

Electronic Supporting Information (ESI)

Structures and paramagnetism of five heterometallic pentanuclear metal strings containing as many as four different metals: $\text{NiPtCo}_2\text{Pd}(\text{tpda})_4\text{Cl}_2$

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Table of Contents

Experimental Section

Physical measurements, Methods and Spin Hamiltonian

Materials and Methods

Synthesis

NMR and Mass Spectra

Figure S1: ^1H NMR spectrum of $[\text{CoPdCo}_3(\text{tpda})_4\text{Cl}_2]$ (**1**) in CDCl_3

Figure S2: ^1H NMR spectrum of $[\text{CoPtCo}_3(\text{tpda})_4\text{Cl}_2]$ (**2**) in CDCl_3

Figure S3: ^1H NMR spectrum of $[\text{CoPdCo}_2\text{Pd}(\text{tpda})_4\text{Cl}_2]$ (**3**) in CD_2Cl_2

Figure S4: ^1H NMR spectrum of $[\text{CoPtCo}_2\text{Pd}(\text{tpda})_4\text{Cl}_2]$ (**4**) in CD_2Cl_2

Figure S5: 2D COSY NMR spectrum of $[\text{CoPtCo}_2\text{Pd}(\text{tpda})_4\text{Cl}_2]$ (**4**) in CD_2Cl_2 (full range)

Figure S6: 2D COSY NMR spectrum of $[\text{CoPtCo}_2\text{Pd}(\text{tpda})_4\text{Cl}_2]$ (**4**) in CD_2Cl_2 (small range)

Figure S7: ^1H NMR spectrum of $[\text{NiPtCo}_2\text{Pd}(\text{tpda})_4\text{Cl}_2]$ (**5**) in CD_2Cl_2

Figure S8: High resolution MALDI spectrum and simulation of $[\text{CoPtCo}_2\text{Pd}(\text{tpda})_4\text{Cl}_2]$ (**4**) and $[\text{NiPtCo}_2\text{Pd}(\text{tpda})_4\text{Cl}_2]$ (**5**)

Crystallographic Section

Figure S9: The crystal structures of $[\text{CoPdCo}_3(\text{tpda})_4\text{Cl}_2]$ (**1**) and $[\text{CoPtCo}_3(\text{tpda})_4\text{Cl}_2]$ (**2**)

Figure S10: The crystal structures of $[\text{CoPdCo}_2\text{Pd}(\text{tpda})_4\text{Cl}_2]$ (**3**) and $[\text{CoPtCo}_2\text{Pd}(\text{tpda})_4\text{Cl}_2]$ (**4**).

Figure S11: The crystal structure of $[\text{CoPtCo}(\text{dpa})_4\text{Cl}_2]$

Figure S12: The selected distances of related compounds

Figure S13: The cumulative intensity distribution of reflection statistics in **3**, **4** and **5**

Table S1: Crystal data and structure refinement details for **1** · 3 CH_2Cl_2

Table S2: Crystal data and structure refinement details for **2** · 3 CH_2Cl_2 .

Table S3: Crystal data and structure refinement details for **3** · CH_2Cl_2

Table S4: Crystal data and structure refinement details for **4** · 0.5 CH_2Cl_2

Table S5: Crystal data and structure refinement details for **5** · 0.5 CH_2Cl_2

Table S6: Crystal data and structure refinement details for $\text{CoPtCo}(\text{dpa})_4\text{Cl}_2 \cdot \text{Et}_2\text{O}$

Experimental Section

Physical measurements, Methods and Spin Hamiltonian

Crystal data was collected on a Bruker SMART Apex and Bruker D8 VENTURE diffractometer with monochromatized Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at $T = 150(2) \text{ K}$. Cell parameters were retrieved and refined using *DENZOSMN* software on all observed reflections. Data reduction was performed with the *DENZOSMN* software. Empirical absorption was based on the symmetry-equivalent reflections and absorption corrections were applied with the SORTAV program. All the structures were solved and refined with *SHELXL-2014* or *SHELXL-2018* by full-matrix least squares on F^2 values with the *Olex2* interface.¹ The diagrams of cumulative intensity distribution in reflection statistics were generated by *Olex2* program.¹ The hydrogen atoms were included in calculated positions and refined with a riding model. IR spectra were obtained with a Nicolet Fourier-Transform in the range 450–4000 cm^{-1} . The mass spectra were measured by Bruker New ultrafleXtreme™ MALDI-TOF mass spectrometer. ¹H NMR spectra were recorded with a Bruker AMX 300 MHz spectrometer.

Magnetic measurements were carried out with a Quantum Design MPMS7 SQUID magnetometer operating at a magnetic field of 3000 G between 4 and 300 K. The diamagnetic corrections were evaluated from Pascal's constants. The program *MagProp* in the DAVE packaged software² was applied to fit the magnetic susceptibility by means of the spin Hamiltonian equations (1) and (2). In compounds **1** and **2**, the equation (1) was applied to obtain the exchange coupling constant J between terminal Co^{2+} ($S_1 = 3/2$) and low spin of tricobalt unit ($S_2 = 1/2$; 4 ~ 150K). The zero-field splitting parameter (D_1) of terminal Co^{2+} is included in this fitting. Unfortunately, we failed to fit the data for the high temperatures region (150 – 300K) due to the uncertainties and the complication of 2nd spin crossover of the inner tricobalt system at high temperatures (refer to *J. Am. Chem. Soc.*, 2000, **122**, 6226-6236). As for the isolated spin center in compound **4**, the ZFS parameter (D) of Co(II) were included in equation (2) (4 ~ 300K). We neglect the higher order terms and the ZFS E term which are two to three orders of magnitude smaller the other terms. Similarly, we applied equation (2) to fit the data for compound **5**.

$$\hat{H} = -2J\hat{S}_1\hat{S}_2 + \beta(g_1\hat{S}_1 + g_2\hat{S}_2)H + D_1[\hat{S}_{1z}^2 - (1/3)S_1(S_1 + 1)] \quad (1)$$

$$\hat{H} = \beta H \cdot g \cdot \hat{S} + D[\hat{S}_z^2 - (1/3)S(S + 1)] \quad (2)$$

Where J is the exchange coupling constant, $g\beta HS$ is the electronic Zeeman interaction, D is the zero-field splitting (ZFS).

Materials and Methods

All manipulations were carried out under argon or nitrogen atmosphere by using standard Schlenk techniques unless indicated otherwise. Solvents were purified by standard methods and freshly distilled under nitrogen atmosphere prior to use. Anhydrous CoCl_2 , Co(OAc)_2 and the $t\text{BuOK}$ were used as

received from commercial sources. The 2,6-bis(2-pyridylamino)pyridine(H_2tpda), ³ Bis(2-pyridyl)amine($Hdpa$) ⁴, $Pt(CH_3CN)_2Cl_2$, ⁵ and $Pd(CH_3CN)_2Cl_2$ ⁶ were synthesized following published procedures.

Synthesis

[$CoPdCo_3(tpda)_4Cl_2$] (1):

In a 250 mL Erlenmeyer flask, H_2tpda (526 mg, 2 mmol), $Pd(CH_3CN)_2Cl_2$ (156 mg, 0.6 mmol) and anhydrous $CoCl_2$ (260 mg, 2 mmol) were mixed with 40 g naphthalene under Argon. The mixture was heated to 150°C for 1 hour. After that, the temperature was adjusted to 220°C for another 2 hours. The brown mixture was cooled to room temperature and the naphthalene was solidified. A solid of *t*-BuOK (421 mg, 3.75 mmol) was added into the flask. This mixture was then heated to 150°C for 15 mins under argon. The brown precipitate was dissolved, and the solution turned to dark red gradually. The temperature was then increased to 220°C (refluxing naphthalene) and kept at this temperature for 8 hours. This dark red solution was cooled to room temperature and treated it with hot hexane (200 mL) to precipitate the metal complex. After filtration, the brown solid was subsequently extracted with 150 ml CH_2Cl_2 . The red solution was condensed to 30 mL. Then, a 40 mL of MeOH was added. The solution was slowly evaporated by rotatory evaporation without water bath until red micro-crystal precipitated. The crystal was collected and washed with ether. The dark red crystal was obtained by diffusion of diethyl ether into the CH_2Cl_2 solution of complex. (200 mg, 27% yield). IR (KBr, cm^{-1}): 1600 m, , 1547 m, 1471 m, 1450 m, 1407 s, 1356 m, 1338 m, 1155 m, 765 m. MS(MALDI) m/z : 1458 $[M]^+$, 1423 $[M-Cl]^+$; ¹ H NMR (300 MHz, $CDCl_3$): δ (ppm) 83.14 (b, 4H), 63.10 (4H), 32.34 (4H), 31.03 (4H) , 17.15 (4H), 14.41 (4H), 10.76 (4H) , 8.63 (4H) , 5.48 (4H) , 4.47 (4H) , 4.15 (4H). Elemental analysis (%): calcd. C 49.42, H 3.04, N 19.21; found: C 49.59, H 3.10, N 19.12

[$CoPtCo_3(tpda)_4Cl_2$] (2):

The compound **2** was synthesized by using the same reaction conditions as above description, except that the $Pt(CH_3CN)_2Cl_2$ (209 mg, 0.6 mmol) was applied as Pt^{2+} precursor. (153 mg, 20% yield). IR (KBr, cm^{-1}): 1600 m, , 1547 m, 1472 m, 1451 m, 1406 s, 1350 m, 1333 m, 1153 m, 766 m. MS(MALDI) m/z : 1547 $[M]^+$, 1511 $[M-Cl]^+$; ¹ H NMR (300 MHz, $CDCl_3$): δ (ppm) 60.74 (b, 4H), 49.84 (4H), 24.89 (4H), 19.81 (4H) , 18.34 (4H), 15.93 (4H), 13.49 (4H) , 9.11 (4H) , 8.23 (4H) , 6.22 (4H) , 3.41 (4H). Elemental analysis (%): calcd. C 46.59, H 2.87, N 18.11; found: C 46.73, H 2.98, N 18.02

[$CoPdCo_2Pd(tpda)_4Cl_2$] (3):

In a 150 mL Erlenmeyer flask, the [$CoPdCo_3(tpda)_4Cl_2$] (1) (95 mg, 0.065 mmol) and anhydrous $Co(OAc)_2$ (35 mg, 0.2 mmol) were mixed with 30 g naphthalene under Argon. The mixture was heated to 200°C and then an 8 mL of $Pd(CH_3CN)_2Cl_2$ (52 mg, 0.2 mmol) in CH_3CN was dropwise added into the flask over a time period of 25 mins. After addition, the temperature was adjusted to 220°C for

another 35 mins. The brown solution was cooled to room temperature. The solidified naphthalene was treated with 100 mL hot hexane. The brown precipitate was collected by filtration and extracted by 100 mL CH₂Cl₂. The crude product was purified by short silica gel column chromatography. The trace of unreacted **1** was flashed off by using 20% (Acetone/CH₂Cl₂) and the product was afforded by using 50% (Acetone/CH₂Cl₂) as eluent. The dark red crystal was obtained by diffusion of ether into the CH₂Cl₂ solution of complex. (39 mg, 40 % yield). IR (KBr, cm⁻¹): 1602 m, , 1575 m, 1544 m, 1474 m, 1452 m, 1421 s, 1355 m, 1335 m, 1154 m, 766 m, 731 m. MS(MALDI) *m/z*: 1470 [M-Cl]⁺ ; ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 96.79 (b, 4H), 77.01 (s, 4H), 34.81 (s, 4H), 11.53 (s, 4H) ,10.51 (d, 4H) , 7.23 (d, 4H), 6.92 (m, 8H), 6.44 (t, 4H) , 4.96 (d, 4H), 4.01 (d, 4H). Elemental analysis (%): calcd. C 47.86, H 2.95, N 18.60; found: C 48.02, H 3.03, N 18.51

[CoPtCo₂Pd(tdpa)₄Cl₂] (4):

The compound **4** was synthesized by using the same reaction conditions as above description, except that the [CoPtCo₃(tdpa)₄Cl₂] (**2**) (100 mg, 0.065 mmol) was used. (42 mg, 41% yield) IR (KBr, cm⁻¹): 1602 m, , 1576 m, 1545 m, 1474 m, 1451 m, 1421 s, 1351 m, 1331 m, 1156 m, 765 m, 732 m. MS(MALDI) *m/z*: 1558 [M-Cl]⁺ ; ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 79.57 (b, 4H), 68.56 (s, 4H), 20.16 (s, 4H), 15.13 (d, 4H) , 12.20 (d, 4H), 9.95 (d, 4H), 9.54 (t, 4H) , 8.21 (t, 4H), 7.23 (t, 4H), 3.49 (s, 8H). Elemental analysis (%): calcd. C 45.20, H 2.78, N 17.57; found: C 45.35, H 2.89, N 17.48

[NiPtCo₂Pd(tdpa)₄Cl₂] (5):

In a 150 mL Erlenmeyer flask, [CoPtCo₂Pd(tdpa)₄Cl₂] (**2**) (100 mg, 0.063 mmol) and Ni(OAc)₂·4H₂O (63 mg, 0.253 mmol) were mixed with 30 g naphthalene for 4 hours under Argon. After cooling to ca. 80 °C, n-hexane (100 mL) was added in the brown solution to precipitate the metal complex. After filtration, the crude material was washed with hexane to remove naphthalene residues. The brown solid was subsequently extracted with 100 ml CH₂Cl₂. The solution was then condensed to ~30 mL. The dark brown crystal was formed by layering the CH₂Cl₂ solution with ether. Yield: 82 mg, 82 %. The dark brown crystal was obtained by diffusion of ether into the CH₂Cl₂ solution of complex. IR (KBr, cm⁻¹): 1602 m, , 1576 m, 1544 m, 1473 m, 1452 m, 1420 s, 1351 m, 1330 m, 1155 m, 767 m, 732 m. MS(MALDI) *m/z*: 1558 [M-Cl]⁺ ; ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 67.41 (b, 4H), 25.28 (b, 4H), 12.20 (b, 4H), 11.17 (b, 4H) , 8.98 (b, 4H), 7.90 (b, 4H), 7.71 (b, 4H) , 7.36 (b, 4H) , 6.57(b, 4H) , 6.01 (b, 4H). Elemental analysis (%): calcd. C 45.21, H 2.78, N 17.57; found: C 45.42, H 2.89, N 17.46

[CoPtCo(dpa)₄Cl₂]:

Hdpa (342 mg, 2 mmol) was dissolved in 30g naphthalene at 150°C by using 150 mL Erlenmeyer flask under air. The Pt(CH₃CN)₂Cl₂ (174 mg, 0.5 mmol) and anhydrous CoCl₂ (130 mg, 1 mmol) were added into the solution. The temperature was raised to refluxed naphthalene (220°C) for 30 minutes. After that, a solid of *t*-BuOK (224 mg, 2 mmol) was added into the flask by several small portions. This mixture was then kept at refluxed temperature for 3 hours under air. This dark orange solution

was cooled to room temperature and treated it with hot hexane (200 mL) to precipitate the metal complex. After filtration, the brown solid was extracted with 50 ml CH_2Cl_2 . The mixture was purified by silica gel column with eluent 10% (Acetone/ CH_2Cl_2). The final product was obtained by layer of CH_2Cl_2 solution with diethyl ether. The dark orange crystal was collected and washed with ether. (316 mg, 59% yield). IR (KBr, cm^{-1}): 1603 m, 1593 m, 1549 m, 1469 s, 1460 s, 1423 s, 1363 m, 1347 m, 1316 m, 1284 m, 1155 m, 767 m. MS(MALDI) m/z : 1064 $[\text{M}]^+$; ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) 35.25 (b, 4H), 24.25 (4H), 14.69 (4H), 7.83 (4H). Elemental analysis (%): calcd. C 45.13, H 3.03, N 15.79; found: C 45.37, H 3.10, N 15.68

Spectroscopic Characterization

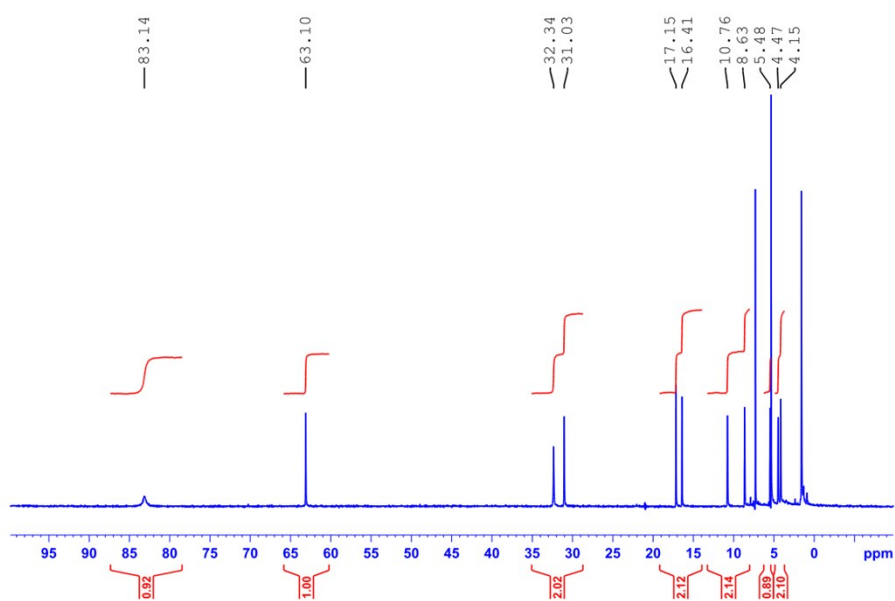


Figure S1: ^1H NMR spectrum of $[\text{CoPdCo}_3(\text{tpda})_4\text{Cl}_2]$ (1) in CDCl_3

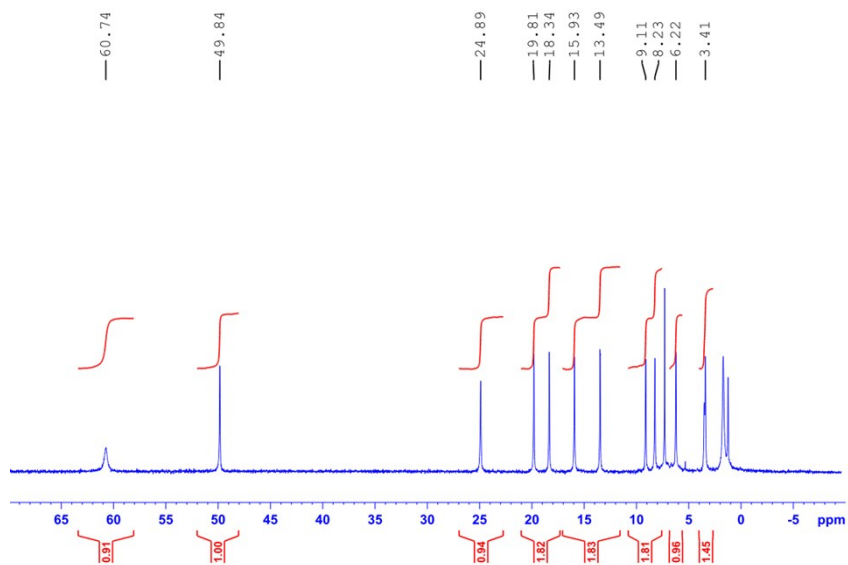


Figure S2: ^1H NMR spectrum of $[\text{CoPtCo}_3(\text{tpda})_4\text{Cl}_2]$ (**2**) in CDCl_3

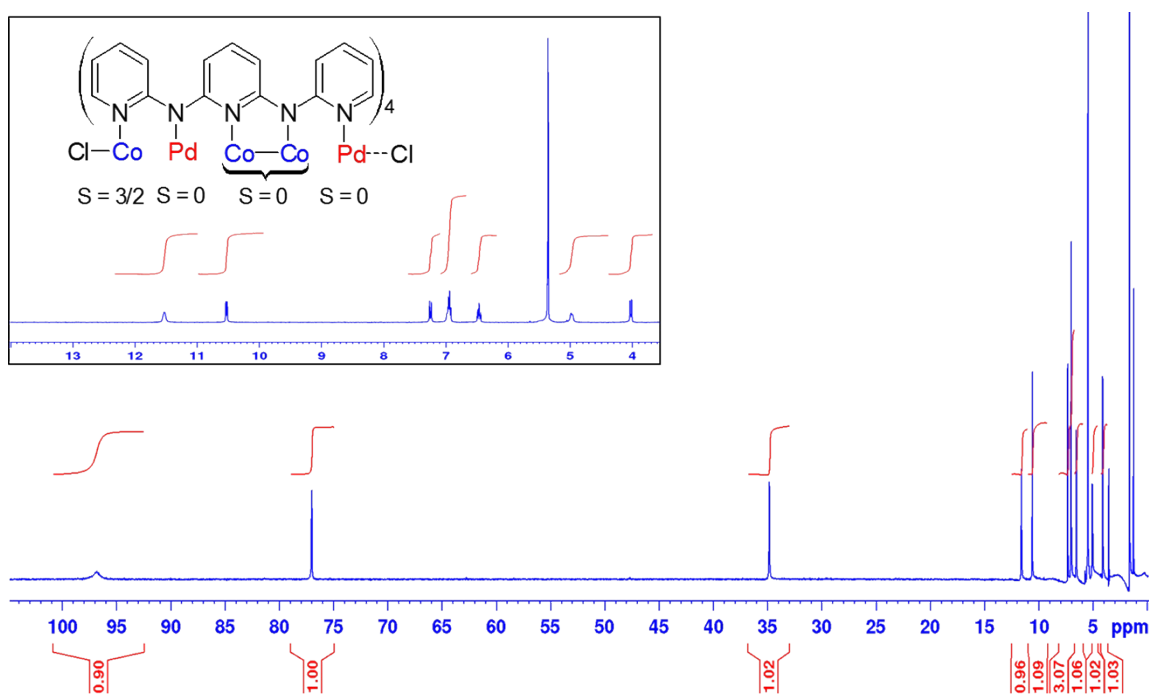


Figure S3: ^1H NMR spectrum of $[\text{CoPdCo}_2\text{Pd}(\text{tpda})_4\text{Cl}_2]$ (**3**) in CD_2Cl_2

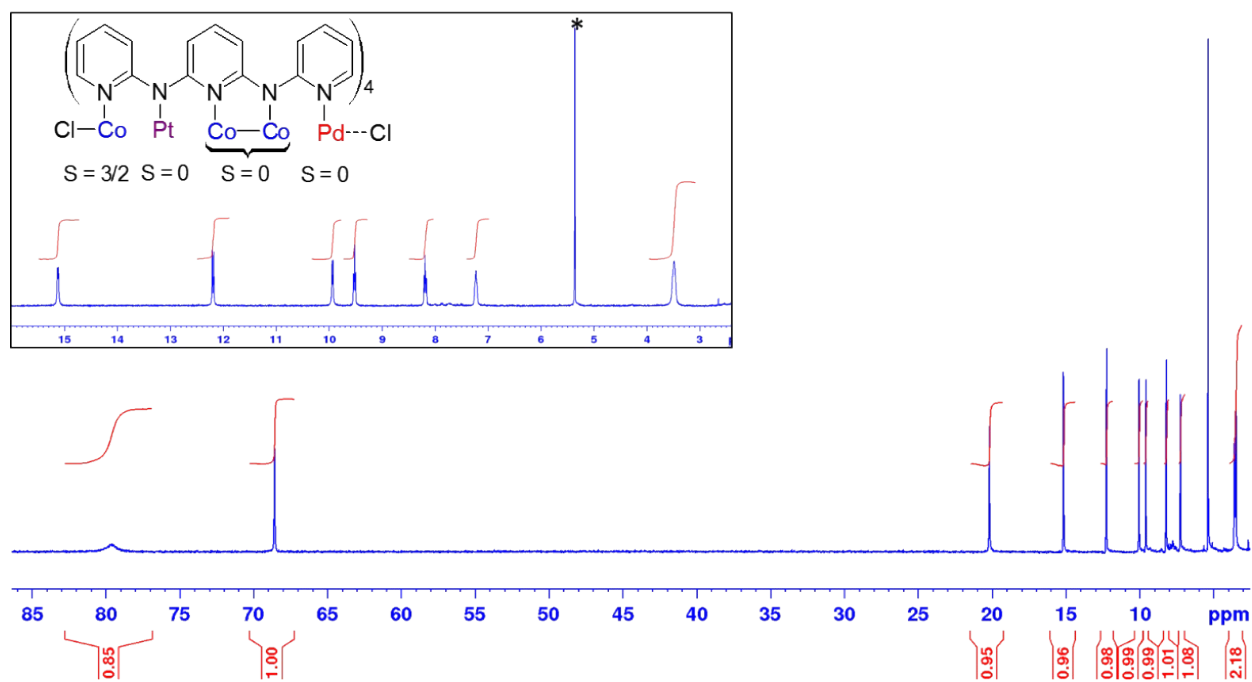


Figure S4: ^1H NMR spectrum of $[\text{CoPtCo}_2\text{Pd}(\text{tpda})_4\text{Cl}_2]$ (**4**) in CD_2Cl_2

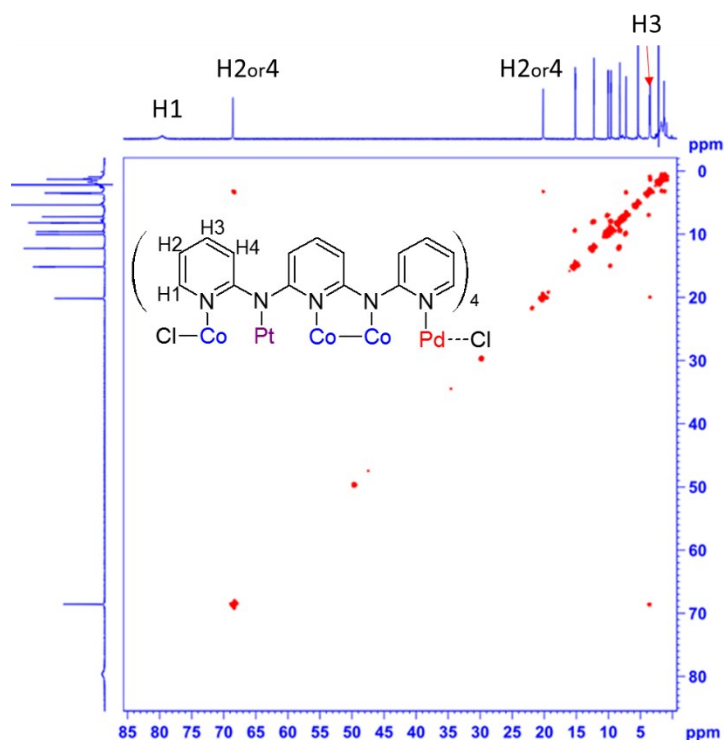


Figure S5: 2D COSY NMR spectrum of $[\text{CoPtCo}_2\text{Pd}(\text{tpda})_4\text{Cl}_2]$ (**4**) in CD_2Cl_2 (full range).

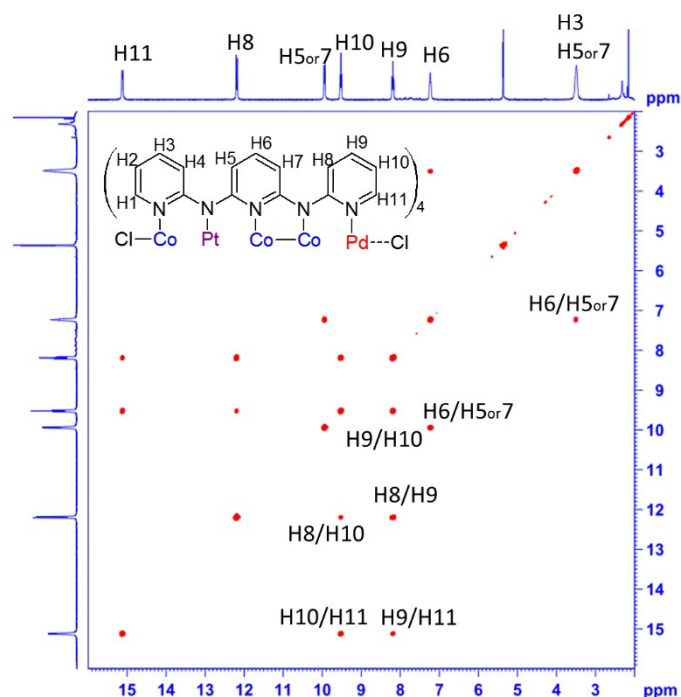


Figure S6: 2D COSY NMR spectrum of $[\text{CoPtCo}_2\text{Pd}(\text{tpda})_4\text{Cl}_2]$ (**4**) in CD_2Cl_2 (small range). The H5 and H7 are indistinguishable from the spectrum. The assignment of H8 and H11 is based on the coupling constant.⁷ ($J_{8,9} = 8.2$ Hz; $J_{10,11} = 5.8$ Hz) The relatively small red dots (lower intensity) at H8/H10 and H9/H11 are from long range coupling.

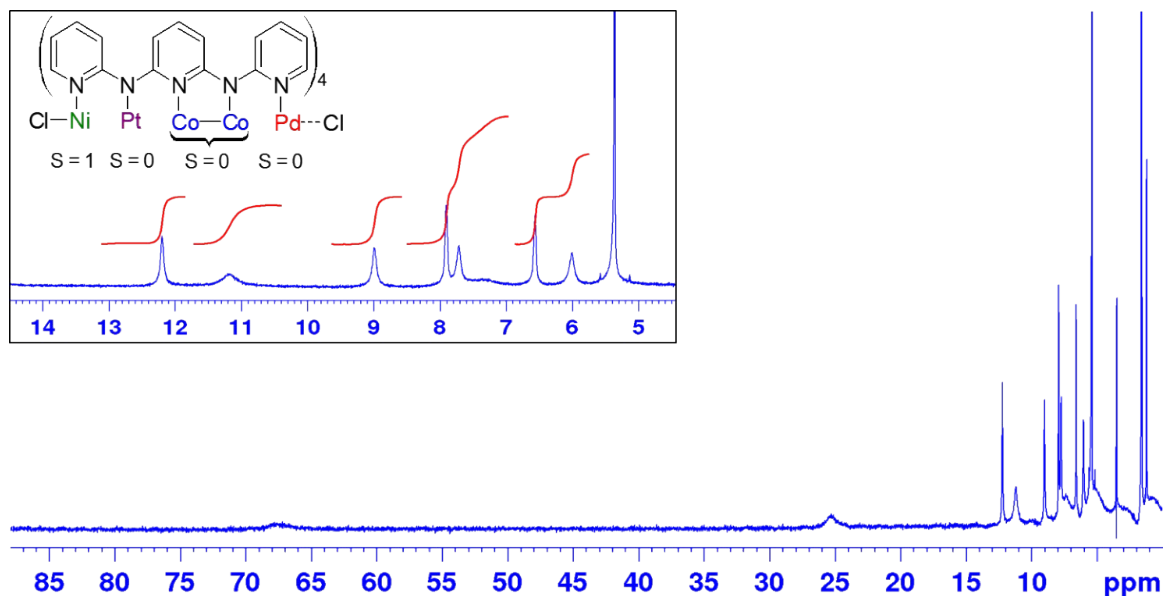


Figure S7: ^1H NMR spectrum of $[\text{NiPtCo}_2\text{Pd}(\text{tpda})_4\text{Cl}_2]$ (**5**) in CD_2Cl_2 . Because of the fast relaxation of protons, the 2D COSY NMR measurement was unsuccessful and one of the eleven peaks is too broad to be detected.

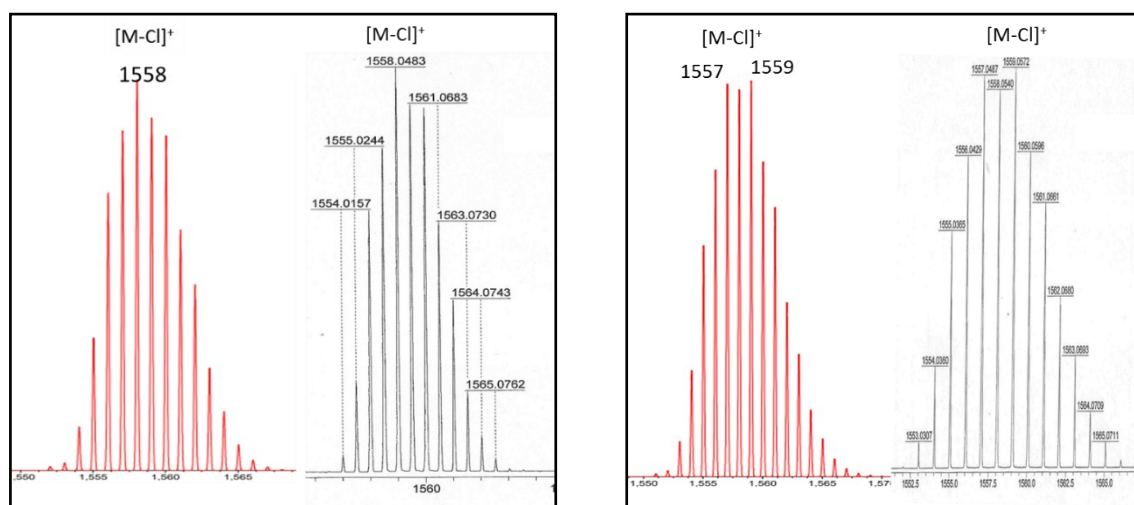


Figure S8: High resolution MALDI spectrum (black line) and their simulation (red line) of $[\text{CoPtCo}_2\text{Pd}(\text{tpda})_4\text{Cl}_2]$ (**4**)(right) and $[\text{NiPtCo}_2\text{Pd}(\text{tpda})_4\text{Cl}_2]$ (**5**)(left). The chloride coordinated on Pd site is weak interaction, which is rather like ion-pair. Therefore, the fragment of loss one Cl ($[\text{M}-\text{Cl}]^+$) is detectable only.

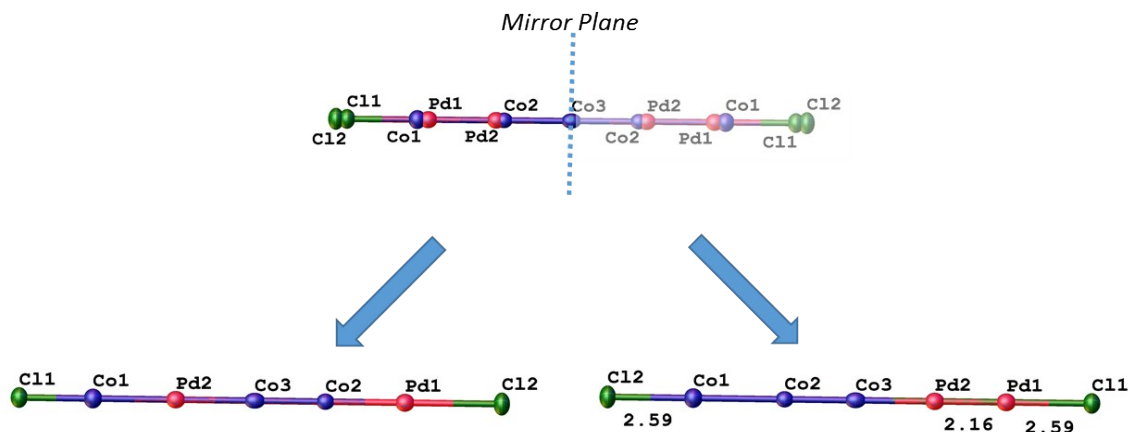
Crystallographic Section:

Structural description, metal identification and refining method:

The complex **1** [CoPdCo₃(tdpa)₄Cl₂] locates at general position with metal cores disorder. The space group is P2₁/c and the number of molecules in the asymmetric unit is one ($Z' = 1$). The Co and Pd at the amide position are disorder due to the composition of unsymmetrical metal cores. The M2 and M4 represent the different combination of Pd and Co occupancy. The FVAR command in *SHELXL* program is applied to determine the metal occupancy of Pd and Co in M2 and M4 position. Likewise, the M2 and M4 in isostructural complex **2** [CoPtCo₃(tdpa)₄Cl₂] are different combination of Pt and Co. The same method is applied to obtain the metal occupancy.

In compounds **3**, **4** and **5**, the cumulative intensity distribution in reflection statistics show that the space group of crystals belongs to centrosymmetric groups. (Figure S13) Therefore, the space group I4/m is chosen for solving crystal structures.^{8,9} In addition, these compounds are isostructure in crystallography. The complex **3** [CoPdCo₂Pd(tdpa)₄Cl₂] locates at special position and the number of molecules in the asymmetric unit is one eighth ($Z' = 0.125$). The whole molecule can be generated by symmetrical operations of a *4-fold* rotation axes along the metal cores and a *mirror* plane that is passing through the center cobalt (Co3) and perpendicular to the molecular plane. Owing to these two operations, the occupancy of all metals and axial chloride are fixed at 0.125 in the input file for refining structure. After the symmetric operation of the *mirror* plane, the metal cores can be generated into two possibilities of arrangement in compound **3**. One is CoPdCoCoPd and the other is CoCoCoPdPd (as shown below). The later one is eliminated due to having too short Pd-Pd distance (2.16 Å). Similarly, there are two sets of metal-chloride distances. One is Co1-Cl1: 2.24 Å / Pd1-Cl2: 2.95 Å and the other is Co1-Cl2: 2.59 Å / Pd1-Cl1: 2.59 Å. The later one is omitted due to having too long Co-Cl distance. Because of the isostructure in crystallography, the same metal identification and refining methods are able to be applied to deal with the structures of compounds **4** and **5**.

The space group of [CoPtCo(dpa)₄Cl₂] is P2₁/c and the number of molecules in the asymmetric unit is one ($Z' = 1$). This complex locates at general position and there is no disorder in structure.



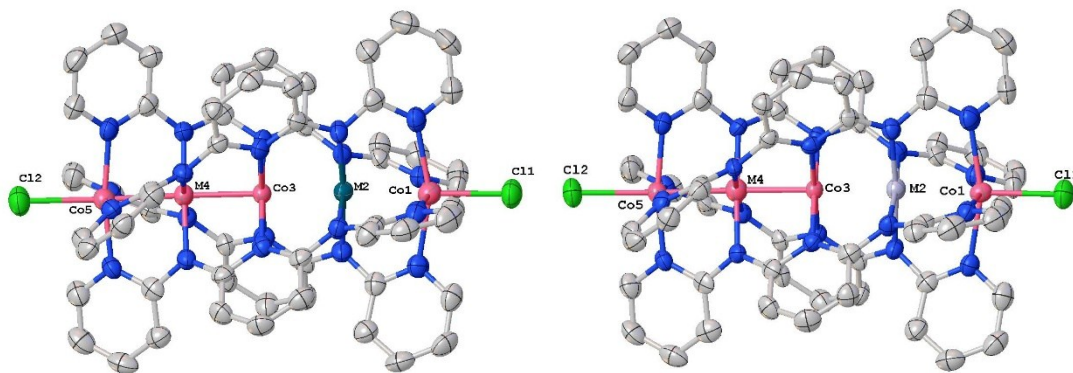


Figure S9: The crystal structures of $[\text{CoPdCo}_3(\text{tdpa})_4\text{Cl}_2]$ (1) (left) and $[\text{CoPtCo}_3(\text{tdpa})_4\text{Cl}_2]$ (2) (right). All atoms are drawn at the 50% probability level. The solvent molecules and hydrogen atoms are omitted for clarity and the crystals with major occupancy are chosen for display. Crystal occupancy contributions: $[\text{CoPdCo}_3(\text{tdpa})_4\text{Cl}_2]$ (1): M2 = 0.885 Pd / 0.115 Co and M4 = 0.885 Co / 0.115 Pd ; $[\text{CoPtCo}_3(\text{tdpa})_4\text{Cl}_2]$ (2): M2 = 0.915 Pt / 0.085 Co and M4 = 0.915 Co / 0.015 Pt.

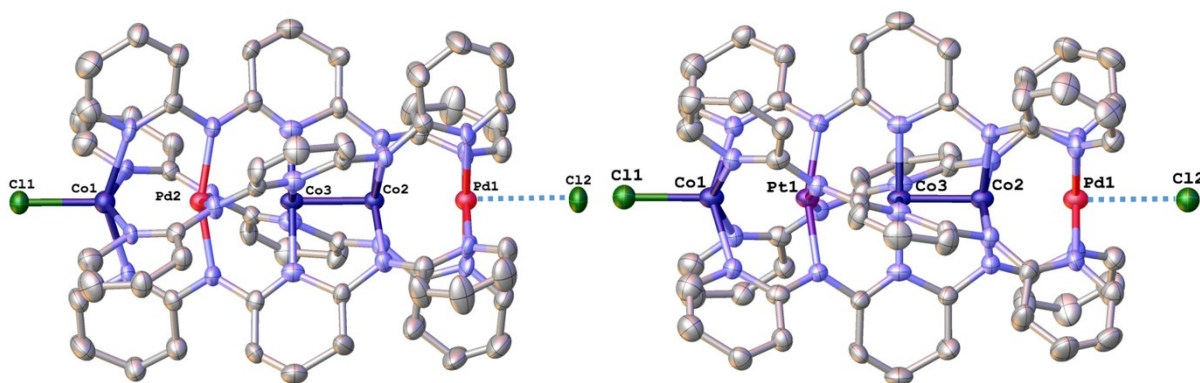


Figure S10: The crystal structures of $[\text{CoPdCo}_2\text{Pd}(\text{tdpa})_4\text{Cl}_2]$ (3) (left) and $[\text{CoPtCo}_2\text{Pd}(\text{tdpa})_4\text{Cl}_2]$ (4) (right). The solvent molecules and hydrogen atoms are omitted for clarity. All atoms are drawn at the 50% probability level.

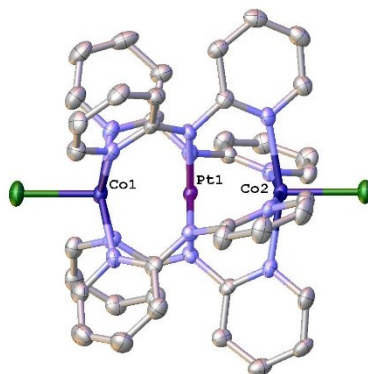


Figure S11: The crystal structure of $[\text{CoPtCo}(\text{dpa})_4\text{Cl}_2]$. The solvent molecules and hydrogen atoms are omitted for clarity. All atoms are drawn at the 50% probability level.

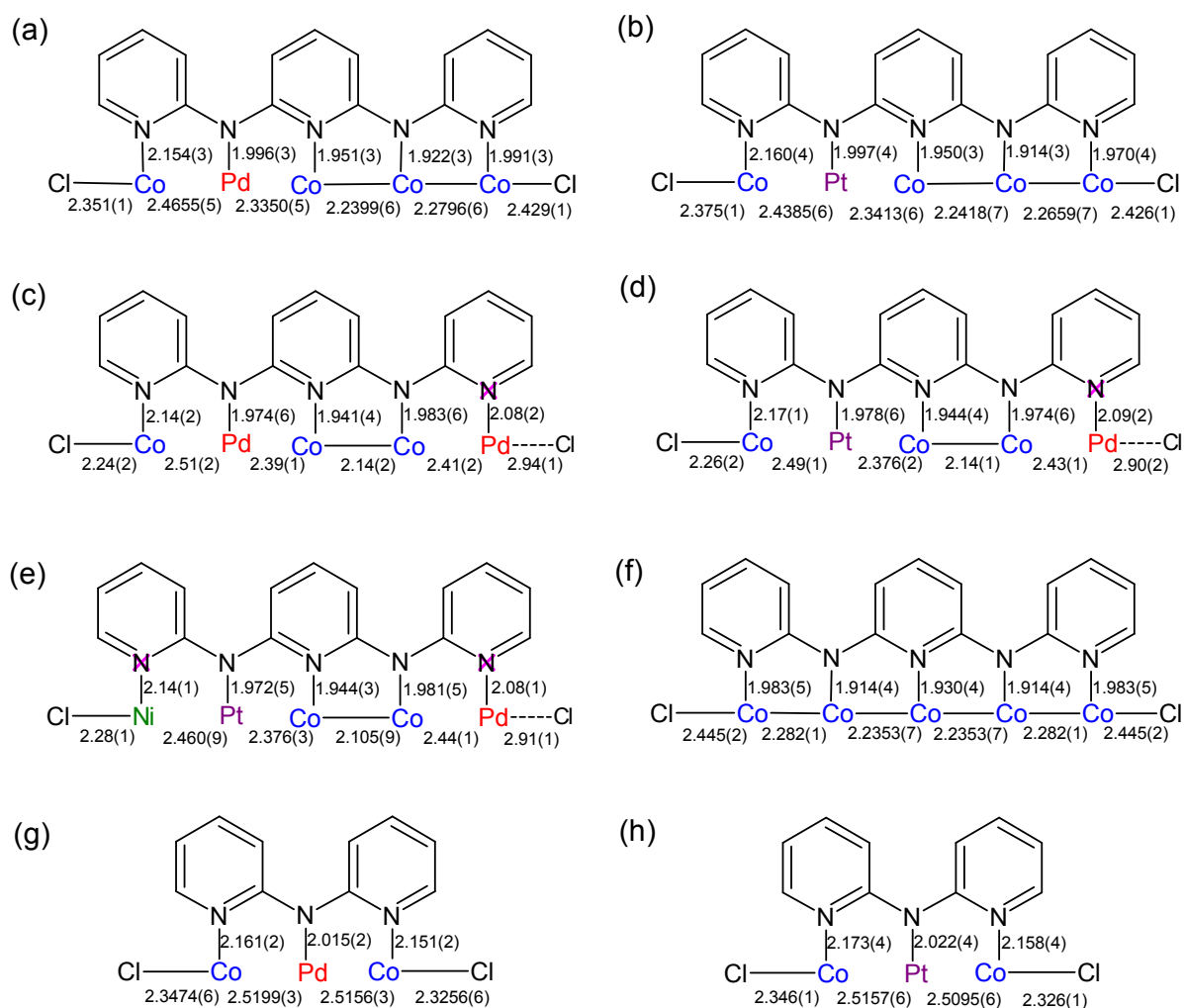


Figure S12: The selected distances of related compounds illustrated in simplified structures.

(a) $[\text{CoPdCo}_3(\text{tdpa})_4\text{Cl}_2]$ (1), (b) $[\text{CoPtCo}_3(\text{tdpa})_4\text{Cl}_2]$ (2), (c) $[\text{CoPdCo}_2\text{Pd}(\text{tdpa})_4\text{Cl}_2]$ (3), (d) $[\text{CoPtCo}_2\text{Pd}(\text{tdpa})_4\text{Cl}_2]$ (4), (e) $[\text{NiPtCo}_2\text{Pd}(\text{tdpa})_4\text{Cl}_2]$ (5), (f) $[\text{Co}_5(\text{tdpa})_4\text{Cl}_2]$ ¹⁰, (g) $[\text{CoPdCo}(\text{dpa})_4\text{Cl}_2]$ ¹¹, (h) $[\text{CoPtCo}(\text{dpa})_4\text{Cl}_2]$. The distances of 1 in (a) and 2 in (b) are selected from the major occupancy of structures (~90%). Because of the minor disorder of metal center, the distances in (1) and (2) are approximately close to the real value, but not the precise value.

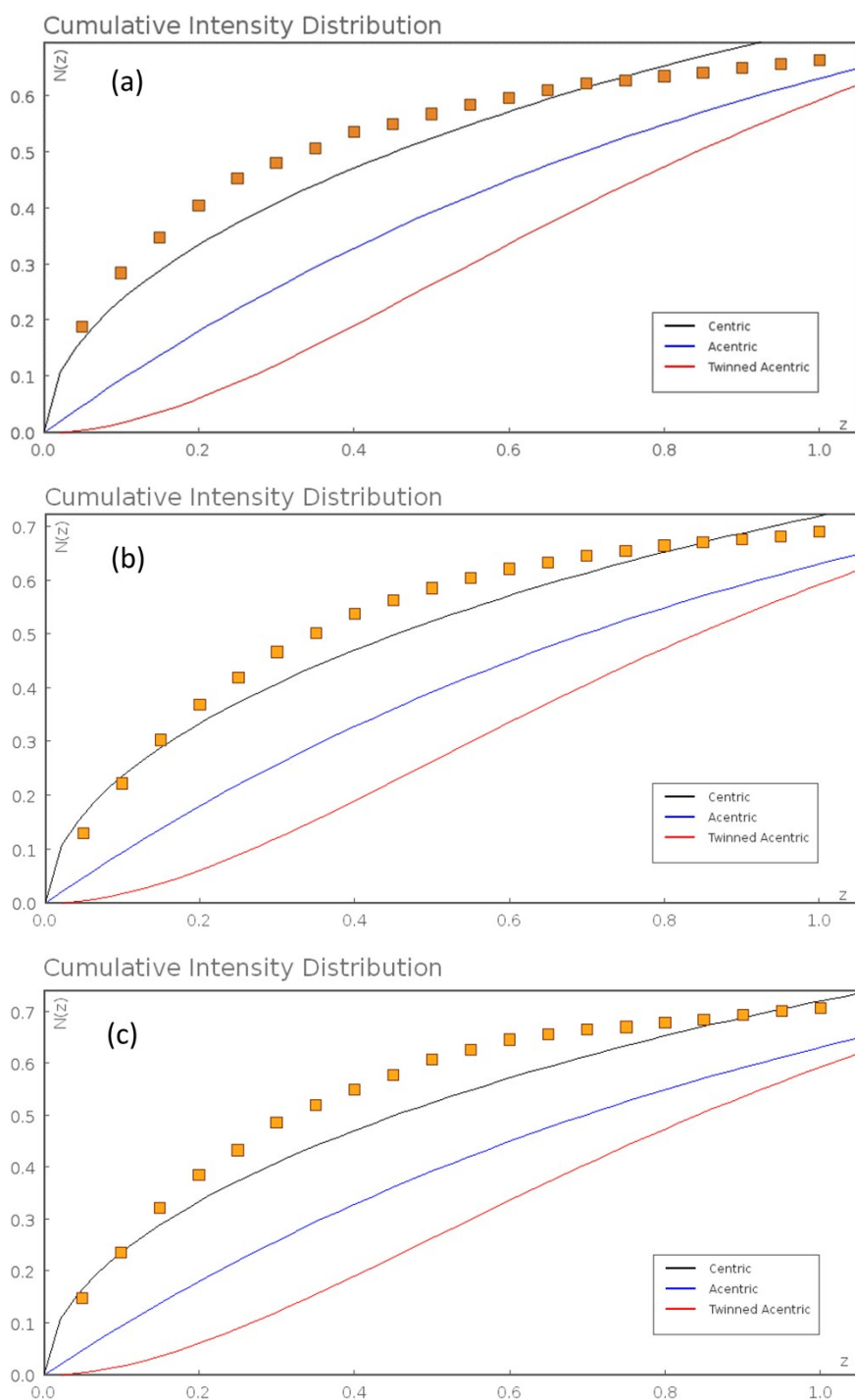


Figure S13: The cumulative intensity distribution of reflection statistics

(a): $[\text{CoPdCo}_2\text{Pd}(\text{tdpa})_4\text{Cl}_2]$ (**3**), (b): $[\text{CoPtCo}_2\text{Pd}(\text{tdpa})_4\text{Cl}_2]$ (**4**), (c): $[\text{NiPtCo}_2\text{Pd}(\text{tdpa})_4\text{Cl}_2]$ (**5**)

The red, blue and black lines represent the theoretical value for twinned, non-centrosymmetric and centrosymmetric crystals, respectively. The orange dots are the experimental data.

Table S1. Crystal data and structure refinement details for **1** · 3CH₂Cl₂

Empirical formula	C63 H50 Cl8 Co4 N20 Pd	
Formula weight	1712.95	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 20.0796(2) Å	α = 90°.
	b = 15.9485(2) Å	β = 108.4299(7)°.
	c = 21.4276(3) Å	γ = 90°.
Volume	6510.02(14) Å ³	
Z	4	
Density (calculated)	1.748 Mg/m ³	
Absorption coefficient	1.657 mm ⁻¹	
F(000)	3432	
Crystal size	0.220 x 0.200 x 0.200 mm ³	
Theta range for data collection	1.623 to 27.499°.	
Index ranges	-26 ≤ h ≤ 26, -20 ≤ k ≤ 20, -27 ≤ l ≤ 27	
Reflections collected	36214	
Independent reflections	14909 [R(int) = 0.0482]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.733 and 0.712	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	14909 / 7 / 873	
Goodness-of-fit on F ²	1.036	
Final R indices [I > 2σ(I)]	R1 = 0.0432, wR2 = 0.0999	
R indices (all data)	R1 = 0.0872, wR2 = 0.1122	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.139 and -1.419 e.Å ⁻³	

Table S2. Crystal data and structure refinement details for $2 \cdot 3\text{CH}_2\text{Cl}_2$.

Empirical formula	C63 H50 Cl8 Co4 N20 Pt	
Formula weight	1801.64	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 20.0753(3) Å	$\alpha = 90^\circ$.
	b = 15.9501(2) Å	$\beta = 108.4468(5)^\circ$.
	c = 21.4567(3) Å	$\gamma = 90^\circ$.
Volume	6517.48(16) Å ³	
Z	4	
Density (calculated)	1.836 Mg/m ³	
Absorption coefficient	3.524 mm ⁻¹	
F(000)	3560	
Crystal size	0.230 x 0.230 x 0.220 mm ³	
Theta range for data collection	1.069 to 27.499°.	
Index ranges	$-26 \leq h \leq 26$, $-16 \leq k \leq 20$, $-26 \leq l \leq 27$	
Reflections collected	38788	
Independent reflections	14929 [R(int) = 0.0464]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.761 and 0.748	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	14929 / 7 / 873	
Goodness-of-fit on F ²	1.057	
Final R indices [I > 2sigma(I)]	R1 = 0.0410, wR2 = 0.0983	
R indices (all data)	R1 = 0.0711, wR2 = 0.1067	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.046 and -1.600 e.Å ⁻³	

Table S3. Crystal data and structure refinement details for $3 \cdot \text{CH}_2\text{Cl}_2$

Empirical formula	C61 H46 Cl4 Co3 N20 Pd2	
Formula weight	1590.57	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I4/m	
Unit cell dimensions	a = 10.5246(4) Å	$\alpha = 90^\circ$.
	b = 10.5246(4) Å	$\beta = 90^\circ$.
	c = 27.1616(11) Å	$\gamma = 90^\circ$.
Volume	3008.6(3) Å ³	
Z	2	
Density (calculated)	1.756 Mg/m ³	
Absorption coefficient	1.634 mm ⁻¹	
F(000)	1586	
Crystal size	0.167 x 0.155 x 0.127 mm ³	
Theta range for data collection	2.075 to 27.482°.	
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -31 ≤ l ≤ 35	
Reflections collected	6289	
Independent reflections	1762 [R(int) = 0.0431]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.789 and 0.646	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1762 / 45 / 200	
Goodness-of-fit on F ²	1.087	
Final R indices [I > 2σ(I)]	R1 = 0.0450, wR2 = 0.1203	
R indices (all data)	R1 = 0.0753, wR2 = 0.1384	
Extinction coefficient	0.0025(4)	
Largest diff. peak and hole	1.566 and -1.135 e.Å ⁻³	

Table S4. Crystal data and structure refinement details for $4 \cdot 0.5\text{CH}_2\text{Cl}_2$

Empirical formula	C60.50 H45 Cl3 Co3 N20 Pd Pt	
Formula weight	1636.79	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I4/m	
Unit cell dimensions	a = 10.5398(6) Å	$\alpha = 90^\circ$.
	b = 10.5398(6) Å	$\beta = 90^\circ$.
	c = 27.1120(14) Å	$\gamma = 90^\circ$.
Volume	3011.8(4) Å ³	
Z	2	
Density (calculated)	1.805 Mg/m ³	
Absorption coefficient	3.608 mm ⁻¹	
F(000)	1608	
Crystal size	0.167 x 0.155 x 0.127 mm ³	
Theta range for data collection	2.969 to 27.479°.	
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -34 ≤ l ≤ 22	
Reflections collected	6035	
Independent reflections	1757 [R(int) = 0.0345]	
Completeness to theta = 25.242°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.636 and 0.563	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1757 / 38 / 196	
Goodness-of-fit on F ²	1.078	
Final R indices [I > 2σ(I)]	R1 = 0.0369, wR2 = 0.1102	
R indices (all data)	R1 = 0.0534, wR2 = 0.1199	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.303 and -0.767 e.Å ⁻³	

Table S5. Crystal data and structure refinement details for $5 \cdot 0.5\text{CH}_2\text{Cl}_2$

Empirical formula	C60.50 H45 Cl3 Co2 N20 Ni Pd Pt	
Formula weight	1636.57	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I4/m	
Unit cell dimensions	a = 10.5523(4) Å	$\alpha = 90^\circ$.
	b = 10.5523(4) Å	$\beta = 90^\circ$.
	c = 27.0046(9) Å	$\gamma = 90^\circ$.
Volume	3007.0(2) Å ³	
Z	2	
Density (calculated)	1.808 Mg/m ³	
Absorption coefficient	3.651 mm ⁻¹	
F(000)	1610	
Crystal size	0.120 x 0.120 x 0.110 mm ³	
Theta range for data collection	2.730 to 27.496°.	
Index ranges	-13 ≤ h ≤ 13, -10 ≤ k ≤ 13, -33 ≤ l ≤ 34	
Reflections collected	9131	
Independent reflections	1774 [R(int) = 0.0232]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6387	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1774 / 39 / 200	
Goodness-of-fit on F ²	1.084	
Final R indices [I > 2σ(I)]	R1 = 0.0287, wR2 = 0.0886	
R indices (all data)	R1 = 0.0365, wR2 = 0.0961	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.707 and -0.694 e.Å ⁻³	

Table S6. Crystal data and structure refinement details for CoPtCo(dpa)₄Cl₂·Et₂O

Empirical formula	C ₄₄ H ₄₀ Cl ₂ Co ₂ N ₁₂ O Pt
Formula weight	1136.73
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 16.0911(2) Å α = 90°. b = 15.7779(2) Å β = 97.7811(8)°. c = 17.0753(2) Å γ = 90°.
Volume	4295.22(9) Å ³
Z	4
Density (calculated)	1.758 Mg/m ³
Absorption coefficient	4.188 mm ⁻¹
F(000)	2248
Crystal size	0.440 x 0.250 x 0.100 mm ³
Theta range for data collection	1.765 to 27.498°.
Index ranges	-20 ≤ h ≤ 20, -20 ≤ k ≤ 20, -17 ≤ l ≤ 22
Reflections collected	22297
Independent reflections	9783 [R(int) = 0.0485]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.637 and 0.382
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	9783 / 0 / 561
Goodness-of-fit on F ²	0.977
Final R indices [I > 2σ(I)]	R1 = 0.0388, wR2 = 0.0813
R indices (all data)	R1 = 0.0631, wR2 = 0.0885
Extinction coefficient	n/a
Largest diff. peak and hole	2.045 and -2.402 e.Å ⁻³

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