Hydrogen-Hydrogen Bonding: A Stabilizing Interaction in Strained Chelating Rings of Metal Complexes in Aqueous Phase

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Supplementary information

Table S1. Physical properties of H-atoms and the localised stabilisation energy, E_{stab} of H–H bonding in the five conformers (C1-C5) of the Zn(NTPA) complex. q(H) is the charge on an H-atom and E(H) is its atomic energy; BL is the bond length in the energy-optimised structure. Atoms printed in bold are involved in the H–H bonding interaction.

Zn(NTPA)	H–H bond	BL / Å	Atom	q(H)/au	E(H)/au	ΔE(H)[a]	E_{stab}[a]
C1	**CH31-H34C**	2.196	**H31**	0.021	-0.62015	-4.83	-7.66
			H30	0.029	-0.61245		
			H34	0.033	-0.61065	-2.83	
			H35	0.040	-0.60614		
	CH27-H28C	2.003	**H27**	0.035	-0.60726	1.03	-3.15
			H26	0.036	-0.60890		
			H28	0.032	-0.62226	-4.19	
			H29	0.026	-0.61559		
C2	**CH31-H32C**	1.962	**H31**	0.034	-0.60830	0.78	-3.66
			H30	0.035	-0.60955		
			H32	0.031	-0.62324	-4.45	
			H33	0.022	-0.61615		
	CH27-H28C	2.062	**H27**	0.034	-0.60993	-3.14	-8.46
			H26	0.042	-0.60493		
			H28	0.030	-0.62409	-5.32	
			H29	0.019	-0.61562		
C3	**CH29-H34C**	1.991	**H29**	0.032	-0.62239	-4.25	-3.94
			H28	0.026	-0.61562		
			H34	0.035	-0.60757	0.31	
			H35	0.037	-0.60806		
	CH27-H30C	2.213	**H27**	0.033	-0.61062	-3.21	-8.34
			H26	0.041	-0.60551		
			H30	0.019	-0.62065	-5.14	
			H31	0.029	-0.61246		

Table S1 continues

Zn(NTPA)	H–H bond	BL / Å	Atom	q(H)/au	E(H)/au	ΔE(H)[a]	E_{stab}[a]
C4	**CH29-H34C**	2.011	**H29**	0.032	-0.62169	-3.84	-2.20
			H28	0.026	-0.61557		
			H34	0.036	-0.60682	1.64	
			H35	0.034	-0.60944		
	CH27-H30C	2.203	**H27**	0.034	-0.60963	-1.76	-5.41
			H26	0.039	-0.60682		
			H30	0.025	-0.61821	-3.65	
			H31	0.029	-0.61240		
C5	**CH31-H32C**	1.958	**H31**	0.034	-0.60868	1.02	-3.49
			H30	0.034	-0.61031		
			H32	0.030	-0.62405	-4.52	
			H33	0.021	-0.61686		
	CH27-H28C	2.051	**H27**	0.034	-0.61021	-2.49	-7.68
			H26	0.041	-0.60625		
			H28	0.030	-0.62439	-5.19	
			H29	0.018	-0.61611		

[a] In kcal mol^{-1}

Table S2. Atomic energies *E*(H) of the same H-atoms in five conformers (C1-C5) of ZnNTPA (atoms in bold are involved in the H-H interaction). $\Delta E = E_H(\text{bonded}) - E_H(\text{non-bonded})$ in kcal mol^{-1}.

Zn(NTPA)	**Atom**	***E*(H) / au**	**ΔE**
C1	**H31**	-0.62015	-4.82
C3	H31	-0.61246	
C3	**H30**	-0.62065	-5.14
C1	H30	-0.61245	
C1	**H31**	-0.62015	-4.86
C4	H31	-0.61240	
C4	**H30**	-0.61821	-3.61
C1	H30	-0.61245	
C4	**H29**	-0.62169	-3.50
C5	H29	-0.61611	
C5	**H28**	-0.62439	-5.53
C4	H28	-0.61557	
C1	**H28**	-0.62409	-5.35
C4	H28	-0.61557	
C4	**H29**	-0.62169	-3.81
C1	H29	-0.61562	
C1	**H28**	-0.62226	-4.17
C3	H28	-0.61562	
C3	**H29**	-0.62239	-4.27
C1	H29	-0.61559	
		Average	-4.51
		StDev	0.73

Table S3. Average differences (DIF) between the AIM-computed bond path angles (BPA) and geometrical bond angles (GBA), DIF = BPA – GBA, in three 6-member rings of five conformers of the Zn(NTPA) complex. Rings are marked in Figure 1.

Ring a			Ring b			Ring c		
Bond Angle	**DIF**	**StDev**	**Bond Angle**	**DIF**	**StDev**	**Bond Angle**	**DIF**	**StDev**
O20-Zn-N	-1.94	0.12	O18-Zn-N	-2.10	0.09	O19-Zn-N	-2.10	0.04
C9-N-Zn	4.26	0.33	C12-N-Zn	1.85	1.05	C15-N-Zn	2.73	1.11
C10-C9-N	-4.19	0.40	C13-C12-N	-3.54	0.40	C16-C15-N	-3.33	0.34
C11-C10-C9	-5.39	0.58	C14-C13-C12	-3.51	0.65	C17-C16-C15	-3.56	0.97
C10-C11-O20	-2.70	0.24	C13-C14-O18	-1.74	0.41	C16-C17-O19	-1.98	0.36
C11-O20-Zn	-9.95	0.38	C14-O18-Zn	-9.10	0.29	C17-O19-Zn	-8.95	0.50

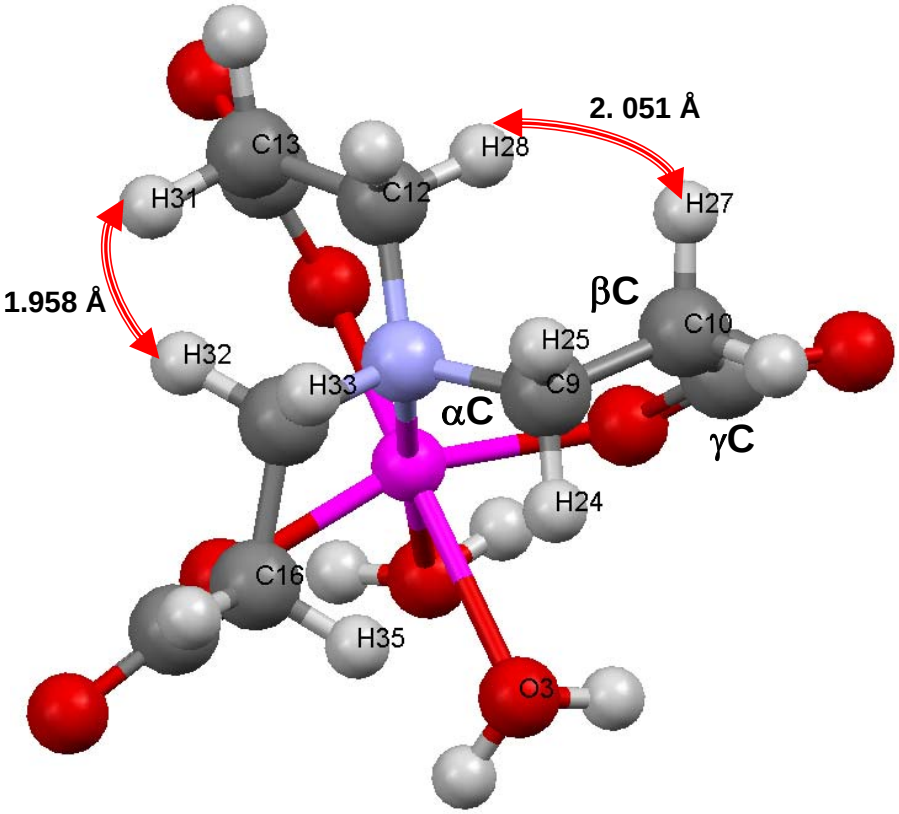
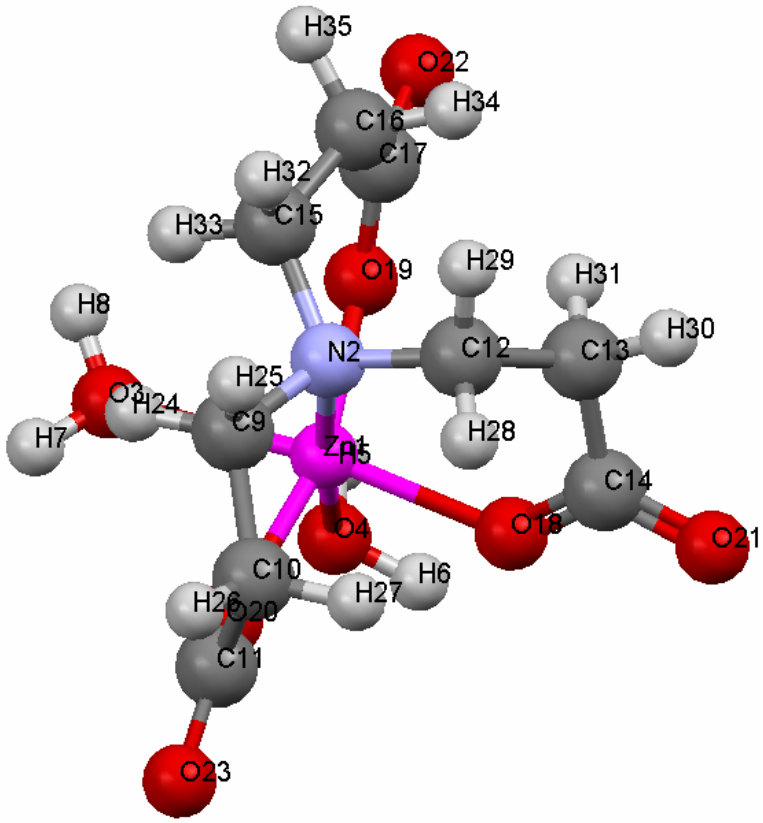


Figure S1. H-H bonding interactions found from the AIM analysis in the conformer C5 of the ZnNTPA complex and numbering of C-atoms used in this work.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H34
C16
C17
H32
C15
H33
O19
H29
H31
H8
N2
C12
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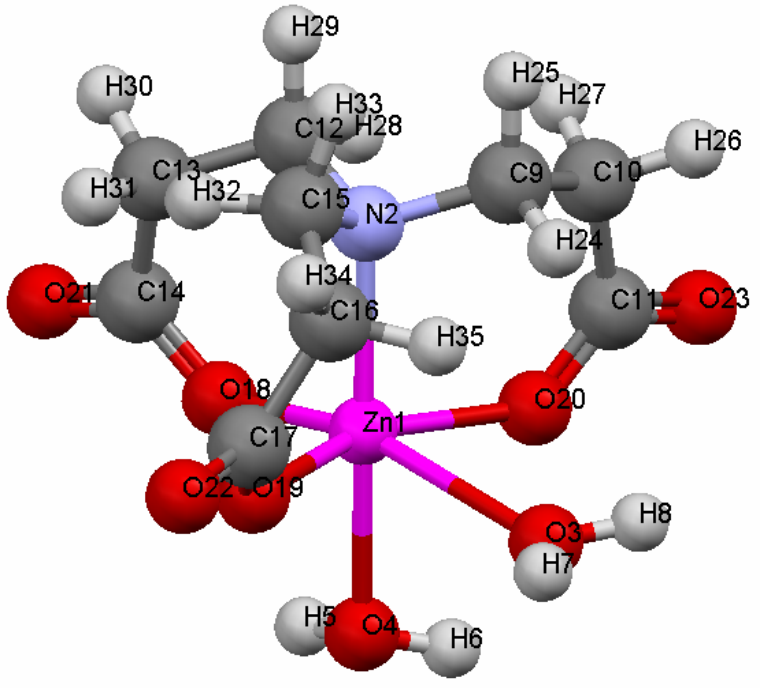
H25
O3
H24
C9
H28
H7
Zn1
H5
C14
O4
O18
O21
C10
H6
H26
H27
O20
C11
O23

C1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H27
H33
C12
H28
H26
C13
C9
C10
H31
H32
C15
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H34
O21
C14
C11
O23
C16
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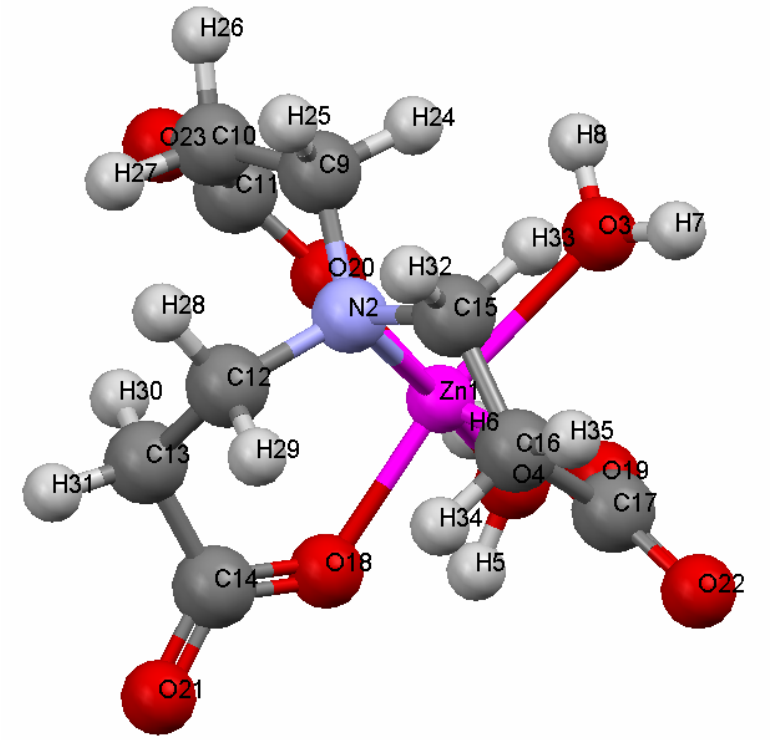
O20
Zn1
C17
O22
O19
O3
H8
H7
H5
O4
H6

C2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C10
H25
H24
H8
H27
C11
C9
O3
H7
H33
O20
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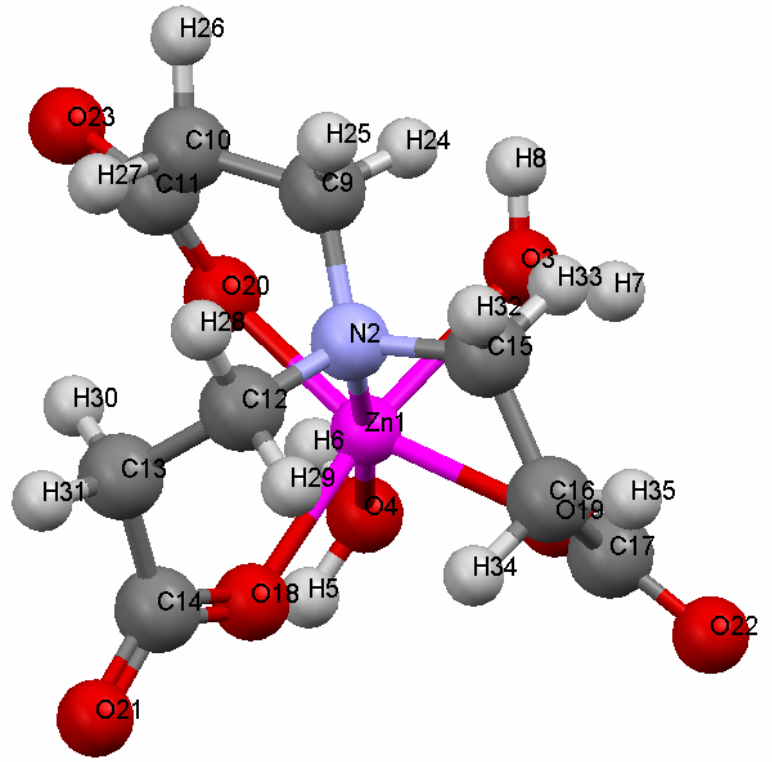
C15
H28
C12
Zn1
H30
H6
C16
H35
C13
H29
O4
O19
H31
C17
H34
O18
H5
C14
O22
O21

C3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O3
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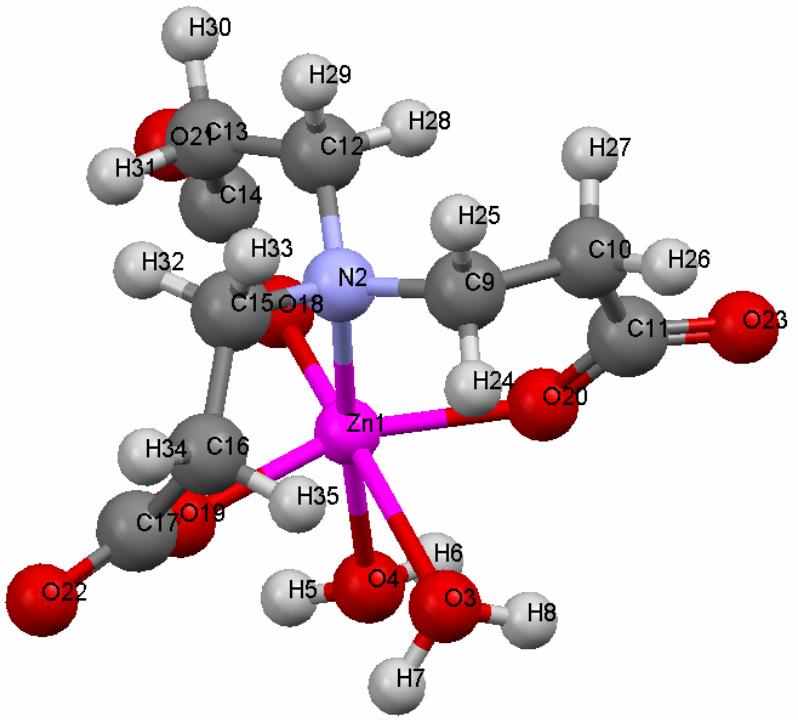
C15
H30
C12
Zn1
H6
C13
H29
C16
H35
H31
O4
O19
C17
H34
C14
O18
H5
O22
O21

C4



C5

Figure S2. Conformers (C1 – C5) of the ZnNTPA complex discussed in this work.

Table S4. Selected dihedral angles (in deg) and the Gibbs free energy values *G*(aq) of five conformers of ZnNTPA seen in Figure S2.

Conformer	**N-C9-C10-C11**	**N-C12-C13-C14**	**N-C15-C16-C17**	***G*(aq) / au**
C1	–73.26	–69.99	62.49	–2788.949610
C2	–58.86	–73.28	–76.86	–2788.952341
C3	–62.28	69.46	72.37	–2788.948761
C4	–62.92	70.94	75.25	–2788.949715
C5	–58.97	–73.33	–75.62	–2788.951271