the intensity of the signals of the dinitrobenzoyl ring protons, H13, occurs after saturation of the methoxy protons, H11, of **1**. This seems to indicate that the dinitrobenzamide N—H---O═C hydrogen bond between **1** and **2** occurs to a some extent but that the *R*–*S* complex has no strongly preferred structure.

The nuclear Overhauser effects noted here provide direct support for the initially proposed chiral recognition model. Such studies can be expected to become essential tests of the validity of future chiral recognition models. However, *intermolecular NOEs* have a vast potential for the structural elucidation of a variety of low molecular weight solution complexes in general and are not restricted to the study of chiral recognition mechanisms.

Acknowledgment. This work was supported by a grant from the NSF. We also thank David Vander Velde for helpful discussion.

Supplementary Material Available: Complete tabulation of ^1H chemical shifts, ^1H T_1 values, and intra- and intermolecular NOE data for both the *R*–*S* and *S*–*S* complex (5 pages). Ordering information is given on any current masthead page.

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[4] The magnetization of spin-$^1/_2$ nuclei on molecules involved in fast-exchange complex formation has been described by Bothner-By and coworkers using the equation

$$m_t = \frac{fT_c m_f + cT_f m_c}{fT_c + cT_f}$$

where m_t is the observed magnetization, m_f and m_c are the equilibrium magnetizations free and complexed, respectively, of the observed nucleus, f and c are the mole fractions of free and complexed forms of the molecule on which the observed nucleus resides, and T_f^{-1} and T_c^{-1} are the rates of approach to equilibrium magnetization of the observed nucleus in the free and complexed forms, respectively. Balaram, P.; Bothner-By, A. A.; Breslow, E. *Biochemistry* **1973**, *12*, 4695. Further studies of complexation between the *S* enantiomers of **1** and **2** indicate that at the concentrations used for this study, approximately 60% of each component is complexed at equilibrium. On the basis of the above equation, then, NOEs observed should be about 60% of the intensity expected for complete complexation between **1** and **2**. A more detailed description of these studies is in preparation. For further discussion of NOE in exchanging systems, see: Borzo, M.; Maciel, G. E. *J. Magn. Reson.* **1981**, *43*, 175.

Decarbonylation of Molybdenum(II) Carbonyl Complexes: A New Route to Quadruply Bonded Molybdenum(II) Dimers

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Multiple metal–metal bonds are now well established and, among them, the quadruple bond between molybdenum(II) atoms has perhaps been the most intensively studied.[1] Despite this, most of the known Mo_2^{4+} derivatives are still prepared via ligand-exchange reaction starting from the molybdenum(II) acetate, its preparation from $Mo(CO)_6$ being the most important route to the formation of the Mo_2^{4+} core. Other synthetic routes to Mo_2^{4+} species from mononuclear precursors generally involve reduction of higher oxidation state compounds, such as MoX_3 (X = Cl, Br),[2] $MoCl_4$,[3] $MoH_4(PMePh_2)_4$,[4] and MoO_3.[5] Only one example seems

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(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Wiley: New York, 1982.

(2) (a) Edwards, D. A.; Maguire, J. J. *Inorg. Chim. Acta* **1977**, *25*, L47. (b) Armstrong, J. E.; Edwards, D. A.; Maguire, J. J.; Walton, R. A. *Inorg. Chem.* **1979**, *18*, 1172.

(3) Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 1430.

(4) Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1716.

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