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Synthesis of Heteronuclear Pt−Tl Complexes with Donor−Acceptor Bonds. X-ray Structures of *cis*-$[Tl(\mu_2\text{-}OOCCH_3)Pt(PPh_3)(C_6F_5)_2]$ and $(NBu_4)_2[\{Pt(C_6F_5)_3\}_2\{(\mu_2\text{-}O,\mu_3\text{-}O'CCH_3)Tl\}_2]$

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Reactions of the anionic platinum complexes $(NBu_4)[Pt(PPh_3)(C_6F_5)_2(OCOCH_3)]$ **(1)** and $(NBu_4)_2[Pt(C_6F_5)_3(S)]$ (S = methanol or acetone) with Tl(I) salts afford the heterometallic neutral *cis*-$[(C_6F_5)_2(PPh_3)Pt(\mu_2\text{-}OOCCH_3)Tl]$ **(2)** and the dimeric dianionic $(NBu_4)_2[\{(C_6F_5)_3Pt\}_2\{(\mu_2\text{-}O,\mu_3\text{-}O'CCH_3)Tl\}_2]$ **(3)**. Both complexes display Pt−Tl bonds with bond lengths of 2.994(1) Å and 2.884(1) Å, respectively, the latter being the shortest Pt−Tl(I) distance reported so far. The structure of both compounds has been established by X-ray studies.

Introduction

Structurally characterized complexes displaying Tl−Pt(II) bonds are scarce: $Tl_2[Pt(CN)_4]$,[1] $[Tl(\text{crown-}P_2)Pt(CN)_2]NO_3$,[2] and *cis*-$[(NH_3)_2Pt(1\text{-}MeT)_2Tl(1\text{-}MeT)_2Pt(NH_3)_2]NO_3 \cdot 7H_2O$.[3] The paramagnetic Tl(II) complex $(NBu_4)_2[Tl\{Pt(C_6F_5)_4\}_2]$[4] has been reported recently. No thallium(I) acetate compounds have been structurally studied, despite the fact that $TlOOCCH_3$ has long been known.[5] We present here the synthesis and structural characterization of two heterometallic PtTl acetate complexes: the neutral *cis*-$[(PPh_3)(C_6F_5)_2Pt(\mu_2\text{-}OOCCH_3)Tl]$ **(2)** and the anionic $(NBu_4)_2[\{(C_6F_5)_3Pt\}_2\{(\mu_2\text{-}O,\mu_3\text{-}O'CCH_3)Tl\}_2]$ **(3)** (Bu = *n*-butyl); the latter, which is the first structurally characterized anionic Pt−Tl complex, displays the shortest Pt(II)−Tl(I) distance (2.884(1) Å) reported to date.

Experimental Section

C, H, and N analyses were carried out on a Perkin-Elmer 240-B or 2400 microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (200−4000 cm^{-1}) using Nujol mulls between polyethylene sheets or KBr disks. ^{31}P, ^{19}F, and ^{195}Pt NMR spectra were recorded on a Varian Unity 300 instrument in acetone-d_6 and CD_2Cl_2 solutions at room temperature. NMR spectra are referenced to 85% aqueous H_3PO_4, $CFCl_3$, and $Na_2[PtCl_6]$.

UV−vis absorption spectra were recorded on a Hitachi U-3400 spectrophotometer. Photoluminescence spectra were measured by excitation with light from a 1000 W tungsten lamp passed through a 0.22 m double monochromator. Fluorescence was detected through a 0.5 m monochromator with a photomultiplier detector. The luminescence spectra were corrected for the instrumental response using a standard calibrated tungsten−halogen lamp.

The starting compounds $(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-}Cl)]_2$[6] and $TlOCOCH_3$[5] were prepared by literature methods.

All reactions were carried out at room temperature.

(a) Preparation of $(NBu_4)[Pt(OCOCH_3)(PPh_3)(C_6F_5)_2]$ (1). $AgOCOCH_3$ (0.0827 g, 0.5 mmol) was added to a methanol/acetone (5/40 mL) solution of $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6F_5)_2]_2$ (0.4000 g, 0.25 mmol), and after 4−5 h of stirring, the precipitate AgCl was filtered off. PPh_3 (0.1300 g, 0.5 mmol) was added to the solution, which, after 5 min, was evaporated to dryness; the residue was washed with Et_2O to render the pale yellow compound $(NBu_4)[Pt(OCOCH_3)(PPh_3)(C_6F_5)_2]$. Yield: 0.4643 g (85%). Anal. Calcd for $PtNPC_{48}H_{54}F_{10}O_2$: C, 52.75; H, 4.98; N, 1.28. Found: C, 52.52; H, 4.97; N, 1.17. Relevant IR absorptions (cm^{-1}): for C_6F_5 groups, 1500 (vs), 1377 (s), 1318 (s), 1062 (vs), 956 (vs), 803 (s), 780 (s); for PPh_3, 1099 (s), 753 (s), 740 (s), 706 (s), 696 (s), 535 (s), 515 (s), 504 (m); for ν(COO), 1627 (vs), 1318 (s).

(b) Preparation of *cis*-$[(C_6F_5)_2(PPh_3)Pt(\mu_2\text{-}OOCCH_3)Tl]$ (2). The synthesis was accomplished through two different procedures: (i) starting from the intermediate compound **(1)** and (ii) directly from $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6F_5)_2]_2$.

Method i. To a methanol/acetone (5/40 mL) solution of **1** (0.2500 g, 0.23 mmol) was added an equimolecular amount of $TlNO_3$ (0.0610 g, 0.23 mmol) which was dissolved after 5 h of stirring The solution was evaporated to dryness, and the residue (a paste) was treated with 20 mL of ^iPrOH to extract NBu_4NO_3. The remaining white solid was identified as *cis*-$[TlPt(\mu_2\text{-}OOCCH_3)(PPh_3)(C_6F_5)_2]$ **(2)**. Yield: 0.1940 g (80%). Anal. Calcd for $PtTlC_{32}F_{10}H_{18}O_2P$: C, 36.43; H, 1.72. Found: C, 35.90; H, 1.70. Relevant IR absorptions (cm^{-1}): for C_6F_5 groups, 1640 (m), 1610 (m), 1378 (s), 1066 (vs), 952 (vs), 808 (s), 785 (s); for PPh_3, 1105 (s), 747 (s), 740 (s), 706 (s), 695 (s), 535 (s), 515 (s), 504 (m); for ν(COO), 1549 (vs), 1404 (s).

Method ii. PPh_3 (0.1300 g, 0.5 mmol) was added to a methanol/acetone (5/40 mL) solution of $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6F_5)_2]_2$ (0.4000 g, 0.25 mmol). After 30 min of stirring, $TlOCOCH_3$ (0.1300 g, 0.5 mmol) was added and the precipitate TlCl was filtered off. $TlNO_3$ (0.1330 g, 0.5 mmol) was added, and after 5 h of stirring, the solution was evaporated to dryness and the residue extracted with ^iPrOH to leave complex **2** (0.4323 g). Yield: 82%.

(c) Preparation of $(NBu_4)_2[(C_6F_5)_3Pt(\mu_2\text{-}O\text{-}\mu_3\text{-}O'CCH_3)Tl]_2$ (3). $AgClO_4$ (0.0426 g, 0.2 mmol) was added to a methanol/acetone (5/40 mL) solution of $(NBu_4)_2[Pt(C_6F_5)_3Cl]$ (0.2500 g, 0.2 mmol). After 1 h of stirring, the precipitate AgCl was filtered off and $TlOCOCH_3$ (0.0541 g, 0.2 mmol) was added to the solution, which, after 4 h of stirring,

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Table 1. Crystal Data for *cis*-[$(C_6F_5)_2(PPh_3)Pt(\mu_2\text{-}OOCCH_3)Tl$] **(2)** and $(NBu_4)_2[\{(C_6F_5)_3Pt\}_2\{(\mu_2\text{-}O\text{-}\mu_3\text{-}O'CCH_3)Tl\}_2]$ **(3)**[a]

	2	**3**
chem formula	$TlPtPO_2F_{10}H_{18}C_{32}$	$TlPtNO_2F_{15}H_{39}C_{36}$
fw	1054.9	1202.14
space group	$P\bar{1}$	$P2_1/n$
a, Å	9.136(1)	13.868(1)
b, Å	9.864(2)	16.704(2)
c, Å	18.148(2)	18.022(2)
α, deg	95.08(1)	90
β, deg	101.89(1)	94.63(1)
γ, deg	102.00(1)	90
V, Å	1550.6(5)	4161.1(7)
Z	2	4
d_{calc}, g/cm^3	2.259	1.919
cryst size, mm	0.2 × 0.15 × 0.08	0.2 × 0.3 × 0.23
μ(Mo Kα), cm^{-1}	98.37	73.24
transm factors	0.9132/0.4897	0.962/0.694
data collecn instrument	Siemens P4	Siemens/ STOE AED2
radiation (Mo Kα), (graphite monochromated), Å	0.710 73	0.710 73
temp, °C	20	20
scan method	$\omega-2\theta$	$\omega-\theta$
data collecn range (2*θ*), deg	4−45	4−45
no. of unique data	4046	5684
no. of data with $F_o > 4\sigma(F_o)$	3014	5418
no. of params refined	425	497
R	0.0365	0.0329
R_w	0.0426	
R_{w2}		0.0611
quality of fit indicator	0.93[b]	1.050[c]

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. $w^{-1} = [\sigma^2(|F_o|) + 0.0035|F_o|^2]$. $R_{w2} = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$; $P[\max(F_o^2;0) + 2F_c^2]/3$. [b] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$. [c] Quality of fit $= [\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$.

was evaporated to dryness; the residue was extracted with Et_2O, the insoluble NBu_4ClO_4 being separated by filtration. The solution was again evaporated to dryness, and the oily residue upon treatment with *n*-hexane rendered the white complex **3**. Yield: 0.1750 g (73%). Anal. Calcd for $Pt_2Tl_2C_{72}F_{30}N_2O_4H_{78}$: C, 35.97; H, 3.27; N, 1.17. Found: C, 36.25; H, 3.42; N, 1.21. The conductivity of the complex **3** in acetone solutions was measured at different concentrations to determinate the slope of the Onsager's equation,[7] which is 889 and indicates that complex **3** behaves as an (1:1) electrolyte in acetone solution. Relevant IR absorptions (cm^{-1}): for C_6F_5 groups, 1634 (m), 1379 (s), 1055 (vs), 951 (vs), 808 (s), 786 (m), 770 (s) for ν(COO), 1546 (vs), 1410 (s).

(d) X-ray Structure Analysis of *cis*-[$(C_6F_5)_2(PPh_3)Pt(\mu_2\text{-}OOCCH_3)$-Tl] (2) and $(NBu_4)_2[(C_6F_5)_3Pt(\mu_2\text{-}O\text{-}\mu_3\text{-}O'CCH_3)Tl]_2$ (3). Colorless crystals of complex **2** or complex **3** were obtained by slow diffusion (ca. 2 weeks at −4 °C) of *n*-hexane into acetone solutions of each complex.

Crystallographic data for these complexes are collected in Table 1. Three check reflections were measured every 97 reflections (complex **2**) or 180 min (complex **3**). No decay was observed. Data reductions included absorption corrections based on azimuthal scans.

The positions of the platinum and thallium atoms were determined from the Patterson map. The remaining of the structures were developed and refined in an alternating sequence of least-squares refinements and difference Fourier maps.

For complex **2** all non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were added at calculated positions and refined with a riding model in which the C−H distance was fixed at 0.96 Å with the isotropic temperature factor refining to 0.074(11) Å^2. The final *R* factors for molecule **2** are $R = 0.0365$ and $R_w = 0.0426$. A total of 3014 data with $F_o > 4\sigma(F_o)$ were used to refine 425 parameters.[8] The final difference Fourier map does not show any peak higher than 1 e/Å^3.

For complex **3**, there are two C atoms of the NBu_4^+ group which are disordered over two atomic sites, C(28) and C(28a), C(36) and C(36a), with 50% occupancy for all of these sites. H atoms, except those bonded to the disordered C atoms, were added at calculated positions using information of the difference Fourier map for the H atoms of the methyl groups[8] and were further refined with a riding model, the C−H distance being fixed at 0.96 Å. Their isotropic displacement parameters were refined at 1.2 (CH_2) or 1.5 (CH_3) times the equivalent anisotropic displacement parameter of the corresponding C atom. All of the non-hydrogen atoms except the disordered ones were refined with anisotropic displacement parameters. The highest peak on the final difference Fourier map corresponds to 0.93 e/Å^3, and it is located in the disordered area. The final *R* factors for the molecule are $R = 0.0329$ and $R_{w2} = 0.0611$. A total of 5418 data were used to refine 497 parameters.[9]

Results and Discussion

(a) Synthesis of $(NBu_4)[(C_6F_5)_2Pt(PPh_3)(OCOCH_3)]$ (1). Complex **1**, the first (pentafluorophenyl)(acetato) platinum(II) complex, can be readily synthesized by reacting $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6F_5)_2]_2$ with $AgOCOCH_3$ (eq 1).

$$(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6F_5)_2]_2 + 2AgOCOCH_3 + 2PPh_3 \rightarrow 2(NBu_4)[(C_6F_5)_2Pt(PPh_3)(OCOCH_3)]\ \mathbf{(1)} + 2AgCl \quad (1)$$

The IR spectrum shows two broad absorptions due to the ν_{asym}(COO) and ν_{sym}(COO) modes of vibration at 1627 and 1318 cm^{-1}, respectively, whose difference $\Delta = 309$ cm^{-1} is in the expected range for unidentate acetate ligands.[10] Three absorptions at 504, 515, and 535 cm^{-1} are due to the PPh_3 ligand. Finally, two strong absorptions at 803 and 780 cm^{-1} are due to two mutually *cis* C_6F_5 groups,[11] as expected, since both the precursor complex and complex **2** contain two C_6F_5 groups in the *cis* position.

(b) Synthesis and Structure of *cis*-[$(C_6F_5)_2(PPh_3)Pt(\mu_2\text{-}OOCCH_3)Tl$] (2). Complex **2** can be obtained either by reaction of complex **1** with $TlNO_3$ in a methanol/acetone solution (eq 2) or directly from $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6F_5)_2]_2$ upon addition of PPh_3 and subsequently of $TlOOCCH_3$ and $TlNO_3$ (eq 3).

$$(NBu_4)[(C_6F_5)_2Pt(PPh_3)(OCOCH_3)] + TlNO_3 \rightarrow cis\text{-}[(C_6F_5)_2(PPh_3)Pt(\mu_2\text{-}OOCCH_3)Tl] + NBu_4NO_3 \quad (2)$$

$$(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6F_5)_2]_2 + 2PPh_3 + 2TlOCOCH_3 + 2TlNO_3 \rightarrow 2cis\text{-}[(C_6F_5)_2(PPh_3)Pt(\mu_2\text{-}OOCCH_3)Tl] + 2TlCl + 2NBu_4NO_3 \quad (3)$$

Yields are similar (80%, eq 2; 82%, eq 3) in both cases.

The IR spectrum of complex **2** shows the two absorptions (at 785 and 808 cm^{-1}) related to the presence of two mutually *cis* C_6F_5 groups and three absorptions (at 535, 515, and 504 cm^{-1}) due to the presence of PPh_3, almost the same values as that in complex **1**. However, the two absorptions due to the acetate ligand appear now at 1549 and 1404 cm^{-1}, with $\Delta = 145$ cm^{-1}; i.e., the acetate group is acting in complex **2** as a bidentate ligand, in accord with the structure (see below) which indicates that the carboxylate group is bridging the Pt and Tl atoms.

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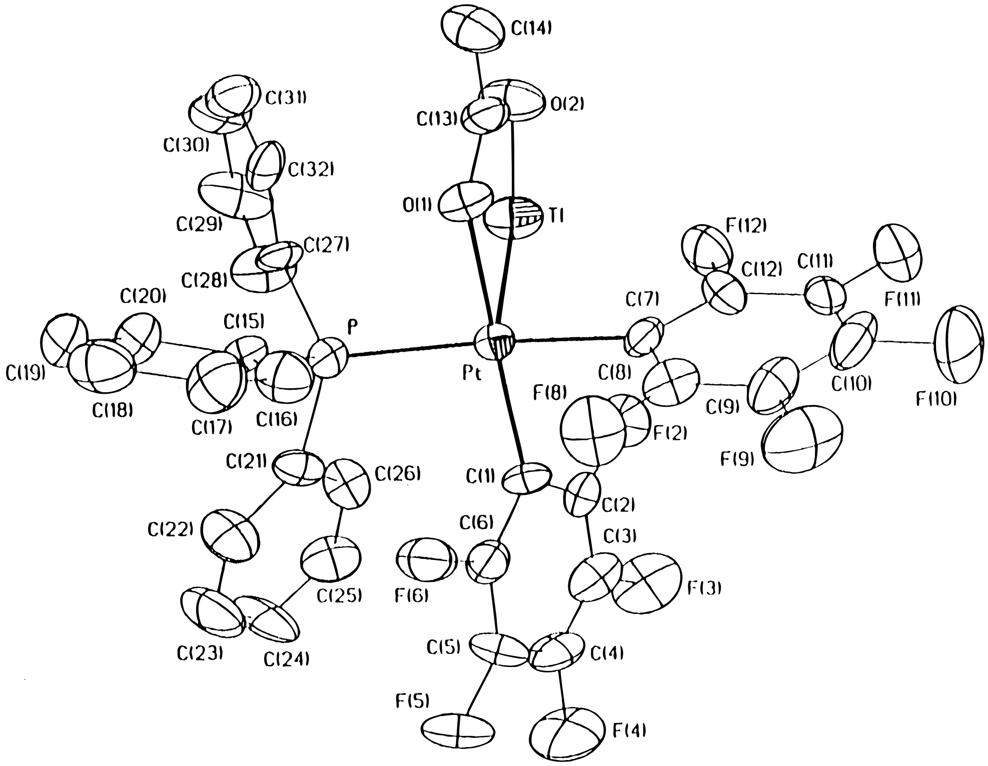

Figure 1. Thermal ellipsoid plot of the complex $[(C_6F_5)_2(PPh_3)Pt(\mu OOCCH_3)Tl]$ **(2)** showing the atom-labeling scheme.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *cis*-$[(C_6F_5)_2(PPh_3)Pt(\mu_2\text{-}OOCCH_3)Tl]$ **(2)**

Pt−Tl	2.994(1)	Tl−O(2)	2.489(8)
Pt−C(1)	2.013(10)	Pt−C(7)	2.067(12)
Pt−O(1)	2.107(7)	Pt−P	2.326(3)
O(1)−C(13)	1.273(16)	O(2)−C(13)	1.236(17)
C(13)−C(14)	1.519(15)		
Tl−Pt−O(1)	85.2(2)	Tl−Pt−C(1)	103.3(4)
O(1)−Pt−C(1)	171.0(4)	Tl−Pt−C(7)	100.5(4)
O(1)−Pt−C(7)	88.2(4)	C(1)−Pt−C(7)	87.2(5)
Tl−Pt−P	87.2(1)	O(1)−Pt−P	90.9(2)
C(1)−Pt−P	92.5(4)	C(7)−Pt−P	172.0(4)
Pt−Tl−O(2)	74.6(2)	Pt−O(1)−C(13)	128.0(7)
Tl−O(2)−C(13)	124.2(8)	O(1)−C(13)−O(2)	124.7(10)
O(1)−C(13)−C(14)	114.4(11)	O(2)−C(13)−C(14)	120.8(12)

At room temperature, the ^{31}P NMR spectrum of complex **2** in acetone-d_6 solution shows a singlet with the corresponding platinum satellites ($\delta = 12.89$ ppm, $J(P-Pt) = 2473.9$ Hz). Addition of the starting material $(NBu_4)[Pt(OCOCH_3)(PPh_3)(C_6F_5)_2]$ ($\delta = 19.20$ ppm, $J(P-Pt) = 2696.18$ Hz) to the solutions of complex **2** results in only one signal, the position of which depends on the amount of $(NBu_4)[Pt(OCOCH_3)(PPh_3)(C_6F_5)_2]$ added, and no signals due to **2** or **1** are detected. This fact indicates that in acetone a dissociative process involving the starting material **1** is operating at room temperature. The very low solubility of **2** in nondonor solvents precludes an NMR study in such solvents.

The structure of this complex has been determined by X-ray diffraction; a drawing of the molecule is given in Figure1, and the main bond distances and angles are collected in Table 2. The structure can be understood as the result of a donor−acceptor bonding interaction between the anionic roughly square-planar $[Pt(C_6F_5)_2(PPh_3)(OCOCH_3)]^-$ and Tl^+ ion to give a Pt−Tl bond which receives the additional support of the bridging acetate ligand. The two mutually *cis* C_6F_5 groups bonded to the Pt atom show Pt−C distances of 2.013(10) and 2.067(12) Å within the usual range in other (pentafluorophenyl)platinum(II) derivatives. The Pt−P distance of 2.325(3) Å is longer than that in $[(PPh_3)Pt(\mu_2\text{-}OAc)_2(\mu_3\text{-}OAc)Ag]_2$ (Pt−P, 2.216(4) Å),[12] probably due to the strong *trans* influence of the one C_6F_5 group *trans* to the P atom.[13,14] A second factor which may contribute to the long Pt−P distance is the neutral character of complex **2**, since for neutral or cationic platinum complexes a tendency to give longer Pt−P distances than similar anionic complexes has been observed before.[15] So, for instance, the Pt−P distance in the anionic $(NBu_4)[Pt(C_6F_5)_3(PPh_3)]$, where the PPh_3 is necessarily *trans* to a C_6F_5 group, is 2.279(3) Å.

The Pt−O(1) distance is 2.107(7) Å, and the Tl−O(2) distance is 2.489(8) Å. None of the covalent thallium(I) acetate complexes have been the subject of structural studies, and the only thallium−carboxylate compound that has been studied by X-ray diffraction is TlL. HL (HL = $HO_2CCH_2OC_6H_4Cl$-*o*)) displays a Tl−O distance of 2.826(7) Å.[16] Previously reported Tl−O distances range from 2.46(6)[17] to 3.2 Å.[18] The Tl−O(2) distance in complex **2** is in the low end of the range. O(2) is also located at 2.983(10) Å from the Tl atom of another molecule. The C−O distances in the carboxylate group are C(13)−O(1) = 1.273(16) Å and C(13)−O(2) = 1.235(17) Å. They are normal for acetate bridging groups, as is the O(2)−C(1)−O(1) angle: 124.7(12)°. There is also a short contact (2.982(9) Å) between the Tl atom and one *o*-F atom of one of the C_6F_5 groups.

The Pt−Tl distance (2.994(1) Å) points to the presence of a bond. This distance is similar to or shorter than that found in

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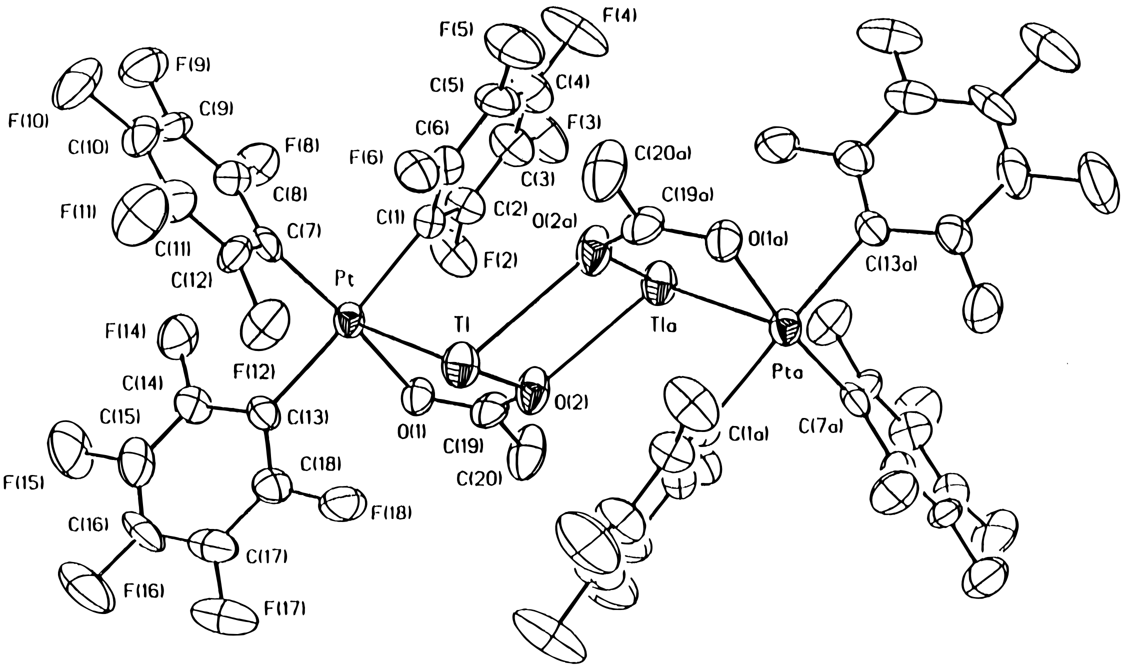

Figure 2. Thermal ellipsoid plot of the dianion $[(C_6F_5)_6Pt_2(\mu\text{-}OOCCH_3)_2Tl_2]^{2-}$ showing the atom-labeling scheme.

other Pt(II)−Tl(I) complexes whose structures have been solved: 3.140(1) Å in $Tl_2[Pt(CN)_4]$,[1] 2.911(2) and 2.958(2) Å in $[Tl(crown\text{-}P_2)Pt(CN)_2]NO_3$,[2] or 3.085(1) Å in *cis*-$[(NH_3)_2Pt(1\text{-}MeT)_2Tl(1\text{-}MeT)_2Pt(NH_3)_2]NO_3{\cdot}7H_2O^3$. However, it is worth mentioning that some other Pt−Tl complexes with Pt and Tl in oxidation states other than II or I, respectively, displaying a wide range of Pt−Tl distances $[TlPt_3(CO)_3(PCy_3)_3][Rh(\eta\text{-}C_8H_{12})Cl_2]$, 3.047 (1) Å;[19] $[Pt_6(\mu_6\text{-}Tl)(\mu\text{-}CO)_6(\mu\text{-}dppp)_3][PF_6]$, 2.860(3) −2.992(3) Å,[20] or $(NBu_4)_2[Tl\{Pt(C_6F_5)_4\}_2]$, 2.698(1) −2.708(1) Å [4]], have been prepared, although the formal oxidation state of the metal centers involved should influence the metal−metal bond distances. Since the presence of a bridging acetate ligand in complex **2** makes the existence of the Pt−Tl bond somewhat questionable, we studied the spectral behavior of complex **2** (and also complex **3**), to confirm the presence of these metal−metal bonds (see below). However, some indirect evidence also points to the existence of the Pt−Tl bond: (a) The Tl−Pt vector is roughly perpendicular to the coordination plane of the Pt(II) atom (angle of 11.0(2)° with the perpendicular to this plane) and the Pt atom is 0.149(1) Å out of this plane in the direction of the Tl atom, a typical situation for donor−acceptor Pt−M bonds. (b) Increasing the donor character of the Pt atom reduces the Pt−Tl distance, as will be seen in the anionic complex **3** in the following discussion.

(c) Synthesis and structure of $(NBu_4)_2[\{(C_6F_5)_3Pt\}_2\{(\mu_2\text{-}O\text{-}\mu_3\text{-}O'CCH_3)Tl\}_2]$ (3). Addition of $TlOCOCH_3$ to methanol/acetone solutions of the complex $(NBu_4)[Pt(C_6F_5)_3S]$ (S = acetone or MeOH)[21] (1:1 ratio) leads to isolation of complex **3** formed after eq 4.

$$2(NBu_4)[Pt(C_6F_5)_3(S)] + 2TlOCOCH_3 \xrightarrow{-2S} (NBu_4)_2[\{(C_6F_5)_3Pt\}_2\{(\mu_2\text{-}O\text{-}\mu_3\text{-}O'CCH_3)Tl\}_2] \quad (4)$$

The IR spectrum of **3** shows one absorption at 880 cm^{-1}, due to NBu_4^+, and three bands at 770, 786, and 808 cm^{-1} which arise from the "$Pt(C_6F_5)_3$" moiety.[11] The two absorptions at 1546 and 1410 cm^{-1} are due to the acetate bridging ligand, since $\Delta = 136$ cm^{-1}.

The ^{19}F NMR spectrum of **3** at room temperature in CD_2Cl_2 shows signals in the *o*-F region ($\delta = -114$ and -120 ppm) and signals in the *m*-F and *p*-F region ($\delta = -164$ and -167 ppm). The *o*-F/*m*+*p*-F ratio should be 2:3 and in the spectrum is ≈ 1.15:3. However, the ^{19}F NMR spectrum of **3** at −85 °C shows the adequate *o*-F/*m*+*p*-F ratio, and in addition half of the *o*-F atoms are coupled to the Tl atom (*o*-F: $\delta = -118.72$ ppm, $J(Tl-F) = 3436.1$ Hz, 1F; $\delta = -117.135$ ppm, $^3J(F-Pt) = 471.8$ Hz, 1F; $\delta = -115.68$ ppm, $J(Tl-F) = 3251.6$ Hz, 2F; $\delta = -118.45$ ppm, $^3J(F-Pt) = 291.1$ Hz, 2F. *m*+*p*-F: $\delta = -165.9$ ppm, 2F; −163.8 ppm, 4F; $\delta = -165.08$ ppm , 1F; $\delta = -163.08$ ppm, 2F). A similar spectroscopic behavior has been observed in other complexes displaying Tl···F interactions.[22,23]

The ^{195}Pt NMR spectrum of $(NBu_4)_2[\{Pt(C_6F_5)_3\}_2\{(\mu_2\text{-}O,\mu_3\text{-}O'CCH_3)Tl\}_2]$ in CD_2Cl_2 at room temperature shows two broad multiplets ($\delta = -2582$ ppm) due to Pt−Tl coupling, $^1J(Pt-Tl) = 7.3$ kHz. The value of this coupling constant is smaller than in a nonisolated Pt−Tl compound for which ^{195}Pt and ^{205}Tl NMR spectra have been reported, although in this case the compound is an intermediate for which formal oxidation states of Pt(II)−Tl(III) or Pt(III)−Tl(II) have been tentatively assigned.[24] The different $^1J(^{195}Pt-^{203}Tl)$, $^1J(^{195}Pt-^{205}Tl)$ coupling constant cannot be measured due to the broadeness of the multiplets owing to the contributions of the coupling with the fluorine atoms of the C_6F_5 rings.

The structure of complex **3** has been determined by X-ray diffraction (Figure 2), and the most important distances are collected in Table 3. The platinum atom is coordinated to three pentafluorophenyl groups, an oxygen atom of the acetate ligand, and a Tl atom. The Pt−C distances are Pt−C(1) = 2.084(8) Å, Pt−C(7) = 1.988(8) Å, and Pt−C(13) = 2.074(8) Å. Two

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for $(NBu_4)_2[\{(C_6F_5)_3Pt\}_2\{(\mu_2\text{-}O,\mu_3\text{-}O'CCH_3)Tl\}_2]$ **(3)**

Pt−Tl	2.884(1)	Pt−C(7)	1.988(8)
Pt−C(1)	2.084(8)	Pt−O(1)	2.092(5)
Pt−C(13)	2.074(7)	Tl−O(2)	2.542(6)
Tl−O(2a)	2.739(6)	O(1)−C(19)	1.273(10)
O(2)−C(19)	1.245(10)	C(19)−C(20)	1.526(11)
C(7)−Pt−C(13)	88.7(3)	C(7)−Pt−C(1)	90.6(3)
C(13)−Pt−C(1)	176.0(3)	C(7)−Pt−O(1)	171.8(3)
C(13)−Pt−O(1)	86.3(3)	C(1)−Pt−O(1)	94.0(3)
C(7)−Pt−Tl	101.4(2)	C(13)−Pt−Tl	102.9(2)
C(1)−Pt−Tl	81.2(2)	O(1)−Pt−Tl	86.0(2)
O(2)−Tl−O(2a)	74.6(2)	O(2)−Tl−Pt	73.96(13)
O(2a)−Tl−Pt	109.13(13)	C(19)−O(1)−Pt	124.2(5)
C(19)−O(2)−Tl	116.8(5)	C(19)−O(2)−Tl(a)	127.1(6)
Tl−O(2)−Tl(a)	105.4(2)	O(2)−C(19)−O(1)	126.4(8)
O(2)−C(19)−C(20)	118.4(8)	O(1)−C(19)−C(20)	115.2(8)

Pt−C distances, corresponding to the two mutually *trans* C_6F_5 groups, are equal, and the shortest Pt−C distance is to the C atom of the C_6F_5 group *trans* to the acetate ligand, owing to the strong *trans* influence of the perfluoroaryl groups.

The Pt−Tl distance, 2.884(1) Å, is the shortest Pt(II)−Tl(I) distance so far reported, including those in complex **2**. Although at first sight one could think that the difference in the Pt−Tl distances between **3** and **2** could be due to the fact that **3**, which is anionic in character, should contain a more basic Pt center, thus producing a stronger Pt−Tl bond, it is necessary to be cautious on this point, since both the platinum environment and also that of thallium (which is the Lewis acid) are different in both cases. Again, the Pt atom in complex **3** is shifted 0.0988(5) Å from the best least squares plane (formed by the three ipso-C of the C_6F_5 groups and the O(1)) toward the Tl atom, and the Pt−Tl vector forms with the perpendicular to the plane an angle of 13.3°. A distinctive structural feature is that two $[(C_6F_5)_3Pt(\mu_2\text{-}OOCCH_3)Tl]^-$ moieties are mutually bonded with the O(2) atom in the acetate ligand also bridging the two Tl atoms (which result in this way three coordinated) in each moiety giving a dinegative dimeric anion, with an angle Tl−O(2)−Tl(a) = 105.4(2)°. The dimeric anion sits on a crystallographic inversion center, whose central part is formed by the two Tl and the two μ_3-O atoms. However, the Tl(a)−O(2) interaction which produces the dimerization seems to be weak in character since **3** behaves as an (1:1) electrolyte in acetone solutions (see Experimental Section), indicating that the dimer is no longer present in this donor solvent. Finally, each Tl atom in complex **3** makes short contacts with two *o*-F atoms (at 3.081(5) and 3.040(5) Å) from F(6) and F(18), respectively.

(d) UV−Vis Absorption and Emission Spectra of Complexes (1−3). It has been shown that Pt−Tl bonds usually give rise to luminescence,[1,25,26] and thereafter optical spectroscopy experiments were performed on complexes $(NBu_4)[(C_6F_5)_2(PPh_3)Pt(OCOCH_3)]$ **(1)**, $[(C_6F_5)_2(PPh_3)Pt(\mu\text{-}OOCCH_3)Tl]$ **(2)**, and $(NBu_4)_2[(C_6F_5)_3Pt(\mu\text{-}OOCCH_3)Tl]_2$ **(3)**.

The left hand side of Figure 3 shows the absorption spectra of these complexes, in CH_2Cl_2 solutions, recorded at room temperature. The absorption spectrum of **1** does not show any absorption maximum, whereas the spectrum of **2** presents one intense band with a maximum at 34 720 cm^{-1} and full width at half-maximum (FWHM) of about 2200 cm^{-1}, together with three less intense shoulders at 30 120, 35 970, and 37 040 cm^{-1}.

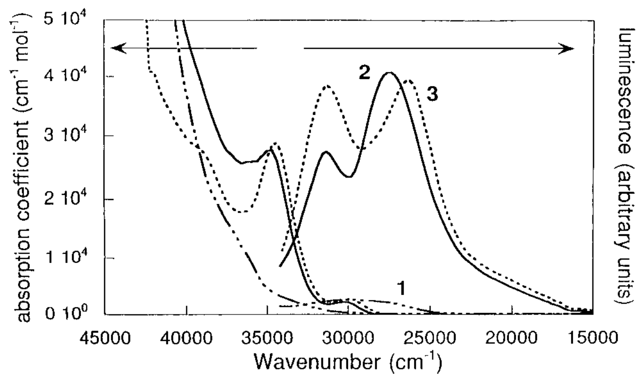

Figure 3. Absorption and emission spectra of compounds (− ··· −) **1**, (—) **2**, and (- -) **3** measured at room temperature. The emission spectra were excited at 37 000 cm^{-1} on solid samples, while the absorption spectra were recorded in a CH_2Cl_2 solution.

The spectrum of complex **3** is similar, with the intense absorption maximum at 34 480 cm^{-1} and FWHM of 2350 cm^{-1} and two less intense absorptions at 29 940 and 38 760 cm^{-1}. Since no peaks are present in the spectrum of complex **1**, which does not contain Tl, the absorption maxima in **2** and **3** are assigned to the existence of Tl−Pt bonds in these complexes. The spectra of solid samples also show absorption maxima at approximately the same positions, but with overall higher intensity when normalized to the complex concentration.

By irradiating solid samples with light in the UV (37 000 cm^{-1}), we obtain the luminescence spectra shown on the right side of Figure 3 (at room temperature, solution samples give no luminescence, possibly owing to an efficient nonradiative deexcitation *via* the numerous energy levels of the solvent in the near IR). Again, the spectra of complexes **2** and **3**, both with Pt−Tl bonds, are very similar, with two strongly overlapped emission bands, with maxima at 31 580 and 27 880 cm^{-1}for **2** and, respectively, 31 390 and 26 520 cm^{-1} for **3**. Another much broader luminescence band extends to lower energies. The solid complex **1** shows only a tiny luminescence band.

The entities which give rise to the luminescence bands at about 31 600 and 27 000 cm^{-1} have been identified as the acetate groups by comparison with the luminescence spectra of $TlOCOCH_3$ and $KOCOCH_3$ which were also measured. These entities are excited with UV radiation of 37 000 cm^{-1}, simultaneously with electrons located close to the Tl atoms, presumably the electrons in the Pt−Tl bond. Additionally, these luminescence bands in the spectra of complexes **2** and **3** display two excitation maxima in the UV (at approximately 37 200 and 32 600 cm^{-1}), whereas by detecting the luminescence at 20 000 cm^{-1} only an excitation maximum at approximately at 36 200 cm^{-1} is observed. This fact points to a different origin of the high-energy emission bands (31 600 and 27 000 cm^{-1}) and the broad band, and reinforces the assignation of the second emission to the existence of the Pt−Tl bond.

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Supporting Information Available: Tables of crystallographic data, complete bond distances and bond angles, atomic coordinates, anisotropic displacement parameters, and H-atom coordinates (9 pages). Ordering information is given on any current masthead page.

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