Supplementary information for the paper

LANTHANIDE COMPLEXES BASED ON NEW BIS-CHELATING CARBACYLAMIDOPHOSPHATE (CAPh) SCORPIONATE LIKE LIGAND

by

- Iryna Olyshevets[a], Vladimir Ovchynnikov[a], Nataliia Kariaka[a], Viktoriya Dyakonenko[b], Svitlana Shishkina[b], Tatiana Sliva[a], Małgorzata Ostrowska[c], Aleksandra Jedyńczuk[c], Elżbieta Gumienna-Kontecka,[c] Vladimir Amirkhanov[a]

[a] Taras Shevchenko National University of Kyiv, Department of Chemistry, 64/13, Volodymyrska Street, Kyiv 01601, Ukraine

[b] Institute for Single Crystals, National Academy of Science of Ukraine, Nauky ave. 60, Kharkiv 61001, Ukraine

[c] Faculty of Chemistry, University of Wroclaw, F. Joliot-Curie 14, Wroclaw, 50383, Poland

Table S1. Crystallographic data for H_2L, NaHL·*i*-PrOH, $[Ln(HL)_2(NO_3)]$·*i*-PrOH.

Compounds	**H_2L**	**NaHL**· *i*-PrOH	**$[Tb(HL)_2(NO_3)]$**· *i*-PrOH	**$[Eu(HL)_2(NO_3)]$**· *i*-PrOH
Empirical formula	$C_{11}H_{19}N_5O_8P_2$	$C_{14}H_{26}NaN_5O_9P_2$	$C_{25}H_{44}N_{11}O_{20}P_4T$	$C_{25}H_{44}N_{11}O_{20}P_4E$
Formula weight	411.25	493.33	1101.51	1093.54
Temperature (K)	293	294	110	294
Crystal system	Monoclinic			
Space group	$P2_1/c$		$P\ 2_1/n$	
Unit cell dimensions				
a (Å)	8.9985(2)	13.740(2)	13.134(2)	13.3844(6)
b (Å)	11.8275(3)	17.912(3)	17.152(2)	17.2947(6)
c (Å)	17.5639(3)	9.9299(15)	19.453(3)	19.5123(8)
α (°)	90.00	90.00	90.00	90.00
β (°)	103.400(2)	108.507(16)	107.506(19)	106.525(5)
γ (°)	90.00	90.00	90.00	90.00
Volume ($Å^3$)	1818.43(7)	2317.5(6)	4179.6(12)	4330.2(3)
Z	4	4	4	4
D_{calc}(g/cm^3)	1.502	1.414	1.751	1.677
Absorption coefficient (mm^{-1})	0.290	0.260	1.935	1.683
F(000)		1032	2224	2212
Reflections collected/Independent	30070/5285	20367/5320	33047/7353	25701/8470
Reflections with I>2 *σ* (I)	3911	2506	4081	5974
R(int)	0.0291	0.1295	0.1810	0.0733
Goodness-of-fit on F2	1.070	1.027	0.983	1.032
Final R indices [I>2*σ* (I)]	$R_1 = 0.0498$, $wR_2 = 0.1299$	$R_1 = 0.0964$, $wR_2 = 0.1778$	$R_1 = 0.0790$, $wR_2 = 0.1685$	$R_1 = 0.0591$, $wR_2 = 0.1412$
R indices (all data)	$R_1 = 0.0710$, $wR_2 = 0.1378$	$R_1 = 0.2012$, $wR_2 = 0.2181$	$R_1 = 0.1448$, $wR_2 = 0.2068$	$R_1 = 0.0862$, $wR_2 = 0.1621$
CCDC	1984336	1984337	1984338	1984339

Table S2. Selected bond lengths (Å) and angles (°) for H_2L, NaHL·*i*-PrOH, $[Tb(HL)_2NO_3]$·*i*-PrOH and $[Eu(HL)_2NO_3]$·*i*-PrOH (Symmetry codes: (i) -*x*+1, -*y*+1, -*z*+1; (ii) *x*, -*y*+3/2, *z*+1/2,

H_2L			
P1—O1A	1.5836 (10)	P2—O6	1.5623 (16)
P1—O2A	1.5736 (10)	P2—O7	1.5453 (14)
P1—O3	1.4555 (14)	P2—O8	1.4580 (15)
P1—N1	1.6264 (18)	P2—N5	1.6544 (16)
P1—O1B	1.5760 (10)	O4—C3	1.203 (2)
P1—O2B	1.5824 (10)	O5—C9	1.226 (2)
NaHL·*i*-PrOH			
P1—O1	1.584 (5)	Na1—O3	2.374 (4)
P1—O2	1.552 (5)	Na1—O3^{i}	2.300 (4)
P1—O3	1.457 (4)	Na1—O4	2.399 (3)
P1—N1	1.597 (4)	Na1—O5^{ii}	2.345 (4)
P2—O6	1.547 (5)	Na1—O8	2.265 (4)
P2—O7	1.549 (5)	O4—C3	1.241 (5)
P2—O8	1.451 (4)	O5—C9	1.227 (6)
P2—N5	1.643 (4)		
O3^{i}—Na1—O3	83.00 (14)	O8—Na1—O3	137.90 (16)
O3—Na1—O4	79.16 (13)	O8—Na1—O3^{i}	103.28 (14)
O3^{i}—Na1—O5^{ii}	102.35 (15)	O8—Na1—O4	88.63 (13)
O5^{ii}—Na1—O3	123.73 (16)	O8—Na1—O5^{ii}	95.97 (15)
O5^{ii}—Na1—O4	89.54 (14)		
$[Tb(HL)_2NO_3]$·*i*-PrOH			
Tb1—O3	2.307 (7)	P2—O8	1.470 (8)
Tb1—O4	2.366 (8)	P2—N5	1.642 (9)
Tb1—O8	2.335 (7)	P3—O9	1.567 (10)
Tb1—O11	2.298 (6)	P3—O10	1.565 (10)
Tb1—O12	2.384 (7)	P3—O11	1.475 (8)
Tb1—O14	2.331 (8)	P3—N6	1.618 (11)
Tb1—O17	2.504 (8)	P4—O14	1.470 (8)
Tb1—O19	2.476 (8)	P4—O15	1.540 (9)
P1—O1	1.602 (8)	P4—O16	1.584 (8)
P1—O2	1.582 (7)	P4—N10	1.632 (9)
P1—O3	1.494 (9)	O4—C3	1.254 (12)
P1—N1	1.595 (9)	O5—C9	1.213 (11)
P2—O6	1.562 (8)	O12—C14	1.256 (13)
P2—O7	1.537 (8)	O13—C20	1.217 (14)
$[Eu(HL)_2NO_3]$·*i*-PrOH			
Eu1—O3	2.328 (4)	P2—O8	1.458 (5)
Eu1—O4	2.362 (4)	P2—N1	1.636 (6)
Eu1—O8	2.372 (4)	P3—O9	1.574 (7)
Eu1—O11	2.332 (5)	P3—O10	1.538 (6)
Eu1—O12	2.412 (4)	P3—O11	1.486 (5)
Eu1—O16	2.370 (5)	P3—N6	1.599 (7)
Eu1—O17	2.525 (5)	P4—O14	1.540 (6)
Eu1—O19	2.513 (5)	P4—O15	1.480 (7)
P1—O1	1.574 (5)	P4—O16	1.472 (5)
P1—O2	1.571 (5)	P4—N10	1.614 (6)
P1—O3	1.489 (5)	O4—C3	1.278 (7)
P1—N5	1.590 (6)	O5—C9	1.228 (7)
P2—O6	1.577 (6)	O12—C14	1.264 (8)
P2—O7	1.511 (6)	O13—C20	1.208 (9)

Table S3. *Hydrogen-bond geometry (Å, º)* **for H_2L**, **NaHL·***i*-PrOH**, [Tb(HL)$_2$NO$_3$]·***i***-PrOH and **[Eu(HL)$_2$NO$_3$]·***i*-PrOH . Symmetry codes: (i) *x*, -*y*+1/2, *z*-1/2; (ii) *x*+1, -*y*+1/2, *z*+1/2, (iii) -*x*+2, -*y*+1, -*z*+1; (iv) *x*, -*y*+3/2, *z*-1/2,(vi) -*x*+3/2, *y*+1/2, -*z*+3/2; (vii) -*x*+1, -*y*+1, -*z*+1.

D—H···A	H···A , Å	D···A, Å	D—H···A, deg
H_2L			
N1—H1···O8^{i}	2.12 (3)	2.810 (2)	160 (3)
N2—H2···O8^{i}	2.39 (3)	3.038 (2)	142 (3)
N4—H4···O3^{ii}	2.08 (3)	2.859 (2)	160 (3)
N5—H5···N3	2.06 (3)	2.685 (2)	136 (2)
N5–H5…O4	2.43(3)	3.135(2)	150(2)
NaHL·*i*-PrOH			
N2—H2···O9^{iii}	2.04	2.885 (5)	167
N4—H4···O4^{iv}	2.00	2.857 (5)	171
N5—H5···N3	2.05	2.663 (5)	128
N5–H5…O4	2.44	3.242(4)	157
O9—H9···N1	2.02	2.834 (5)	175
D—H···A	H···A , Å	D···A, Å	D—H···A, deg
[Tb(HL)$_2$NO$_3$]·*i*-PrOH			
N2—H2···O5^{vi}	1.91	2.765 (11)	164
N5—H5···N3	1.90	2.601 (12)	135
N5–H5…O4	2.31	3.04(1)	141
N9—H9···O20^{vii}	2.06	2.891 (13)	156
N10—H10···N8	1.92	2.581 (13)	131
N10–H10…O12	2.33	3.06(1)	140
O20—H20···N6	2.01	2.826 (13)	163
[Eu(HL)$_2$NO$_3$]·*i*-PrOH			
N1—H1···N3	1.93	2.602 (7)	134
N1–H1…O4	2.34	3.067(6)	143
N4—H4···O5^{vi}	1.94	2.788 (7)	166
N9—H9···O20^{vii}	2.05	2.872 (8)	161
N10—H10···N8	1.93	2.607 (8)	135
N10–H10…O12	2.33	3.070(7)	144
O20—H20···N6	2.04	2.808 (9)	157

Table S4. Criteria for coordination polyhedron determination [i].

Polyhedron form	Angle (°)					
	δ_1 [°]	δ_2 [°]	δ_3 [°]	δ_4 [°]	φ	ω
Hoard's dodecahedron, D_{2d}	29.5	29.5	29.5	29.5	0	90
Bicapped trigonal prism, C_{2v}	0	21.7	48.2	48.2	16.1	-
Square antiprism, D_{4d}	0	0	52.5	52.5	24.7	79.3
[Tb(HL)$_2$NO$_3$]·*i*-PrOH	12.96	19.15	42.11	44.66	10.2	87.75
[Eu(HL)$_2$NO$_3$]·*i*-PrOH	11.95	20.15	41.15	43.75	11.2	87.55

Table S5. Determining the type of polyhedron using the SHAPE program*

NaHL·*i*-PrOH		**[Tb(HL)$_2$NO$_3$]·*i*-PrOH**		**[Eu(HL)$_2$NO$_3$]·*i*-PrOH**	
PP-5	27.725	OP-8	29.268	OP-8	29.310
vOC-5	4.464	HPY-8	22.079	HPY-8	21.269
TBPY-5	2.944	HBPY-8	13.319	HBPY-8	13.278
SPY-5	3.162	CU-8	9.669	CU-8	10.110
JTBPY-5	5.538	SAPR-8	2.087	SAPR-8	2.229
		TDD-8	2.226	TDD-8	2.191
		JGBF-8	11.065	JGBF-8	11.549
		JETBPY-8	27.479	JETBPY-8	27.329
		JBTPR-8	2.584	JBTPR-8	2.649
		BTPR-8	2.253	BTPR-8	2.190
		JSD-8	3.145	JSD-8	3.240
		TT-8	10.493	TT-8	10.880
		ETBPY-8	22.115	ETBPY-8	22.236

* S H A P E v2.1. Continuous Shape Measures calculation, (c) 2013 Electronic Structure Group, Universitat de Barcelona. Contact: llunell@ub.edu

PP-5 D_{5h} Pentagon

vOC-5 C_{4v} Vacant octahedron

TBPY-5 D_{3h} Trigonal bipyramid

SPY-5 C_{4v} Spherical square pyramid

JTBPY-5 D_{3h} Johnson trigonal bipyramid J12

OP-8 D_{8h} Octagon

HPY-8 C_{7v} Heptagonal pyramid

HBPY-8 D_{6h} Hexagonal bipyramid

CU-8 O_h Cube

SAPR-8 D_{4d} Square antiprism

TDD-8 D_{2d} Triangular dodecahedron

JGBF-8 D_{2d} Johnson gyrobifastigium J26

JETBPY-8 D_{3h} Johnson elongated triangular bipyramid J14

JBTPR-8 C_{2v} Biaugmented trigonal prism J50

BTPR-8 C_{2v} Biaugmented trigonal prism

JSD-8 D_{2d} Snub diphenoid J84

TT-8 T_d Triakis tetrahedron

ETBPY-8 D_{3h} Elongated trigonal bipyramid

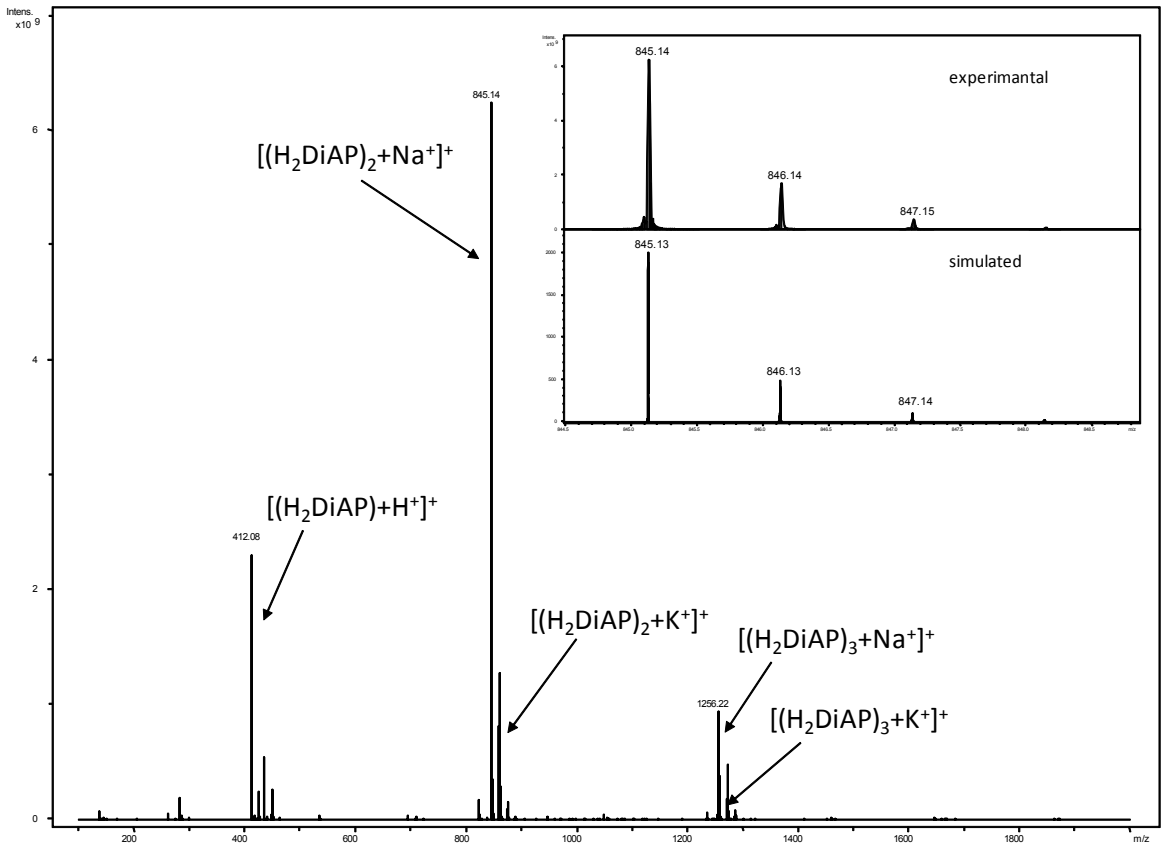
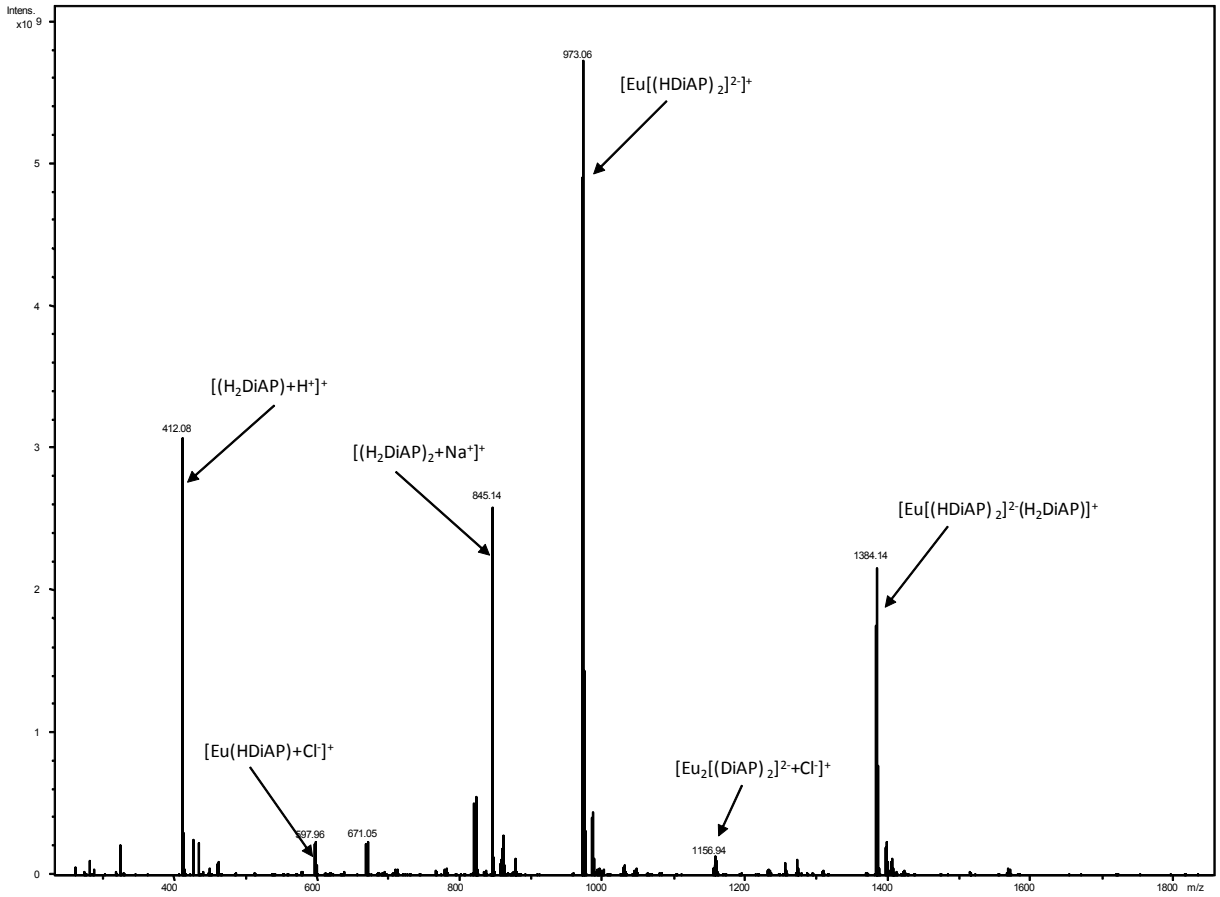


Fig. S1. ESI-MS spectra of H_2L system in methanol/water (1:1) solution.



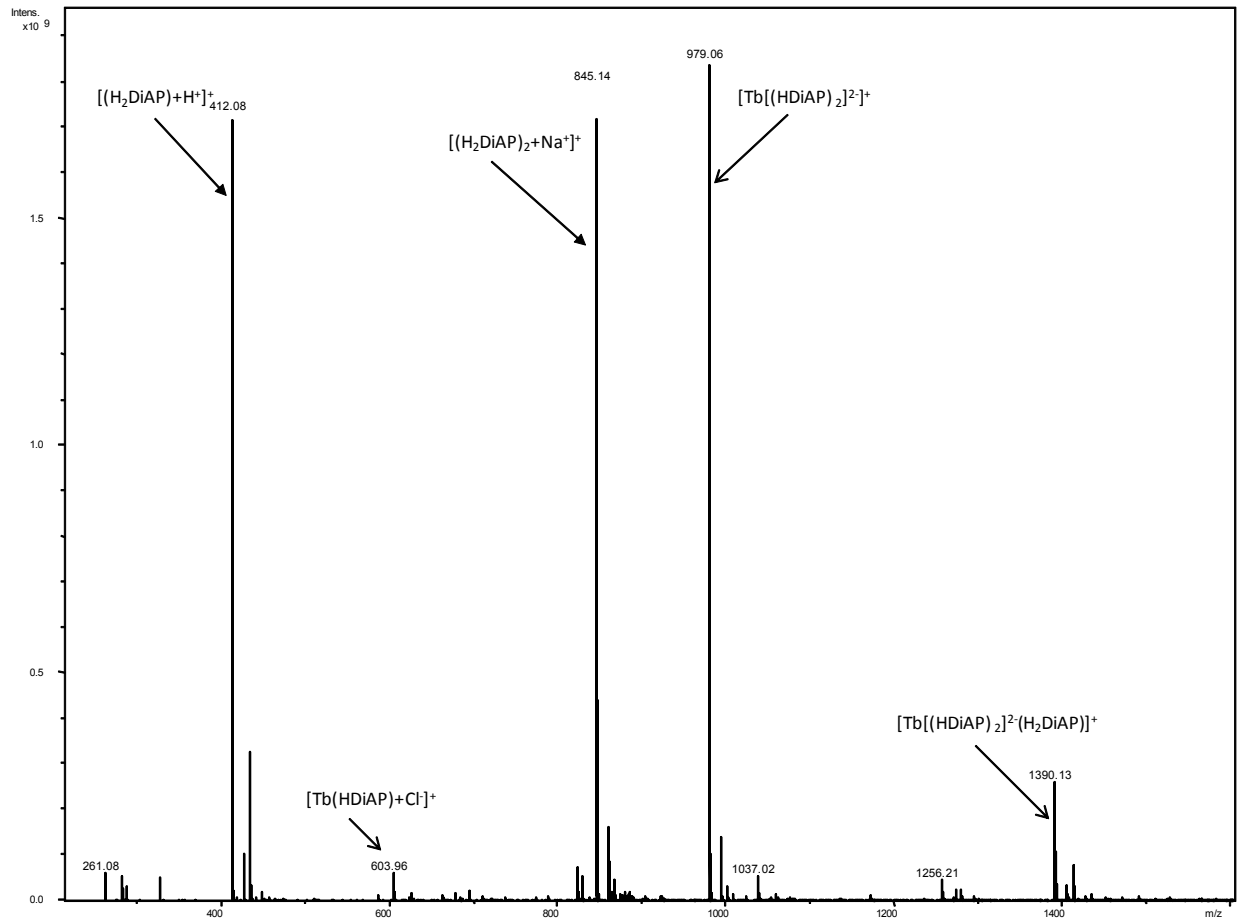


Fig. S2.ESI-MS spectra of the Eu(III)-H_2Land Tb(III)- H_2L systems(pH 3) in methanol/water (1:1)solution.

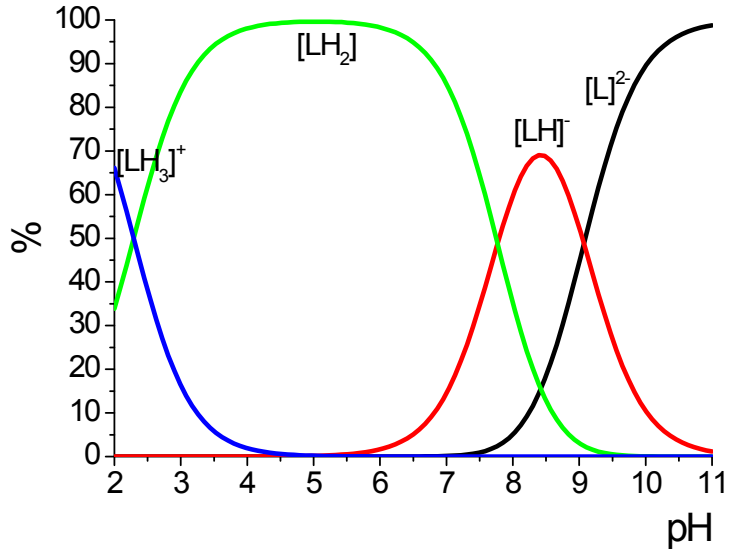


Fig. S3. Species distribution profiles for H_2DiAP. I = 0.1 M ($NaClO_4$), MeOH/H_2O 80:20 w/w, T = (25.0 ± 0.2) C.

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i M.A. Porai-Koshits, L.A. Aslanov. Some aspects of the stereochemistry of eight-coordinate complexes. *J. Struct. Chem.*, **1972**, 13, 244.