Formation of a tetrahedral Tl_4 cluster directed by a novel homoscorpionate ligand

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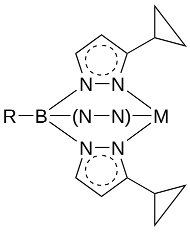
The thallium complex of a novel ligand, hydrotris(3-cyclopropylpyrazol-1-yl)borate, forms a stable tetramer, $[Tl(Tp^{Cpr})]_4$, containing a perfect tetrahedron of Tl atoms, with each Tl in an octahedral environment.

The formation of Tl···Tl bonds, or strong interactions between two Tl atoms, has been found or postulated in a number of thallium(I) compounds, although the exact nature of such bonding remained enigmatic.[1] Most of these examples featured two Tl atoms bridged by one, two, or three ligands enforcing a certain proximity between them, and leading to a Tl···Tl interaction. For instance, a Tl–Tl distance of 3.69 Å was found in a complex structure, containing a triangle consisting of two Tl atoms (further bonded to manganese carbonyl moieties) bridged by a $Mn(CO)_2$ link.[2] The Tl···Tl relationship was considered one of bonding interaction, being only 0.29 Å longer than the metal–metal distance in elemental Tl.[3] Other examples have also been reported,[4] and cited in a review devoted to this subject.[1] Some insight into the nature of the Tl–Tl interaction was elicited from an unbridged species, the quasi-dimer of $[Tl\{C_5(CH_2Ph)_5\}]$, formed about an inversion center, where the Tl···Tl distance is 3.63 Å.[5] It was proposed that bonding interaction results from the mixing of empty p levels into filled s combinations, with the desideratum expressed that 'further work is needed in finding more structures to develop a better understanding of this fascinating problem'.[1] Since that time, other examples appeared,[6] including a fairly unstable tetrameric cluster of the monoalkylthallium compound $[Tl\{C(SiMe_3)\}]_4$, containing Tl in a tetrahedral environment, within a distorted structure.[7] Earlier, similar group 13 analogue structures such as $[In\{C(SiMe_3)_3\}]_4$,[8] and $[Ga\{C(SiMe_3)_3\}]_4$,[9] containing tetrahedra of In and Ga, respectively, have been reported.

In the course of fine-tuning the coordinative behavior of homoscorpionate [hydrotris(pyrazol-1-yl)borate] ligands through modification of their 3-R substituents,[10] we had synthesized hydrotris(3-cyclopropylpyrazol-1-yl)borate (Tp^{Cpr}), isolated it as the stable, high-melting Tl salt,† and determined its structure by X-ray crystallography.‡



$[Tl(Tp^{Cpr})]$ R = H, M = Tl

–(N–N)– represents the third, hidden, 3-(cyclopropyl)pz

To our surprise, this thallium salt, $[Tl(Tp^{Cpr})]$, revealed a highly symmetrical tetrameric structure, containing a perfect tetrahedron of four Tl atoms, each capped by the three nitrogens of a Tp^{Cpr} ligand, thus placing each Tl in an octahedral coordination environment, an unprecedented structure involving Tl^I–Tl^I bonding. Previously, all structures of Tl salts of homoscorpionate ligands, including $[Tl(Tp^{Bu^t})]$,[11] $[Tl(Tp^{Bu^t,Me})]$,[12] $[Tl(Tp^{Bu^t{}_2})]$,[13] $[Tl(Tp^{Menth})]$,[14] $[Tl(Tp^{Mementh})]$,[14] [Tl{tris(1,4-dihydroindeno[1,2-*c*]pyrazol-1-yl)borato}],[15] $[Tl(Tp^{Ant})]$,[16] [Tl{hydrotris(7-*tert*-butylindazol-2-yl)borate}][$Tl(Tp^{3Bo,7Me})$][17] and $[Tl\{HB(3,5\text{-}[p\text{-}C_6H_4\text{-}Bu^t]_2pz)_3\}]$,[18] $[Tl\{HB[pz(CF_3)_2\text{-}3,5]\}]$,[19] and $[Tl(Tp^{Tol})]$,[20] which have been determined by X-ray crystallography, are monomeric or in one case dimeric. In all these cases, Tl is coordinated to the three nitrogen atoms of the ligand, usually with retention of the ligand C_{3v} symmetry, except for the very hindered $Tp^{Bu^t{}_2}$ and Tp^{Ant} derivatives which were distorted. The Tl–N bond lengths ranged from 2.50 to 2.68 Å, and the N–Tl–N angles from 76 to 78° with the exception of the distorted Tp^{Ant}, where the angle was 66°. The only thing resembling a Tl···Tl interaction was noted in the case of $[Tl(Tp^{Tol})]$, the structure of which showed two molecules in a face-to-face conformation, akin to that found in $[Tl\{C_5(CH_2Ph)_5\}]$, with the Tl atoms 3.86 Å apart. However, in contrast to $[Tl\{C_5(CH_2Ph)_5\}]$, which had a *trans*-bent geometry, the $[Tl(Tp^{Tol})]$ 'dimer' was not bent, but had a collinear B–Tl–Tl–B sequence.

The structure of $[Tl(Tp^{Cpr})]_4$ has the Tl_4 tetrahedron as its core (Fig. 1) with each Tl capped by a Tp^{Cpr} ligand, and all Tl–Tl bonds equal at 3.6468(4) Å, with the Tl–Tl–Tl angles the expected 60°. Each Tp^{Cpr} ligand is rotated by about 30° about its threefold axis with respect to a staggered relationship to the triangle of Tl atoms below. The crystals are face-centered cubic, and the unit cell consists of four discrete crystallographically perfect tetrameric tetrahedral thallium clusters (Fig. 2). The Tl–N bonds are 2.532(3) Å, which is close to the short end of the reported values, while the N–Tl–N angles are 76.58(12)°, and thus in the typical range for $[Tl(Tp^x)]$ complexes. All the

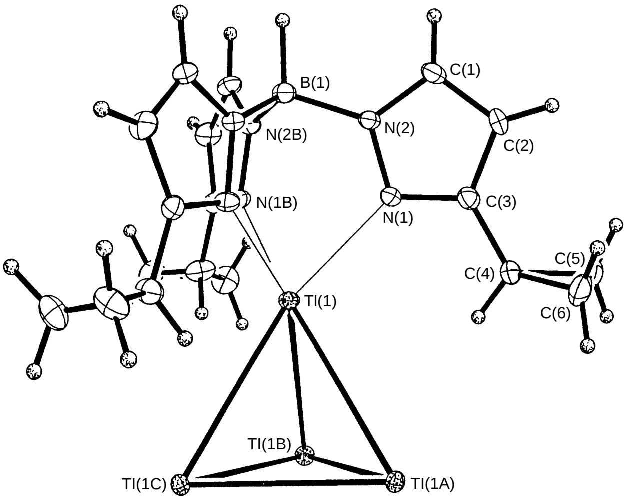


Fig. 1 ORTEP diagram of $[Tl(Tp^{Cpr})]_4$ showing atom labelling scheme. Thermal ellipsoids at 30% probability. Hydrogen atoms and three of the Tp^{Cpr} ligands have been omitted for clarity. Selected distances (Å) and angles (°): Tl(1)–Tl(2) 3.647; Tl(1)–N(1), 2.532; Tl(1)–Tl(2)–Tl(3) 60.0, N(1)–Tl(1)–N(2) 123.2.

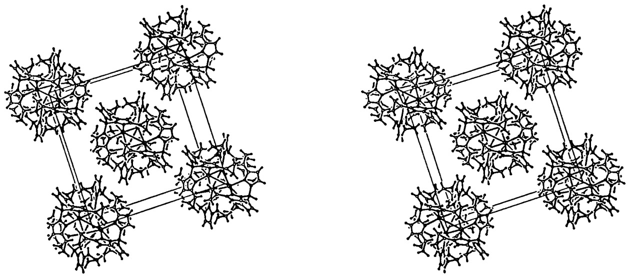


Fig. 2 Stereoview of the unit cell showing discrete tetrameric tetrahedral thallium clusters

cyclopropyl groups are turned in such a way that only the tertiary hydrogen is pointed at the metal.

The reason why the Tl_4 cluster is formed with Tp^{Cpr} but not with any of the other Tp^x ligands cannot be simply a steric one, in the sense that the cyclopropyl group is smaller than any of the 3-R substituents in $[Tl(Tp^x)]$ complexes whose structures are known. We have determined the structure of [Tl(Tp)], the least hindered Tl homoscorpionate, with 3-R = H, and found only unassociated monomers in the crystal with the nearest Tl–Tl distance 4.8 Å, and thus definitely out of bonding range.[21] Since there is no steric hindrance to prevent formation of the Tl_4 cluster, what seems to be missing is an additional driving force for its formation, supplied by the 3-cyclopropyl substituent. Moreover, structures of the closely related $[Tl(Tp^x)]$ compounds with 3-R = Pr^i or 3-R = c-C_4H_9 have also been determined and, again, found to be simple monomers.[21]

Looking at the space-filling model of the structure of $[Tl(Tp^{Cpr})]_4$, we see that the cyclopropyl groups from one ligand cross over past the Tl atom to which the ligand is bonded, and protrude over an adjacent Tl atom, creating an intimately interlocking network of ‘rabbet joints’, which involves all four ligands over the tetrahedral array of Tl atoms. This resembles somewhat the intermeshing of the R groups of Tp^R ligands in octahedral $[M(Tp^R)_2]$ complexes, and makes the whole structure appear spherical (Fig. 2). However, in $[Tl(Tp^{Cpr})]_4$ each Tp^{Cpr} ligand interlocks with three others, thus generating a rather rigid structure, with little rotational freedom for the cyclopropyl groups, or for twisting of the pz groups. It is this unstrained fit of all the components within $[Tl(Tp^{Cpr})]_4$ that seems to be the driving force for the formation of this supramolecular structure and, possibly, for the lowering of surface energy (cluster *vs.* four monomeric units) during crystallization of the monomeric species present in solution. The reported results are obviously unrelated to cases where individual Tp ligands are capping a corner in preformed metallic clusters, as for instance in $[Fe_4S_4]^{2+}$,[22] or in $[VFe_3S_4]^{2+}$.[23]

We have to conclude that the specific nature of the 3-R substituents in homoscorpionate ligands can exert a very subtle, and yet dominant, influence on their coordination chemistry, not always predictable *a priori*.[24]

Footnotes and References

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† *Synthesis*: 3-cyclopropylpyrazole was synthesized in 58% yield from methyl cyclopropyl ketone by the method used for making 3-isopropylpyrazole.[25] Bp 122–124 °C (2.8 Torr.) ^{1}H NMR: δ 12.45 (s, 1 H, NH), 7.46 (s, 1 H, H-5), 5.93 (d, 1 H, H-4), 1.97 (spt, 1 H, tertiary H), 0.93 (dt, 2 H, cyclopropyl) and 0.74 (dt, 2 H, cyclopropyl). ^{13}C NMR: δ 7.89, 101.1, 134.0, 150.6 (the fifth peak is hidden under the δ 7.9 peak). Calc. for $C_6H_8N_2$: C, 66.7; H 7.41; N 25.9. Found: C, 66.9; H, 7.51; N, 25.7%.

$[Tl(Tp^{Cpr})]$ was prepared by heating 3-cyclopropylpyrazole with KBH_4 (3.6 : 1 mole ratio) until the theoretical amount of hydrogen was evolved. After distilling out excess 3-cyclopropylpyrazole *in vacuo*, the residue was dissolved in thf and converted to the Tl salt in 77% yield, by treatment with aqueous $TlNO_3$. Mp 144–146 °C. IR: BH 2438 cm^{-1}. ^{1}H NMR: δ 7.50 (d,1 H, H-5), 5.74 (d, 1 H, H-4), 2.04 (m, 1 H, tertiary H), 0.93 (m, 2 H, cyclopropyl), 0.566 (m, 2 H, cyclopropyl). ^{13}C NMR: δ 8.1, 9.0, 99.7, 135.9, 155.8. Calc. for $C_{18}H_{22}BN_6Tl$: C, 40.2; H, 4.10; N, 15.6. Found: C, 40.1; H, 4.18; N, 15.4%. $CDCl_3$ was used as NMR solvent in all cases. Molecular mass determination by the Signer method in chloroform gave a value of 556 (monomer 537).[26]

‡ *Crystal data* for $[Tl(Tp^{Cpr})]_4$: $C_{72}H_{88}B_4N_{24}Tl_4$: M_w = 537.60, cubic, $F23$, a = 20.5104(2) Å, U = 8628.2(2) Å^3, Z = 4, T = 173(2), D_c = 1.655 g cm^{-1}, μ = 75.00 cm^{-1}, $R(F)$ = 0.0217 and $R(wF^2)$ = 0.0627 for 1708 observed independent reflections ($3 \leqslant 2\theta \leqslant 56°$). CCDC 182/545.

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