Antiferromagnetic Coupling Across a Tetrametallic Unit Through Noncovalent Interactions

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Syntheses.

General Considerations. K\(_2\)PtCl\(_4\) was prepared using a combination of literature preparations. H\(_2\)PtCl\(_6\) was prepared\(^1\) from commercially obtained Pt metal and was converted to K\(_2\)PtCl\(_6\) using a literature preparation.\(^2\) K\(_2\)PtCl\(_4\) was then synthesized from K\(_2\)PtCl\(_6\) using literature methods.\(^3\) All other reagents were obtained commercially and were used without further purifications. [Ni\(_2\)(tba)\(_4\)(EtOH)] was prepared according the literature.\(^4\) All reactions were carried out in air under ambient conditions unless otherwise specified. UV-Vis data were collected with a Shimadzu UV-3600 spectrometer. \(^1\)H NMR spectra for Evans method were recorded on a Varian 500 MHz spectrometer. Elemental analyses were performed by Quantitative Technologies Inc. (QTI, Whitehouse, NJ 08888).

\([\text{PtFe(tba)}_4(\text{H}_2\text{O})]\\cdot(\text{acetone})\) (1): Compound 1 was prepared similarly to 3 until the addition of the first-row metal chloride using the amounts: NaHCO\(_3\) (0.1834 g, 2.183 mmol), Htba (0.2873 g, 2.079 mmol), K\(_2\)PtCl\(_4\) (0.2158 g, 0.520 mmol). A solution of FeCl\(_3\)·6H\(_2\)O (0.1405 g, 0.520 mmol) in ~15 mL H\(_2\)O was added dropwise to the reaction flask causing an immediate precipitation of a dark purple solid. The solution was then heated to 70°C for 30 min, which caused the dark purple solid to turn brown. The brown solid was filtered over celite, washed with H\(_2\)O, then dissolved in ~400 mL acetone forming a red solution. The volume of acetone was reduced to ~10 mL \textit{in vacuo} creating a red solid that precipitated out of solution. Hexanes was added sparingly to force additional precipitation of the red solid. The solid was then filtered and dried \textit{in vacuo}. The red material was redissolved in acetone and recrystallized with hexanes twice more to give a red microcrystalline powder with [PtFe(tba)\(_4\)(H\(_2\)O)]\\cdot(\text{acetone}) composition in 27% yield. Larger red crystals were grown from slow evaporation of acetone for X-ray
crystallography. Anal. calcd: C, 42.52; H 3.22; N 0.00 %. Found: C, 42.46; H, 2.96; N <0.05 %. UV-Vis (DMF) (λ_{max}, nm (ɛ_M, cm^{-1} M^{-1})): 314(32,400), 484(920), 996(13). Evans method (DMF-d7): 5.11 μB.

[PtCo(tba)₄(H₂O)]₂·5THF (2): Compound 2 was prepared similarly to 3 with the same amounts used until the addition of the first-row metal chloride. A solution of CoCl₂·6H₂O (0.2310 g, 0.843 mmol) in ~15 mL of H₂O was added dropwise to the reaction flask and let stir for 24 hours. The light green/beige precipitate that formed was separated from the colorless solution by filtering over celite. The powder was dissolved in THF and recrystallized with addition of hexanes to give a green powder with 64% yield.

Yellow/light brown crystals of 2b were grown from slow evaporation of CH₂Cl₂. Purple block-shaped crystals of 2a were grown from slow evaporation of THF and found to have the [PtCo(tba)₄(H₂O)]₂·10THF composition. Recrystallization of the green/beige material from CH₂Cl₂ and hexanes was found to have the composition [PtCo(tba)_4(H_2O)] (2b). Anal. Calcd. (2a): C, 45.59; H, 4.23; N 0.00 %. Found: C, 45.49; H, 3.98; N <0.05 %. Anal. Calcd. (2b): C, 40.97; H, 2.70; N, 0.00 %. Found: C, 40.97; H, 2.73; N, 0.00 %. UV-Vis (THF) (λ_{max}, nm (ɛ_M, cm^{-1} M^{-1})): 236(62,300), 295(30,500), 307(30,900), 495(28), 579(11), 1275(3). Evans method (DMF-d7): 5.02 μB.

[PtNi(tba)₄(H₂O)]·THF (3): A solution of NaHCO₃ (0.2975 g, 3.541 mmol) in ~100 mL H₂O was added to Thiobenzoic Acid (Htba) (0.4661 g, 3.373 mmol) and swirled by hand at room temp without a stir bar. The solution turned light yellow after ~10 min and was then transferred to another flask – leaving behind any protonated Htba. The stir bar was then added. A solution of K₂PtCl₄ (0.3500 g, 0.843 mmol) in ~15 mL H₂O was added to the flask, let stir for 1-2 min, followed by the dropwise addition of a NiCl₂·6H₂O (0.2308 g, 0.843 mmol) solution in ~15 mL H₂O. Upon addition of the NiCl₂·6H₂O a slight clouding of the solution was observed. After stirring 24 hours, a yellow precipitate was separated from the colorless solution by filtering over celite. The yellow powder was dissolved in THF and recrystallized with addition of Hexanes in a 61% yield and found to have a [PtNi(tba)₄(H₂O)]·2THF composition. Anal. calcd: C, 44.82; H, 3.97; N 0.00 %. Found: C, 44.79; H, 3.78; N <0.05 %. Light green block-shaped crystals of 3 were grown from slow evaporation of THF for X-ray crystallography. After grinding and heating the crystalline powder to 90°C for 30 min, 3 was found to have the [PtNi(tba)₄(H₂O)]·THF composition. Anal. calcd: C, 43.06; H, 3.39; N 0.00 %. Found: C, 43.26; H, 2.92; N <0.05 %. Care was taken to use X-ray quality crystals in all solid-state measurements. UV-Vis (THF) (λ_{max}, nm (ɛ_M, cm^{-1} M^{-1})): 246(56,300), 284(32,600), 321(27,700), 698(9), 820(6), 1337(10). Evans method (DMF-d7): 3.11 μB.

Single Crystal X-ray Diffraction. A crystal of 2a was mounted on a Cryoloop with Paratone-N oil and data was collected at 100 K with Cu Kα radiation at 40 s/frame. Data were corrected for absorption with the SADAB program and structure was solved by direct methods. All non-hydrogen atoms were placed in calculated positions. S and O atoms were disordered over two positions (49.5/50.5) and were
modeled with DFIX commands for Co-O and C-O distances. Disorder (47.0/53.0) with respect to aromatic ring (C23-C28) was treated using a two part model with HFIX 66 restraint and EADP command for C24, C24A, C25, C25A. Residual electron density was treated using the Program Squeeze (found large void volume of 3874 Å³ with electron density of 1511 e⁻) this was associated with 38 (thirty-eight) THF molecules in the unit cell, consistent with the elemental analysis data.

An orange colored crystal of 2b was mounted on a Cryoloop with Paratone-N oil. Data were collected on a Bruker APEX II CCD systems using Mo Kα radiation in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 10 seconds per frame using a scan width of 0.5°. Indexing and unit cell refinement indicated a primitive, monoclinic lattice with space group Pc. Data was corrected for absorption by the program SADABS. Solution by direct methods (SHELXS) and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms except those on the waters of hydration were placed in calculated positions with appropriate riding models. Hydrogen atoms on atoms O5 and O10 (waters of hydration) were found from a Fourier difference map, were restrained using DFIX and DANG commands and were allowed to refine. The structure was found to be twinned with a BASF ration of 72.4/27.6. CHECKCIF indicated a large solvent void but the residual electron density was centered around the Pt atoms and not in the void space.

**DFT Calculations.** All-electron, geometry-optimized, spin-unrestricted calculations were performed on [PtNi(tba)₄], [PtCo(tba)₄], and [PtFe(tba)₄] with idealized C₄ᵥ symmetry, and high-spin electron configurations in each, S = 1, 3/2, and 2 respectively, consistent with the experimental data. The expectation S² values for the three compounds are 6.06921 (PtFe), 3.75601 (PtCo), and 2.00553 (PtNi). In each case the origin was coincident with the 3d/ metal, the Pt-M vector coincident with the z-axis, and the x- and y-axes were aligned with the thiocarboxylate ligands. The 2010 version of ADF⁵,⁶ was used including the GGA-BLYP functional, TZ2P basis sets for all atoms, and ZORA relativistic corrections for the Pt atoms. Frequency calculations on each of the three optimized structures showed genuine minima on the potential energy surface in the absence of any modes with negative frequencies. A comparison of the metal-ligand atom distances for the crystallographic and computational structures are collected in Table S3.

Spin-unrestricted and restricted calculations on C₂ symmetry [PtM(tba)₄(OH₂)], M = Fe, Co, Ni, and D₂ symmetry [PtM(tba)₄(OH₂)₂], M = Co, Ni, were carried out using the SCM ADF2010.2 package.⁵,⁷ Gas-phase geometry optimizations were carried out by the energy gradient minimization method with tight SCF convergence criteria and integration accuracies spanning 4.5-6. Calculations were carried out using the GGA B³LYP⁹ functional and the dispersion-corrected GGA Perdew-Burke-Ernzerhof î(PBE-)
D3\textsuperscript{11}) functional that includes Grimme’s zero-damped third generation dispersion correction to the total bonding energy.\textsuperscript{12} Within the PBE-D3 scheme electron correlation was treated within the local density approximation (LDA) in the PW92 parametrization.\textsuperscript{13} Within the BLYP scheme electron correlation was treated within the local density approximation (LDA) with the Vosko-Wilk-Nusair parametrization.\textsuperscript{14} Use of the PBE-D3 functional, a parent of the native PBE functional, was considered as a reasonable expedient\textsuperscript{15} to the modeling of the geometries of the paramagnetic lantern-type complexes and to a preliminary investigation of their electronic structure.\textsuperscript{16} Relativistic effects were treated in all cases with the ZORA formalism\textsuperscript{17} with recourse to ad-hoc all-electron triple-\(\zeta\) polarized basis sets of Slater-type orbitals (STOs) for all elements including H.\textsuperscript{18} A comparison of the metal-ligand atom distances for the crystallographic and computational structures as well as the corresponding expectation values \(S^2\) for the HS and BS states are collected in Table S3. The Gopinathan-Jug formalism\textsuperscript{19} was used for the geometries to compute two-atom bond indices (written \(n\)) with a value of 0.05 as threshold.

For monomers [PtNi(tba)\textsubscript{4}·H\textsubscript{2}O], [PtCo(tba)\textsubscript{4}·H\textsubscript{2}O] (2b), and [PtFe(tba)\textsubscript{4}·H\textsubscript{2}O] (1), spin-unrestricted geometry optimization was constrained to \(C_2\) symmetry (principal \(z\) axis collinear with the metal-Pt axis) and to high-spin (HS) electron configurations \(S = 1\) (spin polarization = 2), 3/2 (spin polarization= 3), and 2 (spin polarization = 4) respectively, consistent with the experimental data at room temperature. For dimers [PtNi(tba)\textsubscript{4}·H\textsubscript{2}O\textsubscript{2}] and [PtCo(tba)\textsubscript{4}·H\textsubscript{2}O\textsubscript{2}], spin unrestricted geometry optimization was constrained to \(D_2\) symmetry (main \(z\) axis bisecting perpendicularly the Pt-Pt segment) at high spin configuration with \(S= 1\) (spin polarization = 2) and 3 (spin polarization = 6) respectively.

The resulting geometries were used with no symmetry constraint to perform single point computations of low spin configurations of [PtNi(tba)\textsubscript{4}·H\textsubscript{2}O] (\(S^2 = 0\)), [PtCo(tba)\textsubscript{4}·H\textsubscript{2}O] (\(S^2 = 1/2\)), [PtNi(tba)\textsubscript{4}·H\textsubscript{2}O\textsubscript{2}] (\(S = 0\)) and [PtCo(tba)\textsubscript{4}·H\textsubscript{2}O\textsubscript{2}] (\(S = 0\)) by applying the “spin-flip” broken symmetry (BS) method.\textsuperscript{20-22} In each case the high spin configuration was recomputed with no symmetry constraint with tight SCF convergence criteria. The resulting energy differences between the HS and BS configurations reproduced the trends established experimentally as to the relative stability of the low and the high spin states. However, as expected for large many-electrons systems treated within a GGA scheme,\textsuperscript{23, 24} the computed values of spin coupling constants \(J\) were found in all cases to be largely overestimated compared to those determined experimentally for solid-state samples; test computations carried out with the dispersion corrected meta-GGA functional TPSS\textsuperscript{25} (i.e TPSS-D\textsuperscript{11, 12}) led to only slightly improved energy differences\textsuperscript{26} between HS and BS states. Kohn-Sham spin density polarizations in HS and BS states were materialized by subtracting \(\beta\) SCF spin density to \(\alpha\) SCF spin density using ADFview2010. Other plots of the coulombic potential maps over SCF electron density and molecular orbital were also drawn using ADFview.
Analytical frequency calculations on each of the three water-free optimized structures in their high spin state were exempt of imaginary vibrational modes indicating that they were genuine minima on the potential energy surface. However, due to large symmetry constraints on the water molecule (of which the $C_2$ axis was virtually forced to remain colinear with the $C_2$ axis aligned on the M-Pt vector) and due to the repulsive tendency of the M-to-water interaction in the GGA structures of those water-containing complexes, calculations of normal vibrational modes produced systematically an imaginary eigenvalue associated essentially with the disruption of the M-to-water interaction (M= Fe, Co, Ni). This issue associated with the limitations inherent to the use of pure GGA functionals$^{27, 28}$ was not addressed in this preliminary report. Computation of the HS and BS states of [PtNi(tba)$_4$·H$_2$O] at the UPBE0$^{29, 30}$/AE-TZP level improved the description of the BS state by producing a neat $S=0$ state. However the $J$ constant was still largely overestimated, which partly disqualifies this hybrid for the description of the magnetic behaviour of this series of complexes. Resorting to other hybrid functionals$^{31}$ or to higher levels of theory in Jacob’s ladder of methods (such as CI), with careful adjustment of the geometry of the adsorbed water molecule, should enable a better reproduction of those structural features and to a minimization of the delocalized nature of the electronic structure.

A spin restricted geometry optimization was also carried out with the $C_2$-symmetric [PtNi(tba)$_4$·H$_2$O]$_2$ ($S= 0$) to probe the effect of the spin state over the Pt-Pt distance.

**Diffuse Reflectance.** Ultraviolet–visible (UV-vis) reflectance data were collected on a Varian Cary 500 scan UV−vis−NIR spectrophotometer over a spectral range of 200−2000 nm at room temperature. Poly(tetrafluoroethylene) was used as a reference material. Reflectance spectra were converted to absorbance data, using the Kubelka–Munk function.$^{32, 33}$

**Magnetic Measurements.** Magnetic susceptibility data were collected with a Quantum Design MPMS-XL SQUID magnetometer. For measurement between 2 and 300 K, samples were loaded into a gelatin capsule and inserted into drinking straws prior to analysis. Samples of 1 were measured as loosely-packed crystals as well as packed ground-up powders. The latter preparations show loss of solvate acetone, and data were interpreted accordingly.

Since compound 2a decomposes upon grinding, a sample of purple crystalline blocks was left unground, and was measured as loosely-packed crystals and as crystals suspended in a matrix of eicosane to prevent torquing. Although the data are similar, given possible desolvation or reactions with hot eicosane, all data for 2a are reported for crystals only. The crystals do not decompose during SQUID data collection. Data for 2b were collected on light-yellow-colored powdered samples. Samples of 3 were measured in several different ways: as loosely-packed crystals, as crystals suspended in eicosane, as
packed ground-up powders, and as powders suspended in eicosane. The first three preparations provide qualitatively similar data. However, ground samples of 3 mixed with eicosane gave significantly different data and powder XRD measurements did not match predicted patterns, so data from this preparation was not analyzed further. For all measurements, diamagnetic corrections were applied by using Pascal’s constants and by subtracting the diamagnetic susceptibility from the sample holder (including eicosane where appropriate). Where possible, susceptibility data were fit with theoretical models using a relative error minimization routine (julX 1.41). Exchange coupling parameters are based on the Hamiltonian:

\[ \hat{H} = -2J(S_x \cdot S_y) \].

Zero-field splitting parameters obtained with julX are based on the spin Hamiltonian:

\[ \hat{H} = \sum_{i,j} D_i [S_{z,j}^2 - \frac{1}{3} S_i (S_i + 1) + E_i/S_i (S_{x,i}^2 - S_{y,i}^2)] + \sum g \beta S_i \cdot B. \]

Fits of magnetization data were obtained with the ANISOFIT program and are based on the Hamiltonian:

\[ \hat{H} = D \hat{S}_z^2 + E (\hat{S}_x^2 + \hat{S}_y^2) + g_{iso} \beta \hat{S} \cdot B. \]

The MagSaki program was used to simulate magnetic susceptibility data involving axially distorted Co(II)-containing compounds.
<table>
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<th>1</th>
<th>2a</th>
<th>2b</th>
<th>3</th>
</tr>
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*a R=rΣ||Fₒ|-|F_c||/Σ|Fₒ|, b R(ωF²)=√Σ[ω(Fₒ²-F_c²)²]/Σ[ω(Fₒ)²]|¹/²; ω=1/[σ(Fₒ)+aP+bP], P=[2F_c²+max(Fₒ,0)]/3
Table S2. Selected interatomic distances and angles for 1, 2a, 2b, and 3.

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Electronic Supplementary Material (ESI) for Chemical Science
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Table S3. Comparison of crystallographic and computed gas-phase geometries in [PtM(tba)•H₂O] species

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*Average of four. *b) Computed with the symmetry constraint lifted. *c) Mulliken-type spin densities; spin densities at S atoms were found negligible and are therefore not listed in this table.
Figure S1. ORTEP of [PtFe(tba)$_4$(OH$_2$)]·acetone, 1·acetone, with ellipsoids at 50% level and hydrogen atoms removed for clarity. Not shown are intermolecular Pt(1)…S(3) contacts at 3.2596(9) Å.
**Figure S2.** ORTEP of [PtCo(tba)$_4$(OH)$_2$], 2b, with ellipsoids at 50% level and hydrogen atoms removed for clarity. The interdimer contacts are 2.978(1) Å for Pt(1)$\cdots$S(8) and 3.106(1) Å for Pt(2)$\cdots$S(2).
**Figure S3.** ORTEP of [PtNi(tba)$_4$(OH$_2$)]$_2$·THF, 3. Ellipsoids are at the 50% level. THF and hydrogen atoms have been removed for clarity.
Figure S4. $[\text{Ni}_2(\text{tba})_4(\text{HOEt})]$ and $[\text{PtNi}(\text{tba})_4(\text{OH}_2)]$ in THF and in the solid state. The spectrum of $[\text{Ni}_2(\text{tba})_4(\text{HOEt})]$ was reported previously\textsuperscript{4} but was remeasured for comparison convenience.
Figure S5. [PtNi(tba)$_4$(OH$_2$)$_3$] in THF at five different concentrations.
Figure S6. Temperature dependence of magnetic susceptibility for 1, measured at 1000 G. Best fit parameters (via julX) are included in the figure with units of cm$^{-1}$ for $D$ and $T_W$ (the mean field approximation to account for intermolecular interactions) and units of emu/mol for TIP. The raw data is shown in the top figure; the TIP contribution has been subtracted from the data shown in the bottom figure.
Figure S7. Comparison of experimental and calculated powder diffraction data for 1.
Alternative fits and simulations for Co-containing complexes 2a and 2b. In the manuscript, we generate fits to the magnetic susceptibility data for 2a and 2b without including axial anisotropy ($D$) since $S = 0$ and $S = \frac{1}{2}$ states cannot have $D$ ($2b$ acts like $S = \frac{1}{2}$ at low temperature). However, since the spin Hamiltonian used by julX does not explicitly account for unquenched orbital angular momentum and/or spin-orbit coupling, commonly encountered with 6-coordinate Co(II) complexes, we attempted fits where we treat “$D$” simply as a parameter to be varied. For 2a, including “$D$” results in nearly identical parameters and fit quality (Table S4).

Table S4. Comparison of julX-fitted magnetic parameters for 2a.

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<td>$D$ (cm$^{-1}$)</td>
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Alternative fitting scenarios for 2b are shown in Table S5. Attempts to fit 2b as a dimeric Co$_2$Pt$_2$ species yield unsatisfactory results. Tiny $J$ values (intradimer coupling) in entries 1 and 2 support the assumption of minimal Co…Co magnetic interactions and the treatment of 2b as a monomer. The fit shown for entry 3 is reasonably similar to the values obtained for 2a. In fact, fits obtained with $g$ and $D$ values fixed to those found for 2a (entry 4) also refine to similar values. Since the “$D$” value found for entry 3 was negligible, we concluded that reducing the number of parameters presented in the manuscript was warranted (entry 6). These fits include a mean field approximation in monomer and dimer cases: these are consistent with the intermolecular interactions observed in the solid-state crystal structure. Removal of the mean-field correction results in a “$D$” that is physically unreasonable (entry 5). In all cases large TIP values reflect the inability of the julX Hamiltonian to adequately model orbital contributions.

Table S5. Comparison of alternative fitted parameters for 2b.

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In an alternative fitting method, Sakiyama\textsuperscript{37-42} and others\textsuperscript{38, 43, 44} have considered effects of ligand-field distortions on the magnetic behaviour of Co(II) ions. These systems can be modelled by accounting for the spin-orbit coupling ($\lambda$), axial ligand-field splitting ($\Delta$), and an orbital reduction factor ($\kappa$). Results of these simulations are shown in Figure S10.

**Figure S8.** Results of MagSaki simulations for Co-containing complexes 2a and 2b. Solid lines are best fits obtained from MagSaki. The fit shown for 2a has $\theta$ fixed to zero while the fit for 2b has a freely-refined $\theta$.

Simulating the 2b data with MagSaki,\textsuperscript{36} and fixing $S = 3/2$, $g = 2.0$, gives fitted parameters $\Delta = 351$ cm$^{-1}$, $\kappa = 0.7$, $\lambda = -173$ cm$^{-1}$, $\theta = -1.9$ K, and TIP = 1.21×10$^{-4}$ emu/mol. These values are typical for a Co(II) ion in an axially-distorted octahedral ligand field.\textsuperscript{37} If we assume no intermolecular interactions (i.e. $\theta$ fixed to 0 K), similar parameters are obtained: TIP = 0.001 emu/mol (fixed), $\Delta = 658$ cm$^{-1}$, $\kappa = 0.66$, and $\lambda = -173$ cm$^{-1}$; note that $\Delta$ is larger and TIP refines to unreasonably small values, supporting the inclusion of $\theta$.

An attempt was also made to simulate the magnetic data for 2a using the axially distorted model that is built into MagSaki. Here, $\kappa$, $\lambda$, and $\Delta$ were obtained first by fitting the data above 100 K and then $J$ was added to fit all the data. The large TIP value was necessary to reproduce the monotonic behaviour at higher temperatures: $g = 2.0$ (fixed), $\theta = 0$ K (fixed), $J = -11.6$ cm$^{-1}$, TIP = 4.4×10$^{-3}$ emu/mol, $\kappa = 0.92$, $\lambda = -172$ cm$^{-1}$, $\Delta = 15.8$ cm$^{-1}$. For comparison, refining the $\theta$ parameter results in similar values: $g = 2.0$ (fixed), $\theta = -11.11$ K, $J = -11.1$ cm$^{-1}$, TIP = 4.6×10$^{-3}$ emu, $\kappa = 0.92$, $\lambda = -173$ cm$^{-1}$, $\Delta = -15.9$ cm$^{-1}$. 
Lacking independent determinations of simulated values (e.g. g from EPR), the simulation is over-parameterized; nevertheless, the values obtained are consistent with a dinuclear complex containing axially-distorted Co(II) ions.41-44

For the Co-containing complexes studied here, we find that the coupling between spin centers is rather weak, at least compared to the Ni-containing analogue 3. Although structurally both 2a and 2b show intermolecular interactions in the solid state, the paths for possible magnetic exchange are significantly different, such that 2a is best thought of as a (CoPt)₂ species while 2b acts more like a (CoPt) entity.
**Figure S9.** Comparison of calculated X-ray powder diffraction pattern for 2b (red), pre-SQUID 2b (blue), and compound 2b after SQUID measurement (purple). Bottom: comparison of calculated X-ray powder diffraction for 2b (green), calculated X-ray powder diffraction pattern for 2a (red) and compound 2a after grinding and SQUID measurement (black).
**Figure S10.** Temperature dependence of the magnetic susceptibility for ground crystals (powder) sample of 3, measured in a 1000 G field. Best fit parameters (via julX) are provided in Table S6. Note: the TIP contribution has been subtracted from the data.

**Figure S11.** Comparison of calculated X-ray powder diffraction pattern for crystalline 3 (blue), powdered 3 before (purple), and after (black) SQUID measurement.
Table S6. Comparison of julX fits to the magnetic susceptibility data for 3.

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Figure S12. Hydrogen bonding interactions in the lattice of [PtFe(tba)$_4$(OH$_2$)], 1, with distances shown in Ångstroms.
**Figure S13.** Hydrogen bonding interactions in the lattice of [PtCo(tba)$_4$(OH)$_2$]$_2$, 2a, with distances shown in Ångstroms.
Figure S14. Hydrogen bonding interactions in the lattice of [PtCo(tba)₄(OH₂)], 2b, with distances shown in Ångstroms.
Figure S15. Hydrogen bonding interactions in the lattice of [PtNi(tba)₄(OH₂)], 3, with distances shown in Ångstroms.
Figure S16. Energy level diagram and selected orbital pictures for DFT calculation of $[\text{PtNi(tba)}_4(\text{OH}_2)]^-$ under $C_2$ symmetry.
**Figure S17.** Isosurface plots (0.005 e/Å³) of high spin and broken symmetry spin density polarizations in the [CoPt(tba)(H₂O)] monomer (2b) as computed at the (ZORA) PBE-D3/AE-TZP level. Blue and red isosurfaces represent $\alpha$ and $\beta$ spin domains respectively.

**Figure S18.** a) Isosurface (0.005 e/Å³) plot of the spin density polarization (mostly $\alpha$ spins) for the high spin model of [FePt(tba)(H₂O)] (1) computed at the (ZORA) UPBE/AE-TZP level. b) Coulombic potential (values comprised between -0.033 and 0.417 a.u) map drawn over an isosurface (0.03 e/Å³) of the total SCF electron density.
**Figure S19.** Isosurface plots (0.005 e/A³) of high spin and broken symmetry “low spin” spin density polarization in the model of 2a as computed at the (ZORA) UPBE-D3/AE-TZP level. Blue and red isosurfaces represent α and β spin domains respectively.

**Figure S20.** Plots of the singly occupied spin α molecular orbitals for the high spin model of 2a computed at the (ZORA) UPBE-D3/AE-TZP level.
Computational part: Coordinates and energies

1, (ZORA)PBE-D3/AE-TZP, C2 symmetry

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Geometry Convergence Tests

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Convergence tests:
(Energies in hartree, Gradients in hartree/angstrom or radian, Lengths in angstrom, Angles in degrees)

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Pauli Repulsion

- Kinetic (ΔT^0): 163.1125480663177 eV = 4438.5179 kcal/mol = 102354.67 kJ/mol
- Delta V^Pauli LDA-XC: -83.7362015362097 eV = -2278.5733 kcal/mol = -52545.16 kJ/mol
- Delta V^Pauli GGA-Exchange: -20.5723464714561 eV = -559.8020 kcal/mol = -12909.34 kJ/mol
- Delta V^Pauli GGA-Correlation: 1.05754262404999 eV = 28.7772 kcal/mol = 663.62 kJ/mol

Total Pauli Repulsion: 59.62066542192836 eV = 1622.3609 kcal/mol = 37412.54 kJ/mol

Steric Interaction

- Pauli Repulsion (ΔE^Pauli): 59.62066542192836 eV = 1622.3609 kcal/mol = 37412.54 kJ/mol
- Electrostatic Interaction: -12.662985058465141 eV = -344.5774 kcal/mol = -7946.14 kJ/mol

Total Steric Interaction: 46.957680365727697 eV = 1277.7835 kcal/mol = 29466.39 kJ/mol

Orbital Interactions

- A: -30.971375661248349 eV = -842.7740 kcal/mol = -19434.83 kJ/mol
- B: -30.535170113872397 eV = -830.9043 kcal/mol = -19161.11 kJ/mol

Total Orbital Interactions: -61.512041770560394 eV = -1673.8278 kcal/mol = -38599.39 kJ/mol

Alternative Decomposition Orb.Int.

- Kinetic: -148.640438020361046 eV = -4044.7121 kcal/mol = -93273.29 kJ/mol
- Coulomb: 80.793263015258870 eV = 2198.6591 kcal/mol = 50702.92 kJ/mol
- XC: 6.329163737021333 eV = 172.2552 kcal/mol = 3971.61 kJ/mol

Total Orbital Interactions: -61.512041770560415 eV = -1673.8278 kcal/mol = -38599.39 kJ/mol

Dispersion Energy: -0.050267508424341 eV = -1.3678 kcal/mol = -31.54 kJ/mol

Total Bonding Energy: -14.604664057585676 eV = -397.4131 kcal/mol = -9164.57 kJ/mol

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

- Electrostatic Energy: -12.662985058465141 eV = -344.5774 kcal/mol = -7946.14 kJ/mol
- Kinetic Energy: 14.472096768630231 eV = 393.8058 kcal/mol = 9081.38 kJ/mol
- Coulomb (Steric+OrbInt+Res): -0.00035144328638 eV = -0.0010 kcal/mol = -0.02 kJ/mol
- Dispersion Energy: -0.050267508424341 eV = -1.3678 kcal/mol = -31.54 kJ/mol

Total Bonding Energy: -14.604664057585696 eV = -397.4131 kcal/mol = -9164.57 kJ/mol
### 2b, (ZORA) PBE-D3/AE-TZP, C\textsubscript{2} symmetry

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Geometry Convergence Tests

| Energy old | -14.55458387 |
| new        | -14.55459601 |

Convergence tests:
(Energies in hartree, Gradients in hartree/angstr or radian, Lengths in angstrom, Angles in degrees)
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Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

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Geometry Convergence Tests

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Convergence tests:
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| Steric Interaction    |             |            |        |
| Pauli Repulsion (Delta E^Pauli) | 59.4130234247926 | 1616.7106 | 37282.24 | 155988.87 |
| Electrostatic Interaction (Delta V_elstat in the BB paper) | -12.558092255702892 | -341.7231 | -7880.32 | -32971.27 |
| Total Steric Interaction | 46.85493178545030 | 1274.9875 | 29401.92 | 123017.60 |

| Orbital Interactions  |             |            |        |
| Pauli Repulsion (Delta E^Pauli) | -30.725901678906872 | -836.0943 | -19280.80 | -80670.84 |
| A                     | -30.536700420384335 | -830.9459 | -19162.07 | -80174.10 |
| Total Orbital Interactions | -61.269658685740218 | -1667.2322 | -38447.30 | -160863.47 |

| Alternative Decomposition Orb.Int. |             |            |        |
| Kinetic                 | -149.028606839670772 | -4055.2747 | -93516.87 | -391274.55 |
| Coulomb                 | 81.077769124956603  | 2206.2384  | 50877.07  | 212869.65  |
| XC                     | 6.681790298973953    | 181.8041   | 4192.50   | 17541.43   |
| Total Orbital Interactions | -61.269658685740218 | -1667.2322 | -38447.30 | -160863.47 |

| Residu (E=Steric+OrbInt+Res) |             |            |        |
| -0.00007926500815      | -0.0021     | -0.05     | -0.20    |

Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

| Electrostatic Energy   | -12.558092255702892 | -341.7231 | -7880.32 | -32971.27 |
| Kinetic Energy         | 13.910375053067395  | 378.5206  | 8728.89  | 36521.69  |
| Coulomb (Steric+OrbInt) Energy | -2.715710165522367 | -73.8982  | -1704.13 | -7130.10  |
| Dispersion Energy      | -0.052914334374964  | -1.4399   | -33.20    | -138.93    |
### 2a, (ZORA) PBE-D3/AE-TZP, $D_2$ symmetry

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Geometry Convergence Tests

Energy old :    -29.13828927
new :        -29.13847153

Convergence tests:
(Energies in hartree, Gradients in hartree/angstrom or radian, Lengths in angstrom, Angles in degrees)

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Electronic Supplementary Material (ESI) for Chemical Science
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Pauli Repulsion

Kinetic (Delta T^0):  328.051962364114956  8926.7481  205855.74  861300.31
Delta V^Pauli LDA-XC:  -41.385887158124027  -1126.1673  -25970.04  -108658.63
Delta V^Pauli GGA-Exchange:  2.16273697160599  58.8511  1357.14  5678.27
Delta V^Pauli GGA-Correlation:  -0.503385483868119  -13.6978  -315.88  -1321.64

Total Pauli Repulsion:  119.275560110880392  3245.6531  74846.55  313157.94

Electronic Supplementary Material (ESI) for Chemical Science
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Delta $E^{\text{Pauli}}$ in BB paper:

### Steric Interaction

Pauli Repulsion ($\Delta E^{\text{Pauli}}$): 119.275560110880392 3245.6531 74846.55 313157.94

(\text{Electrostatic Interaction} = \Delta V_{\text{elstat}} \text{ in the BB paper})

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### Alternative Decomposition Orb.Int.

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### Residu ($E^{\text{Steric+OrbInt+Res}}$)

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### Summary of Bonding Energy (energy terms are taken from the energy decomposition above)

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### 3, (ZORA) PBE-D3/AE-TZP, $D_2$ symmetry

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### Geometry Convergence Tests

#### Energy

- **old**: -28.95253226
- **new**: -28.95307647

#### Convergence tests:

- **change in energy**: -0.00054421
- **gradient max**: 0.00071707
- **gradient rms**: 0.00019043
- **cart. step max**: 0.00746248
- **cart. step rms**: 0.00171843

#### Hartree, eV, kcal/mol, kJ/mol

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<th>kJ/mol</th>
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#### Electronic Supplementary Material (ESI) for Chemical Science

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Steric Interaction

Pauli Repulsion (Delta E^Pauli): 119.071452200771688 3240.0991 74718.47 312622.05
(Electrostatic Interaction = Delta V_elstat in the BB paper)

Total Steric Interaction: 93.858840999940526 2554.0290 58897.32 246426.35
(Total Steric Interaction = Delta E^0 in the BB paper)

Orbital Interactions

A: -30.850024228674368 -839.4719 -19358.68 -80996.73
B1: -30.504711855987480 -830.0754 -19142.00 -80090.11
B2: -30.508376011042749 -830.1752 -19144.30 -80099.73
B3: -30.792687885281786 -837.9117 -19322.71 -80846.19

Total Orbital Interactions: -122.679680140682990 -3338.2839 -76982.67 -322095.45

Alternative Decomposition Orb.Int.

Kinetic: -300.219382104363660 -8169.3850 -188390.53 -788225.88
Coulomb: 163.820797731790719 4457.7907 102799.11 430111.44
XC: 13.718904231889965 373.3104 8608.74 36018.98

Total Orbital Interactions: -122.679680140682976 -3338.2839 -76982.67 -322095.45

Residu (E=Steric+OrbInt+Res): -0.000221824651469 -0.0060 -0.14 -0.58
Dispersion Energy: -0.131726425425834 -3.5845 -82.66 -345.85


Summary of Bonding Energy [energy terms are taken from the energy decomposition above]

Electrostatic Energy: -25.212611200831169 -686.0701 -15821.15 -66195.70
Kinetic Energy: 28.151753793659509 766.0482 17665.49 73912.42
Coulomb (Steric+OrbInt) Energy: -5.693315134084656 -154.9230 -3572.62 -14947.80
XC Energy: -26.06688442137620 -709.3161 -16357.22 -68438.61
Dispersion Energy: -0.131726425425834 -3.5845 -82.66 -345.85

References: