Structure and isomerization comparison of Zn(II), Cd(II) and Hg(II) perchlorate complexes of 2,6-bis([(2-pyridyl-methyl)amino]methyl)pyridine †

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ELECTRONIC SUPPLEMENTARY INFORMATION

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Table S1. Hydrogen bonding observed in **1** and **2** [Å and °]

Complex	D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
1[a]	N2-H2N...O4B#2	0.98	2.32	3.08(2)	133.9
	N2-H2N...O3A#2	0.98	2.39	3.074(13)	126.3
2	N4-H4...O8B	0.98	2.24	2.92(2)	125.4

[a] Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z #2 x,y,z-1

Table S2. Overview of mononuclear Hg(II) and Cd(II) complexes with two bound[a] perchlorates and five or more other bound atoms.[b]

Metal Ion	CCDC Code	M-$OClO_3$ bond distance		Other bound atoms	Structural Descriptor	Positions of bound per-chlorate O
		Short-est	Long-est			
Hg(II)	DAZWOR[1]	2.845	2.929	N_2O_3	Pentagonal Bipyramid	Eq. Plane
	OQOJUA[2]	2.959	3.082	N_3S_2	Bicapped Square pyramid	Caps
	VUPWIN[3]	2.902	3.053	S_5	Bicapped Square Pyramid	Caps
	YOLLUH[4]	2.712	2.834	N_3O_2	Pentagonal Bipyramid	Axial
	This work	2.834	3.059	N_5	Bicapped Square Pyramid	Caps
Cd(II)	LAJBEF[5]	2.534	2.668	O_4S_2	Bicapped Trigonal Prism	Square Edge
	RUQSIF[6]	2.460	2.460	N_5	Pentagonal Bipyramid	Axial
	RUZMAA[7]	2.360	2.418	N_5	Pentagonal Bipyramid	Axial
	VOPLER[8]	2.947	3.062	N_5	Bicapped Trigonal Prism	Caps
	This work	2.606	2.633	N_5	Bicapped Square Pyramid	Caps

[a] Defined as within the sum of the van der Waals radii for M(II) and O. (1.55 Å for Hg,[9] 1.58 Å for Cd,[9] and 1.54 Å for O[10]).
[b] See Figure S1 for schematic diagrams

Table S3: Dihedral torsional angles (°) for methylene protons of **1**

Torsion angle	Angle(°)
H6A-C6-N2-Hg	83.74
H6B-C6-N2-Hg	158.87
H7A-C7-N2-Hg	88.16
H7B-C7-N2-Hg	154.60
H13A-C13-N4-Hg	152.44
H13B-C13-N4-Hg	90.37
H14A-C14-N4-Hg	96.86
H14B-C14-N4-Hg	146.28

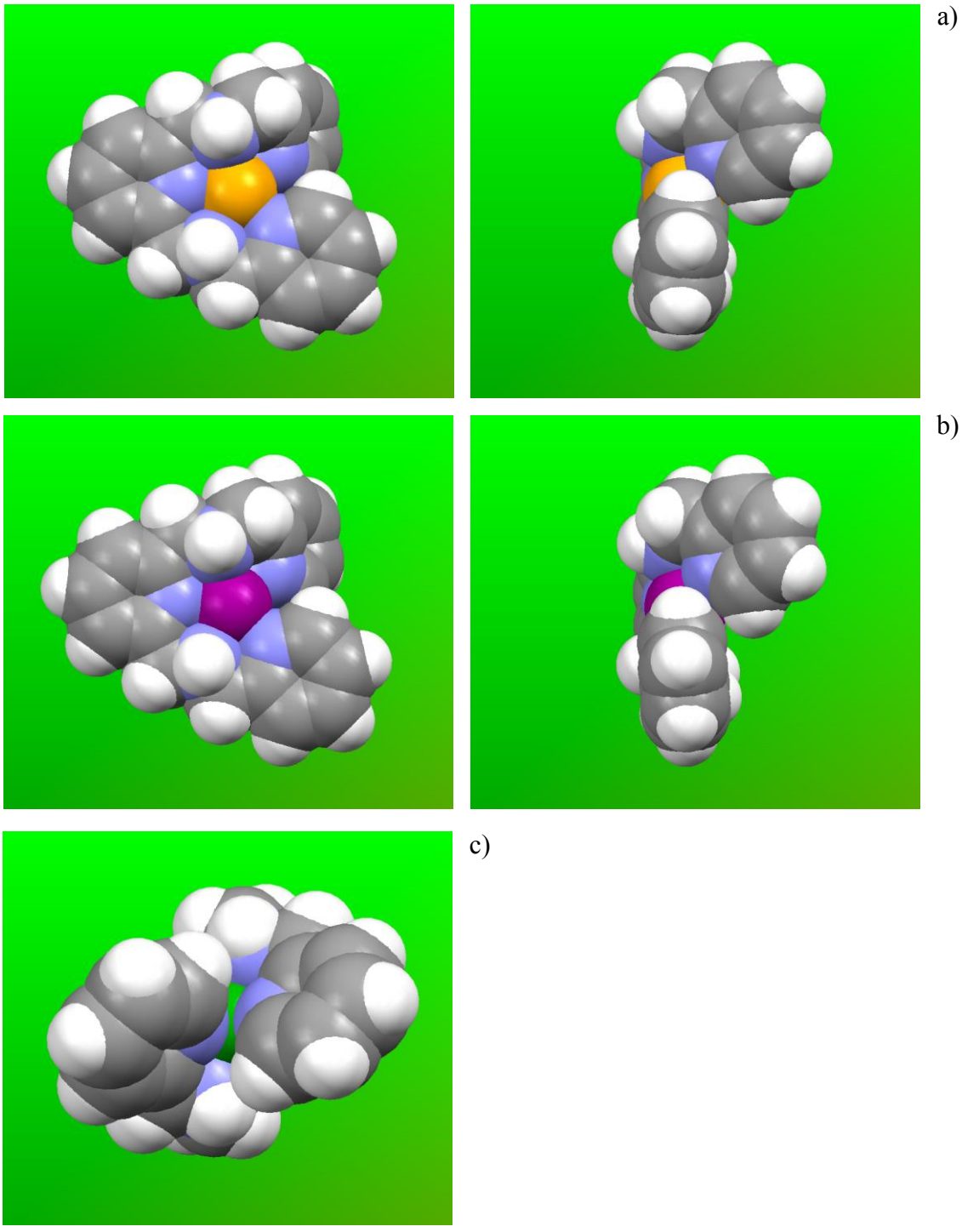

Figure S1. Space fill diagram of a) **1** and b) **2** viewed with the least squares plane of N2-N3-N4-N5 in (left) and perpendicular to (right) the page and c) **3** viewed with the least squares plane of N1-N3-N5 perpendicular to the page. Perchlorates omitted for clarity. Significant overlap of the terminal ligand pyridyl groups results from coiling **L** around M(II) in all three complexes. Note the secondary amine hydrogens have *syn* orientation of in square pyramidal **1** and **2** and *anti* orientation in trigonal bipyramidal **3**. Orange = Hg; Purple = Cd; Green = Zn; Light blue = N; Gray = C; White = H.

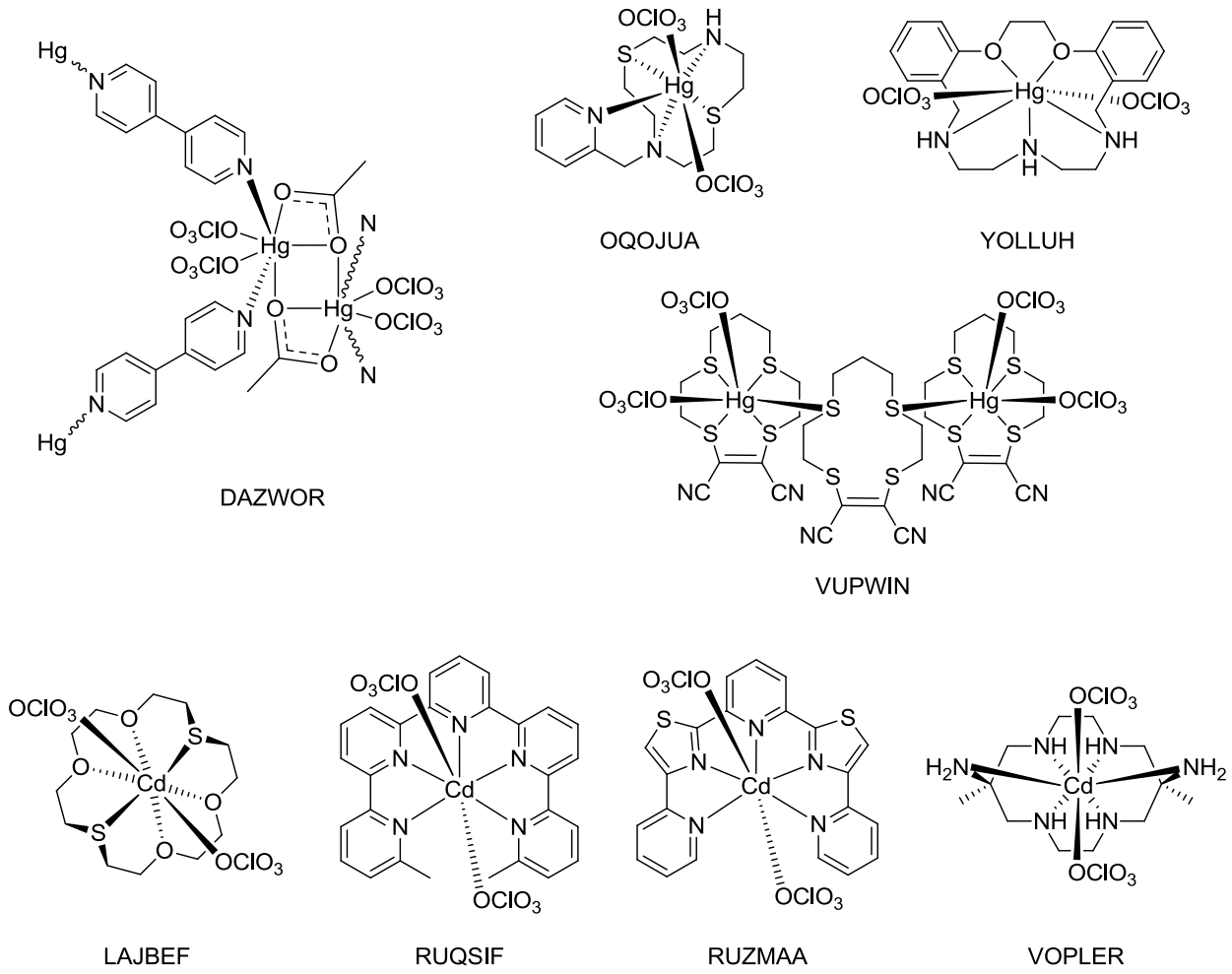

Figure S2. Schematic diagrams of structurally characterized diperchlorate complexes with two oxygens from monodentate perchlorates within the sum of the M-O van der Waals radii for Hg(II)[1-4] and Cd(II)[5-8] bound to five other atoms. See Table S2 for structural details.

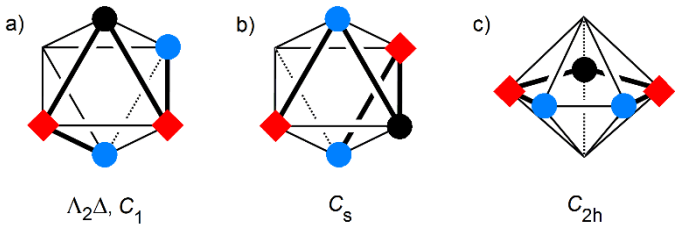

Figure S3. Schematic diagrams of additional ML^{2+} conformations that are not required to explain the experimental data. Blue circles = N1 & N5; Red diamonds = N2 & N3; Black circle = N3. a) Assymetric and b) symmetric octahedral edge conformation requiring crystallographically unprecedented placement of 2,6-bis(aminomethyl)pyridine on a triangular face. c) Bicapped pentagonal planar conformation that would result in loss of geminal proton coupling, but requires substantial elongation of two M-N bonds for placement of both bulking terminal pyridyl rings in a single plane.

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