Supplementary Materials: Ddpd as Expanded Terpyridine: Dramatic Effects of Symmetry and Electronic Properties in First Row Transition Metal Complexes

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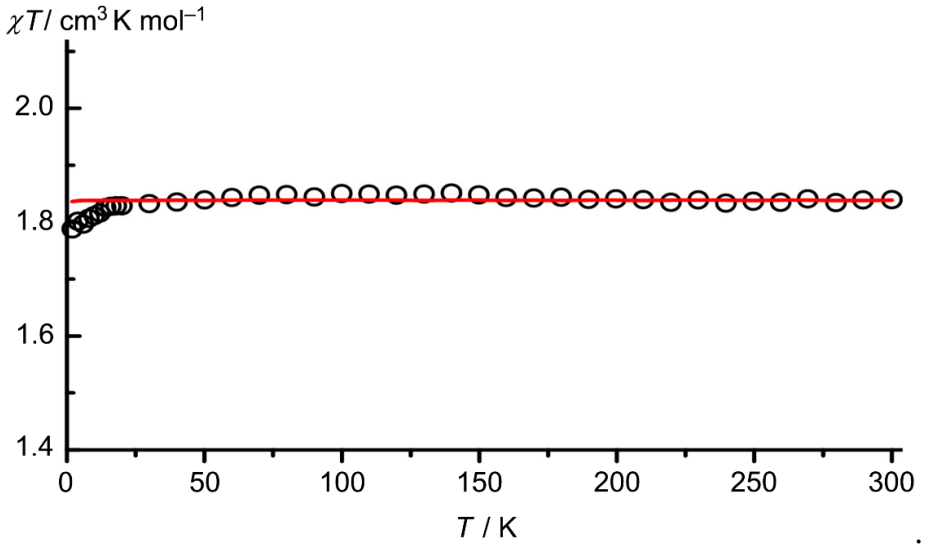


Figure S1. Temperature-dependence of $\chi_M T$ of $[Cr(ddpd)_2][BF_4]_3 \times CH_3CN$ (black circles) with fit (solid red line, $g = 1.980$).

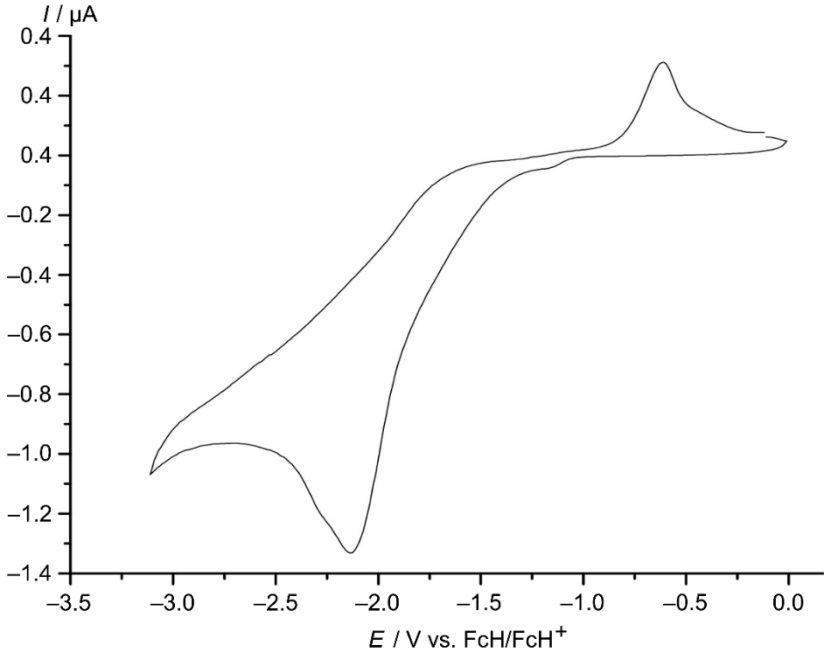


Figure S2. Cyclic voltammogram of $[Ni(ddpd)_2][BF_4]_2$ in CH_3CN in the presence of HOAc and CO_2.

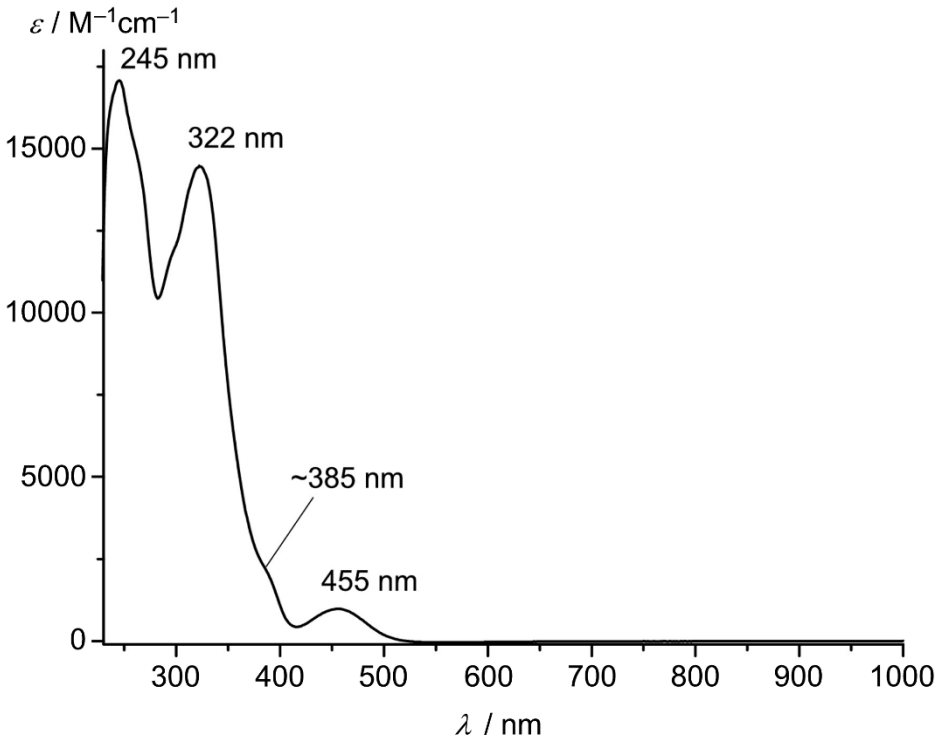


Figure S3. UV/Vis spectrum of *mer*-VCl_3(ddpd) in CH_2Cl_2.

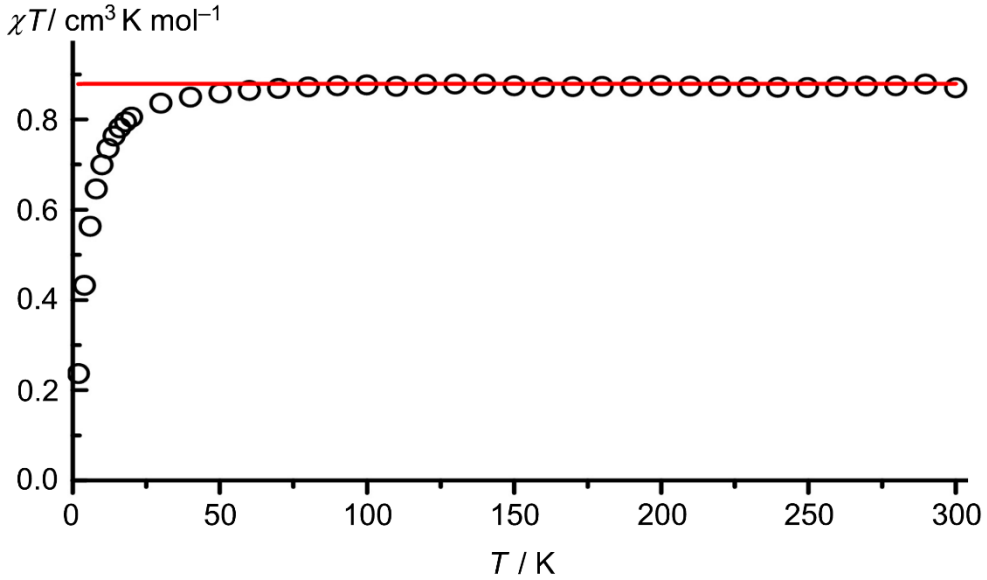
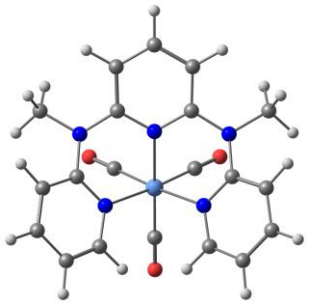


Figure S4. Temperature-dependence of $\chi_M T$ of VCl_3(ddpd) (black circles) with fit (solid red line, g = 1.875).

Cartesian Coordinates of the DFT calculated geometry of *fac*-$Cr(CO)_3$(ddpd).



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6       -1.206027000      3.295754000     -0.792950000
6       -1.166241000      1.919625000     -0.507800000
7        0.000192000      1.276824000     -0.293234000
1        2.148108000      3.807524000     -0.958110000
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6       -1.285415000      0.206261000      2.117877000
8       -2.103421000      0.607925000      2.857598000
8       -0.005850000     -2.981239000      2.566297000
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8        2.107513000      0.607533000      2.853103000
-------------------
GIBBS FREE ENTHALPY
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The Gibbs free enthalpy is G = H - T*S
Total enthalpy                  ...  -2325.29770765 Eh
Total entropy correction        ...     -0.07675478 Eh    -48.16 kcal/mol
-----------------------------------------------------------------------
Final Gibbs free enthalpy       ...  -2325.37446243 Eh
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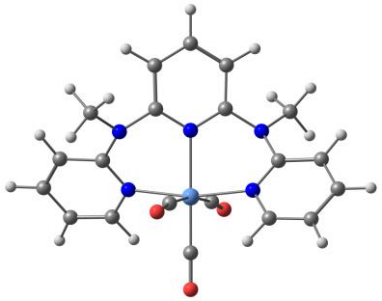
Cartesian Coordinates of the DFT calculated geometry of *mer*-$Cr(CO)_3$(ddpd).



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6       -4.198919000      0.297491000     -0.034069000
6       -2.801107000      0.256686000      0.128299000
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7        2.040578000     -0.673622000      0.485272000
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7       -2.157040000      1.181004000      0.969535000
6       -2.942212000      1.779434000      2.043303000
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1       -3.495499000      0.987121000      2.557096000
1       -2.259865000      2.243867000      2.760686000
7        2.156655000      1.180927000     -0.969752000
6        2.941368000      1.779501000     -2.043776000
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1        2.258724000      2.244263000     -2.760660000
1        0.000501000      5.106327000      0.001283000
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6        0.000097000     -2.680483000      0.000577000
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8       -0.751543000     -1.288547000      2.914920000
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GIBBS FREE ENTHALPY
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The Gibbs free enthalpy is G = H - T*S
Total enthalpy                  ...  -2325.27794198 Eh
Total entropy correction        ...     -0.07599064 Eh    -47.68 kcal/mol
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Final Gibbs free enthalpy       ...  -2325.35393261 Eh
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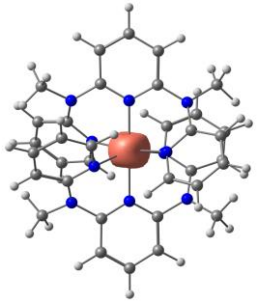
Cartesian Coordinates of the DFT calculated geometry of high spin [*mer*-$Cr(ddpd)_2]^{2+}$ (^5E spin density in orange with an isosurface value of 0.05 a.u.). CPCM(acetonitrile)-RIJCOSX-B3LYP-D3BJ-ZORA/def2-SVP



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1        3.366993436     -3.189462936      1.128412274
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1        4.087387826      3.353634357      0.619299310
1        4.257605626      1.918255886     -0.423480973
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1        0.002334201      5.975261529     -0.002956513
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24      -0.000578920     -0.009379138     -0.001056238
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GIBBS FREE ENTHALPY
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The Gibbs free enthalpy is G = H - T*S
Total enthalpy                  ...  -2916.24132917 Eh
Total entropy correction        ...     -0.09979641 Eh    -62.62 kcal/mol
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Final Gibbs free enthalpy       ...  -2916.34112558 Eh
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