

# Supplementary Material

## Exploring the Spatial Arrangement of Simple 18-Membered Hexaazatetraamine Macrocyclic Ligands in Their Metal Complexes

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**Figure S1.** Two examples of different conformations for the CPy-CH<sub>2</sub>-NH(2)-CH<sub>2</sub> branches of acetylpyridine residues S2

**Table S1.** Crystal data and structure refinement for L·12H<sub>2</sub>O, [DyL(OAc)<sub>2</sub>]OAc·7H<sub>2</sub>O·EtOH and [DyL<sup>Me2</sup>(Cl)<sub>2</sub>]Cl·2H<sub>2</sub>O. S3

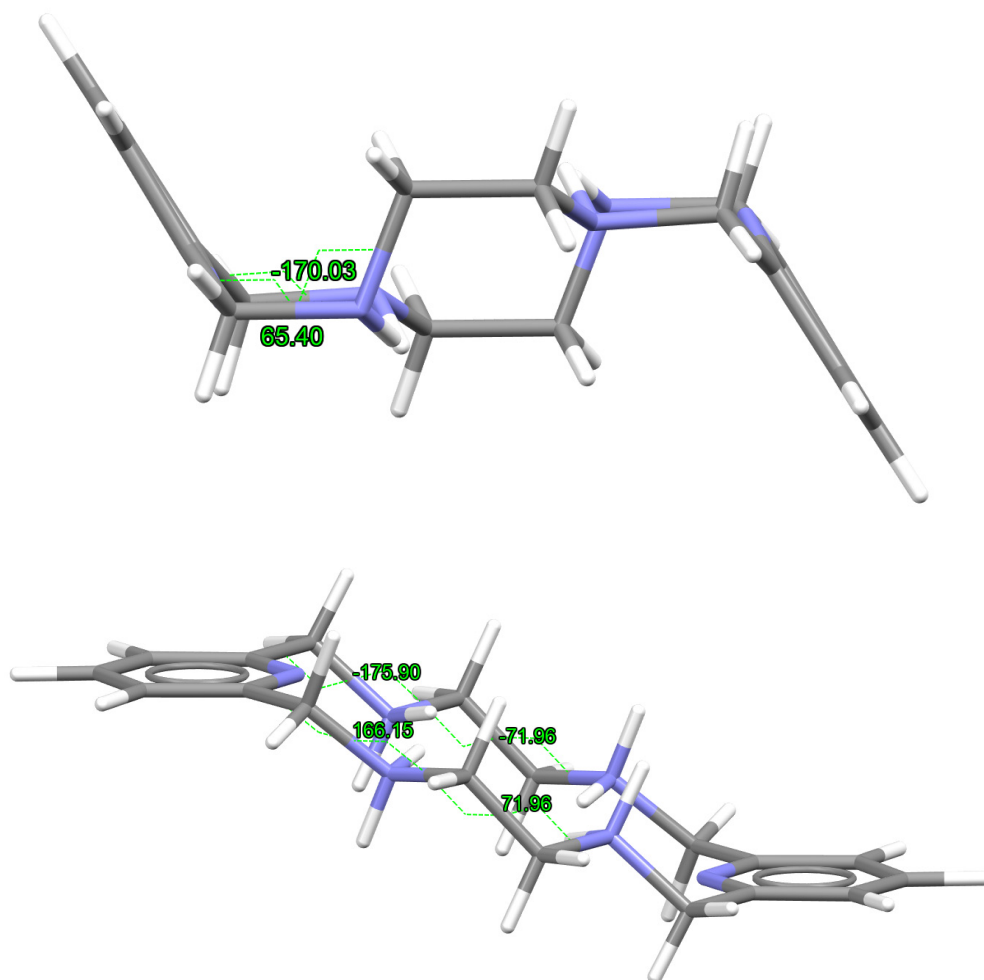
**Table S2.** Main bond distances (Å) and angles (°) for L·12H<sub>2</sub>O. S4

**Table S3.** Some relevant features for lanthanoid complexes of the hexaaza tetraamine ligands crystallographically characterized. S5

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**Table S5.** Main bond distances (Å) and angles (°) for [DyL(OAc)<sub>2</sub>]OAc·7H<sub>2</sub>O·EtOH and [DyL<sup>Me2</sup>(Cl)<sub>2</sub>]Cl·2H<sub>2</sub>O. S8

**Table S6.** SHAPE v2.1. Continuous Shape Measures Calculation (c) 2013 Electronic Structure Group, Universitat de Barcelona. S9



**Figure S1.** Two examples of different conformations for the  $C_{Py}-CH_2-NH_2-CH_2$  branches of acetylpyridine residues: (Top): Gauche and alternate conformations found for L in L·12H<sub>2</sub>O (this work); and bottom: Alternate and alternate for ZUVKUW [21].

**Table S1.** Crystal data and structure refinement for  $\text{L}^{\text{N6}} \cdot 12\text{H}_2\text{O}$ ,  $[\text{DyL}(\text{OAc})_2]\text{OAc} \cdot 7\text{H}_2\text{O} \cdot \text{EtOH}$  and  $[\text{DyL}^{\text{Me2}}(\text{Cl})_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ .

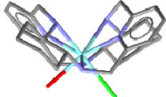
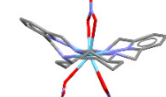
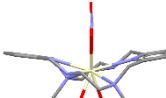
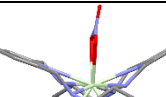
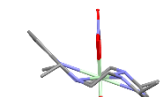
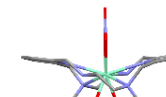
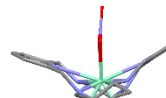
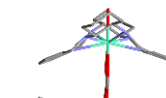
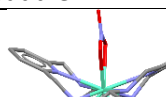
	$\text{L} \cdot 12\text{H}_2\text{O}$	$1 \cdot 7\text{H}_2\text{O} \cdot \text{EtOH}$	$2 \cdot 2\text{H}_2\text{O}$
Empirical formula	$\text{C}_{18}\text{H}_{50}\text{N}_6\text{O}_{12}$	$\text{C}_{24}\text{H}_{49}\text{DyN}_6\text{O}_{13}$	$\text{C}_{20}\text{H}_{34}\text{Cl}_3\text{DyN}_6\text{O}_2$
Molecular weight	542.64	792.19	659.38
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P-1$	$P-1$	$P2_1/n$
Wavelength ( $\text{\AA}$ )	0.71073	0.71073	0.71073
Crystal size ( $\text{mm}^3$ )	0.25 x 0.15 x 0.14	0.10 x 0.05 x 0.02	0.13 x 0.08 x 0.02
Color, shape	Colorless, prism	Pale yellow, plate	Colorless, plate
$T$ (K)	100	250	100
$a$ ( $\text{\AA}$ )	7.5502(4)	9.3422(4)	10.3146(8)
$b$ ( $\text{\AA}$ )	9.6015(5)	12.8831(7)	16.4037(13)
$c$ ( $\text{\AA}$ )	10.6416(5)	14.2999(7)	14.8724(11)
$\alpha$ ( $^\circ$ )	75.945(2)	78.827(2)	90
$\beta$ ( $^\circ$ )	78.182(2)	80.662(2)	91.920(3)
$\gamma$ ( $^\circ$ )	85.489(2)	88.660(2)	90
Volume ( $\text{\AA}^3$ )	732.15(6)	1666.03(14)	2515.0(3)
$Z$	1	2	4
Absorpt. coef. ( $\text{mm}^{-1}$ )	0.102	2.310	3.319
Reflections collected	26696	98996	155377
Independent reflections	3631 [ $R_{\text{int}} = 0.0461$ ]	8256 [ $R_{\text{int}} = 0.0842$ ]	13578 [ $R_{\text{int}} = 0.0445$ ]
Data / restraints / param.	3631 / 0 / 163	8256 / 0 / 400	7688 / 0 / 301
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0420$ $wR_2 = 0.1069$	$R_1 = 0.0315$ $wR_2 = 0.0600$	$R_1 = 0.0159$ $wR_2 = 0.01594$
$R$ indices (all data)	$R_1 = 0.0603$ $wR_2 = 0.1151$	$R_1 = 0.0424$ $wR_2 = 0.0636$	$R_1 = 0.0190$ $wR_2 = 0.0402$

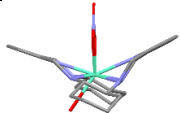
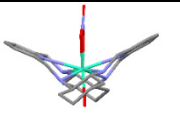
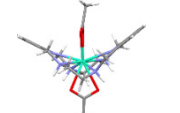
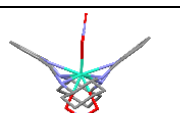
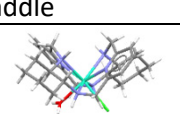
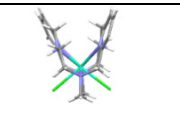
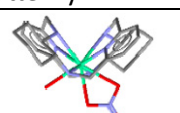
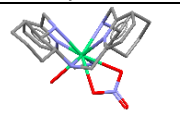
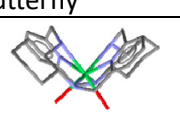
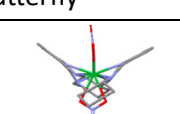
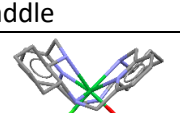
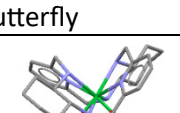
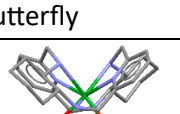
**Table S2.** Main bond distances (Å) and angles (°) for L·12H<sub>2</sub>O.

C1-N1	1.4752(17)	C1-C9#1	1.5142(18)
C2-N1	1.4771(17)	C2-C3	1.5049(19)
C3-N2	1.3405(17)	C3-C4	1.3932(19)
C7-N2	1.3442(17)	C4-C5	1.385(2)
C8-N3	1.4765(17)	C5-C6	1.388(2)
C9-N3	1.4703(17)	C6-C7	1.3886(18)
		C7-C8	1.5117(19)
N1-C1-C9#1	110.94(11)	C4-C3-C2	121.82(12)
N1-C2-C3	109.65(11)	C5-C4-C3	118.52(13)
N2-C3-C4	122.24(12)	C4-C5-C6	119.32(12)
N2-C3-C2	115.84(11)	C5-C6-C7	118.83(13)
N2-C7-C6	121.99(12)	C6-C7-C8	122.91(12)
N2-C7-C8	115.01(11)	C1-N1-C2	110.97(10)
N3-C8-C7	112.56(10)	C3-N2-C7	119.02(11)
N3-C9-C1#1	111.61(11)	C9-N3-C8	112.02(10)

#1: -x+1,-y+2,-z

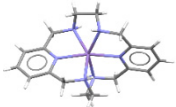

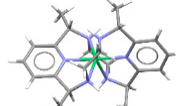
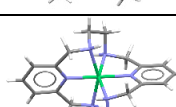
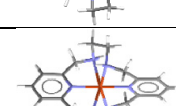
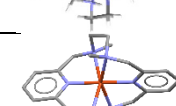
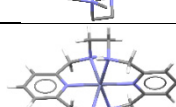
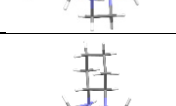
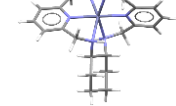
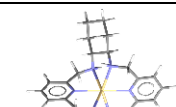
**Table S3.** Some relevant features for lanthanoid complexes of the hexaaza tetraamine ligands crystallographically characterized.

Complex / Counterion / Coord. No.	Chirality	Conformation of the ligand	Ln <sup>III</sup> Radius /Å [31-33]	Deviation from HP-6 ChMS / best ChMS geom.*	CSD- REFCOD Ref.
[Y <sup>L</sup> (H <sub>2</sub> O)Cl] <sup>2+</sup> / Cl <sup>-</sup> 8	C: <i>R,R,R,R</i> , N: <i>S,S,S,S</i>	 Butterfly	1.159 [33]	20.564 10.433 TPR	RIVQIY [7]
[La <sup>L</sup> (NO <sub>3</sub> ) <sub>3</sub> ] 11	C: <i>S,S,S,S</i> N: <i>R,R; R,S*</i>	 Saddle	1.16 [31], 1,250 [32]	2.123	PONZEX [5]
[Ce <sup>L</sup> (NO <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> / NO <sub>3</sub> <sup>-</sup> 10	N: <i>R',S; S,R'</i> 'Me substituted	 Saddle	1.143 [31], 1.220 [32]	4.552	DIJZEE [4]
[Pr <sup>L</sup> (H <sub>2</sub> O)(NO <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup> / NO <sub>3</sub> <sup>-</sup> 10	C: <i>R,R,R,R</i> , N: <i>R,S;S,R</i>	 Saddle	1.126 [31], 1.200 [32]	Pr1: 4.863 Pr2: 4.905	YIPHUB [9]
[Nd <sup>L</sup> (NO <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> / NO <sub>3</sub> <sup>-</sup> 10	C: <i>R,R;S,S</i> , N: <i>S,S;R,R</i>	 Wave	1.109 [31], 1.175 [32]	2.093	SICCOX [8]
[Sm <sup>L</sup> (NO <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> / NO <sub>3</sub> <sup>-</sup> 10	N: <i>R',S; S,R'</i> 'substituted	 Saddle	1.079 [31], 1.140 [32]	4.967	DIJZII [4]
[Sm <sup>L</sup> (H <sub>2</sub> O) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup> / NO <sub>3</sub> <sup>-</sup> 10	C: <i>R,R,R,R</i> , N: <i>R,S;S,R</i>	 Saddle		Sm1: 5.164 Sm2: 5.137	RIVQUK [7]
[Eu <sub>2</sub> (L <sup>cyh2</sup> ) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> (CO <sub>3</sub> ) <sub>3</sub> ] <sup>4+</sup> / Cl <sup>-</sup> 9	C: <i>R,R,R,R</i> , N: <i>R,S;S,R</i>	 Saddle	1.066 [31], 1.120 [32]	5.043	FOFBUA [6]
[Eu <sup>L</sup> (H <sub>2</sub> O)(NO <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup> / NO <sub>3</sub> <sup>-</sup> 10	C: <i>R,R,R,R</i> , N: <i>R,S;S,R</i>	 Saddle		Eu1: 5.197 Eu2: 5.238	YIPJAJ [9]

[EuL <sup>cyh2</sup> (H <sub>2</sub> O)(NO <sub>3</sub> )] <sup>2+</sup> / NO <sub>3</sub> <sup>-</sup> 9	C: <i>R,R; S,S</i> N: <i>R,S;S,R</i>	 Saddle		5.151	YIPJUD [7]
[TbL <sup>cyh2</sup> (H <sub>2</sub> O)(NO <sub>3</sub> )] <sup>2+</sup> / NO <sub>3</sub> <sup>-</sup> 9	C: <i>R,R,R,R</i> , N: <i>R,S;S,R</i>	 Saddle	1.040 [31], 1.090 [32]	5.329	RIVRAR [7]
[DyL(OAc) <sub>2</sub> ] <sup>+</sup> / AcO <sup>-</sup> 10	N: <i>R,S;S,R</i>	 Saddle	1.027 [31], 1.075 [32]	5.559	This work
[DyL <sup>cyh2</sup> (NO <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> / [Dy(NO <sub>3</sub> ) <sub>5</sub> ] <sup>2-</sup> 10	N: <i>R,S;R,S</i> N: <i>R,S;S,R</i>	 Saddle		Dy1: 6.086 Dy2: 5.781	YIPJEN [9]
[DyL <sup>cyh2</sup> (H <sub>2</sub> O)Cl] <sup>2+</sup> / Cl <sup>-</sup> 8	C: <i>R,R,R,R</i> , N: <i>S,S,S,S</i>	 Butterfly		20.479 10.542/TPR	FOFBOU [6]
[DyL <sup>Me2</sup> (Cl)] <sup>+</sup> / Cl <sup>-</sup> 8	N: <i>R',S; S,R'</i> 'substituted	 Butterfly		20.430 / 9.546 TPR	This work
[HoL <sup>cyh2</sup> (H <sub>2</sub> O)(NO <sub>3</sub> )] <sup>2+</sup> / NO <sub>3</sub> <sup>-</sup> 9	C: <i>R,R,R,R</i> , N: <i>S,S,S,S</i>	 Butterfly	1.015 [31], 1.055 [32]	11.871/TPR	RIVPOD [7]
[ErL <sup>cyh2</sup> (H <sub>2</sub> O)(NO <sub>3</sub> )] <sup>2+</sup> / NO <sub>3</sub> <sup>-</sup> 9	C: <i>R,R,R,R</i> , N: <i>S,S,S,S</i>	 Butterfly	1.004 [31], 1.040 [32]	11.875/TPR	RIVPUJ [7]
[TmL <sup>cyh2</sup> (H <sub>2</sub> O) <sub>2</sub> ] <sup>3+</sup> / NO <sub>3</sub> <sup>-</sup> 8	C: <i>R,R,R,R</i> , N: <i>S,S,S,S</i>	 Butterfly	0.994 [31], 1.025 [32]	21.873 11.375/TPR	RIVQAQ [7]
[YbL <sup>cyh2</sup> (NO <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> / [Yb(NO <sub>3</sub> ) <sub>5</sub> ] <sup>2-</sup> 10	C: <i>R,R,R,R</i> , N: <i>R,S;S,R</i>	 Saddle	0.985 [31], 1.010 [32]	Yb1: 6.317 Yb2: 6.036	YIPJIR [9]
[YbL <sup>cyh2</sup> (H <sub>2</sub> O)Cl] <sup>2+</sup> / Cl <sup>-</sup> 8	C: <i>R,R,R,R</i> , N: <i>S,S,S,S</i>	 Butterfly		20.354 12.801/TPR	RIVQOE [7]
[YbL <sup>cyh2</sup> (H <sub>2</sub> O) <sub>2</sub> ] <sup>2+</sup> / NO <sub>3</sub> <sup>-</sup> 8	C: <i>R,R,R,R</i> , N: <i>S,S,S,S</i>	 Butterfly		21.767 11.305/TPR	YIPJOX [9]
[LuL <sup>cyh2</sup> (H <sub>2</sub> O) <sub>2</sub> ] <sup>2+</sup> / NO <sub>3</sub> <sup>-</sup> 8	C: <i>R,R,R,R</i> , N: <i>S,S,S,S</i>	 Butterfly	0.977 [31], 0.995 [32]	21.963 11.242/TPR	RIVQEU [7]

\* Spacers separated by “;” if necessary ; HP-6 (1 D<sub>6h</sub> Hexagon); TPR-6 ( 4 D<sub>3h</sub> Trigonal prism)

**Table S4.** Some relevant features for 3d metal complexes of the hexaazatetraamine ligands crystallographically characterized.

Complex/ anion		Chirality	Conformation of the ligand	Deviation from HP6 ChMS / best ChMS geom.*	CSD- REFCOD/ Ref
[MnL] <sup>2+</sup> / Br <sub>4</sub> Mn <sup>2-</sup>		N: <i>R,R,R,R</i> ; Mn: <i>P</i>	twisted	25.391 6.925/OC	IGESIX [11]
[CoL <sup>Me4</sup> ] <sup>2+</sup> / Cl <sub>4</sub> Co <sup>2-</sup>		N: <i>R,R,R,R</i> ; Co: <i>P</i>	twisted	29.746 4.353/OC	BIHCEA10 [10]
[NiL <sup>Me4a</sup> ] <sup>2+</sup> / ClO <sub>4</sub> <sup>-</sup>		C: <i>R,S; R,S</i> ; <sup>**</sup> N: <i>R,R,R,R</i> , Ni: <i>P</i>	twisted	30.474 3.925/OC	KUBCUG [12]
[NiL] <sup>2+</sup> / ClO <sub>4</sub> <sup>-</sup>		N: <i>S,S,S,S</i> ; Ni: <i>M</i>	twisted	30.218 3.803/OC	WUCYCY [15]
[CuL] <sup>2+</sup> / ClO <sub>4</sub> <sup>-</sup>		N: <i>S,S,S,S</i> ; Cu: <i>M</i>	twisted	29.144 4.578/OC	WUCYIC [15]
[CuL <sup>Me4</sup> ] <sup>2+</sup> / Cl <sub>4</sub> Cu <sup>2-</sup>		N: <i>R,R,R,R</i> Cu: <i>P</i>	twisted	30.723 4.193/OC	BIHCIE10 [10]
[ZnL] <sup>2+</sup> / CF <sub>3</sub> O <sub>3</sub> S <sup>-</sup>		N: <i>R,R,R,R</i> ; Zn: <i>P</i>	twisted	27.611 5.266/OC	WIFWOX [13]
[ZnL <sup>cyh2</sup> ] <sup>2+</sup> / ClO <sub>4</sub> <sup>-</sup>		C: <i>R,R,R,R</i> ; N: <i>S,S,S,S</i> ; Zn: <i>P</i>	twisted	27.819 4.895/OC	PONYUM [5]
[CdL <sup>cyh2</sup> ] <sup>2+</sup> / ClO <sub>4</sub> <sup>-</sup>		C: <i>S,S,S,S</i> ; N: <i>R,R,R,R</i> , Cd: <i>M</i>	twisted	21.397 8.526/OC	PONZAT [5]
[CdL] <sup>2+</sup> / CF <sub>3</sub> O <sub>3</sub> S <sup>-</sup>		N: <i>S,S,S,S</i> Cd: <i>M</i>	twisted	21.503 8.744/OC	ZAXMUG [14]

\* HP-6 (1 D<sub>6h</sub> Hexagon); OC ( Octahedron);

\*\* Spacers separated by “;” if necessary.

**Table S5.** Main bond distances (Å) and angles (°) for [DyL(OAc)<sub>2</sub>]OAc·7H<sub>2</sub>O·EtOH and [DyL<sup>Me2</sup>(Cl)<sub>2</sub>]Cl·2H<sub>2</sub>O.

	[DyL(OAc) <sub>2</sub> ]OAc·7H <sub>2</sub> O·EtOH	[DyL <sup>Me2</sup> (Cl) <sub>2</sub> ]Cl·2H <sub>2</sub> O
Dy1-N1	2.609(3)	2.6186(13)
Dy1-N2	2.536(2)	2.5079(13)
Dy1-N3	2.564(2)	2.5064(13)
Dy1-N4	2.644(3)	2.6326(13)
Dy1-N5	2.565(3)	2.4903(13)
Dy1-N6	2.559(3)	2.5096(13)
Dy1-O1	2.437(2)	-
Dy1-O2	2.504(2)	-
Dy1-O3	2.438(2)	-
Dy1-O4	2.577(2)	-
Dy1-Cl1	-	2.6523(4)
Dy1-Cl2	-	2.6196(4)
N1-Dy1-N4	177.29(8)	155.43(4)
N2-Dy1-N5	145.77(8)	104.82(4)
N3-Dy1-N6	148.28(8)	108.12(4)
Cl1-Dy1-Cl2	-	101.626(14)

**Table S6.** SHAPE v2.1. Continuous Shape Measures Calculation (c) 2013 Electronic Structure Group, Universitat de Barcelona.

Geometries coordination number 10

HD-10	13 D4h	Hexadecahedron (2:6:2) or (1:4:4:1)
TD-10	12 C2v	Tetradecahedron (2:6:2)
SDD-10	11 D2	Staggered Dodecahedron (2:6:2)
JSPC-10	10 C2v	Sphenocorona J87
JATDI-10	9 C3v	Augmented tridiminished icosahedron J64
JMBIC-10	8 C2v	Metabidiminished icosahedron J62
JBCSAPR-10	7 D4d	Bicapped square antiprism J17
JBCCU-10	6 D4h	Bicapped cube J15
PAPR-10	5 D5d	Pentagonal antiprism
PPR-10	4 D5h	Pentagonal prism
OBPY-10	3 D8h	Octagonal bipyramid
EPY-10	2 C9v	Enneagonal pyramid
DP-10	1 D10h	Decagon

Geometries coordination number 8

ETBPY-8	13 D3h	Elongated trigonal bipyramid
TT-8	12 Td	Triakis tetrahedron
JSD-8	11 D2d	Snub diphendoid J84
BTPR-8	10 C2v	Biaugmented trigonal prism
JBTPR-8	9 C2v	Biaugmented trigonal prism J50
JETBPY-8	8 D3h	Johnson elongated triangular bipyramid J14
JGBF-8	7 D2d	Johnson gyrobifastigium J26
TDD-8	6 D2d	Triangular dodecahedron
SAPR-8	5 D4d	Square antiprism
CU-8	4 Oh	Cube
HBPY-8	3 D6h	Hexagonal bipyramid
HPY-8	2 C7v	Heptagonal pyramid
OP-8	1 D8h	Octagon

1·7H<sub>2</sub>O·EtOH

Structure [ML10]	HD-10	TD-10	SDD-10	JSPC-10	JATDI-10	JMBIC-100
	7.045,	4.325,	5.020,	3.565,	19.955,	7.562,
<b>JBCSAPR-10</b>	<b>JBCCU-10</b>	<b>PAPR-10</b>	<b>PPR-10</b>	<b>OBPY-10</b>	<b>EPY-10</b>	<b>DP-1</b>
<b>3.401,</b>	<b>9.794,</b>	<b>12.575,</b>	<b>12.420,</b>	<b>13.551,</b>	<b>25.275,</b>	<b>36.968</b>

2·2H<sub>2</sub>O

Structure [ML8 ]	ETBPY-8	TT-8	JSD-8	BTPR-8	JBTPR-8	JETBPY-8
	, 25.468,	13.941,	4.814,	3.062,	3.441,	27.792,
JGBF-8	<b>TDD-8</b>	SAPR-8	CU-8	HBPY-8	HPY-8	OP-8
14.761,	<b>2.479,</b>	3.486,	13.327,	17.158,	23.890,	29.436