Supplementary Material for:

Periodic Trends within a Series of Five Coordinate, Thiolate–Ligated $[M^{II}(S^{Me2}N_4(tren))]^+$ (M = Mn, Fe, Co, Ni, Cu, Zn) Complexes, Including a Rare Example of a Stable Cu^{II}–Thiolate

Lisa M. Brines, Jason Shearer, Jessica K. Fender, Dirk Schweitzer, Steven C. Shoner, David Barnhart,[§] Werner Kaminsky,[§] Scott Lovell,[§] and Julie A. Kovacs*

The Department of Chemistry, University of Washington: Box 351700 Seattle, WA 98195-1700

Supplementary Figures:

Figure S-1. Chemdrawing of $[Ni^{II}(SN_4(tren)–RS^{dang})]_2 \bullet 2H_2O$ (**3**) showing the co-crystallized H_2O molecules H–bonded to the "dangling" thiolate sulfur.

Figure S-2. Packing diagram for $[Ni^{II}(SN_4(tren)–RS^{dang})]_2 \bullet 2H_2O$ (**3**) showing intermolecular H–bonds to the "dangling" thiolate sulfur.

Figure S-3. A d–orbital splitting diagram illustrating why the trigonal bipyramidal Cu–S bond is not longer than the Ni–S bond, as would be predicted by Shannon radii.

Figure S-4. A d–orbital splitting diagram illustrating why Ni^{2+} adopts an ~ square pyramidal structure. A distorted trigonal–bipyramidal Ni^{2+} structure would have a pair of electrons pointing approximately towards one of the nitrogens in the trigonal plane (d_{xy}). By rearranging to a square pyramidal geometry, each ligand has only one electron pointing directly towards it, and the doubly populated σ^* orbital converts to a π^*, resulting in a structure with stronger bonds.

Figure S-5. Electronic absorption spectrum of $[Co^{II}(S^{Me2}N_4(tren))](PF_6)$ (**6**) in MeCN at ambient temperature.

Figure S-6. Electronic absorption spectrum of $[Mn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**5**) in MeCN at ambient temperature.

Figure S-7. Electronic absorption spectrum of $[Ni^{II}(S^{Me2}N_4(tren))]Cl$ (**4**) in MeCN at ambient temperature.

Figure S-8. Electronic absorption spectrum of $[Cu^{II}(S^{Me2}N_4(tren))](PF_6)$ (**7**) in H_2O at ambient temperature.

Figure S-9. ^1H NMR (298 K) of $[Ni^{II}(S^{Me2}N_4(tren))]Cl$ (**4**) showing that it is paramagnetic.

Figure S-10. Inverse molar magnetic susceptibility ($1/\chi_m$) vs. temperature (T) plot for $[Mn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**5**) fit to an S = 5/2 spin-state.

Figure S-11. Inverse molar magnetic susceptibility ($1/\chi_m$) vs. temperature (T) plot for $[[Ni^{II}(S^{Me2}N_4(tren))]Cl$ (**4**) fit to an S = 1 spin-state.

Figure S-12. X-band EPR spectrum of S= 3/2 $[Co^{II}(S^{Me2}N_4(tren))](PF_6)$ (**6**) at 5 K in MeOH/EtOH (9:1) glass.

Figure S-13. Cyclic voltammogram of $[Ni^{II}(S^{Me2}N_4(tren))]Cl$ (**4**) in MeCN at 298 K (0.1 M $(Bu_4N)PF_6$, glassy carbon electrode, 150 mV/sec scan rate). Peak potentials versus SCE indicated.

Figure S-14. Cyclic voltammogram of $[Cu^{II}(S^{Me2}N_4(tren))](PF_6)$ (**7**) in MeCN at 298 K (0.1 M $(Bu_4N)PF_6$, glassy carbon electrode, 150 mV/sec scan rate). Peak potentials versus SCE indicated.

Figure S-15. Cyclic voltammogram of $[Zn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**8**) in MeCN at 298 K (0.1 M $(Bu_4N)PF_6$, glassy carbon electrode, 150 mV/sec scan rate), showing its ligand–centered oxidation wave. Peak potentials versus SCE indicated.

Supplementary Tables:

Table S–1. Crystal Data for $[Ni^{II}(SN_4(tren)–RS^{dang})]_2 \bullet 2H_2O$ (**3**).

Table S–2. Positional and Equivalent Isotropic Thermal Parameters for $[Ni^{II}(SN_4(tren)–RS^{dang})]_2 \bullet 2H_2O$ (**3**).

Table S–3. Bond Distances (Å) and Angles (deg) for $[Ni^{II}(SN_4(tren)–RS^{dang})]_2 \bullet 2H_2O$ (**3**).

Table S–4. Intramolecular and Intermolecular S...H contacts (Å) and X-H-S angles (deg) for $[Ni^{II}(SN_4(tren)–RS^{dang})]_2 \bullet 2H_2O$ (**3**)

Table S–5. Crystal Data for $[Ni^{II}(S^{Me2}N_4(tren))]Cl$ (**4**)

Table S–6. Positional and Equivalent Isotropic Thermal Parameters for $[Ni^{II}(S^{Me2}N_4(tren))]Cl$ (**4**)

Table S–7. Bond Distances (Å) and Angles (deg) for $[Ni^{II}(S^{Me2}N_4(tren))]Cl$ (**4**)

Table S–8. Anisotropic Thermal Parameters for $[Ni^{II}(S^{Me2}N_4(tren))]Cl$ (**4**)

Table S–9. Hydrogen Atoms for $[Ni^{II}(S^{Me2}N_4(tren))]Cl$ (**4**)

Table S-10. Crystal Data for $[Mn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**5**)

Table S-11. Positional and Equivalent Isotropic Thermal Parameters for $[Mn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**5**)

Table S-12. Bond Distances (Å) and Angles (deg) for $[Mn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**5**)

Table S–13. Anisotropic Thermal Parameters for $[Mn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**5**).

Table S–14. Hydrogen Atoms for $[Mn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**5**).

Table S-15. Crystal Data for $[Co^{II}(S^{Me2}N_4(tren))](PF_6)$ (**6**)

Table S-16. Positional and Equivalent Isotropic Thermal Parameters for $[Co^{II}(S^{Me2}N_4(tren))](PF_6)$ (**6**)

Table S-17. Bond Distances (Å) and Angles (deg) for $[Co^{II}(S^{Me2}N_4(tren))](PF_6)$ (**6**)

Table S–18. Anisotropic Thermal Parameters for $[Co^{II}(S^{Me2}N_4(tren))](PF_6)$ (**6**).

Table S–19. Hydrogen Atoms for $[Co^{II}(S^{Me2}N_4(tren))](PF_6)$ (**6**).

Table S–20. Crystal Data for $[Cu^{II}(S^{Me2}N_4(tren))](PF_6)$ (**7**)

Table S–21. Positional and Equivalent Isotropic Thermal Parameters for $[Cu^{II}(S^{Me2}N_4(tren))](PF_6)$ (**7**)

Table S–22. Bond Distances (Å) and Angles (deg) for $[Cu^{II}(S^{Me2}N_4(tren))](PF_6)$ (**7**)

Table S–23. Anisotropic Thermal Parameters for $[Cu^{II}(S^{Me2}N_4(tren))](PF_6)$ (**7**)

Table S–24. Hydrogen Atoms for $[Cu^{II}(S^{Me2}N_4(tren))](PF_6)$ (**7**)

Table S–25. Crystal Data for $[Zn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**8**)

Table S–26. Positional and Equivalent Isotropic Thermal Parameters for $[Zn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**8**)

Table S–27. Bond Distances (Å) and Angles (deg) for $[Zn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**8**)

Table S–28. Anisotropic Thermal Parameters for $[Zn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**8**)

Table S–29. Hydrogen Atoms for $[Zn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**8**)

Figures.

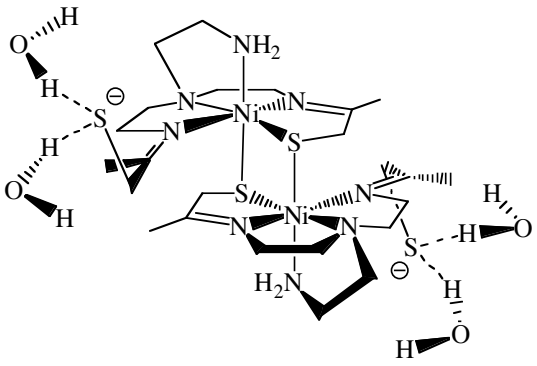
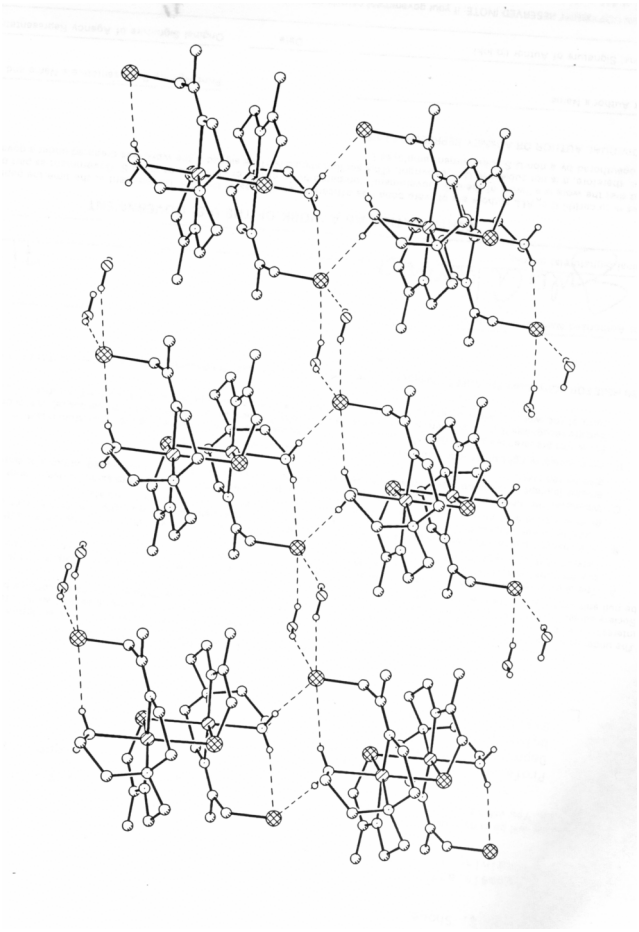


Figure S-1.



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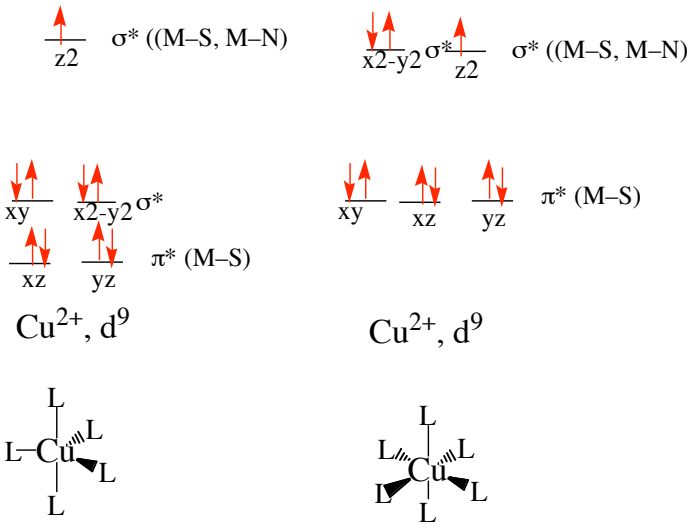

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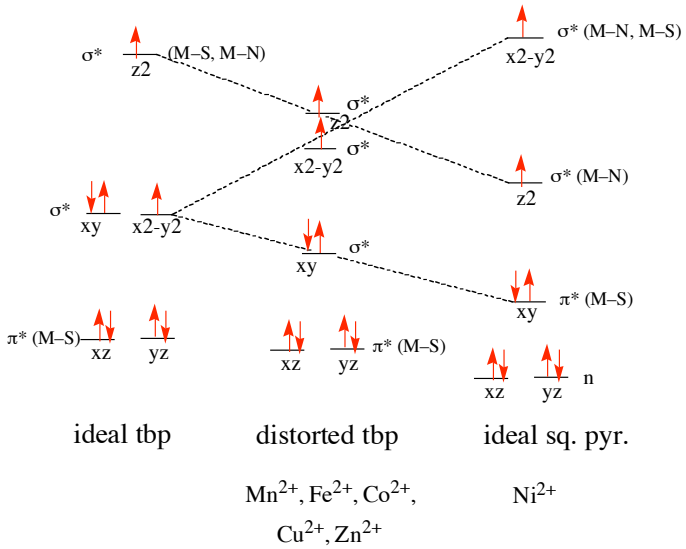

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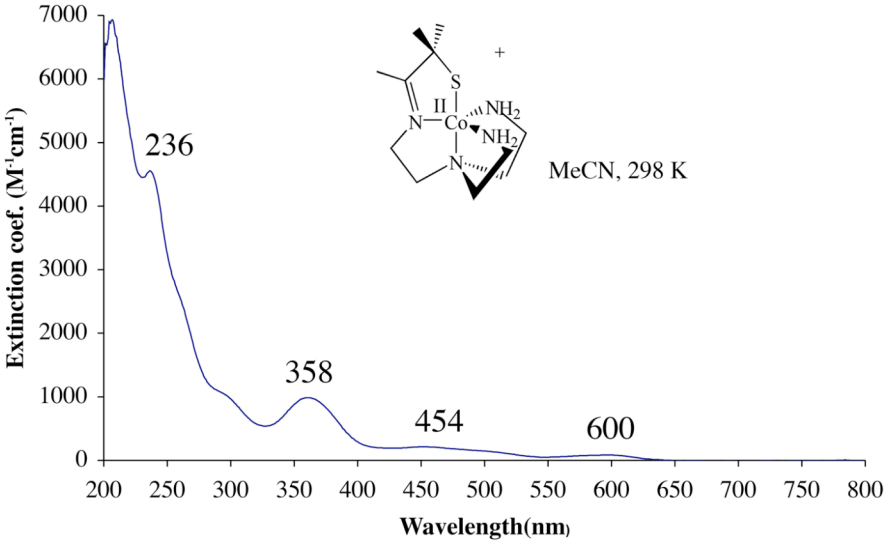

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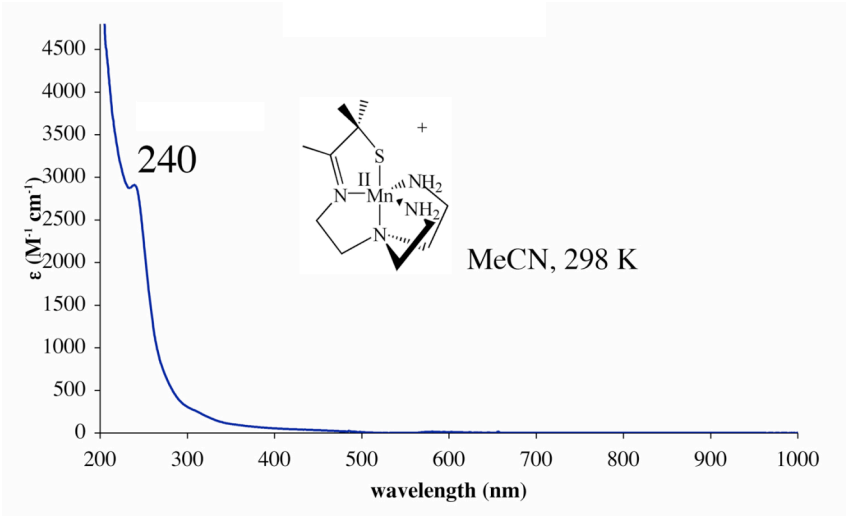

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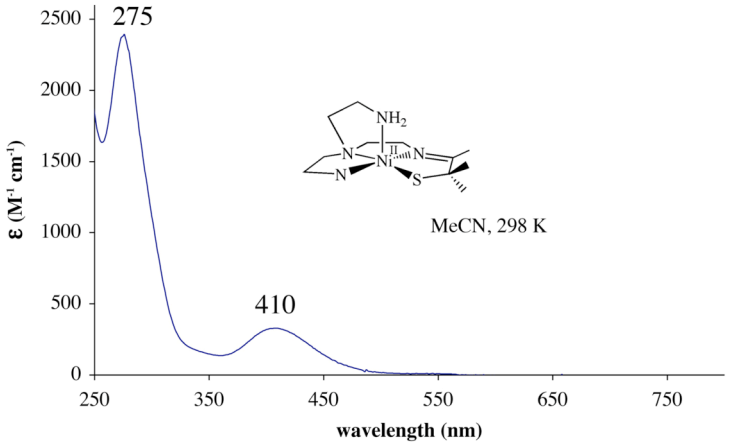

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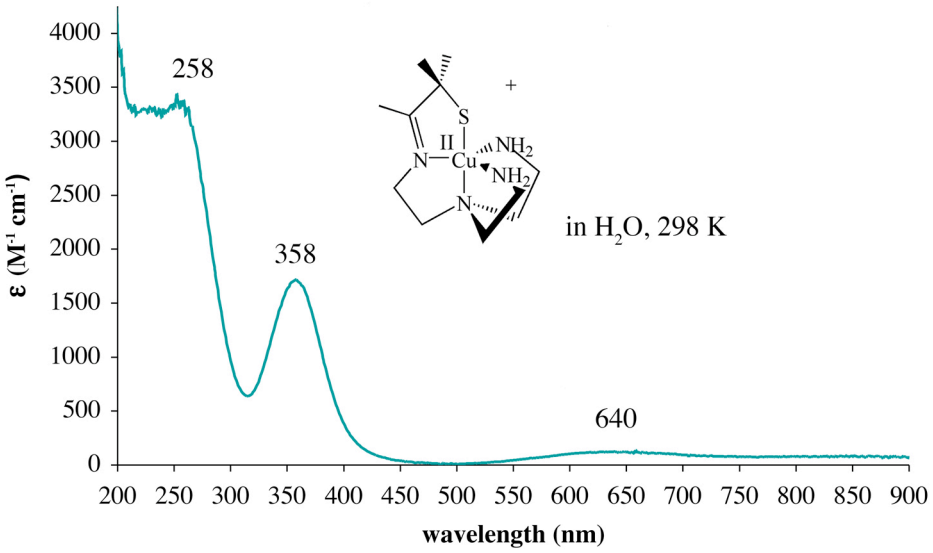
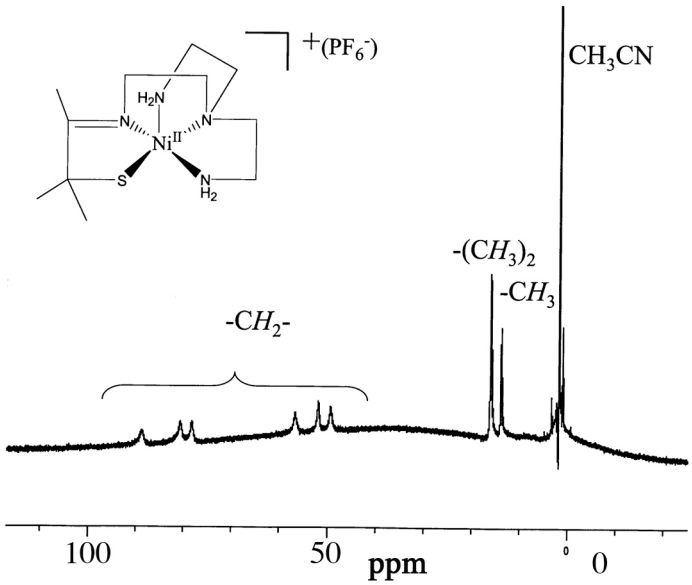


Figure S-8



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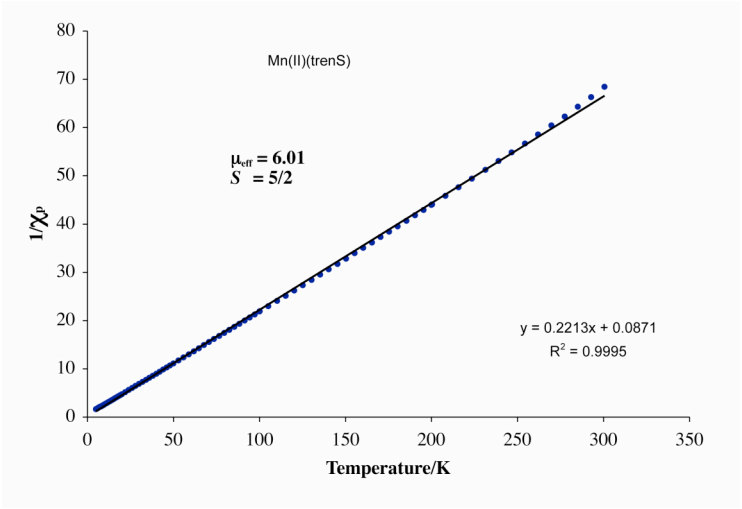

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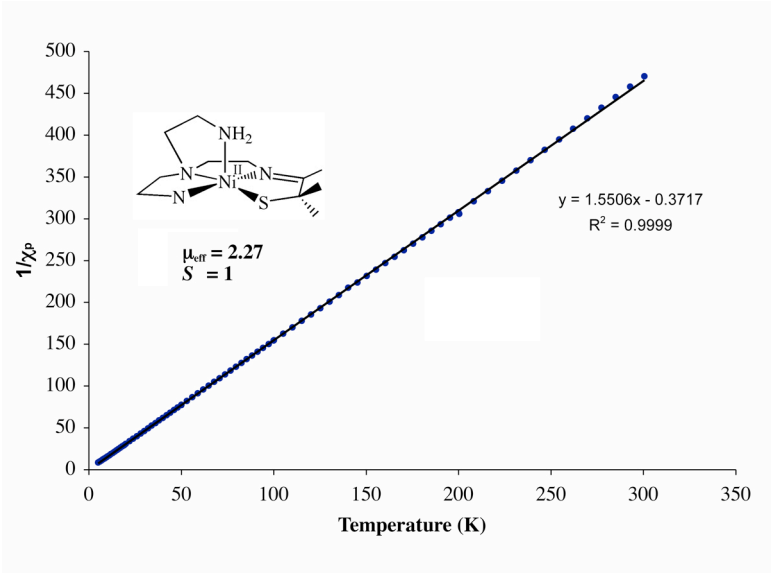

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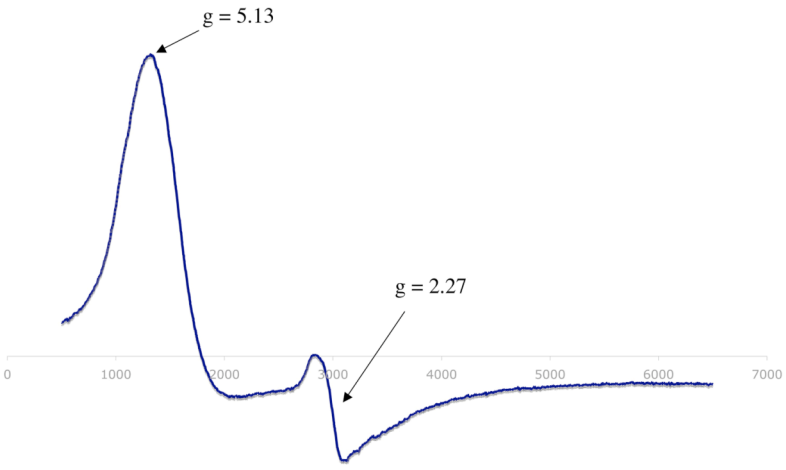

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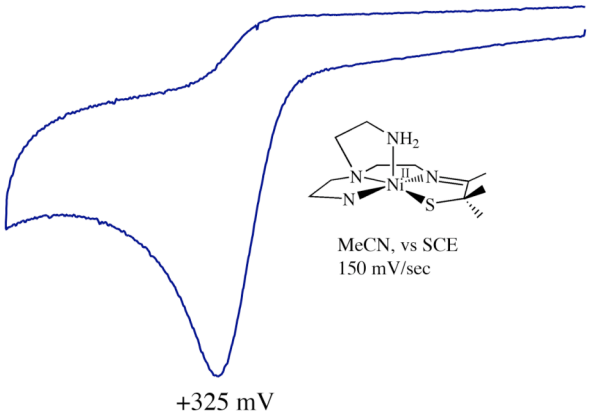

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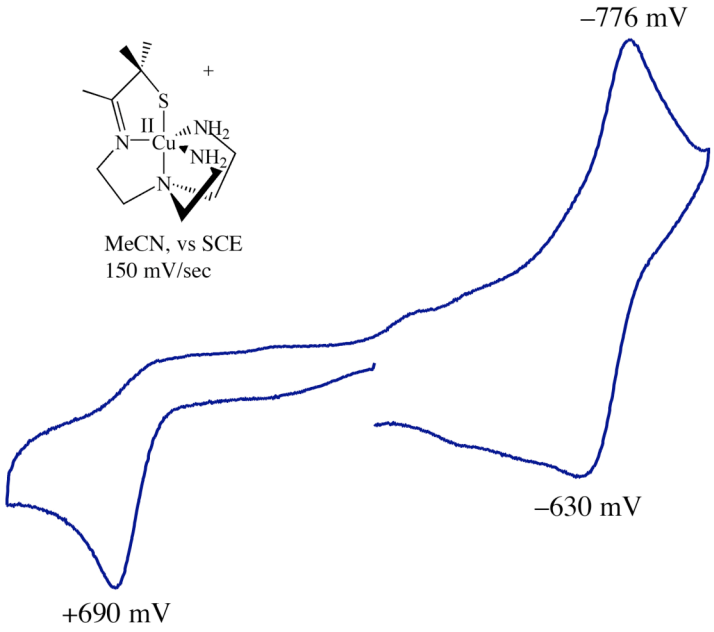

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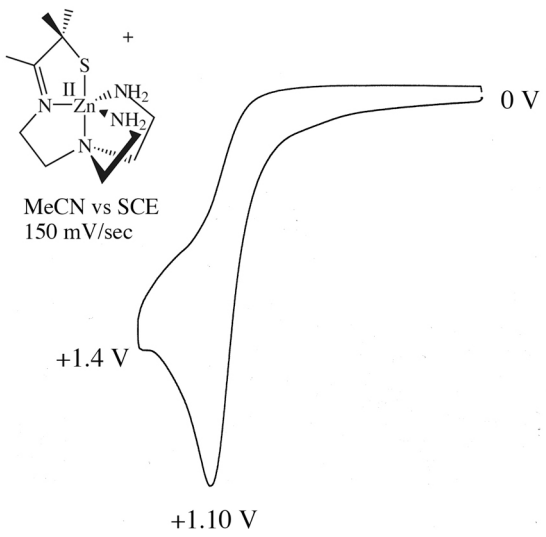

Figure S-15.

Table S–1. Crystal Data for $[Ni^{II}(SN_4(tren)–RS^{dang})]_2 \bullet 2H_2O$ (**3**)

	3
formula	$Ni_2S_4N_8C_{24}H_{52}O_{2.5}$
fw	738.4
unit cell[a]	triclinic
a, Å	8.936(2)
b, Å	10.152(2)
c, Å	10.458(2)
α, deg	61.71(3)
β, deg	81.80(3)
γ, deg	87.39(3)
V, Å^3	826.2(4)
Z	1
σ_{calc}, g/cm^3	1.484
space group	P1
μ, cm^{-1}	14.30
transmission factors	1.000 - .9083[b]
R [c]	0.0470
R_w	0.0675
GOF	1.22

[a] In all cases: Mo Kα (λ= 0.71073 Å) radiation; graphite monochomator; 295 K.
[b] An empirical absorption correction was applied.
[c] $R = \Sigma \, | \, | F_o | - | F_c | \, | \, / \, \Sigma \, | F_o |$; $R_w = \left[\Sigma w \, (\, | F_o | - | F_c | \,)^2 \, / \, \Sigma w F_o^{\,2} \right]^{1/2}$, where $w^{-1} = \sigma^2(F) + C \, F^2$ (C= 0.0063).

Table S–2. Selected Positional Parameters ($\times 10^4$) for $[Ni^{II}(SN_4(tren)–RS^{dang})]_2 \bullet 2H_2O$ (**3**)

Atom	x	y	z
Ni(1)	8389(1)	-4584(1)	15987(1)
S(1)	8826(1)	-5537(1)	14226(1)
S(2)	5297(1)	-1702(1)	12773(1)
N(1)	8648(3)	-6820(3)	17437(3)
N(2)	7958(3)	-4417(3)	17951(3)
N(3)	7971(3)	-2185(3)	15095(3)
N(4)	6005(3)	-4643(3)	16176(3)
O(1)	4876(6)	1801(5)	10299(5)
O(2)	2433(21)	3539(22)	9101(20)
C(1)	8440(4)	-7452(4)	15546(4)
C(2)	8576(3)	-7867(3)	17096(3)
C(3)	8572(5)	-9492(4)	18164(5)
C(4)	8634(5)	-7157(4)	18960(4)
C(5)	8844(5)	-5707(4)	19014(4)
C(6)	8555(5)	-3007(4)	17631(4)
C(7)	7968(5)	-1708(4)	16220(4)
C(8)	7559(4)	-1188(4)	13857(4)
C(9)	7356(4)	-1626(4)	12731(4)
C(10)	7205(6)	439(5)	13468(6)
C(11)	6300(4)	-4490(4)	18395(4)
C(12)	5331(4)	-3968(5)	17127(5)

Table S–3. Selected Bond Distances (Å) and Angles (deg) for $[Ni^{II}(SN_4(tren)–RS^{dang})]_2 \bullet 2H_2O$ (**3**).

Ni(1)-S(1)	2.434(1)	N(1)-C(2)	1.278(5)
Ni(1)-S(1a)	2.470(1)	N(1)-C(4)	1.459(5)
Ni(1)-N(1)	2.073(2)	N(3)-C(8)	1.303(4)
Ni(1)-N(2)	2.119(3)	N(3)-C(7)	1.469(6)
Ni(1)-N(3)	2.192(3)	S(1)-C(1)	1.786(3)
Ni(1)-N(4)	2.112(3)	S(2)-C(9)	1.838(4)
S(2). . . O(1)	3.304	S(2). . . H(4)	2.673
S(2). . . O(1)*	3.287	S(2). . . H(4)'	2.645
S(2). . . N(4)	3.518	S(2). . . H(1)*	2.524
S(2). . . N(4)'	3.534	S(2). . . H(2)	2.504
		Ni. . . Ni	3.606
S(1)-Ni(1)-N(1)	81.4(1)	S(2)-H(2)-O(1)	159.1
N(1)-Ni(1)-N(2)	82.4(1)	S(2)-H(4)-N(4)	156.7
N(2)-Ni(1)-N(3)	79.7(1)	S(2)-H(4)'-N(4)'	169.8
N(3)-Ni(1)-S(1)	116.4(1)	S(2)-H(1)*-O(1)*	154.7
S(1)-Ni(1)-N(2)	163.6(1)		
N(1)-Ni(1)-N(3)	162.1(1)		
N(4)-Ni(1)-N(3)	80.6(1)	S(1a)-Ni(1)-S(1)	85.4(1)
N(4)-Ni(1)-N(2)	83.3(1)	S(1a)-Ni(1)-N(1)	83.7(1)
N(4)-Ni(1)-N(1)	97.2(1)	S(1a)-Ni(1)-N(2)	95.9(1)
N(4)-Ni(1)-S(1)	95.7(1)	S(1a)-Ni(1)-N(3)	98.3(1)
N(4)-Ni(1)-S(1a)	178.7(1)		
N(3)-C(8)-C(9)	119.4(3)	N(1)-C(2)-C1)	118.5(3)
C(8)-C(9)-S(2)	104.9(3)	C(2)-C(1)-S(1)	116.4(3)

Symmetry codes: ' = 1–x, –1–y, 3–z
* = 1–x, –y, 2–z
a = 2–x, -1–y, 3–z

Table S-4. Intramolecular and Intermolecular S...H contacts (Å)[a] and X-H-S angles (deg) for $[Ni^{II}(SN_4(tren)–RS^{dang})]_2 \bullet 2H_2O$ (**3**)

S(2)....H(4A)	2.673	S(2)-H(4)-N(4)	156.7
S(2)....H(4D)'	2.645	S(2)-H(4)'-N(4)'	169.8
S(2)....H(1)*	2.524	S(2)-H(1)*-O(1)*	154.7
S(2)....H(2)	2.504	S(2)-H(2)-O(1))	159.1
S(2)....N(4)	3.518		
S(2)....N(4)'	3.534		
S(2)....O(1)*	3.287		
S(2)....O(1)	3.304		

Symmetry codes: ' = 1–x, –1–y, 3–z
* = 1–x, –y, 2–z

[a] H(1) and H(2) are attached to two different interstitial water molecules, H(4) is attached to the apical nutrogen N(4), and H(4) is attached to apical N(4') from an adjacent unit cell. The hydrogen atoms of the H_2O molecules were located using a difference map, and then refined using a riding model, with O-H(1) of 0.824 Å and O-H(2) of 0.842 Å. Amine hydrogens were placed at calculated positions with N-H of 0.900 Å.

Table S-5. Crystal data and structure refinement for [$Ni^{II}(S^{Me2}N_4(tren))$]Cl (**4**).

Empirical formula	C11 H25 Cl N4 Ni S
Formula weight	339.57
Temperature	161(2) K
Wavelength	0.71070 A
Crystal system, space group	Monoclinic, C 2/c (No. 15)
Unit cell dimensions	a = 19.1240(3) A alpha = 90 deg.
	b = 7.7534(3) A beta = 100.139(2)deg.
	c = 21.3505(7) A gamma = 90 deg.
Volume	3116.33(17) A^3
Z, Calculated density	8, 1.448 Mg/m^3
Reflections used for indexing	904
Absorption coefficient	1.540 mm^-1
F(000)	1440
Crystal description / color	purple / plate
Crystal size	0.23 x 0.16 x 0.08 mm
Theta range for data collection	2.64 to 28.68 deg.
Index ranges	-22<=h<=22, -9<=k<=9, -26<=l<=26
Reflections collected / unique	52638 / 3519 [R(int) = 0.065]
Completeness to 2theta = 28.68	40.8%
Absorption correction	Empirical (SORTAV)
Max. and min. transmission	0.888 and 0.868
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3519 / 0 / 163
Goodness-of-fit on F^2	0.789
Final R indices [I>4sigma(I)]	*R1 = 0.0420, wR2 = 0.0996
R indices (all data)	R1 = 0.0716, *wR2 = 0.1221
*Report these R factors	
Largest diff. peak and hole	0.574 and -0.636 e.A^-3

Table S-6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for [$Ni^{II}(S^{Me2}N_4$(tren))]Cl (**4**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	9500(2)	977(6)	6779(2)	40(1)
C(2)	9570(2)	194(5)	5656(2)	36(1)
C(3)	9072(2)	318(5)	6143(2)	29(1)
C(4)	8797(2)	-1509(5)	6241(2)	29(1)
C(5)	9311(2)	-2903(6)	6493(2)	41(1)
C(6)	7790(2)	-3426(5)	6191(2)	36(1)
C(7)	7028(2)	-3386(5)	5813(2)	35(1)
C(8)	6813(2)	-1274(7)	7079(2)	55(1)
C(9)	6328(2)	-1806(6)	6494(2)	40(1)
C(10)	6149(2)	-1194(5)	5360(2)	37(1)
C(11)	5938(2)	696(5)	5415(2)	39(1)
Cl(1)	8666(1)	-1382(1)	8024(1)	39(1)
N(1)	8118(1)	-1759(4)	6125(1)	28(1)
N(2)	6659(1)	-1748(4)	5918(2)	32(1)
N(4)	7272(2)	173(4)	6962(1)	30(1)
N(3)	6576(1)	1738(4)	5640(2)	31(1)
Ni(1)	7430(1)	204(1)	6038(1)	25(1)
S(1)	8352(1)	1828(1)	5854(1)	30(1)

Table S-7. Bond lengths [A] and angles [deg] for [$Ni^{II}(S^{Me2}N_4(tren))$]Cl (**4**).

C(1)-C(3)	1.544(5)
C(2)-C(3)	1.534(5)
C(3)-C(4)	1.538(5)
C(3)-S(1)	1.830(3)
C(4)-N(1)	1.292(4)
C(4)-C(5)	1.496(5)
C(6)-N(1)	1.454(5)
C(6)-C(7)	1.537(5)
C(7)-N(2)	1.489(5)
C(8)-N(4)	1.474(5)
C(8)-C(9)	1.476(6)
C(9)-N(2)	1.480(4)
C(10)-N(2)	1.465(5)
C(10)-C(11)	1.530(6)
C(11)-N(3)	1.471(4)
N(1)-Ni(1)	2.000(3)
N(2)-Ni(1)	2.097(3)
N(4)-Ni(1)	2.048(3)
N(3)-Ni(1)	2.077(3)
Ni(1)-S(1)	2.2560(9)
C(2)-C(3)-C(4)	107.6(3)
C(2)-C(3)-C(1)	108.7(3)
C(4)-C(3)-C(1)	109.0(3)
C(2)-C(3)-S(1)	109.4(2)
C(4)-C(3)-S(1)	112.3(2)
C(1)-C(3)-S(1)	109.6(3)
N(1)-C(4)-C(5)	122.3(3)
N(1)-C(4)-C(3)	117.9(3)
C(5)-C(4)-C(3)	119.7(3)
N(1)-C(6)-C(7)	108.5(3)
N(2)-C(7)-C(6)	111.6(3)
N(4)-C(8)-C(9)	112.0(4)
C(8)-C(9)-N(2)	113.4(3)
N(2)-C(10)-C(11)	111.4(3)
N(3)-C(11)-C(10)	109.7(3)
C(4)-N(1)-C(6)	123.4(3)
C(4)-N(1)-Ni(1)	121.8(3)
C(6)-N(1)-Ni(1)	113.41(19)
C(10)-N(2)-C(9)	111.3(3)
C(10)-N(2)-C(7)	113.2(3)
C(9)-N(2)-C(7)	112.5(3)
C(10)-N(2)-Ni(1)	103.9(2)
C(9)-N(2)-Ni(1)	108.3(2)
C(7)-N(2)-Ni(1)	106.99(19)
C(8)-N(4)-Ni(1)	111.4(2)
C(11)-N(3)-Ni(1)	111.5(2)
N(1)-Ni(1)-N(4)	96.16(12)
N(1)-Ni(1)-N(3)	158.67(12)
N(3)-Ni(1)-N(4)	99.31(12)
N(1)-Ni(1)-N(2)	84.22(11)
N(4)-Ni(1)-N(2)	83.66(12)
N(3)-Ni(1)-N(2)	83.00(12)
N(1)-Ni(1)-S(1)	85.37(8)
N(4)-Ni(1)-S(1)	115.22(8)

N(3)-Ni(1)-S(1)	101.04(8)
N(2)-Ni(1)-S(1)	159.34(9)
C(3)-S(1)-Ni(1)	98.56(11)

Table S-8. Anisotropic displacement parameters (A^2 x 10^3) for $[Ni^{II}(S^{Me2}N_4(tren))]Cl$ (**4**).
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	36(2)	50(3)	32(2)	-6(2)	1(2)	-1(2)
C(2)	32(2)	39(2)	39(2)	2(2)	10(1)	4(2)
C(3)	20(1)	37(2)	32(2)	3(2)	6(1)	0(1)
C(4)	32(2)	34(2)	20(2)	-3(2)	2(1)	6(2)
C(5)	42(2)	43(2)	39(2)	6(2)	10(2)	11(2)
C(6)	40(2)	29(2)	43(2)	1(2)	16(2)	5(2)
C(7)	45(2)	24(2)	37(2)	-6(2)	7(2)	-4(2)
C(8)	63(3)	58(3)	48(3)	-6(2)	18(2)	-24(2)
C(9)	48(2)	49(3)	27(2)	-1(2)	15(2)	-20(2)
C(10)	29(2)	41(2)	38(2)	-4(2)	0(2)	-9(2)
C(11)	28(2)	41(2)	47(2)	10(2)	2(2)	-2(2)
Cl(1)	38(1)	40(1)	38(1)	3(1)	6(1)	-11(1)
N(1)	26(1)	25(2)	35(2)	-4(1)	10(1)	0(1)
N(2)	32(1)	29(2)	35(2)	-9(1)	9(1)	-8(1)
N(4)	37(2)	24(2)	26(2)	-2(1)	4(1)	-1(1)
N(3)	27(1)	26(2)	39(2)	2(1)	4(1)	1(1)
Ni(1)	24(1)	23(1)	27(1)	1(1)	5(1)	-1(1)
S(1)	25(1)	28(1)	37(1)	4(1)	5(1)	-2(1)

Table S-9. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for [$Ni^{II}(S^{Me2}N_4$(tren))]Cl (**4**).

	x	y	z	U(eq)
H(1A)	9902	88	6906	60
H(1B)	9170	903	7119	60
H(1C)	9594	2352	6737	60
H(2A)	9949	-499	5785	54
H(2B)	9318	-274	5234	54
H(2C)	9653	1152	5576	54
H(5A)	9748	-2496	6515	62
H(5B)	9225	-3870	6272	62
H(5C)	9299	-2895	6983	62
H(6A)	7828	-3589	6568	40
H(6B)	8000	-4442	5974	40
H(7A)	7029	-3285	5468	39
H(7B)	6797	-4662	5934	39
H(8A)	6553	-1045	7494	61
H(8B)	7230	-2406	7270	61
H(9A)	5933	-669	6423	44
H(9B)	6063	-2840	6527	44
H(10A)	5699	-1909	5295	40
H(10B)	6401	-1272	4937	40
H(11A)	5695	629	5741	43
H(11B)	5673	1229	4970	43
H(3A)	7687	301	7233	35
H(3B)	7062	1218	7080	35
H(4A)	6558	2581	5950	32
H(4B)	6648	2491	5292	32

Table S-10. Crystal data and structure refinement for $[Mn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**5**)

Empirical formula	C11 H25 F6 Mn N4 P S
Formula weight	445.32
Temperature	130(2) K
Wavelength	0.71073 A
Crystal description/color	needle / colorless
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 8.194(4)A alpha = 90 deg.
	b = 12.831(5)A beta = 90 deg.
	c = 18.198(8)A gamma = 90 deg.
Volume	1913.3(14) A^3
Z, Calculated density	4, 1.546 Mg/m^3
Absorption coefficient	0.939 mm^-1
F(000)	916
Crystal size	0.59 x 0.26 x 0.26 mm
Reflections for indexing	915
Theta range for data collection	2.24 to 25.32 deg.
Index ranges	-8<=h<=9, -15<=k<=15, -21<=l<=21
Reflections collected / unique	2733 / 2733 [R(int) = 0.0658]
Completeness to theta = 25.00	86.5%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7923 and 0.6073
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2733 / 0 / 220
Goodness-of-fit on F^2	S = 1.036
S = root(sum(w*D*D)/(n-p)), where D = (Fo*Fo - Fc*Fc)	
Final R indices [I>2sigma(I)]	*R1 = 0.0583, wR2 = 0.1199
R indices (all data)	R1 = 0.1571, *wR2 = 0.1592
*Report these R factors.	
R1 = sum||Fo|-|Fc||/sum|Fo|, wR2= root(sum(w*D*D)/sum(w*Fo*Fo)),	
where D = (Fo*Fo - Fc*Fc)	
Weighting scheme	
calc w=1/[\s^2^(Fo^2^)+(0.0700P)^2^+0.2820P] where P=(Fo^2^+2Fc^2^)/3	
Absolute structure parameter	0.04(6)
Largest diff. peak and hole	0.360 and -0.335 e.A^-3

Table S–11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $[Mn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**5**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Mn(1)	9244(2)	1032(1)	120(1)	65(1)
S(1)	9224(3)	2451(2)	-750(1)	70(1)
P(1)	5390(3)	-965(3)	-1566(1)	73(1)
F(1)	6157(7)	-893(6)	-2379(2)	79(2)
F(2)	6687(7)	-134(5)	-1274(3)	79(2)
F(3)	4634(7)	-1029(6)	-757(3)	91(2)
F(4)	4086(7)	-1805(5)	-1855(3)	87(2)
F(5)	4149(8)	-36(5)	-1776(3)	88(2)
F(6)	6615(7)	-1903(6)	-1359(3)	90(2)
N(1)	10200(9)	195(8)	-820(4)	63(3)
N(2)	9618(9)	-651(6)	576(4)	55(2)
N(3)	10596(11)	1339(7)	1142(4)	77(3)
N(4)	6719(10)	535(7)	330(4)	68(3)
C(1)	11596(12)	2200(10)	-1812(6)	86(4)
C(2)	8684(13)	1986(10)	-2181(5)	84(4)
C(3)	9971(13)	1770(10)	-1567(5)	69(3)
C(4)	10159(12)	582(10)	-1478(5)	63(3)
C(5)	10282(12)	-71(10)	-2166(5)	81(4)
C(6)	10404(11)	-946(9)	-724(4)	68(3)
C(7)	10767(12)	-1182(9)	58(4)	69(3)
C(8)	10332(14)	-544(9)	1316(6)	73(3)
C(9)	11461(13)	409(10)	1347(6)	74(3)
C(10)	8053(12)	-1162(10)	590(6)	74(3)
C(11)	6716(12)	-406(8)	836(5)	59(3)

Table S-12. Bond lengths [A] and angles [deg] for [$Mn^{II}(S^{Me2}N_4(tren))](PF_6)$(**5**).

Mn(1)-N(1)	2.166(8)
Mn(1)-N(3)	2.201(8)
Mn(1)-N(4)	2.198(8)
Mn(1)-N(2)	2.334(8)
Mn(1)-S(1)	2.412(3)
S(1)-C(3)	1.831(11)
P(1)-F(2)	1.597(7)
P(1)-F(4)	1.606(7)
P(1)-F(3)	1.599(6)
P(1)-F(1)	1.611(5)
P(1)-F(5)	1.613(7)
P(1)-F(6)	1.612(7)
N(1)-C(4)	1.295(11)
N(1)-C(6)	1.484(12)
N(2)-C(10)	1.441(12)
N(2)-C(8)	1.475(11)
N(2)-C(7)	1.496(11)
N(3)-C(9)	1.438(13)
N(3)-H(3A)	0.9200
N(3)-H(3B)	0.9200
N(4)-C(11)	1.518(12)
N(4)-H(4A)	0.9200
N(4)-H(4B)	0.9200
C(1)-C(3)	1.509(13)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.560(14)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-C(4)	1.541(14)
C(4)-C(5)	1.510(13)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-C(7)	1.484(11)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.534(14)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(11)	1.531(14)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
N(1)-Mn(1)-N(3)	125.0(3)
N(1)-Mn(1)-N(4)	109.5(3)

N(3)-Mn(1)-N(4)	112.2(3)
N(1)-Mn(1)-N(2)	77.0(3)
N(3)-Mn(1)-N(2)	78.4(3)
N(4)-Mn(1)-N(2)	78.1(3)
N(1)-Mn(1)-S(1)	81.9(3)
N(3)-Mn(1)-S(1)	115.0(3)
N(4)-Mn(1)-S(1)	109.1(2)
N(2)-Mn(1)-S(1)	158.85(19)
C(3)-S(1)-Mn(1)	99.8(4)
F(2)-P(1)-F(4)	179.7(4)
F(2)-P(1)-F(3)	89.2(3)
F(4)-P(1)-F(3)	90.5(3)
F(2)-P(1)-F(1)	90.4(3)
F(4)-P(1)-F(1)	89.8(3)
F(3)-P(1)-F(1)	179.6(5)
F(2)-P(1)-F(5)	90.3(4)
F(4)-P(1)-F(5)	89.9(3)
F(3)-P(1)-F(5)	90.7(4)
F(1)-P(1)-F(5)	89.1(3)
F(2)-P(1)-F(6)	90.4(3)
F(4)-P(1)-F(6)	89.4(4)
F(3)-P(1)-F(6)	89.3(4)
F(1)-P(1)-F(6)	90.8(4)
F(5)-P(1)-F(6)	179.3(4)
C(4)-N(1)-C(6)	119.4(9)
C(4)-N(1)-Mn(1)	122.0(8)
C(6)-N(1)-Mn(1)	115.9(6)
C(10)-N(2)-C(8)	112.3(8)
C(10)-N(2)-C(7)	111.3(8)
C(8)-N(2)-C(7)	111.6(7)
C(10)-N(2)-Mn(1)	108.1(6)
C(8)-N(2)-Mn(1)	106.9(6)
C(7)-N(2)-Mn(1)	106.3(6)
C(9)-N(3)-Mn(1)	108.6(7)
C(9)-N(3)-H(3A)	110.0
Mn(1)-N(3)-H(3A)	110.0
C(9)-N(3)-H(3B)	110.0
Mn(1)-N(3)-H(3B)	110.0
H(3A)-N(3)-H(3B)	108.4
C(11)-N(4)-Mn(1)	109.8(6)
C(11)-N(4)-H(4A)	109.7
Mn(1)-N(4)-H(4A)	109.7
C(11)-N(4)-H(4B)	109.7
Mn(1)-N(4)-H(4B)	109.7
H(4A)-N(4)-H(4B)	108.2
C(3)-C(1)-H(1A)	109.5
C(3)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(3)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(3)-C(2)-H(2A)	109.5
C(3)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(3)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5

C(1)-C(3)-C(4)	107.7(9)
C(1)-C(3)-C(2)	108.7(9)
C(4)-C(3)-C(2)	108.6(9)
C(1)-C(3)-S(1)	111.1(9)
C(4)-C(3)-S(1)	114.8(7)
C(2)-C(3)-S(1)	105.7(8)
N(1)-C(4)-C(5)	123.5(11)
N(1)-C(4)-C(3)	118.6(10)
C(5)-C(4)-C(3)	117.8(9)
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(7)-C(6)-N(1)	109.7(8)
C(7)-C(6)-H(6A)	109.7
N(1)-C(6)-H(6A)	109.7
C(7)-C(6)-H(6B)	109.7
N(1)-C(6)-H(6B)	109.7
H(6A)-C(6)-H(6B)	108.2
C(6)-C(7)-N(2)	112.6(8)
C(6)-C(7)-H(7A)	109.1
N(2)-C(7)-H(7A)	109.1
C(6)-C(7)-H(7B)	109.1
N(2)-C(7)-H(7B)	109.1
H(7A)-C(7)-H(7B)	107.8
N(2)-C(8)-C(9)	110.3(9)
N(2)-C(8)-H(8A)	109.6
C(9)-C(8)-H(8A)	109.6
N(2)-C(8)-H(8B)	109.6
C(9)-C(8)-H(8B)	109.6
H(8A)-C(8)-H(8B)	108.1
N(3)-C(9)-C(8)	110.8(9)
N(3)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9A)	109.5
N(3)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	108.1
N(2)-C(10)-C(11)	110.7(10)
N(2)-C(10)-H(10A)	109.5
C(11)-C(10)-H(10A)	109.5
N(2)-C(10)-H(10B)	109.5
C(11)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	108.1
N(4)-C(11)-C(10)	109.0(8)
N(4)-C(11)-H(11A)	109.9
C(10)-C(11)-H(11A)	109.9
N(4)-C(11)-H(11B)	109.9
C(10)-C(11)-H(11B)	109.9
H(11A)-C(11)-H(11B)	108.3

Symmetry transformations used to generate equivalent atoms:

Table S–13. Anisotropic displacement parameters (A^2 x 10^3) for $[Mn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**5**).
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Mn(1)	65(1)	70(1)	60(1)	2(1)	-1(1)	3(1)
S(1)	74(2)	74(2)	62(2)	2(1)	-2(2)	-1(2)
P(1)	64(2)	89(3)	66(2)	-3(2)	-6(1)	0(2)
F(1)	81(4)	101(6)	56(3)	-5(3)	-5(3)	-1(4)
F(2)	62(4)	90(6)	86(4)	-16(4)	-1(3)	-6(4)
F(3)	73(4)	145(6)	57(3)	0(4)	1(3)	-16(5)
F(4)	70(4)	91(6)	99(4)	-7(4)	-12(4)	-27(4)
F(5)	71(4)	98(6)	95(4)	-1(4)	-1(4)	18(4)
F(6)	87(4)	98(7)	84(4)	6(4)	-25(3)	5(4)
N(1)	71(6)	67(8)	52(6)	2(4)	-2(4)	-6(5)
N(2)	48(5)	69(8)	48(5)	-1(4)	-8(4)	1(4)
N(3)	86(7)	76(9)	68(5)	15(4)	-3(5)	5(7)
N(4)	93(6)	53(8)	57(5)	-5(4)	-9(4)	-7(5)
C(1)	70(7)	69(11)	120(10)	18(7)	12(6)	0(8)
C(2)	84(9)	89(11)	78(8)	-2(7)	-3(6)	7(7)
C(3)	72(8)	63(9)	72(8)	-2(6)	-3(6)	10(7)
C(4)	51(6)	98(11)	39(6)	1(6)	8(4)	0(6)
C(5)	58(7)	132(14)	52(7)	-6(7)	1(5)	-7(8)
C(6)	66(7)	91(10)	45(5)	6(6)	4(4)	-14(8)
C(7)	68(6)	89(9)	50(6)	-8(5)	4(5)	-5(8)
C(8)	86(8)	50(9)	84(8)	-8(6)	-2(6)	-4(7)
C(9)	79(8)	63(10)	79(8)	12(7)	10(6)	-1(8)
C(10)	74(8)	63(11)	84(8)	-1(6)	-7(6)	-13(7)
C(11)	59(6)	56(9)	63(6)	5(6)	11(5)	-2(6)

Table S–14. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $[Mn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**5**).

	x	y	z	U(eq)
H(3A)	11320	1878	1072	92
H(3B)	9883	1526	1510	92
H(4A)	6146	1072	544	81
H(4B)	6218	368	-107	81
H(1A)	11914	1873	-2277	104
H(1B)	12423	2050	-1437	104
H(1C)	11507	2955	-1880	104
H(2A)	9024	1641	-2636	101
H(2B)	8601	2739	-2264	101
H(2C)	7620	1714	-2027	101
H(5A)	10474	385	-2590	97
H(5B)	9261	-456	-2238	97
H(5C)	11189	-563	-2118	97
H(6A)	9392	-1309	-874	81
H(6B)	11307	-1198	-1038	81
H(7A)	11897	-959	170	83
H(7B)	10702	-1945	135	83
H(8A)	10959	-1180	1439	88
H(8B)	9448	-465	1683	88
H(9A)	11899	487	1851	89
H(9B)	12393	303	1009	89
H(10A)	8095	-1762	932	89
H(10B)	7793	-1431	93	89
H(11A)	5639	-755	816	71
H(11B)	6918	-182	1348	71

Table S-15. Crystal data and structure refinement for $[Co^{II}(S^{Me2}N_4(tren))](PF_6)$ (**6**).

Empirical formula	C11 H25 Co F6 N4 P S
Formula weight	449.31
Temperature	153(2) K
Wavelength	0.71070 A
Crystal description/color	prism / pleochroic red/green
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 8.1770(6) A alpha = 90 deg.
	b = 12.7180(6) A beta = 90 deg.
	c = 17.9770(13) A gamma = 90 deg.
Volume	1869.5(2) A^3
Z, Calculated density	4, 1.596 Mg/m^3
Absorption coefficient	1.173 mm^-1
F(000)	924
Crystal size	0.50 x 0.38 x 0.30 mm
Reflections for indexing	323
Theta range for data collection	1.96 to 28.26 deg.
Index ranges	-6<=h<=10, -10<=k<=12, -22<=l<=22
Reflections collected / unique	5056 / 3241 [R(int) = 0.047]
Completeness to theta = 28.26	77.6%
Absorption correction	Numerical, SORTAV
Max. and min. transmission	0.7198 and 0.5916
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3241 / 0 / 218
Goodness-of-fit on F^2	1.093
Final R indices [I>2sigma(I)]	*R1 = 0.0375, wR2 = 0.0978
R indices (all data)	R1 = 0.0413, *wR2 = 0.1030
	*Report these R factors
Weighting scheme	calc w=1/[\s^2^(Fo^2^)+(0.0516P)^2^+2.1891P]
	where P=(Fo^2^+2Fc^2^)/3
Absolute structure parameter	-0.006(19)
Extinction coefficient	0.0054(17)
Largest diff. peak and hole	0.487 and -0.488 e.A^-3

Table S-16. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $[Co^{II}(S^{Me2}N_4(tren))](PF_6)$ (**6**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Co(1)	713(1)	4044(1)	9926(1)	11(1)
C(1)	-1616(6)	2754(4)	11783(3)	33(1)
C(2)	1352(6)	2977(4)	12142(2)	28(1)
C(3)	59(5)	3220(3)	11550(2)	16(1)
C(4)	-151(4)	4399(3)	11467(2)	14(1)
C(5)	-345(5)	5042(4)	12178(2)	21(1)
C(6)	-369(4)	5967(3)	10754(2)	15(1)
C(7)	-753(4)	6223(3)	9946(2)	16(1)
C(8)	1988(4)	6156(4)	9401(2)	19(1)
C(9)	3262(5)	5346(4)	9193(2)	18(1)
C(10)	-1510(5)	4585(4)	8685(2)	21(1)
C(11)	-374(5)	5520(4)	8690(2)	21(1)
N(1)	-159(3)	4831(3)	10829(2)	11(1)
N(3)	-620(4)	3657(3)	8974(2)	17(1)
N(2)	367(4)	5648(3)	9436(2)	14(1)
N(4)	3134(3)	4443(3)	9709(2)	16(1)
F(1)	6001(3)	6805(2)	11846(2)	37(1)
F(2)	5846(3)	5044(2)	11807(2)	35(1)
F(3)	3317(3)	5135(2)	11324(1)	26(1)
F(4)	3440(4)	6904(2)	11364(2)	34(1)
F(5)	3888(3)	5961(2)	12405(1)	28(1)
F(6)	5399(3)	5987(3)	10760(1)	42(1)
S(1)	715(1)	2584(1)	10678(1)	15(1)
P(1)	4657(1)	5974(1)	11586(1)	18(1)

Table S-17. Bond lengths [A] and angles [deg] for [$Co^{II}(S^{Me2}N_4(tren))](PF_6)$ (**6**).

Co(1)-N(1)	2.037(3)
Co(1)-N(4)	2.081(3)
Co(1)-N(3)	2.087(3)
Co(1)-N(2)	2.239(3)
Co(1)-S(1)	2.2973(11)
C(1)-C(3)	1.550(6)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.532(6)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-C(4)	1.517(7)
C(3)-S(1)	1.844(4)
C(4)-N(1)	1.272(5)
C(4)-C(5)	1.525(5)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-N(1)	1.461(6)
C(6)-C(7)	1.521(5)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-N(2)	1.487(5)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-N(2)	1.475(5)
C(8)-C(9)	1.512(6)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-N(4)	1.480(5)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-N(3)	1.480(5)
C(10)-C(11)	1.509(6)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-N(2)	1.482(4)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
N(3)-H(2D)	0.9200
N(3)-H(2E)	0.9200
N(4)-H(4A)	0.9200
N(4)-H(4B)	0.9200
F(1)-P(1)	1.594(3)
F(2)-P(1)	1.582(3)
F(3)-P(1)	1.601(3)
F(4)-P(1)	1.596(3)
F(5)-P(1)	1.601(2)
F(6)-P(1)	1.603(3)

N(1)-Co(1)-N(4)	111.26(13)
N(1)-Co(1)-N(3)	125.95(13)
N(4)-Co(1)-N(3)	113.62(13)
N(1)-Co(1)-N(2)	79.73(12)
N(4)-Co(1)-N(2)	79.89(12)
N(3)-Co(1)-N(2)	80.03(12)
N(1)-Co(1)-S(1)	85.85(10)
N(4)-Co(1)-S(1)	107.83(10)
N(3)-Co(1)-S(1)	107.02(10)
N(2)-Co(1)-S(1)	165.39(8)
C(3)-C(1)-H(1A)	109.5
C(3)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(3)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(3)-C(2)-H(2A)	109.5
C(3)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(3)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(4)-C(3)-C(2)	110.3(3)
C(4)-C(3)-C(1)	107.8(3)
C(2)-C(3)-C(1)	110.2(4)
C(4)-C(3)-S(1)	112.5(3)
C(2)-C(3)-S(1)	107.5(3)
C(1)-C(3)-S(1)	108.6(3)
N(1)-C(4)-C(3)	121.1(3)
N(1)-C(4)-C(5)	121.6(4)
C(3)-C(4)-C(5)	117.3(3)
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
N(1)-C(6)-C(7)	109.0(3)
N(1)-C(6)-H(6A)	109.9
C(7)-C(6)-H(6A)	109.9
N(1)-C(6)-H(6B)	109.9
C(7)-C(6)-H(6B)	109.9
H(6A)-C(6)-H(6B)	108.3
N(2)-C(7)-C(6)	110.9(3)
N(2)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7A)	109.5
N(2)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	108.1
N(2)-C(8)-C(9)	109.3(3)
N(2)-C(8)-H(8A)	109.8
C(9)-C(8)-H(8A)	109.8
N(2)-C(8)-H(8B)	109.8
C(9)-C(8)-H(8B)	109.8
H(8A)-C(8)-H(8B)	108.3

N(4)-C(9)-C(8)	108.9(3)
N(4)-C(9)-H(9A)	109.9
C(8)-C(9)-H(9A)	109.9
N(4)-C(9)-H(9B)	109.9
C(8)-C(9)-H(9B)	109.9
H(9A)-C(9)-H(9B)	108.3
N(3)-C(10)-C(11)	108.9(3)
N(3)-C(10)-H(10A)	109.9
C(11)-C(10)-H(10A)	109.9
N(3)-C(10)-H(10B)	109.9
C(11)-C(10)-H(10B)	109.9
H(10A)-C(10)-H(10B)	108.3
N(2)-C(11)-C(10)	110.1(3)
N(2)-C(11)-H(11A)	109.6
C(10)-C(11)-H(11A)	109.6
N(2)-C(11)-H(11B)	109.6
C(10)-C(11)-H(11B)	109.6
H(11A)-C(11)-H(11B)	108.2
C(4)-N(1)-C(6)	120.8(3)
C(4)-N(1)-Co(1)	120.4(3)
C(6)-N(1)-Co(1)	116.9(2)
C(10)-N(3)-Co(1)	110.8(2)
C(10)-N(3)-H(2D)	109.5
Co(1)-N(3)-H(2D)	109.5
C(10)-N(3)-H(2E)	109.5
Co(1)-N(3)-H(2E)	109.5
H(2D)-N(3)-H(2E)	108.1
C(8)-N(2)-C(11)	112.1(3)
C(8)-N(2)-C(7)	111.4(3)
C(11)-N(2)-C(7)	111.1(3)
C(8)-N(2)-Co(1)	107.6(2)
C(11)-N(2)-Co(1)	107.9(2)
C(7)-N(2)-Co(1)	106.5(2)
C(9)-N(4)-Co(1)	111.9(2)
C(9)-N(4)-H(4A)	109.2
Co(1)-N(4)-H(4A)	109.2
C(9)-N(4)-H(4B)	109.2
Co(1)-N(4)-H(4B)	109.2
H(4A)-N(4)-H(4B)	107.9
C(3)-S(1)-Co(1)	98.39(14)
F(2)-P(1)-F(1)	89.89(15)
F(2)-P(1)-F(4)	179.36(17)
F(1)-P(1)-F(4)	90.68(16)
F(2)-P(1)-F(5)	90.15(15)
F(1)-P(1)-F(5)	90.47(15)
F(4)-P(1)-F(5)	89.55(15)
F(2)-P(1)-F(3)	89.77(15)
F(1)-P(1)-F(3)	179.60(16)
F(4)-P(1)-F(3)	89.66(14)
F(5)-P(1)-F(3)	89.74(14)
F(2)-P(1)-F(6)	90.43(17)
F(1)-P(1)-F(6)	90.19(15)
F(4)-P(1)-F(6)	89.86(17)
F(5)-P(1)-F(6)	179.12(14)
F(3)-P(1)-F(6)	89.61(14)

Table S-18. Anisotropic displacement parameters (A^2 x 10^3) for $[Co^{II}(S^{Me2}N_4(tren))](PF_6)$ (**6**).
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Co(1)	12(1)	8(1)	13(1)	0(1)	0(1)	1(1)
C(1)	34(2)	20(3)	44(3)	0(2)	20(2)	-6(2)
C(2)	38(2)	25(3)	20(2)	3(2)	-6(2)	10(2)
C(3)	19(2)	12(3)	18(2)	0(2)	3(2)	-1(2)
C(4)	5(1)	21(3)	15(2)	0(2)	0(1)	-1(1)
C(5)	23(2)	27(3)	14(2)	-6(2)	1(2)	4(2)
C(6)	19(2)	6(3)	20(2)	-1(2)	-1(1)	2(2)
C(7)	18(2)	9(3)	22(2)	2(1)	4(2)	6(1)
C(8)	22(2)	14(3)	21(2)	0(2)	2(2)	-3(2)
C(9)	19(2)	15(3)	22(2)	0(2)	6(2)	-5(2)
C(10)	19(2)	22(3)	22(2)	3(2)	-7(2)	2(2)
C(11)	28(2)	18(3)	17(2)	0(2)	-5(2)	2(2)
N(1)	8(1)	7(2)	18(1)	-5(1)	1(1)	2(1)
N(3)	19(2)	16(2)	16(1)	0(1)	-2(1)	-2(1)
N(2)	16(1)	10(2)	15(1)	0(1)	-1(1)	1(1)
N(4)	15(1)	13(2)	20(1)	-2(1)	2(1)	0(1)
F(1)	32(2)	35(2)	45(2)	-2(1)	-12(1)	-18(1)
F(2)	24(1)	32(2)	47(2)	-9(1)	-7(1)	10(1)
F(3)	20(1)	27(2)	31(1)	-5(1)	-3(1)	-9(1)
F(4)	40(2)	19(2)	42(2)	7(1)	-15(1)	-1(1)
F(5)	32(1)	32(2)	21(1)	0(1)	2(1)	3(1)
F(6)	31(1)	71(2)	25(1)	-1(1)	9(1)	-18(2)
S(1)	19(1)	9(1)	18(1)	1(1)	-2(1)	-1(1)
P(1)	15(1)	20(1)	19(1)	0(1)	-2(1)	-5(1)

Table S-19. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $[Co^{II}(S^{Me2}N_4(tren))](PF_6)$ (**6**).

	x	y	z	U(eq)
H(1A)	-1515	1990	11839	49
H(1B)	-2432	2912	11400	49
H(1C)	-1959	3064	12257	49
H(2A)	1473	2213	12192	41
H(2B)	1010	3275	12620	41
H(2C)	2400	3285	11994	41
H(5A)	-459	5788	12051	32
H(5B)	621	4945	12494	32
H(5C)	-1321	4806	12447	32
H(6A)	643	6333	10909	18
H(6B)	-1274	6209	11077	18
H(7A)	-1898	6026	9835	20
H(7B)	-637	6989	9864	20
H(8A)	2259	6468	9890	23
H(8B)	1973	6726	9026	23
H(9A)	3083	5107	8675	22
H(9B)	4368	5659	9225	22
H(10A)	-2476	4731	9001	25
H(10B)	-1895	4447	8172	25
H(11A)	498	5418	8315	25
H(11B)	-991	6163	8557	25
H(2D)	80	3409	8614	21
H(2E)	-1354	3133	9085	21
H(4A)	3648	4608	10149	19
H(4B)	3662	3873	9505	19

Symmetry transformations used to generate equivalent atoms:

Table S-20. Crystal data and structure refinement for $[Cu^{II}(S^{Me2}N_4(tren))](PF_6)$ (**7**).

Empirical formula	C11 H25 Cu F6 N4 P S
Formula weight	453.92
Temperature	130(2) K
Wavelength	0.71070 A
Crystal description/color	block / green
Crystal system, space group	Orthorhombic, P 21 21 21 (no. 19)
Unit cell dimensions	a = 8.1120(5)A alpha = 90 deg.
	b = 12.7400(4)A beta = 90 deg.
	c = 18.0310(11)A gamma = 90 deg.
Volume	1863.45(17) A^3
Z, Calculated density	4, 1.618 Mg/m^3
Absorption coefficient	1.428 mm^-1
F(000)	932
Crystal size	0.22 x 0.19 x 0.10 mm
Reflections for indexing	592
Theta range for data collection	3.38 to 26.34 deg.
Index ranges	-10<=h<=10, -13<=k<=13, -22<=l<=22
Reflections collected / unique	3509 / 3509 [R(int) = 0.0619]
Completeness to theta = 26.34	93.8%
Absorption correction	HKL-SCALEPACK
Max. and min. transmission	0.8751 and 0.7479
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3509 / 0 / 220
Goodness-of-fit on F^2	S = 0.995

S = root(sum(w*D*D)/(n-p)), where D = (Fo*Fo - Fc*Fc)

Final R indices [I>2sigma(I)]	*R1 = 0.0417, wR2 = 0.0862
R indices (all data)	R1 = 0.0603, *wR2 = 0.0916

*Report these R factors.

R1 = sum||Fo|-|Fc||/sum|Fo|, wR2= root(sum(w*D*D)/sum(w*Fo*Fo)),
where D = (Fo*Fo - Fc*Fc)

Weighting scheme

calc w=1/[\s^2^(Fo^2^)+(0.0457P)^2^+0.0000P] where P=(Fo^2^+2Fc^2^)/3

Absolute structure parameter	0.014(16)
Largest diff. peak and hole	0.412 and -0.448 e.A^-3

Table S-21. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $[Cu^{II}(S^{Me2}N_4(tren))](PF_6)$ (**7**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	6626(6)	2824(4)	3207(3)	40(1)
C(2)	3632(7)	3039(4)	2848(2)	37(1)
C(3)	4928(5)	3293(3)	3432(2)	23(1)
C(4)	5150(5)	4467(3)	3506(2)	18(1)
C(5)	5310(6)	5109(3)	2807(2)	24(1)
C(6)	5415(6)	6023(3)	4252(2)	20(1)
C(7)	5825(5)	6204(3)	5063(2)	22(1)
C(8)	5411(6)	5435(3)	6299(2)	26(1)
C(9)	6512(6)	4483(3)	6301(2)	24(1)
C(10)	3046(5)	6096(3)	5594(2)	22(1)
C(11)	1738(6)	5279(3)	5802(2)	25(1)
N(1)	5182(4)	4891(2)	4147(2)	20(1)
N(2)	4683(4)	5596(2)	5552(2)	17(1)
N(3)	5576(5)	3576(2)	5998(2)	22(1)
N(4)	1864(4)	4409(2)	5276(2)	22(1)
F(1)	10893(3)	143(2)	1790(2)	38(1)
F(2)	8370(3)	1981(2)	1387(2)	34(1)
F(3)	10362(4)	1113(2)	757(1)	42(1)
F(4)	8903(3)	1016(2)	2412(1)	30(1)
F(5)	10967(3)	1911(2)	1848(2)	40(1)
F(6)	8307(3)	214(2)	1326(1)	30(1)
P(1)	9642(2)	1058(1)	1590(1)	23(1)
S(1)	4294(2)	2700(1)	4319(1)	22(1)
Cu(1)	4455(1)	4134(1)	5046(1)	18(1)

Table S-22. Bond lengths [A] and angles [deg] for [$Cu^{II}(S^{Me2}N_4(tren))](PF_6)$ (**7**).

C(1)-C(3)	1.556(6)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.523(6)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-C(4)	1.512(6)
C(3)-S(1)	1.842(4)
C(4)-N(1)	1.275(5)
C(4)-C(5)	1.510(5)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-N(1)	1.466(5)
C(6)-C(7)	1.516(5)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-N(2)	1.495(5)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-N(2)	1.486(5)
C(8)-C(9)	1.506(6)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-N(3)	1.486(5)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-N(2)	1.475(6)
C(10)-C(11)	1.534(6)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-N(4)	1.462(5)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
N(1)-Cu(1)	1.977(3)
N(2)-Cu(1)	2.082(3)
N(3)-Cu(1)	2.068(3)
N(3)-H(3A)	0.9200
N(3)-H(3B)	0.9200
N(4)-Cu(1)	2.171(4)
N(4)-H(4A)	0.9200
N(4)-H(4B)	0.9200
F(1)-P(1)	1.588(3)
F(2)-P(1)	1.606(3)
F(3)-P(1)	1.613(3)
F(4)-P(1)	1.600(2)
F(5)-P(1)	1.597(3)
F(6)-P(1)	1.599(3)
S(1)-Cu(1)	2.2537(10)
C(3)-C(1)-H(1A)	109.5

C(3)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(3)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(3)-C(2)-H(2A)	109.5
C(3)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(3)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(4)-C(3)-C(2)	110.7(4)
C(4)-C(3)-C(1)	107.3(4)
C(2)-C(3)-C(1)	110.4(4)
C(4)-C(3)-S(1)	111.2(3)
C(2)-C(3)-S(1)	108.7(3)
C(1)-C(3)-S(1)	108.4(3)
N(1)-C(4)-C(5)	121.7(4)
N(1)-C(4)-C(3)	120.1(4)
C(5)-C(4)-C(3)	118.2(3)
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
N(1)-C(6)-C(7)	107.6(3)
N(1)-C(6)-H(6A)	110.2
C(7)-C(6)-H(6A)	110.2
N(1)-C(6)-H(6B)	110.2
C(7)-C(6)-H(6B)	110.2
H(6A)-C(6)-H(6B)	108.5
N(2)-C(7)-C(6)	110.7(3)
N(2)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7A)	109.5
N(2)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	108.1
N(2)-C(8)-C(9)	110.4(3)
N(2)-C(8)-H(8A)	109.6
C(9)-C(8)-H(8A)	109.6
N(2)-C(8)-H(8B)	109.6
C(9)-C(8)-H(8B)	109.6
H(8A)-C(8)-H(8B)	108.1
N(3)-C(9)-C(8)	108.8(4)
N(3)-C(9)-H(9A)	109.9
C(8)-C(9)-H(9A)	109.9
N(3)-C(9)-H(9B)	109.9
C(8)-C(9)-H(9B)	109.9
H(9A)-C(9)-H(9B)	108.3
N(2)-C(10)-C(11)	110.0(3)
N(2)-C(10)-H(10A)	109.7
C(11)-C(10)-H(10A)	109.7
N(2)-C(10)-H(10B)	109.7
C(11)-C(10)-H(10B)	109.7
H(10A)-C(10)-H(10B)	108.2
N(4)-C(11)-C(10)	107.9(3)

N(4)-C(11)-H(11A)	110.1
C(10)-C(11)-H(11A)	110.1
N(4)-C(11)-H(11B)	110.1
C(10)-C(11)-H(11B)	110.1
H(11A)-C(11)-H(11B)	108.4
C(4)-N(1)-C(6)	122.5(3)
C(4)-N(1)-Cu(1)	122.0(3)
C(6)-N(1)-Cu(1)	114.3(2)
C(10)-N(2)-C(8)	111.8(3)
C(10)-N(2)-C(7)	111.4(3)
C(8)-N(2)-C(7)	111.1(3)
C(10)-N(2)-Cu(1)	109.2(2)
C(8)-N(2)-Cu(1)	108.0(2)
C(7)-N(2)-Cu(1)	105.1(2)
C(9)-N(3)-Cu(1)	105.2(2)
C(9)-N(3)-H(3A)	110.7
Cu(1)-N(3)-H(3A)	110.7
C(9)-N(3)-H(3B)	110.7
Cu(1)-N(3)-H(3B)	110.7
H(3A)-N(3)-H(3B)	108.8
C(11)-N(4)-Cu(1)	108.3(3)
C(11)-N(4)-H(4A)	110.0
Cu(1)-N(4)-H(4A)	110.0
C(11)-N(4)-H(4B)	110.0
Cu(1)-N(4)-H(4B)	110.0
H(4A)-N(4)-H(4B)	108.4
F(1)-P(1)-F(5)	90.16(15)
F(1)-P(1)-F(6)	90.37(14)
F(5)-P(1)-F(6)	179.42(15)
F(1)-P(1)-F(4)	90.21(14)
F(5)-P(1)-F(4)	90.28(14)
F(6)-P(1)-F(4)	89.97(14)
F(1)-P(1)-F(2)	179.78(17)
F(5)-P(1)-F(2)	90.05(15)
F(6)-P(1)-F(2)	89.43(14)
F(4)-P(1)-F(2)	89.72(14)
F(1)-P(1)-F(3)	90.70(15)
F(5)-P(1)-F(3)	89.87(15)
F(6)-P(1)-F(3)	89.87(14)
F(4)-P(1)-F(3)	179.08(16)
F(2)-P(1)-F(3)	89.38(15)
C(3)-S(1)-Cu(1)	98.98(14)
N(1)-Cu(1)-N(3)	135.86(16)
N(1)-Cu(1)-N(2)	84.05(12)
N(3)-Cu(1)-N(2)	84.57(12)
N(1)-Cu(1)-N(4)	111.52(13)
N(3)-Cu(1)-N(4)	108.81(15)
N(2)-Cu(1)-N(4)	81.86(13)
N(1)-Cu(1)-S(1)	86.29(10)
N(3)-Cu(1)-S(1)	103.29(9)
N(2)-Cu(1)-S(1)	170.27(9)
N(4)-Cu(1)-S(1)	100.68(9)

Symmetry transformations used to generate equivalent atoms:

Table S-23. Anisotropic displacement parameters (A^2 x 10^3) for $[Cu^{II}(S^{Me2}N_4(tren))](PF_6)$ (**7**).
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	38(3)	41(3)	40(3)	-7(2)	18(3)	10(2)
C(2)	57(4)	33(3)	20(3)	-2(2)	-6(3)	-16(2)
C(3)	27(3)	26(2)	15(2)	-3(2)	1(2)	0(2)
C(4)	14(2)	21(2)	18(2)	-1(2)	1(2)	3(2)
C(5)	26(3)	29(2)	18(2)	0(2)	0(2)	0(2)
C(6)	23(2)	14(2)	22(2)	2(2)	3(2)	0(2)
C(7)	27(2)	17(2)	23(2)	-1(2)	7(2)	-3(2)
C(8)	31(3)	29(2)	18(2)	-3(2)	0(2)	-1(2)
C(9)	26(3)	24(2)	22(2)	0(2)	-9(2)	-5(2)
C(10)	26(2)	18(2)	23(2)	1(2)	1(2)	2(2)
C(11)	26(3)	26(2)	24(3)	-2(2)	5(2)	1(2)
N(1)	16(2)	25(2)	20(2)	1(1)	1(2)	-1(2)
N(2)	23(2)	16(2)	14(2)	-2(1)	-3(2)	-1(1)
N(3)	24(2)	21(2)	20(2)	2(1)	1(2)	1(2)
N(4)	20(2)	25(2)	21(2)	1(1)	2(2)	-4(2)
F(1)	32(2)	43(2)	41(2)	-3(1)	-1(2)	9(1)
F(2)	39(2)	25(1)	40(2)	9(1)	-10(2)	4(1)
F(3)	34(2)	69(2)	22(1)	-2(1)	7(1)	-12(2)
F(4)	35(2)	38(1)	18(1)	0(1)	0(1)	4(1)
F(5)	36(2)	39(2)	45(2)	-2(1)	-12(1)	-19(1)
F(6)	26(2)	33(2)	32(2)	-8(1)	-3(1)	-10(1)
P(1)	21(1)	27(1)	20(1)	0(1)	-1(1)	-5(1)
S(1)	31(1)	17(1)	20(1)	0(1)	-2(1)	1(1)
Cu(1)	22(1)	16(1)	16(1)	0(1)	-1(1)	-1(1)

Table S-24. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $[Cu^{II}(S^{Me2}N_4(tren))](PF_6)$ (**7**).

	x	y	z	U(eq)
H(1A)	6978	3127	2733	60
H(1B)	6528	2061	3157	60
H(1C)	7443	2989	3590	60
H(2A)	2601	3400	2970	55
H(2B)	3441	2279	2837	55
H(2C)	4021	3273	2361	55
H(5A)	4249	5440	2692	36
H(5B)	5637	4651	2395	36
H(5C)	6149	5654	2878	36
H(6A)	4397	6406	4117	24
H(6B)	6325	6278	3934	24
H(7A)	6976	5985	5160	27
H(7B)	5732	6961	5178	27
H(8A)	4519	5341	6668	31
H(8B)	6059	6062	6442	31
H(9A)	7500	4616	5993	29
H(9B)	6879	4328	6813	29
H(10A)	2768	6414	5109	27
H(10B)	3064	6662	5970	27
H(11A)	1927	5023	6314	31
H(11B)	625	5595	5778	31
H(3A)	4801	3348	6334	26
H(3B)	6275	3029	5889	26
H(4A)	1316	4572	4845	26
H(4B)	1395	3814	5475	26

Table S-25. Crystal data and structure refinement for $[Zn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**8**).

Empirical formula	C11 H25 F6 N4 P S Zn
Formula weight	455.75
Temperature	130(2) K
Wavelength	0.71070 A
Crystal description/color	block / clear
Crystal system, space group	Orthorhombic, P 21 21 21 (no. 19)
Unit cell dimensions	a = 8.1600(3)A alpha = 90 deg.
	b = 12.7280(4)A beta = 90 deg.
	c = 17.9620(5)A gamma = 90 deg.
Volume	1865.54(10) A^3
Z, Calculated density	4, 1.623 Mg/m^3
Absorption coefficient	1.572 mm^-1
F(000)	936
Crystal size	0.48 x 0.43 x 0.31 mm
Reflections for indexing	1020
Theta range for data collection	3.37 to 28.26 deg.
Index ranges	-10<=h<=10, -16<=k<=16, -22<=l<=23
Reflections collected / unique	4221 / 4221 [R(int) = 0.0492]
Completeness to theta = 28.26	96.0%
Absorption correction	HKL-SCALEPACK
Max. and min. transmission	0.6414 and 0.5191
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4221 / 0 / 220
Goodness-of-fit on F^2	S = 1.015
S = root(sum(w*D*D)/(n-p)), where D = (Fo*Fo - Fc*Fc)	
Final R indices [I>2sigma(I)]	*R1 = 0.0280, wR2 = 0.0674
R indices (all data)	R1 = 0.0318, *wR2 = 0.0691
	*Report these R factors.
R1 = sum||Fo|-|Fc||/sum|Fo|, wR2= root(sum(w*D*D)/sum(w*Fo*Fo)), where D = (Fo*Fo - Fc*Fc)	
Weighting scheme	
calc w=1/[\s^2^(Fo^2^)+(0.0349P)^2^+0.8362P] where P=(Fo^2^+2Fc^2^)/3	
Absolute structure parameter	-0.012(9)
Largest diff. peak and hole	0.318 and -0.367 e.A^-3

Table S-26. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for [$Zn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**8**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	3369(4)	2240(2)	8228(2)	31(1)
C(2)	6332(4)	2018(2)	7844(2)	28(1)
C(3)	5058(3)	1782(2)	8449(1)	17(1)
C(4)	4841(3)	595(2)	8533(1)	14(1)
C(5)	4660(3)	-34(2)	7827(1)	19(1)
C(6)	4609(3)	-976(2)	9250(1)	16(1)
C(7)	4231(3)	-1235(2)	10059(1)	18(1)
C(8)	6994(3)	-1156(2)	10604(1)	19(1)
C(9)	8258(3)	-331(2)	10815(2)	21(1)
C(10)	4612(3)	-537(2)	11317(1)	20(1)
C(11)	3501(3)	418(2)	11324(2)	21(1)
N(1)	4809(2)	169(2)	9174(1)	14(1)
N(2)	5346(2)	-686(2)	10574(1)	16(1)
N(4)	8138(2)	566(2)	10297(1)	16(1)
N(3)	4413(3)	1355(2)	11048(1)	17(1)
F(1)	8306(2)	-136(1)	8684(1)	26(1)
F(2)	8872(2)	-948(1)	7597(1)	27(1)
F(3)	10851(2)	-37(1)	8195(1)	34(1)
F(4)	10398(2)	-992(2)	9244(1)	40(1)
F(5)	8418(2)	-1903(1)	8637(1)	33(1)
F(6)	10982(2)	-1805(1)	8151(1)	37(1)
P(1)	9647(1)	-972(1)	8417(1)	19(1)
S(1)	5753(1)	2426(1)	9310(1)	16(1)
Zn(1)	5708(1)	972(1)	10091(1)	13(1)

Table S-27. Bond lengths [A] and angles [deg] for [$Zn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**8**).

C(1)-C(3)	1.548(4)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.534(4)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-C(4)	1.528(3)
C(3)-S(1)	1.840(2)
C(4)-N(1)	1.272(3)
C(4)-C(5)	1.507(3)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-N(1)	1.473(3)
C(6)-C(7)	1.521(3)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-N(2)	1.474(3)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-N(2)	1.473(3)
C(8)-C(9)	1.521(4)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-N(4)	1.476(3)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-N(2)	1.475(3)
C(10)-C(11)	1.516(4)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-N(3)	1.490(3)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
N(1)-Zn(1)	2.0738(19)
N(2)-Zn(1)	2.3008(19)
N(4)-Zn(1)	2.083(2)
N(4)-H(3A)	0.9200
N(4)-H(3B)	0.9200
N(3)-Zn(1)	2.075(2)
N(3)-H(4A)	0.9200
N(3)-H(4B)	0.9200
F(1)-P(1)	1.5994(16)
F(2)-P(1)	1.6030(15)
F(3)-P(1)	1.5936(18)
F(4)-P(1)	1.6067(17)
F(5)-P(1)	1.6018(18)
F(6)-P(1)	1.5940(17)
S(1)-Zn(1)	2.3220(6)

C(3)-C(1)-H(1A)	109.5
C(3)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(3)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(3)-C(2)-H(2A)	109.5
C(3)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(3)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(4)-C(3)-C(2)	109.9(2)
C(4)-C(3)-C(1)	107.2(2)
C(2)-C(3)-C(1)	110.4(2)
C(4)-C(3)-S(1)	113.15(16)
C(2)-C(3)-S(1)	107.43(17)
C(1)-C(3)-S(1)	108.81(18)
N(1)-C(4)-C(5)	122.1(2)
N(1)-C(4)-C(3)	120.9(2)
C(5)-C(4)-C(3)	117.0(2)
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
N(1)-C(6)-C(7)	109.02(19)
N(1)-C(6)-H(6A)	109.9
C(7)-C(6)-H(6A)	109.9
N(1)-C(6)-H(6B)	109.9
C(7)-C(6)-H(6B)	109.9
H(6A)-C(6)-H(6B)	108.3
N(2)-C(7)-C(6)	111.77(19)
N(2)-C(7)-H(7A)	109.3
C(6)-C(7)-H(7A)	109.3
N(2)-C(7)-H(7B)	109.3
C(6)-C(7)-H(7B)	109.3
H(7A)-C(7)-H(7B)	107.9
N(2)-C(8)-C(9)	110.34(19)
N(2)-C(8)-H(8A)	109.6
C(9)-C(8)-H(8A)	109.6
N(2)-C(8)-H(8B)	109.6
C(9)-C(8)-H(8B)	109.6
H(8A)-C(8)-H(8B)	108.1
N(4)-C(9)-C(8)	109.4(2)
N(4)-C(9)-H(9A)	109.8
C(8)-C(9)-H(9A)	109.8
N(4)-C(9)-H(9B)	109.8
C(8)-C(9)-H(9B)	109.8
H(9A)-C(9)-H(9B)	108.2
N(2)-C(10)-C(11)	110.67(19)
N(2)-C(10)-H(10A)	109.5
C(11)-C(10)-H(10A)	109.5
N(2)-C(10)-H(10B)	109.5
C(11)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	108.1

N(3)-C(11)-C(10)	109.9(2)
N(3)-C(11)-H(11A)	109.7
C(10)-C(11)-H(11A)	109.7
N(3)-C(11)-H(11B)	109.7
C(10)-C(11)-H(11B)	109.7
H(11A)-C(11)-H(11B)	108.2
C(4)-N(1)-C(6)	120.6(2)
C(4)-N(1)-Zn(1)	120.04(16)
C(6)-N(1)-Zn(1)	116.93(15)
C(8)-N(2)-C(7)	113.19(18)
C(8)-N(2)-C(10)	112.94(19)
C(7)-N(2)-C(10)	112.20(19)
C(8)-N(2)-Zn(1)	105.65(14)
C(7)-N(2)-Zn(1)	106.14(13)
C(10)-N(2)-Zn(1)	105.98(14)
C(9)-N(4)-Zn(1)	111.54(15)
C(9)-N(4)-H(3A)	109.3
Zn(1)-N(4)-H(3A)	109.3
C(9)-N(4)-H(3B)	109.3
Zn(1)-N(4)-H(3B)	109.3
H(3A)-N(4)-H(3B)	108.0
C(11)-N(3)-Zn(1)	109.99(15)
C(11)-N(3)-H(4A)	109.7
Zn(1)-N(3)-H(4A)	109.7
C(11)-N(3)-H(4B)	109.7
Zn(1)-N(3)-H(4B)	109.7
H(4A)-N(3)-H(4B)	108.2
F(3)-P(1)-F(6)	90.01(9)
F(3)-P(1)-F(1)	90.02(9)
F(6)-P(1)-F(1)	179.97(9)
F(3)-P(1)-F(5)	179.31(10)
F(6)-P(1)-F(5)	90.55(10)
F(1)-P(1)-F(5)	89.41(9)
F(3)-P(1)-F(2)	89.96(9)
F(6)-P(1)-F(2)	90.39(9)
F(1)-P(1)-F(2)	89.61(9)
F(5)-P(1)-F(2)	89.63(9)
F(3)-P(1)-F(4)	90.47(11)
F(6)-P(1)-F(4)	90.29(10)
F(1)-P(1)-F(4)	89.71(9)
F(5)-P(1)-F(4)	89.93(10)
F(2)-P(1)-F(4)	179.20(9)
C(3)-S(1)-Zn(1)	98.48(8)
N(1)-Zn(1)-N(3)	126.41(8)
N(1)-Zn(1)-N(4)	110.83(8)
N(4)-Zn(1)-N(3)	113.32(8)
N(1)-Zn(1)-N(2)	78.56(7)
N(3)-Zn(1)-N(2)	80.66(7)
N(4)-Zn(1)-N(2)	80.06(8)
N(1)-Zn(1)-S(1)	85.35(6)
N(3)-Zn(1)-S(1)	108.74(6)
N(4)-Zn(1)-S(1)	106.86(6)
N(2)-Zn(1)-S(1)	163.88(5)

Symmetry transformations used to generate equivalent atoms:

Table S-28. Anisotropic displacement parameters (A^2 x 10^3) for $[Zn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**8**).
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	30(2)	25(1)	38(2)	1(1)	-15(1)	9(1)
C(2)	43(2)	24(1)	18(1)	1(1)	7(1)	-8(1)
C(3)	19(1)	16(1)	16(1)	0(1)	-4(1)	1(1)
C(4)	10(1)	18(1)	15(1)	-1(1)	-2(1)	3(1)
C(5)	19(1)	23(1)	16(1)	-2(1)	1(1)	-2(1)
C(6)	17(1)	13(1)	18(1)	-1(1)	-1(1)	-2(1)
C(7)	19(1)	15(1)	20(1)	2(1)	0(1)	-5(1)
C(8)	21(1)	15(1)	21(1)	2(1)	-2(1)	4(1)
C(9)	20(1)	24(1)	20(1)	1(1)	-6(1)	4(1)
C(10)	24(1)	21(1)	14(1)	1(1)	3(1)	-2(1)
C(11)	22(1)	22(1)	18(1)	1(1)	6(1)	-1(1)
N(1)	13(1)	13(1)	16(1)	-1(1)	0(1)	0(1)
N(2)	18(1)	16(1)	14(1)	1(1)	1(1)	-1(1)
N(4)	15(1)	17(1)	17(1)	-2(1)	-1(1)	-1(1)
N(3)	20(1)	17(1)	15(1)	0(1)	1(1)	1(1)
F(1)	21(1)	28(1)	28(1)	-4(1)	4(1)	7(1)
F(2)	30(1)	34(1)	18(1)	1(1)	-1(1)	-4(1)
F(3)	24(1)	37(1)	41(1)	-6(1)	6(1)	-11(1)
F(4)	31(1)	67(1)	23(1)	-1(1)	-7(1)	14(1)
F(5)	37(1)	25(1)	38(1)	8(1)	11(1)	0(1)
F(6)	32(1)	39(1)	40(1)	-3(1)	9(1)	19(1)
P(1)	18(1)	23(1)	17(1)	0(1)	2(1)	5(1)
S(1)	20(1)	12(1)	17(1)	1(1)	2(1)	0(1)
Zn(1)	15(1)	12(1)	12(1)	0(1)	0(1)	-1(1)

Table S-29. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for [$Zn^{II}(S^{Me2}N_4(tren))](PF_6)$ (**8**).

	x	y	z	U(eq)
H(1A)	3002	1917	7762	47
H(1B)	3465	3002	8160	47
H(1C)	2571	2092	8622	47
H(2A)	7358	1654	7962	43
H(2B)	6531	2776	7822	43
H(2C)	5922	1773	7361	43
H(5A)	5695	-392	7716	29
H(5B)	4379	437	7415	29
H(5C)	3789	-556	7891	29
H(6A)	5628	-1337	9094	19
H(6B)	3704	-1222	8927	19
H(7A)	3087	-1031	10172	22
H(7B)	4331	-2003	10136	22
H(8A)	7272	-1459	10112	23
H(8B)	7007	-1731	10975	23
H(9A)	8062	-89	11331	26
H(9B)	9371	-638	10791	26
H(10A)	5493	-445	11690	24
H(10B)	3973	-1169	11453	24
H(11A)	2536	288	11003	25
H(11B)	3107	549	11837	25
H(3A)	8642	395	9855	20
H(3B)	8679	1134	10497	20
H(4A)	5126	1585	11409	21
H(4B)	3687	1889	10946	21

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