Supporting Information

for

Stereochemistry of metal tetramethylcyclam complexes directed by an unexpected anion effect

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Experimental Section

Materials and Methods. All reagents were purchased from commercial suppliers and used as received unless otherwise noted. Optical Spectra were recorded on an Agilent 8453 UV–vis spectrophotometer. Electrospray ionization mass spectra (ESI-MS) were collected on a Waters (Milford, MA, USA) Acquity SQD quadrupole mass instrument, by infusing samples directly into the source using a manual method. The spray voltage was set at 2.5 kV and the capillary temperature at 80 °C. CW X-band (9 GHz) EPR spectra were collected on a Bruker EMX plus 6/1 spectrometer equipped with an Oxford Instrument ESR900 liquid He cryostat using an Oxford ITC 503 temperature controller. Q-band (34 GHz) pulse EPR data were obtained on a Bruker Elexsys E580 spectrometer using an EN5107D2 resonator and Cryogenic temperatures were achieved with an Oxford CF-935 cryostat and Oxford ITC temperature controller.

Preparation of [Cu(TMC)](NO₃)₂(H₂O)_{0.5}. TMC (0.13 g, 0.5 mmol) (TMC = 1,4,8,11tetramethyl-1,4,8,11-tetraazacyclotetradecane) was added to an acetonitrile (CH₃CN) solution (5 mL) of Cu(NO₃)₂·xH₂O (0.09 g, 0.5 mmol). The resulting solution was refluxed for 12 h. After cooling, to room temperature, the solvent was removed under reduced pressure to give a purple powder. The solid was filtered and the filtrate was then washed with diethyl ether and dried in a vacuum. Yield: 0.25 g (95%). UV–vis (H₂O): λ_{max} (ε) = 554 nm (215 M⁻¹ cm⁻¹). ESI-MS (in CH₃CN): *m/z* 157.6 for [Cu(TMC)]²⁺, *m/z* 180.1 for [Cu(TMC)(CH₃CN)]²⁺, and *m/z* 381.2 for [Cu(TMC)(NO₃)]⁺. Anal. Calcd for C₁₄H₃₃CuN₆O_{6.5}: C, 37.12; H, 7.34; N, 18.55. Found: C, 36.68; H, 7.02; N, 18.86. Crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a methanol (MeOH) solution of [Cu(TMC)](NO₃)₂(H₂O)_{0.5}. **Preparation of [Cu(TMC)](ClO₄)₂.** [Cu(TMC)](ClO₄)₂ was prepared following an identical procedure as the one reported for [Cu(TMC)](NO₃)₂ except Cu(ClO₄)₂•xH₂O (0.19 g, 0.5 mmol) was used to give a blue solid. Crystallographic data was obtained from previously reported perchlorate complexes.¹ Yield: 0.25 g (96%). UV–vis (H₂O): λ_{max} (ε) = 615 nm (190 M⁻¹ cm⁻¹). ESI–MS (in CH₃CN): *m/z* 159.5 for [Cu(TMC)]²⁺, *m/z* 180.2 for [Cu(TMC)(CH₃CN)]²⁺, and *m/z* 418.2 for [Cu(TMC)(ClO₄)]⁺. Anal. Calcd for C₁₆H₃₅Cl₂CuN₅O₈: C, 34.32; H, 6.30; N, 12.51. Found: C, 34.05; H, 6.24; N, 12.47.

X-ray Structural Determination. A single crystal of $[Cu(TMC)](NO_3)_2(H_2O)_{0.5}$ was picked from solutions by using a nylon loop (Hampton Research Co.) on a handmade copper plate mounted inside a liquid N₂ Dewar vessel at *ca*. -40 °C and mounted on a goniometer head in a N₂ cryostream. Data collections were carried out on a Bruker SMART APEX II CCD diffractometer equipped with a monochromator in the Mo K α ($\lambda = 0.71073$ Å) incident beam. The CCD data were integrated and scaled using the Bruker-SAINT software package, and the structure was solved and refined using SHELXTL V 6.12.² Hydrogen atoms were located in the calculated positions. All non-hydrogen atoms were refined with anisotropic thermal parameters. Crystal data for [Cu(TMC)](NO₃)₂: C₁₄H₃₂CuN₆O₆, monoclinic, *P*₂₁/n, *Z* = 2, *a* = 7.9917(4), *b* = 15.0923(8), *c* = 8.3426(5) Å, β = 106.381(2)°, *V* = 965.38(9) Å³, μ = 1.175 mm⁻¹, ρ_{calcd} = 1.527 g cm⁻³, R₁ = 0.0264, wR₂ = 0.0883 for 2395 unique reflections, 126 variables. The crystallographic data are summarized in Table S1, and Table 2 lists the selected bond distances and angles.

CW and Pulse EPR Spectroscopy. All EPR measurements were carried out at Korea Basic Science Institute (KBSI) in Seoul, Korea. The simulations of the EPR spectra were performed by

EasySpin.³ CW X-band (9 GHz) EPR spectra were collected on a Bruker EMX plus 6/1 spectrometer equipped with an Oxford Instrument ESR900 liquid He cryostat using an Oxford ITC 503 temperature controller. All spectra were collected with the following experimental parameters: microwave frequency, 9.64 GHz; microwave power, 1.0 mW; modulation amplitude, 10 G; time constant, 62.50 ms; 5 scans; temperature, 5 K. Q-band (34 GHz) pulse EPR data were obtained on a Bruker Elexsys E580 spectrometer using an EN5107D2 resonator and Cryogenic temperatures were achieved with an Oxford CF-935 cryostat and Oxford ITC temperature controller. The measurements were conducted at 15 K. The ESE-EPR spectra were acquired using a pulse sequence, $\pi/2-\tau-\pi$ -echo, with a pulse length $t_{\pi/2} = 32$ ns, $t_{\pi} = 64$ ns and $\tau = 400$ ns. The ¹H Davies ENDOR were performed using the π -T- π /2- τ - π -echo, with microwave pulse lengths of $t_{\pi/2} = 100$ ns, $t_{\pi} = 200$ ns and an inter-pulse time of $\tau = 600$ ns. In this sequence, the RF power is applied during the time $T(20 \ \mu s)$ to drive nuclear spin transitions. The repetition time was 2 ms. The ²H Mims ENDOR were performed using the $\pi/2-\tau-\pi/2-T-\pi/2$ -echo, with microwave pulse lengths of $t_{\pi/2} = 32$ ns and an inter-pulse time of $\tau = 400$ ns. In this sequence, the RF power is applied during the time $T(20 \ \mu s)$ to drive nuclear spin transitions. The repetition time was 2 ms. The ¹⁴N Davies ENDOR were performed using the π -T- π /2- τ - π -echo, with microwave pulse lengths of $t_{\pi/2} = 32$ ns, $t_{\pi} = 64$ ns and an inter-pulse time of $\tau = 400$ ns. In this sequence, the RF power is applied during the time $T(20 \ \mu s)$ to drive nuclear spin transitions. The repetition time was 2 ms.

Simulation parameters for Fig. 4: A = [0.9, -0.45, -0.45] MHz, $e^2 qQ/h = 0.128$ MHz, $\eta = 0$. Conditions for Fig. 4: (a) Microwave frequency = 9.6 GHz, T = 15 K, modulation frequency = 100 kHz, modulation amplitude = 10 G; (b) Microwave frequency = 33.9 GHz, 15 K, microwave pulse sequence 200-100-200 ns, $\tau = 600$ ns, RF pulse length = 20 µs; (c) Microwave frequency = 33.9 GHz, 15 K, microwave pulse sequence 32-32-32 ns, $\tau = 400$ ns, RF pulse length = 20 μ s. Conditions for Fig. 5: Microwave frequency = 33.9 GHz, T = 15 K, pulse sequence = 64-32-64 ns, $\tau = 400$ ns, RF pulse length = 20 μ s.

Computational Details. The DFT models for *trans*-I- and *trans*-III-[Cu(TMC)]²⁺ complexes with nitrate and perchlorate anions were constructed by using the X-ray crystal structures, obtained from this study and reference 1(a) as initial geometries and then performing geometry optimization with the BP86 functional,⁵⁻⁶ the 6-311G* basis set,⁷⁻⁹ and polarizable continuum model (water)¹⁰⁻¹³ using the Gaussian 09 package.¹⁴

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Identification code	$[Cu(TMC)](NO_3)_2$
Empirical Formula	$C_{14}H_{32}CuN_6O_6$
Formula weight	443.99
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal System	Monoclinic
Space group	$P2_{1}/n$
	$a = 7.9917(4)$ Å $\alpha = 90^{\circ}$
Unit cell dimensions	$b = 15.0923(8) \text{ Å} \beta = 106.381(2)^{\circ}$
	$c = 8.3426(5)$ Å $\gamma = 90^{\circ}$
Volume	965.38(9) Å ³
Ζ	2
Density (calculated)	1.527 g/cm^{-3}
Absorption coefficient	1.175 mm ⁻¹
F(000)	470
Reflections collected	39083
Independent reflections	2395
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	2395/0/126
Goodness-of-fit on F^2	0.801
Final R indices [I>2sigma(I)]	R1 = 0.0264, WR2 = 0.0883
R indices (all data)	R1 = 0.0343, $wR2 = 0.0977$

Table S1Crystal data and structure refinement for [Cu(TMC)](NO3)2(H2O)0.5

[Cu(TMC)](NO ₃) ₂ (H ₂ O) _{0.5}					
Cu–N1	2.0825(12)				
Cu–N2	2.0738(13)				
N1–Cu–N2	92.72(5)				

Table S2Selected bond lengths (Å) and angle (°) for $[Cu(TMC)](NO_3)_2(H_2O)_{0.5}$

Complexes	<i>g</i> ₁	<i>g</i> ₂	g_{3}	<i>A</i> ₁ (G)	$A_2(\mathbf{G})$	<i>A</i> ₃ (G)	Reference
[Cu(TMC)](NO ₃) ₂ (H ₂ O) _{0.5}	2.205	2.055	2.035	200	10	0	this work
[Cu(TMC)](ClO ₄) ₂	2.224	2.056	2.034	180	20	0	this work
Cu(II)(TPP)	2.18	2.04	2.04	219	37	37	4

 Table S3
 Spin Hamiltonian parameters of CW-EPR simulations for Cu(II) complexes

	Cu(II)(TPP)	[Cu(TMC)](NO ₃) ₂ (H ₂ O) _{0.5}	[Cu(TMC)](ClO ₄) ₂		
$^{N}A_{1}$ [MHz]	44.1	43.0	37.0	42.0	44.7	
$^{N}A_{2}$ [MHz]	42.8	29.5	24.2	29.5	21.5	
$^{N}A_{3}$ [MHz]	54.2	28.7	24.4	24.0	28.1	
^N A _{iso} [MHz]	47.0	33.7	28.5	31.8	31.6	
Euler angle [α, β, γ]°	_	[0, 90, 0]	[0, 0, 90]	[0, 90, 0]	[0, 90, 0]	
<i>e²qQ/h</i> [MHz]	1.8	1.7	1.6	1.7	3.0	
η	0.15	0.1	0.0	0.1	0.1	
Euler angle [α, β, γ]°		[0, 90, 0]	[90, 90, 0]	[0, 0, 0]	[0, 0, 0]	
Reference	4	this	work	this work		

Table S4 Simulation parameters for 14 N Davies ENDOR of $[Cu(TMC)](NO_3)_2(H_2O)_{0.5}$ and $[Cu(TMC)](ClO_4)_2$



Fig. S1 Crystal packing diagram for [Cu(TMC)](NO₃)₂.



Fig. S2 34 GHz ESE-EPR of $[Cu(TMC)](ClO_4)_2$ (left, black) and $[Cu(TMC)](NO_3)_2(H_2O)_{0.5}$ (left, red) and the derivative ESE-EPR spectra of (a) $[Cu(TMC)](ClO_4)_2$ and (b) $[Cu(TMC)](NO_3)_2(H_2O)_{0.5}$. The experimental data were plotted with solid black lines and simulated data were plotted with dashed red lines. The simulation was performed simultaneously with identical parameters for Table S3. Experimental conditions: microwave frequency = 33.9 GHz, T = 15 K, $t_{\pi/2} = 32$ ns, $\tau = 400$ ns.



Fig. S3 34 GHz ¹H Davies ENDOR of $[Cu(TMC)](ClO_4)_2$ (black) and $[Cu(TMC)](NO_3)_2(H_2O)_{0.5}$ (red). Experimental conditions: microwave frequency = 33.9 GHz, *T* = 15 K, $t_{\pi/2} = 100$ ns, $\tau = 600$ ns, RF pulse length = 20 µs.



Fig. S4 34 GHz ²H Mims ENDOR of $[Cu(TMC)](NO_3)_2(H_2O)_{0.5}$ (solid black line) and its simulated spectra (dashed red line). The simulations were performed with following parameters; A = [0.76, -0.38, -0.38] MHz, $e^2 q Q/h = 0.128$ MHz, $\eta = 0$. Experimental conditions: microwave frequency 33.9 GHz, T = 15 K, $t_{\pi/2} = 32$ ns, $\tau = 400$ ns, RF pulse length = 20 µs.



Fig. S5 34 GHz ¹H Davies ENDOR spectra (in $H_2O - in D_2O$) of (a) [Cu(TMC)](ClO₄) and (b) [Cu(TMC)](NO₃)₂(H₂O)_{0.5}.



Fig. S6 DFT models for (a) *trans*-I-[Cu(TMC)]²⁺ complex with nitrate, (b) *trans*-III-[Cu(TMC)]²⁺ complex with nitrate, (c) *trans*-I-[Cu(TMC)]²⁺ complex with perchlorate, and (d) *trans*-III-[Cu(TMC)]²⁺ complex with perchlorate. Gibbs free energies relative to those of the complexes and distances between the Cu(II) center and the first-sphere coordination ligands are given.