4,9,12,15-Tetrathiatricyclo[5.3.$3^{2,6}$]hexadeca-1,6-diene

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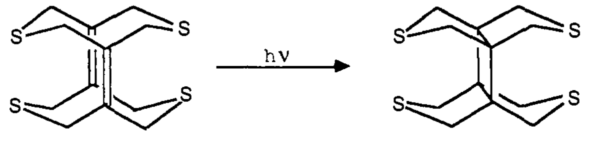
Molecules with carbon-carbon double bonds held near each other in space can display unusual reactivity and have been the subject of many recent studies.[1] We wish to report the synthesis of the tetrathiadiene **1** and its novel photoisomerization to **2**.



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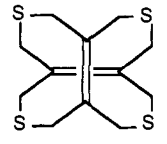

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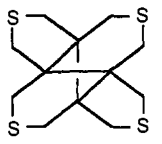

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Compound **1** is formed by the cesium-carbonate-promoted fourfold coupling of tetrakis(thiomethyl)ethene and tetrakis(bromomethyl)ethene.[2] Cesium salts have been touted as being particularly effective in promoting intramolecular reactions of this kind.[3] In the present case, with syringe-pump addition of reagents, yields of **1** greater than 30% can be obtained.[4] The remaining material is insoluble, presumably polymeric, organic material. Using other bases, such as barium carbonate, leads to lower yields and less clean products.

A priori, the cyclized product could be either **1** or **3**, its criss-crossed isomer. Each should have the same general spectroscopic features (a single AB pattern in the ^{1}H NMR spectrum and two signals in the ^{13}C NMR spectrum). The compound is crystalline, but numerous attempts failed to produce crystals appropriate for X-ray analysis.

In an effort to derivatize **1**, a sample of it was photolyzed in triethyl phosphite, the intent being to extrude sulfur from the molecule.[5] Instead, a single compound, isomeric with **1**, was formed. It also shows a single AB pattern in the ^{1}H NMR and two signals in the ^{13}C NMR, consistent with structure **2**. The isomeric cyclobutane, **4**, is not consistent with this data since it has two different sets of diastereotopic hydrogens and three different types of carbon. The structure of **2** was confirmed by Raney nickel[6] desulfurization to give octamethylcyclobutane, a known compound[7] which was identical by NMR, mass spectrometry, and gas chromatographic retention time with an independently prepared sample.

Molecular mechanics calculations using Allinger's MM2 force field[8] suggest that the cyclobutane product is less stable than the diene by about 35 kcal mol^{-1}. In diene **1** the double bonds lie almost directly on top of each other with a spacing of 2.76 Å. The cyclobutane product has nearly equal carbon-carbon bond lengths, 1.56 and 1.57 Å.

The photocyclization of **1** is not limited to triethyl phosphite as a solvent. It occurs readily in THF, chloroform, and acetonitrile. Since compound **1** is only sparingly soluble in these solvents, and **2** is less so, these reactions are heterogeneous. In one experiment, aluminum foil was used to shield the lower portion of the photolysis vessel containing undissolved **1**, and conversion to products occurred at comparable rates, suggesting that the photochemical reaction occurs in solution rather than in the solid state. When identical samples were photolyzed to low conversion with various wavelengths of light, the reaction proceeded only with light in the 300-320-nm range. This result is consistent with the observation of efficient photolysis in Pyrex flasks with Rayonet 300-nm "sunlight" lamps.

While intramolecular 2 + 2 cycloadditions of nonconjugated olefins can be facile with far UV light,[9] we know of no other examples which use near-visible wavelengths. This cycloaddition has been predicted to be particularly facile when the double bonds are separated by three atoms,[10] as in **1**. Compound **3** also has this same spacing, but the intramolecular reaction is likely to be much more difficult due to the lack of overlap of the two double bonds and the higher strain in **4**.

We are currently studying the photochemistry of **1** in more detail and attempting to prepare the isomeric diene **3** by a directed route.

Acknowledgment. We thank the Tulane University Committee on Research for partial support of this work and Professor Harry Ensley for help with the MM2 calculations.

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(4) In a representative preparation, a Sage model 355 dual-syringe pump was used to add solutions of 0.665 g (3.13 mmol) of tetrakis(thiomethyl)ethene and 1.250 g (3.13 mmol) of tetrakis(bromomethyl)ethene, each dissolved in 20 mL of anhydrous DMF, to a stirred suspension of 2.21 g (6.78 mmol) of cesium carbonate in 200 mL of anhydrous DMF under a nitrogen atmosphere over a 3-day period. The solids were washed with water and Soxhlet-extracted with chloroform to give 0.240 g (33%) of **1**: ^{1}H NMR δ 4.74 (d, J = 13.5 Hz, 1 H), 3.23 (d, J = 13.5 Hz, 1H); ^{13}C NMR (multiplicities from INEPT) δ 33.7 (t), 125.9 (s); mass spectrum, *m/e* (relative intensity) 77 (23), 97 (54), 111 (100), 112 (28), 188 (53). Anal. ($C_{12}H_{16}S_4$) C, H, S.

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The Exoclathrate $Al(C_7H_8NO_2)_3\cdot 12H_2O$. A Facial Geometry Imposed by Extensive Hydrogen Bonding with the Ice I Structure

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As part of a program to study the coordination chemistry of posttransition metals, we are examining the complexes formed by aluminum[1,2] and gallium[2] with selected bidentate monobasic ligands. The controversial role of Al in certain (often neurological) disease states[3] and the use of ^{67}Ga in tumor detection[4] are specific reasons for studying these two elements. Subsequent to our reports of the 3-hydroxy-4-pyrone complexes of these group 13 elements,[1,2] we have been studying their complexes with a variety of 3-hydroxy-4-pyridinones[5] (**1**). Our interest in the 3-hydroxy-4-

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* Author to whom correspondence may be addressed.

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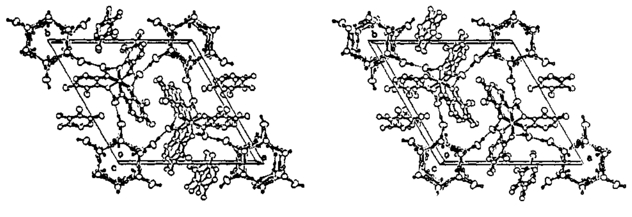
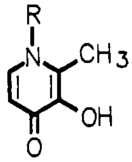


Figure 1. Stereoview (ORTEP) of the unit-cell packing of complex **2**. The view is down the *c* axis.

pyridinones arose from the extreme neurotoxicity of certain of our tris(3-hydroxy-4-pyronato)aluminum(III) complexes.[6] This interest was piqued recently by the reports of Kontoghiorghes[7-9] that 3-hydroxy-1,2-dimethyl-4-pyridinone (Hdpp, **1** R = CH_3) is capable of removing iron from diferric transferrin, an important quantification of the affinity of these species for trivalent metal ions. This evidence lends further credence to our tenet that Al and Ga complexes of these types of ligands will find considerable medical application. The unusual hydrogen bonding network formed by complex **2** when crystallized as a dodecahydrate could not be presaged, however.



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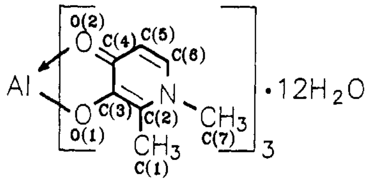

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Complex **2** is prepared in a manner similar to tris(maltolato)aluminum(III).[1,2] Elemental analysis[10] and spectroscopic properties[11-13] are consistent with bidentate, monobasic ligation of Al^{3+} in a tris(ligand) complex of neutral charge. We are attempting to correlate ^{27}Al NMR line widths (aqueous solution) with solution and solid-state structures (*fac* vs. *mer*), so a single-crystal X-ray diffraction study was undertaken on a pink hexagon of **2** crystallized from hot water.[14]

The crystal structure consists of discrete *fac*-$Al(dpp)_3$ units, and water molecules, half (O(4) and O(5)) forming a hexagonal channel and the rest (O(3) and O(6)) bridging between the channel and the adjacent $Al(dpp)_3$ units. A stereoview of the unit-cell packing of $Al(dpp)_3 \cdot 12H_2O$ is shown in Figure 1 looking down the *c* axis. There are intermolecularly bridging water molecules (O(3)) hydrogen bonding between the hydroxy oxygen of one ligand (O(1) in Figure 2) and the keto oxygen (O(2)) of a ligand rotated by 120° and translated by one unit cell (i.e., on the next $Al(dpp)_3$ molecule). As a result, every oxygen coordinating an Al is hydrogen bonded to one water molecule. Each of the intermolecularly bridging waters is itself bridged by another water (O(6)) to the channels of water molecules located at each corner of the unit cell. The rigorous threefold symmetry (3 or C_3) of the *fac*-$Al(dpp)_3$ units is maintained (and no doubt enforced) by this water network.

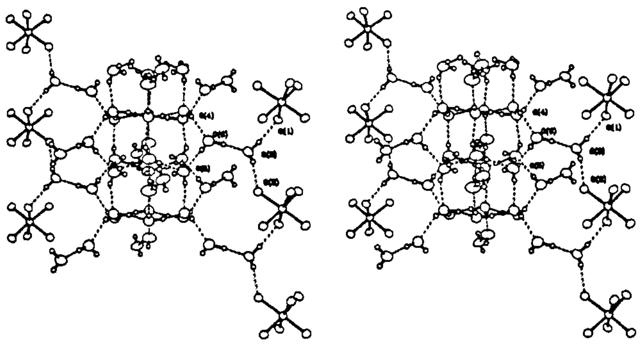

Figure 2. Stereoview (ORTEP) of a part of the hydrogen bonding network of waters and Al complex units. The numbering scheme for the independent O atoms is shown. Only two of the six columns of Al complexes bound to the hexagonal water channels are shown, and all atoms in the complex except AlO_6 are omitted for clarity. The view is down the *a* axis.

The hexagonally symmetric (3 or C_3) channels of water molecules are a unique feature of this structure. In Figure 2 these are shown in a stereoview normal to the *c* axis. Each $(H_2O)_6$ ring has exact $\bar{3}$ or S_6 symmetry. These hexagonal channels of water are closely related to the ice I structure of solid water[15] but are proton ordered (except those protons on O(5) which were twofold disordered and refined as such). Bond distances (supplementary material) vary for ordered O–H from 0.68 (5) to 1.14 (8) Å, for H···O from 1.62 (8) to 2.12 (5) Å, and for O···O from 2.729 (4) to 2.861 (3) Å. Within each six-membered ring, the hydrogen bonding is circular and the circle is homodromic,[16] because all the O–H···O bonds run in the same direction (counterclockwise when viewed down *c* as in Figure 1.) This arrangement is not crystallographically unconstrained, being imposed by the perfect 3(C_3) axis coincident with *c* down the channel. Regardless of the symmetry constraints, it has been suggested[17] that homodromic circles should be the preferred species in water clusters because of a lower dipole moment. These circular hydrogen bonding arrays have been described in the crystal structures of ice[15] and of the clathrate hydrates[18] but to our knowledge have not been reported in inorganic hydrates. In no structures of which we are aware are single hexagonal channels of water observed, although staggered columns have been reported[19] previously. A clathrate hydrate is a crystalline compound formed by a hydrogen bonded water host lattice surrounding a guest ion or molecule, so we have termed $Al(dpp)_3 \cdot 12H_2O$ an exoclathrate, wherein the guest $Al(dpp)_3$ (being too large to be enclosed by a conventional pentagonal- or hexagonal-based polyhedron) is held rigidly *outside* the aquo network. The bridging water molecules hold the structure together so rigidly that all the hydrogen atoms in the cell were located and refined isotropically. According to the classification of Jeffrey and Takagi,[20] all the water–water hydrogen bonds are of the type IA donor–acceptor type.

An O_5 pentagonal hydrophilic channel has been reported recently[21] in a lithium coronand complex where hydrogen bonding interactions were postulated as the primary force in determining the structure of the assembly. In **2**, this certainly obtains, the *fac* geometry being imposed by the hydrophilic network. This also correlates with the narrow aqueous ^{27}Al NMR line width for **2** (580 Hz) vs. that for tris(maltolato)aluminum(III) (900 Hz),[2] which is *mer* in the crystal.[1] It has been suggested[21,22] that the

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(10) Correct elemental analyses (C, H, N) were obtained for both the dodecahydrate $Al(C_7H_8NO_2)_3 \cdot 12H_2O$ (dried in a desiccator overnight) and the anhydrate $Al(C_7H_8NO_2)_3$ (dried in vacuo at 90 °C overnight); mp 300 °C dec.

(11) ^1H NMR (D_2O, 25 °C, 80 MHz) δ 2.42 (s, 3 H, CCH_3), 3.86 (s, 3 H, NCH_3), 6.58 (d, J = 6.8 Hz, 1 H, C*H*C(O)), 7.62 (d, J = 6.8 Hz, 1 H, NC*H*CH); ^{27}Al NMR (H_2O, 25 °C, 78.16 MHz) 39 ppm ($W_{1/2}$ = 580 Hz).

(12) IR (KBr, all strong) 1605 ($\nu_{C=O}$), 1555, 1520, 1490 ($\nu_{C=C}$ ring), 575, 495, 440 cm^{-1} (possible ν_{M-O}).

(13) FAB mass spectrum (glycerol matrix), m/z 744 (relative intensity 0.3, $M_2L_5^+$), 442 (5, $HAlL_3^+ = (M + 1)^+$), 303 (100, ML_2^+).

(14) Crystals of $Al(C_7H_8NO_2)_3 \cdot 12H_2O$ are trigonal, a = 16.600 (2) Å, c = 6.877 (1) Å, Z = 2, space group $P\bar{3}$. The structure was solved by direct methods and was refined by full-matrix least-squares procedures to R = 0.045 and R_w = 0.051 for 1662 independent absorption-corrected reflections with $I \geqslant 3\sigma(I)$ collected at 22 °C with Cu K_α radiation on an Enraf-Nonius CAD4-F diffractometer. All hydrogen atoms were located and refined with isotropic thermal parameters, those associated with water molecule $H_2O(5)$ were found to be twofold disordered.

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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]

Acknowledgment. Acknowledgement is made to NSERC (Canada) for an operating grant and a University Research Fellowship to C.O. and to UBC for a University Graduate Fellowship to W.O.N. We most gratefully thank Professor J. Trotter for the use of his crystallographic facilities.

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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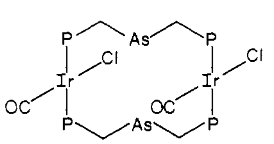
Considerable attention has recently been focused on the photochemical and photophysical properties of a number of luminescent binuclear transition-metal complexes.[1] Much of this work has concerned dimeric planar complexes with a d^8 electronic configuration where a d → p electronic transition is involved 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 unprecedented.



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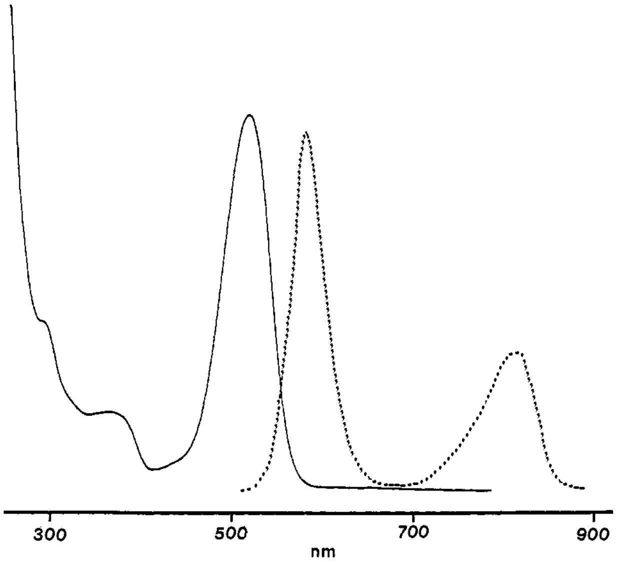

Figure 1. Absorption (solid line) and emission (dashed line) spectra of $[Ir_2Tl(CO)_2Cl_2(\mu\text{-dpma})_2]NO_3$ in dichloromethane solution of 25 °C.

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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(4) Rose/green dichroic needles of $[Ir_2Tl(CO)_2Cl_2(\mu\text{-dpma})_2](NO_3)\cdot 5CH_2Cl_2$ were grown by diffusion of ethyl ether into a dichloromethane solution of the complex. They belong to the monoclinic space group $P2_1/n$, a nonstandard setting of $P2_1/c$ (No. 14) with $a = 15.289$ (5) Å, $b = 21.394$ (5) Å, $c = 24.902$ (7) Å, $\beta = 99.81$ (2)° at 130 K, $Z = 4$, $R = 0.054$, and $R_w = 0.045$ for 7359 reflections with $I > 2\sigma I$ and 528 parameters.

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