**Supplementary Information**

# Determination and prediction of the magnetic anisotropy of Mn ions

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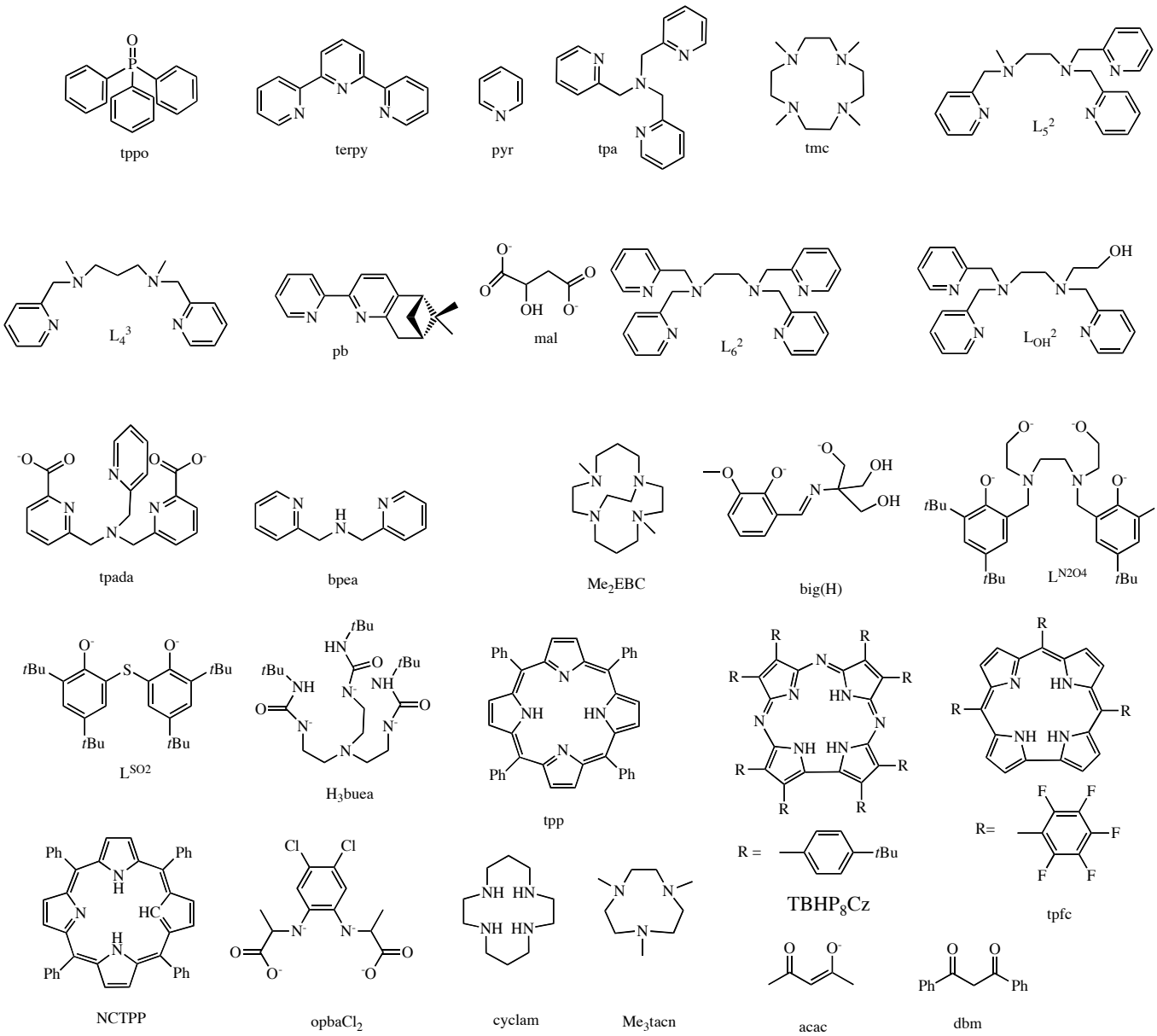
**Figure S1.** Schematic representation of the different ligands

**Figure S2**. Origin of the shape of EPR spectra recorded under anisotropic resonance conditions.

**Table S1.** Additional data regarding the EPR parameters of $Mn^{II}$ complexes.

**Table S2.** Additional data regarding the EPR parameters of $Mn^{III}$ complexes.

**Figure S1:** Schematic representation of the different ligands

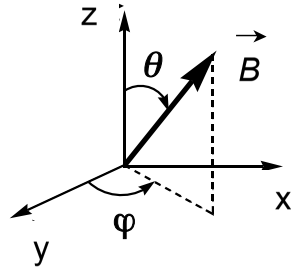


# g-ANISOTROPY

$$\hat{H}_{Zeeman} = \beta_e \left( g_{xx} B_{0x} \hat{S}_x + g_{yy} B_{0y} \hat{S}_y + g_{zz} B_{0z} \hat{S}_z \right)$$

At the resonance

$$B_{0x} = B_0 \, sin\theta \, cos\varphi$$
$$B_{0y} = B_0 \, sin\theta \, sin\varphi$$
$$B_{0z} = B_0 \, cos\theta$$



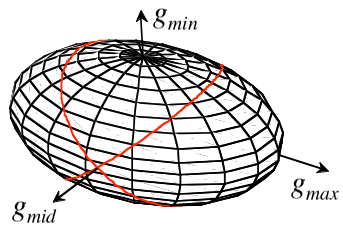

$$h\nu = g(\theta,\varphi)\beta_e B_0(\theta,\varphi)$$

$$g(\theta,\varphi) = \sqrt{g_{xx}^2 \, sin^2\theta \, cos^2\varphi + g_{yy}^2 \, sin^2\theta \, sin^2\varphi + g_{zz}^2 \, cos^2\theta}$$

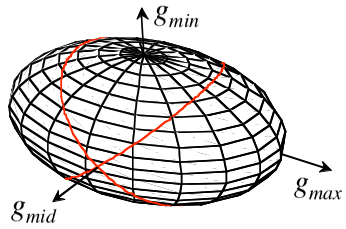
**The intensity and the position of the resonance will depend on its orientation.**

$$g_{min} \leq g(\theta,\varphi) \leq g_{max}$$

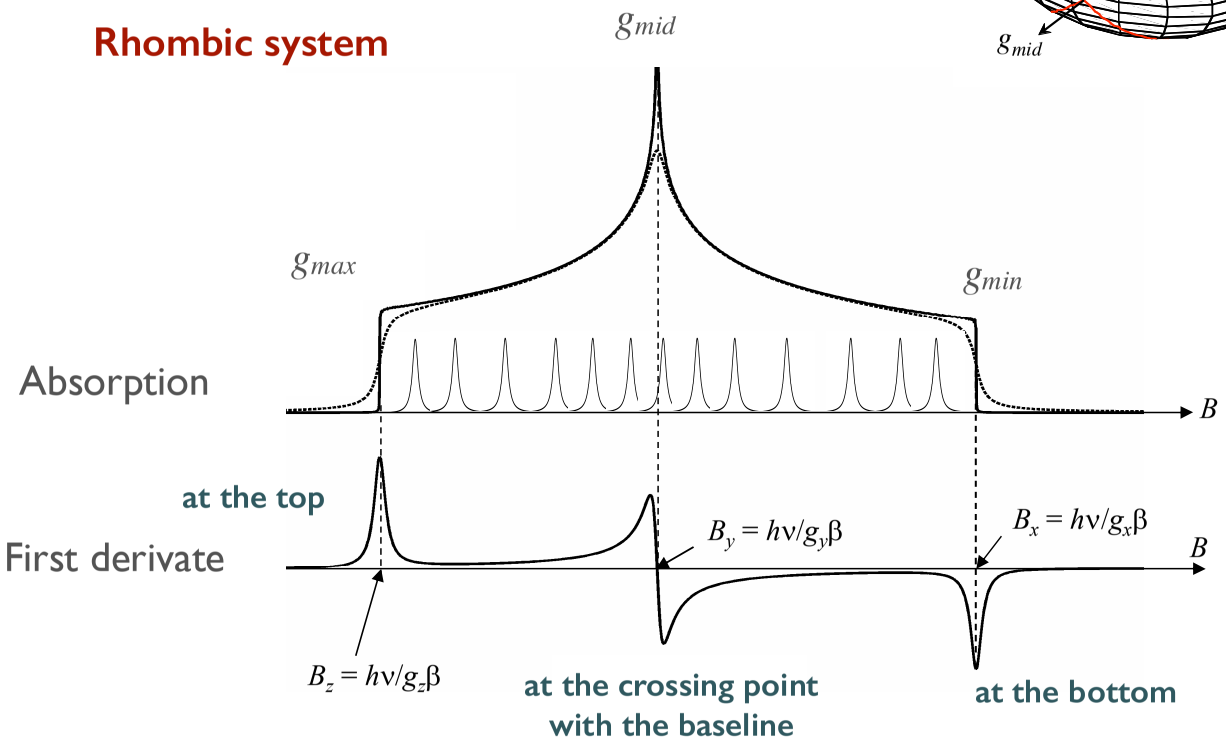
Only one direction for $g_{min}$ and $g_{max}$
Many orientations for $g_{mid}$ (in red)



# g-ANISOTROPY




**Rhombic system**




$g_z > g_y > g_x$

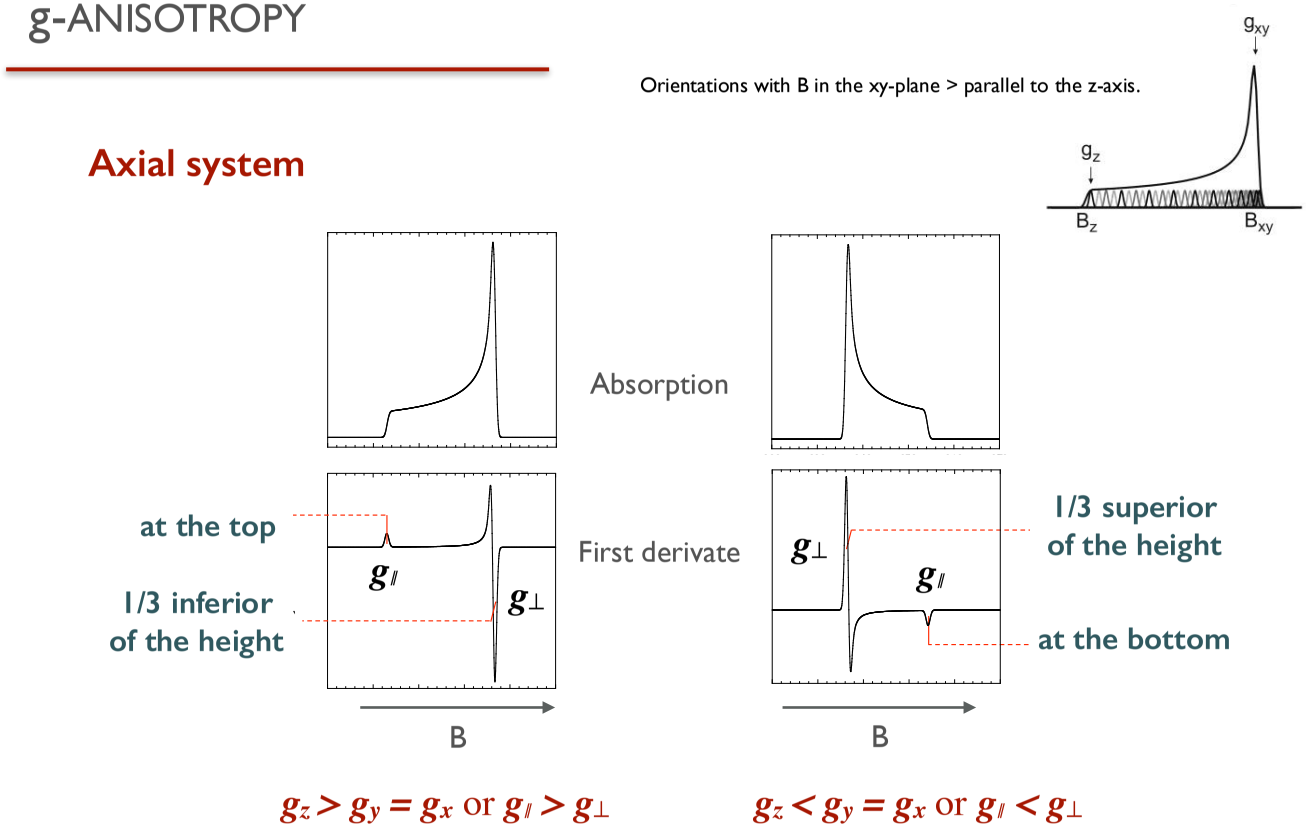



**Figure S2.** These three slides explain the shape of axial or rhombic signals caused by *g*-anisotropy. While the first slide highlights the origin of the three main directions and how EPR can give an access to these preferred directions, the two other slides explain the origin of the turning points that arise from the first derivate of the absorption spectra and that closely correspond with the position of the *g*-values.

**Table S1:** Experimental EPR parameters and calculated *D* values for mononuclear Mn(II) complexes.

| Complex | coord. sphere | $D_{exp}$ [a] ($10^{-4}$ cm$^{-1}$) | $E$ [a] ($10^{-4}$ cm$^{-1}$) | $E/D$ | $g_{iso}$ | $A_{iso}$ [a] ($10^{-4}$ cm$^{-1}$) | $D_{calc}$ ($10^{-4}$ cm$^{-1}$) | ref [b] |
|---|---|---|---|---|---|---|---|---|
| *Iodide complexes* | | | | | | | | |
| *four-coordinate* | | | | | | | | |
| $[Mn(tppo)_2(I)_2]$ | $O_2I_2$ | 0.906 | 0.223 | 0.246 | 2.0039 | | +1.264[c] | 1,2 |
| *five-coordinate* | | | | | | | | |
| $[Mn(terpy)(I)_2]$ | $N_3I_2$ | +1.000 | +0.190 | 0.190 | 1.98/1.99/1.99[d] | | +1.863[e] | 3(2) |
| *six-coordinate* | | | | | | | | |
| *trans*-$[Fe(Mn)(pyr)_4(I)_2]$ | $N_4I_2$ | 0.932 | 0.020 | 0.021 | 2.00 | 77 | | 4 |
| *trans*-$[Mn(pic)_4(I)_2]$ | $N_4I_2$ | 0.999 | 0.005 | 0.005 | 2.001 | | | 5 |
| *trans*-$[Mn(pz)_4(I)_2]$ | $N_4I_2$ | 0.980 | 0.010 | 0.010 | 2.000 | | | 6 |
| *cis*-$[Mn(phen)_2(I)_2]$ | $N_4I_2$ | 0.590 | 0.145 | 0.246 | 2.008 | | | 5 |
| *cis*-$[Mn(tpa)(I)_2]$ | $N_4I_2$ | -0.600 | -0.095 | 0.158 | 1.99/1.98/2.00[d] | | -0.868[e] | 7 |
| *cis*-$[Zn(Mn)(tpa)(I)_2]$ | $N_4I_2$ | 0.635 | 0.120 | 0.189 | 2.00 | 68 | | 8 |
| *Bromide complexes* | | | | | | | | |
| *four-coordinate* | | | | | | | | |
| $[Mn(tppo)_2(Br)_2]$ | $O_2Br_2$ | 0.507 | 0.134 | 0.263 | 1.9985 | | +0.715[c] | 1(2) |
| $[Zn(Mn)(tppo)_2(Br)_2]$ | $O_2Br_2$ | 0.523 | 0.133 | 0.254 | 2.020/2.019/2.017[d] | 73 | | 9 |
| *five-coordinate* | | | | | | | | |
| $[Mn(terpy)(Br)_2]$ | $N_3Br_2$ | +6050 | +0.159 | 0.26 | 1.985 | | +0.983[e] | 3(2) |
| *six-coordinate* | | | | | | | | |
| *trans*-$[Ru(Mn)(pyr)_4(Br)_2]$ | $N_4Br_2$ | 0.665 | 0.001 | 0.002 | 2.00 | 77 | | 4 |
| *trans*-$[Fe(Mn)(pyr)_4(Br)_2]$ | $N_4Br_2$ | 0.586 | 0.003 | 0.005 | 2.00 | 77 | | 4 |
| *trans*-$[Mn(pic)_4(Br)_2]$ | $N_4Br_2$ | 0.626 | 0.003 | 0.005 | 2.002 | | | 5 |
| *trans*-$[Mn(Si\text{-}O\text{-}pyr)_2(Br)_2]$ | $N_4Br_2$ | 0.650 | 0.0007 | 0.01 | 2.00 | | | 10 |
| *cis*-$[Mn(phen)_2(Br)_2]$ | $N_4Br_2$ | 0.359 | 0.074 | 0.21 | 2.002 | | | 5 |
| *cis*-$[Mn(tpa)(Br)_2]$ | $N_4Br_2$ | -0.360 | -0.073 | 0.203 | 2.00/1.98/2.00[d] | | -0.510[e] | 7 |
| *cis*-$[Zn(Mn)(tpa)(Br)_2]$ | $N_4Br_2$ | 0.360 | 0.069 | 0.192 | 2.00 | 68 | | 8 |
| *Chloride complexes* | | | | | | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *four-coordinate* | | | | | | | | |
| $[Mn(tppo)_2(Cl)_2]$ | $O_2Cl_2$ | 0.165 | 0.045 | 0.273 | 2.0000 | | +0.288[c] | [1]([2]) |
| $[Zn(Mn)(tppo)_2(Cl)_2]$ | $O_2Cl_2$ | 0.172 | 0.047 | 0.273 | 2.03/2.02/2.02[d] | 77 | | [9] |
| *five-coordinate* | | | | | | | | |
| $[Mn(terpy)(Cl)_2]$ | $N_3Cl_2$ | -0.260 | -0.075 | 0.29 | 1.994/2.010/2.025[d] | | -0.459[e] | [3]([2]) |
| $[Mn(phenyl\text{-}terpy)(Cl)_2]$ | $N_3Cl_2$ | -0.319 | -0.071 | 0.223 | 1.982/1.970/1.970[d] | | -0.486[e] | [11]([2]) |
| $[Mn(tmc)(Cl)]^+$ | $N_4Cl$ | 0.250 | | 0.25 | | | | [12] |
| *six-coordinate* | | | | | | | | |
| *trans*-$[Ru(Mn)(pyr)_4(Cl)_2]$ | $N_4Cl_2$ | 0.220 | 0 | 0 | 2.00 | 77 | | [4] |
| *trans*-$[Mn(pic)_4(Cl)_2]$ | $N_4Cl_2$ | 0.186 | 0 | 0 | 2.004 | | | [5] |
| *trans*-$[Mn(Si\text{-}O\text{-}pyr)_2(Cl)_2]$ | $N_4Cl_2$ | 0.188 | 0.011 | 0.06 | 2.00 | | | [10] |
| *cis*-$[Mn(phen)_2(Cl)_2]$ | $N_4Cl_2$ | 0.124 | 0.005 | 0.04 | 2.000 | | | [5] |
| *cis*-$[Mn(tpa)(Cl)_2]$ | $N_4Cl_2$ | +0.115 | +0.020 | 0.174 | 1.97/2.00/2.00[d] | | +0.155[e] | [7] |
| *cis*-$[Zn(Mn)(tpa)(Cl)_2]$ | $N_4Cl_2$ | 0.115 | 0.023 | 0.200 | 2.00 | | | [8] |
| *cis*-$[Mn(L_4^2)(Cl)_2]$ | $N_4Cl_2$ | -0.147 | -0.021 | 0.14 | 2.00 | | -0.120[e] | [13] |
| $[Mn(pb)_2Cl_2]$ | N4Cl2 | -0.146 | -0.017 | 0.116 | 2.00 | | -0.180 | [14] |
| $[Mn(L_5^2)(Cl)](PF_6)$ | $N_5Cl$ | 0.180 | 0.060 | 0.33 | 2.00 | | +0.254[e] | [13] |
| $[Mn(L_5^3)(Cl)](PF_6)$ | $N_5Cl$ | +0.157 | 0 | 0 | 2.00 | | +0.223[e] | [13] |
| $[Mn(L_4^3)(Cl)(OH_2)](ClO_4)$ | $N_4OCl$ | +0.110 | +0.016 | 0.14 | 2.00 | | +0.150[e] | [13] |
| *N/O ligands complexes* | | | | | | | | |
| *five-coordinate* | | | | | | | | |
| $[Mn(terpy)(NCS)_2]$ | $N_5$ | -0.300 | -0.050 | 0.17 | 1.99/1.97/1.97[d] | | -0.504[e] | [3] ([15]) |
| $[Mn(tBu\text{-}terpy)(N_3)_2]$ | $N_5$ | -0.250 | -0.044 | 0.176 | 2.000 | | -0.347[e] | [16] ([15]) |
| $[Zn(Mn)(tBu\text{-}terpy)(N_3)_2]$ | $N_5$ | 0.260 | 0.043 | 0.165 | 2.0010/2.0005[f] | 72.5 | | [16] |
| $K_{11}Na[As_2W_{20}Mn(OH_2)_3O_{66}]$ | $O_5$ | +1.460 | +0.033 | 0.23 | 2.01/2 .00/2.02[d] | | | [17] |
| *six-coordinate* | | | | | | | | |
| *trans*-$[Fe(Mn)(pyr)_4(NCS)_2]$ | $N_6$ | 0.010 | 0.003 | 0.300 | 2.00 | 80 | | [4] |
| *cis*-$[Mn(tpa)(NCS)_2]$ | $N_6$ | -0.085 | -0.015 | 0.176 | 2.00 | | -0.075[e] | [15] |
| $[Zn(Mn)(en)_3](NO_3)_2$ | $N_6$ | +0.020 | | | 2.004/2.021[f] | -77 | | [18] |
| $[Cd(Mn)(bpa)_2](ClO_4)_2$ | $N_6$ | -0.018 | 0 | 0 | 2.00 | -77 | | [19] |
| $[Mn(tBu\text{-}terpy)_2](PF_6)_2$ | $N_6$ | -0.073 | -0.015 | 0.205 | 2.00 | | +0.111[e] | [15] |
| $[Mn(terpy)_2](I)_2$ | $N_6$ | -0.042 | -0.005 | 0.190 | 2.00 | | +0.068[e] | [15] |
| $[Zn(Mn)(terpy)_2](PF_6)_2$ | $N_6$ | 0.058 | 0.006 | 0.104 | 2.00 | 71 | | [15] |
| $[Mn(PzOx)_3(BC_6H_5)]Cl$ | N6 | -0.323 | -0.014 | 0.043 | 2.0003/2.0003/1.99 98 | 80 | | [20] |
| $[Mn(L_5^2)(OH_2)](BPh_4)_2$ | $N_5O$ | -0.137 | 0 | 0 | 2.00 | | -0.089[e] | [13] |
| $[Mn(L_5^3)(OH_2)](BPh_4)_2$ | $N_5O$ | -0.090 | 0 | 0 | 2.00 | | -0.080[e] | [13] |
| $[Mn(bpy)_2(CF_3CO_2)_2]$ | N4O2 | -0.035 | -0.005 | 0.154 | 2.00 | | -0.087 | [14] |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $[Mn(pb)(NO_3)(OH_2)](NO_3)$ | N4O2 | -0.074 | -0.009 | 0.122 | 2.00 | | -0.050 | [14] |
| $[Mn(pb)(CF_3CO_2)_2]$ | N4O2 | -0.071 | -0.005 | 0.070 | 2.00 | | -0.029 | [14] |
| $[Mn(terpy)(CF_3CO_2)_2(OH_2)]$ | N3O3 | 0.068 | 0.021 | 0.308 | 2.00 | | -0.041 | [14] |
| $[Pb(Mn)(apy)_6](ClO_4)_2$ | $O_6$ | -0.0009 | | | 2.008 | -87 | | [21] |
| $[Mg(Mn)(apy)_6](ClO_4)_2$ | $O_6$ | -0.004 | | | 2.008 | -87 | | [21] |
| $[Mn(mal)(OH_2)_3]$ | $O_6$ | +0.023 | +0.007 | 0.324 | 1.991 | -86 | | [22] |
| $[Mn(ompa)_3](ClO_4)_2$ | $O_6$ | -0.015 | | | 2.011 /2.010[f] | -99.5 | | [23] |
| $[Hg(Mn)(pyrO)_6](ClO_4)_2$ | $O_6$ | 0.042 | | | 2.009 | -88 | | [24] |
| $[Hg(Mn)(2Me\text{-}pyrO)_6](ClO_4)_2$ | $O_6$ | 0.023 | | | 2.010 | -87 | | [24] |
| $[Hg(Mn)(3Me\text{-}pyrO)_6](ClO_4)_2$ | $O_6$ | 0.050 | | | 2.010 | -87 | | [24] |
| $[Hg(Mn)(4Me\text{-}pyrO)_6](ClO_4)_2$ | $O_6$ | 0.067 | 0.015 | 0.229 | 2.003 | -89 | | [24] |
| $[Hg(Mn)(4CN\text{-}pyrO)_6](ClO_4)_2$ | $O_6$ | 0.022 | | | 2.011 | -84 | | [24] |
| $[Hg(Mn)(4NO_2\text{-}pyrO)_6](ClO_4)_2$ | $O_6$ | 0.047 | 0.002 | 0.041 | 2.012 | -84 | | [24] |
| *seven-coordinate* | | | | | | | | |
| $[Mn(L_6^2)(OH_2)](ClO_4)_2$ | $N_6O$ | -0.127 | 0 | 0 | 2.00 | | -0.030[e] | [13] |
| $[Mn(LX)(OH_2)](ClO_4)_2$ | N5O2 | 0.137 | 0.013 | 0.093 | 1.997 | | | [25] |
| $[Mn(tpada)ClCa(OH_2)_{2.67}(MeOH)_{2.33}]Cl$ | N4O2Cl | -0.098 | -0.013 | 0.133 | 2.00 | | +0.107 | [26] |
| $[Mn(terpy)(NO_3)(OH_2)]$ | $N_3O4$ | -0.068 | -0.010 | 0.147 | 2.00 | | -0.090 | [14] |
| $[Mn(bpea)(NO_3)_2]$ | N3O4 | +0.086 | +0.008 | 0.093 | 2.00 | | +0.075 | |

*[a]The sign is reported when it has been determined; [b] In parenthesis, the reference reporting $D_{calc}$ is notified if it is different from the one reporting $D_{exp}$; [c] Calculations based on the optimized structure ; [d] $g_x/g_y/g_z$; [e] Calculations based on the experimental structures; [f] $g_{para}$ and $g_{perp}$*

**Table S2**: Experimental EPR parameters and calculated *D* values for mononuclear Mn(III) complexes.

| Complex | coord. sphere | Geom. | $D_{exp}$[a] ($cm^{-1}$) | $E$[a] ($cm^{-1}$) | $E/D$ | $B^4_0$ | $g_{iso}$ | Metho. | $D_{calc}$ ($cm^{-1}$) | ref[b] |
|---|---|---|---|---|---|---|---|---|---|---|
| ***S= 2*** | | | | | | | | | | |
| ***6-coordinate*** | | | | | | | | | | |
| $[Mn(bpea)(N_3)_3]$ | N6 | Comp. | +3.50(1) | -.82(1) | +0.234 | | 2.02(1)/1.98(1)/1.95(1) | DFT | +2.56 | 27,28 |
| | | | | | | | | CAS | +3.39 | |
| $[Mn(terpy)(N_3)_3]$ | N6 | Elong. | -3.29(1) | -0.48(1) | -0.146 | | 2.00(0.5)/1.98(0.5)/2.01(0.5) | DFT | -2.79 | 29 |
| | | | | | | | | | -3.45 | |
| $[Mn(opbaCl_2)(py)_2]$ | N4O2 | Elong. | -3.246(2) | -0.115(1) | 0.035 | $B^4_0= B^4_2=0$ $B^4_4= 23(3)\times10^{-4}$ | 2.001(1)/2.000(1)/1.990(3) | DFT | -2.53 | 30 |
| | | | | | | | | CAS | -3.47 | |
| $[Mn(bpia)(OAc)(OCH_3)](PF_6)$ | N4O2 | Comp. | +3.526(3) | +0.588(6) | 0.167 | $B^4_0= -0.00084(7)$ $B^4_2=-0.002(2)$ $B^4_4= -0.0082(5)$ | 1.98(1)/1.952(6)/1.978(5) | DFT | +2.77 | 31 |
| | | | | | | | | CAS | +3.24 | |
| $[MnLK(PF_6)]$ | N3O3 | Comp. | +4.15 | 0.75 | 0.181 | | 2.00 | | | 32 |
| $[Mn(dbm)_2(py)_2](ClO_4)$ | N2O4 | Elong. | -4.504(2) | -0.425(1) | 0.094 | $B^4_0= 1.8(4)\times10^{-4}$ $B^4_2=7(3)\times10^{-4}$ $B^4_4= 48(4)\times10^{-4}$ | 1.993(1)/1.994(1)/1.983(1) | DFT | -3.34 | 28,33 |
| | | | | | | | | CAS | -3.85 | |
| $[Mn(acac)_3]$ | O6 | Elong. | -4.52(2) | 0.25(2) | 0.055 | | 1.99(1) | DFT | -3.12 | 34,35 |
| | | | | | | | | CAS | -3.67 | |
| $[Mn(dbm)_3]$ | O6 | Elong. | -4.35 | 0.26 | -0.60 | | 1.99/1.99/1.97 | | | 36 |
| $[Mn(OH_2)_6]^{2+}$ | O6 | Elong. | -4.491(7) | 0.248(5) | 0.055 | | 1.981(5)/1.993(5)/1.988(5) | DFT | -3.16 | 28,37 |
| | | | | | | | | CAS | -4.13 | |
| $[Mn(bpea)F_3]$ | N3F3 | Elong. | -3.67(2) | 0.70(2) | -0.191 | | 196(1)/1.98(1)/1.98(1) | DFT | -2.43 | 27,28 |
| | | | | | | | | CAS | -3.54 | |
| $[Mn(terpy)F_3]$ | N3F3 | Elong. | -3.82(2) | 0.75(2) | -0.196 | | 1.97(2)/2.04(1)/1.96(1) | DFT | -2.17 | 27,28 |
| | | | | | | | | CAS | -3.66 | |
| $[Mn(terpy)Cl_3]$ | N3Cl3 | Elong. | -3.53 | 0.30 | 0.085 | | 1.98/2.00/2.00 | DFT | -2.25 | 28,38 |
| | | | | | | | | CAS | -3.66 | |
| $[Mn(Phterpy)Cl_3]$ | N3Cl3 | Elong. | -3.46 | 0.43 | 0.124 | | 1.96/2.00/2.00 | DFT | -2.30 | 28,38 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | CAS | -3.69 | |
| [Mn(cyclam)$Br_2$]Br | N4Br2 | Elong. | - 1.1677(7) | - 0.0135(6) | 0.116 | $B^4_0$= 9(3)×$10^{-4}$ $B^4_2$=6(2)×$10^{-4}$ $B^4_4$= 17(3)×$10^{-4}$ | 2.005(4)/2.036(2)/2.015(2) | | | 39 |
| [Mn(cyclam)$I_2$]I | N4I2 | Elong. | +0.604 | +0.034 | 0.056 | | 2.00/2.00/1.99 | | | 40 |
| ***5-coordinate*** | | | | | | | | | | |
| [Mn(NCTPP)$(py)_2$] | N5C | Elong. | -3.084(3) | -0.608(3) | 0.197 | | 2.000(2)/2.000(3)/2.006(4) | | | 41 |
| [Mn(tpfc)($OPPh_3$) | N4O | Elong. | -2.69(2) | -0.030(3) | 0.011 | | 1.994(4)/1.994(4)/1.980(4) | DFT | -1.82 | 28,42 |
| | | | | | | | | CAS | -2.43 | |
| [Mn(tpp)Cl] | N4Cl | Elong. | -2.290(5) | 0.00(1) | 0 | | 1.98/1.98/2.005(3) | DFT | -1.26 | 28,43,44 |
| | | | | | | | | CAS | -1.98 | |
| [Mn(ODMAPz)Cl] | N4Cl | Elong. | -2.33(1) | 0 | 0 | | 1.984 | | | 44 |
| ***4-coordinate*** | | | | | | | | | | |
| [Mn($TBHP_8Cz$)] | N4 | Elong. | -2.60(2) | 0.015 | 0.006 | | 2.00(1) | | | 45 |
| ***S = 1*** | | | | | | | | | | |
| [$Tp_2$Mn]($SbF_6$) | N6 | | +17.97(1) | +0.42(2) | 0.023 | | 2.065(6)/2.073(8)/1.978(6) | LFT | +17.97 | 46 |
| | | | | | | | | DFT | +10.78 | |
| [$Tp^*_2$Mn]($SbF_6$) | N6 | | +15.89(2) | +0.04(1) | 0.003 | | 2.079(7)/2.074(6)/2.075(15) | LFT | +15.89 | 46 |
| | | | | | | | | DFT | +9.94 | |

*[a] the sign is reported when it has been determined; [b] in parenthesis, the reference reporting $D_{calc}$ is notified if it is different from the one reporting $D_{exp}$; [c] calculations based on the optimized structures; [d] $g_x/g_y/g_z$; [e] calculations based on the experimental structures; [f] $g_{//}/g_{\perp}$*

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