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Steric constraint generating large through-space ^{1}H–^{203,205}Tl coupling in a dithallium(I) cryptate

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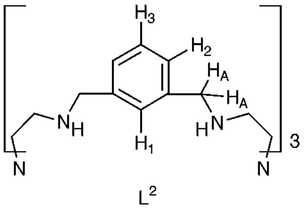
An aminocryptand host enforces approach of encapsulated Tl(I) ions to just within 4.4 Å; despite this relatively large separation, strong Tl(I)···Tl(I) interaction is observed and the aromatic proton of the bridging link exhibits a large through-space coupling to the pair of equivalent Tl nuclei.

In recent years we have become interested in the consequences of enforced proximity between cations encapsulated within azacryptand hosts.[1] In the transition series, this steric enforcement generates a previously uncharacterised bonding situation: a one-electron bond between copper ions in an average-valence +1.5 redox state.[2–6] Steric enforcement of close approach for transition ions implies use of relatively small hosts such as (imBT)† and amBT(= imBT + 12H), while larger hosts such as (N[(CH$_2$)$_2$N=CH(C$_6$H$_4$-*m*)CH=N(CH$_2$)$_2$]$_3$N (L^1) and its amino form L^2 (= L^1 + 12H) have suitable cavity size to accommodate pairs of larger main group cations such as Tl$^+$. Our earlier studies with cryptates of L^2 [7,8] and the analogous iminocryptand ligand, L^1, demonstrate[9,10] that these hosts offer internuclear distances of between 3 and 6 Å according to the preference of the guest cation, as the cryptands can make use of a triple helical twist mechanism[11,12] which allows them to adapt to the preferred coordination site separation of the cationic guests.



L^2

There is interest[13] among bonding theorists in interactions between the formally closed shell low-valent p-block cations. In a number of dimeric and oligomeric structures[13,14] with Tl···Tl distances (some supported by bridging donors) ranging from 3.5 to 4.0 Å, there is evidence for varying degrees of s^2···s^2 interaction. Another point of interest is the possible existence of weakly attractive arene···heavy metal interactions,[15], which could assist the close approach of Tl(I) ions.

The dithallium(I) cryptates of L^2 are synthesised‡ by direct reaction of preformed ligand with the appropriate thallium(I) salt. ^{1}H NMR studies on the triflate salt, T1$_2$L^2(CF$_3$SO$_3$)$_2$ **1,** in the solid state and in solution, suggest a simple and symmetric structure where each Tl(I) cation occupies the site defined by the N4 cap. There is evidence of a low-activation dynamic process in solution in that both methylene-cap signals of **1** present as broad temperature-independent singlet resonances with no discernible fine structure due to geminal or vicinal [^{1}H,^{1}H] methylene coupling. Sharp signals for the H$_2$ and H$_3$ resonances show well defined ortho coupling; however the expected singlet H$_1$ resonance (Ar$_1$), which in analogous L^1 disilver(I) and dicopper(I) iminocryptates[16] is strongly affected by guest encapsulation both in respect of breadth and position, appears here as a severely broadened triplet (apparent ^1J (^{205,203}Tl,^{1}H) ≈ 17 Hz) at δ *ca.* 6.8. The triplet structure is just discernible at 400 MHz; broadening is a function of the magnetic field, approximating to 16 : 9 : 6 for 400, 300 and 250 MHz spectra, in proportion to the square of the magnetic field used [Fig 1(a)]. The signal from the methylene H$_A$ hydrogens adjacent to the aromatic ring is a similarly broadened triplet [Fig 1(b)] and decoupling experiments fail to relate the coupling of the broad triplets to any proton resonance. Also the resonances are not narrowed significantly at high temperature, thus ruling out broadening *via* an exchange process. These observations implicate through-space coupling to thallium, the latter relaxing by a chemical shift anisotropy mechanism.[17] The splitting of the α-methylene signal confirms that the two ^{205,203}Tl nuclei couple to each other with J(Tl,Tl) $>>$ 17 Hz, an example of the strong coupling case.[17b] The size of the coupling to the lone Ar$_1$ hydrogen is unexpected because no formal bond to thallium exists. Nor can it be explained on a through-bond basis as, despite an identical bond pathway, the H$_3$ resonance shows no thallium coupling. It appears that this coupling has to be explained on the basis of interaction between the lone aromatic hydrogen Ar$_1$ and the pair of Tl(I) ions which, although unbonded, are constrained by geometry to lie in close proximity.

The low solubility of **1** in CD$_3$CN allows only a weak ^{13}C solution spectrum where the noise level hinders the unambiguous attribution of ^{205,203}Tl, ^{13}C couplings. There are indications of such coupling in the unique Ar$_1$ carbon resonance which appears at δ *ca.*129.9 as a broadened ≈ 80 Hz triplet. The methylene carbons give rise to two sharp resonances at δ 57.5 and 49.3 with a broader, possibly Tl-coupled, feature at δ 54.1 representing the methylene carbon adjacent to the aromatic ring. In the CP MAS ^{13}C spectrum signal breadth is generally sufficient to conceal any ^{205,203}Tl,^{13}C coupling although splitting of a weak resonance in the region δ 120–130 may derive from such a cause. The weak ^{15}N CP MAS spectrum obtained for **1** likewise fails to show any coupling to thallium; just one relatively broad signal (half-width 150 Hz) centered at

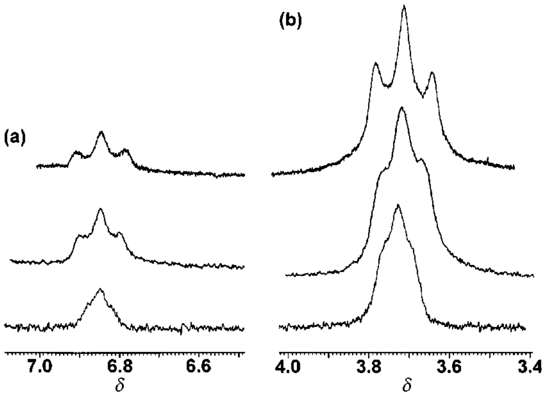


Fig. 1 The Tl-coupled Ar$_1$ (a) and CH$_2$(A) (b) resonances in different magnetic fields: bottom trace, 400; middle trace, 300; top trace, 250 MHz. (Spectra run in CD$_3$CN, 295 K, chemical shift in ppm from SiMe$_4$).

δ -307 (*vs.* NH_4NO_3 standard) appears, representing overlapped cryptand N(H) and N_{br} resonances.

In order to confirm the hypothesis of close approach of Tl nuclei, crystallographic evidence was sought,§ using the synchrotron source at Station 9.8 at CLRC Daresbury. The structure is illustrated in Fig. 2. The $[Tl_2L^2]^{2+}$ cation has $\bar{6}$ point symmetry and the anion lies on a threefold axis, so the asymmetric unit contains one sixth of the cation and one third of the anion. The Tl atom is coordinated to the bridgehead nitrogen (N1) and to three secondary amine groups (N11, N11A and N11B); it is displaced from the plane of the secondary amines by 1.087(3) Å towards the centre of the cavity and the Tl···TlA distance is 4.3755(4) Å. The Tl(I) cations are thus farther from the N_{br} apices than in other dinuclear cryptates we have studied.[1] The Tl–N distances are around 2.7–2.8 Å, at the long end of the range for Tl(I)–N distances,[14,18,19] suggesting a predominantly ionic character for bonding in this complex. The ligand host is fully extended to accommodate the pair of large spherical cations, and there is no helicity of cryptand strands. The structure is thus of unusually high symmetry for a cryptate. The distance between Tl(I) cations and the Ar_1 hydrogen is 3.816 Å. The shortest arene carbon···metal contact is 4.207 Å , almost 0.5 Å longer than the van der Waals sum. Edge to face intermolecular H···π contacts of *ca.* 2.49 Å involve all the arene rings.

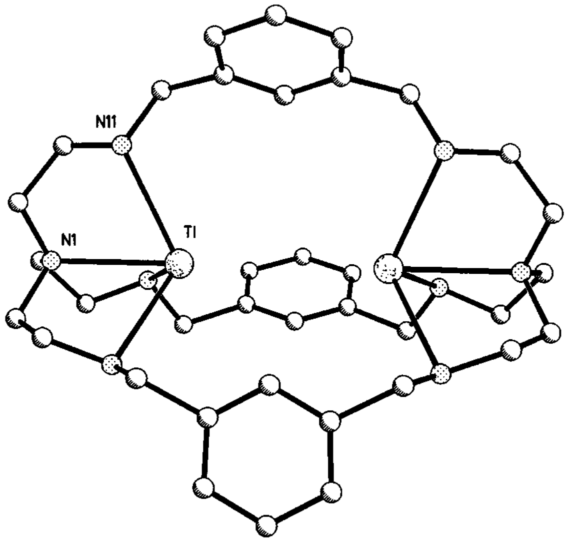


Fig. 2 Structure of $Tl_2L^2(CF_3SO_3)_2$. Selected distances (Å): Tl–N(I) 2.728(5), Tl–N(11) 2.796(3), Tl···Tl 4.3755(4), Tl··H(9) 3.816.

The structural data make it clear that the sizeable coupling between the Ar_1 proton and ^{205,203}Tl is formally through space, although the average separation of these nuclei in the dynamic solution environment may not be identical with that in the crystal where intermolecular H···π packing effects operate. The thallium–thallium coupling of >> 17 Hz must also be classified as a through space effect given the relatively large separation of Tl(I) cations, almost 1 Å greater than the internuclear distance (3.4 Å) in the element. We believe that this represents the largest recorded through-space coupling.

In most dimeric or quasi-dimeric structures,[13,14,19] Tl···Tl distances, in the range 3.6–3.9 Å are significantly shorter than noted here and the closest Tl···arene carbon distance of 3.816 Å in this structure exceeds that typical of weakly interacting arene–heavy metal systems.[19] Nonetheless, we have clear evidence of coupling between both the pair of Tl(I) cations and between this $Tl(I)_2$ pair and the unique aromatic proton Ar_1, despite the ionic character which explains the absence of ^{203,205}Tl, ^{1}H couplings elsewhere in the cryptate spectrum. It is intriguing that the only ^{203,205}Tl, ^{1}H couplings observed in this cryptate are mediated *via* a non-bonded pathway, *e.g.* that involving steric compression of the Tl^+···[H]···Tl^+ moiety. The implication is that coupling information can be efficiently transmitted in large soft cations like Tl(I) by non-directional overlap of electron density.

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Notes and references

† imBT = $N[(CH_2)_2N{=}CHCH{=}N(CH_2)_2]_3N$.

‡ $Tl_2\ L^2(CF_3SO_3)_2 2H_2O{\cdot}MeOH$, **1**: To 0.5 mmol L^2 dissolved in 10 cm^3 MeOH was added 1 mmol Tl(OAc) dissolved in 2 ml water followed by 1 mmol of $LiCF_3SO_3$ as solid. A colourless precipitate was obtained in *ca.* 70% yield on concentrating the pale yellow solution. The final crop of this preparation yielded the small single crystals used for crystallography. Anal. Found (calc.): C, 33.8(34.2); H, 3.9(4.4); N 8.1(8.2)%.

§ *Crystal data*: $[Tl_2L^2](CF_3SO_3)_2$, $C_{38}H_{54}F_6N_8O_6S_2Tl_2$, colourless needle, $0.16 \times 0.06 \times 0.04$ mm, hexagonal, $a = 9.5074(2)$, $c = 29.7005(4)$ Å, $U = 2324.97(8)$ Å^3, space group $P6_3/m$, $Z = 2$, $\mu = 7.088$ mm^{-1}, $F(000) = 1268$. Data were collected at 150(2) K using a SMART CCD with synchrotron radiation ($\lambda = 0.6885$ Å, SRS station 9.8 at Daresbury). A hemisphere of data (16580 reflections, $\theta_{max} = 29.33°$) was collected. The structure was solved by direct methods and refined on F^2, using all 2277 independent reflections ($R_{int} = 0.0346$). Non-hydrogen atoms were refined anisotropically and hydrogen atoms were inserted at calculated positions except for the amine proton, which was located and refined with a fixed ADP. The refinement, on 100 parameters, converged with $wR2 = 0.0835$, GOF = 1.060 (all data) and conventional $R1 = 0.0357$ (2σ data). The only significant residual peaks were close to the Tl atom. All programs used in the structure refinement are contained in the SHELX-97 package.[20] CCDC 182/1483. See http://www.rsc.org/suppdata/cc/a9/a908476b/ for crystallographic files in .cif format.

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