adjacent mercurated calixarenes at the air–water interface. The fact that malonic and not oxalic acid is capable of increasing the cohesiveness of the calix[6]arene monolayer strongly suggests that bridging is, in fact, responsible for this stabilization.[16]

Direct evidence for the porous character of compressed monolayers of **2b** (before and after treatment with malonate) has been obtained by measurement of water evaporation through the film.[17] Placement of a Ni/Cr wire basket, containing 200 mg of dried (170 °C) 6–12 mesh silica desiccant, 5 mm above a monolayer of **2b** for 1 h (20 dyn/cm; 20 μM sodium trifluoroacetate subphase, maintained at 25 °C), resulted in water evaporation which was 92.4 ± 5.6% of that found with use of a clean surface; with a 10 μM malonic acid subphase, the percentage was 88.4 ± 3.6%.[18,20] Similar experiments that were carried out by using a monolayer of 1-hexadecanol (20 dyn/cm; 20 μM sodium trifluoroacetate subphase) showed a water evaporation of 64.0 ± 3.5%. Thus, monolayers of **2b**, compressed to a surface pressure of 20 dyn/cm, maintain a pore structure which offers relatively little resistance toward the permeation of water.[21]

Studies that are now in progress are aimed at fabricating composite membranes based on perforated monolayers derived from **2a–d**, defining their permeability characteristics, and synthesizing related "porous surfactants" for use in the construction of other perforated monolayers.

(16) Monolayers of **2b** have also been stabilized using dithiothreitol (10 μM). In this case, surface pressures fell from 25.4 to 24.7 dyn/cm after 71 min and remained unchanged after 131 min. Transfer of these monolayers to glass slides, however, gave irreproducible transfer ratios that ranged between 0 and 0.9.

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(18) The percentage of water evaporation relative to bare surface is defined as $[(A - C)/(B - C)] \times 100$, where A and B are the percent weight gains in the presence and absence of the monolayer, respectively, and C is the percent weight gain in the laboratory ambient.[19]

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(21) CPK models predict a maximum pore diameter of 6.4 Å, when each of the aromatic rings are approximately perpendicular to the air–water interface. Rotation about the bridging methylenes can further reduce the effective pore size.

The Preparation and Crystal Structures of New Platinum/Phosphonate Complexes

Robert Bau,* Sharon K. S. Huang, Jin-An Feng, and Charles E. McKenna

Department of Chemistry
University of Southern California
Los Angeles, California 90089-0744

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Certain phosphonates [e.g., phosphonoformic acid (PFA), phosphonoacetic acid (PAA), some derivatives of methylene diphosphonate (MDP), and others] are known to inhibit Herpes, influenza, and other viruses.[1-3] Their anti-viral activity is associated with their inhibition of viral polymerases and transcriptases,[4-6] dication-dependent enzymes which catalyze the formtion of a complementary strand of polynucleotide from a single-stranded parent polynucleotide.[6-9] The molecular basis of phosphonate action has not been unambiguously established, but it is strongly suspected tht the phosphonates bind either to an endogenous metal of the enzyme (e.g., Zn^{2+}) or the exogenous coenzymes (e.g., Mg^{2+} or Mn^{2+}) required for enzymatic activity. Thus, the paucity of information about the ligand properties of these compounds, and the structures of their complexes, is somewhat surprising. Only a few structures of MDP[10] and py-

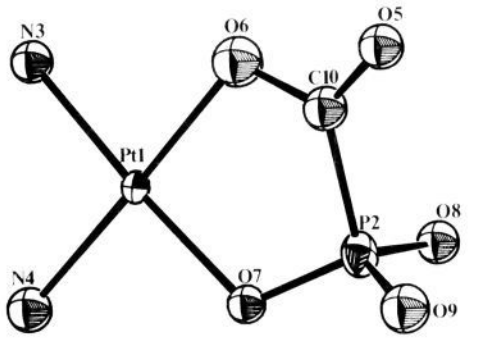

Figure 1. Structure of the [*cis*-Pt$(NH_3)_2$(PFA)]$^-$ anion. Average distances around the periphery of the Pt atom are normal: Pt–N = 2.09 (2), Pt–O(C) = 2.08 (1), C–O = 1.26 (2), C–P = 1.85 (2), P–O = 1.56 (2), and Pt–O(P) = 2.05 (2) Å. Na^+[*cis*-Pt$(NH_3)_2$Pt(PFA)$^-\cdot 3H_2O$ crystallizes in the triclinic space group $P\bar{1}$, with a = 6.366 (8) Å, b = 13.00 (2) Å, c = 6.933 (6) Å, α = 93.30 (9)°, β = 114.22 (8)°, γ = 93.96 (10)°, ρ_c = 2.703 g cm^{-3} for Z = 2. The structure was solved by standard heavy atom techniques and refined a final agreement factor of R = 3.4%, $R(w)$ = 5.8% for 833 reflections. A listing of final atomic coordinates is available.[15]

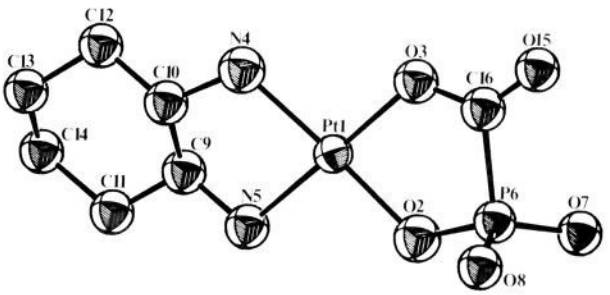

Figure 2. Structure of Na^+[Pt(*trans-l*-dach)(PFA)]$^-$. The compound crystallizes in the cubic space group $P432$, with a = 21.631 (8) Å, V = 10120 (7) Å^3, Z = 24. The structure was solved by using direct methods to locate the platinum atom and refined to present agreement factors of R = 9.9% and $R(w)$ = 7.7% for 842 reflections.

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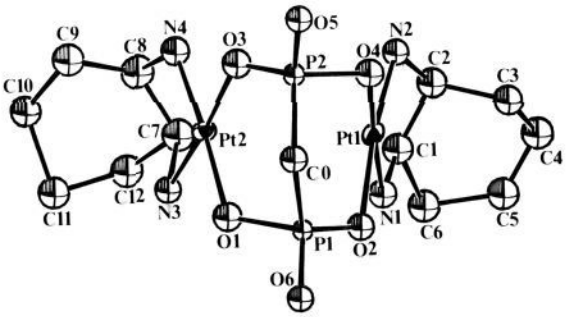

Figure 3. Structure of $[Pt_2(cis\text{-dach})_2(MDP)]$. Distances around the periphery of the Pt are as follows: Pt–N = 2.08 (3), Pt–O = 2.06 (2), O–P = 1.54 (4), Pt–C = 1.83 (2) Å. $[Pt_2(cis\text{-diaminohexane})_2(methylenediphosphonate)]\cdot 9H_2O$ crystallizes in the orthorhombic space group *lba*2, with $a = 21.67$ (1) Å, $b = 12.13$ (1) Å, $c = 23.63$ (1) Å, $V = 6209$ (6) Å^3, $Z = 8$. Automated Patterson search techniques were used to obtain the two Pt atoms, and the rest of the structure was refined to final agreement factors of $R = 3.6\%$ and $R(w) = 3.8\%$ for 1390 reflections.

rophosphate[11] complexes, and some preparative[12] and solution studies[13] of related compounds, have been published. *In this initial study, we have chosen Pt^{2+} as a useful preliminary model for Zn^{2+}.* The well-defined[14] Pt^{2+} square-planar geometry provides a valuable point of departure for evaluation of the less discriminating[14] and more elusive coordination chemistry of Zn^{2+} with phosphonate ligands. This paper describes the preparation and structure determination of three Pt^{II}(bisamine)/phosphonate complexes, $Na^+[cis\text{-}Pt(NH_3)_2(PFA)]^-$, $Na^+[Pt(dach)(PFA)]^-$, and $[Pt_2(dach)_2(MDP)]$ (dach = diaminocyclohexane).

$Na^+[cis\text{-}Pt(NH_3)_2(PFA)]^-$ was prepared by adding 20 mg of $cis\text{-}Pt^{II}(NH_3)_2Cl_2$ to a 10 mL solution of 20 mg of trisodium phosphonoformate (dark, 50 °C, 12 h), followed by concentration to about 2 mL via rotovaporation. Pale yellow plate-like crystals appeared upon slow evaporation. The structure of the $[cis\text{-}Pt(NH_3)_2(PFA)]^-$ anion is shown in Figure 1.[15] The strikingly simple structure of this compound features the expected square-planar geometry of the Pt(II) atom and the phosphoformate ligand forming a five-membered (Pt–O–C–P–O) chelate ring.

$Na^+[Pt(trans\text{-}l\text{-}dach)(PFA)]^-$ is prepared by adding 20 mg of $Pt(trans\text{-}l\text{-}dach)Cl_2$[16] to 10 mL of an aqueous solution containing 17.9 mg of $AgNO_3$, followed by 15.8 mg of trisodium phosphonoformate after AgCl was removed. After stirring in the dark for 12 h, the solution (pH = 5.4) was concentrated to 2 mL, and brick-like colorless crystals appeared in about 2 days. The structure of $[Pt(dach)(PFA)]^-$ is shown in Figure 2.[15] The geometry is very similar to that of the related $[cis\text{-}Pt(NH_3)_2(PFA)]^-$ complex, suggesting again a strong tendency for the five-membered (Pt–O–C–P–O) chelate ring to form.

The third complex, $[Pt_2(dach)_2(MDP)]$, was prepared under similar conditions: 27.0 mg of $Pt(cis\text{-}dach)Cl_2$[16] was added to 10 mL of aqueous $AgNO_3$ (24.1 mg, dark), followed by a 5 mL solution of MDP (12.5 mg; free acid) after AgCl was removed. The pH was adjusted to 7.0 by addition of NaOH, and the mixture was stirred (30 h, room temperature, dark) and concentrated (2.5 mL). Colorless crystals formed in about 10 h upon cooling to 4 °C. The structure of the compound (Figure 3)[15] showed it to be bimetallic, in contrast to the Pt/PFA complexes. This was unanticipated: the preparative procedure described above used a 1:1 ratio of platinum/phosphonate. Each (dach)Pt fragment forms a six-membered (Pt–O–P–C–P–O) ring, and the Pt···Pt distance is nonbonding [3.266 (1) Å].

Our work provides direct confirmation of the proposal[6] that PFA and MDP form five- and six-membered chelate rings, respectively, with metal (II) ions, at least with Pt(II).[17] Work is currently underway on cognate phosphonate complexes of Zn^{2+}, Mn^{2+}, and Mg^{2+}. Pt^{II}(amine)$_2$(phosphonate) complexes were also selected as target molecules in recognition of a recent report that the complex $cis\text{-}[Pt(NH_3)_2(cyclaradine)_2Cl_2]Cl_2$ (cyclaradine = carbocyclicarabinofuranosyladenine) and related compounds are active against topical herpes virus infections,[18] serving presumably as combination drugs. The possibility that appropriately designed PtL_2(phosphonate)-type complexes might prove to be active against various classes of viruses is being explored.[19]

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Supplementary Material Available: Tables of atomic coordinates for $Na^+[cis\text{-}Pt(NH_3)_2(PFA)]^-$, $Na^+[Pt(dach)(PFA)]^-$, and $[Pt_2(dach)_2(MDP)]$ (2 pages). Ordering information is given on any current masthead page.

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Synthesis of the Transient Formyl Complex $[CH_3N(PF_2)_2]_3Co_2(CO)(CHO)^-$ and Observation of Facile Formyl Decomposition To Give the Mixed-Valence Complex $[CH_3N(PF_2)_2]_3Co_2(CO)_2^{\bullet-}$

David S. Dumond and Michael G. Richmond*

Center for Organometallic Research and Education
Department of Chemistry, University of North Texas
Denton, Texas 76203

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Metal formyl complexes continue to derive interest as plausible intermediates in the catalytic reduction of carbon monoxide to alcohols and hydrocarbons.[1] While many mononuclear formyl complexes have been prepared and isolated,[2,3] well-characterized polynuclear formyl complexes remain scarce as a result of enhanced decomposition reactivity relative to their mononuclear counterparts.

The major decomposition pathway in polynuclear formyl complexes, of which the dinuclear formyl complex $[CH_3N(P$-

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