

Stabilisation of a very short Cu–F bond within the protected cavity of a copper(II) compound from a tris(2-aminoethyl)amine derivative†

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The copper(II) coordination compound of an *N*-functionalised derivative of tris(2-aminoethyl)amine forms a cavity that is an excellent fluoride ion host, generating a Cu–F entity with a very short distance (182 pm) and characterised by a fluoride ion devoid of any additional intermolecular interactions.

The tripodal ligand, tris(2-aminoethyl)amine, **tren**, and more elaborate or extended **tren** ligands have found wide application in the preparation of transition-metal complexes.^{1–4} Due to the tripodal arrangement of the four nitrogen donor atoms, these ligands are ideal candidates for the synthesis of trigonal-bipyramidal metal complexes, and a variety of copper(II) coordination compounds with this geometry have been reported.¹ These metal complexes have been used in catalysis and dioxygen binding studies.^{5–7} We have used these ligands to stabilise redox-active oxoanions, such as thiosulfate and thiosulfonates,⁸ and to prepare cyanido-bridged heteropolynuclear clusters with novel magnetic properties.^{9,10} The availability of a single, exchangeable coordination site on the Cu^{II} centre has provided considerable control over the number of reaction products, facilitating their isolation, and over the reactivity of thiosulfate and the thiosulfonates. Of the **tren** derivatives, the aryl substituted versions have been little explored, although various of these have been employed in the formation of transition amido complexes,^{11–14} of which some Mo compounds have been demonstrated to act as catalysts in dinitrogen reduction.^{13,14}

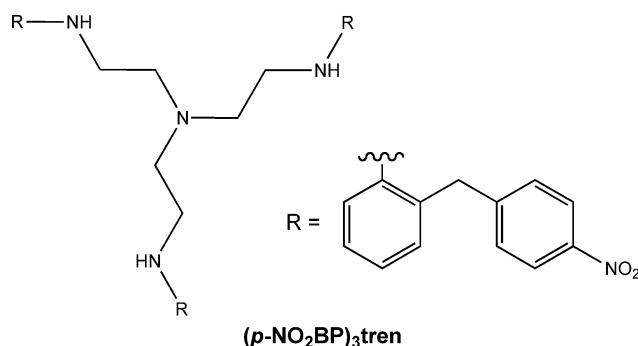
Some of us recently reported on a simple multi-component synthesis of aryl substituted **tren** derivatives containing flexible pendant arms, *i.e.* tris((2-(4-nitrobenzyl)phenylamino)ethyl) amine, (**p-NO₂BP**)₃**tren** (**L**).¹⁵ **L** has a shielded cavity for a metal to bind to the four nitrogen atoms of the **tren** moiety leaving an additional coordination site for binding a small exchangeable ligand, protected by the extended arms of **L**.

Such protected exchangeable ligand binding sites allow the occurrence of interesting and unusual interactions and novel properties. For example, previous studies have shown the possibility of stabilising coordinated small molecules and ions, such as O₂ and N₂.^{13,16} We report herein the use of **L** in the synthesis of a

copper(II) fluoride coordination compound, whose single-crystal X-ray structure reveals the shortest reported Cu–F distance, thus highlighting the ability of this type of ligand to generate products with novel structural features and properties.

The copper(II) fluoride compound, [CuLF]BF₄, was initially isolated in 28% yield from a THF solution of Cu(BF₄)₂·xH₂O and **L** that had been layered with ethanol. The fluoride was generated by gradual decomposition of BF₄[–], a relatively well-known phenomenon observed in a number of copper complexes,^{17–19} mostly with bulky substituted pyridines and pyrazoles,^{18,19} or some amine ligands.¹⁷ The low isolated yield from this reaction led us to develop an alternative synthesis. The use of tetraethylammonium fluoride (Et₄NF), as source of fluoride anions, also produced the desired compound, showing identical IR and solid-state EPR spectra to those of the previously isolated compound, with a yield of 67%.

The X-ray crystal structure of [CuLF]BF₄ is depicted in Fig. 1.† The copper(II) ion is pentacoordinated with an almost ideal trigonal-bipyramidal coordination environment ($\tau = 0.99$)²⁰, as expected for complexes of substituted **tren** ligands. The three equatorial positions are occupied by the aniline nitrogen atoms, N_{eq}, and the axial positions are occupied by the tertiary **tren** nitrogen atom, N_{ax}, and a fluoride anion resulting from BF₄[–] decomposition (see Table 1 for selected bond distances and angles). A BF₄[–] counter-anion is located outside the cavity of the ligand and is non-coordinating (but is hydrogen bonded to the amine groups with N(3)–H(N3)⋯F(12b) = 2.979(5) Å, Table 2).



As is typical for the copper(II) compounds of these tripodal ligands, the copper centre is slightly out of the plane, which is made up of the N_{eq} atoms, displaced towards the fluoride ion (0.192(1) Å above the plane), and the Cu–N_{ax} distance is shorter than the Cu–N_{eq} distances.^{21–23} The general trend for **tren** complexes is that the Cu–N_{eq} distances increase while the Cu–N_{ax} remains constant with the steric bulk, as shown by the series **tren** < **Me₃tren** ≈ **Bz₃tren** < **Me₃Bz₃tren** ≈ **Me₆tren**.^{21,22} (**p-NO₂BP**)₃**tren** would fit at the end of this series, since the direct connection between the aryl group and the secondary amine nitrogen atoms

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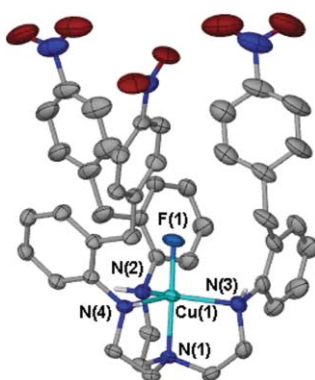
† Electronic supplementary information (ESI) available: Fig. S1–S3, experimental section and crystallographic details. CCDC reference numbers 720265. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b902907a

Table 1 Selected bond lengths and angles

| Bond distances/Å | | Angles/° | |
|------------------|----------|-----------------|-----------|
| Cu(1)–F(1) | 1.821(1) | F(1)–Cu(1)–N(1) | 175.92(7) |
| Cu(1)–N(1) | 2.001(2) | F(1)–Cu(1)–N(2) | 98.36(8) |
| Cu(1)–N(2) | 2.207(2) | F(1)–Cu(1)–N(3) | 95.20(8) |
| Cu(1)–N(3) | 2.160(2) | F(1)–Cu(1)–N(4) | 91.99(7) |
| Cu(1)–N(4) | 2.176(2) | N(1)–Cu(1)–N(2) | 84.79(7) |
| | | N(1)–Cu(1)–N(3) | 85.62(7) |
| | | N(1)–Cu(1)–N(4) | 84.45(7) |
| | | N(2)–Cu(1)–N(3) | 116.71(7) |
| | | N(2)–Cu(1)–N(4) | 110.80(7) |
| | | N(3)–Cu(1)–N(4) | 130.16(7) |

Table 2 Hydrogen bonds

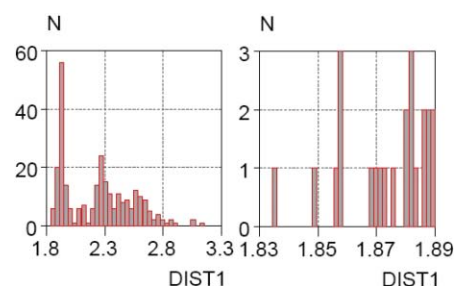
| Hydrogen bonds | <i>d</i> H...F/Å | <i>d</i> C...F/Å | ∠C–H...F/° |
|---------------------|------------------|------------------|------------|
| C(9)–H(9B)...F(1) | 2.34 | 3.114(4) | 135 |
| C(24)–H(24B)...F(1) | 2.19 | 3.044(4) | 145 |
| C(39)–H(39B)...F(1) | 2.40 | 3.192(3) | 137 |
| N(3)–H(N3)...F(12a) | 2.38(3) | 3.008(5) | 130(3) |
| N(3)–H(N3)...F(12b) | 2.20(2) | 2.979(5) | 149(3) |
| N(4)–H(N4)...F(13) | 2.22(2) | 3.000(2) | 148(2) |

**Fig. 1** Diagram of the cation [CuLF]⁺ shown in thermal ellipsoids at 50% probability level. Hydrogen atoms except those associated with the amine groups have been omitted for clarity.

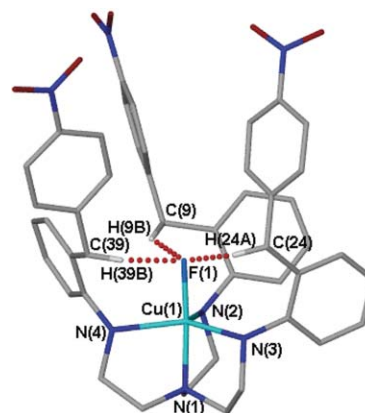
introduces even more steric bulk than is present in the last two members in this series. The novel and most exciting feature of the compound is the extremely short copper fluoride coordination distance. In fact, the Cu–F distance of 1.821(1) Å is the shortest reported so far. A thorough analysis of the Cambridge Structural Database, CSD (version 5.29, Aug 2008), revealed that the shortest previously reported Cu–F distance was 1.836(2) Å for a bispidine copper complex,²⁴ followed by 1.852(4) Å for a [Cu(TPA)F]PF₆ (TPA = tris((2-pyridyl)methyl)amine) complex.¹⁸ There are several structures with much longer Cu–F distances (see Fig. 2).

The fluoride ion in [CuLF]BF₄ is solely bound to the copper(II) centre and does not participate in any other coordinative or hydrogen-bonding interactions. This is extremely unusual as fluoride ions coordinated to copper(II) usually either bridge to a second copper centre,^{17,25,26} or their high electron density is stabilised *via* hydrogen bonding with water or alcohol molecules.^{27,28}

In [CuLF]BF₄, the hydrophobic cavity generated by the pendant arms of **L** prevents the fluoride ligand from forming bridged complexes and from accepting hydrogen bonds from H bond donors. There are, however, weak interactions with an aliphatic

**Fig. 2** Histograms of Cu–F distances found in the CSD (version 5.29, Aug 2008). (a) All distances up to 3.2 Å (*n* = 236). (b) 20 shortest distances.

hydrogen atom of each of the three arms (Fig. 3).^{29,30} These C–H...F contacts (C...F distance 3.044(4) Å, Table 2) can be seen as weak hydrogen bonds, and assemble the pendant arms into a tightly closed binding pocket. A few structures are known in which the delocalisation of the high electron density on the fluoride ion occurs by hydrogen bonding to aromatic and aliphatic hydrogens. These systems also exhibit short Cu–F distances, but not as short as that reported herein.^{18,24,26}

**Fig. 3** Diagram showing hydrogen bonding interactions (red dotted lines) between an aliphatic hydrogen atom of each arm and the fluoride anion.

The packing of the X-ray structure also indicates the presence of unusual nitro–nitro interactions between neighbouring complexes. For example, the O...O distances, *viz.*, O(1)...O(4') 2.883(6) Å and O(3)...O(3') 2.998(9) Å, are shorter than the sum of the van der Waals radii (3.04 Å), and shorter than many reported previously in the CSD (see Fig. S1 and S2, ESI).†

The EPR spectrum of a frozen THF solution of [CuL](BF₄)₂ shows characteristic features indicative of a distorted octahedral coordination geometry (Fig. 4, Table 3).³¹ Addition of one equivalent of Et₄NF caused a drastic change in the spectrum, which is reflected by major changes of the *g* and *A* values. The spectrum is now representative of a trigonal-bipyramidal coordination geometry,^{23,32} and is almost identical to that observed for [Cu(TPA)F]PF₆, whose formation involved the decomposition of a PF₆ anion.¹⁸

Similarly, the UV-vis spectrum showed significant changes on addition of a fluoride source (Fig. S3).† The spectrum of the THF solution containing **L** and Cu(BF₄)₂·H₂O in a 1 : 1 ratio before addition of fluoride exhibited one maximum at 640 nm (ϵ = 380 M^{−1}cm^{−1}), indicative of a distorted octahedral copper complex (*d*_{xz}, *d*_{yz} → *d*_{x²−y²} transition).³³ After addition of Et₄NF,

Table 3 EPR data for a frozen THF solution of a 1 : 1 mixture of **L** and $\text{Cu}(\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$, and a powdered sample of the title compound

| Frozen solution at 77 K | <i>g</i> values ^a | <i>A</i> values ^a /mT |
|---------------------------------|------------------------------|----------------------------------|
| $[\text{CuL}](\text{BF}_4)_2^b$ | $g_x = 2.044$ | $A_x = 6.1$ |
| | $g_y = 2.082$ | $A_y = 7.9$ |
| | $g_z = 1.255$ | $A_z = 10.1$ |
| | $g_x = 2.043$ | $A_x = 0.05$ |
| $[\text{CuLF}]\text{BF}_4^c$ | $g_y = 2.165$ | $A_y = 2.6$ |
| | $g_z = 1.908$ | $A_z = 16.0$ |
| | | |
| Solid | rt | 77 K |
| $[\text{CuLF}]\text{BF}_4$ | $g_x = 2.01$ | $g_x = 2.02$ |
| | $g_y = 2.18$ | $g_y = 2.17$ |
| | $g_z = 2.22$ | $g_z = 2.22$ |

^a Values from simulated spectra.³⁶ ^b Solution prepared by mixing equimolar amounts of **L** and $\text{Cu}(\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$. ^c Previous solution after adding 1 equiv. of tetraethylammonium fluoride.

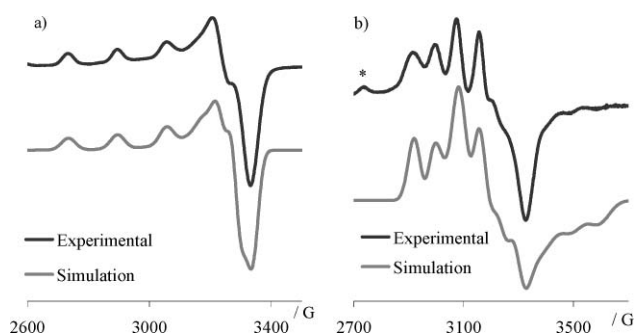


Fig. 4 EPR spectra of a frozen THF solution of (a) $[\text{CuL}](\text{BF}_4)_2$ before addition of fluoride and (b) $[\text{CuLF}]\text{BF}_4$ after addition of 1 equiv. of tetraethylammonium fluoride. Simulated spectra are shown in light-grey.³⁶ * indicates a small amount of impurity present due to some unreacted $[\text{CuL}](\text{BF}_4)_2$.

new absorption peaks were observed at 680 nm ($\epsilon = 370 \text{ M}^{-1} \text{ cm}^{-1}$) and 840 nm ($\epsilon = 460 \text{ M}^{-1} \text{ cm}^{-1}$) in keeping with the formation of a trigonal-bipyramidal complex.^{32,34}

The reflectance vis-NIR spectrum of the powdered compound, showing two peaks at 694 and 938 nm (inset of Fig. S3),[†] is similar to the solution spectrum after the introduction of fluoride anions. The EPR spectrum of the powdered sample also shows *g* values typical for a trigonal-bipyramidal based coordination environment with the unpaired electron in the $d_{x^2-y^2}$ orbital (Table 3).³⁵ These results indicate that the compound adopts the same trigonal-bipyramidal geometry both in solution and in the solid-state.

In summary, a unique trigonal-bipyramidal $\text{Cu}(\text{II})$ coordination compound has been fully characterised, in which the apical fluoride ion is totally embedded in a pocket, and kept in position by the shortest known Cu–F bond, and by weak C–H...F interactions.

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Notes and references

† Crystal structure determination: All non-hydrogen atoms were refined anisotropically. Geometrical and displacement parameter restraints were used to model the BF_4^- group. Displacement parameter restraints were used in modelling one end of one of the ligand arms, even so the ratio of the displacement parameters max–min is around 5 : 1. Splitting the end of the arm was considered, but as it reflected only the movement in the arm and no new chemical information would be gained, it was left as it was. Hydrogen atoms were placed geometrically where possible and refined with a riding model. In the case of the N–H's, these were found in the difference map and these were allowed to refine with a restrained on the N–H distance.

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