culations on the mannopyranosyl cation suggest that its triaxial half-chair conformation is energetically preferred and that most potent mannosidase inhibitors share its binding topography.[19] However, this rationale does not explain why **4** and **5** are as active against bovine β-galactosidase as against β-glu, judging from comparative IC_{50} studies (no K_I's determined). These findings contrast dramatically with findings for 1-dNM and other known glucosidase inhibitors which have relatively little effect on manno- and galactosidases.

With their saccharide-like structures and resonance-stabilized, partially positively charged anomeric carbons, amidinium ions **4**-H^+ and **5**-H^+ represent ideal mimics of the hexopyranosyl cations implicated in enzymic glycoside hydrolysis. As such, their activity against a cross section of glycosidases indicates that recognition and binding of this common transition-state structure, involving favorable electrostatic interactions with one or both active-site carboxylates[20] (Figure 3), overrides any modest stereochemical discrimination which the resting enzymes make between isomeric hexose residues.

Acknowledgment. We thank the National Institutes of Health (GM 35712) for generous financial support. Grants to the Cornell Nuclear Magnetic Resonance Facility from the NSF (CHE 7904825; PGM 8018643) and NIH (RR02002) are also gratefully acknowledged.

Supplementary Material Available: Full experimental details (including physical properties and spectral and analytical data) for the preparation of **4** and **5** plus kinetic data from enzymatic assays with **4** and **5** (10 pages). Ordering information is given on any current masthead page.

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[19] Winkler, D. A.; Holan, G. *J. Med. Chem.* **1989**, *32*, 2084.

[20] Amidinium and guanidinium groups do form tight association complexes with phosphates and carboxylates.[21] However, β-glu's catalytic carboxyl residues are likely perpendicular to the plane of bound inhibitor and thus cannot form the characteristic, in-plane zwitterionic H bonds without severely tilting **4** in the active site. Sterically less demanding amidines like acetamidine or 2-amino-5,5-dimethylpyrroline had no effect on any of the enzymes tested.

[21] (a) Hart, K. W.; Clarke, A. R.; Wigley, D. B.; Waldman, A. D. B.; Chia, W. N.; Barstow, D. A.; Atkinson, T.; Jones, J. B.; Holbrook, J. J. *Biochim. Biophys. Acta* **1987**, *914*, 294. (b) Muller, G.; Riede, J.; Schmidtchen, F. P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1516. (c) Echavarren, A.; Galân, A.; Lehn, J-M.; Mendoza, J. *J. Am. Chem. Soc.* **1989**, *111*, 4994.

Solubilizing the Thallium-Platinum Unit of $Tl_2Pt(CN)_4$. Preparation and Use of a New Crown Ether/Phosphine Hybrid Ligand for Linking Main-Group and Transition-Metal Ions

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Received March 26, 1990

$Tl_2Pt(CN)_4$,[1,2] which has an intense blue luminescence when irradiated in the ultraviolet range, has a novel structure that distinguishes it from other crystalline inorganic compounds derived from $Pt(CN)_4^{2-}$.[3] Generally, these involve a columnar structure with Pt···Pt distances ranging from 3.09 to 3.75 Å, whereas $Tl_2Pt(CN)_4$ forms discrete, well-separated pseudooctahedral units in which the platinum is coordinated to thallium (Pt-Tl distance, 3.140 (1) Å) and the thallium is monocoordinate. $Tl_2Pt(CN)_4$ is soluble only in very polar solvents (water, dimethyl sulfoxide) where it dissociates into Tl^+ and $Pt(CN)_4^{2-}$ ions and loses the luminescence observed in the solid state. We are interested in the general problem of designing complexing agents that allow the transfer of part or all of such solid-state materials into soluble compounds that can be manipulated and studied by typical coordination-chemical techniques. In this case, the Tl-Pt bond is the essential unit that we sought to preserve and solubilize. To that end, we have prepared the new ligand, crown-P_2 (**1**) (Scheme I).

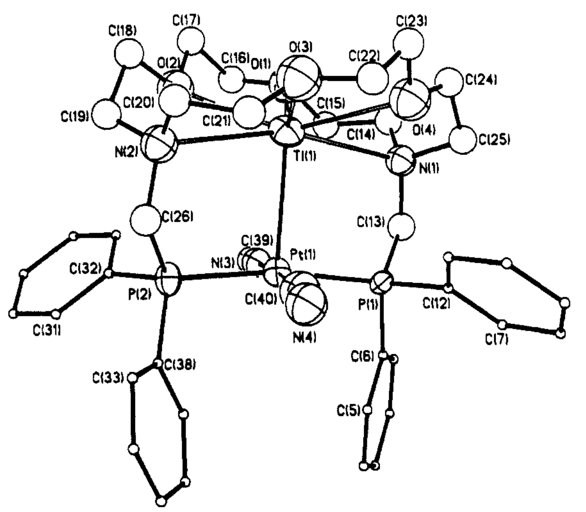
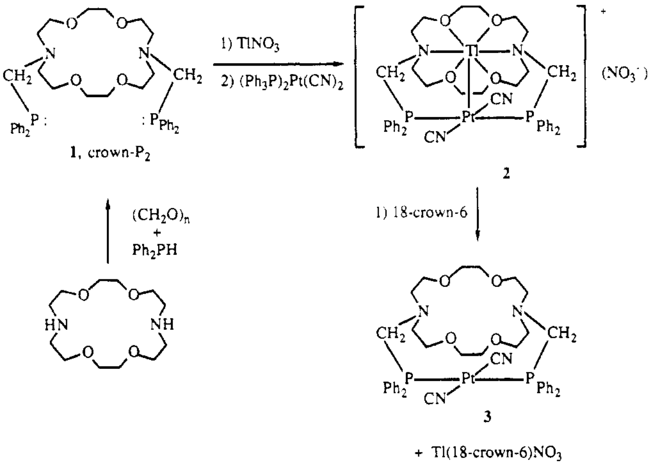


Figure 1. A perspective view of one of the cations in $[Tl(crown\text{-}P_2)Pt(CN)_2]NO_3$ showing 50% thermal contours and uniform, arbitrarily sized circles for the carbon atoms of the crown ligand. Selected bond distances (Å): Pt-Tl, 2.911 (2), 2.958 (2); Pt-P(1), 2.343 (8), 2.312 (11); Pt-P(2), 2.329 (8), 2.333 (10); Tl-O(1), 2.75 (2), 2.77 (3); Tl-O(2), 2.77 (2), 2.91 (2); Tl-O(3), 2.77 (2), 2.77 (2); Tl-O(4), 2.76 (2), 2.87 (2); Tl-N(1), 3.14 (2), 3.05 (2); Tl-N(2), 3.01 (2), 2.98 (2). Bond angles (deg): P(1)-Pt-P(2), 171.0 (3), 172.0 (3); P(1)-Pt-C(39), 85.4 (7), 79.9 (13); P(1)-Pt-C(40), 93.3 (8), 97.7 (11); P(2)-Pt-C(39), 95.4 (7), 100.5 (13); P(2)-Pt-C(40), 85.0 (8), 81.4 (11); Tl-Pt-P(1), 92.8 (2), 92.4 (2); Tl-Pt-P(2), 96.2 (2), 95.5 (3); Tl-Pt-C(39), 89.1 (9), 88.6 (13); Tl-Pt-C(40), 96.4 (11), 94.9 (10).

Scheme I



The aza-crown portion of **1** should create a suitable environment for the thallium ion while phosphorus atoms should be able to substitute for cyano ligands in $Pt(CN)_4^{2-}$. These should not produce a major perturbation of the electronic structure at the platinum. The size of the aza-crown portion situates the two phosphorus atoms so that they comfortably span trans coordination sites on a transition metal, and the facile inversion at nitrogen allows the two phosphorus donors ready access to either side of the macrocycle during complex formation. The methylene linkage between the aza-crown portion and the phosphorus atoms provides the proper spacing to accommodate the Tl-Pt moiety. Moreover, **1** is readily prepared in high yield in a one-step process.[4]

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[1] Nagle, J. K.; Balch, A. L.; Olmstead, M. M. *J. Am. Chem. Soc.* **1988**, *110*, 319.

[2] Zeigler, T.; Nagle, J. K.; Snijderes, J. G.; Baerends, E. J. *J. Am. Chem. Soc.* **1989**, *111*, 5631.

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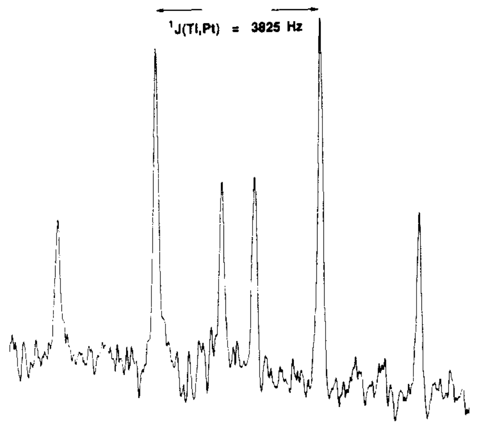

Figure 2. The 64.5-MHz ^{195}Pt$\{^1$H$\}$ NMR spectrum of [Tl(crown-P$_2$)Pt(CN)$_2$][NO$_3$] in chloroform at 20 °C.

Crown-P$_2$ was obtained in 86% yield by the condensation of diphenylphosphine, paraformaldehyde, and diaza-18-crown-6 in toluene at 60 °C.[5,6] Successive addition of thallium(I) nitrate and bis(triphenylphosphine)platinum(II) cyanide to **1** in a 1:1 v/v mixture of toluene and methanol gives a colorless solution from which white needles of [Tl(crown-P$_2$)Pt(CN)$_2$]NO$_3$ (**2**) (IR, ν(CN), 2133 cm^{-1}) were obtained after partial evaporation of the solvent followed by the addition of ethyl ether. The structure of the complex as determined by X-ray diffraction is shown in Figure 1.[7] The complex consists of a planar P$_2$Pt(CN)$_2$ unit that is capped by the diaza-crown portion with the thallium(I) ion sitting within it. Notice that the thallium is shifted out of the rough plane of the aza-crown moiety toward the platinum. The Tl–Pt distances in the two crystallography independent cations in the crystals of **2** (2.911 (2) and 2.958 (2) Å) are similar but considerably shorter than the Tl–Pt distance in Tl$_2$Pt(CN)$_4$ (3.140 (1) Å). Some of this shortening may be brought about by the presence of the ligand bridge, while another contribution arises from the difference in metal–metal bonding between the binuclear Tl–Pt unit in **2** and the trinuclear Tl–Pt–Tl unit in Tl$_2$Pt(CN)$_4$.

Complex **2** is soluble in a range of solvents (chloroform, dichloromethane, acetone), and it retains the Pt–Tl units when dissolved. The ^{31}P$\{^1$H$\}$ NMR spectrum is a convenient probe of this since phosphorus coupling to both ^{195}Pt (33.8% natural abundance, $S = {}^1/_2$) and ^{205}Tl (70.5% natural abundance; ^{203}Tl (39.5%); both $S = {}^1/_2$) is observed (δ = 7.6 ppm, J(Pt,P) = 2293 Hz, J(Tl,P) = 41 Hz) in chloroform. However, the thallium ion can be removed. Treatment of a chloroform solution of **2** with a 20-fold excess of 18-crown-6 results in the disappearance of the ^{31}P NMR spectrum of **2** and the growth of new resonances of thallium-free (crown-P$_2$)Pt(CN)$_2$ (**3**) (δ = 2.0 ppm, J(Pt,P) = 2225 Hz) and no coupling to thallium.

The ^{195}Pt$\{^1$H$\}$ NMR spectrum of **2** produces the first measure of a Tl–Pt one-bond coupling constant. The spectrum recorded in chloroform at 20 °C is shown in Figure 2. It consists of two triplets with δ = −4684 ppm, ^1J(Pt,P) = 2293 Hz, and ^1J(Pt,Tl) = 3825 Hz. This is the first observation of ^1J(Tl,Pt), and it gives, in conjunction with the short Pt–Tl distance, a clear indication that there is a significant covalent component to the Tl–Pt bond. Under the conditions of the experiment, it was not possible to resolve the difference between coupling to ^{205}Tl and ^{203}Tl.

The electronic spectral features of **2** are similar to those of Tl$_2$Pt(CN)$_4$ (luminescence, $\lambda_{\max}$ = 444 nm). In dichloromethane solution at 23 °C, irradiation of **2** in the ultraviolet range produces blue luminescence ($\lambda_{\max}$ = 451 nm). The luminescence is lost when the thallium is removed from **2** through the addition of 18-crown-6.

The hybrid ligand **2** has considerable potential for forming new complexes involving the coordination of transition metals and main group metal ions. Preliminary evidence for formation of Ir$^{\mathrm{I}}$–Tl$^{\mathrm{I}}$ and Ir$^{\mathrm{I}}$–Pb$^{\mathrm{II}}$ bonded units is already at hand,[8] and further extensions are under development.

Acknowledgment. We thank the National Science Foundation (CHE-8941209) for support, Johnson-Matthey, Inc., for a loan of platinum salts, and Dr. Marilyn M. Olmstead for crystallographic advice.

Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, hydrogen atom positions, and data collection parameters for **2** (12 pages). Ordering information is given on any current masthead page.

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(4) For recent work on crown ethers bearing phosphine substituents and related macrocycles, see: Wei, L.; Bell, A.; Ahn, K.-H.; Hall, M. Mm.; Warner, S.; Williams, I. D.; Lippard, S. J. *Inorg. Chem.* **1990**, *29*, 825. Powell, J.; Gregg, M. R.; Kukis, A.; May, C. J.; Smith, S. J. *Organometallics* **1989**, *8*, 2918. Powell, J.; Kukis, A.; May, C. J.; Meindl, P. E.; Smith, S. J. *Organometallics* **1989**, *8*, 2933. Powell, J.; Gregg, M. R.; Meindl, P. E. *Organometallics* **1989**, *8*, 2942 and references in each.

(5) Colorless crystals: mp 110–112 °C dec. ^{31}P$\{^1$H$\}$ NMR: δ = −26 ppm (s) (CDCl$_3$). ^{1}H NMR: δ = 2.96 (4 H, t), 3.43 (2 H, d), 3.53 (8 H, s), 3.55 ppm (4 H, t) in CDCl$_3$.

(6) Maier, L. *Helv. Chim. Acta* **1965**, *110*, 1034. McLain, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 6355. Balch, A. L.; Olmstead, M. M.; Rowley, S. P. *Inorg. Chim. Acta* **1990**, *168*, 255.

(7) Crystals for X-ray diffraction were obtained by diffusion of ethyl ether into a dichloromethane solution of **2**. Colorless **2**, [Tl(crown-P$_2$)Pt(CN)$_2$][NO$_3$]·1.5H$_2$O·0.5CH$_2$Cl$_2$, crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with a = 21.476 (7) Å, b = 14.274 (4) Å, c = 32.660 (9) Å, β = 104.36 (2)°, and Z = 8, at 130 K. R = 0.102 and R_w = 0.078 for 6586 reflections with $I > 2\sigma(I)$ and 435 parameters. The asymmetric unit contains two independent cations and two disordered nitrate ions, as well as lattice water and dichloromethane. The structures of the two cations are similar. When parameters are quoted, the first refers to cation A and the second to cation B. Data were collected with two different X-ray source tubes and merged; see supplementary material for details.

(8) Balch, A. L.; Neve, F., to be published.

Electronic Control of π-Facial Selectivities in Nucleophilic Additions to 7-Norbornanones

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Received March 13, 1990

The role of stereoelectronic effects in controlling the face selectivity during nucleophilic additions to trigonal carbon atoms has come under intense and incisive mechanistic scrutiny in recent years.[1] In particular, substituted cyclohexanones have been explored extensively, although these systems have intrinsic limitations in the sense that the two π-faces of the carbonyl group are sterically nonequivalent and, therefore, not ideally suited for the segregation and assessment of steric vs electronic effects. In a pioneering study, employing sterically unbiased 5-substituted 2-adamantanones, le Noble[2] has drawn attention to the importance of the hyperconjugative assistance by electron-rich σ bonds to the adjacent antibonding orbitals (Cieplak effect)[3] to explain control of diastereoselectivity. It occurred to us that 2,3-endo,endo-disubstituted 7-norbornanones[4,5] can serve as excellent substrates

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(1) For an authoritative background review and comprehensive list of references, see: Cieplak, A. S.; Tait, B. D.; Johnson, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 8447.

(2) (a) Cheung, C. K.; Tseng, L. T.; Lin, M.-H.; Srivastava, S.; le Noble, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 1598. (b) Srivastava, S.; le Noble, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 5873. (c) Lin, M.-H.; Cheung, C. K.; Chung, W. S.; Turro, N. J.; Srivastava, S.; Li, H.; le Noble, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 6562. (d) Chung, W. S.; Turro, N. J.; Srivastava, S.; Li, H.; le Noble, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 7882. (e) Lin, M.-H.; Silver, J. E.; le Noble, W. J. *J. Org. Chem.* **1988**, *53*, 5155.

(3) Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540.

(4) While π-facial selectivities in nucleophilic additions to 7-keto norbornenes[5] and 7-keto benzonorbornenes[5] have been previously investigated, the stereochemical outcome in endo-substituted 7-norbornanones, to our knowledge, has surprisingly not received attention; see: Ashby, E. C.; Noding, S. A. *J. Org. Chem.* **1977**, *42*, 264.

(5) Okada, K.; Tomita, S.; Oda, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 459 and references cited therein.

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