Protonation, coordination chemistry, cyanometallate "supercomplex" formation and fluorescence chemosensing properties of a bis(bipyridino)cyclophane receptor

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Crystals of **1** were of poor quality despite the fact that several attempts were made to obtain better quality crystals. The best crystal was measured at low temperature to minimize the thermal disorder. The remaining disorder can be attributed to the poor quality of the crystals as is reflected in the relatively high values calculated for R(int) and R(sigma) parameters.

Despite that, the structure presents no ambiguity in the position and type of all atoms present and the refinement is stable. Also, the uncertainty of the calculated distances lie within a reasonable values (precision of C-C bonds = 0.018 A as calculated by checkcif).

The quality of the reflections measured give as a result relatively high values of *R1* and *wR2* parameters and some alerts as well most of them related with the disorder. For those alerts we discard wrong assigned scattering type since there is no ambiguity in the atom type as can be compared with structure **2** and is consistent with the synthesis scheme reported. We discard as well errors in the model since there is no alert on space group assignation and there are no unassigned Q peaks.

Table S1: *Crystallographic data for (1) and (2)*

	(1)	(2)
Chemical formula	$C_{34}H_{48}N_{10}\cdot 2(ClO_4)\cdot 4(H_2O)$	$C_{34}H_{50}N_{10}\cdot Ru(CN)_6\cdot 10(H_2O)$
*M*r	867.79	1036.19
Cell setting space group	Monoclinic $P2_1/c$	Monoclinic $P\ 2_1/c$
T (K)	120 (2)	120 (2)
a (Å) *b* (Å) *c* (Å)	20.026 (4) 15.4487 (19) 14.706 (2)	18.4060 (4) 14.9168 (4) 20.8645 (8)
β (°)	108.555 (17)	121.577 (2)
V (Å^3)	4313.2 (12)	4880.3 (3)
Z	4	4
Radiation type	Mo *Kα*	Mo *Kα*
μ (mm^{-1})	0.22	0.39
Crystal size (mm)	0.16 × 0.10 × 0.09	0.24 × 0.19 × 0.14
h, *k*, *l* range	−25→25, −20→19, −19→18	−23→23, −18→18, −19→27

Absorption correction	multi-scan	multi-scan
T_{min}, T_{max}	0.965, 0.981	0.913, 0.945
$R($int)	0.111	0.034
$R[F^2 > 2ó(F^2)]$, $wR(F^2)$, S	0.131 0.473 0.97	0.038 0.103 0.88
Refl. measured Refl. unique	26286 9604	27703 10802
No. of parameters No. of restraints	539 11	735 0

Table S2: Geometric parameters for **1** (Å, °)

C1—N1	1.440(17)	C20—N7	1.497(12)
C1—C32	1.55(2)	N7—C22	1.476(12)
N1—C2	1.496(16)	N7—C21	1.500(13)
N1—H1F	0.89(2)	C22—C23	1.436(15)
C2—C3	1.442(15)	C23—N8	1.491(14)
C3—N2	1.450(12)	N8—C24	1.390(13)
N2—C5	1.464(12)	N8—H8F	0.89(2)
N2—C4	1.485(13)	N9—C25	1.306(16)
C5—C6	1.315(15)	N9—C29	1.333(13)
C6—N3	1.480(12)	C25—C26	1.395(16)
N3—C7	1.372(13)	C26—C27	1.346(15)
C7—C10	1.509(12)	C27—C28	1.380(16)
N4—C8	1.322(10)	C28—C29	1.411(16)
N4—C12	1.331(9)	C29—C33	1.433(18)
C8—C9	1.374(12)	N10—C33	1.367(14)
C9—C10	1.366(12)	N10—C30	1.40(2)
C10—C11	1.403(12)	C30—C31	1.37(2)
C11—C12	1.376(10)	C31—C32	1.375(19)
C12—C13	1.505(11)	C32—C35	1.414(19)
N5—C14	1.324(10)	C35—C33	1.427(18)
N5—C13	1.346(9)	Cl1—O11	1.301(9)
C13—C17	1.375(10)	Cl1—O14	1.362(9)
C14—C15	1.394(12)	Cl1—O12	1.371(11)
C15—C16	1.369(11)	Cl1—O13	1.378(9)
C16—C17	1.367(10)	Cl2—O24	1.261(11)
C16—C18	1.511(11)	Cl2—O23	1.313(12)
C18—N6	1.440(10)	Cl2—O22	1.334(10)
N6—C19	1.471(10)	Cl2—O21	1.381(19)
C19—C20	1.490(13)	O1—H1D	0.8447
O1—H1E	0.7935	O3—H3E	0.8755

O2—H2E	0.8794	O4—H4D	0.8145
O2—H2D	0.7521	O4—H4E	0.8575
O3—H3D	0.7521		
N1—C1—C32	114.3(13)	N6—C19—C20	109.3(8)
C1—N1—C2	115.3(13)	C19—C20—N7	113.0(8)
C1—N1—H1F	121(8)	C22—N7—C20	112.5(9)
C2—N1—H1F	95(8)	C22—N7—C21	108.4(10)
C3—C2—N1	114.6(11)	C20—N7—C21	110.9(8)
C2—C3—N2	111.3(10)	C23—C22—N7	114.2(11)
C3—N2—C5	115.2(9)	C22—C23—N8	109.8(9)
C3—N2—C4	107.6(11)	C24—N8—C23	110.5(10)
C5—N2—C4	109.4(10)	N8—C24—C27	112.6(10)
C6—C5—N2	118.5(10)	C25—N9—C29	114.8(12)
C5—C6—N3	116.2(10)	N9—C25—C26	124.6(12)
C7—N3—C6	117.7(11)	C27—C26—C25	122.1(14)
N3—C7—C10	112.5(9)	C26—C27—C28	114.2(15)
C8—N4—C12	117.9(7)	C26—C27—C24	127.7(16)
N4—C8—C9	123.5(9)	C28—C27—C24	118.1(13)
C10—C9—C8	119.1(9)	C27—C28—C29	121.1(12)
C9—C10—C11	118.3(9)	N9—C29—C28	123.2(13)
C9—C10—C7	121.1(11)	N9—C29—C33	113.4(13)
C11—C10—C7	120.6(11)	C28—C29—C33	123.4(13)
C12—C11—C10	118.3(8)	C33—N10—C30	117.0(16)
N4—C12—C11	122.9(8)	C31—C30—N10	126.8(17)
N4—C12—C13	115.7(7)	C30—C31—C32	118(2)
C11—C12—C13	121.4(8)	C31—C32—C35	116.2(19)
C14—N5—C13	116.6(7)	C31—C32—C1	119.6(19)
N5—C13—C17	122.2(7)	C35—C32—C1	124.1(13)
N5—C13—C12	116.4(7)	C32—C35—C33	125.1(14)
C17—C13—C12	121.4(7)	N10—C33—C35	116.8(17)
N5—C14—C15	124.2(8)	N10—C33—C29	117.6(16)
C16—C15—C14	118.2(8)	C35—C33—C29	125.6(12)

C17—C16—C15	118.0(8)	O11—Cl1—O14	116.2(8)
C17—C16—C18	122.1(8)	O11—Cl1—O12	104.1(10)
C15—C16—C18	119.8(8)	O14—Cl1—O12	108.7(8)
C16—C17—C13	120.7(8)	O11—Cl1—O13	110.0(9)
N6—C18—C16	110.9(7)	O14—Cl1—O13	112.0(7)
C18—N6—C19	115.7(8)	O12—Cl1—O13	104.9(10)
O22—Cl2—O21	97.5(10)	O24—Cl2—O23	114.3(9)
H1D—O1—H1E	97.3	O24—Cl2—O22	120.9(11)
H2E—O2—H2D	116.3	O23—Cl2—O22	114.6(8)
H3D—O3—H3E	111.0	O24—Cl2—O21	97.8(12)
H4D—O4—H4E	95.5	O23—Cl2—O21	107.3(13)

Table S3: Hydrogen-bond geometry for **1** (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1D···N4	0.84	2.07	2.910(8)	178
O1—H1E···O3	0.79	1.98	2.776(9)	178
O2—H2E···N5	0.88	2.09	2.973(12)	179
O2—H2D···O22^{i}	0.75	2.36	3.108(17)	179
O3—H3D···O13^{ii}	0.75	2.27	3.021(13)	179
O3—H3E···N9^{ii}	0.88	2.00	2.877(12)	180
O4—H4E···O23^{iii}	0.86	2.07	2.930(19)	179
N1—H1F···O1^{i}	0.89(2)	2.64(5)	3.478(12)	158(10)
N3—H3Y···O3^{i}	0.92	2.14	3.047(14)	167
N3—H3X···N2	0.92	2.24	2.742(11)	114
N6—H6C···N7	0.92	2.41	2.874(12)	112
N6—H6D···O4^{i}	0.92	2.49	3.362(16)	159
N8—H8F···O1	0.89(2)	2.58(9)	3.237(11)	132(9)

Symmetry codes: (i) *x*, −*y*+1/2, *z*+1/2; (ii) *x*, −*y*+1/2, *z*−1/2; (iii) −*x*+1, *y*+1/2, −*z*+1/2.

Table S4: Geometric parameters for **2** (Å, °)

N4—C8	1.339(4)	C22—C23	1.512(5)
N4—C12	1.350(4)	C23—H23A	0.89(4)
N5—C17	1.341(4)	C23—H23B	1.00(4)
N5—C13	1.349(4)	C24—C27	1.499(4)
N6—C18	1.485(4)	C25—C26	1.382(5)
N6—C19	1.493(4)	C26—C27	1.384(5)
N7—C22	1.426(4)	C26—H26	1.01(3)
N7—C20	1.472(4)	C27—C28	1.391(4)
N7—C21	1.486(5)	C28—C29	1.382(4)
N8—C23	1.489(4)	C29—C30	1.487(4)
N8—C24	1.492(4)	C30—C31	1.391(4)
N8—H8C	0.87(4)	C34—C33	1.381(4)
N8—H8D	0.86(3)	C33—C32	1.381(4)
N12—C25	1.337(4)	C32—C31	1.394(4)
N12—C29	1.350(4)	Ru1—C36	2.031(3)

N13—C30	1.338(4)	Ru1—C36^{i}	2.031(3)
N13—C34	1.349(4)	Ru1—C37^{i}	2.031(3)
N1—C1	1.484(4)	Ru1—C37	2.031(3)
N1—C2	1.495(4)	Ru1—C35^{i}	2.050(3)
N1—H1C	0.90(3)	Ru1—C35	2.050(3)
N1—H1D	0.88(4)	N36—C36	1.166(4)
N2—C4	1.458(4)	N35—C35	1.157(4)
N2—C3	1.466(4)	N37—C37	1.163(4)
N2—C5	1.469(4)	Ru2—C38^{ii}	2.034(3)
N3—C6	1.492(4)	Ru2—C38	2.034(3)
N3—C7	1.496(4)	Ru2—C40^{ii}	2.043(3)
N3—H3C	0.82(3)	Ru2—C40	2.043(3)
N3—H3D	0.86(3)	Ru2—C39^{ii}	2.049(3)
C1—C32	1.504(4)	Ru2—C39	2.049(3)
C2—C3	1.512(5)	N39—C39	1.156(4)
C2—H2A	1.02(3)	N40—C40	1.161(4)
C2—H2B	1.00(3)	N38—C38	1.151(4)
C5—C6	1.514(4)	O1—H1E	0.77(4)
C5—H5A	0.98(3)	O1—H1F	0.78(4)
C5—H5B	0.91(4)	O1—H1E	0.77(4)
C7—C10	1.504(4)	O1—H1F	0.78(4)
C7—H7A	1.07(3)	O2—H2E	0.817(18)
C7—H7B	0.93(3)	O2—H2F	0.800(19)
C10—C11	1.382(4)	O3—H3E	0.7515
C10—C9	1.398(4)	O3—H3F	0.7857
C11—C12	1.394(4)	O4—H4E	0.8280
C11—H11	0.9500	O4—H4F	0.8130
C9—C8	1.372(5)	O5—H5E	0.8074
C8—H8	0.96(3)	O5—H5F	0.8342
C12—C13	1.475(4)	O6—H6E	0.7702
C13—C14	1.390(4)	O6—H6F	0.8526
C17—C16	1.380(4)	O6—H6E	0.7702

C17—H17	0.98(3)	O6—H6F	0.8526
C16—C15	1.385(4)	O7—H7D	0.9773
C16—H16	1.02(3)	O7—H7C	0.9903
C15—C14	1.380(4)	O7—H7C	0.9903
C15—C18	1.507(4)	O7—H7D	0.9773
C18—H18A	0.90(3)	O8—H8E	0.9685
C18—H18B	0.90(3)	O8—H8F	0.9928
C19—C20	1.502(4)	O8—H8E	0.9685
C19—H19A	0.86(4)	O8—H8F	0.9928
C19—H19B	0.91(3)	O9—H9E	0.7791
O10—H10E	0.8435	O9—H9F	0.9215
O10—H10E	0.8435	O10—H10F	0.8232
O10—H10F	0.8232		
C8—N4—C12	117.2(3)	C20—C19—H19B	109(2)
C17—N5—C13	117.1(3)	H19A—C19—H19B	113(3)
C18—N6—C19	113.0(2)	N7—C20—C19	110.1(3)
C22—N7—C20	113.9(3)	N7—C22—C23	111.7(3)
C22—N7—C21	109.5(3)	N8—C23—C22	110.6(3)
C20—N7—C21	110.8(3)	N8—C23—H23A	106(2)
C23—N8—C24	112.0(2)	C22—C23—H23A	113(2)
C23—N8—H8C	111(2)	N8—C23—H23B	106(2)
C24—N8—H8C	114(2)	C22—C23—H23B	109.0(19)
C23—N8—H8D	109(2)	H23A—C23—H23B	111(3)
C24—N8—H8D	110.2(18)	N8—C24—C27	110.5(2)
H8C—N8—H8D	101(3)	N12—C25—C26	124.4(3)
C25—N12—C29	116.2(3)	C25—C26—C27	119.0(3)
C30—N13—C34	117.2(3)	C25—C26—H26	121(2)
C1—N1—C2	113.1(3)	C27—C26—H26	119(2)
C1—N1—H1C	107(2)	C26—C27—C28	117.5(3)
C2—N1—H1C	109(2)	C26—C27—C24	122.0(3)
C1—N1—H1D	110(3)	C28—C27—C24	120.5(3)
C2—N1—H1D	108(3)	C29—C28—C27	119.7(3)

H1C—N1—H1D	110(3)	N12—C29—C28	123.1(3)
C4—N2—C3	110.6(2)	N12—C29—C30	117.5(3)
C4—N2—C5	110.8(3)	C28—C29—C30	119.4(3)
C3—N2—C5	109.9(2)	N13—C30—C31	123.2(3)
C6—N3—C7	113.9(2)	N13—C30—C29	115.9(3)
C6—N3—H3C	110(2)	C31—C30—C29	120.9(3)
C7—N3—H3C	107(2)	N13—C34—C33	123.2(3)
C6—N3—H3D	107(2)	C34—C33—C32	119.5(3)
C7—N3—H3D	110(2)	C33—C32—C31	118.0(3)
H3C—N3—H3D	109(3)	C33—C32—C1	120.6(3)
N1—C1—C32	112.1(2)	C31—C32—C1	121.4(3)
N1—C2—C3	110.2(3)	C30—C31—C32	119.0(3)
N1—C2—H2A	104(2)	C15—C14—C13	119.8(3)
C3—C2—H2A	114(2)	C36—Ru1—C37^{i}	89.96(12)
N1—C2—H2B	106(2)	C36i—Ru1—C37^{i}	90.04(12)
C3—C2—H2B	110(2)	C36—Ru1—C37	90.05(12)
H2A—C2—H2B	112(3)	C36i—Ru1—C37	89.95(12)
N2—C3—C2	112.1(3)	C37i—Ru1—C37	179.997(1)
N2—C5—C6	113.7(3)	C36—Ru1—C35^{i}	88.48(11)
N2—C5—H5A	110.9(19)	C36i—Ru1—C35^{i}	91.52(11)
C6—C5—H5A	103.2(17)	C37i—Ru1—C35^{i}	92.55(11)
N2—C5—H5B	110(2)	C37—Ru1—C35^{i}	87.45(11)
C6—C5—H5B	108(2)	C36—Ru1—C35	91.52(11)
H5A—C5—H5B	110(3)	C36i—Ru1—C35	88.48(11)
N3—C6—C5	110.4(3)	C37i—Ru1—C35	87.45(11)
N3—C7—C10	109.6(2)	C37—Ru1—C35	92.55(11)
N3—C7—H7A	103.4(16)	N36—C36—Ru1	178.8(2)
C10—C7—H7A	110.7(18)	N35—C35—Ru1	177.9(3)
N3—C7—H7B	107.3(18)	N37—C37—Ru1	178.4(3)
C10—C7—H7B	113(2)	C38^{ii}—Ru2—C40^{ii}	91.06(11)
H7A—C7—H7B	113(3)	C38—Ru2—C40^{ii}	88.93(11)
C11—C10—C9	117.7(3)	C38^{ii}—Ru2—C40	88.94(11)

C11—C10—C7	121.5(3)	C38—Ru2—C40	91.07(11)
C9—C10—C7	120.8(3)	C38^{ii}—Ru2—C39^{ii}	91.96(11)
C10—C11—C12	120.2(3)	C38—Ru2—C39^{ii}	88.04(11)
C10—C11—H11	119.9	C40^{ii}—Ru2—C39^{ii}	86.10(12)
C12—C11—H11	119.9	C40—Ru2—C39^{ii}	93.90(12)
C8—C9—C10	118.6(3)	C38^{ii}—Ru2—C39	88.03(11)
N4—C8—C9	124.4(3)	C38—Ru2—C39	91.97(11)
N4—C8—H8	109(2)	C40^{ii}—Ru2—C39	93.90(12)
C9—C8—H8	126(2)	C40—Ru2—C39	86.10(12)
N4—C12—C11	121.8(3)	C39^{ii}—Ru2—C39	180.00(14)
N4—C12—C13	117.2(3)	N39—C39—Ru2	176.0(3)
C11—C12—C13	121.0(3)	N40—C40—Ru2	176.2(3)
N5—C13—C14	122.3(3)	N38—C38—Ru2	179.0(3)
N5—C13—C12	117.5(3)	H1E—O1—H1F	104(4)
C14—C13—C12	120.2(3)	H2E—O2—H2F	115(4)
N5—C17—C16	123.7(3)	H3E—O3—H3F	93.5
N5—C17—H17	114.7(19)	H4E—O4—H4F	101.3
C16—C17—H17	121.6(19)	H5E—O5—H5F	106.0
C17—C16—C15	119.0(3)	H6E—O6—H6F	110.6
C17—C16—H16	116.8(18)	H7D—O7—H7C	103.3
C15—C16—H16	124.1(18)	H8E—O8—H8F	117.7
C14—C15—C16	118.0(3)	H9E—O9—H9F	105.4
C14—C15—C18	121.7(3)	H10F—O10—H10E	100.8
C16—C15—C18	120.3(3)	H18A—C18—H18B	104(3)
N6—C18—C15	112.7(2)	N6—C19—C20	109.7(3)
N6—C18—H18A	105(2)	N6—C19—H19A	108(2)
C15—C18—H18A	115(2)	C20—C19—H19A	114(2)
N6—C18—H18B	106.5(18)	N6—C19—H19B	104(2)
C15—C18—H18B	113(2)		

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x, -y+1, -z$.

Table S5: Hydrogen-bond geometry for **2** (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1C···O2	0.90(3)	2.03(3)	2.862(3)	152(3)
N1—H1D···O6^{iii}	0.88(4)	1.91(4)	2.757(3)	161(3)
N3—H3C···O1	0.82(3)	1.92(3)	2.734(4)	173(3)
N3—H3D···N36^{iv}	0.86(3)	2.13(3)	2.914(4)	151(3)
N6—H6D···O5^{v}	0.92	1.81	2.693(3)	161
N6—H6C···O10	0.92	1.95	2.825(3)	158
N8—H8C···O4^{v}	0.87(4)	1.94(4)	2.794(4)	165(3)
N8—H8D···O10	0.86(3)	2.28(3)	3.054(3)	151(3)
O1—H1E···N12	0.77(4)	2.17(4)	2.934(4)	170(4)
O1—H1F···N40^{vi}	0.78(4)	2.20(4)	2.925(4)	155(4)
O2—H2E···N5	0.817(18)	2.08(2)	2.881(3)	168(4)
O2—H2F···N36^{iv}	0.800(19)	2.02(2)	2.801(4)	166(4)
O3—H3E···O2	0.75	2.15	2.866(3)	161
O3—H3F···N38	0.79	1.95	2.735(3)	176
O4—H4E···N4^{vii}	0.83	2.08	2.896(3)	167
O4—H4F···N35^{i}	0.81	2.09	2.897(3)	173
O5—H5E···N35^{i}	0.81	2.10	2.876(3)	162
O5—H5F···O3^{viii}	0.83	1.93	2.726(3)	158
O6—H6E···N40^{ii}	0.77	2.11	2.861(4)	167
O6—H6F···O9	0.85	1.84	2.679(3)	166
O7—H7C···N39	0.99	2.20	3.171(4)	166
O7—H7D···N38	0.98	2.29	3.175(5)	150
O8—H8E···O4	0.97	2.42	3.009(4)	119
O8—H8F···N37	0.99	2.54	3.012(4)	109
O9—H9E···N37	0.78	2.20	2.969(3)	171
O9—H9F···N39^{ix}	0.92	1.92	2.836(3)	172
O10—H10E···N37	0.84	2.08	2.908(4)	169
O10—H10F···N13	0.82	2.18	3.000(3)	174

Symmetry codes: (iii) $-x, y+1/2, -z+1/2$; (iv) $-x+1, -y+1, -z+1$; (v) $x, -y+1/2, z+1/2$; (vi) $x, -y+3/2, z+1/2$; (vii) $x, -y+1/2, z-1/2$; (i) $-x+1, -y, -z+1$; (viii) $-x+1, y-1/2, -z+1/2$; (ii) $-x, -y+1, -z$; (ix) $-x, y-1/2, -z+1/2$.

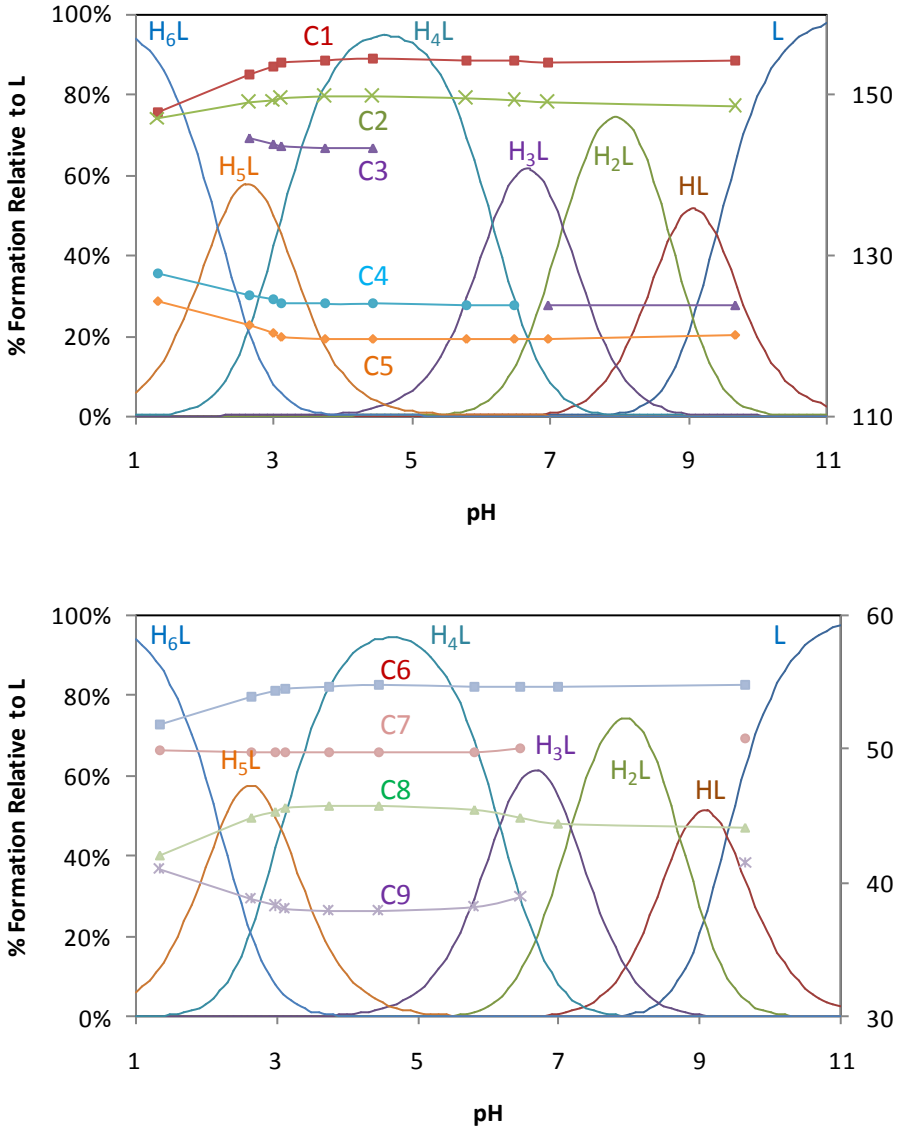

Figure S1.- ^{13}C NMR chemical shifts of L at various pD values in D_2O. Fitting of mole fractions of protonated species were calculated using the following values of Log K: 9.39, 8.73, 7.18, 6.17, 3.20 and 2.30.

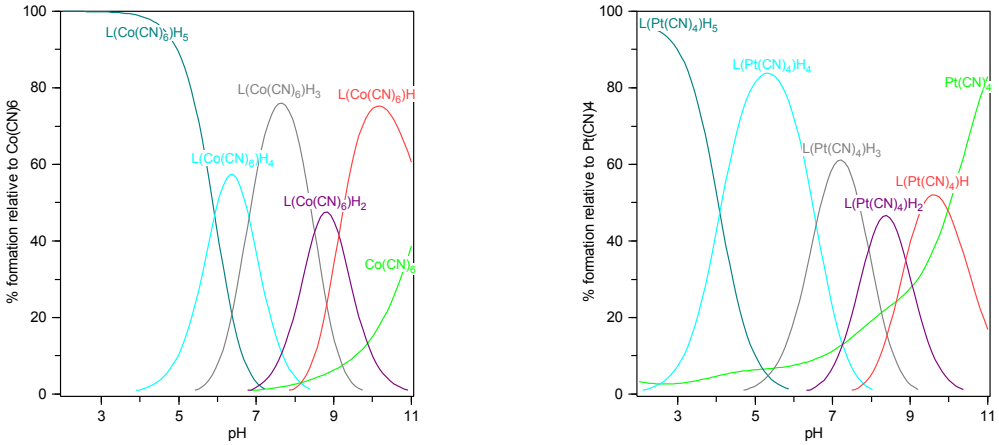

Figure S2.- Distribution diagrams of the species for the **L**/cyanide anion systems $Co(CN)_6^{3-}$ (left) and $Pt(CN)_4^{2-}$ (right) as a function of pH in aqueous solution in 0.15 M at 298.1 K; [L] = $[Co(CN)_6^{3-}]$ = $[Pt(CN)_4^{2-}]$ = 1×10^{-3} M;

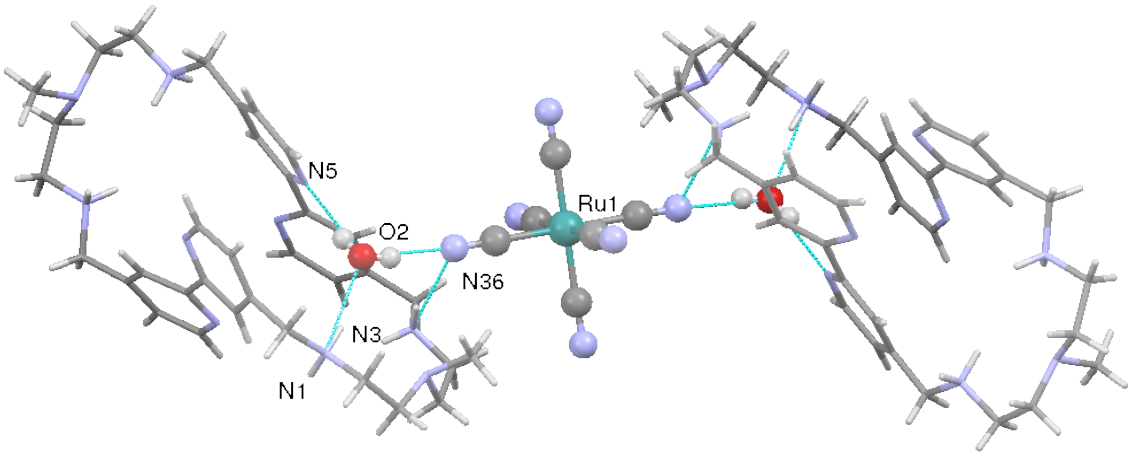

Figure S3.- Views of the hydrogen bond network interconnecting the cyanide anions with the macrocyclic units and the water molecules.

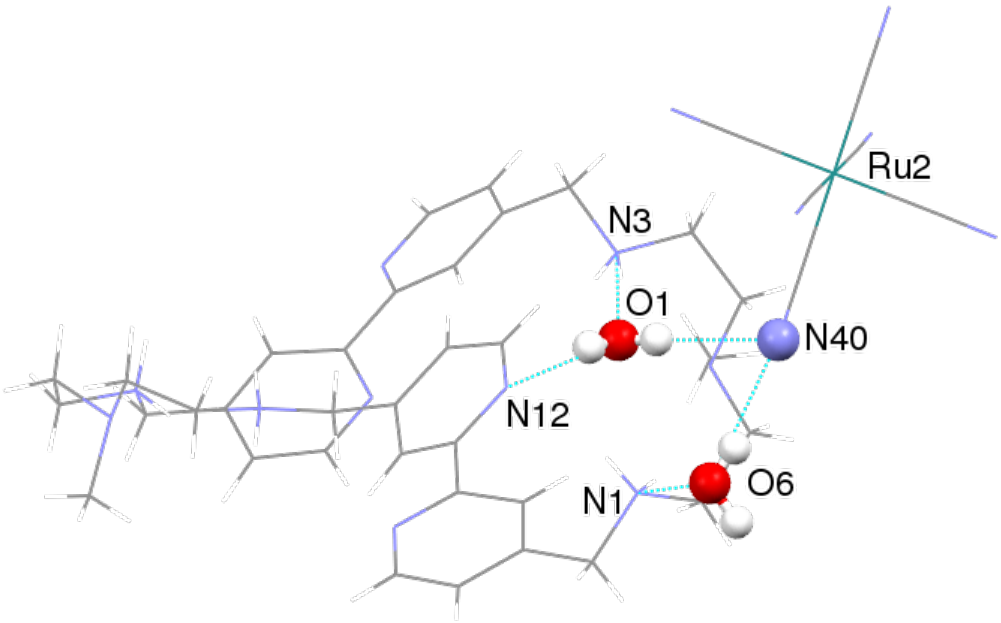

Figure S4.- Views of the hydrogen bond network interconnecting the water molecules with the macrocyclic units and the cyanide anions.

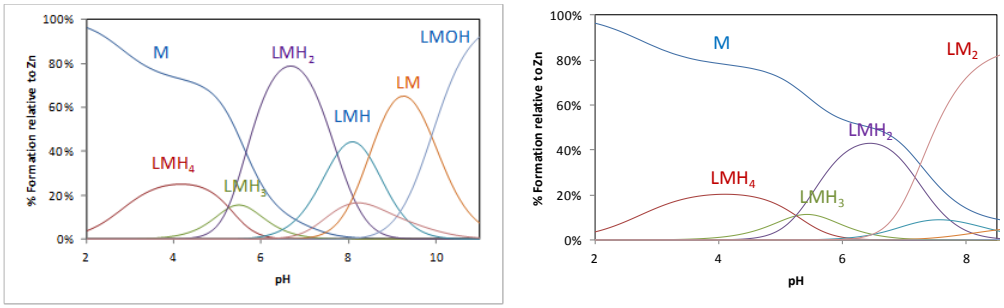

Figure S5.- Distribution diagrams of the species for the **L**/Zn^{+2} systems as a function of pH in aqueous solution in 0.15 M at 298.1 K; [L] = 1 × 10-3 M. (left) $[Zn^{+2}] = 1 \times 10^{-3}$ M, (right) $[Zn^{+2}] = 2 \times 10^{-3}$ M.

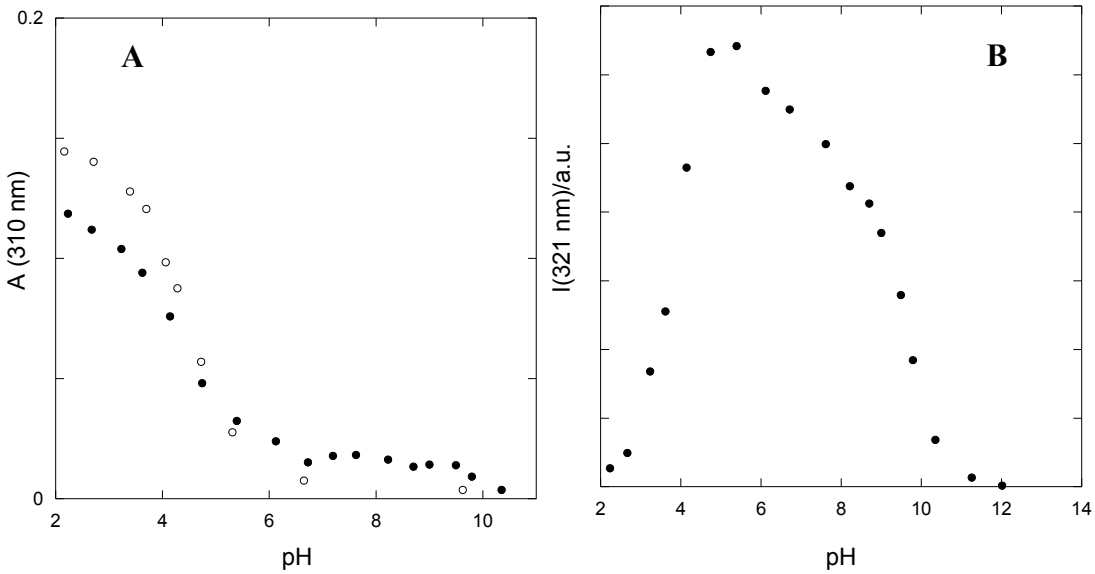

Figure S6.- A - Variation of absorbance at 310 nm as a function of pH for 2,2'-bipyridine in absence (o) and in presence of 1:1 molar ratio of Zn(II) (•) (9.4×10^{-6} M, 0.15 M NaCl, aqueous solution). B - Variation of emission at 321 nm (excitation at 286 nm) as a function of pH for 2,2'-bipyridine in presence of 1:1 molar ratio of Zn(II) (9.4×10^{-6} M, 0.15 M NaCl, aqueous solution).

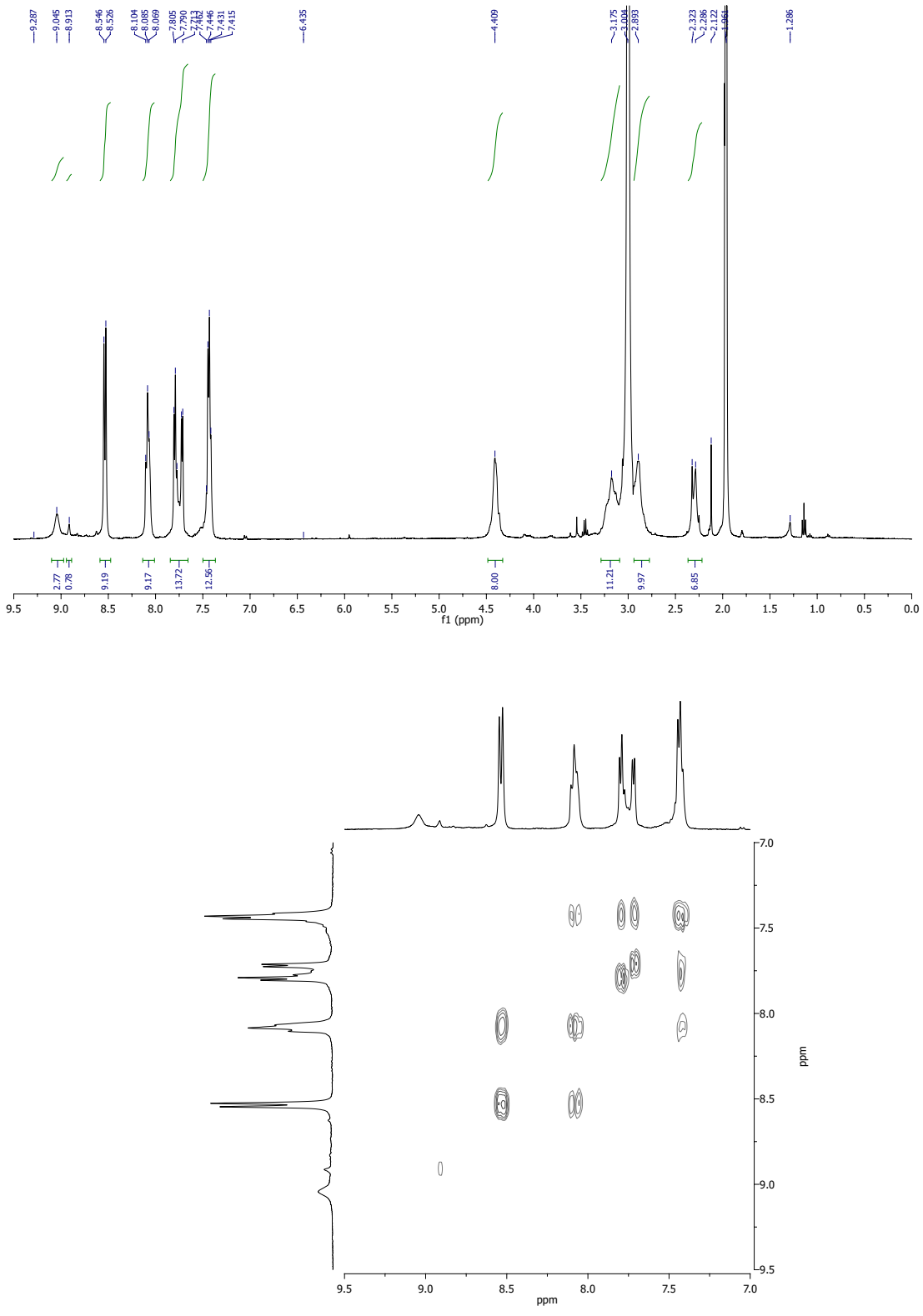

Figure S7.- ^{1}H NMR (top) and COSY (bottom) spectra of $[(Ru(bipy)_2)_2(\mathbf{L})]^{4+}$ in CD_3CN+NaOD, pD≈7, 400.13 MHz, 313 K.