Synthesis and characterisation of a “Pt₃Tl” cluster containing an unprecedented trigonal environment for Tl(I).

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Supporting Information Placeholder

ABSTRACT: The tetranuclear $[\{Pt(CNC)(tht)\}_3Tl](PF_6)$ (tht = tetrahydrothiophene, SC_4H_8 ; $CNC = C,N,C-2,6-NC_5H_3(C_6H_4-2)_2$; **2**) cluster has been prepared by reaction of $[Pt(CNC)(tht)]$ (**1**) and $TlPF_6$ (molar ratio 3:1), and structurally characterized. The Tl(I) atom is bonded to three Pt(II) centers bearing a perfect trigonal coordination. The Pt(II)–Tl(I) bonds are unsupported by any bridging ligand and are the shortest of this kind reported so far (2.9086(5) Å). These intermetallic bonds persist in CD_2Cl_2 solution as it is shown by the $^{195}Pt\{^1H\}$ NMR spectrum of **2** at 193K, in which a Pt–Tl coupling of 8.9 kHz is observed.

Heterometallic compounds featuring metallophilic interactions are interesting chemical species that are currently undergoing an tremendous upsurge.¹ Those interactions mainly involve metal-metal dative bonds between Lewis-acidic (acceptor) and Lewis-basic (donor) metal fragments,¹ and they have been used as a tool in the field of crystal or molecular engineering, linking different subassemblies and resulting in a wide array of types of structural types.^{1,2} In many cases, complexes containing these metal-metal bonds have been shown to exhibit photophysical and photochemical properties, such as luminescence, attributable to the existence of the metallophilic interactions.^{1,2}

Thallium centers in either of its common oxidation states, Tl(I)^{3,4} and Tl(III),^{3d,5} are fairly represented acceptors in this sort of heteropolynuclear clusters. The latter ion has d^{10} electron configuration whereas Tl(I) ($d^{10}s^2$) is a typical case of “inert pair” species.^{3b,4k} The nature of the heterometallic compound $[NBu_4]_2[Tl\{Pt(C_6F_5)_4\}_2]$, formally containing Tl(II) is certainly more complex, since the unpaired electron is almost uniformly delocalized along the Pt–Tl–Pt axis.⁶

Among their donor counterparts, Pt(II)(d^8) is one of the most usual and several structural configuration have been reported: Discrete dinuclear Pt_2Tl ,^{4b-f} trinuclear $PtTl_2$ ^{4a,g-i} or Pt_2Tl “sandwiches”,^{4k-n} tetranuclear “paired” ($PtTl$)₂,^{4b,o-s} or infinite networks.^{4k,n,p,s-u} Often, the Pt–Tl bonds are supported by bridging ligands between the two metallic centres, and/or the Thallium atoms bear additional ligands.

In the course of our current research, we have developed synthetic methods for the preparation of complexes containing Pt–M bonds with the use of strong ligand field cyclometallated $C^{\wedge}N$

ligands, such as 7,8-benzoquinolate (bzq).^{2a,d,7} This strong ligand field causes the d_{z^2} platinum orbital to raise its energy and favours the formation of stronger Pt→M dative bonds.⁸ In this communication we report the use of a Pt precursor containing the tridentate cyclometallated $C,N,C-2,6-NC_5H_3(C_6H_4-2)_2$ (CNC, see Scheme 1) ligand in the preparation of an unprecedented Pt_3Tl cluster with three unsupported Pt(II)→Tl(I) bonds in which the Thallium centre exhibits a symmetric trigonal planar environment.

Complex $[Pt(CNC)(tht)]$ (tht = tetrahydrothiophene, SC_4H_8 , **1**) has been prepared by replacing the dimethyl sulfoxide ligand in $[Pt(CNC)(dmsO)]$ ⁹ with tht. The crystal structure of **1** has been determined by X ray diffraction (see Figure S1, supporting information) and shows, as expected, a square planar coordination for the platinum, with structural parameters very similar to those reported for platinum complexes containing this⁹ or similar tridentate CNC ligands.¹⁰ No intermolecular $\pi\cdots\pi$ interactions between the aromatic rings of the CNC plane ligands are present in **1**, interactions found in the analogous $[Pt(2,6\text{-diphenylisonicotinate})(tht)]$,¹⁰ as well as in other square planar Pt(II) complexes containing planar cyclometallated ligands such as 2,6-diphenylisonicotinate^{2b,10} or bzq.^{2a,7,11}

The reaction of 3 equivalents of **1** with 1 equivalent of $TlPF_6$ in dichloromethane, results, after work up of the solution, in a red solid which spectroscopic and analytical data correspond to the formula $[\{Pt(CNC)(tht)\}_3Tl](PF_6)$ (**2**) (Scheme 1). Regardless of the Pt/Tl ratios used, no compounds with different stoichiometry are detected and always **2** and the corresponding unreacted reactives are obtained.

Scheme 1.

Suitable crystals for X-ray studies of **2** were obtained, and the crystal structure of its cation is represented in Figure 1. As can be seen, **2** is a tetranuclear Pt₃Tl cluster in which the Tl(I) centre lies in a 3-fold axis and thus, the three Pt atoms form a perfect equilateral triangle, in the center of the which lies the thallium atom, being all the Pt–Tl–Pt angles exactly 120°. Due to the molecular symmetry, the three Pt–Tl distances are the same, 2.9088(5) Å. To the best of our knowledge, this value is the shortest reported so far for a Pt(II)–Tl(I) bond unassisted by any bridging ligand or by pairing (PtTl)₂ metallocycle systems. The trigonal environment of the Tl centre seems to indicate the steric inactivity of its lone 6s² electron pair. Some complexes M₃Tl(III) with a symmetrical trigonal environment for the thallium(III) centre are known. These involve carbonyl complexes of low valent metals with general formulae [$\{M(CO)_x(\eta-C_5H_5)\}_3(\mu_3-Tl)\}$ ($x = 3$; $M = Cr, Mo^{5a}$, $x = 2$, $M = Ru^{3d}, Fe^{5b}$) or [$\{M(CO)_4\}_3(\mu_3-Tl)\}^n$ ($n = 0$; $M = Cr^{5b}$, $n = 3$, $M = Fe^{5b}$). Nevertheless, **2** is the first Tl(I) complex in which this striking trigonal environment is found.

Each platinum atom lies in the centre of a square plane which is perpendicular to the corresponding Pt–Tl line, disposition usually found in complexes showing Pt→M dative bonds, and which maximizes the overlapping of the full 5d_{z²} Pt(II) orbital and the empty orbitals of the acidic metal centre.^{4b,f,i} It is more likely that the disposition adopted by the three bulky “Pt(CNC)(tht)” is the optimal (and perhaps the only possible) to accommodate them around the Tl. The tht rings are bent away from the interior of the Pt₃Tl core thus minimizing the repulsion with the CNC ligand of the adjacent unit. Moreover, the plane of the CNC ligands is distorted in such a way that their pyridine rings, the closest to the tht of the adjacent unit, are moved back from the best Pt square plane, while the two phenylene rings, which have less steric hindrance, move slightly inside the centre of the core. It is noteworthy that despite the apparent steric hindrance, the Pt–Tl distances are short for this kind of complexes.

Figure 1. Molecular structure of the cation of complex **2**.

Each of the phenylene rings of the CNC ligands establishes $\pi\cdots\pi$ interactions with another ring of a neighbour cation, and as a result, each [$\{Pt(CNC)(tht)\}_3Tl\}^+$ complex is surrounded by six congeners (see Figure S2, supporting information), with the interplanar distances being about 3.3 Å. As mentioned previously, these $\pi\cdots\pi$

interactions have been found for complexes containing planar cyclometallated ligands.^{2,7,10,11}

As far as we know, there are only other three reports of clusters in which three donor metal atoms are simultaneously bonded to a Tl(I) centre. One is [$\{Pt(1,2\text{-propyldiamine})(NHCO^tBu)_2\}_4Tl_4\}$ –[Pt(CN)₄]₂^{4a} in which infinite Pt–Tl chains are linked *via* half of the Tl atoms, resulting in a 3D network. Nevertheless, in this case, the environment of the Tl connected to three platinum atoms is not symmetric, with longer Pt–Tl bond distances (range 2.986–3.250 Å) and NHCO^tBu ligands bridging Pt and Tl. The other two presents a family of six gold(I) complexes,^{3b,c} which are basically prepared by incorporation of [AuR₂][–] to [AuTl₂]_n (R = C₆Cl₅, 3,5-C₆Cl₂F₃, 2-C₆F₄Br, 2-C₆F₄I) chains and formation of a third Au–Tl bond. The Au–Tl distances range from 2.935 to 3.466 Å and the environments of the Tl atoms are planar, but not symmetrical, being better described as distorted T-shaped.

The ¹H NMR spectra of **1** and **2** in CD₂Cl₂ show the corresponding signals for the CNC and tht ligands (see experimental). On the NMR time scale, both halves of these ligands are equivalent, and thus six and two signals are observed for CNC and tht respectively. The most significant shift of the signals observed in the spectrum of **2** with respect to **1** is the corresponding to the *ortho* phenyl proton (H²) of the CNC ligand, which moves upfield 0.66 ppm.

The presence of Pt(II)→Tl(I) dative bonds in solution is supported by ¹⁹⁵Pt{¹H} NMR spectroscopy. In CD₂Cl₂ solution at room temperature, compound **1** shows a structured ¹⁹⁵Pt resonance at -3914 ppm, due to the quadrupolar nature of ¹⁴N of the CNC ligand, whereas **2** does not show any signal neither at room temperature nor at 193 K. It appears that compound **2** dissociates in solution to give an equilibrium mixture of different Pt/Tl species which are mutually converted on the ¹⁹⁵Pt NMR time scale. However, upon the addition of excess TlPF₆, a ¹⁹⁵Pt NMR signal at -3157 ppm is observed. This downfield shift (*ca.* 760 ppm) is consistent with the formation of Pt→M dative bonds in solution and is caused by the decrease of electron density around the Pt center upon coordination to M⁺.^{2,12} Exactly this same dissociation process at ¹⁹⁵Pt NMR time scale was formerly observed in solutions of compounds with Pt→Cd^{12c} and Pt→Ag^{12a,d} dative bonds.

Variable temperature ¹⁹⁵Pt{¹H} NMR experiments were performed on a CD₂Cl₂ solution of **2** with TlPF₆ in excess (see Figure 2a). At 193 K, it shows a doublet at -3100 ppm due to Pt–Tl coupling ($J_{Pt-Tl} = 8.9$ kHz) which collapse to a broad signal at 243 K. This coupling constant value is similar to that observed in reported compounds with Pt(II)→Tl(I) dative bonds.^{4c-d,13} The $J(^{195}Pt-^{203}Tl)$, $J(^{195}Pt-^{205}Tl)$ coupling constants cannot be measured due to the broadness of the signals. At 193 K, the ¹⁹⁵Pt NMR spectrum of **1** barely changes; it displays a singlet at -3901 ppm (see Figure 2b). Both ¹⁹⁵Pt resonances appear downfield shifted with respect to those at RT and the difference between them has increased up to 801 ppm. The solid state ¹⁹⁵Pt NMR spectra of **1** and **2** have also been recorded and are in agreement with the solution ones at low temperature and with excess of TlPF₆ described here (see Figures S3–S5, Supporting Information).

Thus, from the solution ¹⁹⁵Pt NMR spectra it seems that when an excess of TlPF₆ is added and at low temperature the equilibrium is displaced completely toward the Pt₃Tl tetranuclear complex which is the only one Pt/Tl species present in solution in these conditions

and matches with the X-ray structure. Therefore, the excess of Thallium in the media just prevents the dissociation process. The remarkable downfield shifts (> 750 ppm) in relation to its precursor (**1**) and the extraordinary large value of the Pt(II)-Tl(I) coupling constant (8.9 kHz) are indicative of a fairly strong Pt $\rightarrow$ Tl dative bond.

It is worth noting that the sample with excess of TlPF₆ showed an almost identical ¹H NMR spectrum at 293 K and 193 K to that of compound **2**, supporting the idea that there is only one Pt/Tl species in solution in these conditions.

Figure 2. ¹⁹⁵Pt{¹H} NMR spectra of compounds: **2** + TlPF₆ exc. (a) and **1** (b) in CD₂Cl₂ at variable temperature.

Preliminary studies on solid samples of **1** and **2** have shown that they exhibit luminescent properties, which are currently being investigated.

ASSOCIATED CONTENT

Supporting Information. Details on the experimental procedures and equipment used. NMR data for complexes **1** and **2**. Drawing of the molecular structure of complex **1**. Drawing of the supramolecular arrangement of the cations of complex **2** showing the intermolecular $\pi\cdots\pi$ interactions. Selected bond distances and angles for complexes **1** and **2**. CIF files for the structures of complexes **1** and **2**. Solid ¹⁹⁵Pt NMR spectra of **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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REFERENCES

- (1) Pyykkö, P. *Chem. Rev.* **1997**, 97, 597-636. Moret, M.-E. *Top. Organomet. Chem.* **2011**, 35, 157-184. Bauer, J.; Braunschweig, H.; Dewhurst, R. D. *Chem. Rev.* **2012**, 112, 4329-4346.
- (2) (a) Forniés, J.; Ibáñez, S.; Lalinde, E.; Martín, A.; Moreno, M. T.; Tsiapis, A. C. *Dalton Trans.* **2012**, 41, 3439-3451. (b) Fuertes, S.; Woodall, C. H.; Raithby, P. R.; Sicilia, V. *Organometallics* **2012**, 31, 4228-4240, and the references given therein. (c) Díez, A.; Lalinde, E.; Moreno, M. T. *Co-*

ord. Chem. Rev. **2011**, 255, 2426-2447. (d) Martín, A.; Belío, U.; Fuertes, S.; Sicilia, V. *Eur. J. Inorg. Chem.* **2013**, DOI: 10.1002/ejic.201201528

(3) (a) Fernández, E.; Garau, A.; Laguna, A.; Lasanta, T.; Lippolis, V.; López de Luzuriaga, J. M.; Montiel, M.; Olmos, M. E. *Organometallics* **2010**, 29, 2951-2959. (b) Fernández, E. J.; Laguna, A.; López de Luzuriaga, J. M.; Montiel, M.; Olmos, M. E.; Pérez, J. *Organometallics* **2005**, 24, 1631-1637. (c) Fernández, E. J.; Laguna, A.; Lasanta, T.; López de Luzuriaga, J. M.; Montiel, M.; Olmos, M. E. *Organometallics* **2008**, 27, 2971-2979. (d) Bytheway, I.; Griffith, C. S.; Koutsantonis, G. A.; Skelton, B. W.; White, A. H. *Eur. J. Inorg. Chem.* **2007**, 3240-3246. (e) Casado, M. A.; Pérez-Torrente, J. J.; López, J. A.; Ciriano, M. A.; Lahoz, F. J.; Oro, L. A. *Inorg. Chem.* **1999**, 38, 2482-2488. (f) Halcovitch, N. R.; Vogels, C. M.; Decken, A.; Westcott, S. A. *Can. J. Chem.* **2009**, 87, 139-145. (g) Balch, A. L.; Nagle, J. K.; Olmstead, M. M.; Reddy, P. E. *J. Am. Chem. Soc.* **1987**, 109, 4123. (h) Balch, A. L.; Neve, F.; Olmstead, M. M. *J. Am. Chem. Soc.* **1991**, 113, 2995-3001. (i) Lanci, M. P.; Remy, M. S.; Kaminsky, W.; Mayer, J. M.; Sanford, M. S. *J. Am. Chem. Soc.* **2009**, 131, 15618-15620. (j) Balch, A. L.; Davis, B. J.; Fung, E. Y.; Olmstead, M. M. *Inorg. Chim. Acta* **1993**, 212, 149-156.

(4) (a) Nagle, J. K.; Balch, A. L.; Olmstead, M. M. *J. Am. Chem. Soc.* **1988**, 110, 319-321. (b) Forniés, J.; Fuertes, S.; Martín, A.; Sicilia, V.; Gil, B.; Lalinde, E. *Dalton Trans.* **2009**, 2224-2234. (c) Usón, R.; Forniés, J.; Tomás, M.; Garde, R.; Merino, R. *Inorg. Chem.* **1997**, 36, 1383-1387. (d) Balch, A. L.; Rowley, S. P. *J. Am. Chem. Soc.* **1990**, 112, 6139-6140. (e) Oberbeckmann-Winter, N.; Braunstein, P.; Welter, R. *Organometallics* **2004**, 23, 6311-6318. (f) Forniés, J.; Fortuño, C.; Ibáñez, S.; Martín, A. *Inorg. Chem.* **2008**, 47, 5978-5987. (g) Charmant, J. P. H.; Forniés, J.; Gómez, J.; Lalinde, E.; Merino, R. I.; Moreno, M. T.; Orpen, A. G. *Organometallics* **2003**, 22, 652-656. (h) Liu, F.; Chen, W.; Wang, D. *Chin. J. Struct. Chem.* **2006**, 25, 677. (i) Berenguer, J. R.; Fernández, J.; Lalinde, E.; Sánchez, S. *Chem. Commun.* **2012**, 48, 6384-6386. (j) Song, H. B.; Zhang, Z.-Z.; Hui, Z.; Che, C.-M.; Mak, T. C. W. *Inorg. Chem.* **2002**, 41, 3146-3154. (k) Falvello, L. R.; Forniés, J.; Garde, R.; García, A.; Lalinde, E.; Moreno, M. T.; Steiner, A.; Tomás, M.; Usón, I. *Inorg. Chem.* **2006**, 45, 2543-2552. (l) Renn, O.; Lippert, B.; Mutikainen, I. *Inorg. Chim. Acta* **1993**, 208, 219-223. (m) Chen, W.; Liu, F.; Xu, D. X.; Matsumoto, K.; Kishi, S.; Kato, M. *Inorg. Chem.* **2006**, 45, 5552-5560. (n) Stork, J. R.; Olmstead, M. M.; Fetting, J. C.; Balch, A. L. *Inorg. Chem.* **2006**, 45, 849-857. (o) Forniés, J.; García, A.; Lalinde, E.; Moreno, M. T. *Inorg. Chem.* **2008**, 47, 3651-3660. (p) Stork, J. R.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **2005**, 127, 6512-6513. (q) Díez, A.; Forniés, J.; Gómez, J.; Lalinde, E.; Martín, A.; Moreno, M. T.; Sánchez, S. *Dalton Trans.* **2007**, 3653-3660. (r) Díez, A.; Fernández, J.; Lalinde, E.; Moreno, M. T.; Sánchez, S. *Inorg. Chem.* **2010**, 49, 11606-11618. (s) Berenguer, J. R.; Forniés, J.; Gil, B.; Lalinde, E. *Chem. Eur. J.* **2006**, 12, 785-795. (t) Wu, G.; Wang, D. *J. Cluster Sci.* **2007**, 18, 406-413.

(5) (a) Clarkson, L. M.; Clegg, W.; Hockless, D. C. R.; Norman, N. C.; Marder, T. B. *J. Chem. Soc., Dalton Trans.* **1991**, 2229-2239. (b) van Hal, J. W.; Alemany, L. B.; Whitmire, K. H. *Inorg. Chem.* **1997**, 36, 3152-3159.

(6) Usón, R.; Forniés, J.; Tomás, M.; Garde, R. *J. Am. Chem. Soc.* **1995**, 117, 1837-1838.

(7) Forniés, J.; Sicilia, V.; Casas, J. M.; Martín, A.; López, J. A.; Larraz, C.; Borja, P.; Ovejero, C. *Dalton Trans.* **2011**, 40, 2898-2912.

(8) Aullón, G.; Álvarez, S. *Inorg. Chem.* **1996**, 35, 3137-3144.

(9) Cave, G. W. V.; Alcock, N. W.; Rourke, J. P. *Organometallics* **1999**, 18, 1801-1803.

(10) Fuertes, S.; Brayshaw, S. K.; Raithby, P. R.; Schiffrers, S.; Warren, M. R. *Organometallics* **2012**, 31, 105-119.

(11) Berenguer, J. R.; Lalinde, E.; Moreno, M. T.; Sánchez, S.; Torroba, J. *Inorg. Chem.* **2012**, 51, 11665-11679.

(12) (a) Yamaguchi, T.; Yamazaki, F.; Ito, T. *J. Am. Chem. Soc.* **2001**, 123, 743-744. (b) Berenguer, J. R.; Fernández, J.; Gil, B.; Lalinde, E.; Sánchez, S. *Inorg. Chem.* **2010**, 49, 4232-4244. (c) Yamaguchi, T.; Yamazaki, F.; Ito, T. *J. Am. Chem. Soc.* **1999**, 121, 7405-7406. (d) Janzen, D. E.; Mehne, L. F.; VanDerveer, D. G.; Grant, G. *J. Inorg. Chem.* **2005**, 44, 8182-8184.

(13) Maliarik, M.; Nagle, J. K.; Ilyukhin, A.; Murashova, E.; Mink, J.; Skripkin, M.; Glaser, J.; Kovacs, M.; Horváth, A. *Inorg. Chem.* **2007**, *46*, 4642-4653.

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