

Supplementary Materials

Stabilisation of Exotic Tribromide (Br_3^-) Anions via Supramolecular Interaction with A Tosylated Macrocyclic Pyridinophane. A Serendipitous Case.

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Academic Editor: György Szöllösi

Received: 18 June 2020; Accepted: 08 July 2020; Published: date

Table of anion-ligand interactions for the crystal structures analysed in this work. Table of Hirshfeld surface data for the $(\text{H}_2\text{L-Ts})(\text{Br}_3)_{1.5}(\text{NO}_3)_{0.5}$ crystal structure. ¹H NMR spectrum of the ligand L showing the presence of ca. 2% impurity of L-Ts.

Table S1. Breakdown of main anion-ligand interactions contributing to H-bond tip and anion- π swoosh as found in crystal structures presented in Figures 11-14. Full information can be retrieved from original publications and/or directly from CSD database.

Crystal Structure (Figure)	Anion ^a	H-bond tip (contact distance range) ^{†b}	Anion- π swoosh (contact distance range) ^{†c}
HUDVOU (Fig. 11)	I ⁻ (1)	5 CH...I contacts (3.82-4.03)	1 anion- π contact (3.61)
AVISEE (Fig. 12)	HgBr ₄ ²⁻ (1)	3 CH...Br contacts (3.80-3.94) 8 NH...Br contacts (3.38-3.63)	1 anion- π contact (3.35)
AVISII (Fig. 12)	HgCl ₄ ²⁻ (1)	3 CH...Cl contacts (3.45-3.57) 6 NH...Cl contacts (3.23-3.49)	1 anion- π contact (3.13)
IDIJAJ (Fig. 12)	[Co(CN) ₆] ³⁻ (2) ^d	6 NH...N contacts (2.81-3.03) 6 OH...N contacts (2.68-2.84)	2 anion- π contacts (2.78-3.44)
YOJDAD (Fig. 13)	Br ₃ ⁻ (1)	4 CH...Br contacts (3.60-3.88)	3 anion- π contacts (3.25-3.83)
YOJDEH (Fig. 13)	BrIBr ⁻ (1)	4 CH...Br contacts (3.49-3.84) ^e	2 anion- π contacts (3.28-3.58) ^e
DETRIG (Fig. 14)	F ⁻ /FHF ⁻ (1 each)	10 CH...F contacts (3.25-3.54) 3 O _w H...F contacts (2.36-2.57)	1 anion- π contact (3.01)
DETMOH (Fig. 14)	Cl ⁻ (1)	3 CH...Cl contacts (3.52-3.71) 1 NH...Cl contact (3.06)	1 anion- π contact (3.31)
DETMUN (Fig. 14)	Br ⁻ (1)	5 CH...Br contacts (3.60-3.99) 1 NH...Br contacts (3.23)	1 anion- π contact (3.41)
KAMLOC (Fig. 14)	I ⁻ (2) ^d	5 CH...I contacts (4.01-4.22) 2 NH...I contacts (3.45-3.48)	2 anion- π contacts (3.67-3.70)

† All distances in Å; ^a number of non-equivalent anions within the crystal structure in brackets; ^b given distance range is intended as anion-heavy (non-hydrogen) atom distance; ^c all distances given as anion-centroid distances; ^d in these cases, qualitative image shown in the text represents the closest anion- π contact within the crystal structure; ^e contacts with I cannot be classified as short, yet CH...I and I- π interactions are still distinguishable in the fingerprint plot.

Table S2. Breakdown of $(\text{H}_2\text{L-Ts})^{2+}$ Hirshfeld surface in $(\text{H}_2\text{L-Ts})(\text{Br}_3)_{1.5}(\text{NO}_3)_{0.5}$ crystal structure

$(\text{H}_2\text{L-Ts})^{2+}$							
Inside Atom	Outside Atom						Total
	Br	S	N	H	O	C	
C	2.3	.	0.1	5.5	0.4	3.5	11.8
H	25.6	.	.	40.1	12.2	3.3	81.2
N	0.1	0.1	.	.	0.5	0.1	0.8
O	0.0	.	0.5	4.2	0.9	0.4	6.1
S	.	.	0.1	.	.	.	0.1
Total	28.1	0.1	0.7	49.8	14.1	7.3	

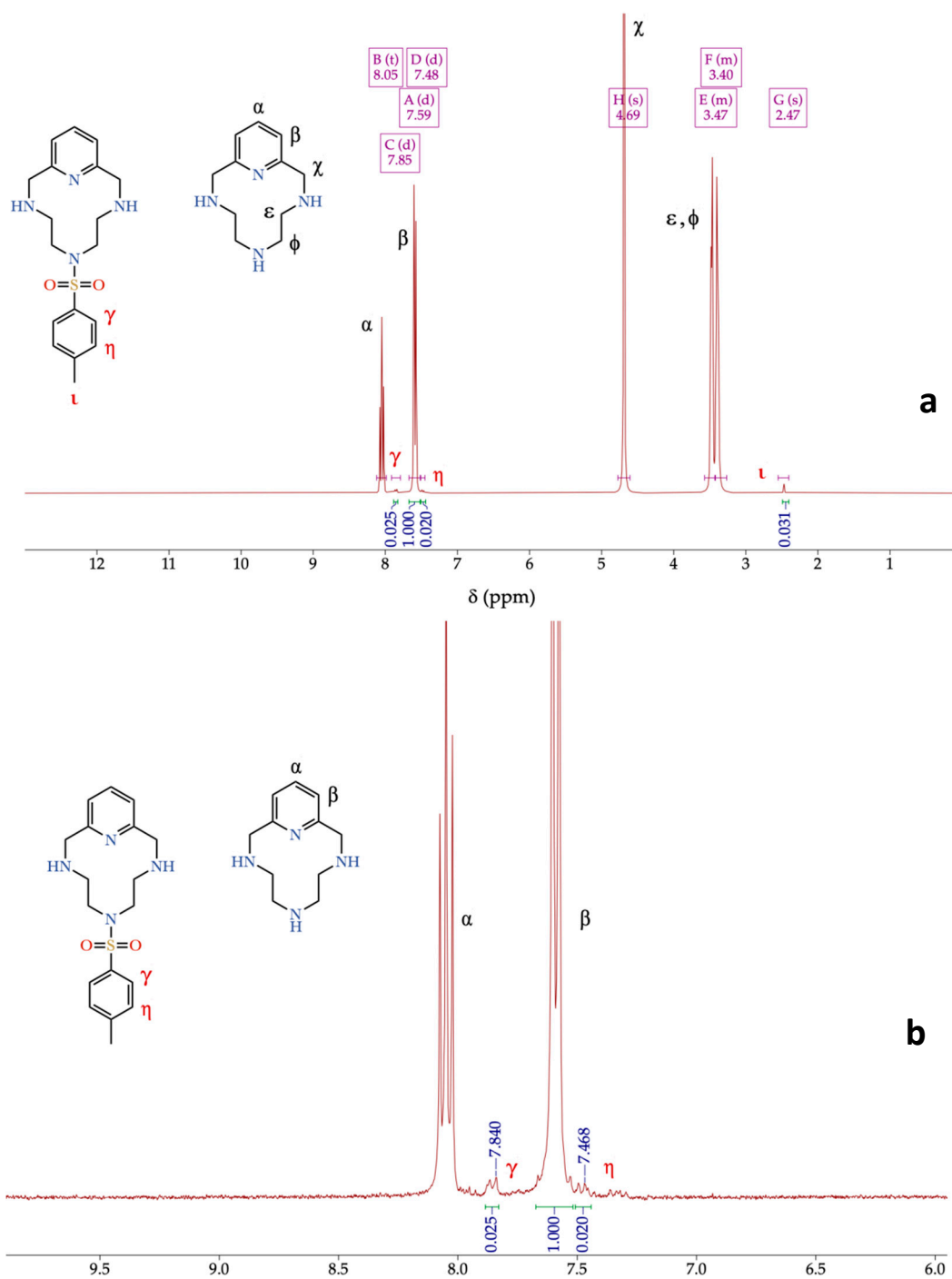


Figure S1. ^1H NMR spectrum recorded on a D_2O solution (pD ca. 3) of L-3HBr. a) Aliphatic and aromatic signals; b) an enlarged detail of aromatic signals. The spectrum allows to detect and quantify the presence of an impurity of L-Ts (monotosylated ligand) in about 2%.