Electronic Supplementary Material for CrystEngComm

Coordination behaviour and network formation with 4,4',6,6'-tetra-carboxy-2,2'-bipyridine and 4,4′-dicarboxy-2,2′-bipyridine ligands with rare and alkaline earth metals

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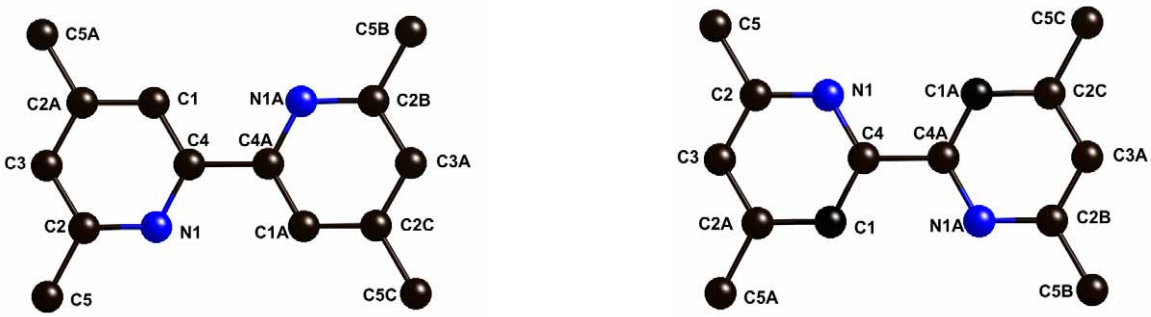
Electronic Supporting Information

Table S1 – Crystal data and structure refinement for **tmbp, 2 and 3.**

Identification code	**tmbp**	**2**	**3**
Empirical formula	$C_{14}H_{16}N_2$	$C_{32}H_{26}GdN_4O_{19}$	$C_{32}H_{27}N_4O_{19}Sm$
Formula weight	212.29	927.82	921.93
Temperature	153(2) K	153(2) K	153(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	*Cmca*	*P*-1	*P*-1
Unit cell dimensions	a = 15.792(1) Å	a = 10.4012(6) Å	a = 10.3547(7) Å
	b = 6.3149(5) Å	b = 10.5076(6) Å	b = 10.6536(7) Å
	c = 11.972(1) Å	c = 16.5788(9) Å	c = 16.651(1) Å
	α = 90°	α = 97.012(1)°	α = 97.717(2)°
	β = 90°	β = 105.144(1)°	β = 104.506(2)°
	γ = 90°	γ = 94.794(1)°	γ = 94.626(2)°
Volume	1193.9(2) $Å^3$	1723.3(2) $Å^3$	1749.7(2) $Å^3$
Z	4	2	2
Density (calculated)	1.181 mg/m^3	1.788 mg/m^3	1.750 mg/m^3
Absorption coefficient	0.070 mm^{-1}	2.017 mm^{-1}	1.770 mm^{-1}
Crystal size (mm)	0.42	0.11	0.08
	0.23	0.07	0.04
	0.09	0.04	0.03
Theta range for data collection	2.58 to 24.99°	1.97 to 25.00°	1.28 to 25.00°
Reflections collected	4377	13800	14042
Independent reflections	551 [R_{int}=0.0205]	6043 [R_{int}=0.0478]	6144 [R_{int}=0.0814]
Max. and min. transmission	1.0000 and 0.7538	1.000 and 0.7296	1.0000 and 0.6946
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / Restraints / Parameters	551 / 0 / 40	6043 / 0 / 504	6144 / 0 / 505
Final R indices [I>2sigma(I)]	R1 = 0.0544	R1 = 0.0554	R1 = 0.0605
	wR2 = 0.1252	wR2 = 0.1195	wR2 = 0.1234
R indices (all data)	R1 = 0.0555	R1 = 0.0724	R1 = 0.0993
	wR2 = 0.1260	wR2 = 0.1262	wR2 = 0.1444

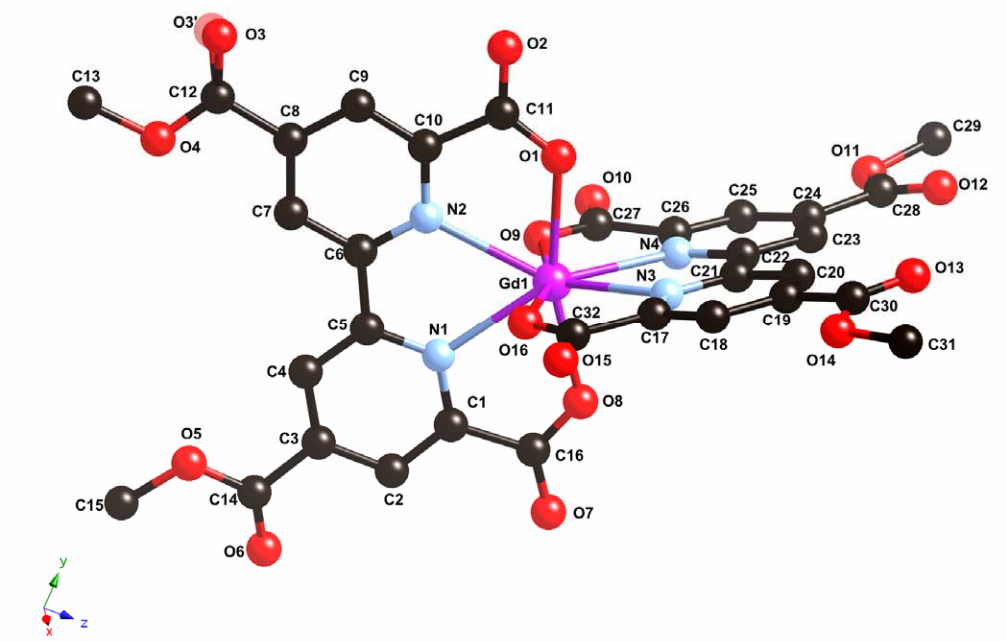
Fig S1. Structural description, molecular structure and atomic numbering scheme for **tmbp**.

The asymmetric unit contains five non hydrogen atoms. Generation of the mirror plane symmetry, that lies in the *yz* plane and is perpendicular to the plane formed by the atoms C3, C2, N1/C1, C4 and C5, creates half the molecule. Application of an inversion symmetry (that lies in the centre of the C4–C4A bond) results in the rest of the molecule being generated. As the carbon atoms C3 and C4 lie on the mirror plane, they are modelled at only half occupancy. Disorder is evident within the crystal structure with the molecule flipping between alternative positions. Consequently, the carbon atoms C1, C2 and C5 and the nitrogen atom N1 only partially occupy the sites. In 50 % of the unit cells the atoms are N1, C2 and C5 and in the remaining 50 % of the unit cells the atoms are C1, C2A and C5A. The two orientations of the ligand are highlighted below.



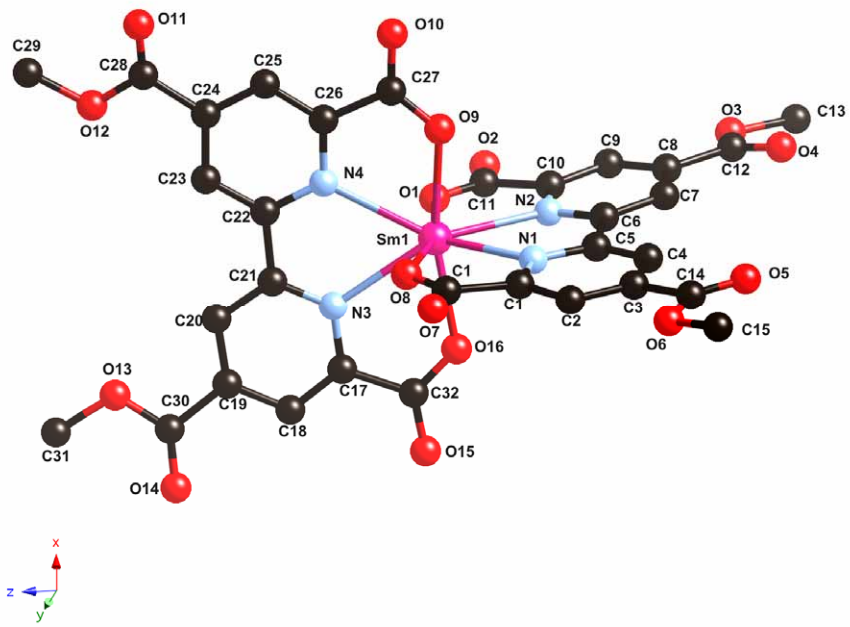
ESI Fig 1 – The structural anti conformations (a and b) of **tmbp** (C, black; N, blue).

Fig S2. Structural description, molecular structure and atomic numbering scheme for **2**. Hydrogen atoms and lattice hydronium ion and water molecules are omitted for clarity.



A 1:2 Gd(III) 4,4',6,6'-H_4tcbp complex has formed with the ligand chelating to the metal centre through its tetradentate bipyridyl-dicarboxylate binding core (N_2O_2), rendering the lanthanide centre eight coordinate. Akin to complex **1**, the carboxylic acid groups in the 4 and 4' positions have esterified to form peripheral methyl ester groups. Disorder is present in **2** at the oxygen atom O3; with O3 disordered over two positions modelled at an occupancy of 50 % at each position (O3 and O3'). Complex **2** is very similar to complex **1**. They appear to differ just by their lanthanide(III) centre and solvent molecules. Their unit cell dimensions and volume are very alike. Unfortunately, hydrogen atoms on the water molecules and the H_3O^+ counterion in **2** could not be modelled. For this reason hydrogen bonding between the discrete complex and solvent molecules is not discussed in detail, but examination proved it to be similar to complex **1**. Hydrogen atoms could not be modelled at fixed positions despite estimating where the positions could be by looking at the packing of the complex and seeing where potential hydrogen bonds lay.

Fig S3. Structural description, molecular structure and atomic numbering scheme for **3**. Hydrogen atoms and lattice hydronium ion and water molecules are omitted for clarity.



A 2:1 4,4',6,6'-H_4tcbp Sm(III) complex has formed with a coordination number of eight about the lanthanide centre. Once again, the peripheral carboxylic acid groups at the 4 and 4' positions of both ligands have esterified yielding methyl ester groups. Complex **3** is similar to both **1** and **2**. Due to the complex diffracting relatively weakly, the data obtained wasn't sufficiently good for hydrogen atoms on solvent water molecules or the H_3O^+ counterion to be modelled. Consequently, it wasn't possible to distinguish between the uncoordinated water molecules and the H_3O^+ counterion. As with **2**, in the absence of hydrogen atoms on the water molecules and the hydronium counterion, hydrogen bonding between the discrete $Sm(dmcdcbp)_2$ units through the solvent and counterion molecules could not be investigated.