**Supplementary information**

Tab. S1. Review of the matrix elements between the atomic-term kets  a

|  |
| --- |
| *Electron repulsion operator*    with the Slater-Condon parameters   or Racah parameters , ,  |
| * The matrix element is - and -independent

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

  with the angular coefficients  * Reduced matrix elements of the (orbital) unit tensor operator using the (genealogic) coefficients of fractional parentage

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

  |

|  |
| --- |
|  *Spin-orbit (one-electron) coupling operator*   |
| * The matrix element is - and -dependent

 * Individual spherical components

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

  |
|  |
|  |

|  |
| --- |
| *Orbital and spin Zeeman operator*   |
| * The orbital Zeeman interaction is -independent

 * The spin Zeeman interaction is -independent

 * Spherical transforms of the magnetic induction

 , ,  |

|  |
| --- |
| *Crystal field operator*   with the crystal field parameters  and the potential constants  with the values of the spherical harmonics  |
| * The matrix element is -independent

 * Reduction according to the Wigner-Eckert theorem

 * + The matrix elements  and  as above (see electron repulsion).
 |

a The formulae require , .

Tab. S2. Energy level diagrams [cm-1] for selected dn systems; not to scale.

d2 system – V(III)



d3 system – Cr(III)



d4 system – Mn(IIII)



high-spin d6 system – Fe(II)



high-spin d7 system – Co(II)



d8 system – Ni(II)



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

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| No |  | Chromophore | Clu-ster | Compound | *gx* | gy | *gz* | *gxy* | *gz - gxy* | *E* | *E*str  | *D* | *D*str  |
|  |  | Abbr. 🡪 |  |  |  |  | gz | gxy | gdif |  |  | D | Dstr |
| 1 | A | {NiN2O2O2}  | 1 | [Ni(pydicar)(pymeoh)]H2O | 2.169 | 2.169 | 2.478 | 2.169 | 0.309 | 0.13 | 1.1 | -12.7 | -24.35 |
| 2 | B | {NiN2O2O2}  | 2 | [Ni(2Meiz)2(fm)2(H2O)2] | 2.000 | 2.001 | 2.038 | 2.000 | 0.038 | 0.07 | 1.1 | -6.00 | -10.13 |
| 3 | C | {NiN4N2} | 2 | [Ni(bzimpy)2](ClO4)2 | 2.120 | 2.120 | 2.149 | 2.120 | 0.029 | 0 | 0 | -4.63 | -10.05 |
| 4 | D | {NiN2O2O2}  | 3 | [Ni(MeSnic)2(fupy)2(H2O)2]  | 2.241 | 2.241 | 2.279 | 2.241 | 0.038 | 0 | 0 | -4.98 | -7.90 |
| 5 | E | {NiN2O2O2}  | 3 | [Ni(MeSnic)2(lut)2(H2O)2] | 2.199 | 2.199 | 2.249 | 2.199 | 0.050 | 0 | 0 | -7.84 | -7.40 |
| 6 | F | {NiN2O2O2}  | 2 | [Ni(Me2iz)2(fm)2(H2O)2] | 2.139 | 2.140 | 2.190 | 2.140 | 0.050 | 0.08 | 1.9 | -7.70 | -6.25 |
| 7 | G | {NiN6} | 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 | {NiN2O2O2}  | 2 | [Ni(iqu)2(ac)2(H2O)2]  | 2.105 | 2.106 | 2.139 | 2.106 | 0.033 | 0.08 | 1.4 | -5.30 | -4.97 |
| 9 | I | {NiN4N2} | 3 | [Ni(Me2fupy)4(NCS)2]⋅6.6H2O | 2.294 | 2.294 | 2.305 | 2.294 | 0.011 | 0 | 0 | -1.65 | -4.3 |
| 10 | J | {NiN2O2O2}  | 3 | [Ni(Mefupy)2(ac)2(H2O)2] | 2.187 | 2.190 | 2.208 | 2.189 | 0.019 | 0.23 | 1.7  | -3.17 | -3.70 |
| 11 | K | {NiN2O2O2}  | 3 | [Ni(bzfupy)2(ac)2(H2O)2] | 2.200 | 2.203 | 2.219 | 2.202 | 0.017 | 0.24 | 0.7 | -2.85 | -2.85 |
| 12 | L | {NiN4N2} | 3 | [Ni(Mefupy)4(NCS)2]⋅1.29H2O | 2.201 | 2.201 | 2.213 | 2.201 | 0.012 | 0 | 0 | -1.93 | -2.60 |
| 13 | M | {NiN2O2O2}  | 2 | [Ni(fupy)2(ac)2(H2O)2]  | 2.147 | 2.149 | 2.179 | 2.148 | 0.031 | 0.15 | 1.0  | -5.00 | -2.32 |
| 14 | N | {NiN4N2} | 3 | [Ni(iqu)4(NCS)2]⋅CH2Cl2 | 2.188 | 2.188 | 2.178 | 2.188 | -0.010 | 0 | 0 | -1.54 | -0.70 |
| 15 | O | {NiN6} | 4 | [Ni(iz)6](Clac)2 | 2.154 | 2.154 | 2.154 | 2.154 | 0.000 | 0 | 0 | 0 | -0.250 |
| 16 | P | {NiN4N2} | 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 | {NiN6} | 4 | [Ni(iz)6](Clprop)2 | 2.155 | 2.155 | 2.150 | 2.155 | -0.005 | 0 | 0 | 0.90 | 2.025 |
| 18 | R | {NiN6} | 5 | [Ni(aepn)2][Ni(CN)4]·H2O | 2.080 | 2.080 | 2.073 | 2.080 | -0.007 | 0 | 0 | 0.99 | 2.125 |
| 19 | S | {NiN4N2} | 4 | [Ni(fupy)4(NCS)2]·THF | 2.199 | 2.200 | 2.180 | 2.200 | -0.020 | 0.11 | 0 | 2.70 | 2.80 |
| 20 | T | {NiN4N2} | 4 | [Ni(bzfupy)4(NCS)2]⋅2H2O | 2.227 | 2.227 | 2.219 | 2.227 | -0.008 | 0 | 0 | 1.15 | 2.95 |
| 21 | U | {NiN6} | 4 | [Ni(Meiz)6]Cl2⋅2H2O | 2.185 | 2.185 | 2.173 | 2.185 | -0.012 | 0 | 0 | 1.96 | 3.510 |
| 22 | W | {NiN4O2}  | 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 | {NiO4O2}  | 4 | [Ni(H2O)4(MeSnic)2]4H2O | 2.351 | 2.351 | 2.180 | 2.351 | -0.171 | 0 | 0 | 4.39 | 8.60 |
| 24 | Y | {NiN4O2}  | 5 | [Ni(Me2iz)4(H2O)2]⋅Cl2⋅3H2O | 2.126 | 2.126 | 2.079 | 2.126 | -0.047 | 0 | 0.7 | 7.42 | 11.35 |
| 25 | Z | {NiN4O2}  | 5 | [Ni(LNN)2(H2O)2] | 2.103 | 2.159 | 2.000 | 2.131 | -0.131 | 1.46 | 3.1 | 11.23 | 15.5 |

Formulae for structural tetragonality (rhombicity): , , . Mean distances: 2.145,  2.070,  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-Me2iz = 1,2-dimethylimidazole, pz = pyrazole, iqu = *iso*-quinoline, fupy = furo[3,2-c]pyridine, Mefupy = 2-methylfuro[3,2-c]pyridine, Me2fupy = 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

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | 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)

|  |  |  |
| --- | --- | --- |
|  | 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 | *gx* | gy | *gxy* | *E* | *E*str  | 2*D* | *D* | *D*str  |
|  |  | Abbr. 🡪 |  |  |  |  | gxy |  |  | D2 |  | Dstr |
| 1 | A | {CoN2O2O2} | 1 | [Co(MeIz)2(ac)2(H2O)2] | 2.530 | 2.530 | 2.530 | 0 | 2.42 | 190.0 | 95.0 | -11.87 |
| 2 | B | {CoO4O2} | 1 | [Co(2OHnic)2(H2O)2] | 2.670 | 2.730 | 2.700 | 0.26 | 0.10 | 159.8 | 79.91 | -9.40 |
| 3 | C | {CoN2O2O2} | 1 | [Co(bylim)2(bz)2(H2O)2] | 2.510 | 2.620 | 2.565 | 0.55 | 1.25 | 158.0 | 79.0 | -9.25 |
| 4 | D | {CoN2O2O2} | 1 | [Co(pic)2(H2O)2] | 2.650 | 2.720 | 2.685 | 2.34 | 3.55 | 168.5 | 84.24 | -8.45 |
| 5 | E | {CoN2O2O2} | 1 | [Co(MeSnic)2(Me2fupy)2(H2O)2] | 2.740 | 2.610 | 2.675 | 1.39 | 2.35 | 199.1 | 99.54 | -7.55 |
| 6 | F | {CoN2O2O2} | 1 | [Co(bz)2(nca)2(H2O)2] | 3.118 | 3.118 | 3.118 | 0 | 2.95 | 211.6 | 105.8 | -6.65 |
| 7 | G | {CoN6} | 1 | [Co(iz)6](HCOO)2 | 2.753 | 2.753 | 2.753 | 0 | 0.71 | 190.0 | 95.00 | -6.10 |
| 8 | H | {CoN2O2O2} | 2 | [Co(iqu)2(ac)2(H2O)2] | 2.587 | 2.689 | 2.638 | 3.01 | 1.80 | 167.9 | 83.96 | -2.80 |
| 9 | I | {CoN2O2O2} | 2 | [Co(pybzfupy)2(ac)2(H2O)2] | 2.607 | 2.758 | 2.683 | 2.84 | 1.50 | 179.2 | 89.59 | -2.30 |
| 10 | J | {CoN2O2O2} | 2 | [Co(bzfupy)2(ac)2(H2O)2] | 2.613 | 2.801 | 2.707 | 6.90 | 1.10 | 206.0 | 103.0 | -0.80 |
| 11 | K | cis{CoN4N2} | 1 | -*cis*-[Co(phen)2(dca)2] | 2.596 | 2.596 | 2.596 | 0 | 0 | 169.6 | 84.8 | -7.80 |
| 12 | L | cis{CoN4N2} | 1 | -*cis*-[Co(phen)2(dca)2] | 2.657 | 2.657 | 2.657 | 0 | 0 | 198.2 | 99.1 | -6.90 |
| 13 | M | cis{CoN4N2} | 2 | [Co(phen)3](tcm)2 | 2.594 | 2.594 | 2.594 | 0 | 0 | 158.6 | 79.3 | -1.00 |
| 14 | N | cis{CoN4N2} | 2 | [{Co(phen)2tcm}2μ2-tcm]tcm·H2O | 2.673 | 2.673 | 2.673 | 0 | 0 | 188.8 | 94.4 | -1.60 |
| 15 | O | cis{CoN2N4} | 2 | *catena*-[Co(bpy)(dca)2] | 2.438 | 2.438 | 2.438 | 0 | 0 | 203.2 | 101.6 | -1.10 |
| 16 | P | cis{CoN2N4} | 2 | *catena*-[Co(bpy)(tcm)2] | 2.633 | 2.633 | 2.633 | 0 | 0 | 206.4 | 103.2 | -0.70 |

*gz* = 2.0 – fixed. Mean distances  2.185,  2.085, and  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, Me2fupy = 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 {CoA2B2} |  | *R*(Co-A) | *R*(Co-B) | **(A-Co-A) | **(B-Co-B) | *D* | *gz*  | *gx*  | *gy* | *D*epr | *gz*epr | *gx*epr | *gy*epr | *E*epr |
| 1 | [CoCl2(dmpz)2] | {CoCl2N2} | C2v | 2.238 | 2.005 | 118.1 | 105.7 | 41.5 | 2.0 | 2.538 | 2.538 |  |  |  |  |  |
| 2 | [CoCl2(ndmiz)2] | {CoCl2N2} | C2v | 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 | [CoCl2(iz)2] | {CoCl2N2} | C1 | 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 | D2d | 1.964 | 1.964 | 113.5 | 113.5 | 5.1 | 2.168 | 2.251 | 2.251 |  |  |  |  |  |
| 4 | Hg[Co(NCS)4] | {CoN4}  | D2d | 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] | {CoN2N2} | C1 | 1.937 | 2.036 | 108.3 | 104.5 |  | 2.133 | 2.250 | 2.250 |  |  |  |  |  |
| 6 | [CoCl2(bziz)2] | {CoCl2N2} | C1 | 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 | Cs3CoCl5  | {CoCl4} | D2d | 2.268 | 2.268 | 107.2 | 107.2 |  |  |  |  | -4.30  | 2.40 | 2.30 | 2.30 |  |
| 8 | [CoCl2(ct)2] | {CoCl2N2} | C1 | 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 | [CoCl2(Mepy)2] | {CoCl2N2} | C1 | 2.232 | 2.051 | 121.4 | 107.4 | -4.88 | 2.523 | 2.123 | 2.123 |  |  |  |  |  |
| 10 | Cs3CoBr5  | {CoBr4} | D2d | 2.399 | 2.399 | 107.6 | 107.6 |  |  |  |  | -5.34  | 2.42 | 2.32 | 2.32 |  |
| 11 | [CoCl2(qu)2] | {CoCl2N2} | C2v | 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 | [CoCl2(ampy)2] | {CoCl2N2} | C2v | 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[CoCl4] | {CoCl4}  | C1 | 2.274 | 2.280 | 118.9 | 113.1 | -12.0 | 2.362 | 2.225 | 2.225 |  |  |  |  |  |
| 14 | [Co(PPh3)2Cl2] | {CoCl2P2}  | C2v | 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(PPh3)2Br2] | {CoBr2P2}  | C2v | 2.349 | 2.385 | 115.2 | 117.4 | -12.5 | 2.164 | 2.006 | 2.006 |  |  |  |  |  |

Convention: *gy* > *gx*.

Data selection for multivariate methods

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| No | Compound  | Chromophore {CoA2B2} | *R*(Co-A) | *R*(Co-B) | **(A-Co-A) | **(B-Co-B) | (**+ **)/2 | (**- **)/2 | *D* | *gz* | *gx* | *gy* | *gxy* | *gz* - *gxy* |
|  | Abbr. 🡪 |  | RA | RB | alpha | beta | Aplus | Aminus | D | gz | gx | gy | gxy | gdif |
| 1 | [CoCl2(dmpz)2] | {CoCl2N2} | 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 | [CoCl2(ndmiz)2] | {CoCl2N2} | 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 | [CoCl2(iz)2] | {CoCl2N2} | 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] | {CoN4}  | 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] | {CoN2N2} | 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 | [CoCl2(bziz)2] | {CoCl2N2} | 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 | Cs3CoCl5  | {CoCl4} | 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 | [CoCl2(ct)2] | {CoCl2N2} | 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 | [CoCl2(Mepy)2] | {CoCl2N2} | 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 | Cs3CoBr5  | {CoBr4} | 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 | [CoCl2(qu)2] | {CoCl2N2} | 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 | [CoCl2(ampy)2] | {CoCl2N2} | 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[CoCl4] | {CoCl4}  | 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(PPh3)2Br2] | {CoBr2P2}  | 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(PPh3)2Cl2] | {CoCl2P2}  | 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(XA2)B2}, set 1

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| No | Ref | Complex | Chromophore{CoXA2B2} | 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 | *gxy*  |
| 1 | [a] | [CoLICl2]  | {CoNN2Cl2} | (4py) | 2.070 | 2.1752.203 | 2.2732.265 | 147.20 | 113.64 | 74.3974.29 | 107.98138.38 | 97.5699.30 | 98.67100.01 | 71.7 | 0 | - | 2.51 |
| 2 | [b] | [CoLC7Cl2]2  | {CoNN2Cl2} | (4py)  | 2.070 | 2.1322.179 | 2.2622.292 | 145.55 | 112.92 | 74.0874.60 | 100.90146.17 | 96.30101.76 | 94.64105.02 | 151 | 11.6 | 1.40 | 3.28 |
| 3 | [c] | [CoLC10Cl2]2  | {CoNN2Cl2} | 3bpy | 2.066 | 2.1302.154 | 2.2852.269 | 149.97 | 112.07 | 75.0475.25 | 119.22128.71 | 96.7098.42 | 97.54100.58 | 86.4 | 5.0 | 1.10 | 3.06 |
| 4 | [a] | [CoLC12Cl2]  | {CoNN2Cl2} | 3bpy | 2.061 | 2.1472.156 | 2.2752.278 | 150.56 | 112.17 | 75.1775.42 | 125.88121.94 | 96.5899.34 | 98.1098.58 | 46.8 | 0 | - | 2.35 |
| 5 | [c] | [CoLC14Cl2]2  | {Co(NN2)Cl2} | (4py) | 2.085 | 2.1352.137 | 2.2632.329 | 141.61 | 111.75 | 73.5473.82 | 95.39152.86 | 98.20101.67 | 96.51106.12 | 70.0 | 4.1 | 1.47 | 2.74 |
| 6 | [g] | [Co(bzimpy)Cl2]·DMF | {CoNN2Cl2} | (4py) | 2.136 | 2.1362.141 | 2.2862.331 | 146.01 | 111.56 | 74.3874.58 | 101.41147.04 | 98.38100.99 | 98.35100.13 | 61.9 | 0 | - | 2.34 |
| 7 | [d] | [Co(terpy)Cl2] | {CoNN2Cl2} | (4py) | 2.074 | 2.1422.161 | 2.2912.325 | 147.82 | 110.29 | 75.3575.63 | 98.74150.95 | 97.20101.41 | 96.03101.84 | 99.5, calc | - | - | (3.157) |
| 8 | [d] | [Co(terpy)(NCS)2] | {CoNN2N‘2} | 3bpy | 2.030 | 2.1452.145 | 1.9811.981 | 154.04 | 103.78 | 77.0277.02 | 128.11128.11 | 93.08102.92 | 93.08102.92 | 49.0, calc | - | - | (2.570) |
| 9 | [e] | [Co(saldptm)] | {CoNN2O2} | 3bpy | 2.124 | 2.0452.054 | 1.9521.944 | 177.11 | 138.63 | 91.4491.36 | 109.68111.69 | 87.7891.95 | 87.5890.72 | 52.0 | 0 | - | 2.60 |
| 10 | [h] | [Co(pno)5](ClO4)2 | {CoOO2O2} | 3bpy | 1.989 | 2.1042.058 | 1.9761.986 | 172.52 | 131.64 | 90.1195.78 | 117.66110.38 | 87.1095.13 | 85.7087.49 | 12.5, epr | 0 | - | (2.15) |
| 11 | [f] | [Co2(PhCOO)4(qu)2] | {CoNO2O2} | 4py | 2.083 | 2.0242.081 | 2.0152.038 | 163.04 | 162.93 | 92.39104.25 | 96.7899.83 | 86.6688.74 | 86.1593.53 | 67.2 | 0 | -1.65 | 2.14 |

calc – ab initio calculations; *D* = **(*gz* – *gxy*)/2 was used in estimating *gxy,* ** = -172 cm-1. epr – estimate by X-band EPR. *gz* = 2.0 – fixed.

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[b] C. Rajnák, J. Titiš, O. Fuhr, M. Ruben and R. Boča, *Inorg. Chem.,* submitted. Note: SMM.

[c] C. Rajnák, PhD. Thesis, University of SS Cyril and Methodius, Trnava, 1014.

[d] F. Habib, O. R. Luca, V. Vieru, M. Shiddiq, I. Korobkov, S. I. Gorelsky, M. K. Takase, L. F. Chibotaru, S. Hill, R. H. Crabtree and M. Murugesu, M. *Angew. Chem. Int. Ed*., 2013, **52**, 11290. Note: SMM.

[e] R. Boča, H. Elias, W. Haase, M. Huber, R. Klement, L. Muller, H. Paulus, I. Svoboda and M. Valko, *Inorg. Chim. Acta*, 1998, **278**, 127; Magnetism: R. Herchel and R. Boča, *Dalton Trans.,* 2005, 1352.

[f] J. Hudák, R. Boča, Ľ. Dlháň, J. Kožíšek and J. Moncoľ, *Polyhedron*, 2011, **30**, 1367.

[g] R. Cariou, J. J. Chirinos, V. C. Gibson, G. Jacobsen, A. K. Tomov, G. J. P. Britovsek and A. J. P. White, *Dalton Trans.,* 2010, **39**, 9039. Magnetism: [a].

[h] I. Bertini, P. Dapporto, D. Gatteschi and A. Scozzafava, *Inorg.Chem.*, 1975, **14**,1639; EPR: M.V. Makinen, L.C. Kuo, M.B. Yim, G.B. Wells, J.M. Fukuyama and J.E. Kim, *J. Am. Chem. Soc.,* 1985, **107**, 5245.

Data for complexes reclassified as a tetragonal pyramid {CoCl(N3Cl’)}, 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 | ** =(**– **)/60 | *J* | *D* | *E* | *gx*  |
|  |  | Abbr. 🡪 | {CoClN3Cl’} | Ra | R3 | R1 | alpha | beta | T1 | T2 | T3 | tau | J | D | E | gx |
| 1 | 1 | [CoL0Cl2]  | {CoClN3Cl’ | 2.265 | 2.0702.1752.203 | 2.273 | 147.20 | 138.38 | 113.64 | 107.98 | 98.67100.01 | 0.15 | 0 | 71.7 | 0 | 2.51 |
| 2 | 1 | [CoL7Cl2]2  | {CoClN3Cl’ | 2.292 | 2.0702.1322.179 | 2.262 | 145.55 | 146.17 | 112.92 | 100.90 | 94.64105.02 | 0.01 | 1.40 | 151 | 11.6 | 3.28 |
| 5 | 1 | [CoL14Cl2]2  | {CoClN3Cl’ | 2.329 | 2.0852.1372.135 | 2.263 | 141.61 | 152.86 | 111.75 | 95.39 | 96.51106.12 | 0.19 | 1.47 | 70.0 | 4.1 | 2.74 |
| 6 | 1 | [Co(bzimpy)Cl2]·DMF | {CoClN3Cl’ | 2.331 | 2.1362.1412.136 | 2.286 | 146.01 | 147.04 | 111.56 | 101.41 | 98.37100.99 | 0.02 | 0 | 61.9 | 0 | 2.34 |
| 7 | 1 | [Co(terpy)Cl2] | {CoClN3Cl’ | 2.325 | 2.0742.1422.161 | 2.291 | 147.82 | 150.95 | 110.29 | 98.74 | 96.03101.84 | 0.05 | 0 | 99.5 | 0 | 3.157 |

|  |  |  |  |
| --- | --- | --- | --- |
|  |  |  |  |
| **(A) < 90, ** > 180, ** > 1 | **(A) < **(B), ** < 180, ** < 1, trigonal bipyramid | **(A) ~ **(B), ** < 180, ** ~ 0, tetragonal pyramid | reclassification to atetragonal 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 | [CoL0Cl2]  | 3.809 | 2.263 |
| 2 | [CoL7Cl2]  | 5.174 | 1.902 |
| 3 | [CoL10Cl2]  | 2.832 | 3.462 |
| 4 | [CoL12Cl2]  | 2.668 | 4.101 |
| 5 | [CoL14Cl2]  | 6.946 | 1.876 |
| 6 | [Co(bzimpy)Cl2]  | 5.047 | 1.697 |
| 7 | [Co(terpy)Cl2] | 5.474 | 1.675 |
| 8 | [Co(terpy)(NCS)2] | 2.974 | 4.482 |
| 9 | [Co(saldptm)Cl2] | 0.835 | 2.340 |
| 10 | [Co(pno)5] | 0.764 | 3.017 |
| 11 | [Co2(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 | **(A) | **(B) | ** –** (A) | ** = (**– **)/2 | **  | *D* | *gx*  | *gx* - *gz* |
|  |  | Abbr. 🡪 | {CoXA2B2} | RX | RA | RB | alpha | beta | thetaA | thetaB | gamma | delta | tau | D | gx | gdif |
| 1 | 1 | [CoL0Cl2]  | {CoNN2Cl2} | 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 | [CoL7Cl2]2  | {CoNN2Cl2} | 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 | [CoL10Cl2]2  | {CoNN2Cl2} | 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 | [CoL12Cl2]  | {CoNN2Cl2} | 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 | [CoL14Cl2]2  | {CoNN2Cl2} | 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)Cl2]·DMF | {CoNN2Cl2} | 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)Cl2] | {CoNN2Cl2} | 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] | {CoNN2N‘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)] | {CoNN2O2} | 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](ClO4)2 | {CoOO2O2} | 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 | [Co2(PhCOO)4(qu)2] | {CoNO2O2} | 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 ** = (** – **)/60; *τ* = 1 for an ideal trigonal bipyramid and *τ* = 0 for an ideal square pyramid; for rigid tridentate ligands ** = (** – **)/60 > 1 where ** = 360 – **.

Data selection for multivariate methods, set 2

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| No | Cluster | Complex | Chromophore | Co-Cl (*z*) | Co-N | Co-Cl’ | N-Co-N’ | N’-Co-Cl’ | ** =|**– **|/60 | *D* | *gx*  | *gx* - *gz* |
|  |  |  | {CoXA2B2} | Co-X (*z*) | Co-A | Co-B | A-Co-A | B-Co-B |  |  |  |  |
|  |  | Abbr. 🡪 | {CoClN3Cl’} | RX | RA | RB | alpha | beta | tau | D | gx | gdif |
| 1 | 1 | [CoL0Cl2]  | {CoClN3Cl’ | 2.265 |  | 2.273 | 147.20 | 138.38 | 0.15 | 71.7 | 2.51 | 0.51 |
| 2 | 1 | [CoL7Cl2]2  | {CoClN3Cl’ | 2.292 |  |  | 145.55 | 146.17 | 0.01 | 151 | 3.28 | 1.28 |
| 3 | 1 | [CoL10Cl2]2  | {CoNN2Cl2} | 2.066 | 2.142 | 2.277 | 149.97 | 112.07 | 1.63 | 86.4 | 3.06 | 1.06 |
| 4 | 1 | [CoL12Cl2]  | {CoNN2Cl2} | 2.061 | 2.151 | 2.276 | 150.56 | 112.17 | 1.62 | 46.8 | 2.35 | 0.25 |
| 5 | 1 | [CoL14Cl2]2  | {CoClN3Cl’ |  |  |  | 141.61 | 152.86 | 0.19 | 70.0 | 2.74 | 0.74 |
| 6 | 1 | [Co(bzimpy)Cl2]·DMF | {CoClN3Cl’ |  |  |  | 146.01 | 147.04 | 0.02 | 61.9 | 2.34 | 0.34 |
| 7 | 1 | [Co(terpy)Cl2] | {CoClN3Cl’ |  |  |  | 147.82 | 150.95 | 0.05 | 99.5 | 3.157 | 1.16 |
| 8 | 1 | [Co(terpy)(NCS)2] | {CoNN2N‘2} | 2.030 | 2.145 | 1.981 | 154.04 | 103.78 | 1.70 | 49.0 | 2.570 | 0.57 |
| 9 | 2 | [Co(saldptm)] | {CoNN2O2} | 2.124 | 2.049 | 1.948 | 177.11 | 138.63 | 0.64 | 52.0 | 2.60 | 0.60 |
| 10 | 2 | [Co(pno)5](ClO4)2 | {CoOO2O2} | 1.989 | 2.081 | 1.981 | 172.52 | 131.64 | 0.68 | 12.5 | 2.15 | 0.15 |
| 11 | 2 | [Co2(PhCOO)4(qu)2] | {CoNO2O2} | 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 |