Supplementary Material (ESI) for PCCP

The physical chemistry of coordinated aqua-, ammine-, and mixed-ligand Co^{2+} complexes: DFT studies on the structure, energetics, and topological properties of the electron density

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Supplementary Information

Computational Details

The form of the B3LYP exchange-correlation functional E_{xc}^{B3LYP} is given by eqn. S1, whilst for X3LYP, eqn. S2 applies.

$$E_{xc}^{B3LYP} = a_0 E_x^{Exact} + (1-a_0)E_x^{Slater} + a_x\Delta E_x^{B88} + a_c E_c^{VWN} + (1-a_c)E_c^{LYP} \quad \text{(S1)}$$

$$E_{xc}^{X3LYP} = a_0 E_x^{Exact} + (1-a_0)E_x^{Slater} + a_x\Delta E_x^{X} + a_c E_c^{VWN} + (1-a_c)E_c^{LYP} \quad \text{(S2)}$$

Both the functionals use the VWN functional III[1] based on correlation of the homogeneous electron gas in the random phase approximation, the Lee–Yang–Parr[2] correlation functional, plus a hybrid exchange functional of three terms: a portion of the Hartree-Fock exact exchange, Slater local exchange, and the non-local gradient correction of Becke88.[3] The hybrid parameter set (a_0, a_x, a_c) is (0.20, 0.72, 0.19) for B3LYP.[3] The third term of eqn. 2 is an admixture of the B88 and PW91 exchange

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functionals ($a_x\Delta E_x^X = a_{x1}E_x^{B88} + a_{x1}E_x^{PW91}$), and therefore, the hybrid parameters (a_0, a_{x1}, a_{x2}, a_c) are (0.218, 0.542, 0.167, 0.129) for the X3LYP functional.[4]

Table S1. The Co–O Bond Lengths in Structures of $[Co(H_2O)_6]^{2+}$ Reported in the CSD.*

CSD REF CODE	Co—O bond length /Å						Symmetry
AJETEO	2.062	2.072	2.076	2.083	2.083	2.125	C_1
BECREH	2.058	2.064	2.074	2.085	2.099	2.148	C_1
BIZSOT	2.076	2.078	2.078	2.085	2.085	2.090	C_1
CAGVOV01	2.063	2.072	2.072	2.108	2.108	2.124	C_1
CAGVOV03	2.069	2.085	2.085	2.121	2.121	2.129	C_1
DIJSIZ	2.048	2.112	2.085	2.085	2.048	2.112	C_1
HEKDOQ	2.020	2.067	2.075	2.090	2.095	2.120	C_1
IDAPAF	2.057	2.074	2.077	2.083	2.130	2.134	C_1
KERNEB	2.069	2.071	2.085	2.089	2.130	2.133	C_1
LIWJEH	2.022	2.047	2.094	2.103	2.127	2.135	C_1
NAMNIZ	2.070	2.073	2.079	2.081	2.106	2.147	C_1
OCDCOC	2.043	2.057	2.082	2.090	2.090	2.118	C_1
PAVXIU	2.061	2.063	2.068	2.069	2.093	2.095	C_1
SIWWIE10	2.041	2.041	2.048	2.129	2.129	2.204	C_1
TICPOL	2.055	2.059	2.064	2.086	2.097	2.117	C_1
UDEDEM	2.049	2.073	2.089	2.089	2.122	2.133	C_1
VENDIB	2.062	2.093	2.096	2.114	2.124	2.125	C_1
VOCDAS	2.011	2.064	2.064	2.115	2.143	2.181	C_1
WABLIU	2.007	2.039	2.062	2.079	2.128	2.133	C_1
WACZOQ	2.053	2.057	2.084	2.087	2.104	2.124	C_1
WOQZUX	2.064	2.088	2.096	2.097	2.109	2.121	C_1
ZZZPAU01	2.049	2.077	2.087	2.109	2.121	2.158	C_1
AGOJUB	2.062	2.062	2.082	2.082	2.141	2.141	D_2h
AJETEO	2.073	2.073	2.093	2.093	2.121	2.121	D_2h
AQCOAM	2.040	2.040	2.097	2.097	2.115	2.115	D_2h
AQCOAM01	2.036	2.036	2.098	2.098	2.109	2.109	D_2h
ASGLCO	2.049	2.049	2.073	2.073	2.129	2.129	D_2h
ASUDIB	2.067	2.067	2.090	2.090	2.149	2.149	D_2h
AYABOR	2.088	2.088	2.102	2.102	2.120	2.120	D_2h
BAVYOM	2.053	2.053	2.070	2.070	2.092	2.092	D_2h
BAVYOM01	2.038	2.038	2.038	2.038	2.058	2.058	D_2h
BEZYUA	2.067	2.067	2.078	2.078	2.100	2.100	D_2h
BIFWAP	2.066	2.066	2.073	2.073	2.077	2.077	D_2h
BIPBUY	2.070	2.070	2.070	2.070	2.078	2.078	D_2h

CSD REF CODE	Co—O bond length /Å						Symmetry
BIYTUY	2.061	2.061	2.080	2.080	2.107	2.107	D_2h
BIZSOT	2.065	2.080	2.085	2.085	2.087	2.087	D_2h
BUGFEO	2.097	2.097	2.097	2.097	2.103	2.103	D_2h
CAGVOV	2.048	2.048	2.063	2.063	2.114	2.114	D_2h
CAGVOV02	2.049	2.049	2.073	2.073	2.120	2.120	D_2h
CAWTEZ	2.070	2.070	2.096	2.096	2.122	2.122	D_2h
COHDPH	2.013	2.013	2.104	2.104	2.128	2.128	D_2h
COHDPH	2.047	2.047	2.054	2.054	2.151	2.151	D_2h
COHDPH01	1.998	1.998	2.114	2.114	2.140	2.140	D_2h
COHDPH02	2.077	2.077	2.080	2.080	2.116	2.116	D_2h
COXSIR	2.087	2.087	2.113	2.113	2.118	2.118	D_2h
DIJREU	2.077	2.077	2.082	2.082	2.099	2.099	D_2h
DIJROE	2.061	2.061	2.090	2.090	2.119	2.119	D_2h
DIJSEV	2.078	2.078	2.080	2.080	2.107	2.107	D_2h
ECEPEH	2.062	2.062	2.084	2.084	2.114	2.114	D_2h
ENSUCO	2.058	2.058	2.091	2.091	2.137	2.137	D_2h
EWOPEL	2.063	2.063	2.076	2.076	2.104	2.104	D_2h
FEGMAF	2.062	2.062	2.085	2.085	2.105	2.105	D_2h
FEPPUM	2.051	2.051	2.064	2.064	2.078	2.078	D_2h
FIWQOR	2.055	2.055	2.112	2.112	2.117	2.117	D_2h
FIWTUA	2.066	2.066	2.068	2.068	2.102	2.102	D_2h
FIWTUA	2.056	2.056	2.061	2.061	2.101	2.101	D_2h
FONQUV	2.042	2.042	2.042	2.042	2.113	2.113	D_2h
FUNQAG	2.075	2.075	2.084	2.084	2.096	2.096	D_2h
GEPGUE	2.042	2.042	2.084	2.084	2.124	2.124	D_2h
GIYDAU	2.041	2.041	2.094	2.094	2.098	2.098	D_2h
HAHKOR	2.117	2.117	2.118	2.118	2.119	2.119	D_2h
HEFSAM	2.039	2.039	2.082	2.082	2.119	2.119	D_2h
HIQJUN	1.987	1.987	2.046	2.046	2.069	2.069	D_2h
HTBZCO	2.072	2.072	2.083	2.083	2.109	2.109	D_2h
HULMAC	2.045	2.045	2.107	2.107	2.141	2.141	D_2h
IMAFIL	2.073	2.073	2.079	2.079	2.094	2.094	D_2h
IQUDON	2.106	2.106	2.118	2.118	2.148	2.148	D_2h
IQUDON	2.092	2.092	2.136	2.136	2.149	2.149	D_2h
IRONIM	2.041	2.041	2.102	2.102	2.109	2.109	D_2h
IWONIR	2.077	2.077	2.081	2.081	2.084	2.084	D_2h
JEHKOW	2.051	2.051	2.085	2.085	2.086	2.086	D_2h
JEHKOW01	2.031	2.031	2.082	2.082	2.084	2.084	D_2h
JEYMUW	2.049	2.049	2.085	2.085	2.129	2.129	D_2h
JIRREI	2.010	2.010	2.062	2.062	2.142	2.142	D_2h
JIRREI	2.054	2.054	2.078	2.078	2.079	2.079	D_2h
KAGMUB	2.050	2.050	2.085	2.085	2.113	2.113	D_2h

CSD REF CODE	Co—O bond length /Å						Symmetry
LEFXUQ	2.038	2.038	2.088	2.088	2.109	2.109	D_2h
LICPIX	2.037	2.037	2.075	2.075	2.113	2.113	D_2h
LIYYAT	2.053	2.053	2.077	2.077	2.081	2.081	D_2h
LIYYAT01	2.056	2.056	2.082	2.082	2.083	2.083	D_2h
MAZGAV	2.071	2.071	2.087	2.087	2.096	2.096	D_2h
MAZVIT	2.049	2.049	2.088	2.088	2.133	2.133	D_2h
MGHBZB10	2.101	2.101	2.106	2.106	2.128	2.128	D_2h
MGHBZB20	2.101	2.101	2.106	2.106	2.128	2.128	D_2h
NAZVOZ	2.055	2.055	2.062	2.062	2.116	2.116	D_2h
NENDOA	2.048	2.048	2.109	2.109	2.130	2.130	D_2h
NESFIB	2.065	2.065	2.071	2.071	2.127	2.127	D_2h
NIHSOM01	2.067	2.067	2.095	2.095	2.117	2.117	D_2h
NIQGID	2.052	2.052	2.099	2.099	2.118	2.118	D_2h
OJOPEI	1.975	1.975	2.034	2.034	2.116	2.116	D_2h
OLOLIK	2.044	2.044	2.097	2.097	2.120	2.120	D_2h
PACJUZ	2.043	2.043	2.121	2.121	2.127	2.127	D_2h
PDACCO	2.058	2.058	2.066	2.066	2.120	2.120	D_2h
PIGRED	2.046	2.046	2.110	2.110	2.127	2.127	D_2h
PIWFOQ	2.079	2.079	2.086	2.086	2.116	2.116	D_2h
PUNSIA	2.063	2.063	2.081	2.081	2.103	2.103	D_2h
QANFUH	2.065	2.065	2.094	2.094	2.127	2.127	D_2h
QAXFAX	2.051	2.051	2.091	2.091	2.115	2.115	D_2h
QEQTAH	2.052	2.052	2.101	2.101	2.124	2.124	D_2h
QEQTEM	2.081	2.081	2.082	2.082	2.098	2.098	D_2h
QESFUP	2.096	2.096	2.100	2.100	2.102	2.102	D_2h
QESFUP	2.091	2.091	2.096	2.096	2.106	2.106	D_2h
QESFUP01	2.096	2.096	2.104	2.104	2.105	2.105	D_2h
QIZFUA01	2.057	2.057	2.058	2.058	2.129	2.129	D_2h
RAXMEJ	2.075	2.075	2.078	2.078	2.133	2.133	D_2h
RAXMIN	2.081	2.081	2.082	2.082	2.148	2.148	D_2h
RENRIM	2.073	2.073	2.082	2.082	2.122	2.122	D_2h
RISPEP	2.054	2.054	2.117	2.117	2.125	2.125	D_2h
SAYVEU	2.062	2.062	2.101	2.101	2.113	2.113	D_2h
SEFXEH	2.068	2.068	2.085	2.085	2.157	2.157	D_2h
SETQOX	2.045	2.045	2.052	2.052	2.110	2.110	D_2h
SEVTIX	2.083	2.083	2.089	2.089	2.090	2.090	D_2h
SEVTIX	2.066	2.066	2.071	2.071	2.104	2.104	D_2h
SIJJOL	2.057	2.057	2.058	2.058	2.097	2.097	D_2h
SIJJOL	2.048	2.048	2.097	2.097	2.115	2.115	D_2h
SUJPES	2.053	2.053	2.087	2.087	2.103	2.103	D_2h
SUJQET	2.025	2.025	2.084	2.084	2.088	2.088	D_2h
SUJQET01	2.049	2.049	2.081	2.081	2.096	2.096	D_2h

CSD REF CODE	Co—O bond length /Å						Symmetry
SUVBUG	2.052	2.052	2.077	2.077	2.086	2.086	D_2h
TAQXUF	2.061	2.061	2.063	2.063	2.144	2.144	D_2h
TELBAN	2.079	2.079	2.083	2.083	2.124	2.124	D_2h
TERKIK	2.046	2.046	2.085	2.085	2.110	2.110	D_2h
TEVQIV	2.041	2.041	2.105	2.105	2.144	2.144	D_2h
UDEDEM	2.047	2.047	2.062	2.062	2.093	2.093	D_2h
UNAGEV	2.059	2.059	2.088	2.088	2.126	2.126	D_2h
UNAGEV01	2.054	2.054	2.086	2.086	2.122	2.122	D_2h
VAHCIR	2.034	2.034	2.063	2.063	2.084	2.084	D_2h
VAWXAS	2.079	2.079	2.105	2.105	2.120	2.120	D_2h
VAWXAS01	2.075	2.075	2.083	2.083	2.118	2.118	D_2h
VILQIR	2.086	2.086	2.090	2.090	2.122	2.122	D_2h
VILQUD	2.070	2.070	2.108	2.108	2.135	2.135	D_2h
VIWPEX	2.025	2.025	2.081	2.081	2.095	2.095	D_2h
VOPMOC	2.046	2.046	2.078	2.078	2.119	2.119	D_2h
WABLIU10	2.072	2.072	2.072	2.072	2.075	2.075	D_2h
WADBEJ	2.039	2.039	2.087	2.087	2.137	2.137	D_2h
WAJKUO	2.071	2.071	2.098	2.098	2.105	2.105	D_2h
WANREJ	2.059	2.059	2.091	2.091	2.100	2.100	D_2h
WIGTUC	2.052	2.052	2.083	2.083	2.106	2.106	D_2h
WIZGIW	2.065	2.065	2.079	2.079	2.111	2.111	D_2h
WUCYOI	2.033	2.085	2.104	2.104	2.116	2.116	D_2h
WUTGOH	2.080	2.080	2.087	2.087	2.098	2.098	D_2h
WUYHUT	2.063	2.063	2.101	2.101	2.125	2.125	D_2h
XILNOW	2.075	2.075	2.086	2.086	2.103	2.103	D_2h
XIYMEY	2.067	2.067	2.072	2.072	2.075	2.075	D_2h
XOBKOO	2.059	2.059	2.062	2.062	2.096	2.096	D_2h
YITNOE	2.053	2.053	2.075	2.075	2.115	2.115	D_2h
YIVSUS	2.069	2.069	2.082	2.082	2.085	2.085	D_2h
ZASREQ	2.051	2.051	2.105	2.105	2.116	2.116	D_2h
ZEBSII	2.035	2.035	2.113	2.113	2.145	2.145	D_2h
AQCOAM02	2.043	2.043	2.104	2.104	2.116	2.116	D_2h
COCXOI	2.076	2.076	2.090	2.090	2.107	2.107	D_2h
MOBFIT	2.061	2.061	2.099	2.099	2.157	2.157	D_2h
QODBOB	2.071	2.071	2.082	2.082	2.093	2.093	D_2h
YOBWUI	2.084	2.084	2.101	2.101	2.102	2.102	D_2h
IDANUX	2.090	2.090	2.110	2.110	2.110	2.110	D_{4h}
NUTMEU	2.056	2.056	2.081	2.081	2.081	2.081	D_{4h}
QESFUP01	2.086	2.086	2.106	2.106	2.106	2.106	D_{4h}
SIDKAS	2.105	2.105	2.106	2.106	2.106	2.106	D_{4h}
VIXCAH	2.054	2.054	2.095	2.095	2.095	2.095	D_{4h}
GINVUV	2.082	2.082	2.082	2.082	2.082	2.082	O_h

CSD REF CODE	Co—O bond length /Å						Symmetry
ODIMEU	2.080	2.080	2.080	2.080	2.080	2.080	O_h
UDEDEM	2.117	2.117	2.117	2.117	2.117	2.117	O_h
XAJPOO	2.118	2.118	2.118	2.118	2.118	2.118	O_h

* The position of the H atoms is ignored when assigning the point group

Table S2. Comparison of Bond Lengths and Bond Angles Involving Heavy Atoms in the Structures of $[Co(H_2O)_6]^{2+}$ Energy-Minimised in the C_1 and C_i Point Groups

Bond lengths

C_1				C_i			
Number	Atom1	Atom2	Length	Number	Atom1	Atom2	Length
1	Co1	O17	2.123	1	Co1	O8	2.124
2	Co1	O8	2.122	2	Co1	O16	2.122
3	Co1	O5	2.124	3	Co1	O4	2.122
4	Co1	O2	2.124	4	Co1	O14	2.122
5	Co1	O14	2.122	5	Co1	O10	2.124
6	Co1	O11	2.122	6	Co1	O2	2.122
	Mean		**2.123**				**2.123**
	σ		**0.001**				**0.001**

Bond Angles

C_1					C_i				
Number	Atom1	Atom2	Atom3	Angle	Number	Atom1	Atom2	Atom3	Angle
1	O17	Co1	O8	88.0	1	O8	Co1	O16	88.0
2	O17	Co1	O5	92.0	2	O8	Co1	O4	88.0
3	O17	Co1	O2	179.9	3	O8	Co1	O14	92.0
4	O17	Co1	O14	92.0	4	O8	Co1	O10	180.0
5	O17	Co1	O11	88.0	5	O8	Co1	O2	92.0
6	O8	Co1	O5	87.9	6	O16	Co1	O4	91.9
7	O8	Co1	O2	92.0	7	O16	Co1	O14	180.0
8	O8	Co1	O14	180.0	8	O16	Co1	O10	92.0
9	O8	Co1	O11	92.1	9	O16	Co1	O2	88.1
10	O5	Co1	O2	88.0	10	O4	Co1	O14	88.1
11	O5	Co1	O14	92.0	11	O4	Co1	O10	92.0
12	O5	Co1	O11	179.9	12	O4	Co1	O2	180.0
13	O2	Co1	O14	88.0	13	O14	Co1	O10	88.0
14	O2	Co1	O11	91.9	14	O14	Co1	O2	91.9
15	O14	Co1	O11	88.0	15	O10	Co1	O2	88.0
	Mean	Cis		**90.0**					**90.0**
	σ			**2.1**					**2.1**
	Mean	Trans		**179.9**					**180.0**
	σ			**0.0**					**0.0**

Table S3. The Co–N Bond Lengths in Structures of $[Co(NH_3)_6]^{2+}$ Reported in the CSD.*

CSD REFCODE	Co-N bond length /Å						Symmetry
CAFWEM	1.965	1.965	1.968	1.968	1.979	1.979	D_{2h}
	1.965	1.965	1.972	1.972	1.984	1.984	D_{2h}
FIRJIZ	1.940	1.940	1.954	1.954	1.955	1.955	D_{4h}
	1.937	1.937	1.938	1.938	1.958	1.958	D_{4h}
OKOCAS	1.947	1.952	1.953	1.962	1.974	1.978	C_1
RAJNIZ	2.135	2.135	2.187	2.187	2.195	2.195	D_{4h}

* The position of the H atoms is ignored when assigning the point group

Table S4. Bond Lengths and Bond Angles Involving Heavy Atoms in the Energy-Minimised Structure of $[Co(NH_3)_6]^{2+}$

Number	Atom1	Atom2	Length /Å
1	Co1	N14	2.257
2	Co1	N2	2.258
3	Co1	N8	2.249
4	Co1	N17	2.257
5	Co1	N11	2.249
6	Co1	N5	2.258

Number	Atom1	Atom2	Atom3	Angle /deg
1	N14	Co1	N2	87.9
2	N14	Co1	N8	92.3
3	N14	Co1	N17	175.7
4	N14	Co1	N11	90.8
5	N14	Co1	N5	89.2
6	N2	Co1	N8	88.3
7	N2	Co1	N17	89.2
8	N2	Co1	N11	177.5
9	N2	Co1	N5	93.9
10	N8	Co1	N17	90.8
11	N8	Co1	N11	89.7
12	N8	Co1	N5	177.5
13	N17	Co1	N11	92.3
14	N17	Co1	N5	87.9
15	N11	Co1	N5	88.3

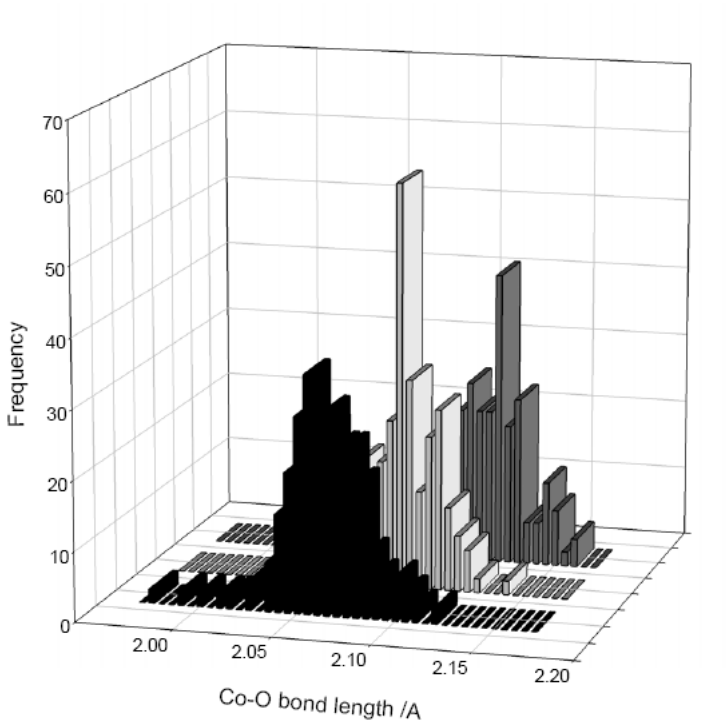

Figure S1. Observed Co–O bond lengths in 132 structures of $[Co(H_2O)_6]^{2+}$ with D_{2h} symmetry, arranged in clusters of the shortest, intermediate and longest bond lengths in each structure.

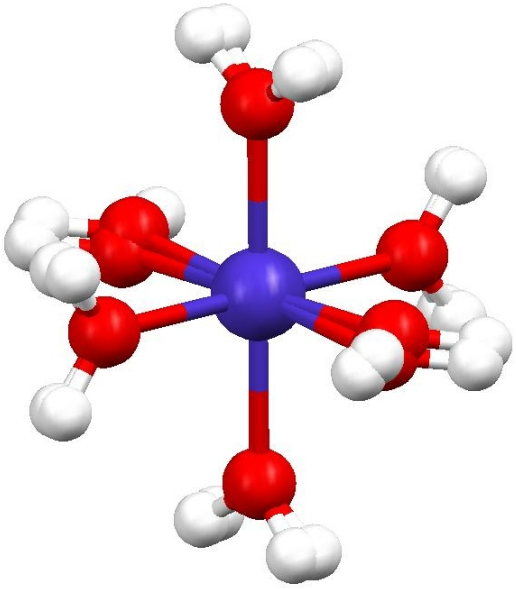

Figure S2. Overlay of the energy-minimised structure of $[Co(H_2O)_6]^{2+}$ energy minimised in the C_1 and the C_i point groups.

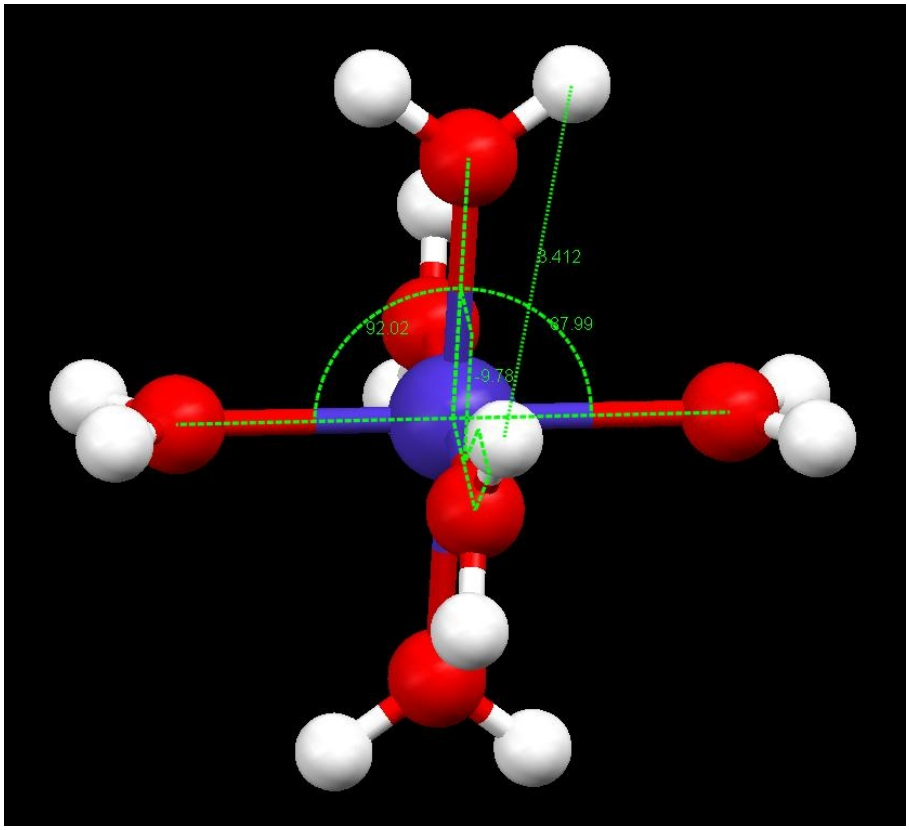

Figure S3. The energy-minimised structure of $[Co(H_2O)_6]^{2+}$ is distorted O_h (ignoring the H atoms) with some O–Co–O angles near 88° (and their complementary angles near 92°, see Table S2), and the O–Co–O–H torsions near 10°. H atoms on neighbouring H_2O ligands are not in close contact.

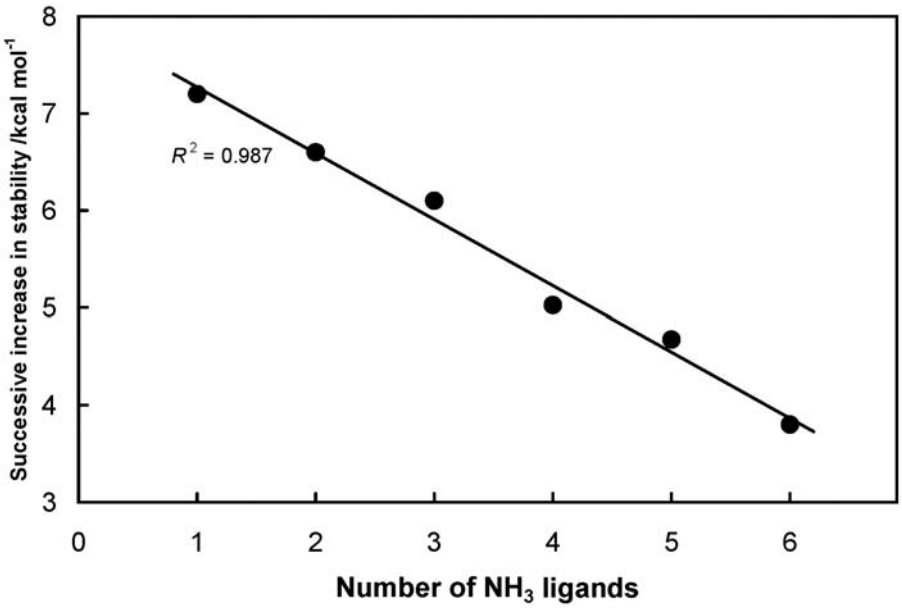

Figure S4. The differential increase in complex stability of $[Co(NH_3)_n(H_2O)_{6-n}]^{2+}$ decreases linearly with the number of NH_3 ligands, n.

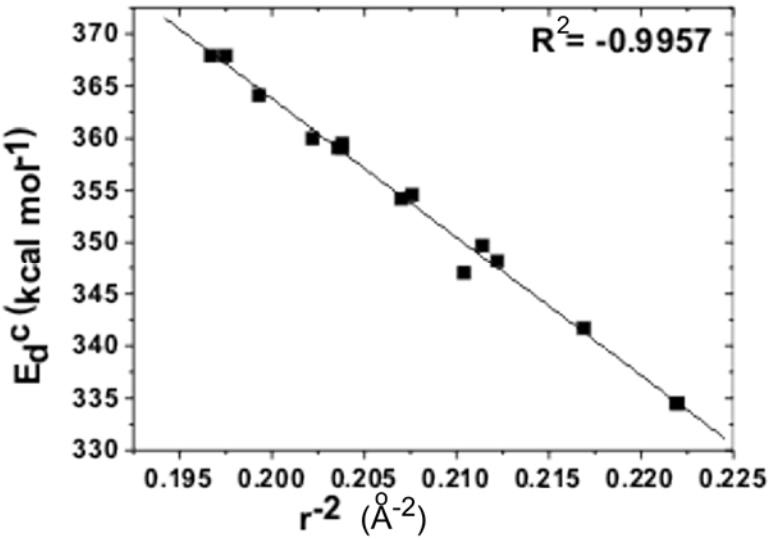

Figure S5. Dependence of calculated zero-point corrected stabilization energy (E_d^c) on the inverse-square mean metal-ligand bond distance (r).

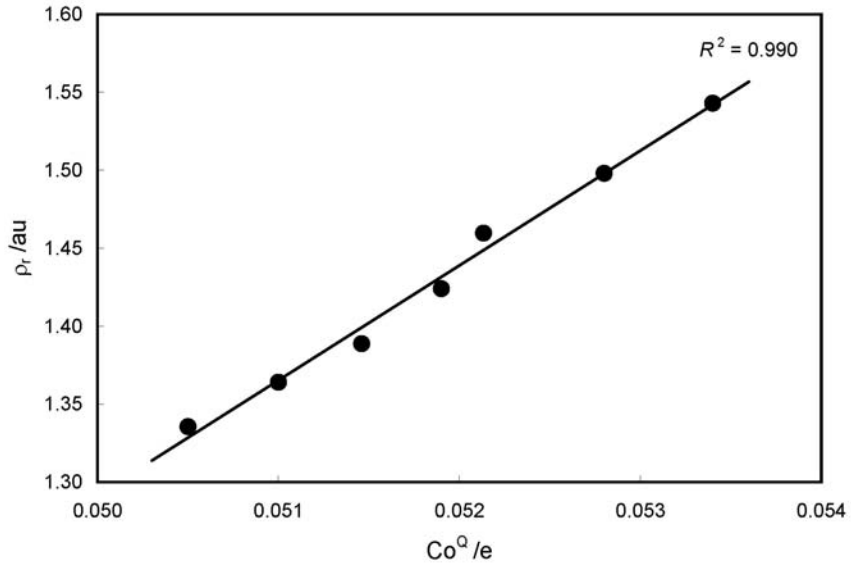

Figure S6 Correlation between the mean electron charge density (ρ_b) at the Co–ligand bond critical points and the partial charge on the Co ion. Mean values for each n in $[Co(NH_3)_n(H_2O)_n]^{2+}$ have been used.

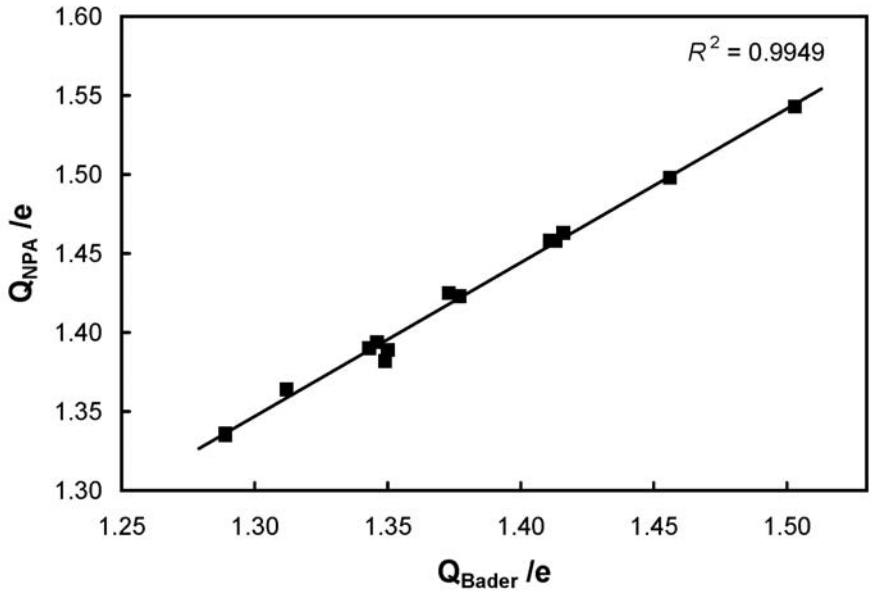

Figure S7. Correlation between the NPA and Bader charges on Co^{2+} in $[Co(NH_3)_n(H_2O)_{6-n}]^{2+}$

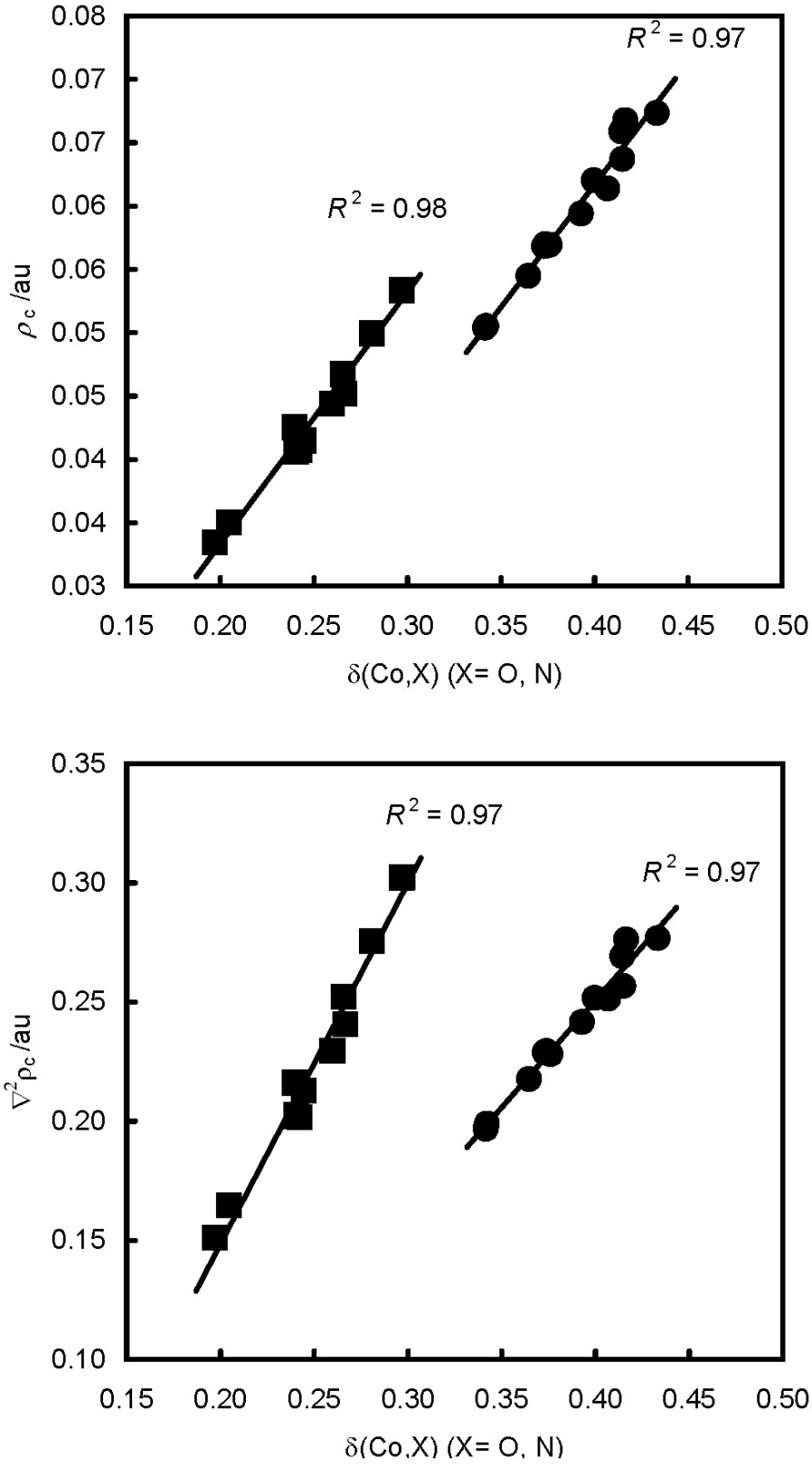

Figure S8. Correlation between the delocalization index δ(Co,O) (■) and δ(Co,N) (●) for Co–O and Co–N bonds with the electron density at the bond critical point (top) and its Laplacian (bottom).

References

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