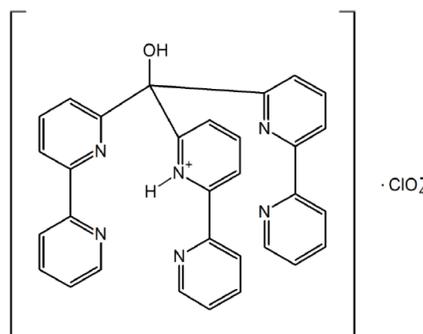# Crystal Structure of the Monoprotonated Tripodal Ligand Tris(2,2'-bipyrid-6-yl) Methanol

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Abstract: The tripodal bipyridine-based ligand tris(2,2'-bipyrid-6-yl) methanol (L^1) was shown in our previous work to have a strong steric preference for trigonal prismatic co-ordination environments with a series of transition metals. We now report the crystal structure of the ligand framework, isolated in its monoprotonated form with a perchlorate counterion. The structure was solved in a monoclinic space group C2/c with cell parameters, a = 21.5885(3), b = 11.7485(3), c = 24.6939(6) Å, α = 90°, β = 110.790(1) °, γ = 90°, volume = 5855.4(2) Å^3, Z = 8. The ^{1}H NMR of the protonated ligand is similar to the parent ligand and showed the compound retained its 3-fold symmetry and all bipyridine groups were equivalent.

We report the crystal structure of the protonated form a tripodal bipyridine-based ligand framework with a strong steric preference for trigonal prismatic co-ordination environments.

Keywords: Bipyridine, crystal structure, trigonal prismatic, tripodal ligand.

INTRODUCTION

Self assembly is common place in nature [1] and coordination chemists have provided a new dimension to this natural phenomenon through the driven self assembly of various metal ions with multidentate ligands. For six co-ordinate complexes, the octahedral geometry is overwhelming more common than the trigonal prismatic arrangement. However such arrangements have received intermittent interest in comparison to their octahedral counterparts and recently, they have been investigated for their usefulness to generate molecular assemblies ranging from the macroscale [2] to nano scale [3].

In order to rationalize why specific six-coordinate complexes are biased towards trigonal prismatic character, we generally consider repulsive ligand-ligand interactions, sterochemical predispositions of a ligand as well as the stereo-electronic preferences of metal ions [4].

Pioneering work of L. Pauling and R. G. Dickinson's on the study of mineral molybdenite [5], in which sulfur atoms surrounds the molybdenum in a trigonal prismatic coordination arrangement, initially invoked interest in the subject. Consequently, a range of analogous compounds were investigated and shown to exhibit TP or pseudo TP arrangements [6, 7]. Several other structurally rigid and non rigid ligand systems were also reported. The structurally rigid systems utilised a variety of ligands, such as the bimacrocyclic ligands, bicapped-TRENCAM (BCT) and bicapped-TPTCAM (BCTPT) [8], *N,N,N',N'*-tetramethylethylenediamine (tmeda)[9], (py)$_3$tach, (py)$_3$tame and clathrochelates [10], to name but a few. More recently, tris(pyrazolyl)borate (Tp^{py}) based ligand systems were coordinated with Co (II) by Ward and McCleverty *et al.* [11], and the trigonal prismatic conformation was observed, however other metal ions yielded tetrameric complexes containing octahedrally co-ordinated metals.

Recently, we have investigated the metal driven self assembly of a six-coordinate tripodal ligand, tris(2,2'-bipyrid-6-yl)methanol with series of transition metals [12]. Furthermore, we have focussed our attention in investigating the

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relationship between octahedral and trigonal prismatic character while varying d electron configuration. It was established that unlike the monoanionic Tp^{Py}, the bipy based ligand naturally favours monomeric complexes as the formation of tetrameric complexes will induce unfavourable electrostatic repulsion. It was concluded that configurationally restrained ligand framework was responsible for enforcing this comparatively rare geometry with respect to an octahedron. In this work we wished to investigate the solid state and solution state structure of the ligand without a metal ion co-ordinated to it. Single crystals of this ligand have been isolated for the first time in the protonated form as a perchlorate salt. We have determined the structure of this species, as well as obtaining the ^{1}H NMR spectra of the ligand and its protonated form. These finding will be discussed below.

EXPERIMENTAL SECTION

All materials were of reagent grade and used as received from commercial sources. Solvents were distilled before use. Ligand L^1 (Fig. **1**) was prepared as described in our previous work [12]. L^1 (50 mg, 0.10 mmol) was dissolved in methanol (15 mL) and then added dropwise to an aqueous solution of praseodymium(III) perchlorate (110 mg, 101 mmol; 40 wt % aqueous solution). The solution was stirred for 20 minutes and left at 4°C for 2 days. A light brown precipitate was filtered off and the remaining filtrate was left to slowly evaporate at room temperature, yielding rectangular shaped crystals suitable for X-ray diffraction (30%). ^{1}H NMR (400 MHz; CD$_3$CN): 8.63 (*d*, 3H, *J* = 8.64 Hz, py-H$_8$), 8.40 (*d*, 3H, *J* = 8.53 Hz, py-H$_4$), 8.35 (*d*, 3H, *J* = 8.5 Hz, py-H$_5$), 8.13 (*t*, 3H, *J* = 8.38 Hz, py-H$_3$), 8.05 (*d*, 3H, *J* = 8.35 Hz, py-H$_2$), 8.00 (*t*, 3H, *J* = 8.32 Hz, py-H$_6$), 7.55 (t, 3H, *J* = 8.09 Hz, py-H$_7$).

X-RAY CRYSTALLOGRAPHY

All single crystal X-ray data was collected at 150 K on a Bruker/Nonius Kappa CCD diffractometer using graphite monochromatic Mo-Kα radiation (λ = 0.71073 Å), equipped with an Oxford Cryostream cooling apparatus. Crystal parameters and details of the data collection, solution and refinement are presented in Table **1**. The data was corrected for Lorentz and polarisation effects and for absorption using SORTAV [13]. Structure solution was achieved by direct methods (Sir- 92 program system [14] and refined by full-matrix least-squares on F^2 (SHELXL-97 [15] with all non-hydrogen atoms assigned anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were placed in idealised positions and allowed to ride on the relevant carbon atom. In the final cycles of refinement, a weighting scheme that gave a relatively flat analysis of variance was introduced and refinement continued until convergence was reached. Molecular structures in the figures were drawn with ORTEP 3.0 for Windows (version 1.08) [16]. Crystallographic data for **1** in CIF format have been deposited with the Cambridge Crystallographic Data Centre (CCDC 783585). Copies of these later data may be obtained free of charge via www.ccdc.cam.ac.uk/data_request/Cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting the CCDC, 12 Union Road, Cambridge CB2 IEZ, UK; Fax: +44-1223-336033.
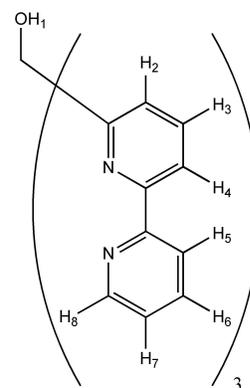

Fig. (1). Ligand L^1 showing the proton numbering.

Table 1.   Crystal data and structure refinement for 1.

Empirical formula	C31 H29 Cl N6 O8
Formula weight	649.05
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 21.5885(3) Å, α = 90°
	b = 11.7485(3) Å, β = 110.790(1)°
	c = 24.6939(6) Å, γ= 90°
Volume	5855.4(2) Å^3
Z	8
Density (calculated)	1.473 Mg/m^3
Absorption coefficient	0.195 mm-1
F(000)	2704
Crystal size	0.20 x 0.20 x 0.20 mm^3
Theta range for data collection	2.90 to 27.47°.
Index ranges	-27<=h<=28, -14<=k<=15, -32<=l<=31
Reflections collected	12065
Independent reflections	6670 [$R_{(int)}$ = 0.0444]
Completeness to θ = 27.47°	99.60%
Absorption correction	Empirical
Max. and min. transmission	0.9620 and 0.9620
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	6670 / 9 / 441
Goodness-of-fit on F^2	1.035
Final R indices [$I \geq 2\sigma(I)$]	R_1 = 0.0514, wR_2 = 0.1087
R indices (all data)	R_1 = 0.0822, wR_2 = 0.1231
Extinction coefficient	0.0067(3)
Largest diff. peak and hole	0.245 and -0.454 e.Å^{-3}

RESULTS AND DISCUSSION

The crystal structure of **1** is depicted in Fig. (**2**). The ligand consists of three bipy groups linked *via* a methine bridge. One of these bipy groups is monoprotonated and is held in a *cisoid* configuration by an intramolecular hydrogen bond (Table **2**). The dihedral angle between the least-squares planes of these two pyridyl units is just 9.27°. The two remaining bipy groups are not configurationally restrained by any such intramolecular interactions and each exhibits a *transoid* configuration around the interannular bond. Accordingly, the dihedral angle for the N3/N4-containing bipy group is 22.27° and for the N5/N6-containing bipy group this value is larger at 36.54°. The three bipy arms adopt an oblique configuration (Fig. **3**), spreading further apart as the sterical influence conferred from the methine bridge is reduced. The C-N and mean C-C bond lengths for the protonated pyridine are 1.355(3) Å and 1.384(3) Å respectively. The corresponding values for the neutral pyridyl units are statistically identical at 1.344(3) Å and 1.385(3) Å. These bond lengths are in excellent agreement with literature values for both 2,2'-bipyridine [17] and 2,2'-bipyridinium (bis)perchlorate [18].
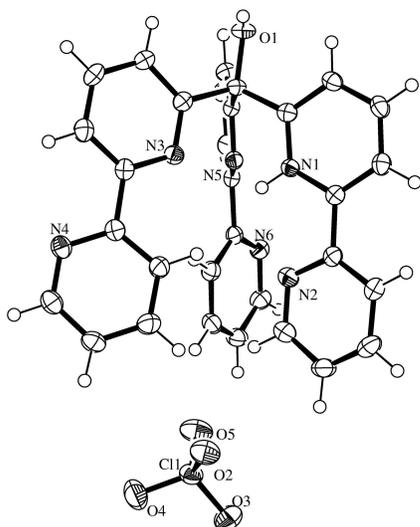
Fig. (2). Perspective view of the asymmetric unit. Displacement ellipsoids are shown at the 50% probability level. H atoms are represented by circles of arbitrary size. Three water molecules within the lattice have been excluded for clarity.
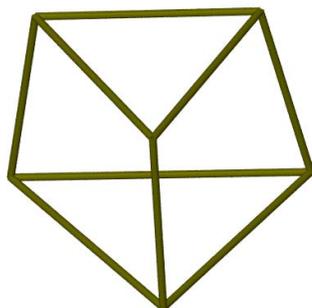
Fig. (3). Highlighting the distorted trigonal prism formed between pyridyl centroids in which the upper triangular face in close proximity to the methine bridge is significantly smaller than the lower triangle formed by the more distant centroids.

Another feature of interest is the orientation of the pyridine rings directly bonded to the bridgehead carbon of the tripod (the proximal pyridine donors). The crystallographic data for tris(2-pyridyl)methanol [19] shows these rings positioned such that all three lone pairs on the nitrogens are pointing away from each other.

However, when protonated, two rings interact with the proton, leading to a N-N distance of 2.656 Å [20]. In contrast, protonated tris(2,2'-bipyrid-6-yl) methanol has all three lone pairs of the proximal pyridine donors pointing towards the proton. In addition, one distal pyridine is also hydrogen bonding to the proton. This distal pyridine (N2-C7/C11) is part of the bipyridyl unit to which the proton is most strongly associated. The N-N distances between the pyridinium moiety (N1-C2/C6) and the two other proximal pyridines is 2.786(3) Å (N1-N5) and 2.852(3) Å (N1-N3), while the remaining N-N distance between these proximal donors is 3.048(3) Å (N3-N5). The N-N distance between the proximal pyridinium unit and its distal pyridine is 2.667(3) Å (N1-N2).

The molecular packing is consolidated by various intermolecular interactions, such as π-stacking between N1-C2/C6 and N2-C7/C11 (symmetry code: 2-x, 1-y, -z; Fig. **4**) and several H-bonds involving the perchlorate counterion and three water molecules. The alcohol group (O1) is also acting as an H-bond donor to a water molecule (O8) within the lattice.
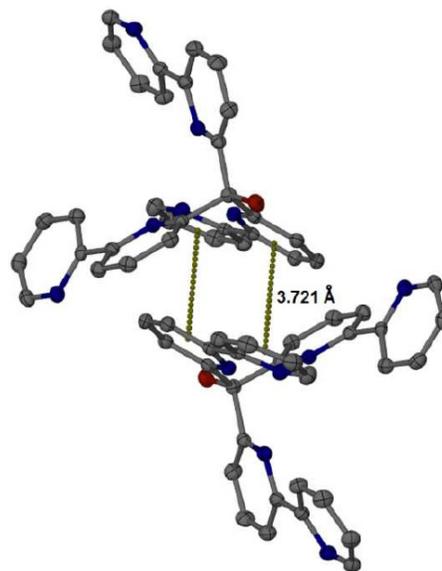
Fig. (4). Fragment of the title structure, viewed along the c-axis showing the π-stacking interactions (gold dotted lines) between symmetrically related molecules (symmetry code: 2-x, 1-y, -z) which support the molecular packing. Hydrogen atoms have been excluded for clarity.

The ^{1}H NMR 2-D COSY spectra of both the monoprotonated and neutral forms of **1** were measured in order to elucidate the coupling behaviour within the aromatic region and thus unambiguously assign the resonances (Fig. **5** and Fig. **6**, respectively). First, one can note that the addition of a single proton to the tripod structure does not destroy the C_3 symmetry of the molecule and all bipyridyl moieties are still

Table 2.   H-bonding geometry (Å, °) for 1.

Donor --- H....Acceptor	D – H	H...A	D...A	D - H...A
Intra N(1)---H(1)....N(2)	0.88	2.29	2.667(3)	106
Intra N(1)---H(1)....N(3)	0.88	2.33	2.852(3)	118
Intra N(1)---H(1)....N(5)	0.88	2.36	2.786(3)	110
O(1)---H(1A)....O(8)^i	0.84	1.83	2.649(3)	164
O(6)---H(6A)....O(7)	0.81(5)	2.06(5)	2.866(3)	176(5)
O(6)---H(6B)....O(3)	0.90(6)	2.23(6)	3.116(4)	166(5)
O(7)---H(7A)....N(4)^{ii}	0.90(5)	2.03(5)	2.917(3)	165(4)
O(7)---H(7B)....N(6)^{iii}	0.89(4)	2.07(4)	2.953(3)	170(4)
O(8)---H(8A)....O(5)	0.89(4)	1.99(5)	2.866(3)	168(4)
O(8)----H(8B)....O(2)^{iv}	0.88(4)	2.04(4)	2.902(3)	165(4)

Symmetry codes: *i* = ½+x, ½-y, ½+z, *ii* = x, -y, z-1/2, *iii* = x, 1-y, z-1/2, *iv* = 3/2-x, ½+y, -z-1/2
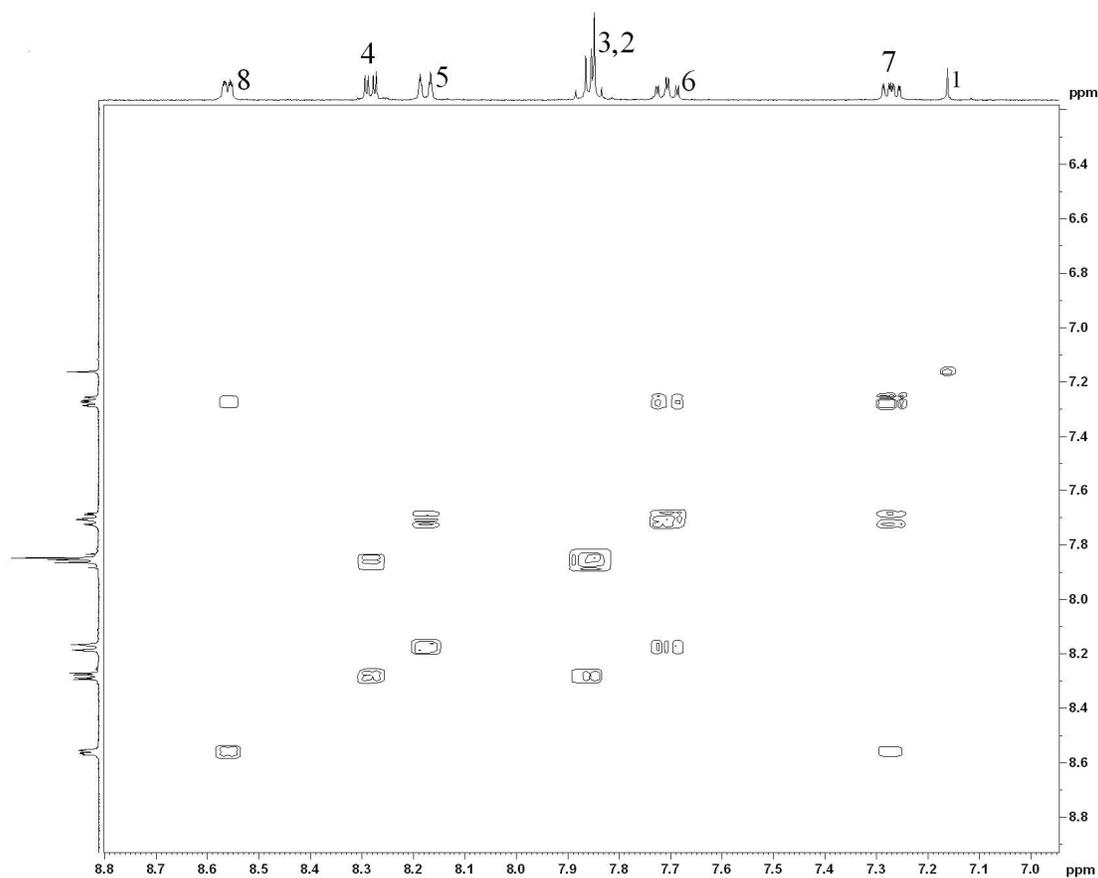
Fig. (5). A COSY map showing the expanded aromatic region of the neutral unprotonated ligand taken at 293K in CD_3CN.

equivalent. This would be consistent with fluxional behaviour of the proton, faster than the NMR timescale. Also, whilst the proton resonance frequencies for both the monoprotonated and neutral ligand exhibit similar ordering, those of the protonated form are shifted slightly downfield as one would expect from the deshielding effect of adding a proton to the pyridine ring [21].

In both cases, there exists strong coupling between vicinal protons around each of the pyridine groups. This allow us to unambiguously group the resonances for each pyridyl ring ((H_2, H_3, H_4,) vs (H_5, H_6, H_7, H_8)), when considering the cross peaks. By then assigning the peak which the highest ppm to H_8 (ortho to the nitrogen atom), this allows the full assignment of all peaks. This is particularly useful in
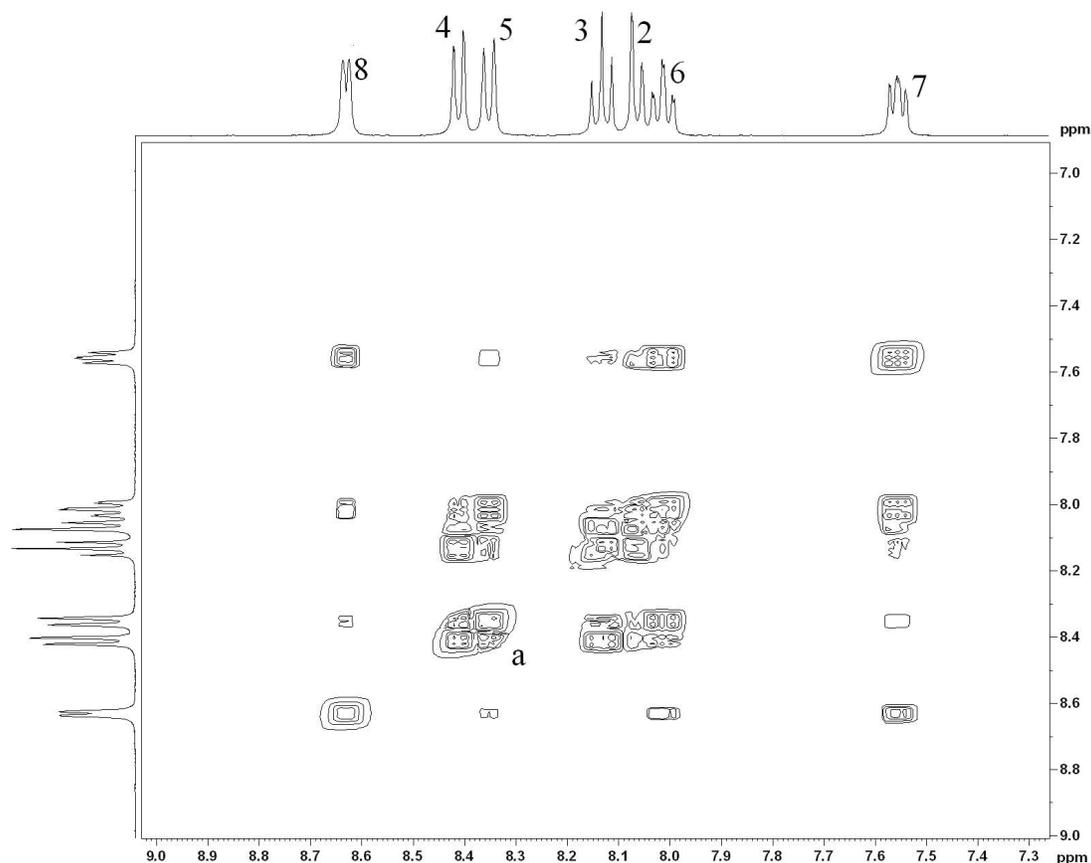
Fig. (6). A COSY map showing the expanded aromatic region of the protonated ligand taken at 293K in CD_3CN.

discriminating between H_4 and H_5 as well as H_3 and H_6. This allows us to determine that the relative ordering of all resonances is unchanged between the protonated and free ligand and suggests there is no preferencial localisation of the proton on one of the two different pyridyl rings.

The protonated ligand also reveals evidence of long range coupling between the two pyridines, which are in a *cisoid* arrangement, specifically through H_4 and H_5 (labelled a).

CONCLUSION

In conclusion, we have shown that the solid state structure of the protonated form of the ligand L^1 has a structure consisting of the three bipyridyl moieties connected to a central carbon. The pyridyl rings connected directly to the central carbon all having their nitrogen donor pointing to the centre of the molecule, perhaps suggesting they all interact with the proton. The other three nitrogen donors on the outermost pyridines vary in their behaviour, with two having a transoid arrangement within the bipyridine moieties and one being *cis*. However, this asymmetric arrangement is not observed in the solution state as ^{1}H NMR identifies C_3 symmetry in the complex. COSY NMR has allowed us to unambiguously assign the proton resonances. Interestingly, the similar ordering of the resonances, in the free ligand compared to its protonated form, suggests little difference in the relative electron density within a compound.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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