correlation between solution and solid structures in high hydrates should be considerable because of the "aqueous-like"[21] crystalline environment. We have recently determined the structure of the Ga analogue which is isostructural and a detailed discussion of these and related complexes with Al and Ga is forthcoming.[5]

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Supplementary Material Available: Preparative procedure and tables of final positional and equivalent isotropic thermal parameters, anisotropic thermal parameters, bond lengths, bond angles, bond lengths and angles involving hydrogen atoms, hydrogen bonding distances and angles and intraannular torsion angles for **2** (6 pages); tables of measured and calculated structure factor amplitude (10 pages). Ordering information is given on any current masthead page.

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Formation of Luminescent, Bent Ir–Tl–Ir and Ir–Pb–Ir Chains through the Binding of Thallium(I) and Lead(II) to the Iridium Metallomacrocycle $Ir_2(CO)_2Cl_2\{\mu\text{-}(Ph_2PCH_2)_2AsPh\}_2$

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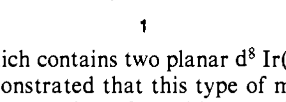
Considerable attention has recently been focused on the photochemical and photophysical properties of a number of luminescent binuclear transition-metal complexes.[1] Much of this work has concerned dimeric planar complexes with a d^8 electronic configuration where a d → p electronic transition is involved in the novel photolytic behavior. Here we report our observations of the formation of new trinuclear complexes that are luminescent in solution at room temperature. These involve binding of simple thallium(I) and lead(II) ions by the metallomacrocycle $Ir_2(CO)_2Cl_2(\mu\text{-dpma})_2$, **1** (dpma is bis(diphenylphosphinomethyl)phenylarsine), which contains two planar d^8 Ir(I) ions.[2] Previous studies have demonstrated that this type of metallomacrocycle is capable of binding a variety of transition-metal ions in the central cavity with the arsenic atoms playing an important role in coordination of the added metal ion.[2,3] However the binding of the main-group ions, thallium(I) and lead (II), is wholly unprecendented.



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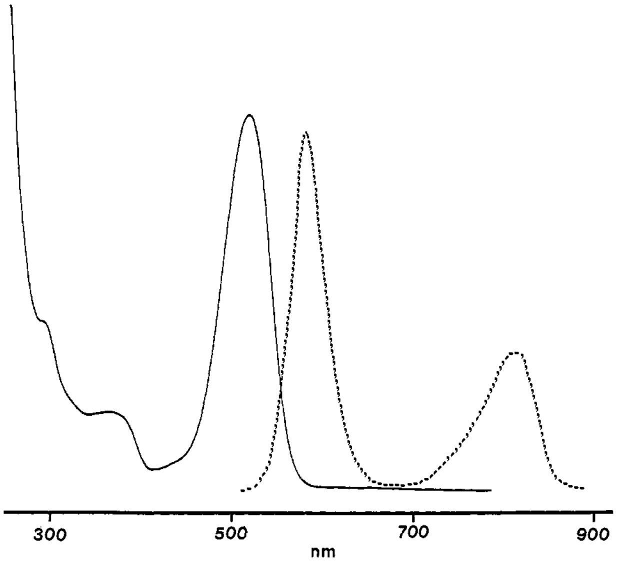

Figure 1. Absorption (solid line) and emission (dashed line) spectra of $[Ir_2Tl(CO)_2Cl_2(\mu\text{-dpma})_2]NO_3$ in dichloromethane solution of 25 °C.

Addition of a colorless methanolic solution of thallium(I) nitrate to a yellow solution of **1** in dichloromethane produces an orange solution from which crystals of $[Ir_2Tl(CO)_2Cl_2(\mu\text{-dpma})_2]NO_3$, **2**, precipitate upon addition of methanol. The ^{31}P NMR spectrum of **2** (singlet at 20.5 ppm in dichloromethane) is distinct from that of **1** (singlet at 18.6 ppm). The infrared spectrum indicated that **2** (ν(CO), 1973 cm^{-1}) contains terminal carbonyl groups (similar to those in **1**; 1964, 1974 cm^{-1}). The electronic absorption spectrum of **2** in dichloromethane solution at 25 °C (shown in Figure 1) is characterized by an intense band at 516 nm (ϵ 33 000) while the emission spectrum (uncorrected) shows two strong features at 580 and 814 nm which appear to be due to fluorescene and phosphorescence, respectively. The metallomacrocycle **1** shows no emission in dichloromethane at 25 °C. The formation of **2** appears to be uniquely dependent on the binuclear nature of **1**, since, under comparable conditions, there is no reaction between thallium(I) nitrate and $Ir(CO)Cl(PPh_3)_2$.

The structure of $[Ir_2Tl(CO)_2Cl_2(\mu\text{-dpma})_2]NO_3\cdot 5CH_2Cl_2$ as determined by X-ray crystallography[4] is shown in Figure 2. The cation has approximate (noncrystallographic) C_{2v} symmetry. The thallium(I) ion is bound through coordination to the two iridium ions. The Tl–Ir distances (2.958 (1), 2.979 (1) Å) are nearly equal and are shorter than the sum (3.06 Å) of the metallic radii of these elements.[5] The Ir–Tl–Ir unit is bent at an angle of 139.4 (1)°. The arsenic atoms are not bound to the thallium ion. The Tl⋯As distances (3.295 (3), 3.308 (3) Å) are significantly longer than the Tl–Ir distances, and the lone pairs on the arsenic atoms are pointed 40° away from the thallium ion. The geometry of the $IrP_2(CO)Cl$ units is not perturbed by the presence of the thallium ion. The units are planar with bond distances and angles similar to those in $Ir(CO)Cl(P(p\text{-tolyl})_3)_2$.[6] The nitrate ion is not co-

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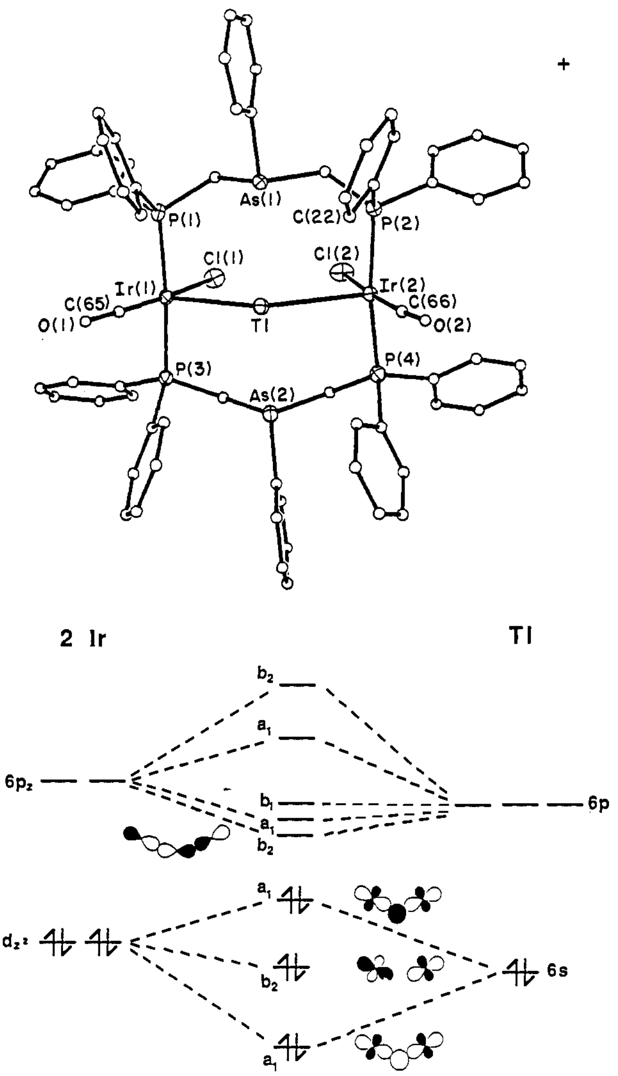

Figure 2. Top: perspective drawing of $[Ir_2Tl(CO)_2Cl_2(\mu\text{-dpma})_2]^+$ showing 50% thermal elipsoids for heavy atoms and uniform arbitrarily sized circles for carbon and oxygen atoms. Selected interatomic distances (Å): Ir(1)-Tl, 2.958 (1); Ir(2)-Tl, 2.979 (1); Ir(1)-P(1), 2.323 (4); Ir(1)-P(3), 2.332 (4); Ir(1)-Cl (1), 2,369 (4); Ir(1)-C(65), 1.79 (1); Ir(2)-P(2), 2.328 (4); Ir(2)-P(4), 2.339 (4); Ir(2)-Cl(2), 2.358 (4); Ir(2)-C(66), 1.83 (2); Tl···As(1), 3.295 (3); Tl···As(2), 3.308 (3). Selected interatomic angles (deg): Ir(1)-Tl-Ir(2), 139.4 (1); P(1)-Ir(1)-P(3), 170.0 (1); Cl(1)-Ir-C(65), 170.9 (5); P(1)-Ir(1)-Cl(1), 86.4 (1); P(1)-Ir(1)-C(65), 92.7 (5); P(3)-Ir(1)-Cl(1), 89.0 (1); P(3)-Ir(1)-C(65), 90.4 (5); P(2)-Ir(2)-P(4), 168.9 (1); Cl(2)-Ir(2)-C(66), 173.0 (5); P(2)-Ir(2)-Cl(2), 87.7 (1); P(2)-Ir(2)-C(66), 92.3 (5); P(4)-Ir(2)-Cl(2), 87.7 (1); P(4)-Ir(2)-C(66), 91.1(5). Bottom: qualitative molecular orbital diagram for the Ir_2Tl unit.

valently bound to the cation. It rests in front of the thallium ion and in the Ir_2Tl plane, but the shortest Tl···O separation is 2.798 Å, much longer than the Tl-O separation of 2.46 Å found in gaseous $TlNO_3$[7] and of 2.101 Å found in gaseous Tl_2O.[8]

Lead(II), which is isoelectronic with thallium(I), also forms a complex with **1**. Addition of lead(II) nitrate in methanol to **1** in dichloromethane produces a pink solution from which $[Ir_2Pb(CO)_2Cl_2(\mu\text{-dpma})_2](NO_3)_2$, **3**, has been isolated as shocking pink crystals. Its spectroscopic properties (^{31}P NMR 24.4 ppm; infrared, ν(CO), 1978, 1984 cm^{-1}) are similar to those of **2**. Like **2**, **3** shows an intense band (538 nm; ϵ 62 000) in the visible absorption spectrum and two strong emission bands (uncorrected) at 563 and 825 nm.

Generally, the few known examples of thallium(I) (or lead(II)) transition-metal bonding are considered to involve primarily ionic interactions.[9] However, this is clearly not the case in **2** and **3**. We view the primary thallium-iridium bonding as involving the interaction of the filled $5d_{z^2}$ orbitals and empty $6p_z$ on iridium with the filled 6s and empty $6p_y$ and $6p_z$ orbitals on thallium (local Tl x axis perpendicular to the Ir-Tl-Ir plane, z axis bisects the Ir-Tl-Ir angle). A simple group theory treatment using these orbitals leads to the diagram shown in Figure 2.[10] Mixing between levels will stabilize the filled a_1, b_2, and a_1 orbitals relative to their empty counterparts, thereby imparting stability to the Ir-Tl-Ir unit. It is proposed that the lowest energy absorption bands leading to luminescence in **2** and **3** result from an a_1 to a b_2 or a_1 transition localized within the Ir-Tl-Ir moiety.

Acknowledgment. We thank the National Science Foundation (CHE 8519557) for support, Bowdoin College for study leave support for J.K.N., Dow Corning Corp. for a Fellowship to P.E.R., and Johnson Matthey Inc. for a loan of iridium.

Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, hydrogen atom positions, and data collection parameters for **2** (9 pages). Ordering information is given on any current masthead page.

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Organosulfones as Chemical Chameleons. A Ring Expansion to α-Methoxy and α-Phenylthio Ketones

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The importance of ring-expansion methods in organic synthesis and the weakness of existing ones is underscored by the large continuing effort to develop new approaches.[1-3] Of prime im-

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