Communications to the Editor

Synthesis and Structure of $(NBu_4)_2[Tl\{Pt(C_6F_5)_4\}_2]$, the First Paramagnetic Compound Containing Thallium(II)[‡]

Rafael Usón,* Juan Forniés, Milagros Tomás, and
Raquel Garde

Departamento de Química Inorgánica
Instituto de Ciencia de Materiales de Aragón
Universidad de Zaragoza, CSIC, 50009 Zaragoza, Spain

Pablo J. Alonso

Instituto de Ciencia de Materiales de Aragón
Universidad de Zaragoza, CSIC, 50009 Zaragoza, Spain

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To our knowledge, no stable paramagnetic thallium(II) compound has been reported to date; only a dithallium compound $[\{(Me_3Si)_3Si\}_2TlTl\{Si(SiMe_3)_3\}_2]$ has very recently been synthesized and structurally characterized.[1] We report here the synthesis, magnetic behavior, and structure of the first paramagnetic Tl(II) compound, $(NBu_4)_2[Tl\{Pt(C_6F_5)_4\}_2]$, **1**.

Compound **1** is a dark blue solid obtained in 90% yield by the 1:1.5 reaction between $(NBu_4)_2[Pt(C_6F_5)_4]$[2] and $[Tl_2(\mu\text{-}Cl)_2(C_6F_5)_4]$[3] in dichloromethane solution.[4]

Measurements at 2 K of the molar magnetization *M* (μB/f.u.) as a function of field strength (*H*/*T* from 0 to 25 000 Oe) point to the presence of one unpaired electron, with $g = 2.1$ and $\mu_{eff} = 1.82\ \mu_B$.[5] The EPR spectra of **1**, taken at room temperature in both the X- and Q-bands, show a quintet structure as in Figure 1, which gives the trace of the X-band spectrum. The spectrum can be interpreted in terms of two factors: (a) the existence of two Tl isotopes (^{203}Tl and ^{205}Tl, with natural abundances 29.5% and 70.5%) with $I = ^1/_2$, and of a Pt isotope (^{195}Pt, 33.8%) also with $I = ^1/_2$; and (b) sharing of the unpaired electron by the three metals.[6]

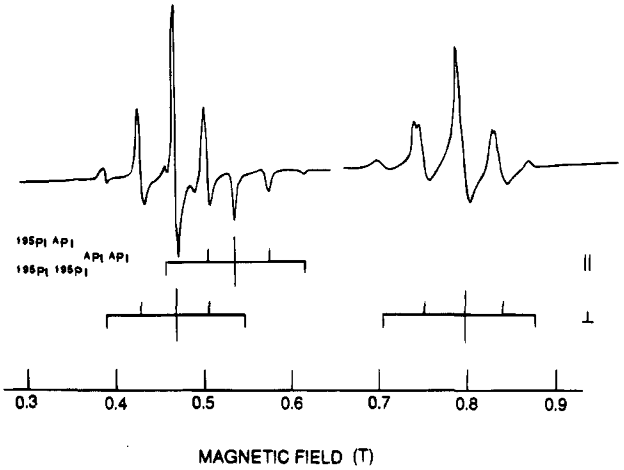

Figure 1. X-band EPR spectrum (room temperature) of 1. The sticks indicate the transition associated with the different isotopes of Pt nuclei.

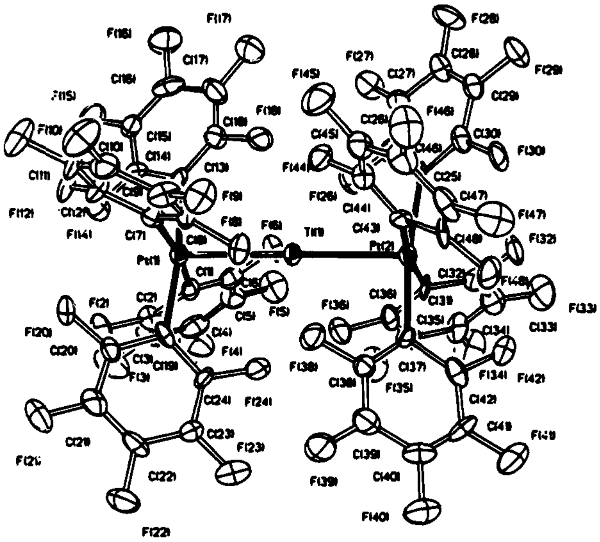

Figure 2. Thermal ellipsoid plot of the dianion $[Tl\{Pt(C_6F_5)_4\}_2]^{2-}$ showing the atom-labeling scheme.

The crystal structure of **1** has been determined,[7] and a drawing of the anion is given in Figure 2. It consists of two square pyramids with a shared apex at the thallium(II) atom, which is linearly bonded (Pt–Tl–Pt 179(1)°) to the two Pt centers in the $[Pt(C_6F_5)_4]^{2-}$ groups. Each Pt atom is shifted (by 0.163(2) and 0.144(2) Å for Pt(1) and Pt(2), respectively) from the basal plane (formed by the four ipso-C atoms of the C_6F_5 groups) toward the Tl center. The two basal planes are parallel to each other (dihedral angle 4.27(5)°) and almost eclipsed (mean ipso-C–Pt••Pt–ipso-C torsion angle 2.77°). The two Tl–Pt bonds are practically perpendicular to the basal planes (deviation: 0.9(2)° for Pt(1)–Tl and 2.7(3)° for Pt(2)–Tl). The Pt–Tl distances (Tl–Pt(1), 2.708(1); Tl–Pt(2), 2.698(1) Å) are considerably shorter than those found for Pt(II)–Tl(I) bonds: 3.140(1) Å in $Tl_2Pt(CN)_4$;[8] 2.911(2) and 2.958(2) Å in $[Tl(crown\text{-}P_2)Pt(CN)_2]NO_3$;[9] 3.085(1) Å in *cis*-$[(NH_3)_2Pt(1\text{-}MeT)_2Tl(1\text{-}MeT)_2Pt(NH_3)_2]NO_3{\cdot}7H_2O$.[10] The presumably smaller size of Tl(II), along with a Tl(II)–Pt bond order higher than 1, could

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[‡] Dedicated to Professor Hubert Schmidbaur, T.U. Munich (Germany), on the occasion of his 60th birthday.

(1) Henkel, S.; Klinkhammer, K. W.; Schwarz, W. *Angew. Chem., Int. Ed.* **1994**, *33*, 681.

(2) Usón, R.; Forniés, J.; Martinez, F.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1980**, 888.

(3) Usón, R.; Laguna, A. In *Inorg. Synth.*; Fackler, J. P., Jr., Ed.; Wiley: New York, 1982; Vol. 21, p 71.

(4) $(NBu_4)_2[Pt(C_6F_5)_4]$ (1 g, 0.741 mmol) and $[TlCl(C_6F_5)_2]_2$ (0.638 g, 1.112 mmol) were stirred for 24 h in CH_2Cl_2 (30 mL); evaporation to dryness and addition of C_6H_6 (40 mL) yielded 0.8 g (90%) of $(NBu_4)_2[Tl\{Pt(C_6F_5)_4\}_2]$. Calcd for $C_{80}H_{72}N_2F_{40}TlPt_2$: C, 39.73; H, 2.98; N, 1.16. Found: C, 39.48; H, 2.94; N, 1.23. Relevant IR absorptions for C_6F_5 groups: 1502 s, 1057 s, 955 vs, 792 s. Λ_M (5×10^{-4} M acetone solutions): 203 $\Omega^{-1}\ cm^{-1}\ mol^{-1}$.

(5) A Quantum Design MPMS-5S instrument was used.

(6) The EPR spectra of powdered 1 packed in a quartz tube were measured at room temperature with a Bruker ESP380E instrument. The magnetic field was measured with a ER35m Bruker gaussmeter, and the DPPH signal was used for calibrating the microwave frequency. The observed EPR signal (Figure 1) can be described using a standard spin-Hamiltonian with *g* principal $g_{\parallel} = 1.924$ and $g_{\perp} = 2.489$ and including an axial hyperfine interaction with a Tl nucleus ($A_{\parallel} = 33.97$ GHz and $A_{\perp} = 35.88$ GHz) and with two equivalent Pt nuclei, the statistical distribution of ^{195}Pt and *Pt nuclei being responsible for the quintet structure. The interactions with the magnetic platinum nucleus are given by $^{Pt}A_{\parallel} = 2.17$ GHz and $^{Pt}A_{\perp} = 2.87$ GHz.

(7) Crystal data for complex **1**: triclinic, space group $P\bar{1}$, $a = 15.088(5)$ Å, $b = 16.664(5)$ Å, $c = 21.641(5)$ Å, $\alpha = 105.15(2)°$, $\beta = 96.91(2)°$, $\gamma = 114.01(2)°$, $V = 4636(3)$ Å^3, $Z = 2$, $D_{calcd} = 1.717$ g cm^{-3}, 12 138 unique reflections measured, 7279 observed [$F_o > 5\sigma(F_o)$], $R = 0.0547$, $R_w = 0.0788$. The structure was solved by the heavy atom method.

(8) Nagle, J. K.; Balch, A. J.; Olmstead, M. M. *J. Am. Chem. Soc.* **1988**, *110*, 319.

(9) Balch, A. L.; Rowley, S. P. *J. Am. Chem. Soc.* **1990**, *112*, 6139.

(10) Renn, O.; Lippert, B.; Mutikainen, I. *Inorg. Chim. Acta* **1993**, *208*, 219.

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account for the short Tl(II)−Pt(II) distance in complex **1**. In addition, one *o*-fluorine atom of each C_6F_5 group makes a short contact (2.839(10)−3.065(12) Å) to the Tl(II) center, replicating the structural features in the isostructural $(NBu_4)_2[Pb\{Pt(C_6F_5)_4\}_2]$, prepared by the reaction between $(NBu_4)_2[Pt(C_6F_5)_4]$ and $Pb(NO_3)_2$.[11]

The formation of complex **1** is, however, a complicated process; and more data is necessary to formulate a reasonable reaction path: (a) Despite the presence of only one Tl atom in **1**, a molar ratio Pt/Tl = 2/3 is required; if a lower proportion of the thallium reagent is used, the yield is lowered and unreacted $(NBu_4)_2[Pt(C_6F_5)_4]$ is recovered; (b) $F_5C_6C_6F_5$ (detected by both ^{19}F NMR and mass spectroscopy) is also a reaction product, which implies the expulsion of a $^{\bullet}C_6F_5$ radical, which subsequently dimerizes. Neither Cl_2 nor ClC_6F_5 figures among the reaction products. (c) After separation of complex **1**, the mother liquors contain a mixture of anionic Tl(III) complexes, which give unseparable oily mixtures, possibly of $[TlCl(C_6F_5)_3]^-$ and $[TlCl_2(C_6F_5)_2]^-$, and given the well-known lability of such Tl(III) complexes, perhaps also other interconversion products.

In sum, these observations, along with the structural and magnetic findings, fit reasonably well with the following stoichiometric equation.

Finally, the bonding in the Pt−Tl−Pt core of the complex can be interpreted as the result of donor−acceptor interactions,

$$2(NBu_4)_2[Pt(C_6F_5)_4] + {}^3/_2[Tl(\mu\text{-}Cl)(C_6F_5)_2]_2 \xrightarrow{Cl_2CH_2} (NBu_4)_2[Tl\{Pt(C_6F_5)_4\}_2] + {}^1/_2C_{12}F_{10} + (NBu_4)[TlCl(C_6F_5)_3] + (NBu_4)[TlCl_2(C_6F_5)_2] \quad (1)$$

with the Tl(II) atom using sp hybrid orbitals to accommodate electron density donated by the Pt atoms of the anionic $[Pt(C_6F_5)_4]^{2-}$ ligands, as is the case[12] in other Pt→M bonds. This leaves the unpaired electron on a p orbital perpendicular to the Pt−Tl−Pt axis, which would interact with suitable empty orbitals of the Pt atoms to give a π molecular orbital with the unpaired electron shared by the three metals, in accordance with the hyperfine interaction (Figure 1) and the departure of the principal *g* values from those of the free electron.

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Supplementary Material Available: Listing of crystallographic data, description of the crystal structure determination, complete bond distances and bond angles, atomic coordinates, and anisotropic displacement parameters (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[12] Usón, R.; Forniés, J. *Inorg. Chim. Acta* **1992**, *198−200*, 165.