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Electronic Supplementary Information

Theoretical aspects on the enhancement of metal binding affinity by intramolecular hydrogen bonding and modulating pK_a values

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Table S1. Comparison of the calculated and experimental minimum bond lengths (in Å) available in two of the studied complexes. The calculated bond lengths are at the level of M06-2X/6-31+G*

compound	Zn-O	Mg-O	C-O
Zn^{2+} complex (RELDUH)[a]	2.0478		1.4138
Zn^{2+}-AL1-3an	1.9460		1.3972
Mg^{2+} complex (ODAKEJ)[b]		2.0256	1.4494
Mg^{2+}-AL1		1.9617	1.4825

[a] CSD entry for a Zn^{2+} complex which resembles to the studied complex Zn^{2+}-AL1-3an. The experimental bond lengths are reported in this row.

[b] CSD entry for a Mg^{2+} complex which resembles to the studied complex Mg^{2+}-AL1. The experimental bond lengths are reported in this row.

Table S2. Selected bond lengths (in Å) for different studied complexes of AL3 at the level of M06-2X/6-31+G*

compound	Bond	Mg^{2+}	Ca^{2+}	Zn^{2+}
AL3	M…O3	1.93	2.28	1.92
	M…O2	1.93	2.29	1.92
	M…O1	1.92	2.25	1.94
	H3…O5	1.60	1.67	1.58
	H2…O6	1.61	1.67	1.59
	H1…O4	1.54	1.61	1.53
	H4…O7	1.78	1.80	1.78
AL3-an	M…O3	1.95	2.30	1.97
	M…O2	1.95	2.31	1.96
	M…O1	1.84	2.15	1.85
	H3…O5	1.69	1.74	1.71
	H2…O6	1.71	1.74	1.71
	H4…O1	1.83	1.77	1.87
	H7…O4	1.98	1.97	1.99
AL3-2an	M…O3	2.00	2.35	2.06
	M…O2	1.85	2.16	1.84
	M…O1	1.87	2.18	1.88
	H3…O5	1.78	1.81	1.81
	H6…O2	1.84	1.79	1.87
	H4…O1	1.75	1.69	1.77
	H7…O4	1.93	1.91	1.94
AL3-3an	M…O3	1.89	2.21	1.89
	M…O2	1.89	2.20	1.89
	M…O1	1.90	2.21	1.94
	H5…O3	1.77	1.73	1.80
	H6…O2	1.78	1.73	1.80
	H4…O1	1.64	1.58	1.65
	H7…O4	1.88	1.86	1.88

Table S3. NBO charges for different metals in AL3 complexes at the level of M06-2X/6-311++G**

compound	Mg^{2+}	Ca^{2+}	Zn^{2+}
AL3	1.72	1.82	1.60
AL3-an	1.70	1.76	1.56
AL3-2an	1.65	1.71	1.52
AL3-3an	1.63	1.69	1.49

Table S4. Dissociation energies (ΔE), enthalpies (ΔH) and free energies (ΔG) of the studied metal cation complexes at M06-2X/6-311++G** level of theory in methanol solvent. All energies are BSSE-corrected in kcal/mol.

	Mg^{2+}			Ca^{2+}			Zn^{2+}		
compound	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG
AL1	30.70	31.29	21.13	15.11	15.70	6.51	31.00	31.59	21.13
AL1-an	53.96	54.55	44.42	28.24	28.83	19.75	57.77	58.36	48.03
AL1-2an	94.93	95.52	85.19	58.11	58.70	49.18	103.20	103.79	93.36
AL1-3an	122.16	122.76	111.62	54.57	55.16	44.76	142.49	143.08	132.01
AL2	32.64	33.24	23.58	15.89	16.49	8.00	33.01	33.60	23.72
AL2-an	54.15	54.75	45.17	28.36	28.95	19.68	58.20	58.79	49.02
AL2-2an	102.73	103.32	94.81	68.28	68.87	60.92	109.95	110.54	101.89
AL2-3an	147.30	147.89	138.28	91.06	91.65	82.09	157.16	157.75	147.86
AL3	41.82	42.41	32.33	21.67	22.26	13.16	41.95	42.54	32.61
AL3-an	54.73	55.32	45.92	29.00	29.59	20.54	56.77	57.37	47.77
AL3-2an	91.62	92.22	84.13	59.56	60.16	52.10	96.55	97.14	88.40
AL3-3an	131.14	131.73	123.42	93.08	93.67	85.56	138.04	138.63	130.44

Table S5. Electron densities, in e/a.u.^{3}, Laplacian of the electron densities, in e/a.u.^{5}, and different energy densities at BCP, in a.u., derived from AIM analysis at the level of M06-2X/6-311++G**

		Mg^{2+}					Ca^{2+}					Zn^{2+}				
compound	BCP	$\rho(r)$	$G(r)$	$V(r)$	$H(r)$	$\nabla^2\rho(r)$	$\rho(r)$	$G(r)$	$V(r)$	$H(r)$	$\nabla^2\rho(r)$	$\rho(r)$	$G(r)$	$V(r)$	$H(r)$	$\nabla^2\rho(r)$
AL3	M-O3	0.0534	0.0964	-0.0822	0.0142	0.4424	0.0437	0.0549	-0.0494	0.0055	0.2417	0.0894	0.1410	-0.1497	-0.0087	0.5296
	M-O2	0.0526	0.0943	-0.0802	0.0141	0.4336	0.0424	0.0531	-0.0475	0.0056	0.2346	0.0896	0.1411	-0.1497	-0.0085	0.5303
	M-O1	0.0553	0.1005	-0.0863	0.0141	0.4584	0.0471	0.0596	-0.0541	0.0054	0.2598	0.0854	0.1320	-0.1408	-0.0088	0.4931
	H3-O5	0.0565	0.0504	-0.0610	-0.0106	0.1593	0.0465	0.0433	-0.0480	-0.0048	0.1541	0.0602	0.0526	-0.0656	-0.0130	0.1586
	H2-O6	0.0546	0.0494	-0.0586	-0.0093	0.1603	0.0470	0.0439	-0.0488	-0.0049	0.1559	0.0583	0.0518	-0.0634	-0.0116	0.1610
	H1-O4	0.0668	0.0587	-0.0757	-0.0170	0.1670	0.0548	0.0503	-0.0595	-0.0092	0.1646	0.0675	0.0589	-0.0764	-0.0175	0.1656
	H4-O7	0.0357	0.0345	-0.0347	-0.0002	0.1375	0.0341	0.0330	-0.0326	0.0004	0.1337	0.0357	0.0345	-0.0346	-0.0002	0.1372
AL3-an	M-O3	0.0497	0.0879	-0.0741	0.0138	0.4070	0.0407	0.0511	-0.0454	0.0057	0.2273	0.0785	0.1184	-0.1256	-0.0072	0.4448
	M-O2	0.0492	0.0872	-0.0732	0.0140	0.4049	0.0402	0.0506	-0.0447	0.0059	0.2259	0.0800	0.1232	-0.1300	-0.0068	0.4654
	M-O1	0.0715	0.1380	-0.1252	0.0128	0.6036	0.0654	0.0828	-0.0813	0.0016	0.3375	0.1132	0.1831	-0.2021	-0.0190	0.6564
	H3-O5	0.0438	0.0413	-0.0447	-0.0034	0.1514	0.0392	0.0375	-0.0388	-0.0013	0.1446	0.0426	0.0403	-0.0431	-0.0028	0.1499
	H2-O6	0.0417	0.0398	-0.0422	-0.0024	0.1498	0.0389	0.0374	-0.0385	-0.0011	0.1454	0.0421	0.0401	-0.0427	-0.0026	0.1503
	H4-O1	0.0336	0.0320	-0.0319	0.0000	0.1281	0.0388	0.0365	-0.0381	-0.0017	0.1392	0.0305	0.0292	-0.0283	0.0009	0.1203
	H7-O4	0.0234	0.0222	-0.0201	0.0021	0.0975	0.0241	0.0230	-0.0208	0.0021	0.1003	0.0230	0.0218	-0.0197	0.0021	0.0957
AL3-2an	M-O3	0.0431	0.0735	-0.0607	0.0127	0.3447	0.0358	0.0443	-0.0386	0.0058	0.2005	0.0635	0.0896	-0.0956	-0.0061	0.3339
	M-O2	0.0685	0.1329	-0.1187	0.0143	0.5889	0.0612	0.0809	-0.0777	0.0032	0.3363	0.1123	0.1829	-0.2001	-0.0173	0.6624
	M-O1	0.0659	0.1232	-0.1104	0.0128	0.5437	0.0597	0.0750	-0.0725	0.0025	0.3101	0.1039	0.1644	-0.1797	-0.0153	0.5962
	H3-O5	0.0353	0.0341	-0.0340	0.0001	0.1366	0.0332	0.0321	-0.0313	0.0008	0.1314	0.0331	0.0320	-0.0313	0.0008	0.1312

AL3-3an	H6-O2	0.0332	0.0308	-0.0308	0.0000	0.1230	0.0379	0.0346	-0.0361	-0.0015	0.1325	0.0308	0.0288	-0.0281	0.0007	0.1178
	H4-O1	0.0412	0.0384	-0.0411	-0.0027	0.1429	0.0476	0.0431	-0.0489	-0.0058	0.1493	0.0381	0.0359	-0.0373	-0.0014	0.1381
	H7-O4	0.0259	0.0248	-0.0228	0.0020	0.1072	0.0267	0.0256	-0.0237	0.0019	0.1101	0.0255	0.0244	-0.0224	0.0020	0.1057
	M-O3	0.0616	0.1131	-0.0999	0.0132	0.5051	0.0549	0.0696	-0.0663	0.0032	0.2912	0.1001	0.1569	-0.1701	-0.0132	0.5747
	M-O2	0.0615	0.1139	-0.1001	0.0138	0.5106	0.0557	0.0700	-0.0667	0.0033	0.2931	0.1002	0.1568	-0.1700	-0.0132	0.5747
	M-O1	0.0601	0.1091	-0.0963	0.0128	0.4876	0.0546	0.0712	-0.0672	0.0040	0.3009	0.0885	0.1336	-0.1447	-0.0111	0.4898
AL2	H5-O3	0.0391	0.0357	-0.0378	-0.0021	0.1347	0.0444	0.0396	-0.0439	-0.0044	0.1408	0.0365	0.0336	-0.0347	-0.0010	0.1305
	H6-O2	0.0383	0.0348	-0.0365	-0.0018	0.1319	0.0439	0.0390	-0.0432	-0.0042	0.1391	0.0364	0.0335	-0.0345	-0.0010	0.1301
	H4-O1	0.0542	0.0476	-0.0572	-0.0096	0.1524	0.0635	0.0537	-0.0691	-0.0154	0.1531	0.0526	0.0464	-0.0550	-0.0086	0.1511
	H7-O4	0.0287	0.0274	-0.0259	0.0015	0.1158	0.0299	0.0286	-0.0273	0.0013	0.1195	0.0287	0.0274	-0.0259	0.0015	0.1158
	M-O3	0.0514	0.0916	-0.0775	0.0140	0.4224	0.0413	0.0515	-0.0459	0.0056	0.2286	0.0875	0.1369	-0.1450	-0.0080	0.5157
	M-O2	0.0505	0.0892	-0.0755	0.0138	0.4122	0.0398	0.0489	-0.0434	0.0055	0.2174	0.0871	0.1356	-0.1435	-0.0079	0.5107
	M-O1	0.0526	0.0946	-0.0805	0.0142	0.4351	0.0445	0.0563	-0.0505	0.0058	0.2484	0.0813	0.1237	-0.1315	-0.0078	0.4636

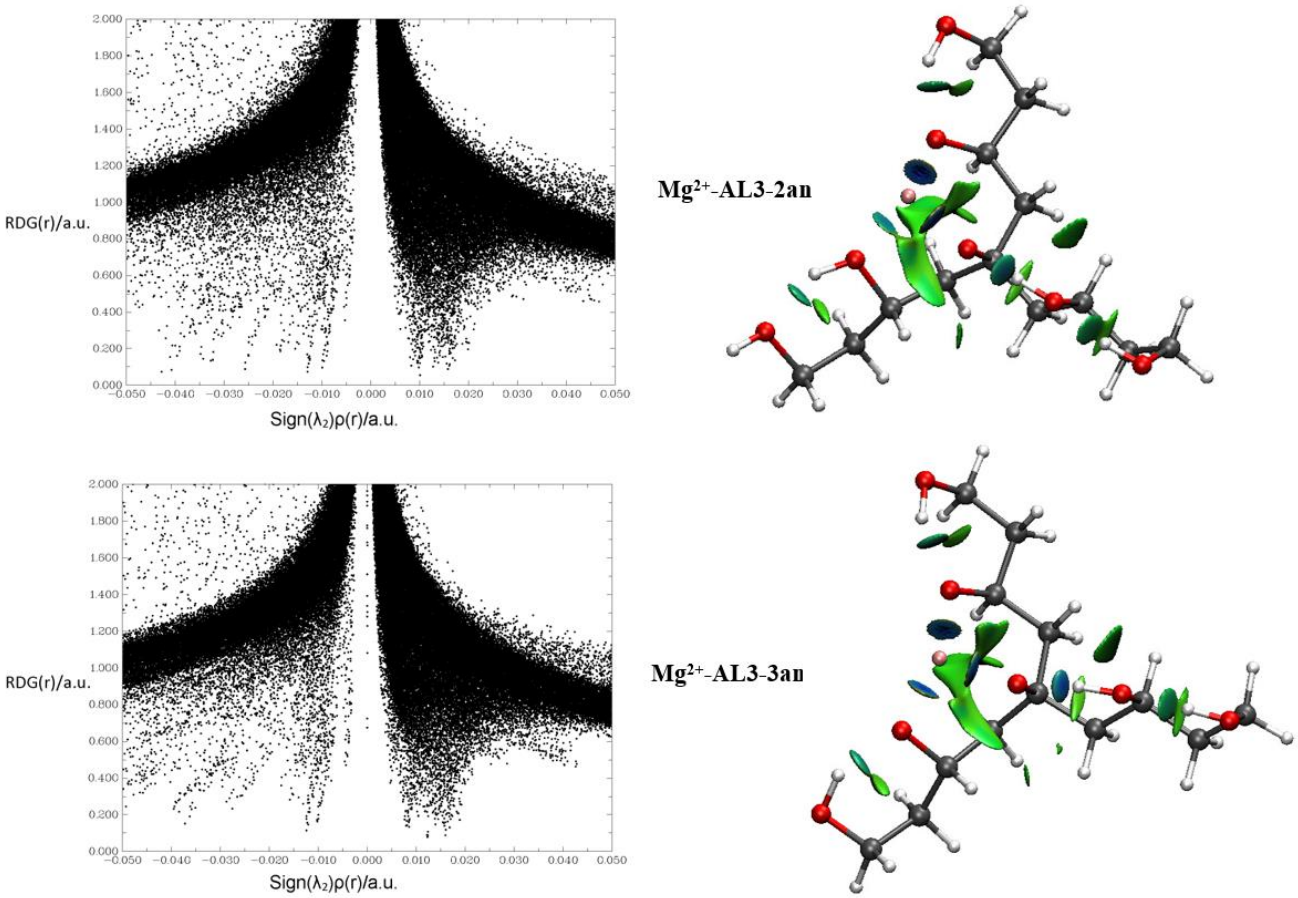

Fig. S1. The scatter diagrams (left) and color-filled RDG isosurface maps (right) at the M06-2X/6-311++G** level of theory