Electronic Supplementary Information (ESI) for "Spin crossover in the $Fe(3PyMe)_2[M(CN)_4]$ series with M = Ni, Pd, Pt, and 3PyMe = 3-pyridinemethanol. The role of intermolecular interactions".

M. C. Vázquez, Y. Avila, L. Sánchez, A. Ortiz, O. Piedra, M. González, M. Ávila*, E. Reguera*

Instituto Politécnico Nacional, Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada, Unidad Legaria, 11500 Mexico City, Mexico.

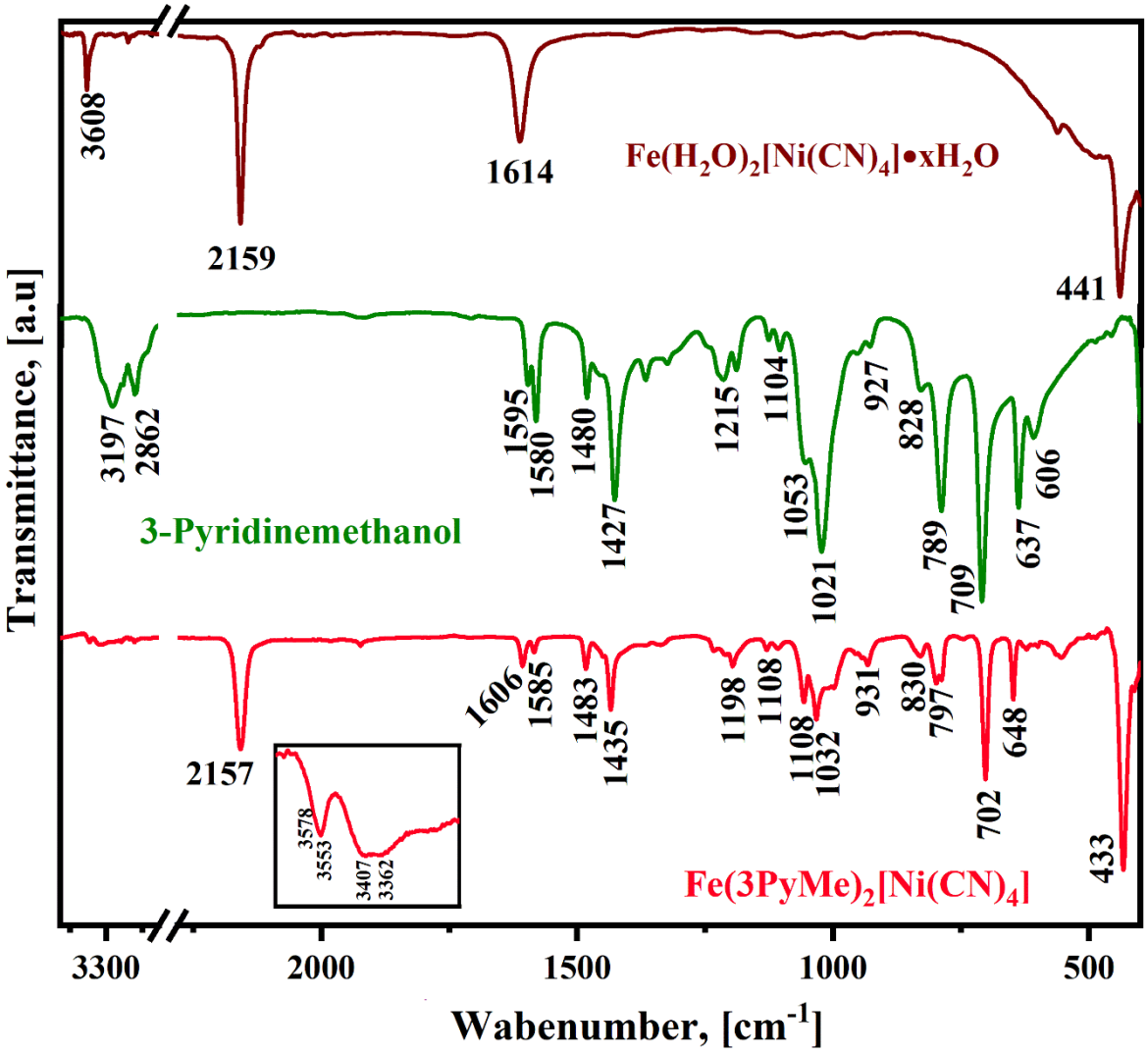

Figure S1. IR spectra for $Fe(H_2O)_2[Ni(CN)_4]\cdot xH_2O$; 3-pyridine methanol as a pillar molecule; and the formed solid by incorporation of bimolecular pillars between adjacent layers

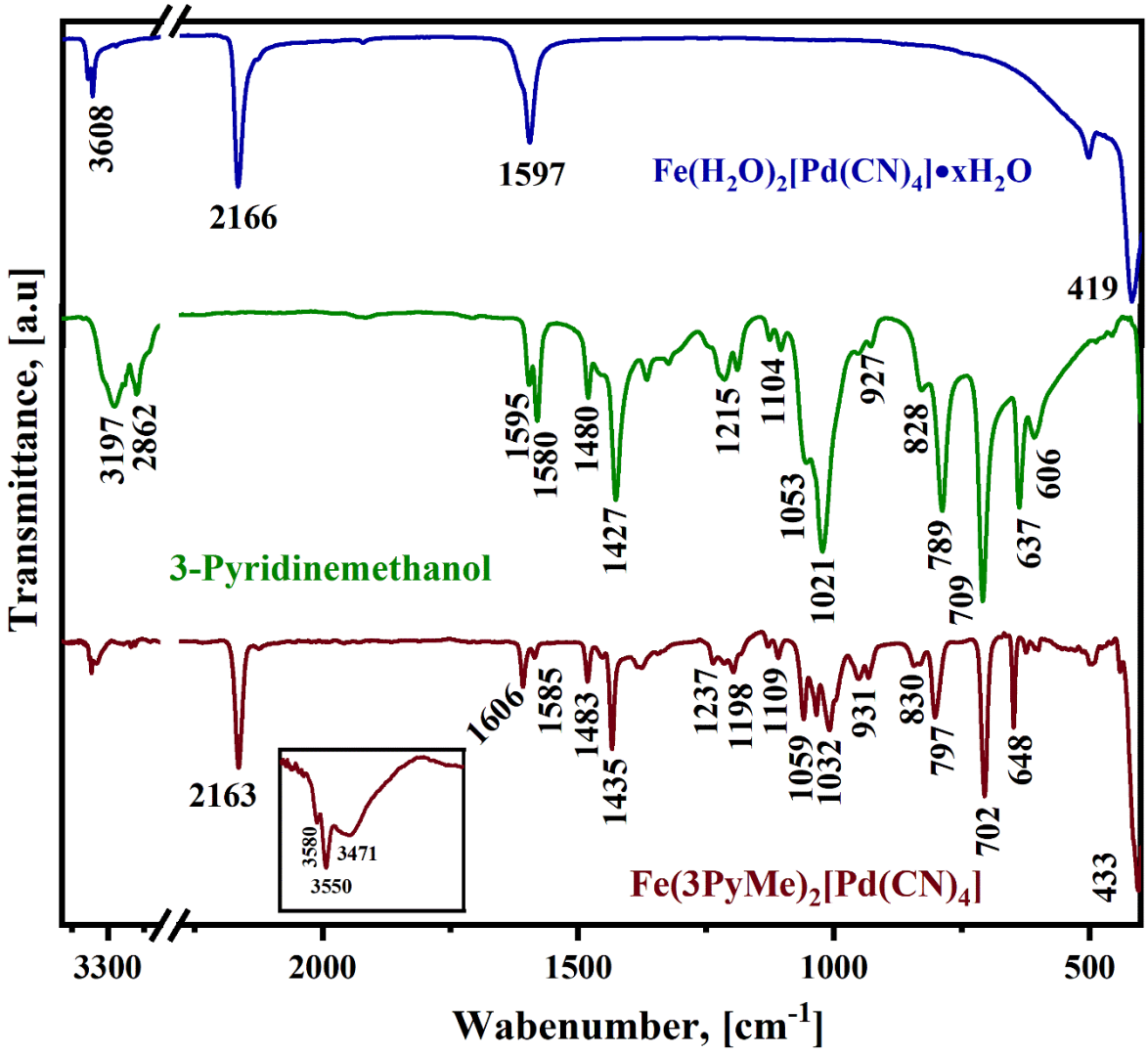

Figure S2. IR spectra for $Fe(H_2O)_2[Pd(CN)_4]\cdot xH_2O$; 3-pyridine methanol as a pillar molecule; and the formed solid by incorporation of bimolecular pillars between adjacent layers

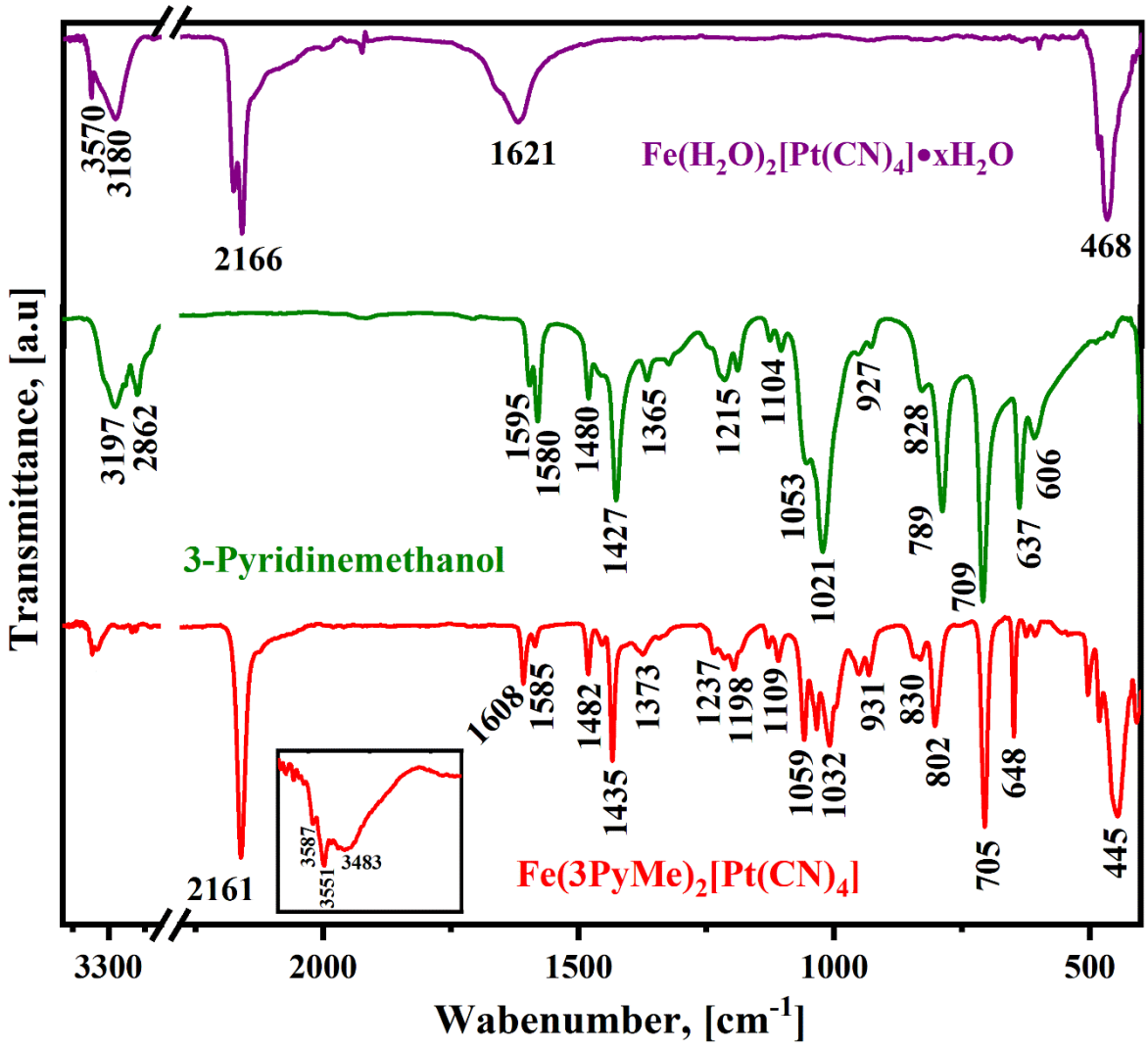

Figure S3. IR spectra for $Fe(H_2O)_2[Pt(CN)_4]\cdot xH_2O$; 3-pyridine methanol as a pillar molecule; and the formed solid by incorporation of bimolecular pillars between adjacent layers

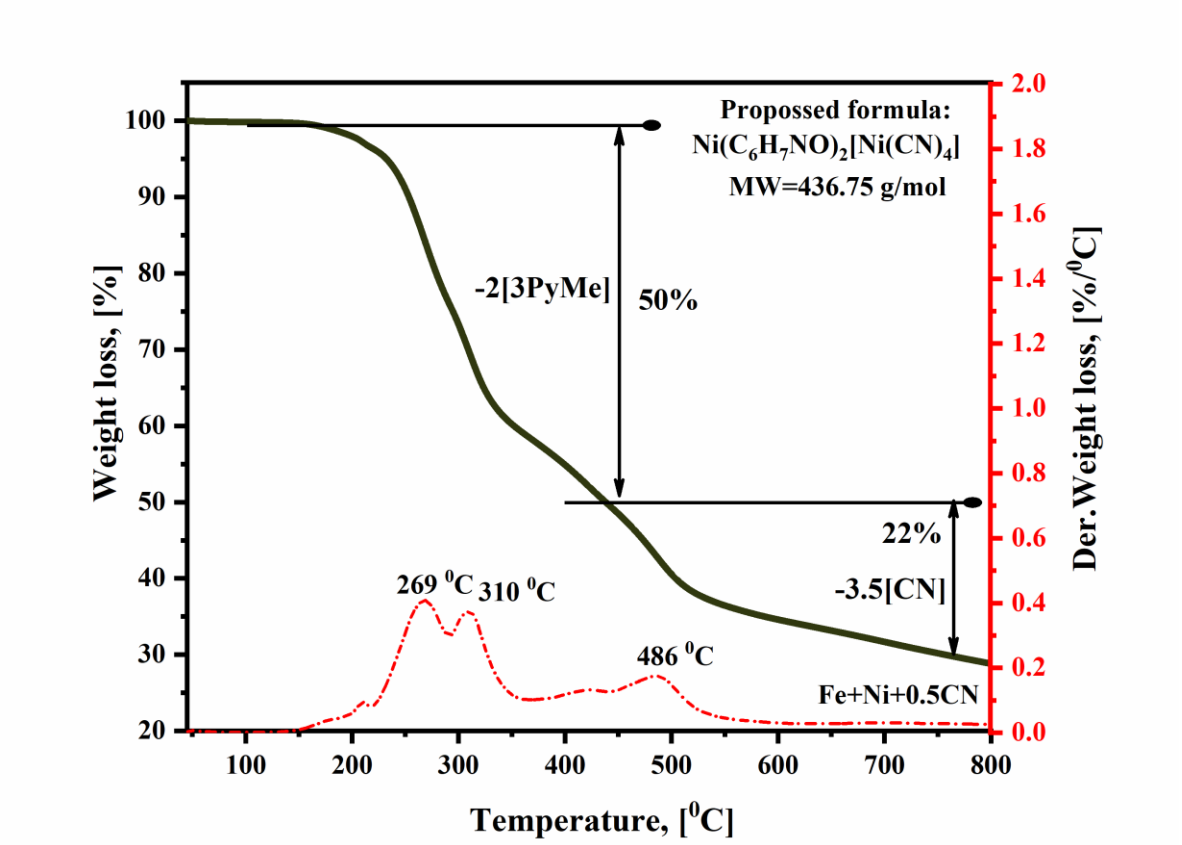

Figure S4. TG curve for the solid formed from the precipitation reaction of aqueous solutions of $K_2[Ni(CN)_4]$, Mohr salt, and the organic ligand (3PyMe).

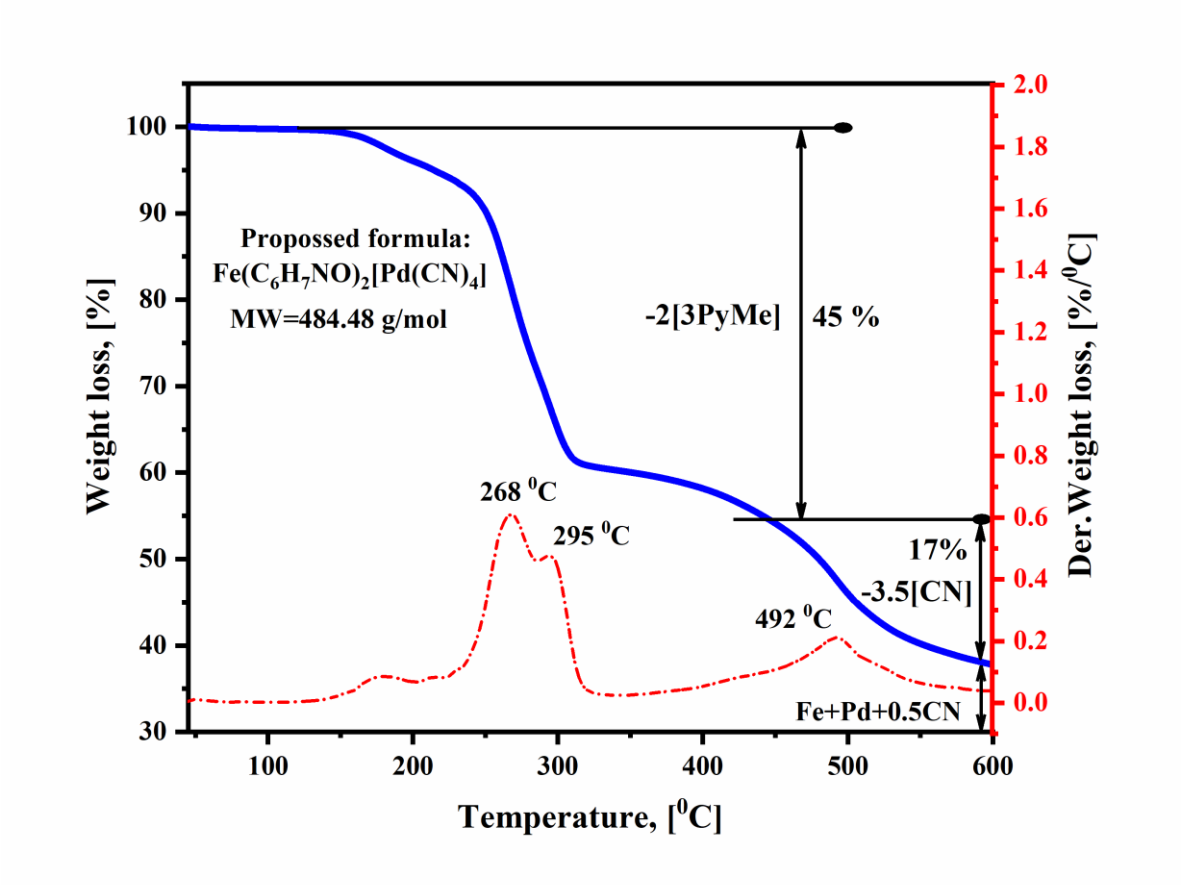

Figure S5. TG curve for the solid formed from the precipitation reaction of aqueous solutions of $K_2[Pd(CN)_4]$, Mohr salt, and the organic ligand (3PyMe).

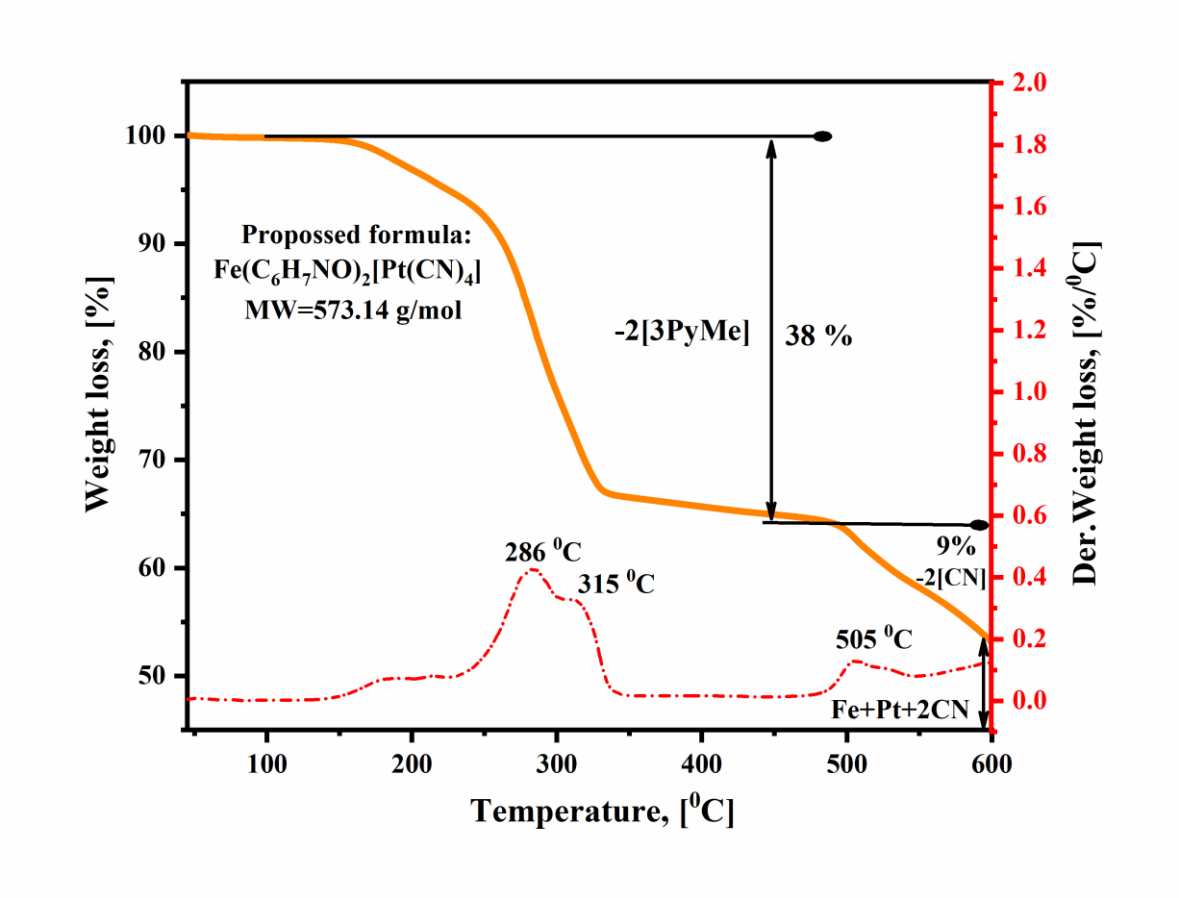

Figure S6. TG curve for the solid formed from the precipitation reaction of aqueous solutions of $K_2[Pt(CN)_4]$, Mohr salt, and the organic ligand (3PyMe).

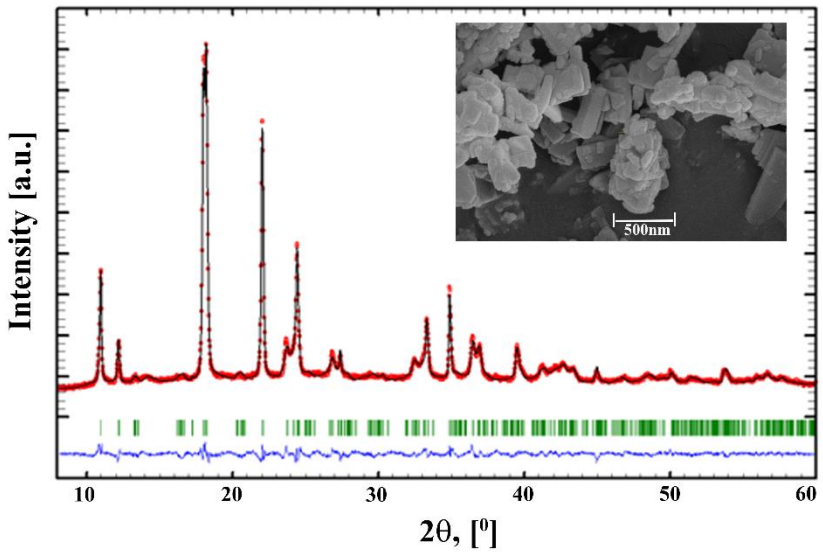

Figure S7. XRD powder pattern experimental (red), calculated (black), and profile fitting difference (blue) for the Rietveld refinement of the composition $Fe(3PyMe)_2[Ni(CN)_4]$ at room temperature. Inset: SEM image of the formed polycrystalline solid with M = Ni.

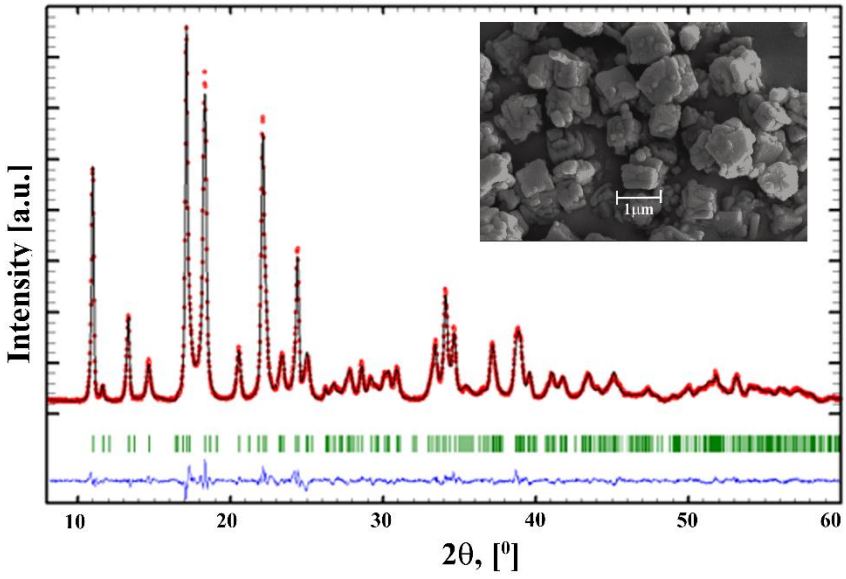

Figure S8. XRD powder pattern experimental (red), calculated (black), and profile fitting difference (blue) for the Rietveld refinement of the composition $Fe(3PyMe)_2[Pt(CN)_4]$ at room temperature. Inset: SEM image of the formed polycrystalline solid with M = Pt.

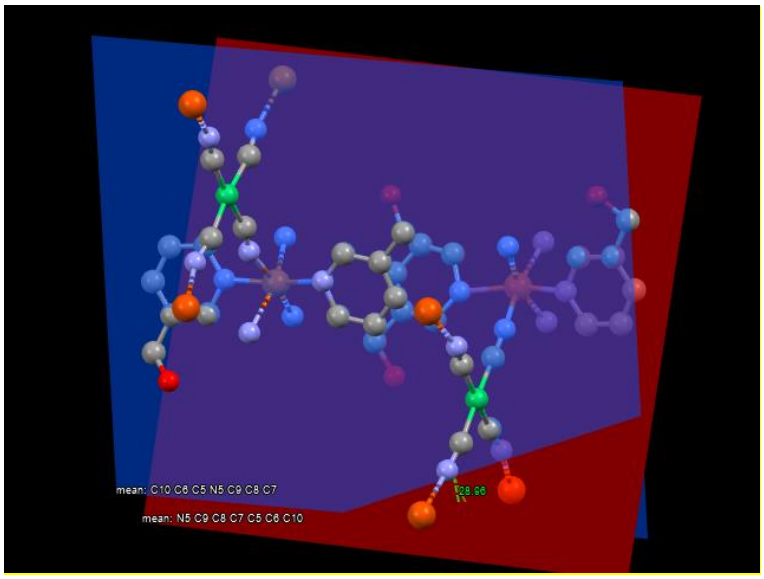

Figure S9. Dihedral angles of the benzene rings for $Fe(3PyMe)_2[Ni(CN)_4]$

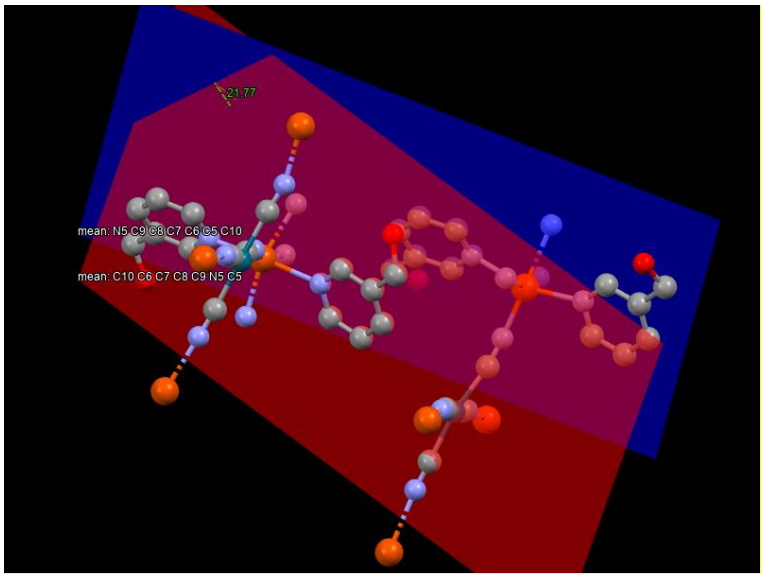

Figure S10. Dihedral angles of the benzene rings for $Fe(3PyMe)_2[Pd(CN)_4]$

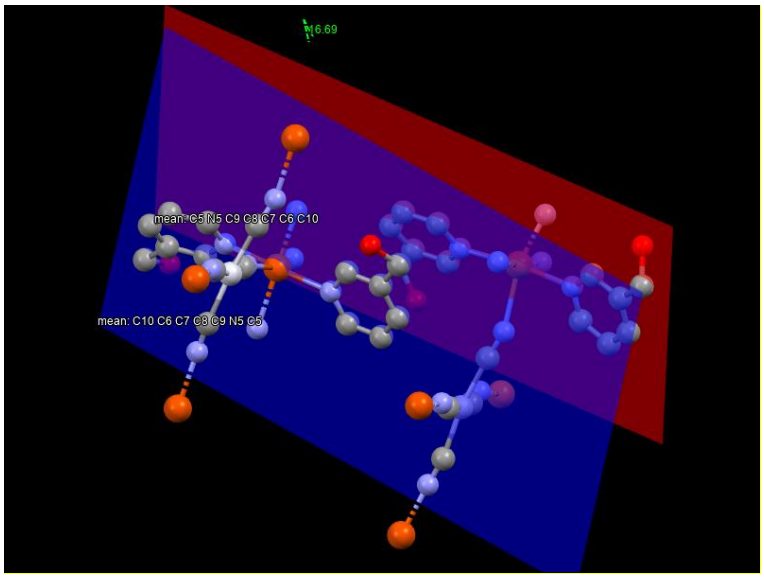

Figure S11. Dihedral angles of the benzene rings for $Fe(3PyMe)_2[Pt(CN)_4]$.

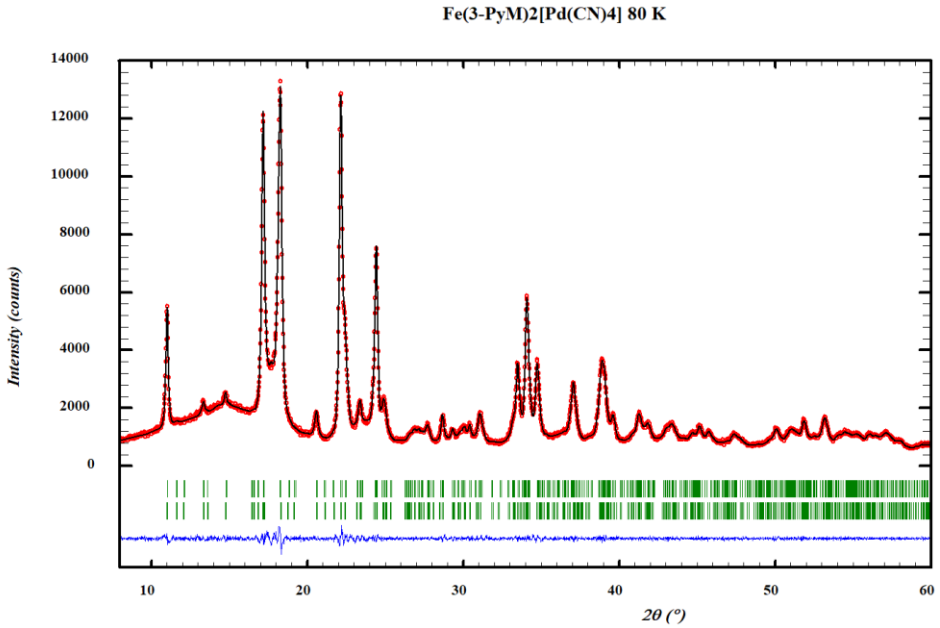

Figure S12. XRD pattern recorded at 80 K for the $Fe(3PyMe)_2[Pd(CN)_4]$ sample, fitted as the superposition of two monoclinic unit cells in the $P2_1$ space group, corresponding to the HS and LS phases at that temperature.

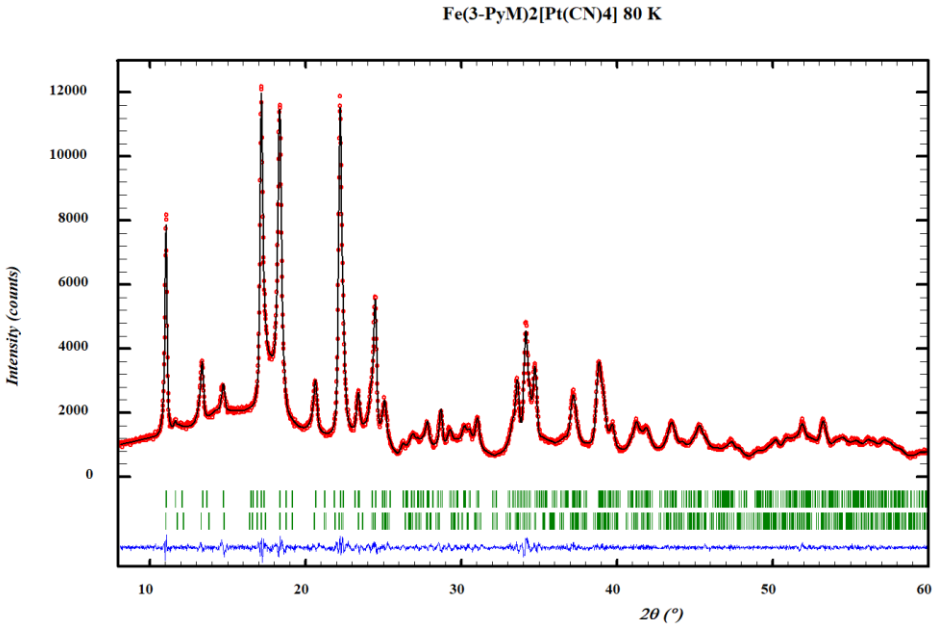

Figure S13. XRD pattern recorded at 80 K for the $Fe(3PyMe)_2[Pt(CN)_4]$ sample, fitted as the superposition of two monoclinic unit cells in the $P2_1$ space group, corresponding to the HS and LS phases at that temperature.

Table S1: Chemical analysis results for the obtained polycrystalline materials

Sample	**%Fe**		**%M**		**%C**		**%N**		**%O**		**%H**	
	Cal.	**Exp.**	**Cal.**	**Exp.**	**Cal.**	**Exp.**	**Cal.**	**Exp.**	**Cal.**	**Exp.**	**Cal.**	**Exp.**
Ni	12.78	14.29	13.43	15.62	43.99	46.02	19.23	17.25	7.32	5.13	3.23	1.49
Pd	11.52	13.39	21.96	22.94	39.66	40.11	17.34	18.12	6.60	4.27	2.91	1.05
Pt	9.74	11.26	34.03	34.56	33.52	34.17	14.66	15.29	5.58	3.21	2.46	1.19

Table S2. Details of the room temperature crystal structures refined by the Rietveld method

Composition	**$Fe(3\text{-}PyM)_2[Ni(CN)_4]$**	**$Fe(3\text{-}PyM)_2[Pd(CN)_4]$**	**$Fe(3\text{-}PyM)_2[Pt(CN)_4]$**
Data collection			
Difractometer	Bruker D8 Advanced Eco	Bruker D8 Advanced Eco	Bruker D8 Advanced Eco
Wavelenght (Å)	1.5418	1.5418	1.5418
2θ range (°)	8.12670-60.01189	8.12670-60.01189	8.12670-60.01189

Step size (°)	0.020443	0.020443	0.020443
Number of points	2540	2540	2540
Temperature (K)	296(1)	296(1)	296(1)
Crystal data			
Empirical formula	$C_{16}H_{14}FeN_6NiO_2$	$C_{16}H_{14}FeN_6O_2Pd$	$C_{16}H_{14}FeN_6O_2Pt$
Empirical formula weight	436.87	484.58	573.26
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 2_1 [4]	P 2_1 [4]	P 2_1 [4]
Unit cell dimensions	a=7.2527(5) Å	a=7.6821(5) Å	a=7.6869(4) Å
	b=7.2809(1) Å	b=7.3014(6) Å	b=7.2881(1) Å
	c=16.1197(4) Å	c=16.2751(3) Å	c=16.2866(3) Å
	β=91.530(6)°	β=98.736(1)°	β=99.433(5)°
Volume ($Å^3$)	850.92(6)	902.28(10)	900.09(5)
Z	2	2	2
Calculated Density (g/cm^3)	1.705	1.784	2.115
F(000)	444.0	480.0	544.0
Refinement			
Effective reflections	57	71	64
Constrain distances	8	8	8
Profile refined parameters	14	14	14
Structural refined parameters	47	47	47
Rexp	2.1062	3.1511	2.7809
Rwp	3.6097	5.4717	4.7915
Bragg R-factor	4.1590	2.9452	2.7923
Goodness of fit	1.714	1.736	1.723

Table S3. Details of the low temperature crystalline phases refined by the Le Bail method

Composition	**$Fe(3\text{-}PyM)_2[Ni(CN)_4]$ 80 K**	**$Fe(3\text{-}PyM)_2[Pd(CN)_4]$ 80 K**	**$Fe(3\text{-}PyM)_2[Pt(CN)_4]$ 80 K**
Data collection			
Difractometer	Bruker D8 Advanced Eco	Bruker D8 Advanced Eco	Bruker D8 Advanced Eco
Wavelenght (Å)	1.5418	1.5418	1.5418
2θ range (°)	8.07765-60.00372	8.11045-60.01199	8.11515-60.01669
Step size (°)	0.012263	0.018399	0.018399

Number of points	4236	2823	2823
Temperature (K)	80(1)	80(1)	80(1)
Crystal data			
Empirical formula	$C_{16}H_{14}FeN_6NiO_2$	$C_{16}H_{14}FeN_6O_2Pd$	$C_{16}H_{14}FeN_6O_2Pt$
Empirical formula weight	436.87	484.58	573.26
F(000)	444.0	480.0	544.0
Z	2	2	2
Crystalline phase 1			
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 2_1 [4]	P 2_1 [4]	P 2_1 [4]
Unit cell dimensions	a=7.2594(3) Å	a=7.6924(3) Å	a=7.6988(2) Å
	b=7.2715(2) Å	b=7.2862(2) Å	b=7.2660(7) Å
	c=16.0555(3) Å	c=16.2059(4) Å	c=16.2040(5) Å
	β=92.063(4)°	β=98.431(8)°	β=99.199(4)°
Volume (Å^3)	846.97(5)	898.51(2)	894.79(4)
Crystalline phase 2			
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 2_1 [4]	P 2_1 [4]	P 2_1 [4]
Unit cell dimensions	a=7.2453(4) Å	a=7.6999(3) Å	a=7.6262(2) Å
	b=7.2863(4) Å	b=7.2817(2) Å	b=7.3240(3) Å
	c=16.1039(1) Å	c=16.2432(1) Å	c=16.2584(4) Å
	β=91.582(3)°	β=98.808(3)°	β=99.321(3)°
Volume (Å^3)	849.83(3)	899.99(3)	896.12(4)

Table S4. Atomic coordinates, isotropic thermal factors and occupation factors for the refined crystal structures at room temperature

Composition	Site	x	y	z	Uiso (Å^2)	Occ
$Fe(3\text{-}PyM)_2[Ni(CN)_4]$						
Fe	2a	0.4966(4)	0.5051(4)	0.2605(4)	0.045(2)	1
Ni	2a	0.0069(4)	0.0036(5)	0.2436(5)	0.042(4)	1
C1	2a	0.1871(3)	0.1921(5)	0.2478(4)	0.053(4)	1
N1	2a	0.3162(4)	0.2815(6)	0.2410(2)	0.053(4)	1
C2	2a	0.1969(4)	-0.1704(2)	0.2449(2)	0.053(4)	1
N2	2a	0.3015(3)	-0.2853(2)	0.2336(4)	0.053(4)	1
C3	2a	-0.1882(1)	-0.1656(3)	0.2414(4)	0.053(4)	1
N3	2a	-0.3114(2)	-0.2602(1)	0.2525(3)	0.053(4)	1
C4	2a	-0.1635(3)	0.1973(3)	0.2518(4)	0.053(4)	1

N4	2a	-0.2810(4)	0.3014(4)	0.2437(5)	0.053(4)	1
N5	2a	0.4600(5)	0.4426(3)	0.3874(3)	0.055(3)	1
C5	2a	0.3158(2)	0.4185(4)	0.4408(4)	0.058(3)	1
H5	2a	0.1991	0.3866	0.4201	0.058	1
C6	2a	0.3461(4)	0.4420(5)	0.5251(4)	0.058(3)	1
C7	2a	0.5203(4)	0.4897(1)	0.5551(5)	0.058(3)	1
H7	2a	0.5407	0.5056	0.6119	0.058	1
C8	2a	0.6646(4)	0.5138(3)	0.5017(4)	0.058(3)	1
H8	2a	0.7812	0.5456	0.5224	0.058	1
C9	2a	0.6342(1)	0.4902(3)	0.4173(3)	0.058(3)	1
H9	2a	0.7301	0.5063	0.3808	0.058	1
C10	2a	0.1904(2)	0.4164(1)	0.5843(4)	0.058(3)	1
H10A	2a	0.1899	0.2909	0.6045	0.058	1
H10B	2a	0.2075	0.4977	0.6316	0.058	1
O1	2a	0.0198(6)	0.4558(5)	0.5427(4)	0.058(3)	1
H1	2a	0.0691	0.5485	0.5249	0.058	1
N6	2a	0.4937(3)	0.4833(4)	0.1397(5)	0.055(3)	1
C11	2a	0.6667(4)	0.4644(1)	0.1067(1)	0.058(3)	1
H11	2a	0.7709	0.4571	0.1414	0.058	1
C12	2a	0.6837(3)	0.4562(4)	0.0214(1)	0.058(3)	1
C13	2a	0.5275(1)	0.4671(4)	-0.0297(3)	0.058(3)	1
H13	2a	0.5389	0.4616	-0.0869	0.058	1
C14	2a	0.3543(2)	0.4860(5)	0.0037(4)	0.058(3)	1
H14	2a	0.2501	0.4934	-0.031	0.058	1
C15	2a	0.3372(4)	0.4941(2)	0.0887(5)	0.058(3)	1
H15	2a	0.2216	0.5067	0.1117	0.058	1
C16	2a	0.8715(4)	0.4355(5)	-0.0158(4)	0.058(3)	1
H16A	2a	0.8612	0.3647	-0.0666	0.058	1
H16B	2a	0.9206	0.5556	-0.0289	0.058	1
O2	2a	0.9920(1)	0.3451(1)	0.0419(3)	0.058(3)	1
H2	2a	0.8988	0.2929	0.0572	0.058	1

Composition	**Site**	**x**	**y**	**z**	**Uiso (Å^2)**	**Occ**
$Fe(3\text{-}PyM)_2[Pd(CN)_4]$						
Fe	2a	0.4859(3)	0.4760(1)	0.2354(4)	0.046(2)	1
Pd	2a	0.0034(3)	-0.0002(4)	0.2502(1)	0.044(2)	1
C1	2a	0.1685(4)	0.2007(5)	0.2315(4)	0.049(4)	1
N1	2a	0.2663(3)	0.3166(4)	0.2323(2)	0.049(4)	1
C2	2a	0.2032(1)	-0.1744(2)	0.2480(5)	0.049(4)	1
N2	2a	0.3089(1)	-0.2810(4)	0.2432(3)	0.049(4)	1
C3	2a	-0.1992(1)	-0.1719(5)	0.2502(3)	0.049(4)	1
N3	2a	-0.3101(2)	-0.2755(3)	0.2502(2)	0.049(4)	1
C4	2a	-0.1830(2)	0.1882(6)	0.2537(1)	0.049(4)	1
N4	2a	-0.2900(5)	0.2920(2)	0.2602(4)	0.049(4)	1
N5	2a	0.5201(5)	0.5031(6)	0.3752(6)	0.048(3)	1
C5	2a	0.3686(5)	0.5063(5)	0.4116(6)	0.053(2)	1

H5	2a	0.2598	0.5282	0.3794	0.053	1
C6	2a	0.3799(4)	0.4768(2)	0.4961(1)	0.053(2)	1
C7	2a	0.5427(5)	0.4446(6)	0.5434(2)	0.053(2)	1
H7	2a	0.5503	0.4248	0.6002	0.053	1
C8	2a	0.6943(1)	0.4414(2)	0.5070(5)	0.053(2)	1
H8	2a	0.803	0.4196	0.5392	0.053	1
C9	2a	0.6828(4)	0.4710(4)	0.4224(3)	0.053(2)	1
H9	2a	0.7839	0.4694	0.3973	0.053	1
C10	2a	0.2160(6)	0.4798(4)	0.5369(5)	0.053(2)	1
H10A	2a	0.1694	0.3567	0.5389	0.053	1
H10B	2a	0.2445	0.5249	0.5934	0.053	1
O1	2a	0.0879(4)	0.5952(2)	0.4906(6)	0.053(2)	1
H1	2a	0.0608	0.6853	0.5159	0.053	1
N6	2a	0.5330(4)	0.5000(5)	0.1031(2)	0.048(3)	1
C11	2a	0.6808(3)	0.5225(3)	0.0650(3)	0.053(2)	1
H11	2a	0.7895	0.5478	0.0966	0.053	1
C12	2a	0.6657(5)	0.5068(4)	-0.0206(3)	0.053(2)	1
C13	2a	0.5032(4)	0.4690(6)	-0.0669(5)	0.053(2)	1
H13	2a	0.4931	0.4585	-0.1243	0.053	1
C14	2a	0.3554(5)	0.4467(2)	-0.0284(2)	0.053(2)	1
H14	2a	0.2467	0.4215	-0.06	0.053	1
C15	2a	0.3703(5)	0.4621(6)	0.0569(1)	0.053(2)	1
H15	2a	0.2719	0.4472	0.0832	0.053	1
C16	2a	0.8257(1)	0.5309(5)	-0.0632(1)	0.053(2)	1
H16A	2a	0.8156	0.453	-0.1119	0.053	1
H16B	2a	0.8333	0.657	-0.0809	0.053	1
O2	2a	0.9794(5)	0.4839(5)	-0.0071(4)	0.053(2)	1
H2	2a	0.9585	0.3958	0.021	0.053	1

Composition	**Site**	**x**	**y**	**z**	**Uiso (Å^2)**	**Occ**
Fe(3-PyM)$_2$[Pt(CN)$_4$]						
Fe	2a	0.5165(4)	0.5296(4)	0.2634(5)	0.041(5)	1
Pt	2a	0.0018(4)	0.0028(4)	0.2534(1)	0.036(5)	1
C1	2a	0.1781(1)	0.1998(4)	0.2442(4)	0.043(2)	1
N1	2a	0.2855(4)	0.3000(5)	0.2332(4)	0.043(2)	1
C2	2a	0.1969(3)	-0.1763(2)	0.2502(5)	0.043(2)	1
N2	2a	0.3222(4)	-0.2604(2)	0.2508(5)	0.043(2)	1
C3	2a	-0.2026(3)	-0.1673(2)	0.2467(4)	0.043(2)	1
N3	2a	-0.3168(4)	-0.2593(2)	0.2571(2)	0.043(2)	1
C4	2a	-0.1833(2)	0.1874(6)	0.2660(4)	0.043(2)	1
N4	2a	-0.2503(2)	0.3238(5)	0.2747(1)	0.043(2)	1
N5	2a	0.5092(5)	0.5036(2)	0.4018(4)	0.045(4)	1
C5	2a	0.3500(5)	0.5242(4)	0.4301(6)	0.047(3)	1
H5	2a	0.2465	0.5418	0.3926	0.047	1
C6	2a	0.3461(1)	0.5185(5)	0.5146(4)	0.047(3)	1
C7	2a	0.5011(3)	0.4922(4)	0.5700(4)	0.047(3)	1

H7	2a	0.4983	0.4884	0.6268	0.047	1
C8	2a	0.6603(2)	0.4716(5)	0.5416(4)	0.047(3)	1
H8	2a	0.7638	0.4541	0.5792	0.047	1
C9	2a	0.6644(1)	0.4773(6)	0.4571(5)	0.047(3)	1
H9	2a	0.7707	0.4636	0.4374	0.047	1
C10	2a	0.1735(5)	0.5408(3)	0.5462(5)	0.047(3)	1
H10A	2a	0.1753	0.4687	0.5964	0.047	1
H10B	2a	0.1567	0.6685	0.5598	0.047	1
O1	2a	0.0328(2)	0.4816(4)	0.4844(5)	0.047(3)	1
H1	2a	0.0469	0.3732	0.4735	0.047	1
N6	2a	0.4961(6)	0.5372(4)	0.1313(4)	0.045(4)	1
C11	2a	0.6374(2)	0.5350(2)	0.0885(5)	0.047(3)	1
H11	2a	0.7496	0.5663	0.1153	0.047	1
C12	2a	0.6101(5)	0.4857(5)	0.0054(2)	0.047(3)	1
C13	2a	0.4424(2)	0.4394(5)	-0.0338(4)	0.047(3)	1
H13	2a	0.4242	0.4063	-0.0898	0.047	1
C14	2a	0.3012(4)	0.4417(4)	0.0090(5)	0.047(3)	1
H14	2a	0.189	0.4103	-0.0178	0.047	1
C15	2a	0.3282(2)	0.4911(5)	0.0922(4)	0.047(3)	1
H15	2a	0.2341	0.4932	0.1215	0.047	1
C16	2a	0.7627(6)	0.4824(6)	-0.0424(2)	0.047(3)	1
H16A	2a	0.8132	0.3602	-0.0405	0.047	1
H16B	2a	0.7215	0.5138	-0.1002	0.047	1
O2	2a	0.8927(1)	0.6105(3)	-0.0066(3)	0.047(3)	1
H2	2a	0.9569	0.644	0.0359	0.047	1

Table S5: Selected bond distances and bond angles for the refined crystal structures at room temperature

Composition	Atoms	Bond distance (Å)	Atoms	Bond angle (°)
$Fe(3\text{-}PyM)_2[Ni(CN)_4]$	Ni-C1	1.895(5)	Ni-C1-N1	166.1(4)
	Ni-C2	1.872(4)	Ni-C2-N2	169.0(4)
	Ni-C3	1.876(4)	Ni-C3-N3	169.3(6)
	Ni-C4	1.882(4)	Ni-C4-N4	167.4(6)
	C1-N1	1.148(4)	Fe-N1-C1	158.2(4)
	C2-N2	1.147(3)	Fe-N2-C2	159.1(5)
	C3-N3	1.146(2)	Fe-N3-C3	165.7(2)
	C4-N4	1.145(4)	Fe-N4-C4	166.4(7)
	Fe-N1	2.107(5)		
	Fe-N2	2.118(4)		
	Fe-N3	2.210(3)		
	Fe-N4	2.213(4)		
	Fe-N5	2.119(8)		
	Fe-N6	1.953(10)		
$Fe(3\text{-}PyM)_2[Pd(CN)_4]$	Pd-C1	1.993(4)	Pd-C1-N1	170.7(5)

	Pd-C2	1.998(3)	Pd-C2-N2	175.2(5)
	Pd-C3	1.999(4)	Pd-C3-N3	177.3(3)
	Pd-C4	1.993(4)	Pd-C4-N4	176.0(4)
	C1-N1	1.130(4)	Fe-N1-C1	166.2(3)
	C2-N2	1.136(3)	Fe-N2-C2	171.22(19)
	C3-N3	1.139(3)	Fe-N3-C3	170.0(3)
	C4-N4	1.135(4)	Fe-N4-C4	163.8(5)
	Fe-N1	2.044(3)		
	Fe-N2	2.251(3)		
	Fe-N3	2.386(3)		
	Fe-N4	2.173(4)		
	Fe-N5	2.259(12)		
	Fe-N6	2.244(7)		
$Fe(3\text{-}PyM)_2[Pt(CN)_4]$	Pt-C1	1.997(4)	Pt-C1-N1	172.7(4)
	Pt-C2	1.995(4)	Pt-C2-N2	171.4(3)
	Pt-C3	1.990(4)	Pt-C3-N3	168.3(5)
	Pt-C4	1.993(4)	Pt-C4-N4	161.2(3)
	C1-N1	1.138(4)	Fe-N1-C1	159.2(6)
	C2-N2	1.140(4)	Fe-N2-C2	165.3(3)
	C3-N3	1.139(4)	Fe-N3-C3	165.6(3)
	C4-N4	1.139(5)	Fe-N4-C4	155.9(3)
	Fe-N1	2.431(5)		
	Fe-N2	2.125(4)		
	Fe-N3	2.016(4)		
	Fe-N4	2.321(4)		
	Fe-N5	2.272(10)		
	Fe-N6	2.132(10)		

Table S6. Relevant interatomic distances and angles of the iron atom coordination environment in the $Fe(3PyMe)_2[M(CN)_4]$ series with M = Ni, Pd, and Pt.

Metal	**Phase**	**$Fe–N_{3OHPy}$ (Å)**	**$Fe–N_{CN}$ (Å)**	**Ring-ring (Å)**	**Ring-ring (°)**
Ni	HS (296 K), XRD	2.036(8)	2.162(5)	3.758	28.96
Pd	HS (296 K), XRD	2.201(7)	2.213(4)	3.938	21.77
Pt	HS (296 K), XRD	2.252(10)	2.223(4)	3.676	16.69