ELECTRONIC SUPPLEMENTARY INFORMATION

Copper(II) Complexes of Quinoline Polyazamacroclyic Scorpiand-Type Ligands: X-Ray, Equilibrium and Kinetic Studies

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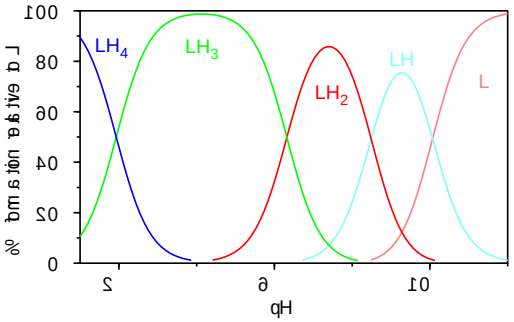

Figure S1. Distribution diagrams for the protonated species of **L1**.

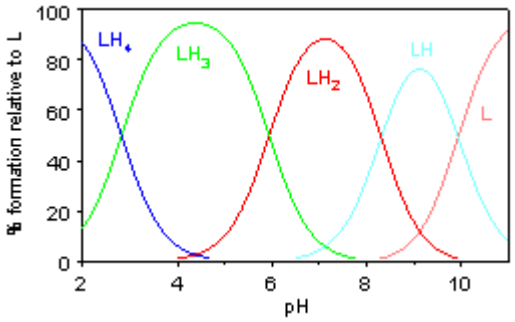

Figure S2. Distribution diagrams for the protonated species of **L2**.

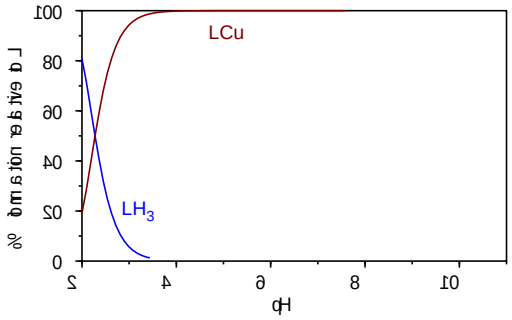

Figure S3. Distribution diagrams for the copper complexes of **L1**.

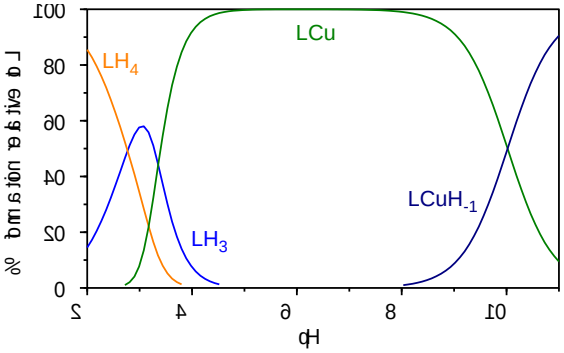

Figure S4. Distribution diagrams for the copper complexes of **L2**.

Table S1. Shift of the NMR Δ(Δδ) signals in ppm observed upon formation of the different protonated forms of the **L1** ligand.[a]

	Protonation process[b]			
NMR signal[c]	$L \rightarrow HL^{+}$	$HL^{+} \rightarrow H_2L^{2+}$	$H_2L^{2+} \rightarrow H_3L^{3+}$	$H_3L^{3+} \rightarrow H_4L^{4+}$
H1	0.32	0.26	0.51	-0.02
H2	0.46	0.31	0.21	-0.02
H3	0.61	0.19	0.02	-0.04
H4	0.36	0.17	0.16	-0.06
H5	0.21	0.13	0.52	0.07
H6	0.03	0.39	0.28	0.21
C1	-2.0	-0.9	0.6	0.0
C2	1.3	0.4	-1.0	-0.1
C3	-0.2	-1.5	-2.0	-0.1
C4	-0.3	-0.6	-1.8	-0.1
C5	-0.4	-0.6	-1.7	1.0
C6	0.8	-0.7	-2.8	-2.9

[o] The values are only approximate because the different protonated forms of the ligand usually do not reach 100% formation at any pH value. [b] The shifts in the signals were obtained from the spectra recorded at pD values where the different species reach its maximum concentration: 12.11 for L, 9.22 for HL^{+}, 7.53 for H_2L^{2+}, 4.10 for H_3L^{3+} and 0.93 for H_4L^{4+}. [c] For simplicity, only the most relevant proton and carbon signals are included.

Table S2. Shift of the NMR signals observed upon formation of the different protonated forms of the **L2** ligand.[a]

	Protonation process[b]			
NMR signal[c]	$L \rightarrow HL^{+}$	$HL^{+} \rightarrow H_2L^{2+}$	$H_2L^{2+} \rightarrow H_3L^{3+}$	$H_3L^{3+} \rightarrow H_4L^{4+}$
H1	0.43	0.42	0.33	-0.17
H2	0.55	0.33	0.24	-0.17
H3	0.59	0.14	0.08	-0.18
H4	0.41	0.11	0.17	-0.16
H5	0.25	0.03	0.60	-0.07
H6	0.00	0.08	0.71	0.11
C1	-1.4	-0.9	0.6	-0.3
C2	0.6	0.6	-0.8	-0.5
C3	-0.9	-2.1	-1.8	-0.3
C4	-0.1	-0.3	-3.8	-0.6
C5	-0.2	-0.5	-1.9	0.3
C6	0.1	-0.4	-0.8	-0.4

[a] The values are only approximate because the different protonated forms of the ligand usually do not reach 100% formation at any pH value. [b] The shifts in the signals were obtained from the spectra recorded at pD values where the different species reach its maximum concentration: 12.38 for L, 9.17 for HL^{+}, 7.36 for H_2L^{2+}, 4.34 for H_3L^{3+}, and 0.00 for H_4L^{4+}.[c] For simplicity, only the most relevant proton and carbon signals are included in the Table. Nevertheless, complete spectra can be found in ref 9.

Table S3. Selected bond lengths (Å) and angles (deg) for complex [Cu(**L1**)]$(ClO_4)_2 \cdot H_2O$.

Bond Distances (Å)		**Bond Angles**	
Cu1-N1	1.979(5)	N1-Cu1-N2	78.8(2)
Cu1-N2	2.309(6)	N1-Cu1-N3	91.8(2)
Cu1-N3	2.183(6)	N1-Cu1-N4	78.9(2)
Cu1-N4	2.276(6)	N1-Cu1-N5	175.0(3)
Cu1-N5	1.976(7)	N1-Cu1-N6	104.4(2)
Cu1-N6	2.173(5)	N2-Cu1-N3	81.1(2)
		N2-Cu1-N4	150.2(2)
		N2-Cu1-N5	98.9(3)
		N2-Cu1-N6	104.0(2)
		N3-Cu1-N4	80.0(2)
		N3-Cu1-N5	83.5(3)
		N3-Cu1-N6	163.7(2)
		N4-Cu1-N5	101.6(3)
		N4-Cu1-N6	100.5(2)
		N5-Cu1-N6	80.4(2)

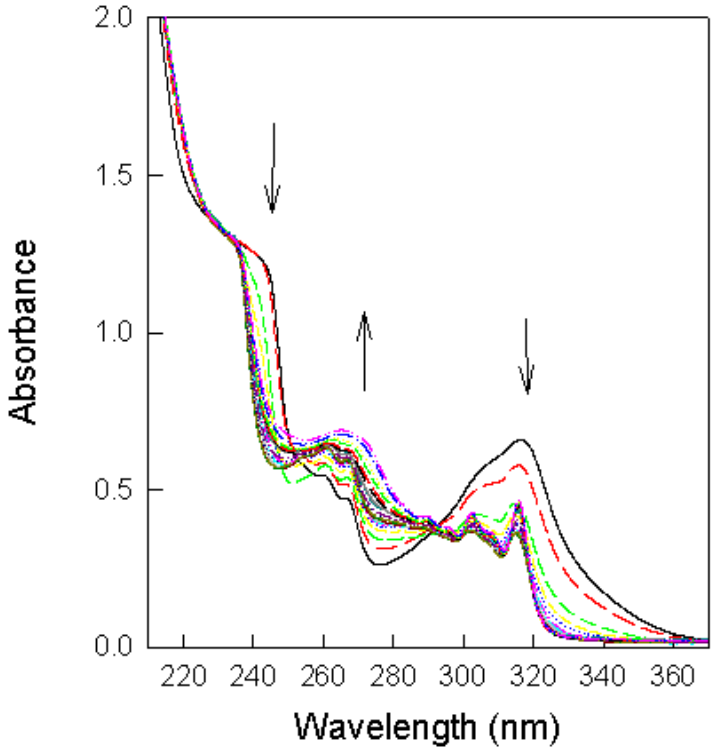

Figure S5. Spectral changes recorded during the titration of **L1**. The spectra were recorded at the following pH values: 1.09, 1.56, 2.10, 2.47, 2.90, 3.61, 4.00, 4.53,5.11, 5.55, 6.06, 6.56, 6.99, 7.51, 8.08, 8.67, 8.98, 9.46, 9.95, 10.50, and 11.03 , and the arrows indicate the direction of changes when the pH is increased.

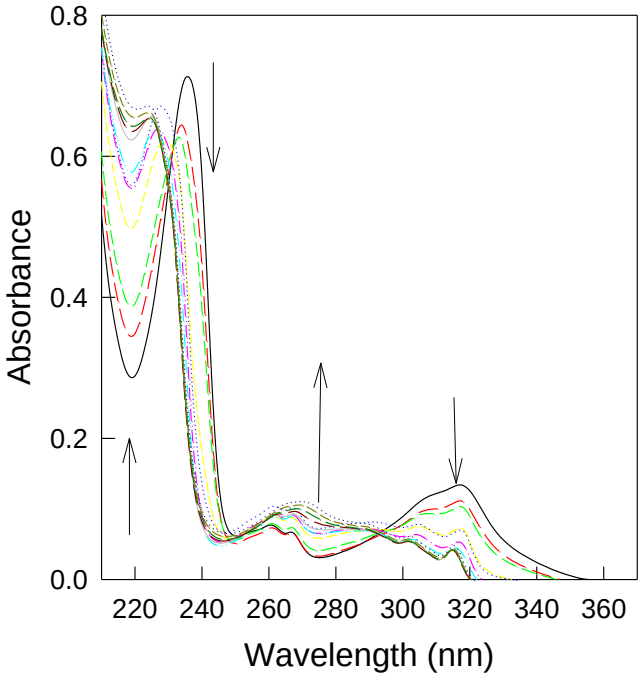

Figure S6. Spectral changes recorded during the titration of **L2**. The spectra were recorded at the following pH values: 2.05, 2.74,3.01,3.85,4.46, 5.15,5.81,6.87,8.18,8.94,9.62 and 10.12, and the arrows indicate the direction of changes when the pH is increased.