Properties and Structures of Thallium(I) Derivatives of Aromatic Diols

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The reaction of thallium(I) salts (acetate, formate) with aromatic 1,2-diols $R(OH)_2$ ($R = C_6H_4$, C_6Cl_4, C_6Br_4, $C_6H_2Bu^t{}_2$, biphenyl-2,2′-diyl) yields $Tl_2[O_2R]$, $Tl[OR(OH)]$, or $Tl[O_2R^\bullet]$ depending on the solution conditions and the nature of R. The compound $Tl[OC_{12}H_8(OH)]$, derived from 2,2′-dihydroxybiphenyl, crystallizes in the space group *C*2/*m*, with $a = 7.911(2)$ Å, $b = 10.775(3)$ Å, $c = 11.955(4)$ Å, $\beta = 93.33(2)$°, $V = 1012.8(4)$ Å^3, and $Z = 2$. Refinement converged at $R = 0.0388$, $R_w = 0.0445$ for 639 reflections at 24 °C. The molecule is a dimer, based on a Tl_2O_2 ring. Only one OH of the diol is deprotonated, so that there is no chelation, and the lattice involves intermolecular Tl•••HO bonding.

Introduction

In two recent papers from this laboratory, we reported the synthesis of compounds in which an aromatic diol forms a singly charged ligand by the loss of one proton, giving rise to complexes of the type M[OR(OH)]. One of these, the copper(I) derivative $Cu_2[OC_6Cl_4(OH)]_2(dppm)_2$ (dppm = bis(diphenylphosphino)methane), was synthesized by the electrochemical oxidation of a copper anode in a solution of $C_6Cl_4(OH)_2$-1,2 and dppm in acetonitrile. The structure involves two copper(I) atoms bridged by two dppm ligands, giving an eight-membered CuPCPCuPCP ring; the copper coordination is completed by the phenoxy oxygen of the monodentate $[OC_6Cl_4(OH)]^-$ ligand. Intramolecular hydrogen bonding between the OH of one ligand and the O^- of the second was identified from the crystal structure.[1] The other work also involved direct electrochemical synthesis with solutions of aromatic diols in acetonitrile, using indium anodes, and in this case a series of $In^I[OR(OH)]$ compounds was obtained. It was not possible to prepare crystalline products, but the oxidation of these unusual indium(I) species to indium(III) derivatives, by I_2, and other reactions, were studied.[2] Similar procedures with aliphatic dithiols yielded $In^I[SR(SH)]$ compounds, whose chemistry is analogous to that of the oxygen compounds.[3]

In an attempt to further explore the properties of such compounds, we have repeated the preparation of the thallium(I) derivatives of 2,2′-dihydroxybiphenyl, first reported by Brady and Hughes in 1933.[4] These authors found that the reaction between the biphenol and thallium(I) acetate in aqueous ammonia yielded either Tl_2O_2R or Tl[OR(OH)] (R = biphenyl) depending on the experimental conditions. We obtained crystals of the latter species and determined the molecular structure; the reactions of Tl[OR(OH)] have also been explored, as has the synthesis of other related thallium(I) derivatives of aromatic diols, and it appears that the situation is more complicated than was originally suggested.

Experimental Section

General Data. All reagents were used as supplied; solvents were dried before use. Since the products are generally air-stable, no special experimental precautions were used other than to carry out the preparations under nitrogen in the early stages of the work; this was later abandoned and reactions were performed in air.

Thallium analysis was by atomic absorption spectrophotometry, using an IL-251 instrument. Microanalysis was carried out by Canadian Microanalytical Laboratories. Infrared spectra were recorded on a Nicolet 5DX instrument, with samples incorporated into CsI disks; ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer. Electron paramagnetic resonance (EPR) spectra were run on a Varian E12 instrument calibrated with an NMR gaussmeter; the klystron frequency was determined from the EPR spectrum of diphenylpicrylhydrazide.

Preparation of $Tl[OC_{12}H_8(OH)]$. Thallium(I) acetate (2.5 g, 9.5 mmol) dissolved in water (23 mL) was mixed with ethanol (6.25 mL), and gaseous ammonia was bubbled through the solution. The addition of a warm solution of $C_{12}H_8(OH)_2$-2,2′ (2.25 g, 12 mmol) in ethanol (6.25 mL) produced a clear solution from which needlelike crystals were thrown down almost immediately. The mixture was allowed to stand for 24 h, after which the product, $Tl[OC_{12}H_8(OH)]$, was collected by filtration, washed with ethanol, and dried in vacuo. Yield: 97%. Mp: 227 °C (lit.[4] 227−229 °C). The initial product was pale brown; well-developed crystals could be grown from hot water, in which the compound is sparingly soluble. Slow evaporation of a saturated solution at room temperature in a desiccator, or the slow diffusion of ethanol into a saturated solution, produced crystals suitable for X-ray crystallography (see below).

The ^1H NMR spectrum in $(CD_3)_2SO$ consisted of three multiplets centered at 6.61 (2H), 7.01 (1H), and 7.20 ppm (1H) (aromatic) and a broad absorption at 10.51 ppm (OH) ($Me_4Si = 0$). The ^{13}C spectrum of the parent $C_{12}H_8(OH)_2$-2,2′ in the same solvent had resonances assigned as 154.3 (C^2), 131.5 (C^6), 128.1 (C^1), 126.0 (C^4), 118.9 (C^5), and 115.7 (C^3) ppm ($Me_4Si = 0$), while the spectrum of the thallium derivative consists of a series of sharp singlets at 161.2, 129.8, 129.4, 127.2, 118.7, and 115.6 ppm, showing significant changes at C^2, C^6, C^1, and C^4 (dmso, room temperature).

Reactions of $Tl[OC_{12}H_8(OH)]$, 1. (i) Solubility. The parent compound is slightly soluble in cold water, appreciably soluble at 80 °C, but insoluble in ethanol and other common organic solvents; the solubility in dmso is sufficient to permit NMR spectroscopy. We have confirmed the observation of Brady and Hughes[4] that **1** (e.g., 0.5 g) is soluble in chloroform (10 mL) in the presence of excess $C_{12}H_8(OH)_2$-1,2 (2 g), giving a clear brown solution. Evaporation of this solution gave crystals of **1**. We also tested the effect of similar quantities of catechol, *p*-nitrophenol, *N,N,N′,N′*-tetramethylenediamine (tmen), tet-

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(3) Geloso, C.; Mabrouk, H. E.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* **1989**, 1759.

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rabromocatechol, and 1,2-ethanediamine (en) on the solubility of **1** in $CHCl_3$, but only in the case of en was the solubility affected. Removal of the solvent from this mixture gave an oil, whose IR and ^1H NMR spectra confirmed the presence of both **1** and en, but we were not able to obtain solid material suitable for further investigation.

(ii) Complexation with 18-Crown-6. A sample of **1** (1.0 g, 2.57 mmol) was suspended in ethanol (10 mL) and 18-crown-6 (0.83 g, 3.15 mmol) added. The mixture was stirred at ca. 50 °C for 40 min, yielding a clear yellow solution which on subsequent evaporation gave pale brown crystals of $Tl[OC_{12}H_8(OH)]\cdot$18-crown-6 in essentially quantitative yield. Anal. Calcd for $C_{24}H_{33}O_8Tl$: C, 44.1; H, 5.10. Found: C, 43.8; H, 5.25. The IR and NMR (^1H, ^{13}C) spectra were in agreement with the formulation of this substance as a 1:1 adduct.

(iii) Oxidation Reactions. Following the earlier results with $In[OR(OH)]$ species,[2] we attempted to study the oxidation of $Tl[OC_{12}H_8(OH)]$ by iodine. The reaction with I_2 appears to be affected by the solvent used; in later experiments, ethanediamine (en) was added to the reaction mixture in order to encourage the removal of the proton of the ligand, but without apparent success, and the substitution of en by Et_3N did not improve matters.

Reaction in toluene resulted in the discharge of the color of I_2 and the formation of a yellow product (~78% of mass of reactants), which contained ligand, en, Tl, and I but whose elemental analysis did not correspond to any reasonable product. When $Tl[OC_{12}H_8(OH)]$ (0.25 g, 0.64 mmol) suspended in chloroform (5 mL) was treated with an equimolar quantity of I_2 in the presence of en (0.32 g, 5.4 mmol), a clear solution was obtained. This gradually became yellow; after 30 min of heating at 70 °C to bring about complete consumption of I_2, a yellow powder was formed (0.20 g). This material, which is only slightly soluble in acetone or dmso, was washed (3 mL of $CHCl_3$, 3 mL of Et_2O) and dried. Iodine analysis (found 39.3%) identified this substance as $I_2Tl[OC_{12}H_8(OH)]$ (calcd 39.5%). This same product was obtained when $Tl[OC_{12}H_8(OH)]$ was treated with I_2 in $CHCl_3$ in the presence of excess 2,2′-dihydroxybiphenyl; the sequence of color changes was similar to that just described.

Other Thallium(I) Compounds. (i) Derivative of Tetrachlorocatechol. Thallium(I) acetate (2.0g, 7.6 mmol) was dissolved in water (1 mL), ethanol (2.5 mL), and Et_3N (2 mL) to give a clear solution, to which was added $C_6Cl_4(OH)_2$ (1.88 g, 7.6 mmol) in ethanol (5 mL). The mixture was refluxed; after about 5 min, the brown solution gave a brown precipitate, which became yellow-green as the reaction progressed. After 2 h, this solid was collected, washed (5 mL of EtOH, 20 mL of Et_2O), and dried in vacuo; yield 2.97 g. The ^1H NMR spectrum showed the presence of ethanol in the final product, and the analysis was close to that required for $Tl[OC_6Cl_4(OH)]\cdot C_2H_5OH$. Anal. Calcd for $C_8H_7O_3Cl_4Tl$: C, 19.3; H, 1.42; Tl, 41.1. Found: C, 20.2; H, 1.78; Tl, 41.3. A similar reaction starting with thallium(I) formate gave a product which was also apparently contaminated with solvent, and this system was not investigated further.

(ii) Derivatives of Tetrabromocatechol. Thallium(I) acetate (1.0 g, 3.8 mmol) was dissolved in H_2O (0.5 mL), and the solution was treated successively with ethanol (2.5 mL), concentrated aqueous ammonia (0.3 mL), and a solution of $C_6Br_4(OH)_2$ (1.62 g, 3.8 mmol) in ethanol (2.5 mL). The addition of the latter precipitated a yellow solid, which instantly redissolved; over a further period of 15 min, an orange precipitate appeared in the stirred solution. This was collected, washed with ethanol (20 mL), and dried in vacuo. Yield: 2.46 g. This product is $Tl[OC_6Br_4(OH)]$. Anal. Calcd for $C_6HO_2Br_4Tl$: C, 11.5; H, 0.16; O, 5.09. Found: C, 11.2; H, 0.50; O, 5.50. This compound is soluble in dmso and *N,N*-dimethylformamide.

In a second experiment, the same quantities of TlOAc and $C_6Br_4(OH)_2$ were dissolved in water (0.5 mL) and ethanol (5 mL), and ammonia gas bubbled through the stirred solution for 20 min. A yellow solid appeared, redissolved, and then finally precipitated once again. This solid was collected, washed ($EtOH-H_2O$ (9:1), 10 mL), and dried in vacuo; yield 1.54 g. A similar reaction using thallium(I) formate as the starting material gave the same product, identified as $Tl_2[O_2C_6Br_4]$. Anal. Calcd: Tl, 49.1; C, 8.66. Found: Tl, 49.5; C, 9.00; H, <0.1. The solubilities are similar to those of the earlier compound; ^{13}C NMR resonances are at 105.9, 114.3, and 160.2 ppm ($Me_4Si = 0$), compared with 113.8, 116.8, and 114.7 ppm for the parent diol.

(iii) Derivative of Catechol. Thallium(I) acetate (2.0 g, 7.6 mmol) was dissolved in water (1 mL) plus ethanol (2.5 mL) and Et_3N (2 mL), and a solution of catechol (0.85 g, 7.7 mmol) was added. After rapid precipitation and redissolution of a yellow solid, a beige precipitate quickly formed. The mixture was then gently refluxed for 2 h, turning deep brown; the solid which was collected by filtration had a shiny gray appearance. Yield: 1.78 g. Anal. Calcd for $C_6H_4O_2Tl$: C, 23.1; H, 1.29; Tl, 65.4. Found: C, 23.0; H, 1.41; Tl, 65.3.

The compound is slightly soluble in dmso and dmf, giving an olive green solution in each case. A dilute solution in 4-methylpyridine gave an ESR spectrum consisting of two triplets centered at $g = 1.998$. This spectrum was simulated by assuming two hyperfine coupling constants, $a_H = 3.27$ G and $a_{Tl} = 101$ G, which identify the gray product as the thallium(I) semiquinone, $Tl[O_2C_6H_4{}^\bullet]$.

(iv) Derivatives of 3,5-Di-*tert*-butylcatechol. (a) We attempted to prepare a monothallium derivative of 3,5-$C_6H_2Bu^t{}_2(OH)_2$ (H_2dbc), using the standard methods. Thallium(I) formate (1.00 g, 4.2 mmol) was dissolved in methanol (5 mL) and ammonia bubbled through the solution for 10 min, after which dbc (0.93 g, 4.2 mmol) in the same solvent (5 mL) was added. The mixture became deep green and produced a copious precipitate; further methanol (20 mL) was added, and the mixture was refluxed gently for 24 h to give a deep blue solution. A variety of techniques were applied in attempts to isolate a stable and identifiable product from this solution, which we believe contained a thallium(I) semiquinone, but without success.

(b) The direct reaction between elemental thallium (0.60 g, 2.95 mmol) and 3,5-di-*tert*-butylbenzoquinone (dbq) (0.65 g, 2.95 mmol) in refluxing toluene (30 mL) under dry nitrogen produced reaction mixtures which were successively red, green (after 15 min), and deep brown (14 h). The final solution was filtered; the absence of thallium metal showed that the reaction had gone to completion. Removal of solvent in vacuo gave a dark brown solid, which was washed (diethyl ether) and dried; yield 1.11 g, 88%. This solid, which we identify as thallium(I) 3,5-di-*tert*-butylbenzosemiquinone, is soluble in toluene, tetrahydrofuran, and dichloromethane, although in each case the solution deposits a yellowish precipitate after a few days. Anal. Calcd for Tl(dbsq$^\bullet$), $C_{14}H_{20}O_2Tl$: C, 39.5; H, 4.7. Found: C, 37.3; H, 4.5. Infrared spectroscopy showed the absence of ν(C=O) of the quinone. The EPR spectrum (solid state, frozen or room-temperature solution) showed a typical free radical spectrum as expected for thallium(I) 3,5-di-*tert*-butylbenzosemiquinone, with $g = 1.998$, $A_H = 3.3$ G, and $A_{Tl} = 44$ (±2) G.

(c) Na(dbsq$^\bullet$) was prepared by reducing H_2dbc (0.51 g, 2.28 mmol) with NaH (0.055 g, 2.28 mmol) in $CHCl_3$ (30 mL). After 30 min, the stirred blue solution was treated with thallium(I) acetate (0.60 g, 2.28 mmol) in the same solvent, and the mixture was refluxed for 3 h. Filtration yielded NaOAc (found 0.19 g; calcd 0.18 g); removal of solvent from the filtrate gave a deep green solid, (found 0.89 g; calcd 0.97 g), which on standing in a drybox for a few days became red-brown. The EPR spectrum of this solid had $g = 1.996$ and $A_{Tl} = 47$ (±2) G; A_H was not detected because of poor resolution. An analogous procedure using $TlNO_3$ gave similar results.

(d) Cyclopentadienylthallium(I) (0.5 g, 1.86 mmol) and dbq (0.41 g, 186 mmol) in toluene (30 mL) were refluxed for 8 h to give a brown solution. Removal of a small quantity of dark yellow solid by filtration, and of solvent by evaporation, yielded a dark brown solid (0.78 g, 86%). The IR and EPR spectra of this material were essentially identical to those noted above, and the solid was also considered to be Tl(dbsq$^\bullet$).

(e) Approximately 0.2 g of the brown solid prepared by route b above was dissolved in toluene (20 mL), and the solution was stored at room temperature in a stoppered vessel. The small quantity of yellow-white solid which precipitated over a 2 week period was collected by filtration, washed with diethyl ether, and dried. Thallium content: found, 63.1%; calcd for $C_{14}H_{20}O_2Tl_2$, 64.9%. This solid is sparingly soluble in $CDCl_3$, and the ^1H NMR spectrum in this solvent had resonances at 1.1 (^{t}Bu) and 6.3−7.5 (phenyl) ppm; ^{13}C resonances at 29.1 (^{t}Bu) and 112 (C^4), 118 (C^6), 143 (C^5), 144 (C^3), 147 (C^2), and 148 (C^1) ppm are in keeping with earlier results on phosphorane derivatives of dbc.[5] The intensities were too weak to allow further interpretation but confirm the presence of the dbc residue in the precipitated solid, and we believe that this solid is Tl_2(dbc).

General X-ray Diffraction Data Collection, Solution, and Refinement. The diffraction experiment was performed on a four-circle

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Table 1. Summary of X-ray Crystallographic Data for $\{Tl[\mu\text{-}O(C_6H_4)(C_6H_4)OH]\}_2$

formula	$C_{24}H_{18}O_4Tl_2$	Z	2
fw	779.14	ρ, g/cm^3	2.55
a, Å	7.911(2)	λ, Å	0.710 69
b, Å	10.775(3)	μ, cm^{-1}	158.97
c, Å	11.955(4)	T, °C	24
β, deg	96.33(2)	$R(F_o)$,[a] %	3.88
V, Å^3	1012.8(4)	$R_w(F_o)$,[a] %	4.45
space group	$C2/m$ (No. 12)		

[a] $R = \sum||F_o| - |F_c|/\sum|F_o||$; $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$, $w = 1/\sigma^2(F)$.

Rigaku AFC6 diffractometer with graphite-monochromatized Mo Kα radiation. The unit cell constant and an orientation matrix for data collection were obtained from 25 centered reflections (15 ° < 2θ < 35°). Machine parameters, crystal data, and data collection parameters are summarized in Table 1 and in the supplementary material. The intensities of three standard reflections recorded every 150 reflections showed no statistically significant changes over the duration of the data collection. The intensity data were collected using the $\omega-2\theta$ scan technique, in four shells (2θ < 30, 40, 45, 50°). A large absorption coefficient (μ = 158.97) was calculated, and an absorption correction was applied to the data, which were processed using the TEXSAN software package[6] running on an SGI computer. Refinement was carried out by using full-matrix least-squares techniques on F, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$ and F_o and F_c are the observed and calculated structure factors. Atomic scattering factors[7] and anomalous dispersion terms[8,9] were taken from the usual sources. Fixed H atom contributions were included, with C−H distances of 0.95 Å and thermal parameters 1.2 times the isotropic thermal parameter of the bonded C atoms. Hydrogen atoms were not refined, but all values were updated as the refinement proceeded.

Structure Determination of $\{Tl[\mu\text{-}O(C_6H_4)(C_6H_4)OH]\}_2$, 1. Tan crystals of the title compound were grown by vapor diffusion of ethanol into an aqueous solution of the compound. A statistical analysis of the intensity distributions and a determination of observed extinctions were consistent with the space group $C2/m$, and this was confirmed by a successful solution refinement. Of the total of 938 reflections collected, 639 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The position of the thallium atom was determined by the Patterson method, and the remaining non-hydrogen atoms were located from difference map calculations. In the final cycles of refinement, the thallium atom and oxygen atoms were assigned anisotropic thermal parameters and the biphenyl units were input as rigid phenyl groups with the carbon atoms being assigned isotropic thermal parameters. The structure refined to $R = \sum||F_o| - |F_c|/\sum|F_o|| = 0.0388$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.0445$; a goodness of fit calculation resulted in a value of 1.46 at final convergence. The final difference map calculation showed no peaks of chemical significance; the largest was 0.8 e/Å^3 and was associated with the thallium atom.

Atomic positional parameters are summarized in Table 2, and bond distances and angles are summarized in Table 3. Anisotropic thermal parameters and hydrogen atom parameters are deposited as supplementary material.

Table 2. Positional Parameters for $\{Tl[\mu\text{-}O(C_6H_4)(C_6H_4)OH]\}_2$

atom	x	y	z	B(eq), Å^2
Tl	0.1025(1)	0	0.34942(8)	2.90(5)
O(1)	0.196(2)	0	0.558(1)	3.0(7)
O(2)	0.265(2)	0.225(2)	0.653(2)	3(1)
C(1)	0.331(2)	−0.048(2)	0.616(1)	2.4(9)
C(2)	0.423(2)	−0.133(2)	0.559(1)	3.8(9)
C(3)	0.555(2)	−0.200(2)	0.618(2)	3.2(9)
C(4)	0.594(2)	−0.182(2)	0.734(2)	3.9(9)
C(5)	0.502(2)	−0.097(2)	0.790(1)	2.9(9)
C(6)	0.370(2)	−0.030(2)	0.731(1)	2.2(9)
C(7)	0.279(2)	0.063(2)	0.800(1)	1.4(9)
C(8)	0.236(2)	0.181(2)	0.758(1)	3.0(9)
C(9)	0.150(2)	0.264(1)	0.821(2)	2.5(9)
C(10)	0.107(2)	0.229(2)	0.927(1)	2.8(9)
C(11)	0.150(2)	0.111(2)	0.970(1)	3.6(9)
C(12)	0.236(2)	0.028(1)	0.906(1)	1.9(9)

Table 3. Bonding Parameters for $\{Tl[\mu\text{-}O(C_6H_4)(C_6H_4)OH]\}_2$

	Bond Distances (Å)[a]		
Tl−O(1)	2.52(1)	Tl′-O(1)	2.71(1)
O(1)-C(1)	1.31(2)	O(2)-C(8)	1.38(2)
C(6)-C(7)	1.53(2)		
	Nonbonding Intradimer Distances (Å)		
Tl•••Tl′	4.109(2)	Tl•••O(2)	4.44(2)
Tl•••O(2)′	3.78(2)	O(1)•••O(1)′	3.25(2)
O(1)•••O(2)	2.71(2)		
	Nonbonding Interdimer Distances (Å)		
Tl•••Tl″	6.675(1)	Tl•••O(2)″	3.14(2)
	Bond Angles (deg)[a]		
O(1)-Tl-O(1)′	76.7(4)	Tl-O(1)-Tl′	103.3(4)
Tl-O(1)-C(1)	131(1)	Tl′-O(1)-C(1)	119(1)
O(1)-C(1)-C(2)	116(1)	O(1)-C(1)-C(6)	123(1)
C(1)-C(6)-C(7)	123(1)	C(5)-C(6)-C(7)	116(1)
C(6)-C(7)-C(8)	121(1)	C(6)-C(7)-C(12)	119(1)
O(2)-C(8)-C(7)	126(2)	O(2)-C(8)-C(9)	114(2)

[a] Phenyl rings are included as rigid groups having ideal D_{6h} symmetry with C−C bond distances of 1.40 Å and C−C−C angles of 120°.

Results

The preparative work with $C_{12}H_8(OH)_2$-2,2′ has confirmed the original experiments by Brady and Hughes,[4] in that a thallium(I) complex of a partially deprotonated diol is formed. The dimeric structure which has been found is different from that proposed by Brady and Hughes and, in fact, is related to the copper(I) complex discussed in the Introduction. The molecule is also interesting in that it is centered on a four-membered Tl_2O_2 ring, found in other thallium(I) complexes. The compound can be oxidized by iodine to the appropriate thallium(III) species. We have also shown that the initial reaction conditions affect the stoichiometry of the product, not only in the original case of 2,2′-dihydroxybiphenyl but also with $C_6Br_4(OH)_2$, where both Tl[OR(OH)] and $Tl_2[O_2R]$ were obtained.

In addition, it is clear that the electronic properties of the substituted phenyl group concerned are also critical, in that thallium(I)−semiquinone derivatives can be obtained in the case of catechol and dbc, over and above any competing formation of Tl[OR(OH)] or $Tl_2[O_2R]$. In the case of Tl(dbsq•), which can be obtained by a variety of routes, the compound appears to be intrinsically unstable, and slow decomposition to Tl_2(dbc) was observed.

Discussion

Molecular Structure of $\{Tl[\mu\text{-}O(C_6H_4)\text{-}(C_6H_4OH]\}_2$, 1. The structure of **1** in the solid state is that of a dimer, $\{Tl[\mu\text{-}O(C_6H_4)(C_6H_4)OH]\}_2$, with an asymmetric Tl_2O_2 core; Tl−O(1) 2.52(1) and Tl−O(1) 2.71(1) Å. The asymmetry is in contrast to the otherwise related $[2,4,6\text{-}(CF_3)_3C_6H_2OTl]_2$ where the Tl_{br}−O bonds are identical within experimental error;[10] average Tl−O 2.465 Å. These bond lengths are in keeping with those reported for Tl^I−O bonds in thallium(I) ascorbate[11] (average 2.76 Å) and (hexafluoroacetylacetonato)thallium(I)[12] (average 2.87 Å), and both these structures involve extensive intermo-

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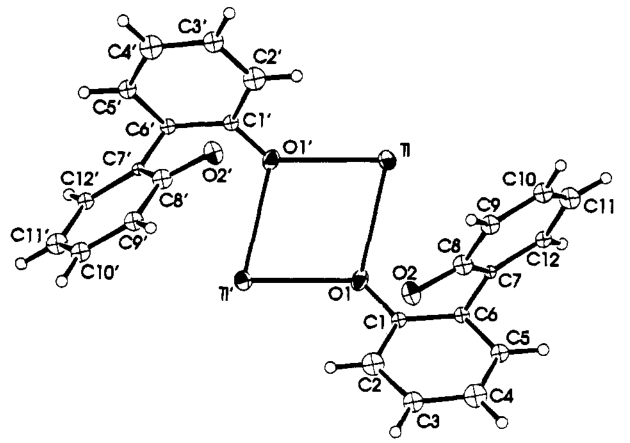

Figure 1. ORTEP diagram for $\{Tl[\mu\text{-}O(C_6H_4)(C_6H_4)OH]\}_2$, **1**, with atoms shown as 30% probability ellipsoids.

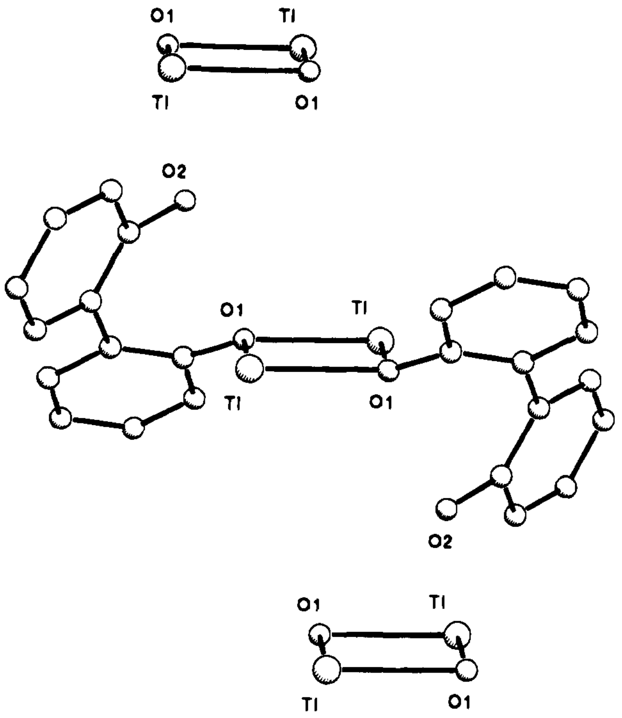

Figure 2. Packing of dimeric units in the lattice of **1**.

lecular interactions. The other interesting feature is that the Tl_2O_2 ring in **1** shows a larger O−Tl−O angle (76.7(4)°) than the phenoxide dimer **2** (70.8(4)°). The Tl_2O_2 ring is at an angle of 13.0° to the C_6H_4O ring to which it is attached, and the latter makes a torsional angle of 42.4° with the pendant $C_6H_4(OH)$ ring. The intramolecular distances and angles may imply an intermolecular interaction between the nonligating OH group and the thallium atom of the next nearest dimeric unit in terms of a OH···Tl hydrogen bond, Tl···O(2) 3.14(2) Å. This distance is reasonable for such an interaction, since similar distances have been reported for the extensive hydrogen bonding in the lattice of thallium(I) ascorbate.[11]

We have commented elsewhere on the usefulness of the C−O bond distance in distinguishing among *o*-quinone, *o*-semiquinone, and catecholate derivatives.[13,14] In keeping with these arguments, r(C−O) for the thallium-bonded oxygen in **1** is close to what would be expected from the above argument, at 1.31(2) Å. This value and that of 1.38(2) Å for the nonbonded OH are close to those found in several substituted catecholate derivatives of main group elements.

The results show that the original chelate structure reasonably postulated by Brady and Hughes does not in fact exist in **1** and that the nonbonding OH group of the ligand is apparently involved in intermolecular hydrogen bonding, which serves to stabilize the lattice. Given the structural similarities between the indium(I) and thallium(I) derivatives of $(CF_3)_3C_6H_2OH$,[10,15] it seems reasonable to conclude that the corresponding In[OR(OH)] and Tl[OR(OH)] species are also structurally related and that the insolubility reported for the indium(I) species derived from substituted catechols[2] is due in part to intermolecular bonding. One quantitative difference is that the removal of the nonbonding proton of the ligand occurs more readily with the indium(I) compounds than is the case for thallium analogues.

One other significant difference is that while the indium(I) compounds are easily oxidized to the corresponding +III state by iodine, this reaction did not occur smoothly with iodine alone and **1**. In the presence of en or excess ligand, the compound $I_2Tl[OC_{12}H_8(OH)]$ was obtained, suggesting that dissociation of the initial dimer may be required before oxidation can occur.

Thallium-Ligand Interactions. The preparative results show that a variety of products can be obtained from the reaction of a thallium(I) salt with a substituted catechol. A change in the concentration of base in the reaction solution may lead to either Tl[OR(OH)] or $Tl_2[O_2R]$ when R = $C_{12}H_8$ or C_6Br_4, and this is most simply seen as shifting the dissociative equilibria of the diol. In other cases, such as catechol itself or 3,5-di-*tert*-butylcatechol, the reaction product was identified as the thallium(I) semiquinone analogous in the latter case to the indium(I) semiquinone reported earlier.[16] No product was isolated in the initial reaction with H_2dbc, and the material obtained via three other routes was obviously unstable, but the spectroscopic evidence for the presence of dbsq• in the reaction products is clear. The instability of this compound in the presence of organic solvents, giving rise to Tl_2dbc, can be seen as the effect of the solution equilibrium $2Tl(dbsq^\bullet) \rightleftharpoons Tl_2dbc + dbq$ where dbq is the parent 3,5-di-*tert*-butylbenzosemiquinone. The mechanism of the processes by which the $Tl_2[O_2R]$ or Tl[OR(OH)] species formed in the initial reactions are converted to semiquinone derivatives is far from clear, but since the reactions were carried out in the presence of dissolved oxygen in basic aqueous solution, conditions which are known to favor electron transfer to give semiquinone derivatives, it is reasonable that such species be formed. What is not clear is the nature of the quantitative parameters which might be used to predict the reaction product from these interesting interactions between aromatic diols and thallium(I) salts, but clearly further work on these systems is required, since there is much more in these thallium(I)−catechol systems than was previously suspected.

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Supplementary Material Available: Tables giving X-ray crystallographic details, anisotropic thermal parameters, and hydrogen atom parameters (2 pages). Ordering information is given on any current masthead page.

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