Supplementary information

Tab. S1. Review of the matrix elements between the atomic-term kets $\left|l^n vLM_L SM_S\right\rangle$ [a]

Electron repulsion operator

$$\hat{V}^{\mathrm{ee}} = \left(\frac{e^2}{4\pi\varepsilon_0}\right)\sum_i^n\sum_{j>i}^n\sum_{k=0}^{\infty}\left[r_>^{-(k+1)}\cdot r_<^k\right]\sum_{q=-k}^{+k}(-1)^q\hat{C}_{-q}^k(1)\hat{C}_q^k(2)$$

with the Slater-Condon parameters $F_{ll}^k = \left(\frac{e^2}{4\pi\varepsilon_0}\right)\left\langle \alpha l,\alpha l\left|r_>^{-(k+1)}\cdot r_<^k\right|\alpha l,\alpha l\right\rangle$

or Racah parameters $A = F_{\mathrm{dd}}^0 - (49/441)F_{\mathrm{dd}}^4$, $B = F_{\mathrm{dd}}^2/49 - (5/441)F_{\mathrm{dd}}^4$, $C = (35/441)F_{\mathrm{dd}}^4$

- The matrix element is M_L- and M_S-independent

$$\left\langle l^n vLSM_L M_S\left|\hat{V}^{\mathrm{ee}}\right|l^n v'L'S'M_L'M_S'\right\rangle = \left\langle l^n vLS\left\|\hat{V}^{\mathrm{ee}}\right\|l^n v'L'S'\right\rangle\delta_{M_L,M_L'}\delta_{M_S,M_S'}$$

- Reduced matrix elements connect the terms of different seniority *v*

$$\left\langle l^n vLS\left\|\hat{V}^{\mathrm{ee}}\right\|l^n v'L'S'\right\rangle = \delta_{L,L'}\delta_{S,S'}\sum_{k=0,2,4}F_{ll}^k\cdot c^k(l^n vv'LS)$$

with the angular coefficients

$$c^k(l^n vv'LS) = \frac{1}{2}\left\langle l\left\|\mathbf{C}^k\right\|l\right\rangle^2\cdot\left\{\frac{1}{(2L+1)}\sum_{v''L''}\left\langle l^n vLS\left\|\mathbf{U}^k\right\|l^n v''L''S\right\rangle\cdot\left\langle l^n v'LS\left\|\mathbf{U}^k\right\|l^n v''L''S\right\rangle - \frac{n}{2l+1}\delta_{v,v'}\right\}$$

$$c^0(l^n vv'LS) = \frac{n(n-1)}{2}\delta_{v,v'}$$

- Reduced matrix elements of the (orbital) unit tensor operator using the (genealogic) coefficients of fractional parentage $G_{n-1,\mathrm{children}}^{n,\mathrm{parent}}$

$$\left\langle l^n vLS\left\|\mathbf{U}^k\right\|l^n v'L'S'\right\rangle = n\delta_{S,S'}(2L+1)^{1/2}(2L'+1)^{1/2}\cdot\sum_{v_1,L_1,S_1}^{\mathrm{parents}}(G_{n-1,v_1L_1S_1}^{n,vLS})^*\cdot G_{n-1,v_1L_1S_1}^{n,v'L'S'}\cdot(-1)^{L_1+L+l+k}\begin{Bmatrix}L & L' & k\\ l & l & L_1\end{Bmatrix}$$

- Reduced matrix element of the Racah operator (rationalized spherical harmonics)

$$\left\langle l\left\|\mathbf{C}^k\right\|l'\right\rangle = (-1)^l[(2l+1)(2l'+1)]^{1/2}\begin{pmatrix}l & k & l'\\ 0 & 0 & 0\end{pmatrix}$$

Spin-orbit (one-electron) coupling operator

$$\hat{H}^{\mathrm{so}} = \hbar^{-2}\sum_{i=1}^n\xi_i(\vec{l}_i\cdot\vec{s}_i) = \hbar^{-2}\xi_l\{\mathbf{L}^1\otimes\mathbf{S}^1\}^0 = \hbar^{-2}\xi_l\mathbf{V}^{11}$$

- The matrix element is M_L- and M_S-dependent

$$\left\langle l^n vLSM_L M_S\left|\kappa\hat{H}^{\mathrm{so}}\right|l^n v'L'S'M_L'M_S'\right\rangle$$

$$= \kappa\xi_l\left\langle l\left\|\mathbf{l}^1\right\|l\right\rangle\cdot\left\langle l^n vLSM_L M_S\left|-\mathbf{V}_{-1,+1}^{11}+\mathbf{V}_{0,0}^{11}-\mathbf{V}_{+1,-1}^{11}\right|l^n v'L'S'M_L'M_S'\right\rangle\hbar^{-2}$$

- Individual spherical components

$$\left\langle l^n vLSM_L M_S\left|\mathbf{V}_{q,r}^{11}\right|l^n v'L'S'M_L'M_S'\right\rangle$$

$$= \left\langle l^n vLS\left\|\mathbf{V}^{11}\right\|l^n v'L'S'\right\rangle\cdot(-1)^{L-M_L}\cdot\begin{pmatrix}L & 1 & L'\\ -M_L & q & M_L'\end{pmatrix}\cdot(-1)^{S-M_S}\cdot\begin{pmatrix}S & 1 & S'\\ -M_S & r & M_S'\end{pmatrix}$$

- Reduced matrix element of the double tensor (orbit-spin) operator between the atomic-term kets

$$\left\langle l^n vLS \left\| \mathbf{V}^{11} \right\| l^n v'L'S' \right\rangle = \hbar^2 n[s(s+1)(2s+1)]^{1/2}[(2L+1)(2L'+1)]^{1/2}[(2S+1)(2S'+1)]^{1/2}$$

$$\cdot \sum_{v_1,L_1,S_1}^{\text{parents}} (-1)^{L_1+S_1+L+S+l+s} (G^{n,vLS}_{n-1,v_1L_1S_1})^* \cdot G^{n,v'L'S'}_{n-1,v_1L_1S_1} \cdot \begin{Bmatrix} L & L' & 1 \\ l & l & L_1 \end{Bmatrix} \cdot \begin{Bmatrix} S & S' & 1 \\ s & s & S_1 \end{Bmatrix}$$

Orbital and spin Zeeman operator

$$\hat{H}^{\mathrm{Z}} = \mu_{\mathrm{B}} \hbar^{-1} \sum_{i=1}^{n} (\kappa \vec{l}_i + g_{\mathrm{e}} \vec{s}_i) \cdot \vec{B} = \mu_{\mathrm{B}} \hbar^{-1} \sum_{q=-1}^{+1} (-1)^q \mathbf{B}^1_{-q} (\kappa_q \mathbf{L}^1_q + g_{\mathrm{e}} \mathbf{S}^1_q)$$

- The orbital Zeeman interaction is M_S -independent

$$\left\langle l^n vLSM_L M_S \left| \hbar^{-1} \mu_{\mathrm{B}} \kappa (\vec{B} \cdot \vec{L}) \right| l^n v'L'S'M'_L M'_S \right\rangle = \delta_{v,v'} \delta_{L,L'} \delta_{S,S'} \delta_{M_S,M'_S} [L(L+1)(2L+1)]^{1/2} (-1)^{L-M_L} \mu_{\mathrm{B}}$$

$$\cdot [-\mathbf{B}^1_{+1} \begin{pmatrix} L & 1 & L' \\ -M_L & -1 & M'_L \end{pmatrix} \kappa_{-1} + \mathbf{B}^1_0 \begin{pmatrix} L & 1 & L' \\ -M_L & 0 & M'_L \end{pmatrix} \kappa_0 - \mathbf{B}^1_{-1} \begin{pmatrix} L & 1 & L' \\ -M_L & +1 & M'_L \end{pmatrix} \kappa_{+1}]$$

- The spin Zeeman interaction is M_L -independent

$$\left\langle l^n vLSM_L M_S \left| \hbar^{-1} \mu_{\mathrm{B}} g_{\mathrm{e}} (\vec{B} \cdot \vec{S}) \right| l^n v'L'S'M'_L M'_S \right\rangle = \delta_{v,v'} \delta_{L,L'} \delta_{S,S'} \delta_{M_L,M'_L} [S(S+1)(2S+1)]^{1/2} (-1)^{S-M_S} \mu_{\mathrm{B}} g_{\mathrm{e}}$$

$$\cdot [-\mathbf{B}^1_{+1} \begin{pmatrix} S & 1 & S' \\ -M_S & -1 & M'_S \end{pmatrix} + \mathbf{B}^1_0 \begin{pmatrix} S & 1 & S' \\ -M_S & 0 & M'_S \end{pmatrix} - \mathbf{B}^1_{-1} \begin{pmatrix} S & 1 & S' \\ -M_S & +1 & M'_S \end{pmatrix}]$$

- Spherical transforms of the magnetic induction

$\mathbf{B}^1_{+1} = -(1/\sqrt{2})(B_x + \mathrm{i}B_y)$, $\mathbf{B}^1_{-1} = +(1/\sqrt{2})(B_x - \mathrm{i}B_y)$, $\mathbf{B}^1_0 = B_z$

Crystal field operator

$$\hat{V}^{\mathrm{cf}} = \left(\frac{e^2}{4\pi\varepsilon_0} \right) \sum_{i=1}^{n} \sum_{K=1}^{N} z_K \sum_{k=0,2,4}^{2l} \left[r_>^{-(k+1)} \cdot r_<^k \right] \sum_{q=-k}^{+k} (-1)^q \hat{C}^k_{-q}(K) \hat{C}^k_q(i) = \sum_{k=0,2,4}^{2l} \sum_{q=-k}^{+k} a^k_q \cdot \hat{U}^k_q$$

with the crystal field parameters $F_k(R_K) = \left(\frac{e^2}{4\pi\varepsilon_0} \right) \left\langle r_>^{-(k+1)} \cdot r_<^k \right\rangle \approx \left(\frac{e^2}{4\pi\varepsilon_0} \right) R_K^{-(k+1)} \cdot \left\langle r^k \right\rangle$

and the potential constants $a^k_q = \left\langle l \left\| \mathbf{C}^k \right\| l \right\rangle \sum_{K=1}^{N} z_K F_k(R_K) \cdot (-1)^q \hat{C}^k_{-q}(\vartheta_K, \varphi_K)$

with the values of the spherical harmonics $(-1)^q \hat{C}^k_{-q}(\vartheta_K, \varphi_K) = \sqrt{4\pi/(2k+1)} \cdot Y^*_{k,q}(\vartheta_K, \varphi_K)$

- The matrix element is M_S -independent

$$\left\langle l^n vLSM_L M_S \left| \hat{V}^{\mathrm{cf}} \right| l^n v'L'S'M'_L M'_S \right\rangle = \delta_{S,S'} \delta_{M_S,M'_S} \sum_{k=0,2,4}^{2l} \sum_{q=-k}^{+k} a^k_q \cdot \left\langle l^n vLSM_L \left| \hat{U}^k_q \right| l^n v'L'S'M'_L \right\rangle$$

- Reduction according to the Wigner-Eckert theorem

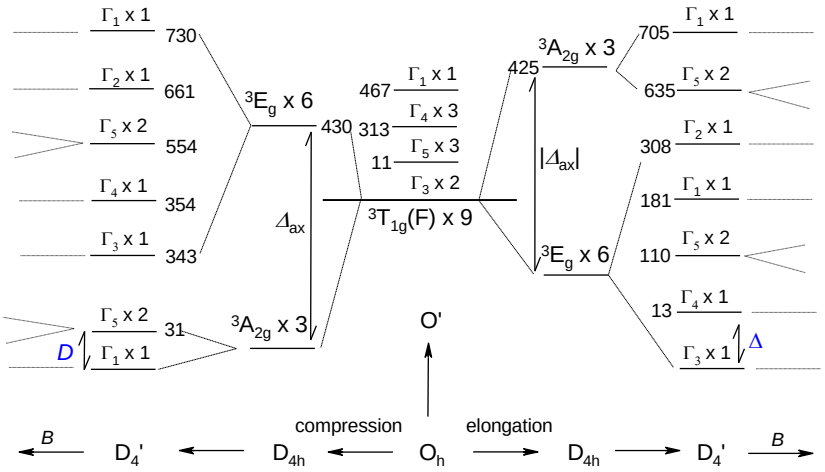
$$\left\langle l^n vLSM_L \left| \hat{U}^k_q \right| l^n v'L'S'M'_L \right\rangle = (-1)^{L-M_L} \begin{pmatrix} L & k & L' \\ -M_L & q & M'_L \end{pmatrix} \cdot \left\langle l^n vLS \left\| \mathbf{U}^k \right\| l^n v'L'S' \right\rangle$$

- The matrix elements $\left\langle l^n vLS \left\| \mathbf{U}^k \right\| l^n v'L'S' \right\rangle$ and $\left\langle l \left\| \mathbf{C}^k \right\| l' \right\rangle$ as above (see electron repulsion).

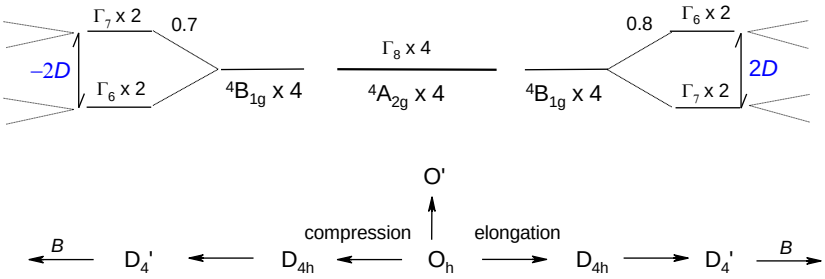
[a] The formulae require $l = 2$, $s = 1/2$.

Tab. S2. Energy level diagrams [cm^{-1}] for selected d^n systems; not to scale.

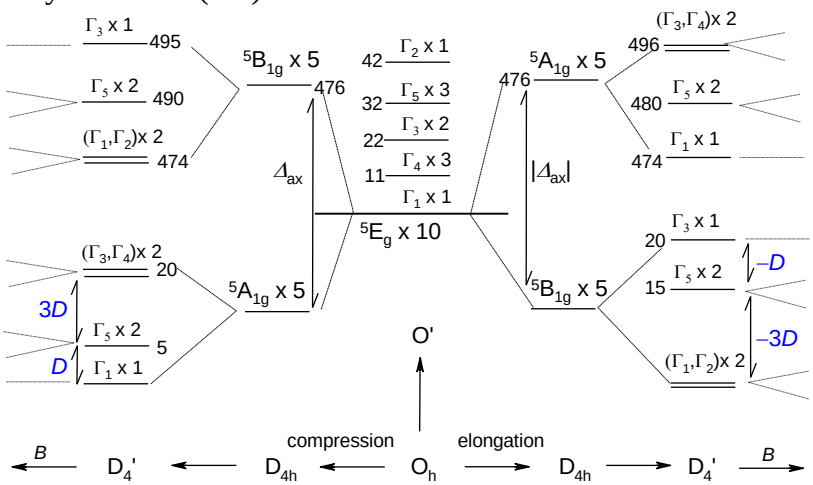
d^2 system – V(III)



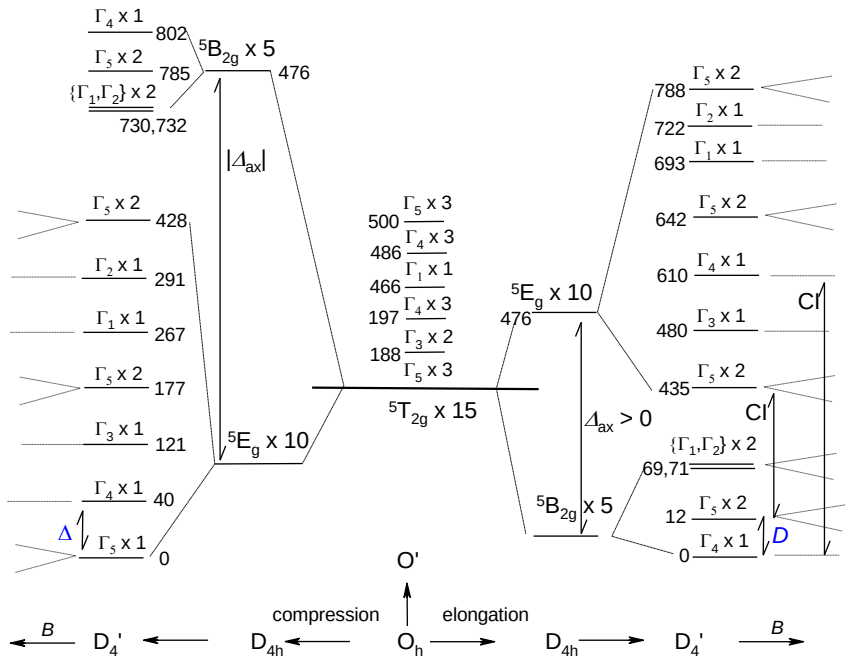
d^3 system – Cr(III)



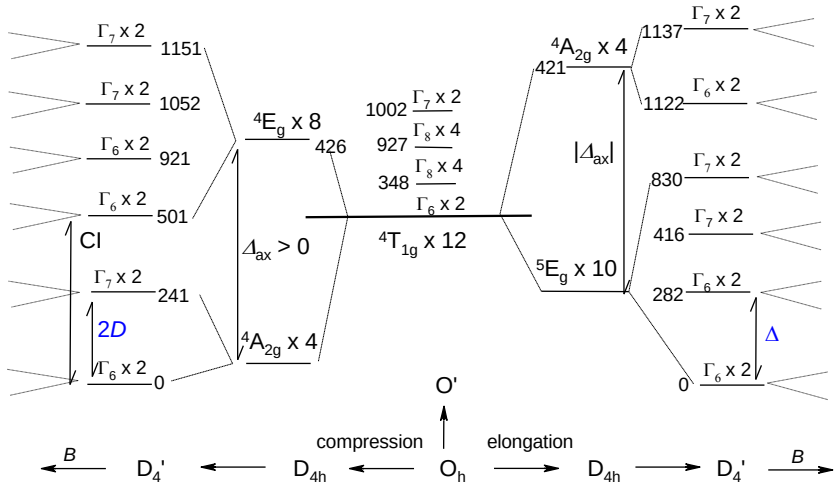
d^4 system – Mn(IIII)



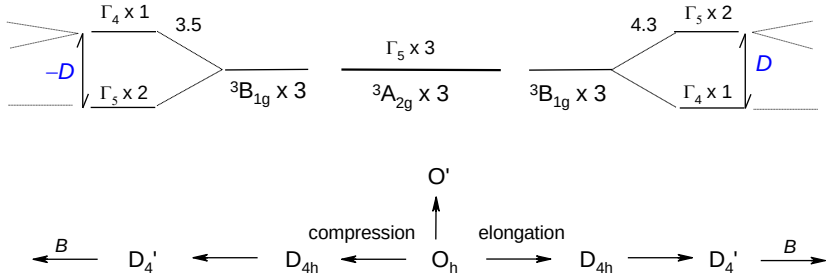
high-spin d^6 system – Fe(II)



high-spin d^7 system – Co(II)



d^8 system – Ni(II)



Tab. S3. HEXAcoordinate Ni(II) complexes: structural and magnetic parameters [pm, cm^{-1}]

No		Chromophore	Clu-ster	Compound	g_x	g_y	g_z	g_{xy}	g_z - g_{xy}	E	E_{str}	D	D_{str}
		Abbr. →					gz	gxy	gdif			D	Dstr
1	A	$\{NiN_2O_2O_2\}$	1	$[Ni(pydicar)(pymeoh)]\cdot H_2O$	2.169	2.169	2.478	2.169	0.309	0.13	1.1	-12.7	-24.35
2	B	$\{NiN_2O_2O_2\}$	2	$[Ni(2Meiz)_2(fm)_2(H_2O)_2]$	2.000	2.001	2.038	2.000	0.038	0.07	1.1	-6.00	-10.13
3	C	$\{NiN_4N_2\}$	2	$[Ni(bzimpy)_2](ClO_4)_2$	2.120	2.120	2.149	2.120	0.029	0	0	-4.63	-10.05
4	D	$\{NiN_2O_2O_2\}$	3	$[Ni(MeSnic)_2(fupy)_2(H_2O)_2]$	2.241	2.241	2.279	2.241	0.038	0	0	-4.98	-7.90
5	E	$\{NiN_2O_2O_2\}$	3	$[Ni(MeSnic)_2(lut)_2(H_2O)_2]$	2.199	2.199	2.249	2.199	0.050	0	0	-7.84	-7.40
6	F	$\{NiN_2O_2O_2\}$	2	$[Ni(Me_2iz)_2(fm)_2(H_2O)_2]$	2.139	2.140	2.190	2.140	0.050	0.08	1.9	-7.70	-6.25
7	G	$\{NiN_6\}$	2	$[Ni(iz)_6](fm)_2$	2.029	2.029	2.051	2.029	0.022	0.08	0	-3.43	-5.165
8	H	$\{NiN_2O_2O_2\}$	2	$[Ni(iqu)_2(ac)_2(H_2O)_2]$	2.105	2.106	2.139	2.106	0.033	0.08	1.4	-5.30	-4.97
9	I	$\{NiN_4N_2\}$	3	$[Ni(Me_2fupy)_4(NCS)_2]\cdot 6.6H_2O$	2.294	2.294	2.305	2.294	0.011	0	0	-1.65	-4.3
10	J	$\{NiN_2O_2O_2\}$	3	$[Ni(Mefupy)_2(ac)_2(H_2O)_2]$	2.187	2.190	2.208	2.189	0.019	0.23	1.7	-3.17	-3.70
11	K	$\{NiN_2O_2O_2\}$	3	$[Ni(bzfupy)_2(ac)_2(H_2O)_2]$	2.200	2.203	2.219	2.202	0.017	0.24	0.7	-2.85	-2.85
12	L	$\{NiN_4N_2\}$	3	$[Ni(Mefupy)_4(NCS)_2]\cdot 1.29H_2O$	2.201	2.201	2.213	2.201	0.012	0	0	-1.93	-2.60
13	M	$\{NiN_2O_2O_2\}$	2	$[Ni(fupy)_2(ac)_2(H_2O)_2]$	2.147	2.149	2.179	2.148	0.031	0.15	1.0	-5.00	-2.32
14	N	$\{NiN_4N_2\}$	3	$[Ni(iqu)_4(NCS)_2]\cdot CH_2Cl_2$	2.188	2.188	2.178	2.188	-0.010	0	0	-1.54	-0.70
15	O	$\{NiN_6\}$	4	$[Ni(iz)_6](Clac)_2$	2.154	2.154	2.154	2.154	0.000	0	0	0	-0.250
16	P	$\{NiN_4N_2\}$	5	$[Ni(dien)(mea)\{Ni(CN)_4\}]$	2.077	2.077	2.050	2.077	-0.027	0	0	4.19	2.02
17	Q	$\{NiN_6\}$	4	$[Ni(iz)_6](Clprop)_2$	2.155	2.155	2.150	2.155	-0.005	0	0	0.90	2.025
18	R	$\{NiN_6\}$	5	$[Ni(aepn)_2][Ni(CN)_4]\cdot H_2O$	2.080	2.080	2.073	2.080	-0.007	0	0	0.99	2.125
19	S	$\{NiN_4N_2\}$	4	$[Ni(fupy)_4(NCS)_2]\cdot THF$	2.199	2.200	2.180	2.200	-0.020	0.11	0	2.70	2.80
20	T	$\{NiN_4N_2\}$	4	$[Ni(bzfupy)_4(NCS)_2]\cdot 2H_2O$	2.227	2.227	2.219	2.227	-0.008	0	0	1.15	2.95
21	U	$\{NiN_6\}$	4	$[Ni(Meiz)_6]Cl_2\cdot 2H_2O$	2.185	2.185	2.173	2.185	-0.012	0	0	1.96	3.510
22	W	$\{NiN_4O_2\}$	4	$[Ni(pz)_4(ac)_2]$	2.170	2.170	2.146	2.170	-0.024	0	0.4	3.88	6.65
23	X	$\{NiO_4O_2\}$	4	$[Ni(H_2O)_4(MeSnic)_2]\cdot 4H_2O$	2.351	2.351	2.180	2.351	-0.171	0	0	4.39	8.60
24	Y	$\{NiN_4O_2\}$	5	$[Ni(Me_2iz)_4(H_2O)_2]\cdot Cl_2\cdot 3H_2O$	2.126	2.126	2.079	2.126	-0.047	0	0.7	7.42	11.35
25	Z	$\{NiN_4O_2\}$	5	$[Ni(L_{NN})_2(H_2O)_2]$	2.103	2.159	2.000	2.131	-0.131	1.46	3.1	11.23	15.5

Formulae for structural tetragonality (rhombicity): $D_{str} = \Delta_z - (\Delta_y + \Delta_x)/2$, $E_{str} = (\Delta_y - \Delta_x)/2$, $\Delta_a = (R_a - \bar{R}_a)$. Mean distances: $\bar{d}(\mathrm{Ni-N}) =$ 2.145, $\bar{R}(\mathrm{Ni-NCS}) =$ 2.070, $\bar{d}(\mathrm{Ni-O}) =$ 2.055 Å. Magnetic *E*-values are only tentative.

Abbreviations of ligands: fm^- = formato, ac^- = acetato, $Clac^-$ = chloroacetato, $Clprop^-$ = 2-chloropropionato, $MeSnic^-$ = 2-methyl-sulfanyl-nicotinato, $pydicar^-$ = pyridine-2,6-dicarboxylato, iz = imidazole, Meiz = 1-methylimidazole, 2Meiz = 2-methylimidazole, 1,2-Me_2iz = 1,2-dimethylimidazole, pz = pyrazole, iqu = *iso*-quinoline, fupy = furo[3,2-c]pyridine, Mefupy = 2-methylfuro[3,2-c]pyridine, Me_2fupy = 2,3-dimethylfuro[3,2-c]pyridine, bzfupy = benzo[4,5]furo[3,2-c]pyridine, pymeoh = 2,6-bis(hydroxymethyl)pyridine, lut = 3,5-lutidine.

Correlation coefficients between variables using 25 datapoints for hexacoordinate Ni(II) complexes

	D	Dstr	gz	gxy
Dstr	0.9485			
gz	-0.5997	-0.6184		
gxy	0.0957	0.1435	0.6002	
gdif	-0.8241	-0.8918	0.6630	-0.2008

Component weights (PCA analysis) for hexacoordinate Ni(II) complexes

	Component 1	Component 2
D	0.517	0.123
Dstr	0.530	0.152
gz	-0.430	0.501
gxy	-0.012	0.827
gdif	-0.515	-0.159

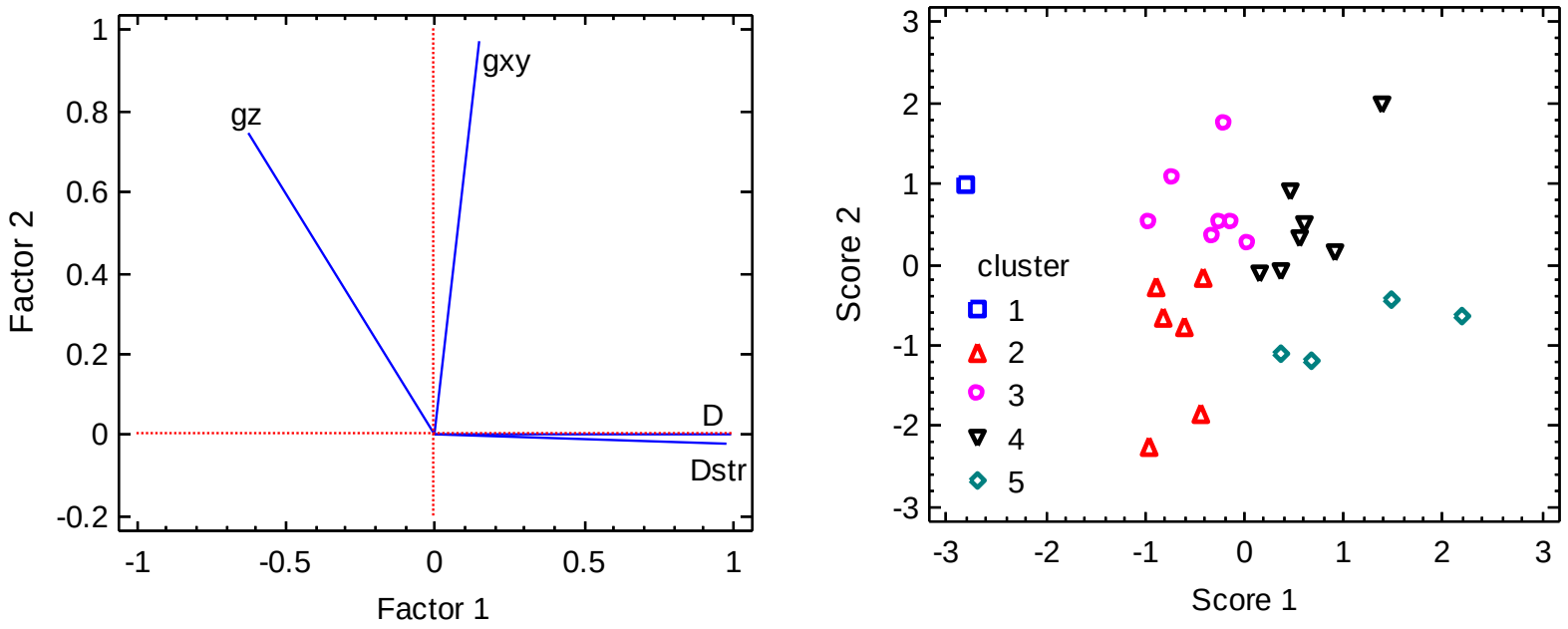


Fig. S1. FA biplot after varimax rotation for hexacoordinate Ni(II) complexes. The points are the individual objects.

Tab. S4. HEXAcoordinate Co(II) complexes: structural and magnetic parameters [pm, cm^{-1}]

No		Chromophore	Clu-ster	Compound	g_x	g_y	g_{xy}	E	E_{str}	$2D$	D	D_{str}
		Abbr. →					gxy			D2		Dstr
1	A	$\{CoN_2O_2O_2\}$	1	$[Co(MeIz)_2(ac)_2(H_2O)_2]$	2.530	2.530	2.530	0	2.42	190.0	95.0	-11.87
2	B	$\{CoO_4O_2\}$	1	$[Co(2OHnic)_2(H_2O)_2]$	2.670	2.730	2.700	0.26	0.10	159.8	79.91	-9.40
3	C	$\{CoN_2O_2O_2\}$	1	$[Co(bylim)_2(bz)_2(H_2O)_2]$	2.510	2.620	2.565	0.55	1.25	158.0	79.0	-9.25
4	D	$\{CoN_2O_2O_2\}$	1	$[Co(pic)_2(H_2O)_2]$	2.650	2.720	2.685	2.34	3.55	168.5	84.24	-8.45
5	E	$\{CoN_2O_2O_2\}$	1	$[Co(MeSnic)_2(Me_2fupy)_2(H_2O)_2]$	2.740	2.610	2.675	1.39	2.35	199.1	99.54	-7.55
6	F	$\{CoN_2O_2O_2\}$	1	$[Co(bz)_2(nca)_2(H_2O)_2]$	3.118	3.118	3.118	0	2.95	211.6	105.8	-6.65
7	G	$\{CoN_6\}$	1	$[Co(iz)_6](HCOO)_2$	2.753	2.753	2.753	0	0.71	190.0	95.00	-6.10
8	H	$\{CoN_2O_2O_2\}$	2	$[Co(iqu)_2(ac)_2(H_2O)_2]$	2.587	2.689	2.638	3.01	1.80	167.9	83.96	-2.80
9	I	$\{CoN_2O_2O_2\}$	2	$[Co(pybzfupy)_2(ac)_2(H_2O)_2]$	2.607	2.758	2.683	2.84	1.50	179.2	89.59	-2.30
10	J	$\{CoN_2O_2O_2\}$	2	$[Co(bzfupy)_2(ac)_2(H_2O)_2]$	2.613	2.801	2.707	6.90	1.10	206.0	103.0	-0.80
11	K	cis$\{CoN_4N_2\}$	1	α-*cis*-$[Co(phen)_2(dca)_2]$	2.596	2.596	2.596	0	0	169.6	84.8	-7.80
12	L	cis$\{CoN_4N_2\}$	1	β-*cis*-$[Co(phen)_2(dca)_2]$	2.657	2.657	2.657	0	0	198.2	99.1	-6.90
13	M	cis$\{CoN_4N_2\}$	2	$[Co(phen)_3](tcm)_2$	2.594	2.594	2.594	0	0	158.6	79.3	-1.00
14	N	cis$\{CoN_4N_2\}$	2	$[\{Co(phen)_2tcm\}_2\mu^2\text{-}tcm]tcm\cdot H_2O$	2.673	2.673	2.673	0	0	188.8	94.4	-1.60
15	O	cis$\{CoN_2N_4\}$	2	*catena*-$[Co(bpy)(dca)_2]$	2.438	2.438	2.438	0	0	203.2	101.6	-1.10
16	P	cis$\{CoN_2N_4\}$	2	*catena*-$[Co(bpy)(tcm)_2]$	2.633	2.633	2.633	0	0	206.4	103.2	-0.70

g_z = 2.0 – fixed. Mean distances $\bar{R}(\mathrm{Co-N}) = 2.185$, $\bar{R}(\mathrm{Co-O}) = 2.085$, and $\bar{R}(\mathrm{Co-Cl}) = 2.475$ Å.

Abbreviations for ligands: fm^- = formato, ac = acetato$^-$, bz^- = benzoato, pic^- = picolinato, MeSnic = 2-methylthionicotinato$^-$, 2OHnic = 2-hydroxynicotinato$^-$, dca^- = dicyanoamide, tcm^- = tricyanomethanide, iz = 1H-imidazole, bzfupy = benzofuro[3,2-c]pyridine, bylim = 1-phenyl-1H-imidazole, iqu = *iso*-quinoline, Meiz = methylimidazole, Me_2fupy = 2,3-dimethylfuro[3,2-c]pyridine, pybzfupy = 1-(pyridine-3-yl)benzofuro[3,2-c]pyridine, nca = nicotinamide, L = 2-[(2,2-diphenylethylimino)methyl]pyridine-1-oxide, phen = 1,10-phenanthroline, bpy = 4,4‘-bipyridine, ampy = aminopyrimidine, abpt = 4-amino-3,5-bis(2-pyridyl)-1,2,4-triazole.

Correlation coefficients using 16 datapoints

	D2	Dstr	gxy
D2			
Dstr	0.2718		
gxy	0.3159	-0.0805	

Component weights (PCA analysis)

	Component 1	Component 2
gxy	0.527	-0.647
D2	0.739	0.031
Dstr	0.418	0.761

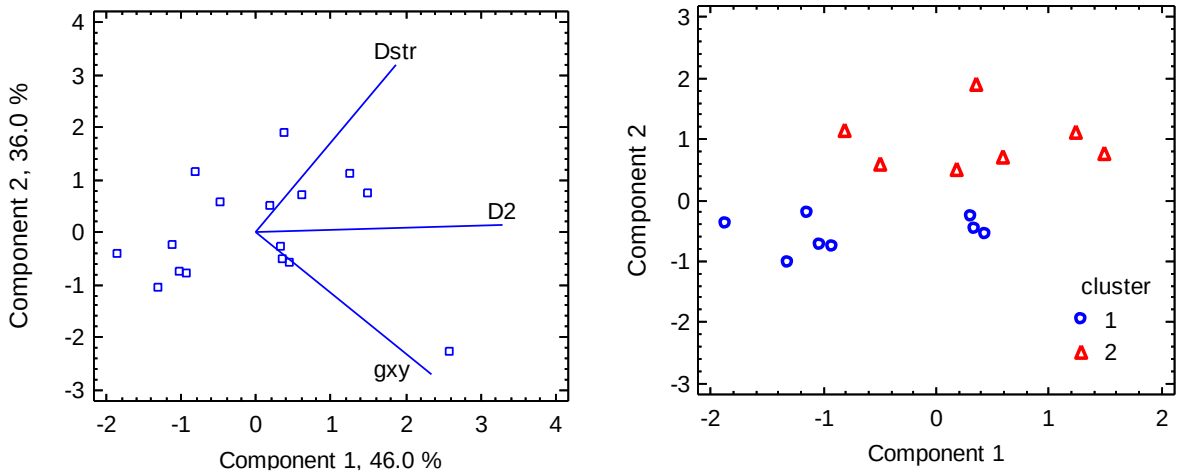


Fig. S2. PCA biplot for hexacoordinate Co(II) complexes. The points are the individual objects.

Tab. S5. TETRAcoordinate Co(II) complexes: structural and magnetic parameters [Å, deg, cm^{-1}]

								Magnetic data				HF/HF-EPR data				
No	Compound	Chromophore $\{CoA_2B_2\}$		*R*(Co-A)	*R*(Co-B)	α(A-Co-A)	β(B-Co-B)	*D*	g_z	g_x	g_y	*D*epr	$g_z$epr	$g_x$epr	$g_y$epr	*E*epr
1	$[CoCl_2(dmpz)_2]$	$\{CoCl_2N_2\}$	C_{2v}	2.238	2.005	118.1	105.7	41.5	2.0	2.538	2.538					
2	$[CoCl_2(ndmiz)_2]$	$\{CoCl_2N_2\}$	C_{2v}	2.231	2.034	111.0	102.4	11.13	2.115	2.240	2.515	11.38	2.16	2.09	2.37	2.36
3	$[CoCl_2(iz)_2]$	$\{CoCl_2N_2\}$	C_1	2.250	1.993	111.2	105.3	5.67	2.079	2.270	2.335	9.15	2.245	2.245	2.245	1.00
4	$Hg[Co(NCS)_4]$	single crystal	D_{2d}	1.964	1.964	113.5	113.5	5.1	2.168	2.251	2.251					
4	$Hg[Co(NCS)_4]$	$\{CoN_4\}$	D_{2d}	1.964	1.964	113.5	113.5	3.86	2.223	2.292	2.292	5.50	2.20	2.15	2.15	0
5	$[Co(NCS)_2(qu)_2]$	$\{CoN_2N_2\}$	C_1	1.937	2.036	108.3	104.5	5.00	2.133	2.250	2.250					
6	$[CoCl_2(bziz)_2]$	$\{CoCl_2N_2\}$	C_1	2.247	2.007	111.9	106.2	2.18	2.304	2.415	2.529	3.33	2.236	2.221	2.24	0.93
7	Cs_3CoCl_5	$\{CoCl_4\}$	D_{2d}	2.268	2.268	107.2	107.2					-4.30	2.40	2.30	2.30	
8	$[CoCl_2(ct)_2]$	$\{CoCl_2N_2\}$	C_1	2.299	2.055	103.4	110.4	-5.23	2.248	2.173	2.201	-4.31	2.253	2.220	2.233	0.23
9	$[CoCl_2(Mepy)_2]$	$\{CoCl_2N_2\}$	C_1	2.232	2.051	121.4	107.4	-4.88	2.523	2.123	2.123					
10	Cs_3CoBr_5	$\{CoBr_4\}$	D_{2d}	2.399	2.399	107.6	107.6					-5.34	2.42	2.32	2.32	
11	$[CoCl_2(qu)_2]$	$\{CoCl_2N_2\}$	C_{2v}	2.244	2.070	113.4	107.2	-6.35	2.496	2.075	2.113	-5.88	2.194	2.210	2.220	1.54
12	$[CoCl_2(ampy)_2]$	$\{CoCl_2N_2\}$	C_{2v}	2.243	2.041	110.4	114.5	-9.99	2.362	2.193	2.197	-7.99	2.220	2.225	2.246	2.23
13	$(Hiz)_2[CoCl_4]$	$\{CoCl_4\}$	C_1	2.274	2.280	118.9	113.1	-12.0	2.362	2.225	2.225					
14	$[Co(PPh_3)_2Cl_2]$	$\{CoCl_2P_2\}$	C_{2v}	2.212	2.384	117.3	115.9	-11.6	2.265	2.215	2.215	-14.7	2.240	2.168	2.168	1.14
15	$[Co(PPh_3)_2Br_2]$	$\{CoBr_2P_2\}$	C_{2v}	2.349	2.385	115.2	117.4	-12.5	2.164	2.006	2.006					

Convention: $g_y > g_x$.

Data selection for multivariate methods

No	Compound	Chromophore $\{CoA_2B_2\}$	*R*(Co-A)	*R*(Co-B)	α(A-Co-A)	β(B-Co-B)	$(\alpha+\beta)/2$	$(\alpha-\beta)/2$	*D*	g_z	g_x	g_y	g_{xy}	g_z - g_{xy}
	Abbr. →		RA	RB	alpha	beta	Aplus	Aminus	D	gz	gx	gy	gxy	gdif
1	$[CoCl_2(dmpz)_2]$	$\{CoCl_2N_2\}$	2.238	2.005	118.1	105.7	111.90	6.20	41.5	2.000	2.538	2.538	2.538	-0.538
2	$[CoCl_2(ndmiz)_2]$	$\{CoCl_2N_2\}$	2.231	2.034	111.0	102.4	106.70	4.30	11.38	2.16	2.09	2.37	2.230	-0.070
3	$[CoCl_2(iz)_2]$	$\{CoCl_2N_2\}$	2.250	1.993	111.2	105.3	108.25	2.95	9.15	2.245	2.245	2.245	2.245	0.000
4	$Hg[Co(NCS)_4]$	$\{CoN_4\}$	1.964	1.964	113.5	113.5	113.50	0.00	5.50	2.20	2.15	2.15	2.150	0.050
5	$[Co(NCS)_2(qu)_2]$	$\{CoN_2N_2\}$	1.937	2.036	108.3	104.5	106.40	1.90	5.00	2.133	2.250	2.250	2.250	-0.117
6	$[CoCl_2(bziz)_2]$	$\{CoCl_2N_2\}$	2.247	2.007	111.9	106.2	109.05	2.85	3.33	2.236	2.221	2.24	2.231	0.005
7	Cs_3CoCl_5	$\{CoCl_4\}$	2.268	2.268	107.2	107.2	107.20	0.00	-4.30	2.40	2.30	2.30	2.300	0.100
8	$[CoCl_2(ct)_2]$	$\{CoCl_2N_2\}$	2.299	2.055	103.4	110.4	106.90	-3.50	-4.31	2.253	2.220	2.233	2.227	0.026
9	$[CoCl_2(Mepy)_2]$	$\{CoCl_2N_2\}$	2.232	2.051	121.4	107.4	114.40	7.00	-4.88	2.523	2.123	2.123	2.123	0.400
10	Cs_3CoBr_5	$\{CoBr_4\}$	2.399	2.399	107.6	107.6	107.60	0.00	-5.34	2.42	2.32	2.32	2.320	0.100

11	$[CoCl_2(qu)_2]$	$\{CoCl_2N_2\}$	2.244	2.070	113.4	107.2	110.30	3.10	-5.88	2.194	2.210	2.220	2.215	-0.021
12	$[CoCl_2(ampy)_2]$	$\{CoCl_2N_2\}$	2.243	2.041	110.4	114.5	112.45	-2.05	-7.99	2.220	2.225	2.246	2.236	-0.015
13	$(Hiz)_2[CoCl_4]$	$\{CoCl_4\}$	2.274	2.280	118.9	113.1	116.00	2.90	-12.0	2.362	2.225	2.225	2.225	0.137
14	$[Co(PPh_3)_2Br_2]$	$\{CoBr_2P_2\}$	2.349	2.385	115.2	117.4	116.30	-1.10	-12.5	2.164	2.006	2.006	2.006	0.158
15	$[Co(PPh_3)_2Cl_2]$	$\{CoCl_2P_2\}$	2.212	2.384	117.3	115.9	116.60	0.70	-14.7	2.240	2.168	2.168	2.168	0.072

Correlation coefficients between variables (15 datapoints)

	D	RA	RB	alpha	beta	Aplus	Aminus	gz	gxy
RA	-0.2373								
RB	-0.5852	0.5153							
alpha	0.0629	-0.0189	0.0764						
beta	-0.5897	0.1113	0.4938	0.2491					
Aplus	-0.3167	0.0551	0.3500	0.8089	0.7710				
Aminus	0.5147	-0.1031	-0.3216	0.6525	-0.5713	0.0822			
gz	-0.5846	0.3329	0.3571	0.0459	0.0529	0.0623	-0.0025		
gxy	0.7303	0.0506	-0.2347	-0.1467	-0.5328	-0.4200	0.2926	-0.2845	
gdif	-0.8135	0.1922	0.3737	0.1156	0.3451	0.2856	-0.1721	0.8306	-0.7702

Component weights (PCA analysis)

	Component 1	Component 2	Component 3	Component 4
RA	0.161	-0.124	-0.265	-0.662
RB	0.330	-0.061	-0.005	-0.497
alpha	0.093	0.663	-0.117	-0.054
beta	0.367	0.131	0.470	-0.105
Aplus	0.284	0.515	0.208	-0.100
Aminus	-0.208	0.459	-0.467	0.036
D	-0.448	0.169	0.015	-0.112
gz	0.291	-0.116	-0.564	0.064
gxy	-0.374	-0.035	-0.084	-0.430
gdif	0.412	-0.057	-0.326	0.293

Tab. S6. PENTAcoordinate Co(II) complexes: structural and magnetic parameters [Å, deg, cm^{-1}]

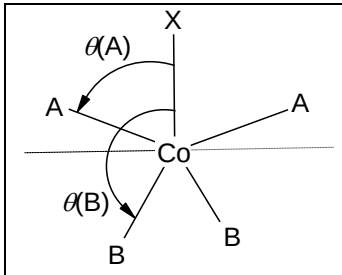
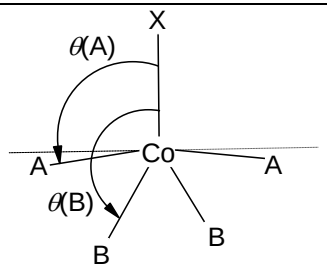
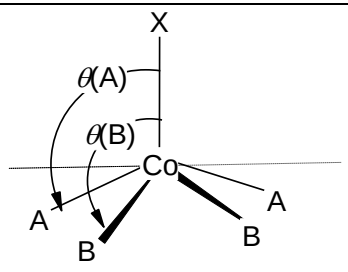
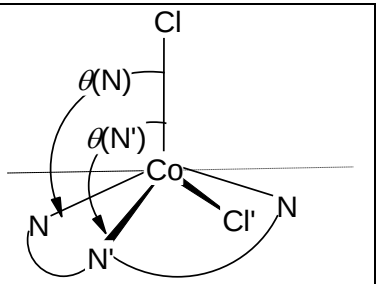
Data for complexes classified as a trigonal bipyramid {$Co(XA_2)B_2$}, set 1

No	Complex	Chromophore {$CoXA_2B_2$}	Geometry	Co-X (z) /Å	Co-A /Å	Co-B /Å	A-Co-A	B-Co-B	X-Co-A	X-Co-B	A-Co-B	A-Co-B	*D* /cm^{-1}	*E* /cm^{-1}	*J* /cm^{-1}	g_{xy}
1	$[CoL^{I}Cl_2]$	{$CoNN_2Cl_2$}	(4py)	2.070	2.175 2.203	2.273 2.265	147.20	113.64	74.39 74.29	107.98 138.38	97.56 99.30	98.67 100.01	71.7	0	-	2.51
2	$[CoL^{C7}Cl_2]_2$	{$CoNN_2Cl_2$}	(4py)	2.070	2.132 2.179	2.262 2.292	145.55	112.92	74.08 74.60	100.90 146.17	96.30 101.76	94.64 105.02	151	11.6	1.40	3.28
3	$[CoL^{C10}Cl_2]_2$	{$CoNN_2Cl_2$}	3bpy	2.066	2.130 2.154	2.285 2.269	149.97	112.07	75.04 75.25	119.22 128.71	96.70 98.42	97.54 100.58	86.4	5.0	1.10	3.06
4	$[CoL^{C12}Cl_2]$	{$CoNN_2Cl_2$}	3bpy	2.061	2.147 2.156	2.275 2.278	150.56	112.17	75.17 75.42	125.88 121.94	96.58 99.34	98.10 98.58	46.8	0	-	2.35
5	$[CoL^{C14}Cl_2]_2$	{$Co(NN_2)Cl_2$}	(4py)	2.085	2.135 2.137	2.263 2.329	141.61	111.75	73.54 73.82	95.39 152.86	98.20 101.67	96.51 106.12	70.0	4.1	1.47	2.74
6	$[Co(bzimpy)Cl_2]\cdot DMF$	{$CoNN_2Cl_2$}	(4py)	2.136	2.136 2.141	2.286 2.331	146.01	111.56	74.38 74.58	101.41 147.04	98.38 100.99	98.35 100.13	61.9	0	-	2.34
7	$[Co(terpy)Cl_2]$	{$CoNN_2Cl_2$}	(4py)	2.074	2.142 2.161	2.291 2.325	147.82	110.29	75.35 75.63	98.74 150.95	97.20 101.41	96.03 101.84	99.5, calc	-	-	(3.157)
8	$[Co(terpy)(NCS)_2]$	{$CoNN_2N'_2$}	3bpy	2.030	2.145 2.145	1.981 1.981	154.04	103.78	77.02 77.02	128.11 128.11	93.08 102.92	93.08 102.92	49.0, calc	-	-	(2.570)
9	[Co(saldptm)]	{$CoNN_2O_2$}	3bpy	2.124	2.045 2.054	1.952 1.944	177.11	138.63	91.44 91.36	109.68 111.69	87.78 91.95	87.58 90.72	52.0	0	-	2.60
10	$[Co(pno)_5](ClO_4)_2$	{$CoOO_2O_2$}	3bpy	1.989	2.104 2.058	1.976 1.986	172.52	131.64	90.11 95.78	117.66 110.38	87.10 95.13	85.70 87.49	12.5, epr	0	-	(2.15)
11	$[Co_2(PhCOO)_4(qu)_2]$	{$CoNO_2O_2$}	4py	2.083	2.024 2.081	2.015 2.038	163.04	162.93	92.39 104.25	96.78 99.83	86.66 88.74	86.15 93.53	67.2	0	-1.65	2.14

calc – ab initio calculations; $D = \lambda(g_z - g_{xy})/2$ was used in estimating g_{xy}, $\lambda = -172$ cm^{-1}. epr – estimate by X-band EPR. $g_z = 2.0$ – fixed.

Data for complexes reclassified as a tetragonal pyramid {CoCl(N_3Cl')}, set 2

No	Cluster	Complex	Chromophore	Co-Cl (z)	Co-N	Co-Cl'	N-Co-N	N'-Co-Cl'	Cl-Co-Cl'	Cl-Co-N'	Cl-Co-N	$\tau = (\alpha - \beta)/60$	*J*	*D*	*E*	g_x
		Abbr. →	{$CoClN_3Cl'$}	Ra	R3	R1	alpha	beta	T1	T2	T3	tau	J	D	E	gx
1	1	$[CoL^0Cl_2]$	{$CoClN_3Cl'$	2.265	2.070 2.175 2.203	2.273	147.20	138.38	113.64	107.98	98.67 100.01	0.15	0	71.7	0	2.51
2	1	$[CoL^7Cl_2]_2$	{$CoClN_3Cl'$	2.292	2.070 2.132 2.179	2.262	145.55	146.17	112.92	100.90	94.64 105.02	0.01	1.40	151	11.6	3.28
5	1	$[CoL^{14}Cl_2]_2$	{$CoClN_3Cl'$	2.329	2.085 2.137 2.135	2.263	141.61	152.86	111.75	95.39	96.51 106.12	0.19	1.47	70.0	4.1	2.74
6	1	[Co(bzimpy)Cl_2] ·DMF	{$CoClN_3Cl'$	2.331	2.136 2.141 2.136	2.286	146.01	147.04	111.56	101.41	98.37 100.99	0.02	0	61.9	0	2.34
7	1	[Co(terpy)Cl_2]	{$CoClN_3Cl'$	2.325	2.074 2.142 2.161	2.291	147.82	150.95	110.29	98.74	96.03 101.84	0.05	0	99.5	0	3.157

			
θ(A) < 90, γ > 180, τ > 1	θ(A) < θ(B), γ < 180, τ < 1, trigonal bipyramid	θ(A) ~ θ(B), γ < 180, τ ~ 0, tetragonal pyramid	reclassification to a tetragonal pyramid for set 2

Analysis by SHAPE; agreement factor [S. Alvarez and M. Llunell, *J. Chem. Soc*., *Dalton Trans*., 2000, 3288.]

	Complex	Trigonal bipyramid	Square pyramid
1	$[CoL^{0}Cl_2]$	3.809	2.263
2	$[CoL^{7}Cl_2]$	5.174	1.902
3	$[CoL^{10}Cl_2]$	2.832	3.462
4	$[CoL^{12}Cl_2]$	2.668	4.101
5	$[CoL^{14}Cl_2]$	6.946	1.876
6	$[Co(bzimpy)Cl_2]$	5.047	1.697
7	$[Co(terpy)Cl_2]$	5.474	1.675
8	$[Co(terpy)(NCS)_2]$	2.974	4.482
9	$[Co(saldptm)Cl_2]$	0.835	2.340
10	$[Co(pno)_5]$	0.764	3.017
11	$[Co_2(PhCOO)_4(qu)_2]$	5.842	0.423

Data selection for multivariate methods, set 1

No	Cluster	Complex	Chromophore	Co-X (z)	Co-A	Co-B	A-Co-A	B-Co-B	θ(A)	θ(B)	$\gamma = 360 - 2\theta$(A)	$\delta = (\alpha - \beta)/2$	τ	D	g_x	g_x - g_z
		Abbr. →	{$CoXA_2B_2$}	RX	RA	RB	alpha	beta	thetaA	thetaB	gamma	delta	tau	D	gx	gdif
1	1	[CoL^0Cl_2]	{$CoNN_2Cl_2$}	2.070	2.189	2.269	147.20	113.64	74.34	123.18	211.32	16.78	1.65	71.7	2.51	0.51
2	1	[$CoL^7Cl_2]_2$	{$CoNN_2Cl_2$}	2.070	2.155	2.277	145.55	112.92	74.34	123.53	211.32	16.31	1.69	151	3.28	1.28
3	1	[$CoL^{10}Cl_2]_2$	{$CoNN_2Cl_2$}	2.066	2.142	2.277	149.97	112.07	75.14	123.96	209.72	18.95	1.63	86.4	3.06	1.06
4	1	[$CoL^{12}Cl_2$]	{$CoNN_2Cl_2$}	2.061	2.151	2.276	150.56	112.17	75.29	123.91	209.42	19.19	1.62	46.8	2.35	0.25
5	1	[$CoL^{14}Cl_2]_2$	{$CoNN_2Cl_2$}	2.085	2.136	2.296	141.61	111.75	73.68	124.12	212.64	14.93	1.78	70.0	2.74	0.74
6	1	[$Co(bzimpy)Cl_2$]·DMF	{$CoNN_2Cl_2$}	2.136	2.138	2.308	146.01	111.56	74.48	124.22	211.04	17.22	1.71	61.9	2.34	0.34
7	1	[$Co(terpy)Cl_2$]	{$CoNN_2Cl_2$}	2.074	2.151	2.308	147.82	110.29	75.49	124.84	209.02	18.76	1.70	99.5	3.16	1.16
8	1	[$Co(terpy)(NCS)_2$]	{$CoNN_2N'_2$}	2.030	2.145	1.981	154.04	103.78	77.02	128.11	205.96	25.13	1.70	49.0	2.57	0.57
9	2	[Co(saldptm)]	{$CoNN_2O_2$}	2.124	2.049	1.948	177.11	138.63	91.40	110.68	177.20	19.24	0.64	52.0	2.60	0.60
10	2	[$Co(pno)_5](ClO_4)_2$	{$CoOO_2O_2$}	1.989	2.081	1.981	172.52	131.64	92.94	114.02	174.12	20.44	0.68	12.5	2.15	0.15
11	2	[$Co_2(PhCOO)_4(qu)_2$]	{$CoNO_2O_2$}	2.083	2.052	2.026	163.04	162.93	98.32	98.30	163.36	0.05	0	67.2	2.14	0.14

Trigonality parameter $\tau = (\alpha - \beta)/60$; $\tau = 1$ for an ideal trigonal bipyramid and $\tau = 0$ for an ideal square pyramid; for rigid tridentate ligands $\tau = (\gamma - \beta)/60 > 1$ where $\gamma = 360 - \alpha$.

Data selection for multivariate methods, set 2

No	Cluster	Complex	Chromophore	Co-Cl (z)	Co-N	Co-Cl'	N-Co-N'	N'-Co-Cl'	$\tau = \lvert\alpha - \beta\rvert/60$	D	g_x	g_x - g_z
			{$CoXA_2B_2$}	Co-X (z)	Co-A	Co-B	A-Co-A	B-Co-B				
		Abbr. →	{$CoClN_3Cl'$}	RX	RA	RB	alpha	beta	tau	D	gx	gdif
1	1	[CoL^0Cl_2]	{$CoClN_3Cl'$	2.265		2.273	147.20	138.38	0.15	71.7	2.51	0.51
2	1	[$CoL^7Cl_2]_2$	{$CoClN_3Cl'$	2.292			145.55	146.17	0.01	151	3.28	1.28
3	1	[$CoL^{10}Cl_2]_2$	{$CoNN_2Cl_2$}	2.066	2.142	2.277	149.97	112.07	1.63	86.4	3.06	1.06
4	1	[$CoL^{12}Cl_2$]	{$CoNN_2Cl_2$}	2.061	2.151	2.276	150.56	112.17	1.62	46.8	2.35	0.25
5	1	[$CoL^{14}Cl_2]_2$	{$CoClN_3Cl'$				141.61	152.86	0.19	70.0	2.74	0.74
6	1	[$Co(bzimpy)Cl_2$]·DMF	{$CoClN_3Cl'$				146.01	147.04	0.02	61.9	2.34	0.34
7	1	[$Co(terpy)Cl_2$]	{$CoClN_3Cl'$				147.82	150.95	0.05	99.5	3.157	1.16
8	1	[$Co(terpy)(NCS)_2$]	{$CoNN_2N'_2$}	2.030	2.145	1.981	154.04	103.78	1.70	49.0	2.570	0.57
9	2	[Co(saldptm)]	{$CoNN_2O_2$}	2.124	2.049	1.948	177.11	138.63	0.64	52.0	2.60	0.60
10	2	[$Co(pno)_5](ClO_4)_2$	{$CoOO_2O_2$}	1.989	2.081	1.981	172.52	131.64	0.68	12.5	2.15	0.15
11	2	[$Co_2(PhCOO)_4(qu)_2$]	{$CoNO_2O_2$}	2.083	2.052	2.026	163.04	162.93	0	67.2	2.14	0.14

Correlation coefficients between variables (11 datapoints), set 1

	D	gx	RX	RA	RB	alpha	beta	thetaA	thetaB	gamma	tau
gx	0.8278										
RX	0.3005	0.1195									
RA	0.4133	0.4562	-0.0826								
RB	0.5577	0.4934	0.3091	0.7561							
alpha	-0.5621	-0.4741	-0.1783	-0.8516	-0.8790						
beta	-0.2502	-0.5079	0.0936	-0.8649	-0.5968	0.7012					
thetaA	-0.4535	-0.5700	-0.1351	-0.9256	-0.8063	0.8791	0.9328				
thetaB	0.2511	0.5091	-0.0899	0.8644	0.5969	-0.7006	-1.0000	-0.9332			
gamma	0.4535	0.5700	0.1351	0.9256	0.8063	-0.8791	-0.9328	-1.0000	0.9332		
tau	0.3812	0.5605	0.0517	0.9075	0.7345	-0.8234	-0.9755	-0.9877	0.9758	0.9877	
dis	-0.1765	0.2671	-0.2984	0.4133	0.0119	-0.0448	-0.7436	-0.4826	0.7442	0.4826	0.5948

Component weights (PCA analysis), set 1

	Component 1	Component 2
RX	-0.028	0.453
RA	-0.330	-0.047
RB	-0.286	0.285
alpha	0.309	-0.213
beta	0.333	0.231
gamma	-0.353	-0.003
thetaA	0.353	0.003
thetaB	-0.333	-0.230
tau	-0.350	-0.092
D	-0.182	0.475
gx	-0.229	0.218
dis	-0.176	-0.525