Supplementary material for:

Fe(II) and Co(II) *N*-methylated CYCLEN complexes as paraSHIFT agents with large temperature dependent shifts

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Table of Contents **Page**

Materials and Methods

Instrumentation. A Varian Inova 500 MHz NMR spectrometer equipped with FTS Systems TC-84 Kinetics Air Jet Temperature Controller was used to collect ^{1}H NMR spectra. ^{13}C NMR spectra were acquired using a Varian Mercury 300 MHz NMR spectrometer operating at 75 MHz. A Fisher Scientific™ accumet™ micro glass mercury-free combination pH electrode connected to a Thermo Scientific™ Orion Star™ A211 pH benchtop meter was used for pH measurements. ThermoFinnigan LCQ Advantage IonTrap LC/MS equipped with a Surveyor HPLC system was used to collect mass spectral data.

Materials. All solvents and reagents were reagent grade, and they were used as received without additional purification. 1,4,7,10-Tetraazacyclododecane (CYCLEN) was obtained from Strem Chemicals, Inc. (Newburyport, MA). Iodomethane (≥99%), *N*,*N*-diisopropylethylamine (DIPEA) and 18-crown-6 (≥99.5%) were obtained from Sigma-Aldrich (St. Louis, MO). 2-Bromomethyl-6-methylpyridine (97%), benzyl chloroformate (95%), cobalt(II) chloride hexahydrate (98%) and iron(II) chloride tetrahydrate (98%) were received from Alfa Aesar (Ward Hill, MA). 3-(Trimethylsilyl)-1-propanesulfonic acid sodium salt (>98%) (TMSP) was purchased from TCI America (Portland, OR). Basic alumina (50-200 µm) and neutral alumina (60-325 µm) were obtained from Dynamic Adsorbents, Inc. (Norcross, GA) and ThermoFisher Scientific (Waltham, MA), respectively.

Magnetic moments. The effective magnetic moment (μ_{eff}, BM) was calculated by using modified Evans' method for small molecules at 298 K as in Eq. S1 – S2.[1] Solutions (8-10 mM) of **[Fe(BMPC)]Cl$_2$**, **[Co(BMPC)]Cl$_2$**, **[Fe(2MPC)]Cl$_2$** and **[Co(2MPC)]Cl$_2$** in deuterium oxide, pD 6.5 – pD 7.0, containing 5% *tert*-butanol (v/v) and 100 mM NaCl were placed in NMR tube inserts, while a reference solution containing 5% *tert*-butanol (v/v) and 100 mM NaCl in deuterium oxide, pD 7.0, was placed into NMR tubes. The paramagnetic molar susceptibility χ_M^p (cm^3·mole^{-1}) at 25 °C was calculated using eq. S1:

$$\chi_M^p = -\frac{3\Delta f \cdot M^p}{4\pi \nu_0 m} - \chi_M^{dia} \qquad \text{Eq. S1}$$

$$\mu_{eff} = 2.83(\chi_M^p T)^{1/2} \qquad \text{Eq. S2}$$

where Δf is the shift in frequency (Hz); M^p is the molecular mass of the dissolved paramagnetic compound (g·mole^{-1}); ν_0 is the operating frequency of NMR spectrometer (Hz); *m* is the concentration of the solute (g·cm^{-3}); χ_M^{dia} is diamagnetic contribution to the molar susceptibility (cm^3·mole^{-1}), which is neglected for small molecules.[1c] Three independently measured values of μ_{eff} were averaged.

Crystallization and X-ray diffraction data collection

Uniform crystals of [Co(BMPC)]Cl_2 complex were formed from neat methanol at 4 ^{o}C after 10 days. Single crystals were mounted on glass fibers with oil on a Bruker SMART APEX-II CCD diffractometer installed at a rotating anode source (MoKα radiation, λ = 0.71073 Å). The crystals were kept at 90(2) K during data collection using an Oxford Cryosystems 700 series Cryostream cooler. The data was collected by the rotation method with 0.5° frame width (ω scan) and 120 s exposure times per frame. Two sets of data (360 frames in each set) were collected for the sample nominally covering complete reciprocal space. The structure was solved using Olex2[2] with the olex2.solve[3] structure solution program using Charge Flipping and refined with the XL[4] refinement package using Least Squares minimization. The hydrogen atoms bound to all nitrogen atoms of secondary amines were observed in an electron density difference map, and all other protons were placed in idealized positions and subsequently refined. The twist angles (θ) for this complex were calculated as dihedral angles defined by the centroids of two mean planes and two atoms, one from each plane, as described previously.[5]

***T_1* measurements.** The 60-100 mM solutions of complexes in deuterium oxide, pD 6.8-7.0, were used for the inversion-recovery T_1 experiments at 25 ^{o}C. The standard two-pulse sequence (180^{o} pulse followed by 90^{o} pulse) was employed. The 90-degree pulse width was calibrated routinely before each set of measurements. The minimum expected T_1, the maximum expected T_1 and the total time (maximum 2 hours used) of each experiment were varied and optimized. The ^{1}H NMR spectrum of each complex was divided into several regions to ensure effective inversion of the spin populations, as well as to avoid having off-axis magnetization and fold-overs when the observed pulse was applied. The baseline correction was performed for all spectra. In order to determine the value of T_1, the array of values of the parameter *d2*, which is between min T_1 and max T_1, were fit by an exponential curve as in eq. S3:

$$M(t) = (M(0) - M_0) \cdot exp\left(-\frac{t}{T_1}\right) + M_0 \qquad \text{Eq. S3}$$

where M_0 is the equilibrium *Z* magnetization and *M*(0) is the magnetization at time zero, which is immediately after the 180^{o} pulse for an inversion recovery T_1 experiment. The T_1 values were obtained by averaging data from at least two independent experiments.

Dissociation of complexes. Acid-induced dissociation was studied on the D_2O solutions containing 10-12 mM of complexes and 100 mM NaCl at pD 3.5(1). Biological anion-induced dissociation was studied on the D_2O solutions containing 10-12 mM of complexes, 100 mM NaCl, 0.40 mM Na_2HPO_4, and 25 mM K_2CO_3 at pD 7.0-7.4. All samples contained 10 mM 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (TMSP) as an internal ^{1}H NMR standard. ^{1}H NMR spectra (25 °C) were collected periodically over 24 hours using samples which were incubated at 37 °C. Integrated intensities of the paramagnetically shifted methyl and aromatic protons were compared to integrated intensities of methyl protons of TMSP for the quantification of % dissociation.[6]

Synthetic Methods

1,7-Bis(benzyloxycarbonyl)-1,4,7,10-tetraazacyclododecane (**1**) was synthesized according to the published procedure.[7]

***1,7-Bis(benzyloxycarbonyl)-4,10-bis[(6-methyl-2-pyridyl)methyl]-1,4,7,10-tetraazacyclododecane* (2a).** 2-Bromomethyl-6-methylpyridine (0.66 g, 3.52 mmol, 2.1 equiv.) was added to argon-purged solution of **1** (0.74 g, 1.68 mmol, 1.0 equiv.) and DIPEA (0.73 mL, 4.20 mmol, 2.5 equiv.) in acetonitrile (60 mL) at 70 °C (Scheme 2). The reaction mixture was stirred at 70 °C under argon for 3 h. The reaction mixture was cooled to room temperature and solvent was removed *in vacuo* producing brown oil. This oil was partitioned between chloroform (100 mL) and water (50 mL). Organic layer was isolated, and the aqueous layer was additionally washed with chloroform (3 × 100 mL). Organic extracts were combined, dried over Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo* producing brown residue. The crude product was purified by column chromatography using basic Al_2O_3 packed with methylene chloride. The product was eluted by a solvent gradient containing 0% to 2% of methanol in methylene chloride. Yield: 0.69 g, 1.06 mmol, 63%. ^{1}H NMR, 500 MHz (DMSO-d_6, 55 °C, ppm): δ = 7.49 t (2H, J = 10 Hz, Ar), 7.34 – 7.23 m (6H, Ar), 7.18 d (4H, J = 5 Hz, Ar), 7.10 d (2H, J = 10 Hz, Ar), 7.05 d (2H, J = 10 Hz, Ar), 4.89 s (4H, $2CH_2$), 3.65 s (4H, $2CH_2$), 3.38 m (8H, $4CH_2$), 2.65 m (8H, $4CH_2$), 2.41 s (6H, $2CH_3$). ^{13}C NMR, 500 MHz (DMSO-d_6, 55 °C, ppm): δ = 158.05, 156.59, 155.26, 136.70, 136.05, 127.95, 127.45, 127.35, 127.12, 120.80, 119.76, 65.73, 60.15, 53.96, 49.11, 23.72. ESI-MS (m/z), calculated: 651.4 $[M+H^+]$. Found: 651.4 (100%) $[M+H^+]$ and 326.4 (35%) $[(M+2H^+)/2]$.

***1,7-Bis[(6-methyl-2-pyridyl)methyl]-1,4,7,10-tetrazacyclododecane* (BMPC).** Compound **2a** (0.30 g, 0.46 mmol) was dissolved in 40 mL of methanol, and the solution was added to a Parr hydrogenator ready flask containing 0.10 g of 10 wt.% Pd/C (5 mol %) under Ar atmosphere followed by addition of catalytic amount of acetic acid (60 µL). Hydrogenation was carried out at 50 psi of H_2 for 18 h (Scheme 2). Reaction mixture was filtered *via* Celite, and filtrate was concentrated *in vacuo* producing yellowish oil. This oil was further purified on a plug of basic Al_2O_3 using 5% MeOH in DCM as an eluent. The solvent was removed *in vacuo*, and the resultant colorless oil solidified in a fridge. Yield: 0.17 g, 0.44 mmol, 97%. ^{1}H NMR, 500 MHz ($CDCl_3$, ppm): δ = 7.53 t (2H, *J* = 10 Hz, Ar), 7.26 d (2H, *J* = 10 Hz, Ar), 7.01 d (2H, *J* = 10 Hz, Ar), 3.77 s (4H, $2CH_2$), 2.68 m (16H, $8CH_2$), 2.50 s (6H, $2CH_3$). ^{13}C NMR, 75 MHz (CD_3OD, ppm): δ = 159.71, 159.23, 139.01, 123.61, 122.12, 62.05, 52.78, 46.25, 24.23. ESI-MS (*m*/*z*), calculated: 383.3 [$M+H^+$]. Found: 383.4 (100%) [$M+H^+$].

1,7-Bis(benzyloxycarbonyl)-4,10-dimethyl-1,4,7,10-tetraazacyclododecane **(2b).** Compound **1** (0.83 g, 1.88 mmol, 1.0 equiv.) was dissolved in acetonitrile (120 mL) followed by addition of K_2CO_3 (0.57 g, 4.14 mmol, 2.2 equiv.) and catalytic amount of 18-crown-6 (0.02 g, 0.08 mmol, 4 mol%). Iodomethane (0.26 mL, 4.14 mmol, 2.2 equiv.) dissolved in 40 mL of acetonitrile was added drop-wise over 40 min to the reaction mixture stirred at 65 °C (Scheme 2). After addition is complete, the reaction mixture was further stirred at 70 °C under Ar atmosphere. After 12 h at 70 °C the reaction mixture was cooled to r.t., and insoluble solids were removed by filtration. The filtrate was concentrated *in vacuo*, and the residue was re-suspended in 80 mL of DCM. After stirring for 30 min the inorganic solids were removed by filtration again. The solvent (DCM) was evaporated, and the crude product was purified by column chromatography using basic Al_2O_3 packed with 100% DCM. A solvent gradient of 0 to 1% methanol in DCM was used as an eluent. The fractions containing pure product were concentrated affording compound **2b** as yellow oil. Yield: 0.28 g, 0.60 mmol, 32%. ^{1}H NMR, 500 MHz ($CDCl_3$, ppm): δ = 7.38 – 7.24 m (10H, Ar), 5.14 s (4H, $2CH_2$), 3.50 – 3.20 m (8H, $4CH_2$), 2.66 – 2.54 m (8H, $4CH_2$), 2.32 – 2.15 m (6H, $2CH_3$). ^{13}C NMR, 75 MHz ($CDCl_3$, ppm): δ = 156.30, 136.83, 128.31, 128.13, 128.05, 127.76, 127.67, 66.82, 56.82, 46.74, 42.60. ESI-MS (*m*/*z*), calculated: 469.3 [$M+H^+$]. Found: 469.3 (100%) [$M+H^+$].

1,7-Dimethyl-1,4,7,10-tetraazacyclododecane **(3b).** Compound **2b** (0.56 g, 1.20 mmol) was dissolved in 50 mL of methanol, and the solution was added to a Parr hydrogenator ready flask containing 80 mg of 10% Pd/C under Ar atmosphere followed by addition of catalytic amount of acetic acid (50 µL). The hydrogenation was carried out at 50 psi of H_2 for 24 h (Scheme 2). Palladium black was removed by filtration on Celite, and filtrate was concentrated *in vacuo* producing a yellowish oil. Yield: 0.24 g, 1.19 mmol, 99%. ESI-MS (*m*/*z*), calculated: 201.2 [$M+H^+$]. Found: 201.3 (100%) [$M+H^+$] and 223.3 (60%) [$M+Na^+$]. The crude **3b** was used for the next step without purification.

1,7-Bis[(6-methyl-2-pyridyl)methyl]-4,10-dimethyl-1,4,7,10-tetrazacyclododecane **(2MPC).** 2-Bromomethyl-6-methylpyridine (0.45 g, 2.40 mmol, 2.0 equiv.) was added to an argon-purged solution of crude **3b** (0.24 g, 1.19 mmol, 1.0 equiv.) and DIPEA (0.52 mL, 3.00 mmol, 2.5 equiv.) in acetonitrile (50 mL) at 70 ^{o}C (Scheme 2). The reaction mixture was stirred at 70 ^{o}C under argon for 8 h. The reaction mixture was cooled to room temperature and solvent was removed *in vacuo,* producing a yellow oil. The crude product was further purified by column chromatography using neutral Al_2O_3 and a solvent gradient containing 0 to 8% of methanol in methylene chloride. Yield: 0.22 g, 0.54 mmol, 45%. ^{1}H NMR, 500 MHz ($CDCl_3$, ppm): δ = 7.62 dt (2H, J_1 = 65 Hz, J_2 = 10 Hz, Ar), 7.18 dd (2H, J_1 = 13 Hz, J_2 = 10 Hz, Ar), 7.06 t (2H, J_1 = 5 Hz, Ar), 3.76 s (4H, $2CH_2$), 2.82 m (8H, $4CH_2$), 2.62 m (8H, $4CH_3$), 2.50 s (6H, $2CH_3$), 2.46 s (6H, $2CH_3$). ^{13}C NMR, 75 MHz (CD_3OD, ppm): δ = 159.64, 158.43, 138.90, 123.84, 123.04, 62.59, 57.66, 51.72, 44.02, 24.34. ESI-MS (*m/z*), calculated: 411.3 [$M+H^+$]. Found: 411.4 (100%) [$M+H^+$] and 433.5 (80%) [$M+Na^+$].

Synthesis of Fe(II) and Co(II) complexes. The Fe(II) complexes of BMPC and 2MPC ligands are prepared from the corresponding metal(II) salts in acetonitrile/water mixtures, while the Co(II) complexes are synthesized in neat acetonitrile. These syntheses have been previously reported for **[Fe(TMPC)]$^{2+}$** and **[Co(TMPC)]$^{2+}$**, respectively.[5] The general procedures are described below.

Synthesis of [Fe(2MPC)]Cl$_2$. 2MPC (40 mg, 97 μmol) was dissolved in a mixture of acetonitrile (0.3 mL) and water (0.6 mL) followed by addition of $FeCl_2{\cdot}4H_2O$ (18 mg, 93 μmol, 0.95 equiv.). Small aliquots (1.0-2.0 μL) of 0.1-1.0 M NaOH aqueous solution were gradually added under constant stirring to adjust to pH 7.0. The reaction mixture was stirred for 40 min under constant pH 6.8-7.0. The brown cloudy impurities were removed by centrifugation, and resultant clear yellow solution was concentrated by using a SpeedVac centrifugal evaporator. The yellow solids were washed with diethyl ether and dried *in vacuo*. Yield: 32 mg, 60 μmol, 62%. ESI-MS (*m/z*), found: 233.4 (100%) [M/2], 501.3 (20%) [$M+Cl^-$].

Synthesis of [Fe(BMPC)]Cl$_2$ was carried out similar to the synthesis of **[Fe(2MPC)]Cl$_2$**, and the product was isolated as a pale solid. ESI-MS (*m/z*), found: 220.3 (70%) [M/2], 437.3 (100%) [$M–H^+$], 473.2 (20%) [$M+Cl^-$].

Synthesis of [Co(2MPC)]Cl$_2$. 2MPC (60 mg, 0.15 mmol) and $CoCl_2{\cdot}6H_2O$ (36 mg, 0.15 mmol, 1.0 equiv.) were stirred in acetonitrile (0.9 mL) under argon for 12 h. The blue solids were collected by centrifugation, washed with diethyl ether and dried *in vacuo*. Yield: 45 mg, 84 μmol, 57%. ESI-MS (*m/z*), found: 234.8 (100%) [M/2], 505.1 (20%) [$M+Cl^-$]

Synthesis of [Co(BMPC)]Cl$_2$ was carried out similar to the synthesis of **[Co(2MPC)]Cl$_2$**, and the product was isolated as a light blue solid. ESI-MS (*m/z*), found: 220.9. (100%) [M/2], 476.2 (20%) [M+Cl].

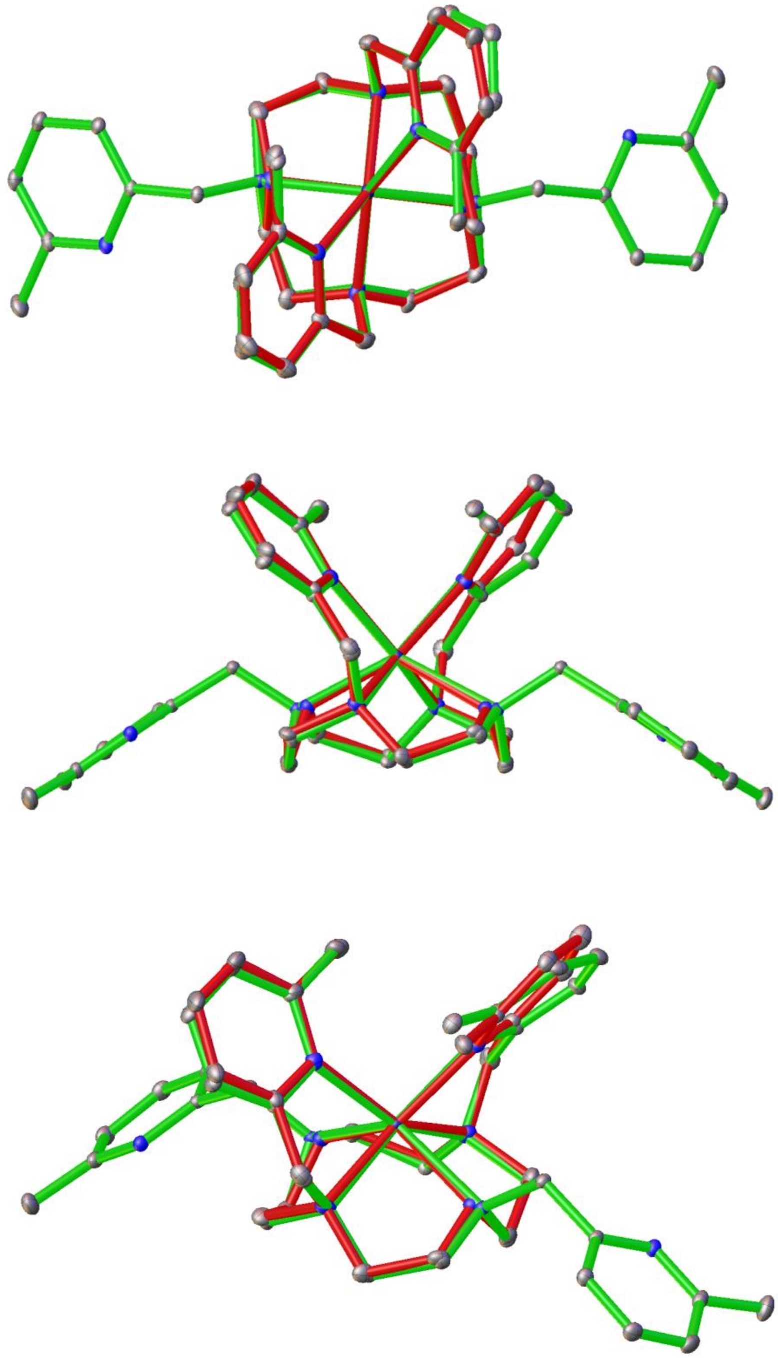

Figure S1. Overlap of structures of **[Co(TMPC)]$^{2+}$** (green) and **[Co(BMPC)]$^{2+}$** (red). The structure of **[Co(TMPC)]$^{2+}$** is adapted from reference [5].

Table S1. T_1 values of selected proton resonances of complexes in D_2O at 25 °C.*

	T_1 (ms)				
[Fe(BMPC)]$^{2+}$	**H1**	**Ar1**	**Ar2**	**Ar3**	**CH_3-Pyr**
	241.4 ppm	55 ppm	45 ppm	11.3 ppm	-22.5 ppm
	0.97 ± 0.02	5.98 ± 0.04	4.53 ± 0.04	12.74 ± 0.14	0.62 ± 0.01
[Co(BMPC)]$^{2+}$	**H5**	**Ar1**	**Ar2**	**Ar3**	**CH_3-Pyr**
	152.62 ppm	56.30 ppm	52.71 ppm	19.25 ppm	-80.51 ppm
	0.67 ± 0.01	0.95 ± 0.01	1.75 ± 0.01	3.05 ± 0.01	0.30 ± 0.00
[Fe(2MPC)]$^{2+}$	**CH_3-N**	**Ar1**	**Ar2**	**Ar3**	**CH_3-Pyr**
	104.78 ppm	54.0 ppm	53.6 ppm	10.88 ppm	-45.49
	1.1 ± 0.1	10.1 ± 0.1	5.4 ± 0.1	18.1 ± 0.1	1.0 ± 0.0
[Co(2MPC)]$^{2+}$	**CH_3-N**	**Ar1**	**Ar2**	**Ar3**	**CH_3-Pyr**
	164.43 ppm	70.60 ppm	55.28 ppm	24.0 ppm	-112.53 ppm
	0.18 ± 0.01	1.4 ± 0.2	2.7 ± 0.0	4.2 ± 0.1	0.44 ± 0.01

* – Measured in 60-100 mM solutions of complexes containing 100 mM NaCl in D_2O, pD 6.8-7.4.

Table S2. R_1 and R_2 values for complexes at 11.7 T, 25 °C.

Complex	**Type of CH_3**	**R_1 (s^{-1})**	**R_2 (s^{-1})***	**R_1/R_2**
[Fe(BMPC)]$^{2+}$	CH_3-Pyr	1610	1510	≈1
[Fe(2MPC)]$^{2+}$	CH_3-N	909	1130	0.80
	CH_3-Pyr	1000	1230	0.81
[Co(BMPC)]$^{2+}$	CH_3-Pyr	3330	3610	0.92
[Co(2MPC)]$^{2+}$	CH_3-N	5560	6230	0.89
	CH_3-Pyr	2272	2660	0.85

* R_2 calculated as π(FWHM) of ^1H resonances in Table 1.

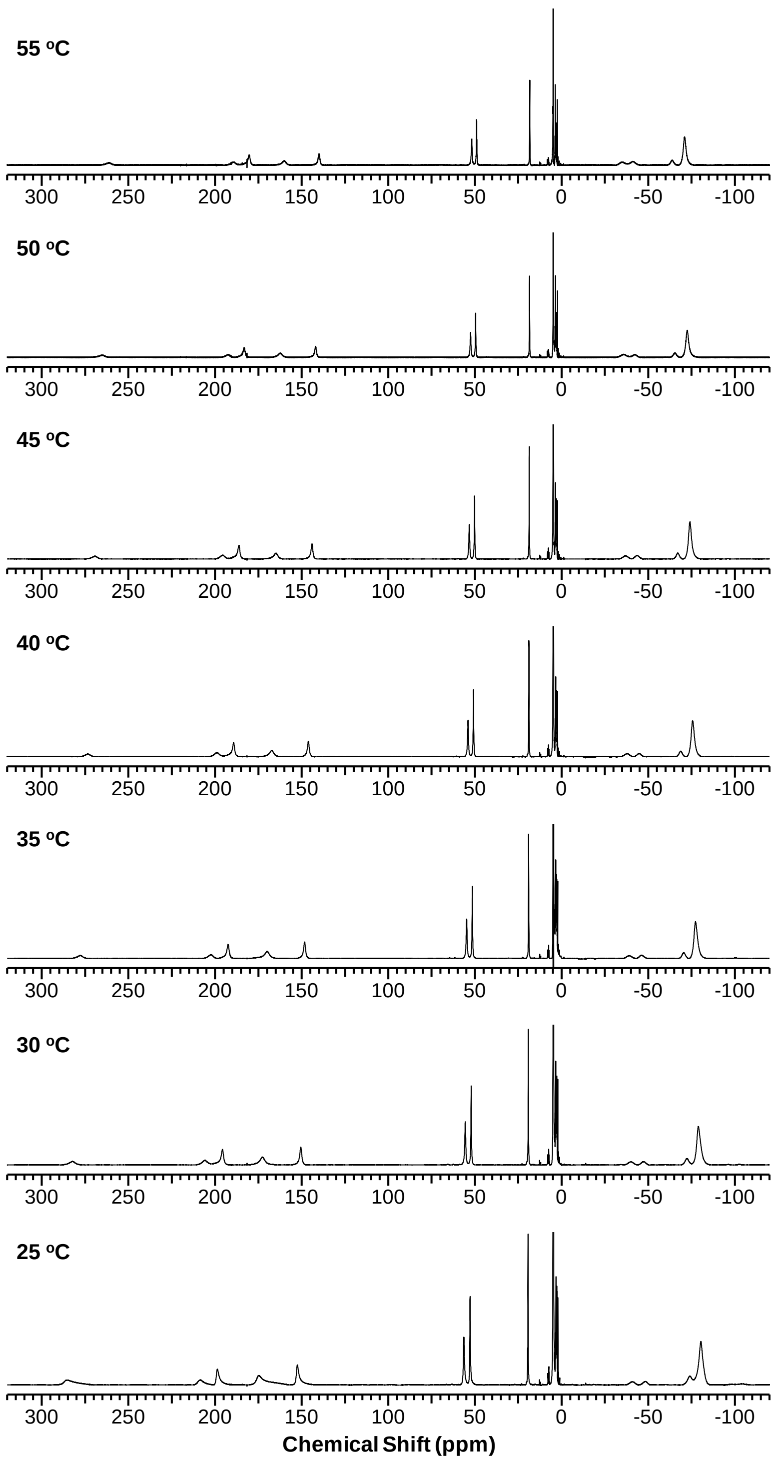

Figure S2. Variable temperature proton NMR spectra of **[Co(BMPC)]$^{2+}$**, 100 mM NaCl in D_2O, pD 7.3.

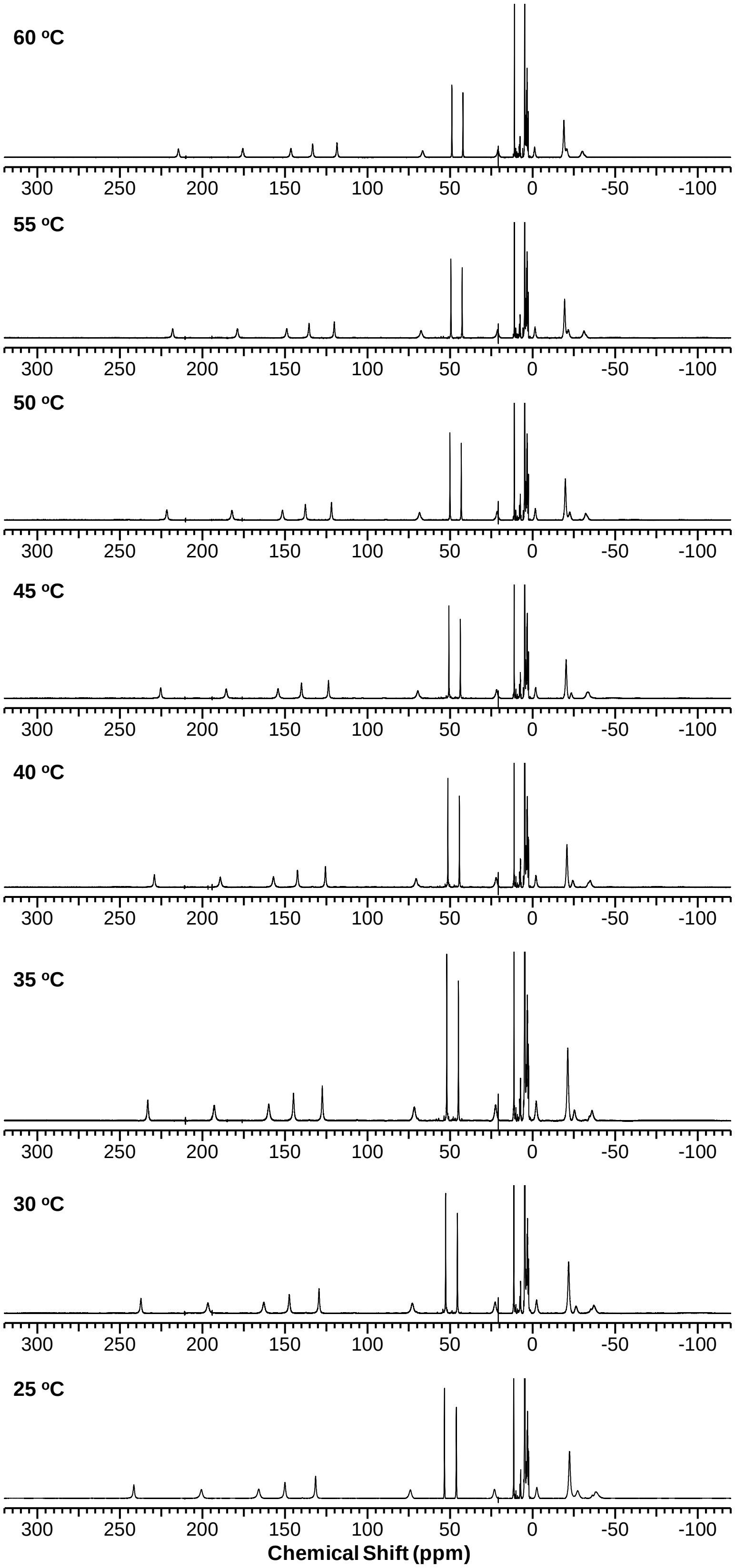

Figure S3. Variable temperature proton NMR spectra of **[Fe(BMPC)]$^{2+}$**, 100 mM NaCl in D_2O, pD 7.2.

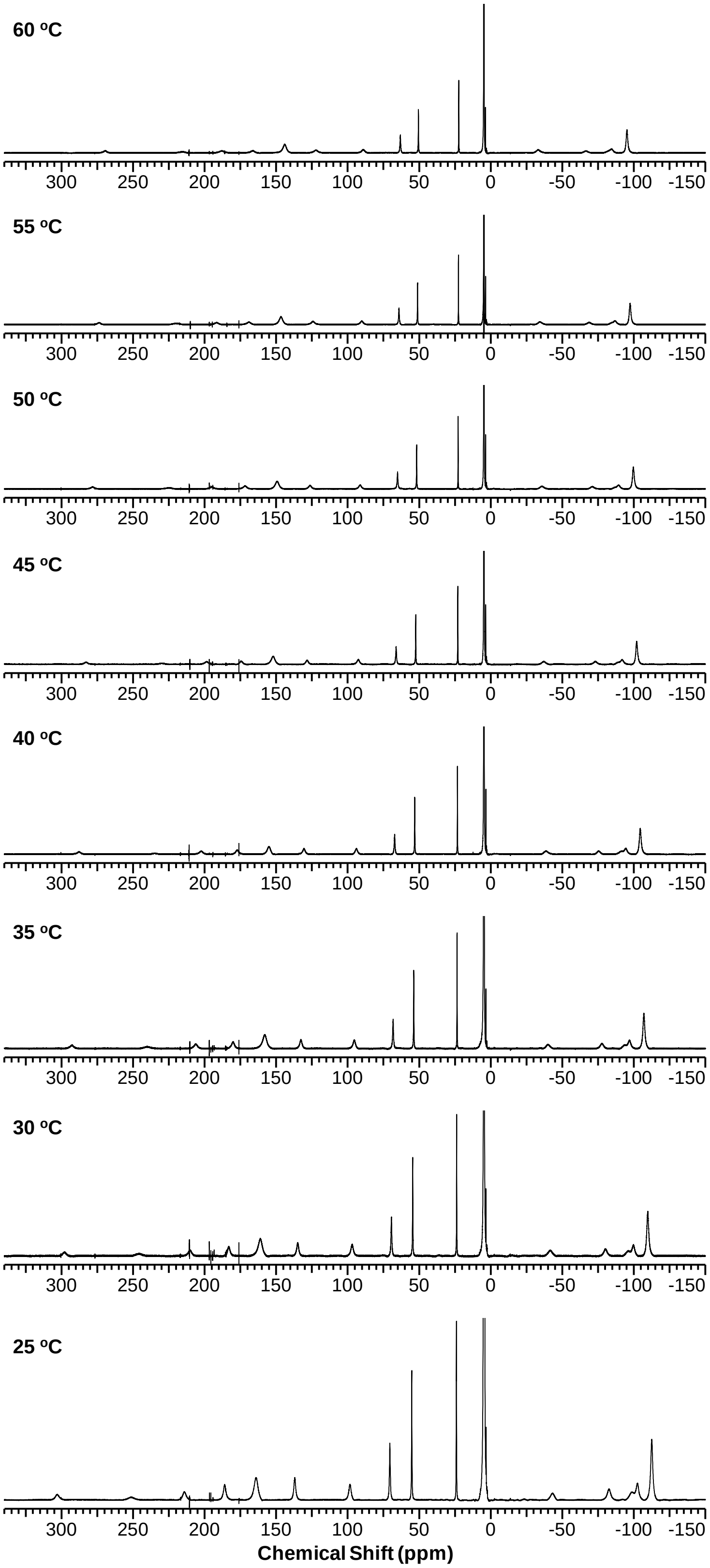

Figure S4. Variable temperature proton NMR spectra of **[Co(2MPC)]**$^{2+}$, 100 mM NaCl in D_2O, pD 6.9.

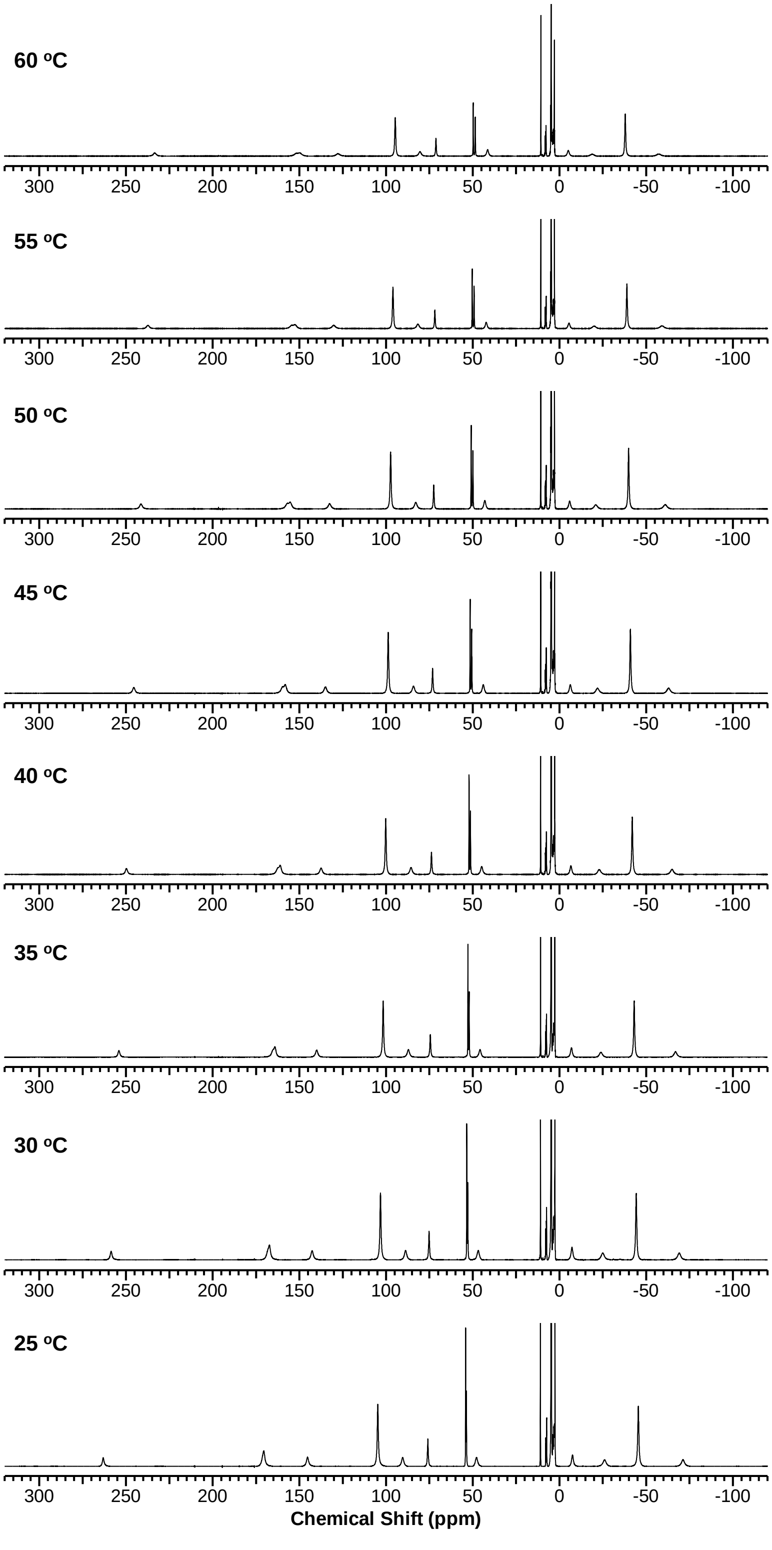

Figure S5. Variable temperature proton NMR spectra of **[Fe(2MPC)]$^{2+}$**, 100 mM NaCl in D_2O, pD 7.0.

Table S3. Dissociation properties of **$[Co(BMPC)]^{2+}$**, **$[Fe(BMPC)]^{2+}$**, **$[Co(2MPC)]^{2+}$** , **$[Fe(2MPC)]^{2+}$** at 37 °C [a]

	% Dissociation Acidic [b]		**% Dissociation Anions** [c]	
Complex:	24 h	48 h	24 h	48 h
$[Co(BMPC)]^{2+}$	3	4	2	2
$[Fe(BMPC)]^{2+}$	5	6	2	2
$[Co(2MPC)]^{2+}$	3	3	ND	ND
$[Fe(2MPC)]^{2+}$	10	14	12	17

[a] Solutions contained 10-12 mM complex;

[b] 100 mM NaCl in D_2O, pD 3.5(1);

[c] 100 mM NaCl, 0.40 mM NaH_2PO_4, 25 mM K_2CO_3 in D_2O, pD 7.0–7.4;

ND – No dissociation was detectable by ^1H NMR technique.

Appendixes I: NMR spectroscopic characterization

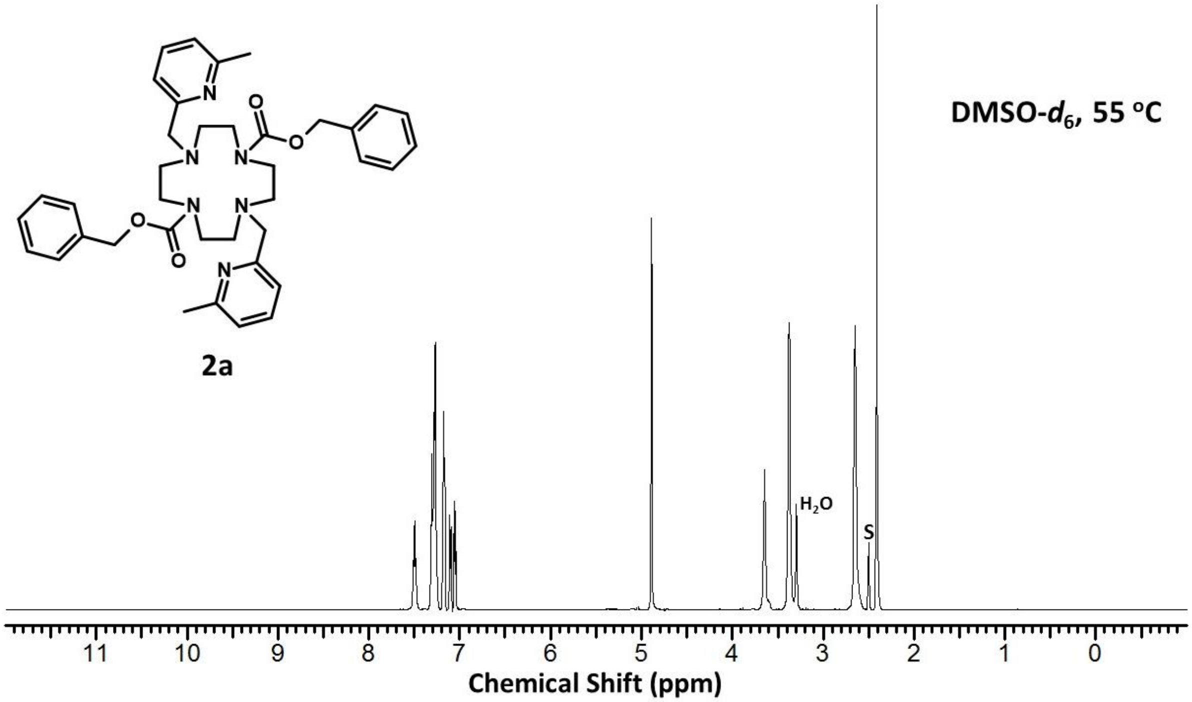

Figure S6. ^{1}H NMR of **2a** in DMSO-d_6 at 55 °C. Solvent signal is labeled “S”.

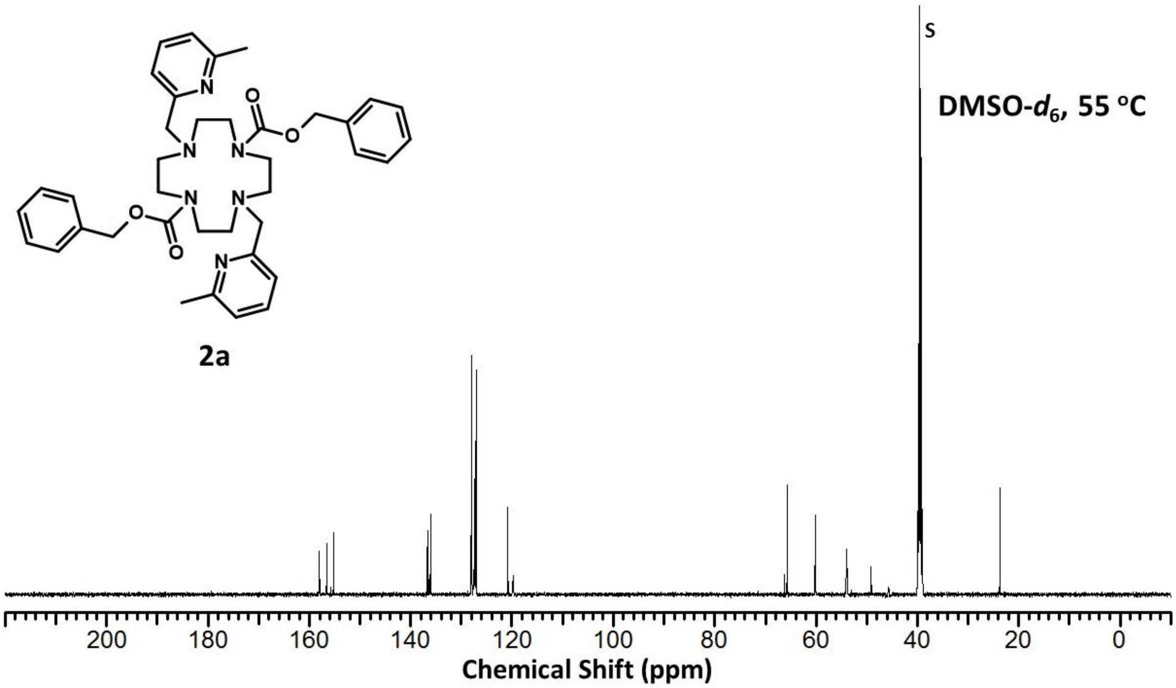

Figure S7. ^{13}C NMR of **2a** in DMSO-d_6 at 55 °C. Solvent signal is labeled “S”.

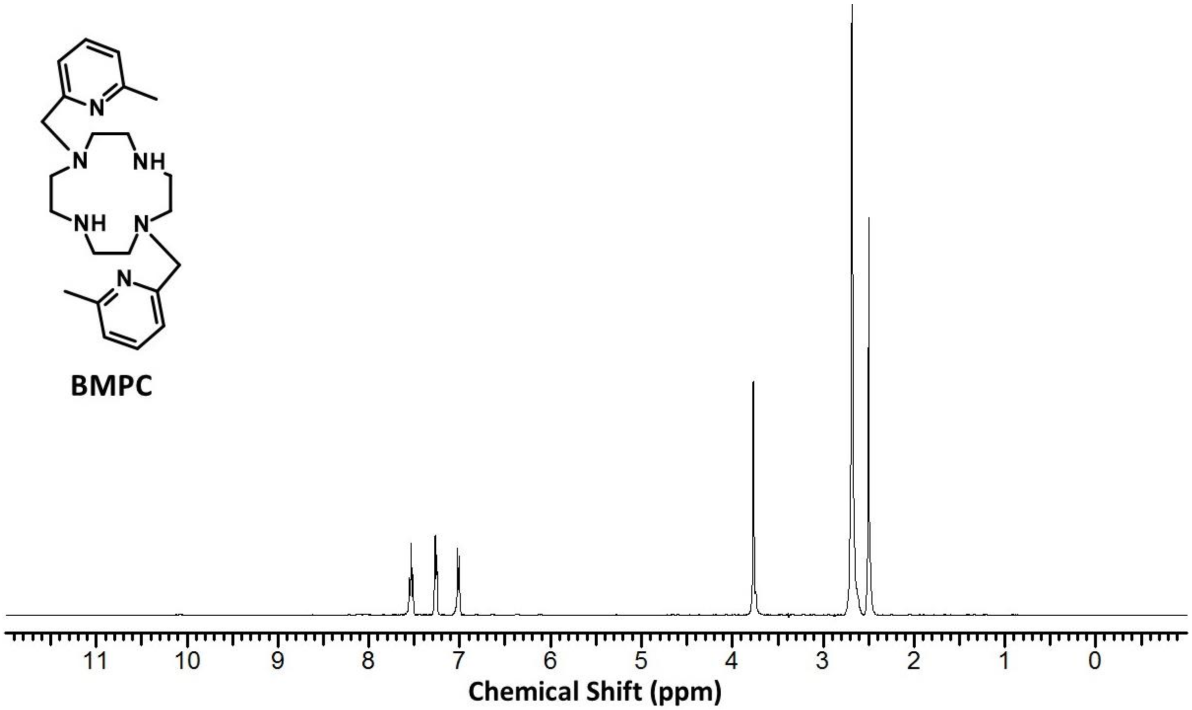

Figure S8. ^{1}H NMR of **BMPC** in $CDCl_3$.

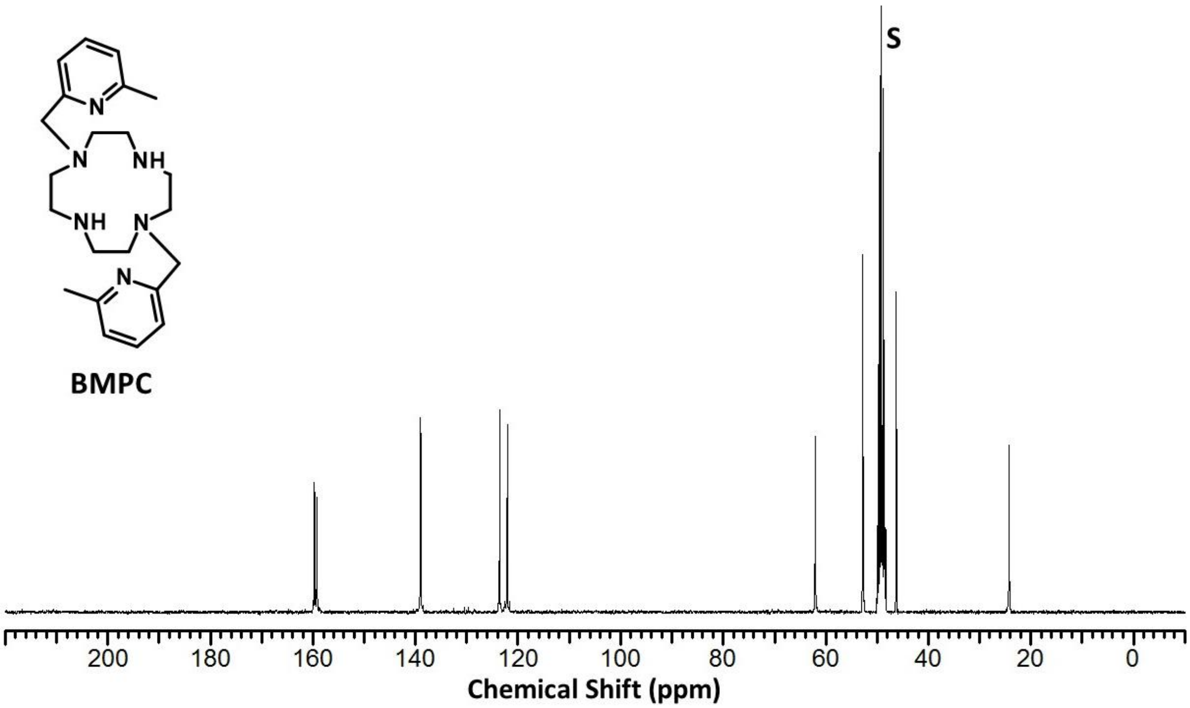

Figure S9. ^{1}H NMR of **BMPC** in CD_3OD. Solvent signal is labeled “S”.

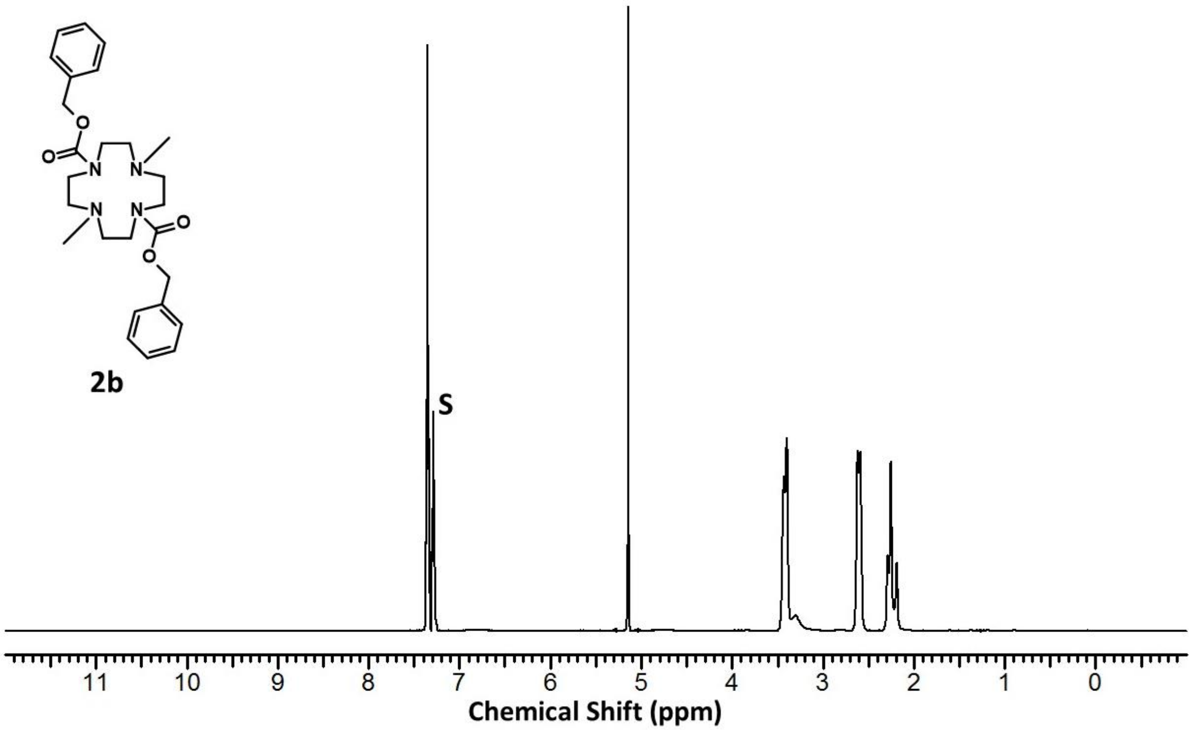

Figure S10. ^{1}H NMR of **2b** in $CDCl_3$. Solvent signal is labeled “S”.

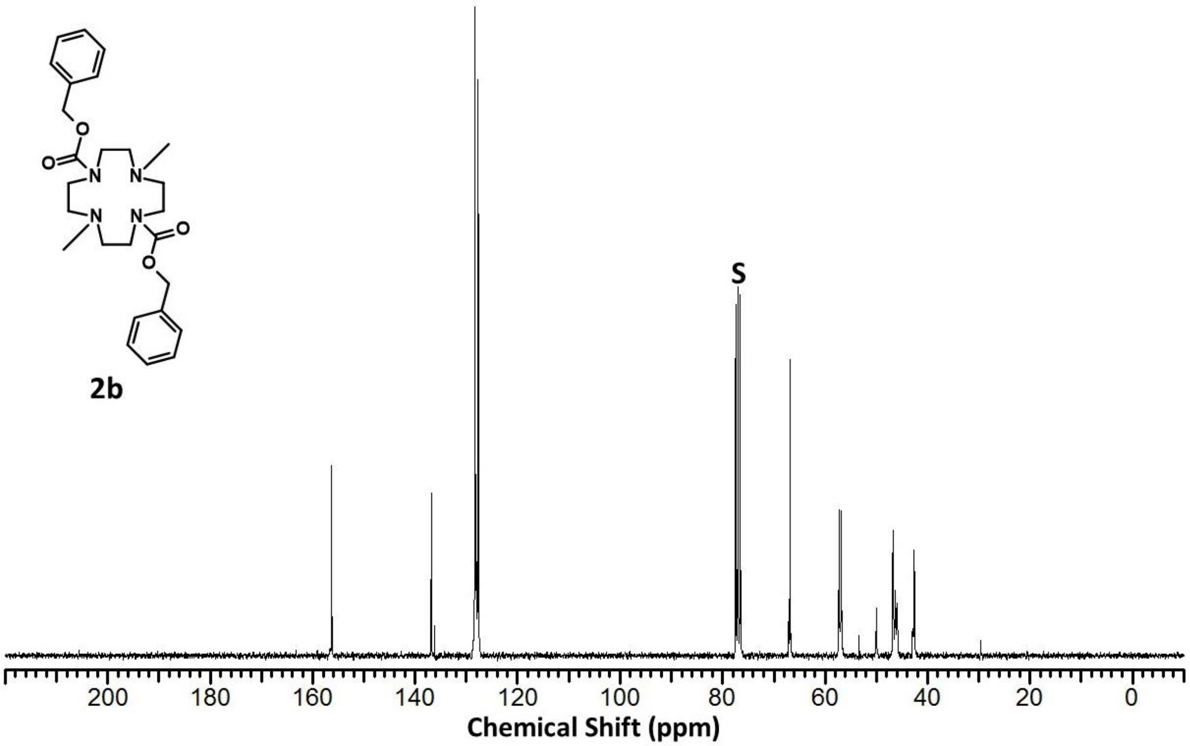

Figure S11. ^{13}C NMR of **2b** in $CDCl_3$. Solvent signal is labeled “S”.

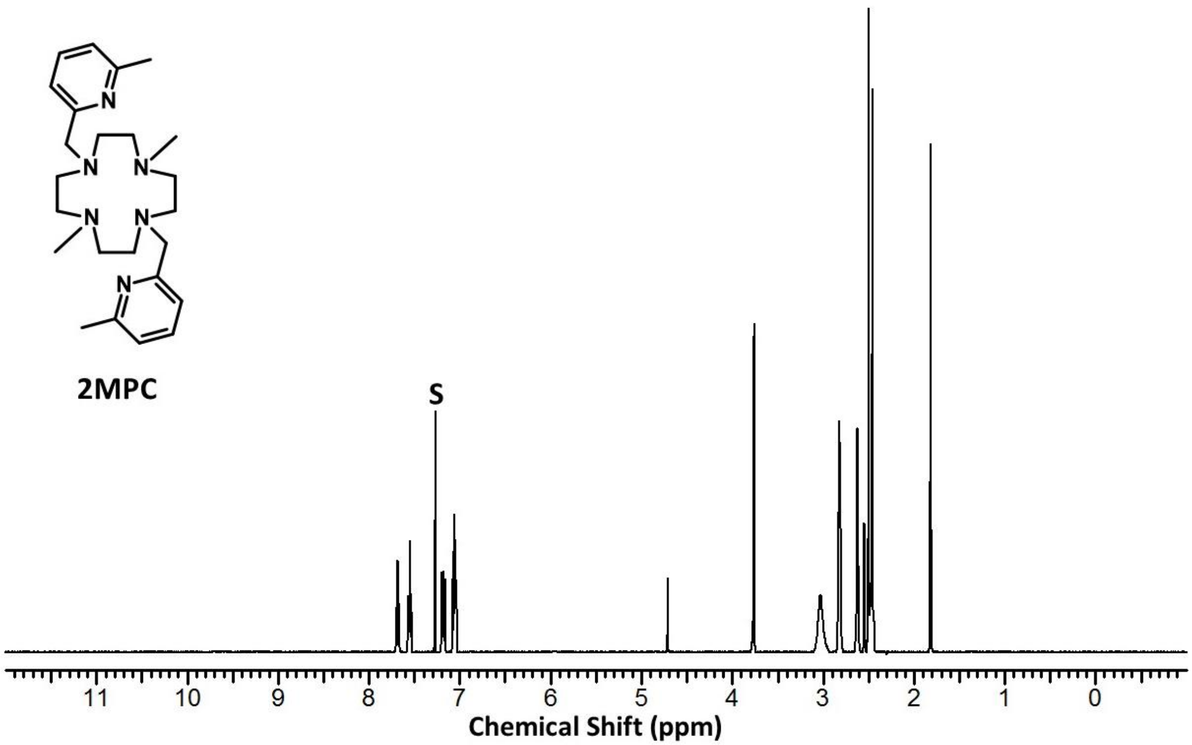

Figure S12. ^{1}H NMR of **2MPC** in $CDCl_3$. Solvent signal is labeled “S”.

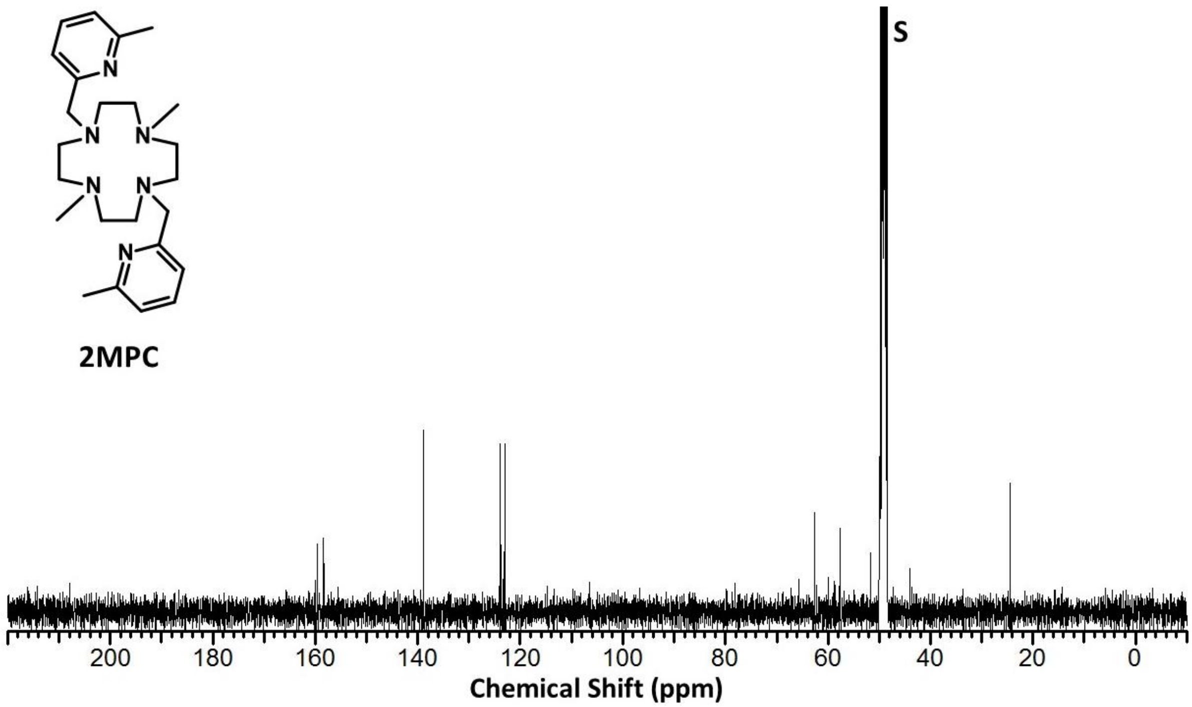

Figure S13. ^{13}C NMR of **2MPC** in CD_3OD. Solvent signal is labeled “S”.

<u>Appendixes II:</u> Crystallographic Data

Table S4. Crystal data and structure refinement for **[Co(BMPC)]$^{2+}$**.

Identification code	Co(BMPC)
Empirical formula	$C_{22}H_{34}Cl_4Co_2N_6$
Formula weight	642.21
Temperature/K	90
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.8045(5)
b/Å	12.9067(5)
c/Å	15.2447(6)
α/°	90
β/°	104.3640(8)
γ/°	90
Volume/Å^3	2631.25(17)
Z	4
ρ_{calc}g/cm^3	1.621
μ/mm^{-1}	1.691
F(000)	1320.0
Crystal size/mm^3	0.24 × 0.1 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.566 to 67.514
Index ranges	$-21 \leq h \leq 21$, $-20 \leq k \leq 20$, $-23 \leq l \leq 23$
Reflections collected	72080
Independent reflections	10527 [R_{int} = 0.0250, R_{sigma} = 0.0154]
Data/restraints/parameters	10527/0/309
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0228, wR_2 = 0.0593
Final R indexes [all data]	R_1 = 0.0274, wR_2 = 0.0617
Largest diff. peak/hole / e Å^{-3}	0.98/-0.47

Table S5. Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times10^3$) for Co(BMPC). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Co1	5165.5(2)	6879.3(2)	7469.1(2)	8.65(3)
Co2	2508.3(2)	1736.9(2)	5087.4(2)	12.65(3)
Cl1	2905.5(2)	890.0(2)	3902.6(2)	15.07(4)
Cl2	2168.1(2)	514.2(2)	6043.4(2)	14.44(4)
Cl3	3888.4(2)	2678.5(2)	5772.8(2)	17.34(5)
Cl4	1221.1(2)	2867.1(2)	4587.5(2)	26.91(6)
N1	5125.7(6)	8523.5(6)	7177.8(5)	10.74(13)
N2	3518.0(6)	6746.2(6)	6925.6(6)	11.17(13)
N6	6409.5(6)	6759.1(6)	6819.4(6)	12.22(14)
N3	6413.1(6)	7518.8(7)	8547.3(5)	12.39(14)
N5	4955.2(6)	5292.6(6)	6902.2(6)	11.75(13)
N4	5030.7(6)	6006.9(7)	8653.5(6)	12.85(14)
C22	7306.2(7)	7648.4(8)	8182.5(7)	15.11(17)
C1	6038.2(8)	8532.3(8)	8758.8(7)	15.92(17)
C20	6317.2(8)	5841.3(8)	6228.6(7)	15.00(17)
C10	5288.8(8)	4915.3(8)	8519.7(7)	14.80(17)
C14	2263.7(8)	5626.7(9)	6026.3(7)	17.32(18)
C13	3250.4(7)	5932.8(7)	6357.7(6)	12.61(15)
C21	7359.9(7)	6775.7(8)	7532.7(7)	15.51(17)
C7	4325.3(8)	8354.9(8)	5559.0(7)	14.97(17)
C2	5567.6(7)	9110.0(7)	7900.8(7)	12.78(15)
C16	1785.2(8)	7033.1(9)	6842.5(8)	19.14(19)
C8	6627.0(8)	6832.0(8)	9348.7(7)	15.26(17)
C6	4727.5(7)	9005.2(7)	6383.5(6)	11.65(15)
C12	4097.2(8)	5375.5(7)	6102.0(7)	14.04(16)
C3	5588.9(8)	10177.9(8)	7875.2(8)	16.89(18)
C11	4714.6(8)	4579.5(8)	7584.2(7)	14.65(17)
C19	5870.7(8)	4948.5(7)	6650.2(7)	14.76(17)
C17	2793.9(7)	7290.4(8)	7174.8(7)	13.75(16)
C9	5655.0(8)	6427.0(9)	9510.5(7)	16.09(17)
C15	1517.5(8)	6199.4(10)	6268.6(8)	20.8(2)
C4	5137.1(8)	10672.9(8)	7068.6(8)	18.39(19)
C5	4716.1(7)	10081.4(8)	6316.2(7)	15.53(17)
C18	3091.6(8)	8175.3(8)	7818.7(8)	18.71(19)

Table S6. Anisotropic Displacement Parameters ($Å^2\times10^3$) for Co(BMPC). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Co1	8.83(5)	8.52(5)	8.94(5)	0.70(4)	2.84(4)	0.41(4)
Co2	13.76(6)	12.36(6)	12.96(6)	1.88(4)	5.44(5)	1.42(4)
Cl1	15.21(10)	18.03(10)	13.54(9)	-2.42(7)	6.51(7)	-4.23(8)
Cl2	13.99(9)	15.13(10)	15.73(10)	3.04(7)	6.56(8)	0.84(7)
Cl3	22.88(11)	10.62(9)	18.47(10)	-0.62(8)	5.05(9)	-3.08(8)
Cl4	22.34(12)	28.16(14)	32.65(14)	17.43(11)	11.36(11)	11.86(10)
N1	10.0(3)	10.1(3)	12.4(3)	-0.7(3)	3.2(3)	-0.4(2)
N2	11.3(3)	10.2(3)	12.4(3)	2.0(3)	3.8(3)	0.4(2)
N6	12.8(3)	11.9(3)	13.1(3)	1.9(3)	5.3(3)	1.1(3)
N3	11.5(3)	14.3(3)	11.4(3)	1.4(3)	3.0(3)	0.2(3)
N5	13.4(3)	9.4(3)	13.3(3)	2.1(3)	5.0(3)	1.4(3)
N4	11.6(3)	15.1(4)	12.5(3)	2.8(3)	4.2(3)	1.6(3)
C22	10.4(4)	18.7(4)	15.9(4)	1.3(3)	2.7(3)	-2.2(3)
C1	18.1(4)	16.3(4)	12.2(4)	-3.3(3)	1.4(3)	0.0(3)
C20	18.8(4)	14.2(4)	14.9(4)	0.4(3)	9.7(3)	2.2(3)
C10	15.2(4)	14.1(4)	16.0(4)	5.8(3)	5.7(3)	2.5(3)
C14	15.7(4)	18.6(4)	15.4(4)	4.0(3)	-0.3(3)	-4.5(3)
C13	13.5(4)	11.1(4)	12.4(4)	2.7(3)	1.7(3)	-1.3(3)
C21	10.9(4)	18.5(4)	17.8(4)	3.0(3)	5.0(3)	2.2(3)
C7	15.3(4)	15.4(4)	12.8(4)	2.0(3)	1.0(3)	-1.4(3)
C2	12.0(4)	12.7(4)	14.0(4)	-2.4(3)	3.9(3)	-0.8(3)
C16	11.7(4)	25.7(5)	20.8(5)	5.9(4)	5.4(3)	2.7(4)
C8	13.6(4)	20.1(4)	10.8(4)	2.9(3)	0.7(3)	1.1(3)
C6	9.0(3)	11.8(4)	14.7(4)	1.7(3)	4.1(3)	0.3(3)
C12	17.5(4)	10.7(4)	13.1(4)	-1.3(3)	2.2(3)	0.1(3)
C3	16.1(4)	12.2(4)	22.3(5)	-4.5(3)	4.7(4)	-1.3(3)
C11	16.6(4)	10.7(4)	17.6(4)	4.4(3)	6.2(3)	-0.4(3)
C19	17.6(4)	11.0(4)	17.6(4)	0.8(3)	8.0(3)	3.9(3)
C17	12.6(4)	15.2(4)	14.7(4)	4.1(3)	5.8(3)	2.4(3)
C9	16.0(4)	22.1(5)	10.6(4)	3.0(3)	4.2(3)	1.5(3)
C15	12.2(4)	29.4(5)	19.3(5)	6.0(4)	1.0(3)	-4.0(4)
C4	17.1(4)	9.6(4)	28.4(5)	-0.6(4)	5.6(4)	0.8(3)
C5	13.3(4)	11.5(4)	22.0(5)	3.5(3)	4.8(3)	1.7(3)
C18	18.8(5)	18.6(5)	21.7(5)	-1.8(4)	10.6(4)	2.9(4)

Table S7. Bond Lengths for Co(BMPC).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	N1	2.1660(8)	N5	C11	1.4866(12)
Co1	N2	2.2256(8)	N5	C19	1.4775(13)
Co1	N6	2.1905(8)	N4	C10	1.4797(13)
Co1	N3	2.2236(8)	N4	C9	1.4782(13)
Co1	N5	2.2137(8)	C22	C21	1.5140(15)
Co1	N4	2.1746(8)	C1	C2	1.5058(14)
Co2	Cl1	2.2911(3)	C20	C19	1.5223(14)
Co2	Cl2	2.2747(3)	C10	C11	1.5129(15)
Co2	Cl3	2.2827(3)	C14	C13	1.3874(14)
Co2	Cl4	2.2791(3)	C14	C15	1.3902(16)
N1	C2	1.3514(12)	C13	C12	1.5040(14)
N1	C6	1.3508(12)	C7	C6	1.4988(14)
N2	C13	1.3526(12)	C2	C3	1.3794(14)
N2	C17	1.3510(12)	C16	C17	1.3985(15)
N6	C20	1.4743(13)	C16	C15	1.3782(17)
N6	C21	1.4820(13)	C8	C9	1.5161(15)
N3	C22	1.4823(13)	C6	C5	1.3927(13)
N3	C1	1.4716(13)	C3	C4	1.3888(16)
N3	C8	1.4786(13)	C17	C18	1.4957(15)
N5	C12	1.4783(13)	C4	C5	1.3804(15)

Table S8. Bond Angles for Co(BMPC).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Co1	N2	91.58(3)	C12	N5	C11	110.47(8)
N1	Co1	N6	87.68(3)	C11	N5	Co1	109.27(6)
N1	Co1	N3	76.32(3)	C19	N5	Co1	109.99(6)
N1	Co1	N5	146.31(3)	C19	N5	C12	111.66(8)
N1	Co1	N4	132.41(3)	C19	N5	C11	110.46(7)
N6	Co1	N2	132.03(3)	C10	N4	Co1	107.79(6)
N6	Co1	N3	79.06(3)	C9	N4	Co1	113.13(6)
N6	Co1	N5	78.44(3)	C9	N4	C10	111.32(8)
N3	Co1	N2	146.76(3)	N3	C22	C21	109.99(8)
N5	Co1	N2	76.13(3)	N3	C1	C2	110.44(8)
N5	Co1	N3	129.38(3)	N6	C20	C19	109.45(8)
N4	Co1	N2	88.80(3)	N4	C10	C11	108.35(8)
N4	Co1	N6	125.24(3)	C13	C14	C15	118.49(10)
N4	Co1	N3	77.80(3)	N2	C13	C14	122.80(9)
N4	Co1	N5	79.35(3)	N2	C13	C12	115.51(8)
Cl2	Co2	Cl1	107.574(10)	C14	C13	C12	121.70(9)
Cl2	Co2	Cl3	110.953(11)	N6	C21	C22	108.22(8)
Cl2	Co2	Cl4	112.988(11)	N1	C2	C1	116.18(8)
Cl3	Co2	Cl1	106.202(10)	N1	C2	C3	123.04(9)
Cl4	Co2	Cl1	111.161(12)	C3	C2	C1	120.78(9)
Cl4	Co2	Cl3	107.772(13)	C15	C16	C17	120.09(10)
C2	N1	Co1	113.47(6)	N3	C8	C9	109.74(8)
C6	N1	Co1	128.22(6)	N1	C6	C7	118.54(8)
C6	N1	C2	118.31(8)	N1	C6	C5	121.31(9)
C13	N2	Co1	112.94(6)	C5	C6	C7	120.12(9)
C17	N2	Co1	127.90(7)	N5	C12	C13	109.63(8)
C17	N2	C13	118.67(9)	C2	C3	C4	118.47(10)
C20	N6	Co1	111.99(6)	N5	C11	C10	109.04(8)
C20	N6	C21	112.73(8)	N5	C19	C20	110.14(8)
C21	N6	Co1	108.53(6)	N2	C17	C16	120.96(10)
C22	N3	Co1	109.17(6)	N2	C17	C18	118.66(9)
C1	N3	Co1	104.00(6)	C16	C17	C18	120.38(9)
C1	N3	C22	110.63(8)	N4	C9	C8	109.15(8)
C1	N3	C8	111.15(8)	C16	C15	C14	118.96(10)
C8	N3	Co1	110.33(6)	C5	C4	C3	119.03(9)
C8	N3	C22	111.31(8)	C4	C5	C6	119.72(10)
C12	N5	Co1	104.83(6)				

Table S9. Torsion Angles for Co(BMPC).

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Co1	N1	C2	C1	2.25(10)	C1	C2	C3	C4	-179.52(9)
Co1	N1	C2	C3	-177.16(8)	C20	N6	C21	C22	-171.23(8)
Co1	N1	C6	C7	-5.49(12)	C10	N4	C9	C8	85.67(10)
Co1	N1	C6	C5	176.62(7)	C14	C13	C12	N5	-140.29(9)
Co1	N2	C13	C14	171.99(7)	C13	N2	C17	C16	-1.08(14)
Co1	N2	C13	C12	-8.18(10)	C13	N2	C17	C18	178.68(9)
Co1	N2	C17	C16	-172.46(7)	C13	C14	C15	C16	-1.41(15)
Co1	N2	C17	C18	7.30(13)	C21	N6	C20	C19	86.70(10)
Co1	N6	C20	C19	-36.04(9)	C7	C6	C5	C4	-176.49(9)
Co1	N6	C21	C22	-46.57(9)	C2	N1	C6	C7	174.17(8)
Co1	N3	C22	C21	-36.08(9)	C2	N1	C6	C5	-3.72(13)
Co1	N3	C1	C2	-46.06(9)	C2	C3	C4	C5	-2.28(16)
Co1	N3	C8	C9	-39.65(9)	C8	N3	C22	C21	85.96(10)
Co1	N5	C12	C13	-49.24(8)	C8	N3	C1	C2	-164.77(8)
Co1	N5	C11	C10	-35.33(9)	C6	N1	C2	C1	-177.46(8)
Co1	N5	C19	C20	-39.51(9)	C6	N1	C2	C3	3.13(14)
Co1	N4	C10	C11	-48.60(8)	C12	N5	C11	C10	-150.15(8)
Co1	N4	C9	C8	-35.88(10)	C12	N5	C19	C20	76.43(10)
N1	C2	C3	C4	-0.13(15)	C3	C4	C5	C6	1.69(15)
N1	C6	C5	C4	1.36(15)	C11	N5	C12	C13	68.36(10)
N2	C13	C12	N5	39.87(11)	C11	N5	C19	C20	-160.22(8)
N6	C20	C19	N5	50.33(11)	C19	N5	C12	C13	-168.29(8)
N3	C22	C21	N6	55.89(10)	C19	N5	C11	C10	85.80(10)
N3	C1	C2	N1	31.29(12)	C17	N2	C13	C14	-0.63(14)
N3	C1	C2	C3	-149.29(9)	C17	N2	C13	C12	179.20(8)
N3	C8	C9	N4	49.76(11)	C17	C16	C15	C14	-0.22(16)
N4	C10	C11	N5	56.70(10)	C9	N4	C10	C11	-173.20(8)
C22	N3	C1	C2	71.03(10)	C15	C14	C13	N2	1.89(15)
C22	N3	C8	C9	-161.02(8)	C15	C14	C13	C12	-177.93(9)
C1	N3	C22	C21	-149.94(8)	C15	C16	C17	N2	1.51(15)
C1	N3	C8	C9	75.18(10)	C15	C16	C17	C18	-178.24(10)

Table S10. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Co(BMPC).

Atom	***x***	***y***	***z***	**U(eq)**
H6	6394.84	7387.61	6432.69	15
H4	4316.08	6031.97	8684.82	15
H22A	7917.2	7647.67	8686.48	18
H22B	7269.22	8321.17	7863.99	18
H1A	6597.71	8944.44	9127.58	19
H1B	5537.65	8430.82	9117.04	19
H20A	6984.03	5641.96	6152.44	18
H20B	5882.16	6004.44	5623.91	18
H10A	5109.34	4470.17	8984.25	18
H10B	6016.56	4850.06	8577.59	18
H14	2101.78	5039.05	5642.62	21
H21A	7929.89	6886.83	7257.14	19
H21B	7458.46	6106.13	7859.61	19
H7A	4880.84	8017.45	5376.89	22
H7B	3957.05	8795.86	5064.55	22
H7C	3875.14	7826.11	5696.35	22
H16	1283.84	7433.52	7012.67	23
H8A	6998.65	7220.86	9887.2	18
H8B	7047.91	6244.11	9249.28	18
H12A	3876.88	4674.45	5873.26	17
H12B	4300.02	5759.62	5614.43	17
H3	5905.38	10565.8	8397.34	20
H11A	4900.83	3861.39	7466.69	18
H11B	3987.59	4596.65	7542.46	18
H19A	5707.62	4368.89	6212.96	18
H19B	6364.72	4696.82	7195.33	18
H9A	5796.52	5876.34	9977.08	19
H9B	5294.62	6994.6	9730.95	19
H15	833.87	6018.92	6042.07	25
H4A	5118.07	11407.93	7035.18	22
H5	4419.93	10407.09	5754.92	19
H18A	3716.22	8004.94	8262.7	28
H18B	2564.09	8303.38	8133.13	28
H18C	3189.44	8797.45	7482.34	28

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