Supporting Information

Copper(II) and Zinc(II) Complexation with *N*-Ethylenehydroxycyclams and Consequences on the Macrocyclic Backbone Configuration

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TE1EtOH
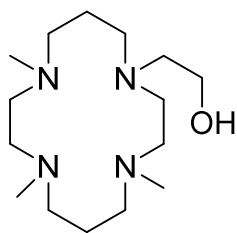
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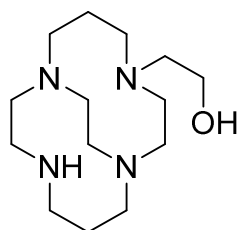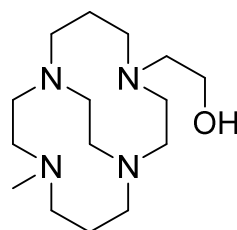
CB-TE1EtOH

CB-TEMeEtOH

TE1EtOH: 2-(1,4,8,11-tetraazacyclotetradecan-1-yl)ethan-1-ol

TE3MeEtOH: 2-(4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecan-1-yl)ethan-1-ol

CB-TE1EtOH: 2-(1,4,8,11-tetraazabicyclo[6.6.2]hexadecan-4-yl)ethan-1-ol

CB-TEMeEtOH: 2-(11-methyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecan-4-yl)ethan-1-ol

Synthesis and characterization of simple and cross-bridged *N*-ethylenehydroxy-functionalized cyclam ligands

1. Synthesis of 2-(1,4,8,11-tetraazacyclotetradecan-1-yl)ethan-1-ol [TE1EtOH]
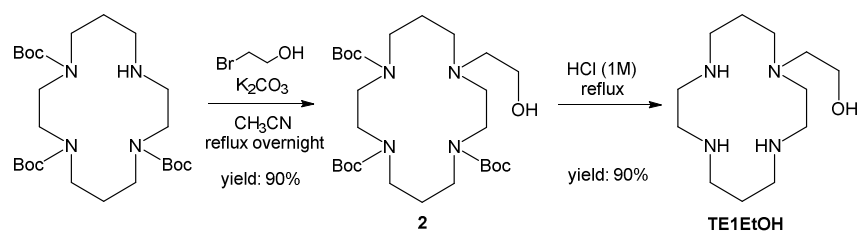
Compound 2: Bromoethanol (2.25 g, 1.28 mL, 18.0 mmol) was rapidly added to a solution of tri-Boc-cyclam (1.80 g, 3.6 mmol) in CH_3CN (50 mL) with K_2CO_3 (1.00 g, 7.2 mmol) and the mixture was stirred at reflux overnight. The solution was filtered and solvent was removed under reduced pressure. The obtained white foam was dissolved in NaOH solution (4 M, 15 mL) and stirred for 3 hours at room temperature. Aqueous layer was extracted with $CHCl_3$ (4 x 40 mL). Organic layers were combined, dried over $MgSO_4$ and evaporated. Compound **2** was then purified on silica column (CH_2Cl_2/AcOEt 50/50 then AcOEt) and was obtained as a white powder (1.76 g, 90 %).

^{13}C Jmod NMR (125 MHz, CD_3CN, 343 K): δ = [156.9, 156.8, 156.7] (C_q=O), [80.3, 80.2, 80.1] (C(CH$_3$)$_3$), [60.7, 58.7, 55.7, 53.8, 49.1, 48.7, 48.4, 48.3, 47.9, 47.2] (CH$_2$-α-N, CH$_2$-α-OH), [29.9, 28.3] (CH$_2$-β-N), 29.0 ppm (C(CH$_3$)$_3$).

^{1}H NMR (500 MHz, CD_3CN, 298 K): δ = 3.53-3.48 (m, 2H), 3.33-3.27 (m, 10H), 3.22-3.20 (m, 2H), 2.60-2.58 (m, 2H), 2.52-2.49 (m, 2H), 2.45-2.43 (m, 2H), 1.86-1.81 (m, 2H), 1.66-1.63 (m, 2H), 1.43 ppm (s, 27H, C(CH$_3$)$_3$).

HRMS (ESI): *m/z* calcd for $C_{27}H_{53}N_4O_7^+$ [M+H]$^+$ 545.3909, found 545.3910.

TE1EtOH: Compound **2** (3.70 g, 6.8 mmol) was stirred at reflux 4 h in HCl solution (1 M, 20 mL). After cooling down, aqueous layer was washed with Et_2O to remove organic impurities. At 0 °C, NaOH pellets were added till pH > 12 and aqueous layer was extracted with $CHCl_3$ (4 x 50 mL). Organic layers were combined, dried over $MgSO_4$ and evaporated. **TE1EtOH** was obtained as a white solid (1.49 g, 90 %).

^{13}C Jmod NMR (75 MHz, CDCl$_3$, 298 K): δ = [62.5, 58.1, 58.0, 57.5, 51.6, 50.6, 50.4, 49.0, 48.5, 48.1] (CH_2-α-N, CH_2-α-OH), [28.8, 26.6] ppm (CH_2-β-N).

^1H NMR (300 MHz, CDCl$_3$, 298 K): δ = 3.59-3.56 (m, 2H, CH_2-α-OH), 3.50 (br s, 3H, N-H), 2.81-2.70 (m, 8H), 2.64-2.53 (m, 10H), 1.85-1.69 ppm (m, 4H, CH_2-β-N).

HRMS (ESI): *m/z* calcd for $C_{12}H_{29}N_4O^+$ [M+H]$^+$ 245.2336, found 245.2333, calcd for $C_{12}H_{30}N_4O^{2+}$ [M+2H]$^{2+}$ 123.1204, found 123.1202.

2. Synthesis of 2-(4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecan-1-yl)ethan-1-ol [TE3MeEtOH]
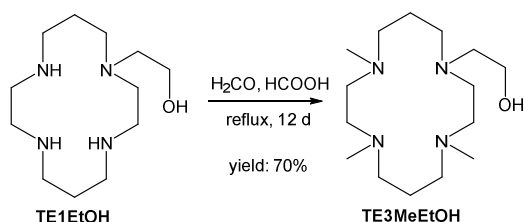
TE3MeEtOH: **TE1EtOH** (1.00 g, 4.1 mmol) was dissolved in 37 % formaldehyde in water (5.00 mL, 1.50 g, 49.9 mmol) and formic acid (5.00 mL, 6.10 g, 132.0 mmol). The solution was stirred at reflux for 12 days, 1.00 mL of formic acid was added after 4 days and 8 days. The mixture was evaporated under reduced pressure and NaOH solution (4 M, 10 mL) was added. This solution was stirred at reflux for 2 h and alkaline aqueous layer was extracted with $CHCl_3$ (4 x 40 mL). Organic layers were combined, dried over $MgSO_4$ and evaporated under reduced pressure.

TE3MeEtOH was purified on silica column (CH_2Cl_2/iPr-NH_2 98/2 to 96/4) and was obtained as a colorless oil (0.82 g, 70 %).

^{13}C Jmod NMR (125 MHz, $CDCl_3$, 298 K): δ = [61.3, 56.2, 55.9, 55.8, 55.3, 54.7, 52.6, 52.3, 52.2, 50.0] (CH_2-α-N, CH_2-α-OH), [44.0, 43.2, 42.7] (N-CH_3), [25.5, 25.0] ppm (CH_2-β-N).

^1H NMR (500 MHz, $CDCl_3$, 298 K): δ = 3.46-3.44 (m, 2H, CH_2-α-OH), 2.52-2.32 (m, 18H, CH_2-α-N), 2.17 (s, 3H), 2.13 (s, 3H), 2.12 (m, 3H), 1.64-1.54 ppm (m, 4H, CH_2-β-N).

HRMS (ESI): *m/z* calcd for $C_{15}H_{35}N_4O^+$ [M+H]$^+$ 287.2805, found 287.2803, calcd for $C_{15}H_{36}N_4O^{2+}$ [M+2H]$^{2+}$ 144.1439, found 144.1435.

3. Synthesis of 2-(1,4,8,11-tetraazabicyclo[6.6.2]hexadecan-4-yl)ethan-1-ol [CB-TE1EtOH]
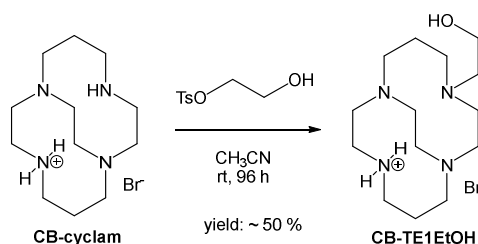
CB-TE1EtOH: Ethylenehydroxy-tosylate (0.22 g, 1.0 mmol) in CH_3CN (10 mL) was slowly added (20 h with syringe driver) to a solution of **CB-cyclam** (0.23 g, 1.0 mmol) in CH_3CN (200 mL). The mixture was stirred 4 days till all the ethylenehydroxy-tosylate was consumed. Reaction progress was tracked by silica TLC (Thin Layer Chromatography). Solvent was evaporated under reduced pressure, 10 mL of NaOH solution (4 M) was added and aqueous layer was extracted with $CHCl_3$ (4 x 20 mL). Organic layers were combined, dried over $MgSO_4$ and solvent was evaporated. **CB-TE1EtOH** was purified (a) on alumina column (CH_2Cl_2/ MeOH 99/1 to 95/5) to obtain beige oil (0.15 mg, 55 %) and (b) by flash chromatography on a C18 column in a mixture of H_2O/CH_3CN (a gradient of 0 to 100% of H_2O) to obtain a beige oil (0.14 mg, 51%).

^{13}C Jmod NMR (75 MHz, CDCl$_3$, 298 K): δ = [61.7, 59.2, 59.0, 55.7, 55.5, 54.9, 53.8, 53.4, 51.9, 51.0, 46.7, 45.0] (CH$_2$-α-N), [28.7, 22.2] ppm (CH$_2$-β-N).

^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ = 3.83-3.73 (m, 2H, CH$_2$-α-OH), 3.54-3.50 (m, 1H), 3.30-3.25 (m, 1H), 2.99-2.37 (m, 22H), 1.90-1.76 (m, 2H), 1.71-1.59 ppm (m, 2H).

HRMS (ESI): *m/z* calcd for C$_{14}$H$_{31}$N$_4$O$^+$ [M+H]$^+$ 271.2492, found 271.2493, calcd for C$_{14}$H$_{32}$N$_4$O^{2+} [M+2H]$^{2+}$ 136.1283, found 136.1283.

4. Synthesis of 4-methyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane iodide [CB-TEMeEtOH]
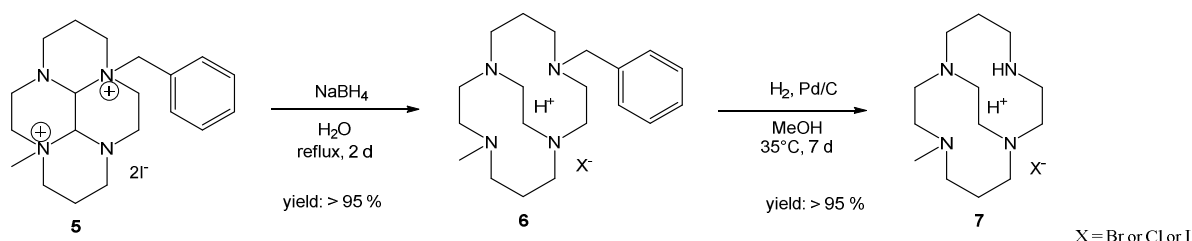
Compound 6: To a solution of compound **5** (1.70 g, 2.9 mmol) in ethanol (50 mL), NaBH$_4$ (1.10 g, 29.2 mmol) was slowly added and the mixture was stirred at reflux 2 days. Solvent was evaporated under reduced pressure and white residue was dissolved in NaOH solution (4 M, 15 mL). The aqueous layer was extracted with CHCl$_3$ (4 x 40 mL). Organic layers were combined, dried over MgSO$_4$ and evaporated. Compound **6** was obtained as brown oil (1.35 g, quantitative).

^{13}C Jmod NMR (125 MHz, CDCl$_3$, 298 K): δ = 140.8 (C$_{q, ar}$), [128.7, 127.9, 126.3] (CH$_{ar}$), [59.8, 59.2, 57.7, 56.5, 56.4, 56.0, 55.9, 54.8, 53.9, 52.0, 51.8] (CH$_2$-α-N), 42.7 (N-CH$_3$), [27.7, 26.8] ppm (CH$_2$-β-N).

^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ = 7.31-7.22 (m, 5H$_{ar}$), 4.43 (d, J=14 Hz, 1H), 4.03 (d, J = 14 Hz, 1H), 3.43-3.29 (m, 2H), 3.22-3.14 (m, 1H), 3.10-3.01 (m, 1H), 2.99-2.80 (m, 6H), 2.66-2.57 (m, 2H), 2.50-2.41 (m, 2H), 2.47 (s, 3H), 2.36-2.25 (m, 4H), 2.10-1.97 (m, 3H), 1.81-1.76 (m, 1H), 1.54-1.45 ppm (m, 2H).

HRMS (ESI): *m/z* calcd for $C_{20}H_{35}N_4^+$ [M+H]$^+$ 331.2856, found 331.2856. m/z calcd for $C_{13}H_{28}N_4^+$ [M-Bn+H]$^+$ 241.2387, found 241.2386.

Compound 7: Compound **6** (1.45 g, 3.2 mmol) was dissolved in methanol (50 mL) with Pd/C 10% (0.80 g, 0.8 mmol). The mixture was stirred at 35 °C under H_2 atmosphere for 7 days. The palladium was removed by filtration on celite and the solvent was evaporated to give compound **7** as brown oil (1.10 g, 95 %).

^{13}C Jmod NMR (75 MHz, CDCl$_3$, 298 K): δ = [58.2, 56.8, 55.4, 54.7, 53.9, 53.4, 51.2, 49.9, 46.4, 44.2] (CH$_2$-α-N), 44.9 (N-CH$_3$), [26.7, 22.2] ppm (CH$_2$-β-N).

^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ = 10.81 (br s, 1H, acidic H), 3.38-3.32 (m, 1H), 3.21-3.16 (m, 1H), 2.97-2.61 (m, 13H), 2.53-2.34 (m, 5H), 2.41 (s, 3H), 1.86-1.50 ppm (m, 4H).

HRMS (ESI): *m/z* calcd for $C_{13}H_{29}N_4^+$ [M+H]$^+$ 241.2387, found 241.2386, calcd for $C_{13}H_{30}N_4^{2+}$ [M+2H]$^{2+}$ 121.1229, found 121.1230.
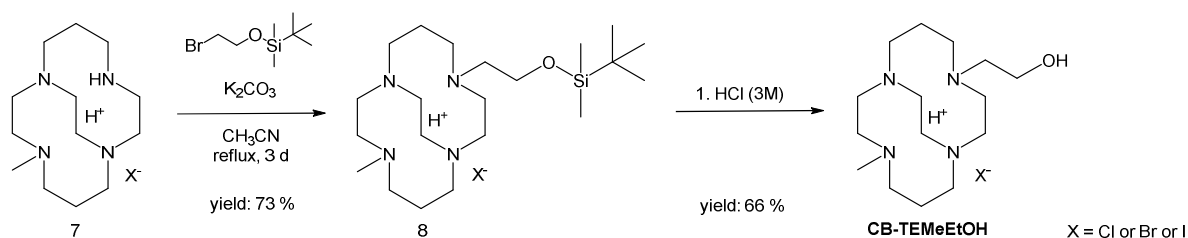
Compound 8: A solution of 2-Bromo-1-tert-butyldimethylsilyloxy-ethane (0.24 g, 1.0 mmol) in CH$_3$CN (10 mL) was slowly added on a solution of **7** (0.20 g, 0.5 mmol) in CH$_3$CN (20 mL) with K$_2$CO$_3$ (0.42 g, 3.0 mmol). Then the solution was stirred at reflux for 3 days. K$_2$CO$_3$ was filtered out and solvent was evaporated under reduced pressure. The mixture was purified on silica column (CH$_2$Cl$_2$/MeOH.NH$_3$ (7N) 98/2 to 90/10) to give compound **8** as a brown oil (0.16 g, 73 %).

13C Jmod NMR (75 MHz, CDCl₃, 298 K) : δ = [60.1, 58.7, 58.3, 55.9, 55.2, 54.5, 54.2, 54.1, 54.1, 52.3, 50.9, 49.9] (CH₂-α-N, CH₂-α-OH), 42.1 (N-CH₃), 25.7 (C(CH₃)₃), [25.1, 23.3] (CH₂-β-N), 18.1 (Si-C$_q$), -5.4 ppm (Si-CH₃).

1H NMR (300 MHz, CDCl₃, 298K) : δ = 3.90-3.82 (m, 1H), 3.78-3.67 (m, 2H), 3.49-3.33 (m, 3H), 3.25-3.20 (m, 1H), 3.17-3.12 (m, 1H), 3.09-3.05 (m, 1H), 3.03-2.92 (m, 7H), 2.86-2.76 (m, 5H), 2.68-2.64 (m, 2H), 2.59-2.55 (m, 1H), 2.34 (s, 3H, CH₃), 1.80-1.77 (m, 2H), 1.64-1.60 (m, 2H), 0.87 (s, 9H, Si-C(CH₃)₃), 0.04 ppm (s, 6H, Si-CH₃).

HRMS (ESI): *m/z* calcd for $C_{21}H_{47}N_4OSi^+$ [M+H]⁺ 399.3514, found 399.3514, calcd for $C_{21}H_{48}N_4OSi^{2+}$ [M+2H]²⁺ 200.1793, found 200.1798, calcd for $C_{15}H_{32}N_4^{2+}$ [M-OTBDMS]²⁺ 134.1308, found 134.1310.

CB-TEMeEtOH: Compound **8** (0.30 g, 0.8 mmol) was dissolved in HCl (3 M, 15 mL) and the mixture was stirred at reflux 2 h. The aqueous layer was washed with Et₂O (3 x 20 mL) and evaporated under reduced pressure. At 0°C, NaOH solution (3 M, 10mL) was added and the aqueous layer was extracted with CHCl₃ (3 x 30mL). Organic layers were combined, dried over MgSO₄ and evaporated under reduce pressure to give **CB-TEMeEtOH** as brown solid (0.16 g, 66 %).

13C Jmod NMR (75 MHz, CDCl₃ , 298 K): δ = [58.8, 58.7, 57.9, 56.7, 56.4, 54.4, 54.2, 53.5, 53.2, 52.8, 52.3, 51.0] (CH₂-α-N, CH₂-α-OH), 42.2 (N-CH₃), [24.6, 23.7] ppm (CH₂-β-N).

1H NMR (300 MHz, CDCl₃, 298 K): δ = 3.84-3.63 (m, 3H), 3.34-3.15 (m, 4H), 3.04-2.98 (m, 4H), 2.92-2.87 (m, 2H), 2.81-2.78 (m, 2H), 2.72-2.60 (m, 8H), 2.25 (s, 3H, CH 3), 1.68-1.54 ppm (m, 4H).

HRMS (ESI): *m/z* calcd for $C_{15}H_{33}N_4O^+$ [M+H]⁺ 285.2649, found 285.2651, calcd for $C_{15}H_{34}N_4O^{2+}$ [M+2H]²⁺ 143.1361, found 143.1361.

Synthesis and characterization of cyclam complexes with copper(II) and zinc(II)

5. Characterization of Copper(II) 2-(1,4,8,11-tetraazacyclotetradecan-1-yl)ethan-1-ol dichloride [Cu(TE1EtOH)]Cl$_2$

TE1EtOH (48.9 mg, 0.200 mmol), CuCl$_2$ (29.6 mg, 0.220 mmol).

Complex was obtained as purple powder (47mg, 60 %).

HRMS (ESI) (positive, H$_2$O): *m/z* calcd. for [C$_{12}$H$_{28}$CuN$_4$O]$^{2+}$, 153.5774, found 153.5776 [Cu(TE1EtOH)]$^{2+}$, calcd. for [C$_{12}$H$_{27}$CuN$_4$O]$^+$, 306.1475, found 306.1473 [Cu(TE1EtOH)-H]$^+$.

6. Characterization of Zinc(II) 2-(1,4,8,11-tetraazacyclotetradecan-1-yl)ethan-1-ol dichloride [Zn(TE1EtOH)]Cl$_2$

TE1EtOH (48.9 mg, 0.200 mmol), ZnCl$_2$ (30.0 mg, 0.220 mmol).

Complex was obtained as white powder (43 mg, 55 %).

HRMS (ESI) (positive, H$_2$O): *m/z* calcd. for [C$_{12}$H$_{28}$N$_4$OZn]$^{2+}$, 154.0772, found 154.0772 [Zn(TE1EtOH)]$^{2+}$, calcd. for [C$_{12}$H$_{27}$N$_4$OZn]$^+$, 307.1471, found 307.1408 [Zn(TE1EtOH)-H]$^+$.

^{1}H NMR (500 MHz, D$_2$O, 298 K): complex mixture of 3 forms δ = 4.00-3.83 (mm, 2H, CH$_2$-α-OH), 3.33-2.43 (m, 18H, CH$_2$-α-N), 2.0-1.64 ppm (m, 4H, CH$_2$-β-N).

^{13}C NMR (125 MHz, D$_2$O, 298 K): Isomer 1: δ = [63.0, 61.5, 61.3, 57.5, 53.3, 52.8, 51.8, 50.6, 50.4, 48.4] (CH$_2$-α-N, CH$_2$-α-OH), [30.6, 28.2] ppm (CH$_2$-β-N). Isomer 2: δ = [59.7, 59.0, 57.5, 54.4, 53.7, 52.8, 51.6, 50.8, 48.2, 47.5] (CH$_2$-α-N, CH$_2$-α-OH), [27.3, 26.5] ppm (CH$_2$-β-N). Isomer 3: δ = [59.9, 58.9, 54.5, 54.2, 53.7, 53.5, 51.9, 50.0, 48.7, 48.0] (CH$_2$-α-N, CH$_2$-α-OH), [29.9, 26.7] ppm (CH$_2$-β-N).

7. Characterization of Copper(II) 2-(4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecan-1-yl)ethan-1-ol dichloride [Cu(TE3MeEtOH)]Cl₂

TE3MeEtOH (57.2 mg, 0.200 mmol), CuCl₂ (29.6 mg, 0.220 mmol).

Complex was obtained as a blue powder (55.4 mg, 64 %).

HRMS (ESI) (positive, H₂O): *m/z* calcd. for $[C_{15}H_{34}CuN_4O]^{2+}$, 174.6009, found 174.6014 $[Cu(TE3MeEtOH)]^{2+}$, calcd. for $[C_{15}H_{34}CuN_4O]^+$, 349.2023, found 349.2018 $[Cu(TE3MeEtOH)]^+$.

8. Characterization of Zinc(II) 2-(4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecan-1-yl)ethan-1-ol dichloride [Zn(TE3MeEtOH)]Cl₂

TE3MeEtOH (57.2 mg, 0.200 mmol), ZnCl₂ (30.0 mg, 0.220 mmol).

Complex was obtained as white powder (61 mg, 70 %).

HRMS (ESI) (positive, H₂O): *m/z* calcd. for $[C_{15}H_{34}N_4OZn]^{2+}$, 175.1007, found 175.1014 $[Zn(TE3MeEtOH)]^{2+}$, calcd. for $[C_{15}H_{33}N_4OZn]^+$, 349.1940, found 349.1942 $[Zn(TE3MeEtOH)-H]^+$, calcd. for $[C_{15}H_{33}ClN_4OZn]^+$, 385.1707, found 385.1707 $[Zn(TE3MeEtOH)+Cl]^+$.

¹H NMR (500 MHz, D₂O, 298 K): δ = 4.15-4.04 (m, 2H, CH₂-α-OH), 3.45 (td, J=13.0, 6.4 Hz, 1H), 3.29-3.20 (m, 7H), 3.12-3.07 (m, 1H), 2.94-2.92 (m, 4H), 2.61 (s, 3H, CH₃), 2.53 (s, 3H, CH₃), 2.51 (s, 3H, CH₃), 2.61-2.51 (m, 5H), 2.43-2.36 (m, 2H, CH₂-β-N), 1.77-1.71 ppm (m, 2H, CH₂-β-N).

¹³C NMR (125 MHz, D₂O, 298 K): δ = [65.0, 64.0, 62.3, 60.1, 59.6, 59.5, 59.1, 53.9, 52.4] (CH₂-α-N), 59.9 (CH₂-α-OH), [48.1, 44.4, 43.6] (N-CH₃), [23.5, 23.1] ppm (CH₂-β-N).

9. Characterization of Copper(II) 2-(1,4,8,11-tetraazabicyclo[6.6.2]hexadecan-4-yl)ethan-1-ol dichloride [Cu(CB-TE1EtOH)]Cl₂

CB-TE1EtOH (22 mg, 0.081 mmol), CuCl₂ (13.12 mg, 0.098 mmol).

Complex was obtained as a blue powder (31.3 mg, 95 %).

HRMS (ESI) (positive, H₂O): m/z calcd. for $[C_{14}H_{30}CuN_4O]^{2+}$, 166.5852, found 166.5858 [Cu(CB-TE1EtOH)]$^{2+}$, calcd. for $[C_{14}H_{29}CuN_4O]^+$, 332.1631, found 332.1635 [Cu(CB-TE1EtOH)-H]$^+$, calcd. for $[C_{14}H_{30}ClCuN_4O]^+$, 368.1398, found 368.1400 [Cu(CB-TE1EtOH)-Cl]$^+$.

10. Characterization of Zinc(II) 2-(1,4,8,11-tetraazabicyclo[6.6.2]hexadecan-4-yl)ethan-1-ol dichloride [Zn(CB-TE1EtOH)]Cl₂

CB-TE1EtOH (16.5 mg, 0.061 mmol), CuCl₂ (10 mg, 0.073 mmol).

Complex was obtained as a beige powder (4.9 mg, 19 %).

HRMS (ESI) (positive, H₂O): m/z calcd. for $[C_{14}H_{30}N_4OZn]^{2+}$, 167.0850, found 167.0856 [Zn(CB-TE1EtOH)]$^{2+}$, calcd. for $[C_{14}H_{29}N_4OZn]^+$, 333.1627, found 333.1629 [Cu(CB-TE1EtOH)-H]$^+$, calcd. for $[C_{14}H_{30}ClN_4OZn]^+$, 369.1394, found 369.1397 [Cu(CB-TE1EtOH)-Cl]$^+$.

¹H NMR (500 MHz, D₂O, 298 K): δ = 4.00-3.93 (m, 2H), 3.41-3.33 (m, 1H), 3.30-3.24 (m, 1H), 3.14-2.94 (m, 19H), 2.78-2.71 (m, 2H), 2.66-2.62 (dd, 1H), 2.32-2.18 (m, 2H), 1.72-1.67 (m, 1H), 1.62-1.58 (m, 1H) ppm.

¹³C NMR (125 MHz, D₂O, 298 K): δ = [60.9, 59.8, 59.6, 58.6, 58.4, 57.6, 56.9, 51.6, 51.2, 49.2, 48.9, 41.0] (CH₂-α-N and CH₂-α-OH), [23.0, 21.50] ppm (CH₂-β-N).

11. Characterization of Copper(II) 2-(4-methyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane iodide)ethan-1-ol dichloride [Cu(CB-TEMeEtOH)]Cl₂

CB-TEMeEtOH.3HCl (63.5 mg, 0.161 mmol), CuCl₂ (26.0 mg, 0.193 mmol).

Complex was obtained as a blue powder (35.1 mg, 52 %).

HRMS (ESI) (positive, H2O): m/z calcd. for $[C_{15}H_{32}CuN_4O]^{2+}$, 173.5931, found 173.5935 [Cu(CB-TEMeEtOH)]$^{2+}$, calcd. for $[C_{15}H_{31}CuN_4O]^+$, 346.1788, found 346.1784 [Cu(CB-TEMeEtOH)-H]$^+$.

12. Characterization of Zinc(II) 2-(4-methyl-1,4,8,11 tetraazabicyclo[6.6.2]hexadecane iodide)ethan-1-ol dichloride [Zn(CB-TEMeEtOH)]Cl$_2$

CB-TEMeEtOH.3HCl (63.5 mg, 0.161 mmol), ZnCl$_2$ (26.4 mg, 0.193 mmol).

Complex was obtained as beige powder (40.0 mg, 59 %).

HRMS (ESI) (positive, H$_2$O): *m/z* calcd. for [C$_{15}$H$_{32}$N$_4$OZn]$^{2+}$, 174.0928, found 174.0930 [Zn(CB-TEMeEtOH)]$^{2+}$, calcd. for [C$_{15}$H$_{31}$N$_4$OZn]$^+$, 347.1784, found 347.1779 [Zn(CB-TEMeEtOH)-H]$^+$, calcd. for [C$_{15}$H$_{32}$ClN$_4$OZn]$^+$, 383.1551, found 383.1555 [Zn(CB-TEMeEtOH)+Cl]$^+$.

^{1}H NMR (500 MHz, D$_2$O, 298 K): δ = 3.96-3.93 (m, 2H, CH$_2$-α-OH), 3.37-3.31 (m, 2H), 3.25-3.21 (m, 2 H), 3.12-2.74 (m, 12H), 2.70 (dd, J=13.0, 4.1 Hz, 1H), 2.63 (dd J=15.4, 5.3 Hz, 1H), 2.51 (s, 3H, CH$_3$), 2.41 (dd, J=15.2, 4.5 Hz, 1H), 2.31-2.22 (m, 2H, CH$_2$-β-N), 1.72-1.68 (m, 2H, CH$_2$-β-N).

^{13}C NMR (125 MHz, D$_2$O, 298 K): δ = [63.7, 63.4, 62.6, 62.0, 61.5, 60.8, 58.4, 54.3, 53.8, 53.7, 52.0] (CH$_2$-α-N), 60.8 (CH$_2$-α-OH), 51.3 (N-CH$_3$), [25.8, 25.7] ppm (CH$_2$-β-N).

NMR characterization of cyclam ligands

13. ^1H and ^{13}C NMR characterization of TE1EtOH
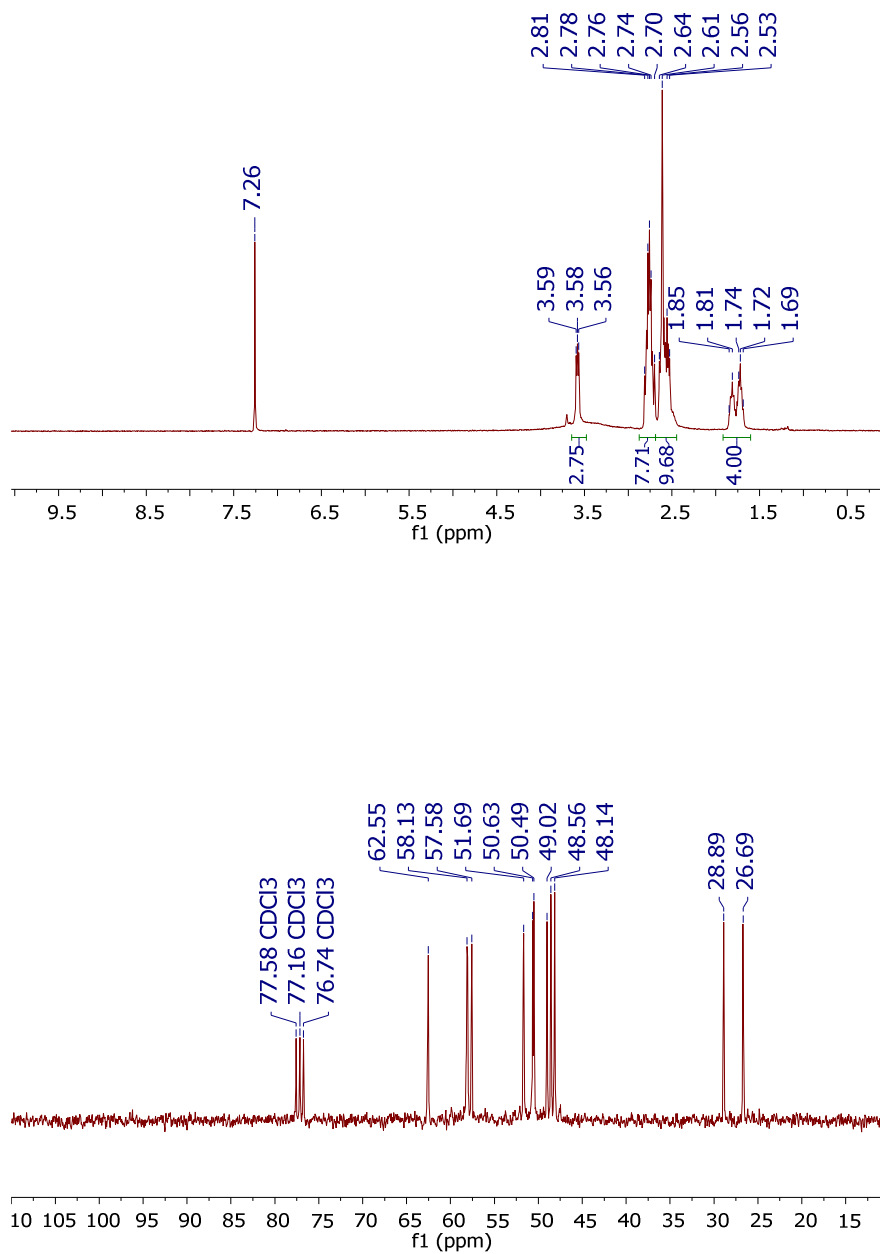
Figure S 1. ^1H (up) and ^{13}C(down) NMR (300 and 75 MHz, CDCl$_3$, 298 K) spectra of TE1EtOH.

14. ¹H and ¹³C NMR characterization of TE3MeEtOH
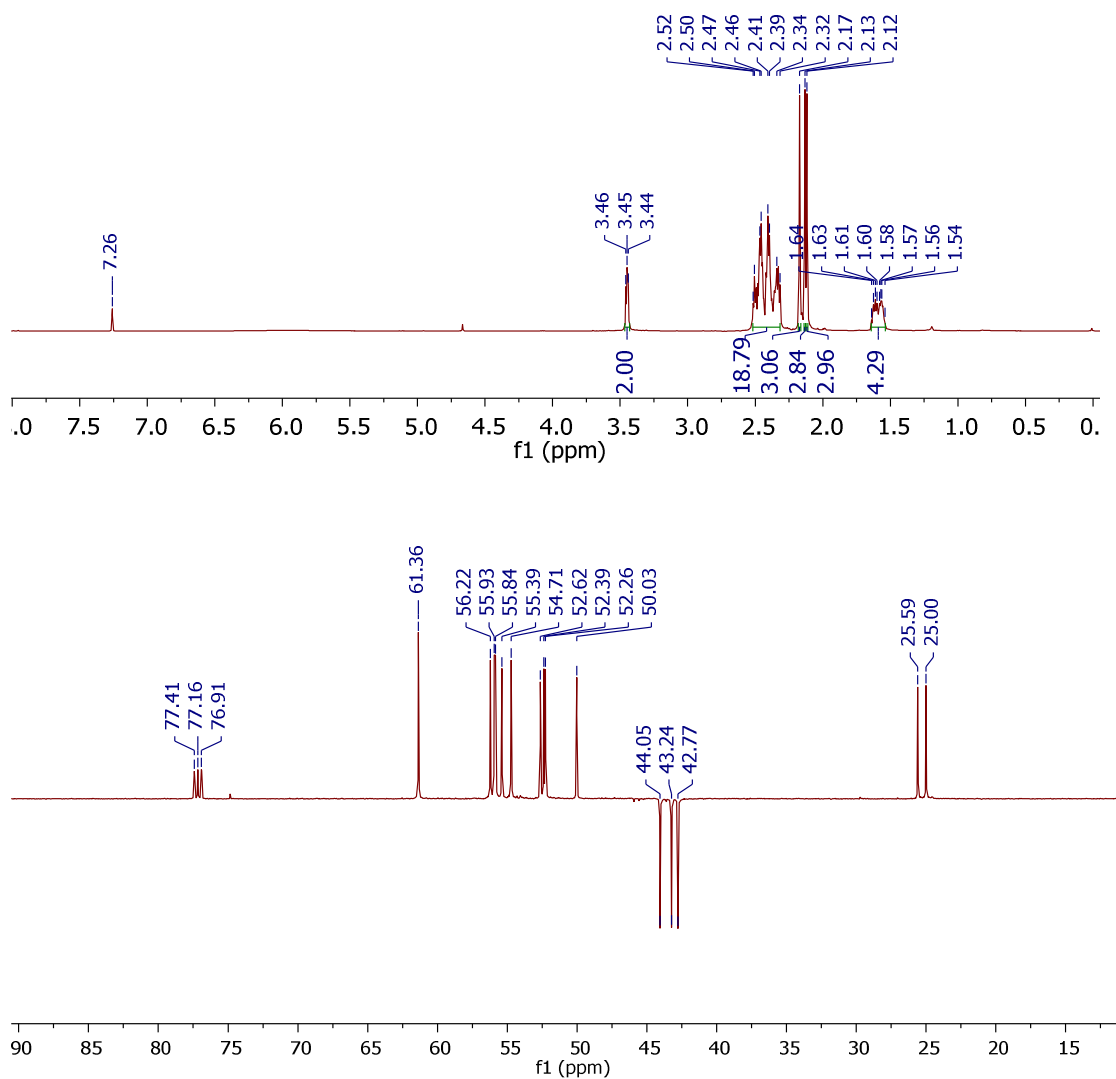
Figure S2. NMR ¹H (up) and ¹³C Jmod (down) (500 and 125 MHz, CDCl₃, 298 K) spectra of TE3MeEtOH.

15. ^{1}H and ^{13}C NMR characterization of CB-TEEtOH
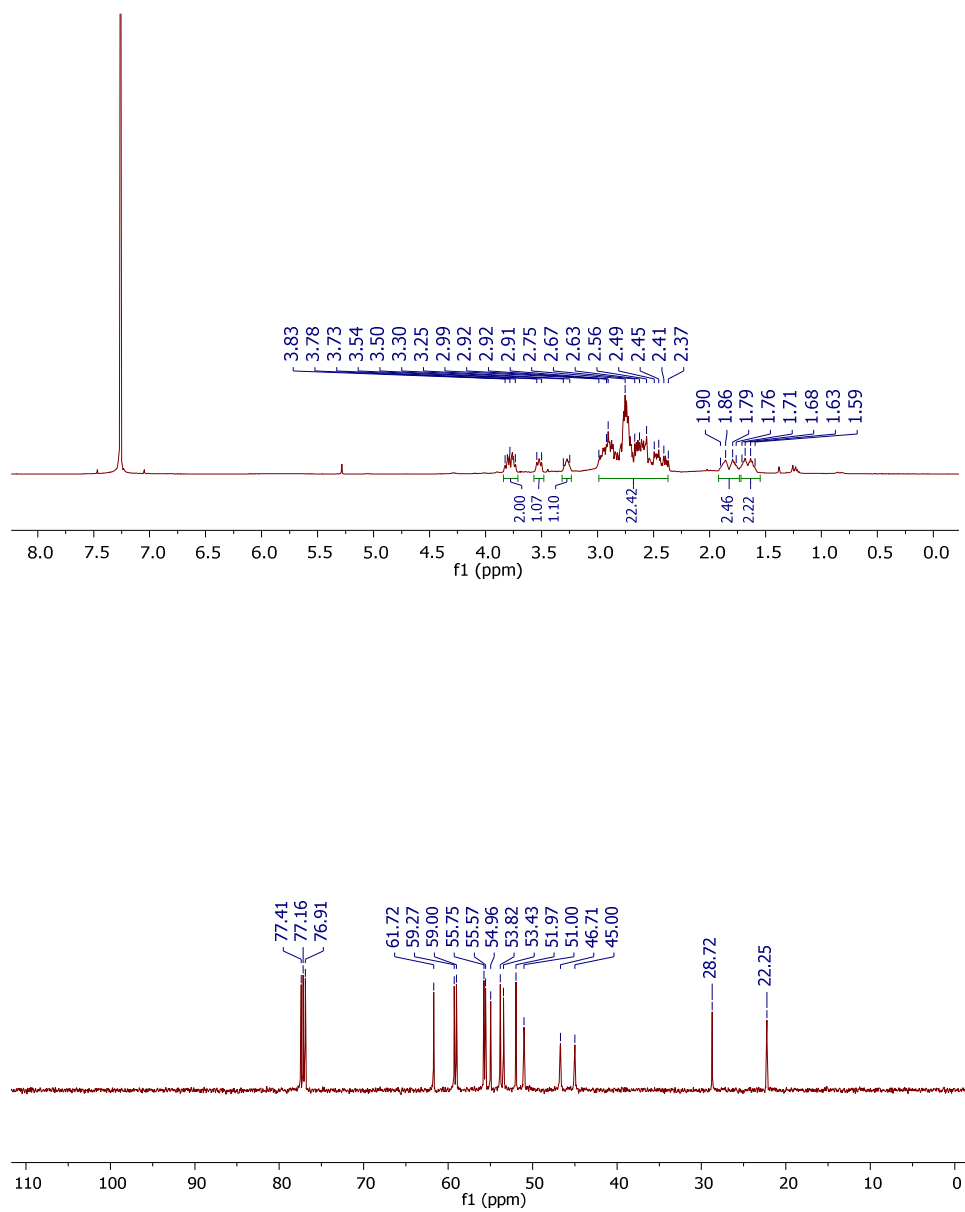
Figure S3. ^{1}H (up) and ^{13}C (down) NMR (500 and 125 MHz, CDCl$_3$, 298 K) spectra of CB-TE1EtOH.

16. ^{1}H and ^{13}C NMR characterization of CB-TEMeEtOH
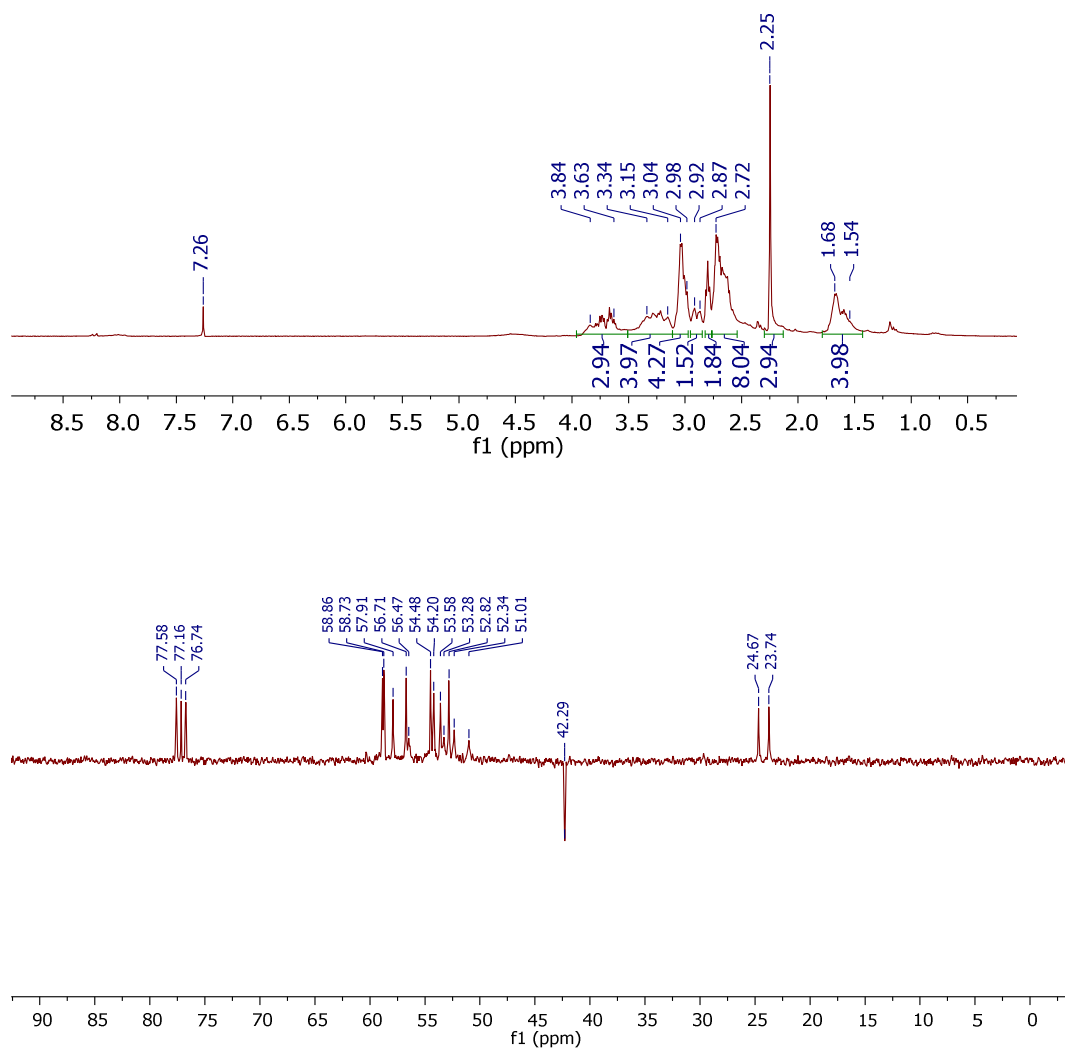
Figure S4. ^{1}H (up) and ^{13}C Jmod (down) NMR (300 and 75 MHz, CDCl$_3$, 298 K) spectra of CB-MeTEEtOH.

HR-MS characterization of cyclam ligands
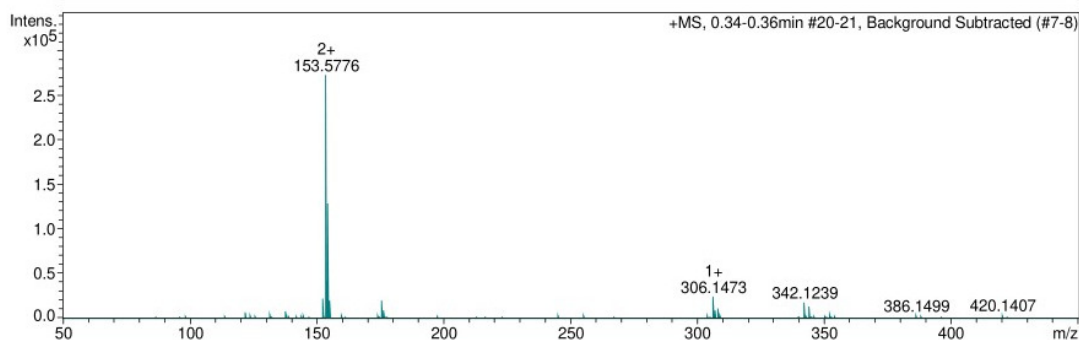
Figure S5. ESI-MS spectrum of [Cu(TE1EtOH)Cl$_2$].
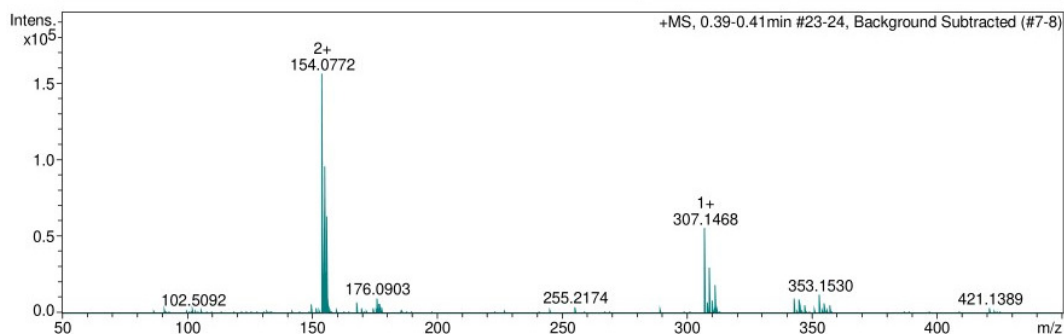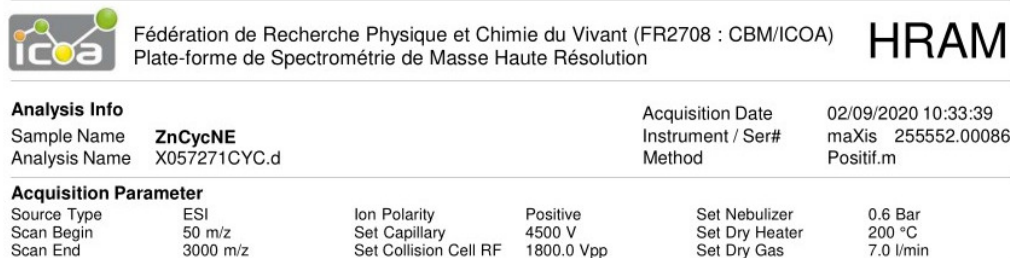
Figure S6. ESI-MS spectrum of [Zn(TE1EtOH)Cl$_2$].

Figure S 7. ESI-MS spectrum of [Cu(TE3MeEtOH)Cl₂].

Figure S8. ESI-MS spectrum of [Zn(TE3MeEtOH)Cl₂].

Figure S10. ESI-MS spectrum of [Cu(CB-TE1EtOH)Cl₂].

Figure S9. ESI-MS spectrum of [Zn(CB-TE1EtOH)Cl₂].

Figure S12. ESI-MS spectrum of [Cu(CB-TEMeEtOH)Cl₂].

Figure S11. ESI-MS spectrum of [Zn(CB-TEMeEtOH)Cl₂].

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NMR Characterization of cyclam-Zinc(II) complexes

17. 1D and 2D NMR characterization of [Zn(TE1EtOH)]Cl$_2$
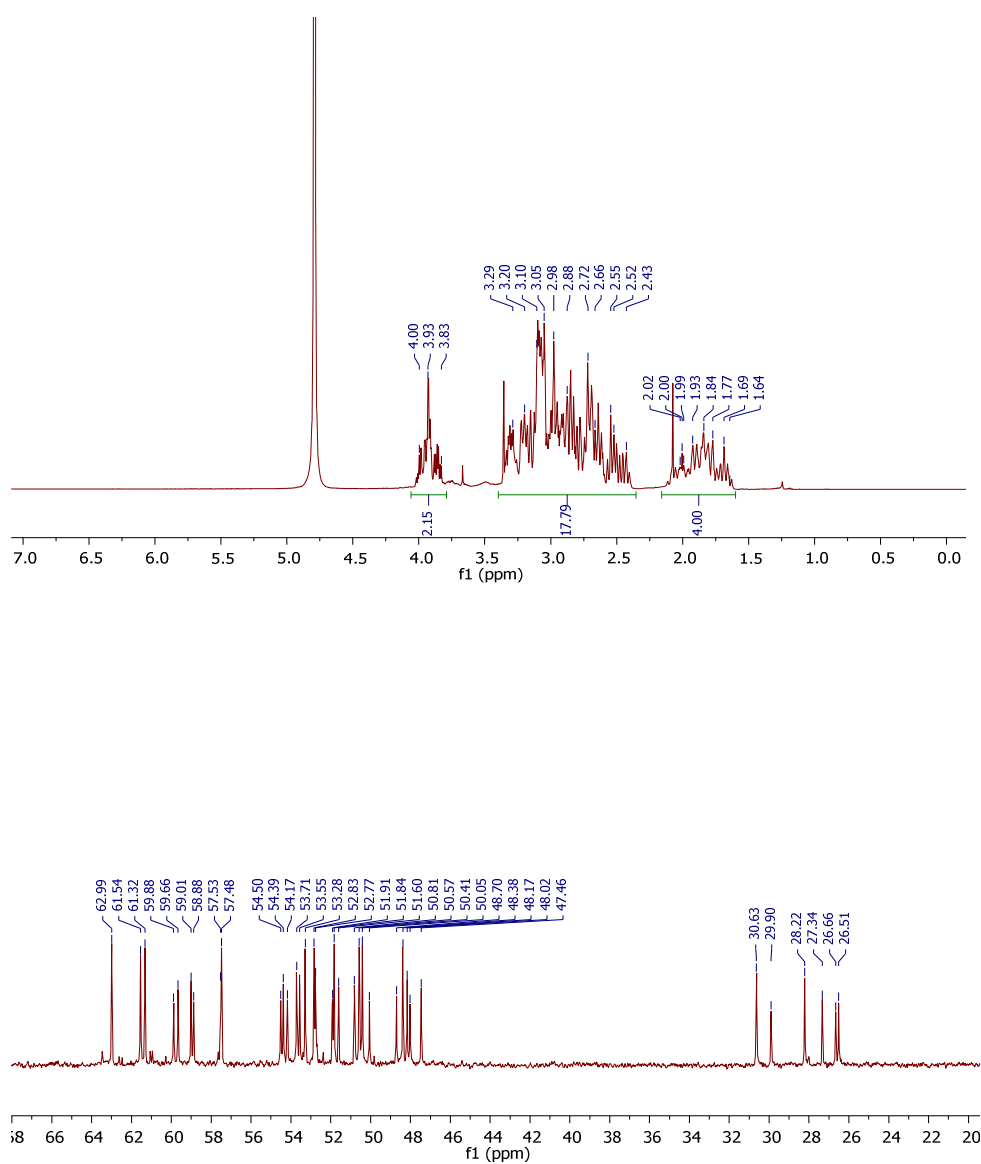
Figure S13. ^{1}H (up) and ^{13}C (down) NMR (500 and 125 MHz, D$_2$O, 298 K) spectra of [Zn(TE1EtOH)]Cl$_2$.
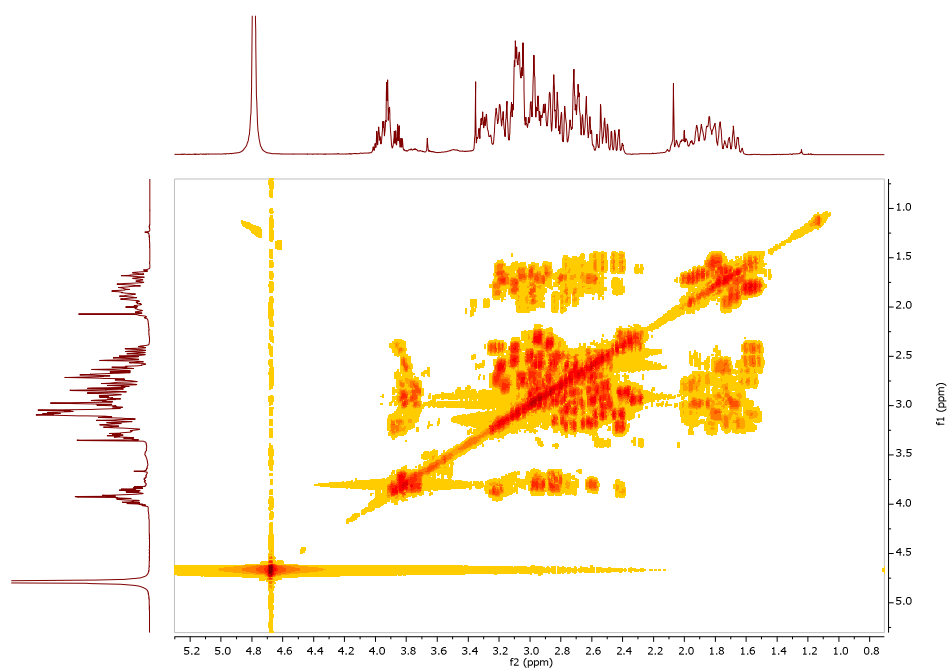
Figure S14. 2D COSY ^{1}H-^{1}H NMR (500 MHz, D$_2$O, 298 K) spectrum of [Zn(TE1EtOH)]Cl$_2$.
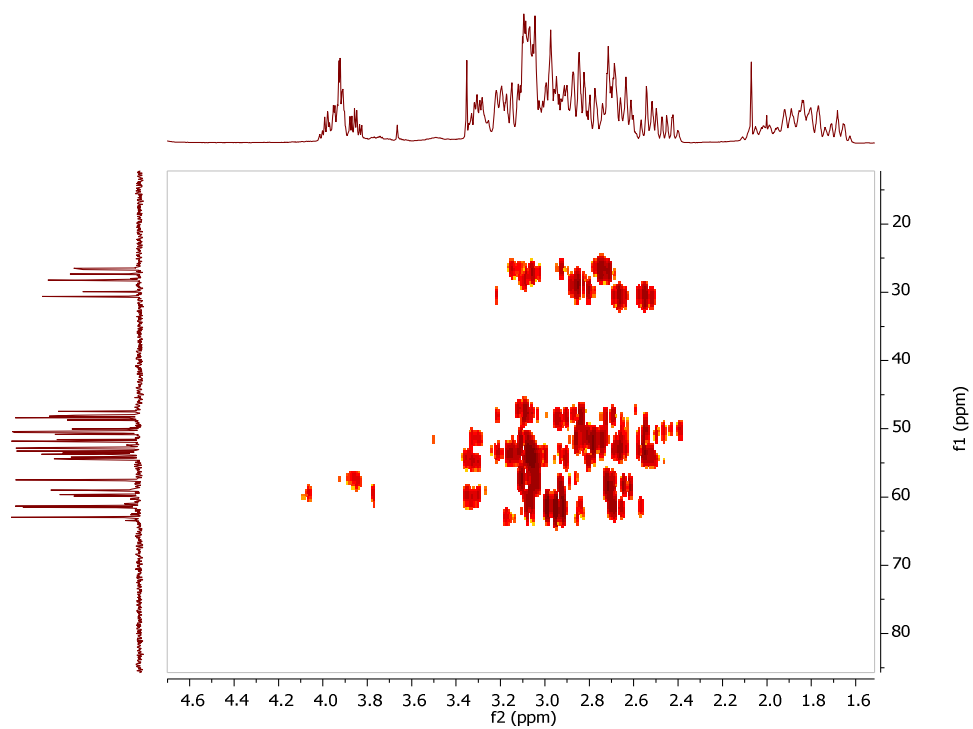
Figure S15. 2D HMBC ^{1}H-^{13}C NMR (500 MHz, 125 MHz, D$_2$O, 298 K) spectrum of [Zn(TE1EtOH)]Cl$_2$.
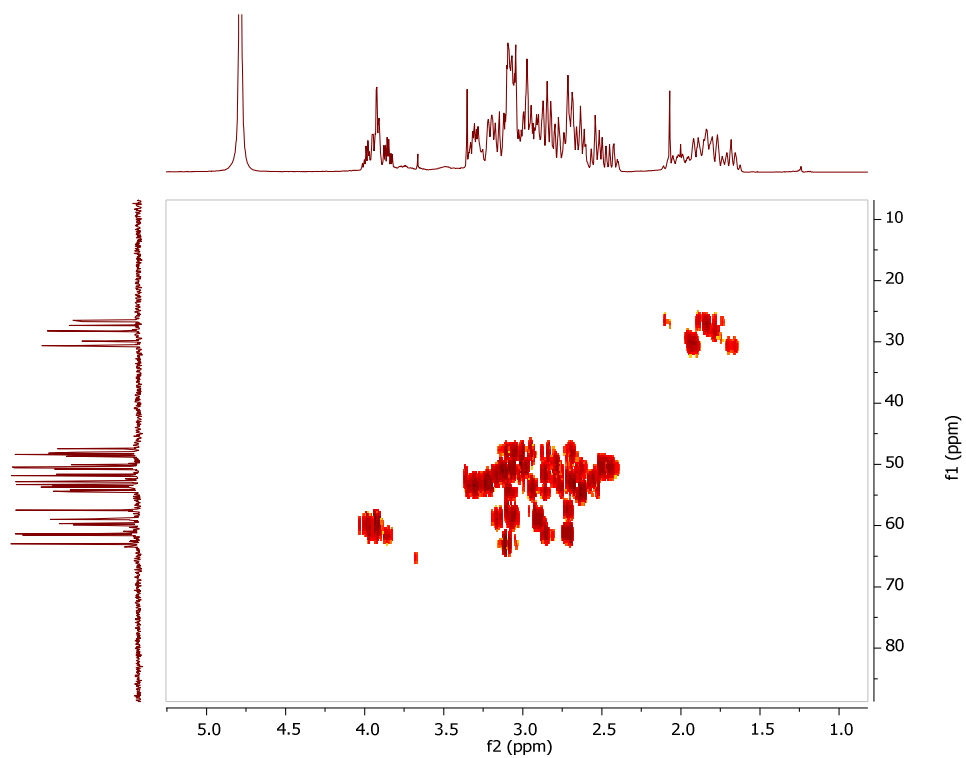
Figure S16. 2D HMQC ^{1}H-^{13}C NMR (500 MHz, 125 MHz, D$_2$O, 298 K) spectrum of [Zn(TE1EtOH)]Cl$_2$.

18. 1D and 2D NMR characterization of [Zn.TE3MeEtOH]Cl$_2$
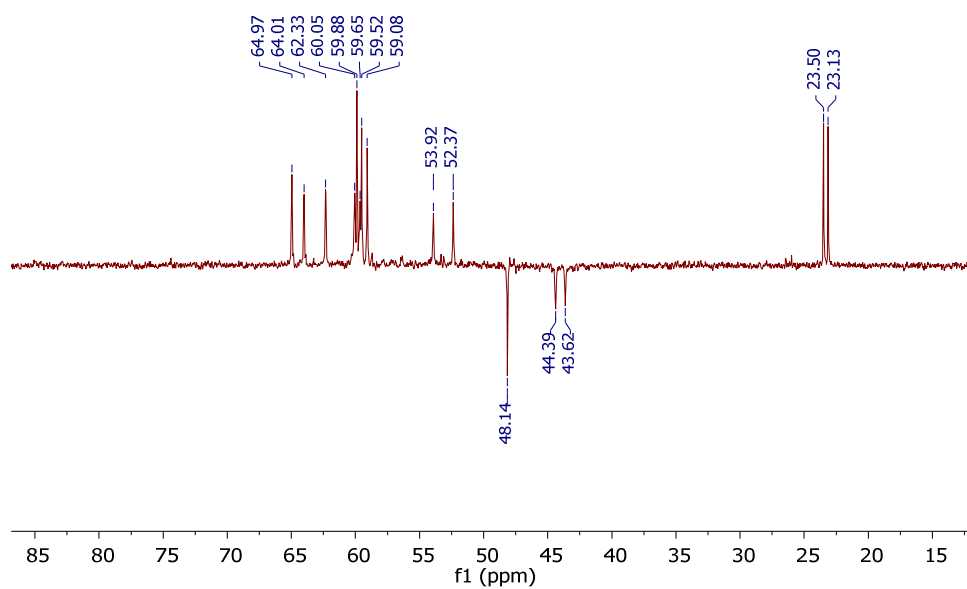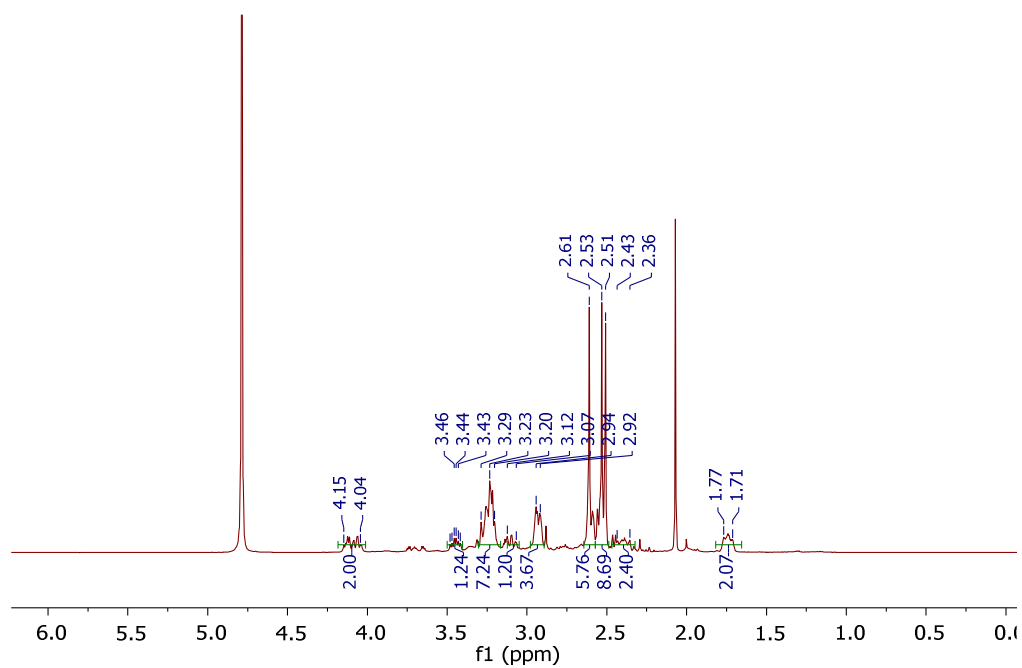
Figure S17. ^{1}H (up) and ^{13}C (down) NMR (500 and 125 MHz, D$_2$O, 298 K) spectra of [Zn(TE3MeEtOH)]Cl$_2$.
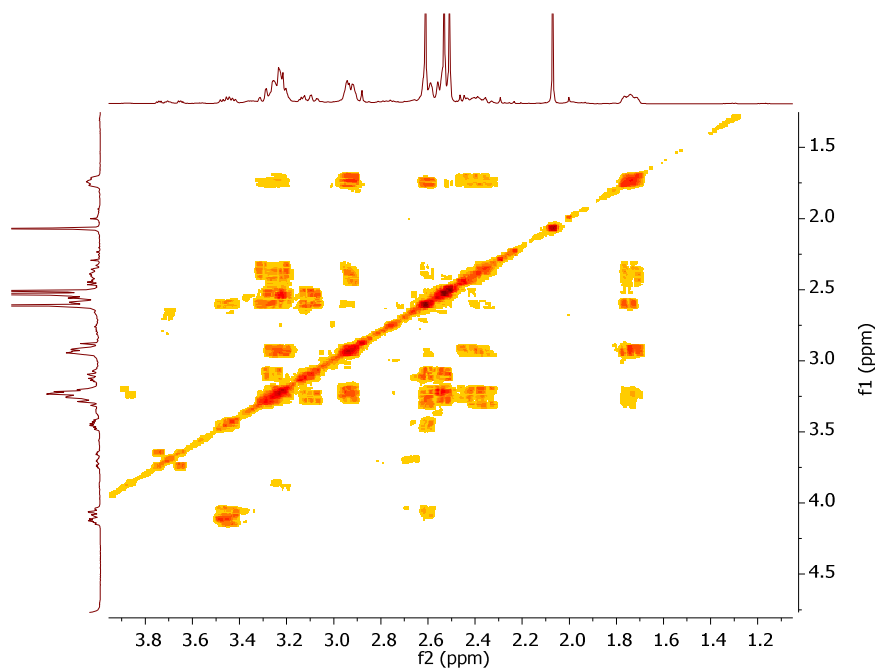
Figure S18. 2D COSY ^{1}H-^{1}H NMR (500 MHz, D$_2$O, 298 K) spectrum of [Zn(TE3MeEtOH)]Cl$_2$.
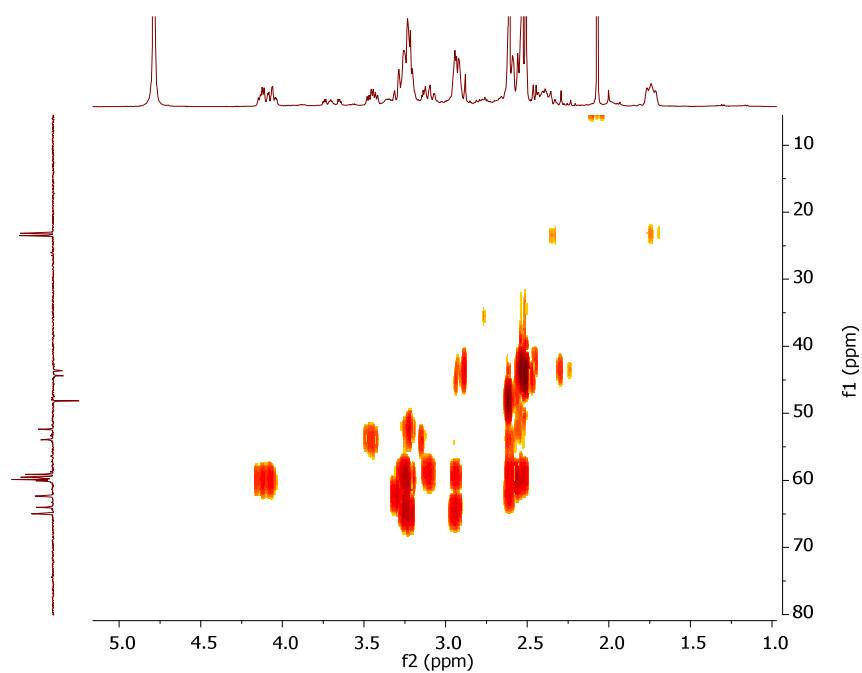
Figure S19. 2D HMQC ^{1}H-^{13}C NMR (500 MHz, 125 MHz, D$_2$O, 298 K) spectrum of [Zn(TE3MeEtOH)]Cl$_2$.
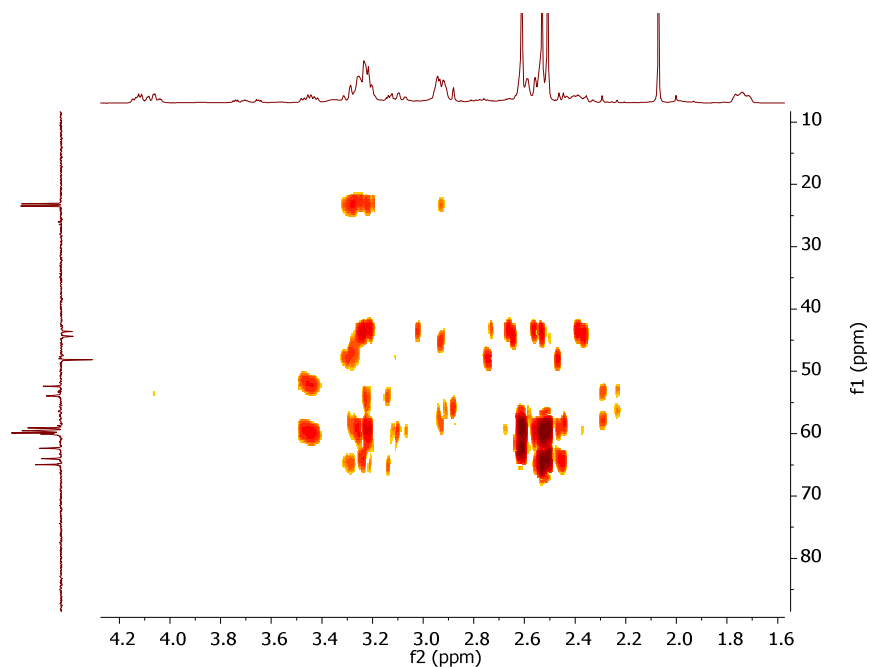
Figure S20. 2D HMBC ^{1}H-^{13}C NMR (500 MHz, 125 MHz, D$_2$O, 298 K) spectrum of [Zn(TE3MeEtOH)]Cl$_2$.

19. 1D and 2D NMR characterization of [Zn(CB-TE1EtOH)]Cl$_2$
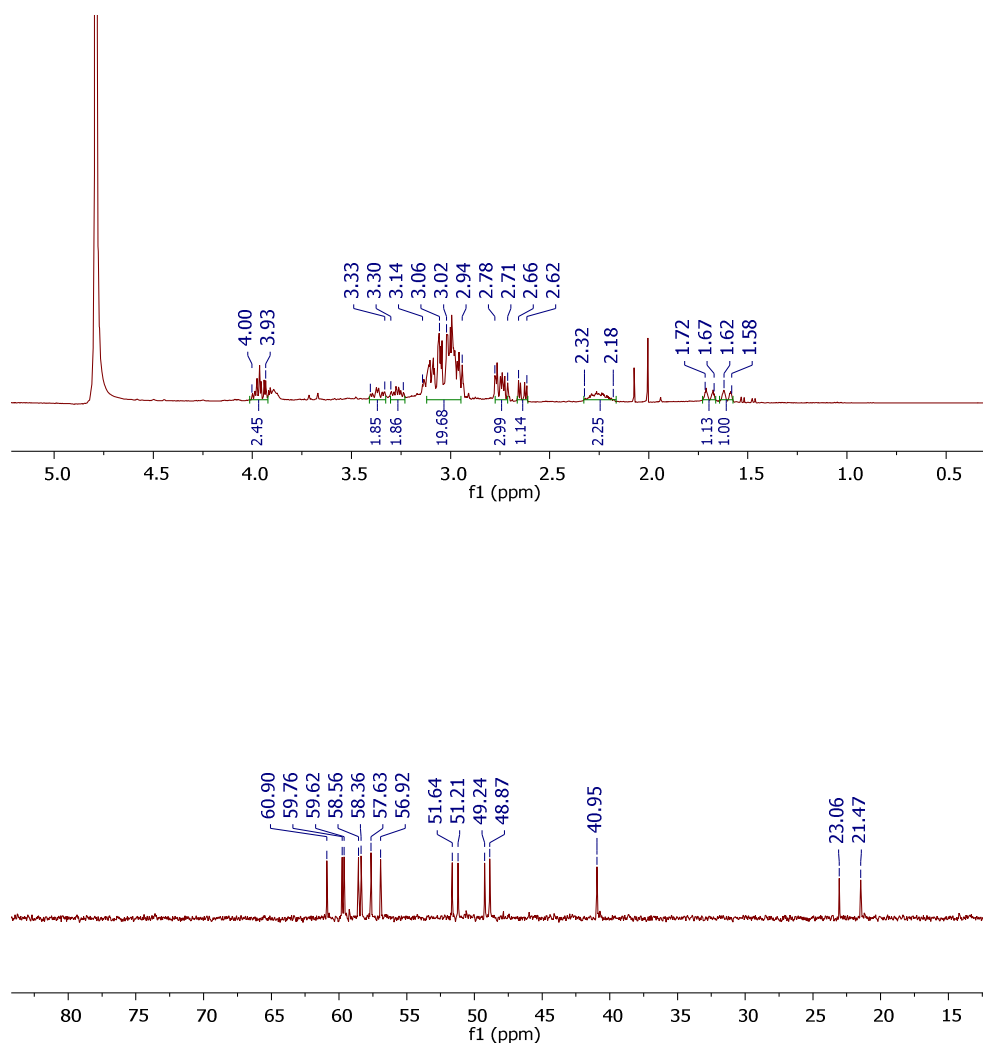
Figure S21. ^{1}H (up) and ^{13}C Jmod (down) NMR (500 and 125 MHz, D$_2$O, 298 K) spectra of [Zn(CB-TE1EtOH)]Cl$_2$
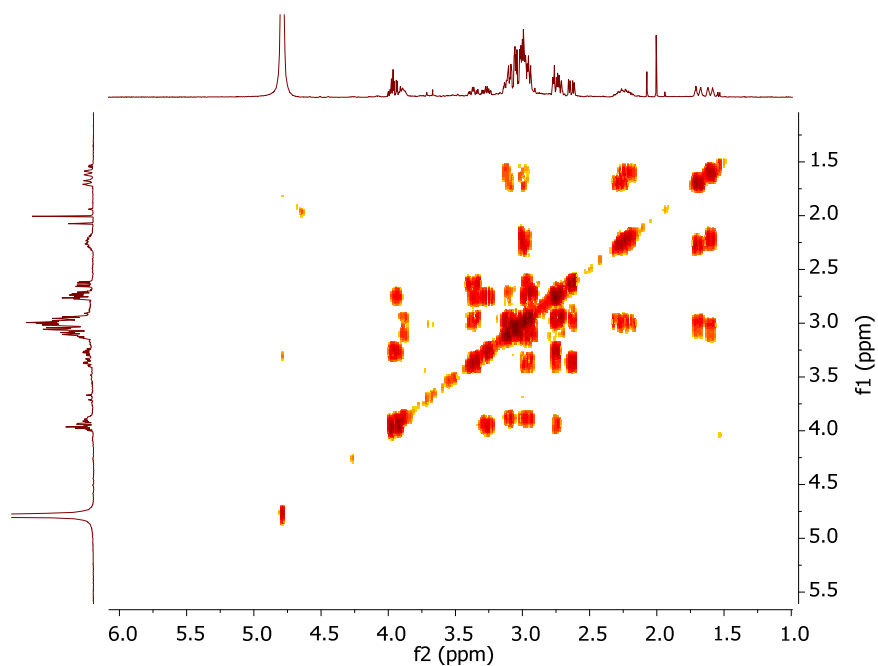
Figure S 22. COSY ^{1}H-^{1}H NMR (500 MHz, D$_2$O, 298 K) spectrum of [Zn(CB-TE1EtOH)]Cl$_2$.
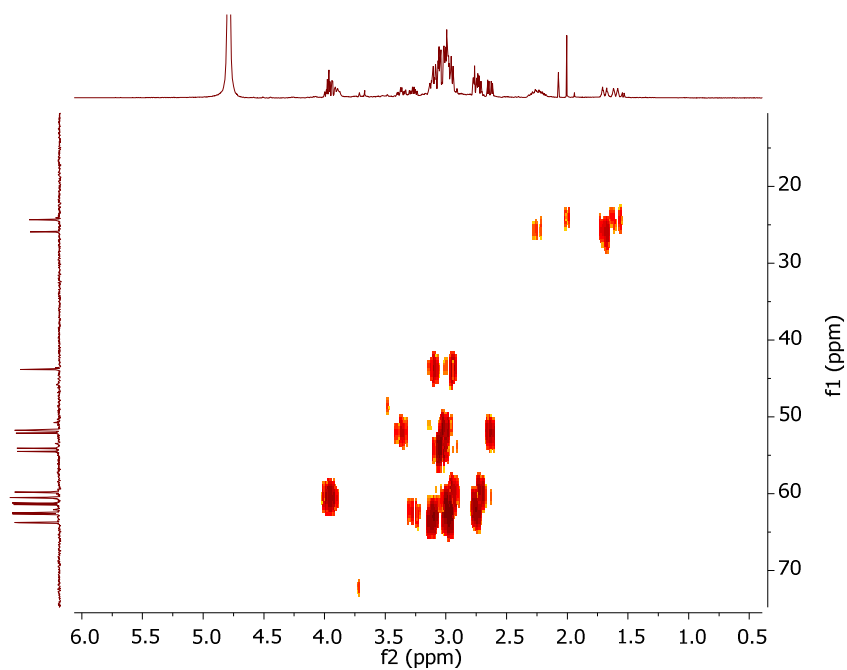
Figure S 23. 2D HMQC ^{1}H-^{13}C NMR (500 MHz, 125 MHz, D$_2$O, 298 K) spectrum of [Zn(CB-TE1EtOH)]Cl$_2$.
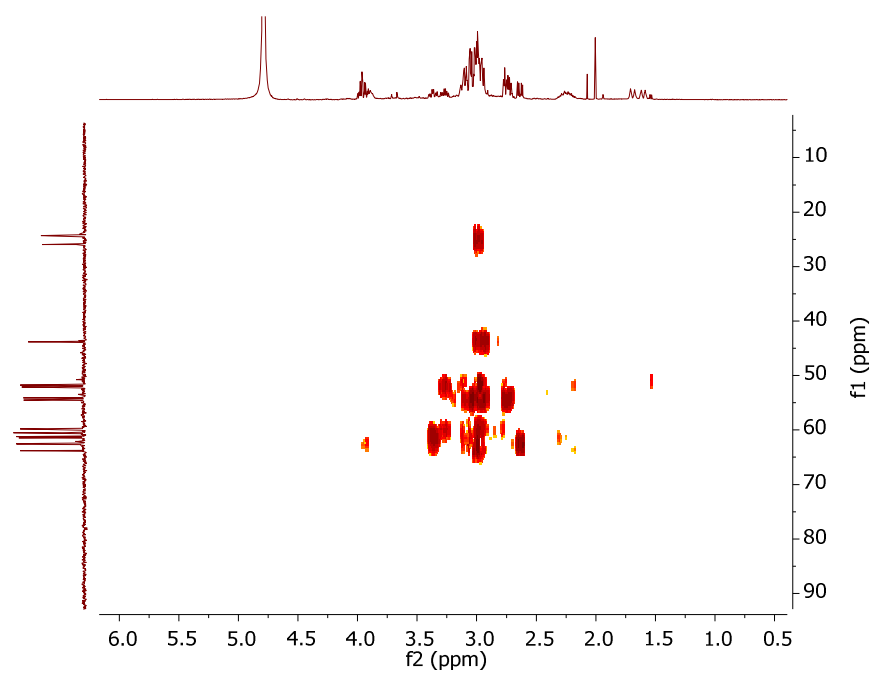
Figure S 24. 2D HMBC ^{1}H-^{13}C NMR (500 MHz, 125 MHz, D$_2$O, 298 K) spectrum of [Zn(CB-TE1EtOH)]Cl$_2$.

20. 1D and 2D NMR characterization of [Zn(CB-TEMeEtOH)]Cl₂
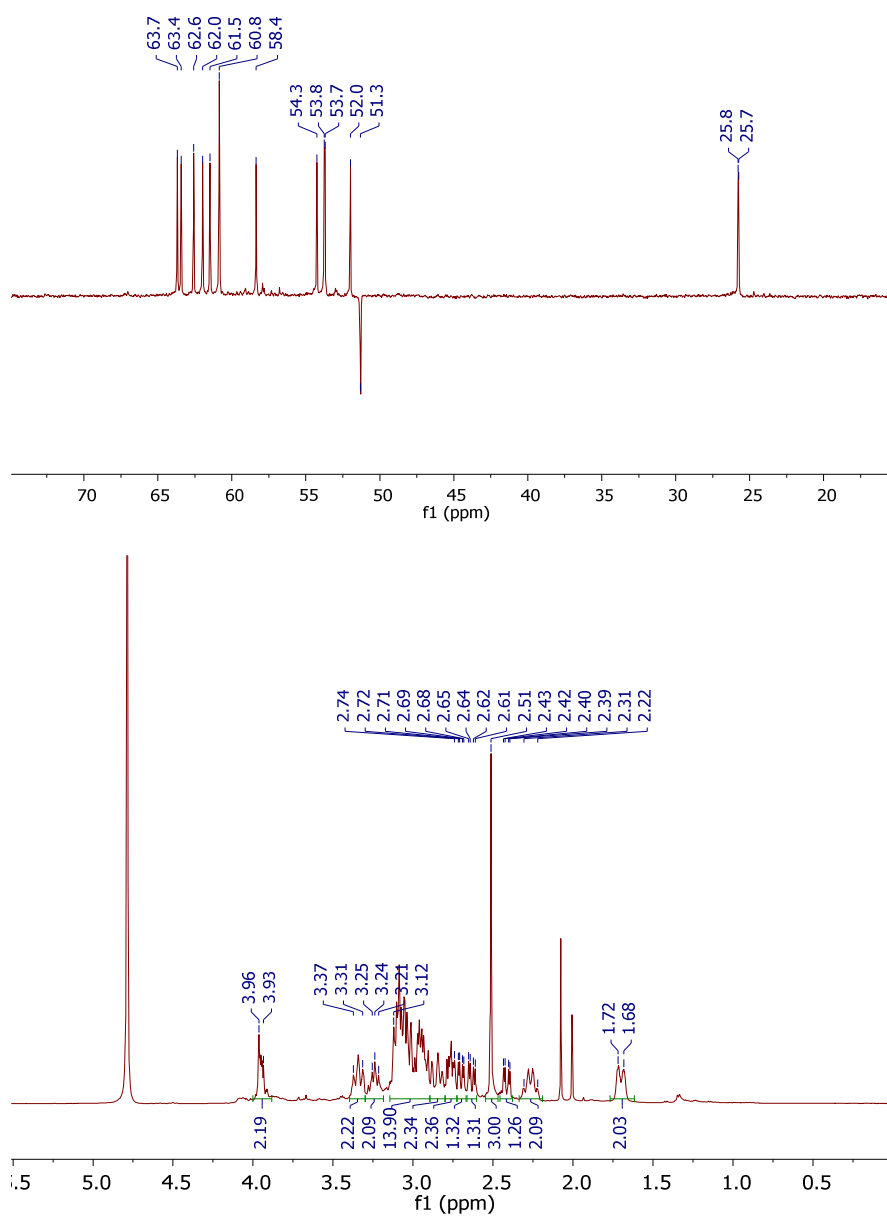
Figure S25. ¹H (up) and ¹³C Jmod (down) NMR (500 and 125 MHz, D₂O, 298 K) spectra of [Zn(CB-TEMeEtOH)]Cl₂.
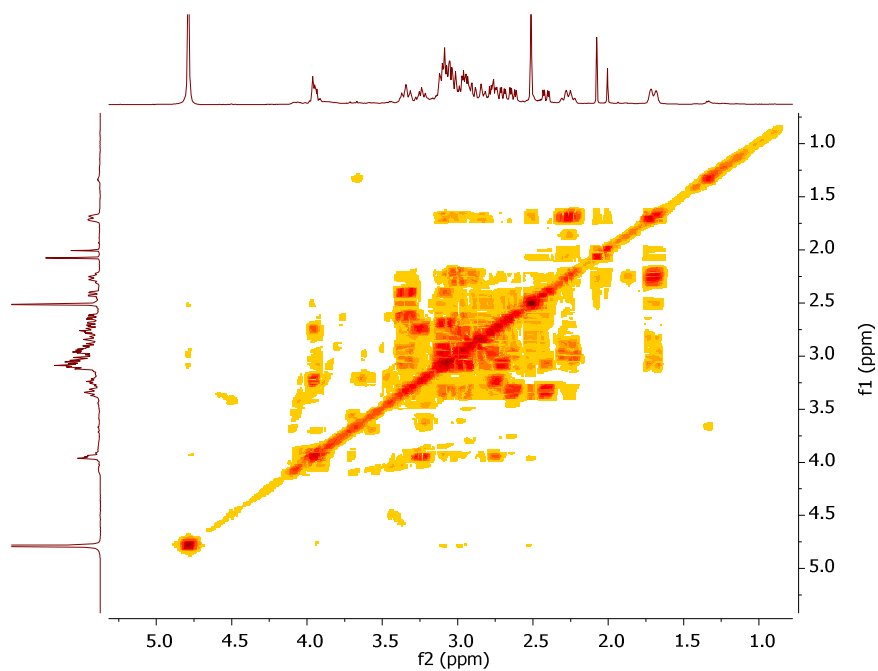
Figure S26. 2D COSY ¹H-¹H NMR (500 MHz, D₂O, 298 K) spectrum of [Zn(CB-TEMeEtOH)]Cl₂.
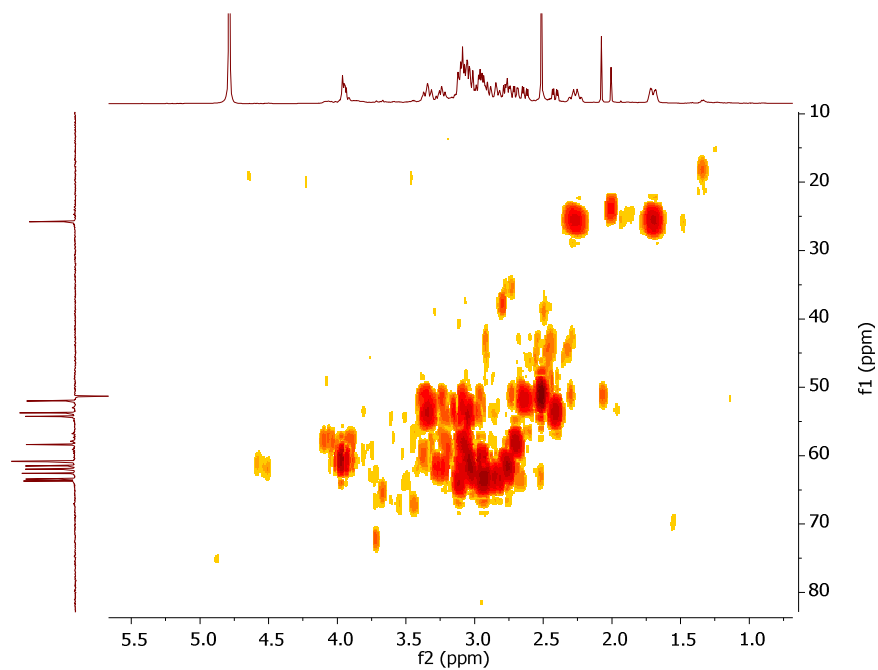
Figure S27. 2D HMQC 1H-13C NMR (500 MHz, 125 MHz, D₂O, 298 K) spectrum of [Zn(CB-TEMeEtOH)]Cl₂.
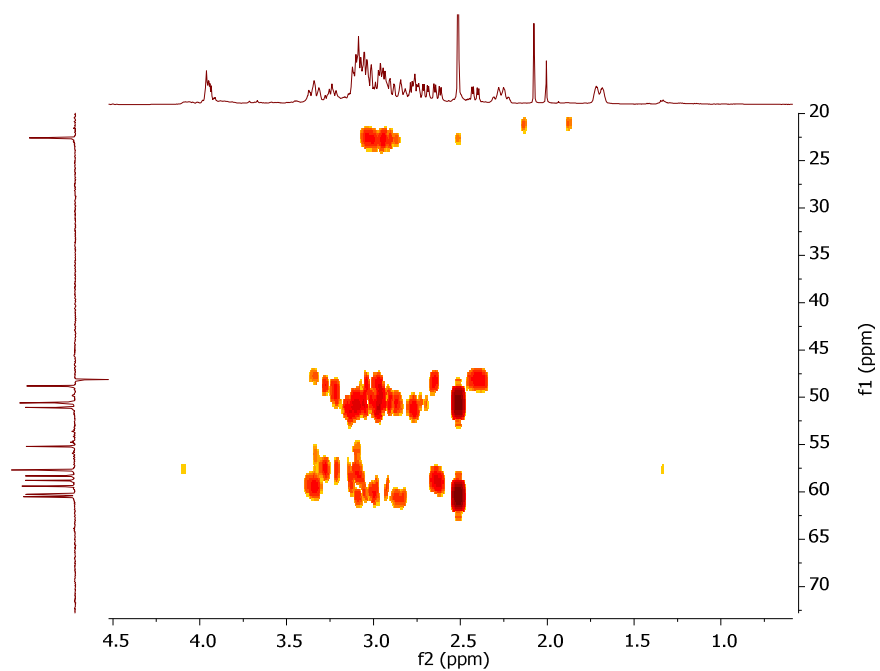
Figure S28. 2D HMBC ^{1}H-^{13}C NMR (500 MHz, 125 MHz, D$_2$O, 298 K) spectrum of [Zn(CB-TEMeEtOH)]Cl$_2$.

Table S2. Crystallographic data of [Zn(TE1EtOH)Cl]Cl.

Empirical formula	$C_{12}H_{28}Cl_2N_4OZn$
Formula weight	380.65 g/mol
Temperature	150(2) K
Radiation type	Mo-Kalpha
Wavelength	0.71073 Å
Crystal system	monoclinic, P 21/n
Unit cell dimensions	a = 6.8923(4) Å, b = 14.6166(10) Å, c = 17.0777(9) Å, β = 92.962(2)°
Volume	1718.14(18) Å^3
Z, Calculated density	4, 1.472 g.cm^{-3}
Absorption coefficient	1.742 mm^{-1}
F(000)	800
Crystal size	0.350 x 0.210 x 0.130 mm
Crystal color	colorless
Crystal description	prism
θ range for data collection	2.388 to 27.513 °
(sinθ/λ)max (Å-1)	0.650
h_min, h_max	-8, 8
k_min, k_max	-16, 18
l_min, l_max	-19, 22
Reflections collected / unique	12108 / 3884 [R(int) = 0.0778]
Reflections [I>2sigma(I)]	3066

Completeness to θmax	0.987
Absorption correction type	multi-scan
Max. and min. transmission	0.797, 0.520
Refinement method	Full-matrix least-squares on F^2
H-atom treatment	H-atom parameters treated by a mixture of independent and constrained refinement
Data / restraints / parameters	3884 / 1 / 184
Goodness-of-fit	1.067
Final R indices [I>2sigma(I)]	R1 = 0.0708
R indices (all data)	R1 = 0.0901
Largest diff. peak and hole	1.302 and -0.617 e.$Å^{-3}$

Table S3. Cartesian coordinates (Å) of [Zn(TE1EtOH)Cl]Cl.

Zn1	**0.49515(8)**	**0.29968(4)**	**0.15625(3)**
Cl1	0.75344(17)	0.39979(8)	0.14499(8)
O1	0.5448(8)	0.3123(3)	0.4612(3)
H1O	0.551(13)	0.346(6)	0.512(3)
N1	0.4666(7)	0.2893(3)	0.2851(3)
N2	0.2459(6)	0.3821(3)	0.1607(2)
H2	0.130974	0.34222	0.147455
N3	0.4194(6)	0.2839(3)	0.0337(3)
H3	0.29439	0.249133	0.028655
N4	0.6394(7)	0.1759(3)	0.1410(3)
H4	0.780901	0.191376	0.14388
C1	0.5800(11)	0.3846(5)	0.4081(4)
H1A	0.693575	0.42065	0.42824
H1B	0.465953	0.425811	0.40436
C2	0.6185(9)	0.3476(4)	0.3273(4)
H2A	0.644002	0.400494	0.293116
H2B	0.739884	0.311303	0.332081
C3	0.2669(9)	0.3269(4)	0.2930(3)
H3A	0.249553	0.34314	0.348447
H3B	0.169827	0.279466	0.277549
C4	0.2322(8)	0.4115(4)	0.2418(3)
H4A	0.102041	0.437417	0.249784

H4B	0˚331161	0˚458794	0˚255184
C5	0˚2411(7)	0˚4584(3)	0˚1030(3)
H5A	0˚362623	0˚494282	0˚109731
H5B	0˚131164	0˚499592	0˚113227
C6	0˚2192(8)	0˚4237(4)	0˚0200(4)
H6A	0˚194125	0˚476773	-0˚01511
H6B	0˚10307	0˚383861	0˚015504
C7	0˚3915(9)	0˚3704(4)	-0˚0096(3)
H7A	0˚36845	0˚357292	-0˚066178
H7B	0˚510728	0˚408022	-0˚002953
C8	0˚5731(9)	0˚2245(4)	0˚0049(4)
H8A	0˚696808	0˚258801	0˚003843
H8B	0˚536989	0˚203338	-0˚048916
C9	0˚5964(8)	0˚1432(4)	0˚0600(4)
H9A	0˚47546	0˚106591	0˚057798
H9B	0˚703587	0˚103696	0˚043536
C10	0˚6168(9)	0˚1024(4)	0˚1992(4)
H10A	0˚712994	0˚053599	0˚190591
H10B	0˚485469	0˚075354	0˚191572
C11	0˚6445(9)	0˚1372(4)	0˚2817(4)
H11A	0˚76175	0˚176345	0˚285136
H11B	0˚669604	0˚084188	0˚316907
C12	0˚4757(9)	0˚1914(4)	0˚3119(4)

H12A	0.352908	0.160641	0.294496
H12B	0.484991	0.190239	0.369885
Cl2	0.10871(19)	0.15072(10)	0.13962(9)

Table S4. Crystallographic data of [Cu(TE1EtOH)Cl]Cl.

Empirical formula	$C_{12}H_{31}Cl_2CuN_4O_2.50$
Formula weight	405.85 g/mol
Temperature	150 K
Wavelength	0.71073 Å
Crystal system	monoclinic, C 2/c
Unit cell dimensions	a = 17.5231(10) Å, b = 9.0433(5) Å, c = 23.9772(13) Å,
	α = 90 °, β = = 105.052(2) °, γ = 90 °
Volume	3669.2(4) Å^3
Z, Calculated density	8, 1.469 g.cm^{-3}
Absorption coefficient	1.494 mm^{-1}
F(000)	1712
Crystal size	0.360 x 0.280 x 0.100 mm
Crystal color	violet
Crystal description	prism
θ range for data collection	2.407 to 27.505 °
(sinθ/λ)max (Å-1)	0.65
h_min, h_max	-22, 22
k_min, k_max	-11, 10

l_min, l_max	-31, 31		
Reflections collected / unique	24504 / 4151 [R(int) = 0.0705]		
Reflections [I>2sigma(I)]	3827		
Completeness to θ_max	0.985		
Absorption correction type	multi-scan		
Max. and min. transmission	0.861		
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	4151 / 5 / 215		
Goodness-of-fit	1.064		
Final R indices [I>2sigma(I)]	R1 = 0.0442		
R indices (all data)	R1 = 0.0475		
Largest diff. peak and hole	0.520 and -1.197 e.Å^{-3}		

Table S5. Cartesian coordinates (Å) of [Cu(TE1EtOH)Cl]Cl.

Cu1	**0.22085(2)**	**0.02511(3)**	**0.10689(2)**
Cl1	0.16857(4)	0.07920(7)	-0.01050(2)
O1	0.25976(12)	-0.0216(2)	0.21044(8)
H1O	0.3015(14)	0.032(3)	0.2346(13)
N1	0.13955(13)	-0.1381(2)	0.10071(9)
H1	0.143454	-0.174329	0.14076
N2	0.15516(13)	0.1847(2)	0.13477(9)
N3	0.30131(13)	0.1855(2)	0.10716(9)
H3	0.292745	0.217199	0.066034

N4	0.28792(14)	-0.1318(3)	0.08182(10)
H4	0.27784	-0.119564	0.039076
C1	0.05577(16)	-0.0963(3)	0.07495(12)
H1A	0.021571	-0.182967	0.075772
H1B	0.049041	-0.068068	0.034064
C2	0.02946(17)	0.0315(4)	0.10681(14)
H2A	0.039669	0.005082	0.148161
H2B -	0.028275	0.044849	0.091492
C3	0.07022(16)	0.1780(3)	0.10197(13)
H3A	0.066395	0.197462	0.060699
H3B	0.041377	0.258048	0.115988
C4	0.19083(17)	0.3265(3)	0.12016(11)
H4A	0.173811	0.41022	0.140663
H4B	0.172469	0.345399	0.078127
C5	0.28028(17)	0.3140(3)	0.13803(11)
H5A	0.304602	0.405106	0.127506
H5B	0.299313	0.299453	0.180295
C6	0.38611(16)	0.1484(3)	0.12785(12)
H6A	0.39836	0.121698	0.169271
H6B	0.418026	0.236338	0.124052
C7	0.40893(18)	0.0202(4)	0.09402(14)
H7A	0.391651	0.043596	0.052299
H7B	0.467228	0.011125	0.104677

C8	0.37380(18)	-0.1275(4)	0.10418(15)
H8A	0.397414	-0.206398	0.085372
H8B	0.387714	-0.148157	0.146165
C9	0.25327(19)	-0.2776(3)	0.09000(13)
H9A	0.268395	-0.305685	0.13132
H9B	0.272454	-0.354862	0.067721
C10	0.16392(18)	-0.2617(3)	0.06851(12)
H10A	0.148671	-0.240447	0.026563
H10B	0.137702	-0.354458	0.07528
C11	0.16372(17)	0.1795(3)	0.19885(11)
H11A	0.11208	0.20377	0.206157
H11B	0.201861	0.256548	0.217702
C12	0.19134(18)	0.0314(3)	0.22660(11)
H12A	0.203983	0.041583	0.269128
H12B	0.148105	-0.041712	0.21473
Cl2	0.10664(4)	0.63306(7)	0.19944(3)
O2	0	0.4019(4)	0.25
H2O	0.032(2)	0.467(4)	0.2351(18)
O3	0	0.8625(4)	0.25
H3O	0.038(2)	0.806(5)	0.238(2)
O4	-0.0634(4)	0.1280(6)	0.2033(3)
H4O	-0.042(6)	0.041(6)	0.223(4)
H5O	-0.038(5)	0.215(6)	0.220(4)

Table S6. Crystallographic data of [Zn(TE3MeEtOH)](ZnCl$_4$).

Empirical formula	C$_{15}$H$_{38}$Cl$_4$N$_4$O$_3$Zn$_2$
Formula weight	595.03 g/mol
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic, Pbca
Unit cell dimensions	a = 14.919(2) Å, b = 17.057(2) Å, c = 19.439(2) Å
Volume	4946.7(10) Å^3
Z, Calculated density	8, 1.598 mg/m^3
Absorption coefficient	2.394 mm^{-1}
F(000)	2464
Crystal description	Plate // (1 0 0)
Crystal color	Colorless
Crystal size	0.23 x 0.21 x 0.04 mm
θ range for data collection	3.44 to 26.37°
Limiting indices	-18<=h<=11, -20<=k<=21, -24<=l<=15
Reflections collected / unique	17758 / 5059 [R(int) = 0.0512]
Completeness to θ = 26.37	99.80%
Absorption correction	Analytical
Max. and min. transmission	0.9103 and 0.6089
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5059 / 17 / 260
Goodness-of-fit on F^2	1.049

Final R indices [I>2sigma(I)]	R1 = 0.0629		
R indices (all data)	R1 = 0.0930		
Largest diff. peak and hole	0.894 and -1.221 e.Å^{-3}		

Table S7. Cartesian coordinates (Å) of [Zn(TE3MeEtOH)](ZnCl$_4$).

C1	**0.2018(6)**	**0.2824(5)**	**0.2299(4)**
C2	0.2985(5)	0.2552(5)	0.2161(4)
C3	0.4045(5)	0.2194(4)	0.1272(4)
C4	0.4289(6)	0.2040(5)	0.0558(5)
C5	0.3728(6)	0.1397(5)	0.0211(4)
C6	0.2299(6)	0.0854(5)	-0.0146(4)
C7	0.1916(5)	0.0418(4)	0.0452(4)
C8	0.1116(5)	0.0527(4)	0.1533(3)
C9	0.0618(5)	0.0979(5)	0.2051(4)
C10	0.1154(6)	0.1639(5)	0.2389(4)
C11I	0.0501(12)	0.2698(12)	0.1815(11)
C12I	0.0657(11)	0.3266(9)	0.1178(7)
C11J	0.2789(10)	0.2253(9)	-0.0410(8)
C12J	0.1783(10)	0.2574(10)	-0.0431(7)
C13	0.3187(5)	0.3416(4)	0.1179(5)
C14I	0.2561(11)	0.2150(9)	-0.0507(7)
C14J	0.0571(12)	0.2849(11)	0.1775(11)
C15	0.0452(5)	0.1058(4)	0.0491(3)

N1	0.1337(4)	0.2295(4)	0.1933(3)
N2	0.3150(3)	0.2575(3)	0.1413(3)
N3	0.2774(4)	0.1624(4)	0.0082(3)
N4	0.1306(3)	0.0940(3)	0.0874(2)
O1I	0.1133(6)	0.2858(5)	0.0657(5)
O1J	0.1485(7)	0.2758(6)	0.0246(5)
Zn1	0.2010(1)	0.1998(1)	0.0981(1)
Cl1	0.3545(1)	0.0217(1)	0.1948(1)
Cl2	0.3213(1)	0.1022(1)	0.3719(1)
Cl3	0.1849(1)	-0.0631(1)	0.3083(1)
Cl4	0.4307(1)	-0.0956(1)	0.3445(1)
Zn2	0.3256(1)	-0.0091(1)	0.3078(1)
O2	0.5347(5)	0.0199(6)	0.1074(3)
O3I	0.1457(8)	0.3957(7)	-0.0308(6)
O3J	0.0928(8)	0.4193(7)	0.0216(5)

Table S8. Crystallographic data of [Cu(TE3MeEtOH)](ClO$_4$)$_2$.

Empirical formula	$C_{15}H_{34}Cl_2CuN_4O_9$
Formula weight	548.9 g/mol
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P n a 21

Unit cell dimensions	a = 15.2412(16) Å, b = 14.7907(17) Å, c = 10.0443(13) Å
Volume	2264.3(5) Å^3
Z	1.610 Mg/m^3
Absorption coefficient	1.254 mm^{-1}
F(000)	1148
Crystal description	Plate // (1 0 -1)
Crystal color	Blue
Crystal size	0.23 x 0.15 x 0.03 mm
Theta range for data collection	3.36 to 26.37°
Limiting indices	-18<=h<=19, -13<=k<=18, -12<=l<=12
Reflections collected / unique	13091 / 4480 [R(int) = 0.0887]
Completeness to θ = 26.37	99.70%
Absorption correction	Analytical
Max. and min. transmission	0.9633 and 0.7613
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4480 / 963 / 275
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0741
R indices (all data)	R1 = 0.1278
Absolute structure parameter	0.49(6)
Largest diff. peak and hole	0.940 and -0.501 e. Å^{-3}

Table S9. Cartesian coordinates (Å) of [Cu(TE3MeEtOH)](ClO₄)₂.

C1I	**0.2320(20)**	**0.0693(18)**	**0.6140(20)**
C2I	0.2815(15)	0.1551(15)	0.5850(30)
C3I	0.3880(20)	0.2108(17)	0.4250(30)
C4I	0.4256(16)	0.2089(18)	0.2930(20)
C5I	0.3660(20)	0.1991(15)	0.1790(30)
C6I	0.2838(15)	0.1090(30)	0.0310(20)
C7I	0.1915(14)	0.1285(18)	0.0670(30)
C8I	0.0774(13)	0.0934(15)	0.2350(20)
C9I	0.0597(17)	0.0440(20)	0.3600(20)
C10I	0.1034(18)	0.0731(19)	0.4840(20)
C11I	0.1856(16)	-0.0701(15)	0.5030(30)
C12I	0.2596(12)	-0.1250(12)	0.4490(20)
C13I	0.4091(17)	0.0660(18)	0.5470(30)
C14I	0.4090(15)	0.423(17)	0.1390(30)
C15I	0.1530(20)	-0.0257(15)	0.1110(30)
N1I	0.1923(12)	0.0263(13)	0.4888(19)
N2I	0.3468(12)	0.1257(16)	0.4749(18)
N3I	0.3355(11)	0.1032(14)	0.1660(20)
N4I	0.1633(12)	0.0640(12)	0.1732(18)
O1I	0.2916(9)	-0.0846(10)	0.3410(20)
C1J	0.2209(12)	0.0446(14)	0.0631(17)
C2J	0.2756(15)	0.1280(17)	0.0750(30)

C3J	0.3729(15)	0.2178(12)	0.2270(18)
C4J	0.4217(12)	0.2223(15)	0.3518(18)
C5J	0.3677(14)	0.2028(12)	0.4730(19)
C6J	0.2882(10)	0.1020(15)	0.6088(18)
C7J	0.1933(10)	0.1204(14)	0.5790(20)
C8J	0.0752(17)	0.0980(20)	0.4290(30)
C9J	0.0364(10)	0.0(11)	0.3093(16)
C10J	0.0863(16)	0.0640(20)	0.1860(20)
C11J	0.1654(13)	-0.0788(13)	0.2010(20)
C12J	0.2510(20)	-0.1230(20)	0.2350(50)
C13J	0.4207(14)	0.0698(16)	0.1620(30)
C14J	0.4223(12)	0.0512(16)	0.4980(20)
C15J	0.1485(18)	-0.0313(13)	0.5280(30)
N1J	0.1739(11)	0.0187(13)	0.1924(16)
N2J	0.3425(12)	0.1244(12)	0.1907(19)
N3J	0.3414(12)	0.1045(14)	0.4790(20)
N4J	0.1636(11)	0.0589(12)	0.4667(17)
O1J	0.3074(11)	-0.0741(10)	0.3092(16)
Cu1	0.2627(1)	0.0678(1)	0.3322(3)
O2I	0.2646(9)	0.3931(14)	0.3220(20)
O3I	0.1191(8)	0.4430(7)	0.3545(16)
O4I	0.1531(11)	0.3460(12)	0.1832(12)
O5I	0.1574(10)	0.2933(9)	0.4007(13)

Cl1I	0.1740(7)	0.3691(7)	0.3162(8)
O2J	0.2620(8)	0.3973(14)	0.3370(20)
O3J	0.1147(9)	0.4228(8)	0.2801(14)
O4J	0.1497(12)	0.3580(12)	0.4854(12)
O5J	0.1701(9)	0.2737(7)	0.2931(13)
Cl1J	0.1737(6)	0.3636(6)	0.3474(7)
O6I	-0.0798(9)	0.2477(13)	0.8190(30)
O7I	0.0442(12)	0.1581(9)	0.8560(20)
O8I	0.0461(18)	0.2699(18)	0.6881(19)
O9I	0.0470(15)	0.3120(13)	0.9160(20)
Cl2I	0.0138(10)	0.2488(10)	0.8188(17)
O6J	0.0712(14)	0.3053(15)	0.7570(20)
O7J	0.0250(20)	0.1589(12)	0.8000(30)
O8J	0.0430(20)	0.2600(20)	0.9771(18)
O9J	-0.0735(10)	0.2786(16)	0.8260(40)
Cl2J	0.0145(7)	0.2518(6)	0.8431(10)
O6K	-0.0214(12)	0.2091(14)	0.7184(18)
O7K	0.1232(10)	0.2135(13)	0.7940(20)
O8K	0.0107(13)	0.1978(13)	0.9477(17)
O9K	0.0305(11)	0.3362(8)	0.8370(30)
Cl2K	0.0347(6)	0.2383(5)	0.8226(13)

DFT calculations and results
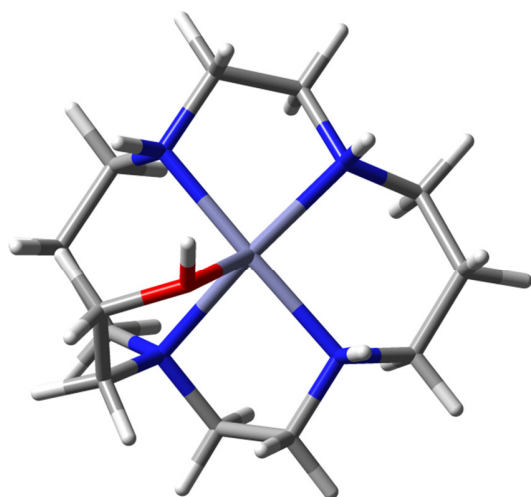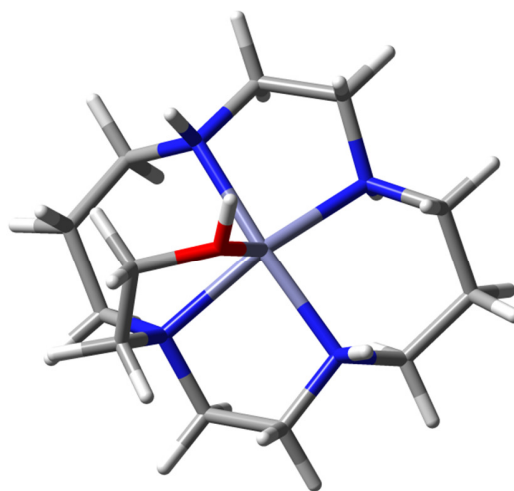
trans-I   *trans*-II
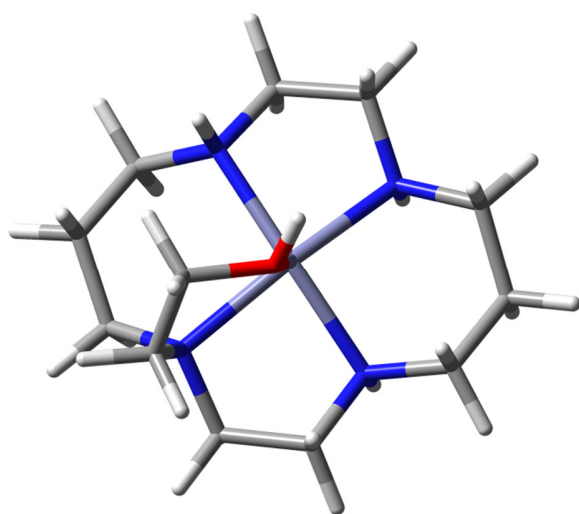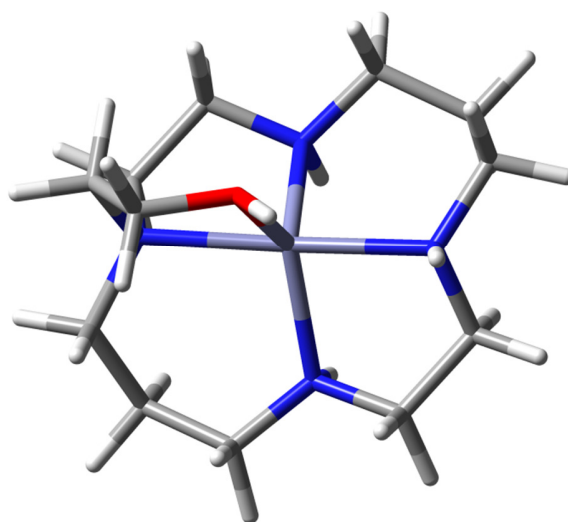
trans-III   *cis*-V

Figure S 29. Structures of the different isomers of [Zn(TE1EtOH)]²⁺ optimized with DFT calculations (rtpssh/Def2-TZVPP; scrf=(pcm,solvent=water)).
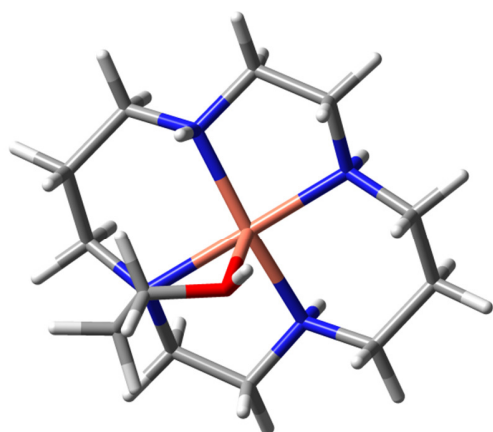
[Cu(TE1EtOH)]$^{2+}$ (*trans*-III)
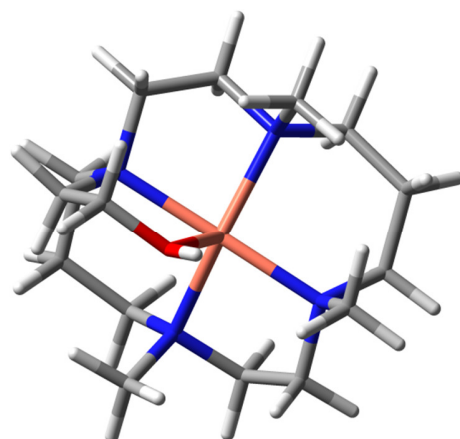
[Cu(TE3MeEtOH)]$^{2+}$ (*trans*-I)
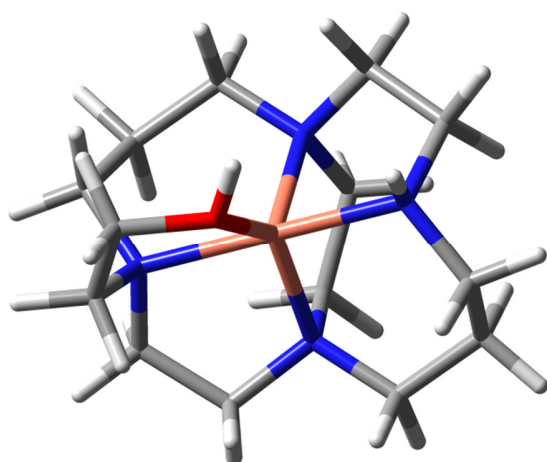
[Cu(CB-TE1EtOH)]$^{2+}$ (*cis*-V)
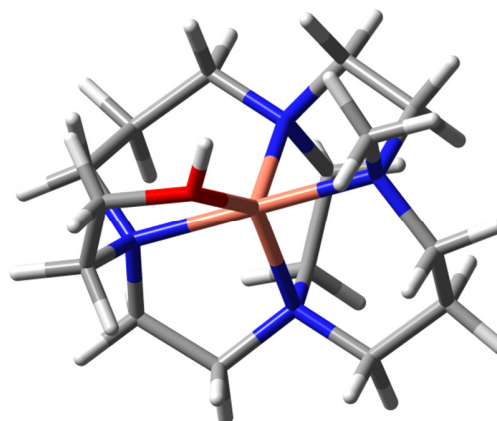
[Cu(CB-TEMeEtOH)]$^{2+}$ (*cis*-V)

Figure S 30. Structures of the Cu(II) complexes optimized with DFT calculations (utpssh/Def2-TZVPP; scrf=(pcm,solvent=water)).

Table S 10. ^{13}C NMR chemical shifts for the central carbon of the propylene units of [Zn(TE1EtOH)]Cl$_2$ and the values calculated with DFT.

	Exp.	Calcd.	Population / %
trans-III	30.6	32.5	44
	28.2	30.3	
trans-I	29.9	31.6	31
	26.7	30.0	
cis-V	27.3	28.6	25
	26.5	28.0	

Table S 11. Cartesian coordinates of [Zn(TE1EtOH)]$^{2+}$ (*trans*-I) optimized with DFT calculations (rtpssh/Def2-TZVPP; scrf=(pcm,solvent=water)).

```
---------------------------------------------------------------------
Center     Atomic                      Coordinates (Angstroms)
Number     Number                  X            Y            Z
---------------------------------------------------------------------
    1         7              -1.954451     1.034763     0.161976
    2         7              -0.904893    -1.871793    -0.268297
    3         7               1.763844    -1.080663     0.343343
    4         7               0.801443     1.922970    -0.104086
    5         6              -2.801051     0.589994    -0.977698
    6         1              -2.266609     0.823914    -1.900636
    7         1              -3.728116     1.171443    -0.976136
    8         6              -3.123835    -0.899408    -0.926071
    9         1              -3.930492    -1.082061    -1.639897
   10         1              -3.523367    -1.167102     0.057988
   11         6              -1.971804    -1.824396    -1.302107
   12         1              -2.351552    -2.836117    -1.474813
   13         1              -1.506501    -1.483923    -2.229211
   14         6               0.233515    -2.724088    -0.682125
   15         1              -0.048761    -3.779638    -0.701815
   16         1               0.503817    -2.433771    -1.698243
   17         6               1.404292    -2.519623     0.267896
   18         1               1.129481    -2.842855     1.273031
   19         1               2.258871    -3.118217    -0.059253
   20         6               2.655752    -0.652503    -0.768717
```

```
   21             1                    2.142050    -0.860881    -1.708826
   22             1                    3.566267    -1.259359    -0.748116
   23             6                    3.023027     0.827208    -0.700726
   24             1                    3.442841     1.073050     0.278923
   25             6                    1.913865     1.801748    -1.090573
   26             1                    2.345594     2.795349    -1.256399
   27             1                    1.468681     1.475149    -2.032179
   28             6                   -0.330587     2.676877    -0.712843
   29             1                   -0.464001     2.299035    -1.727415
   30             1                   -0.094499     3.743428    -0.781066
   31             6                   -1.612693     2.477032     0.085654
   32             1                   -1.496552     2.844489     1.105008
   33             1                   -2.423113     3.044324    -0.379791
   34             1                    3.835381     0.985602    -1.414387
   35            30                   -0.103727    -0.001028     0.383771
   36             1                    2.268268    -0.938459     1.213710
   37             1                   -1.311409    -2.279484     0.573054
   38             1                   -2.484254     0.880637     1.016107
   39             6                    1.250274     2.606083     1.148948
   40             1                    0.503373     3.352535     1.414841
   41             1                    2.188932     3.135858     0.970173
   42             6                    1.422586     1.659366     2.322270
   43             1                    1.506515     2.231267     3.246871
   44             1                    2.307067     1.028314     2.222437
   45             8                    0.235744     0.835269     2.370133
   46             1                    0.273428     0.245720     3.134585
 ------------------------------------------------------------------
```
E(RTPSSh) = -2547.8884658 Hartree
Zero-point correction = 0.422766
Thermal correction to Energy = 0.441114
Thermal correction to Enthalpy = 0.442058
Thermal correction to Gibbs Free Energy = 0.379084
Sum of electronic and zero-point Energies = -2547.465700
Sum of electronic and thermal Energies = -2547.447352
Sum of electronic and thermal Enthalpies = -2547.446408
Sum of electronic and thermal Free Energies = -2547.509381

Table S 12. Cartesian coordinates of [Zn(TE1EtOH)]$^{2+}$ (*trans*-II) optimized with DFT calculations (rtpssh/Def2-TZVPP; scrf=(pcm,solvent=water)).

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	1	1.210153	-3.630195	-0.243600
2	6	-0.749628	-2.715955	-0.279489
3	1	-0.925098	-2.787138	0.796422
4	1	0.891053	-2.635156	-1.664392
5	6	0.741968	-2.705639	-0.585498
6	1	-1.261915	-1.413290	-1.764477

7	7	−1.330955	−1.439514	−0.749114
8	6	−2.739290	−1.216434	−0.353472
9	1	1.661076	−1.773139	0.979932
10	7	1.395275	−1.517063	0.031433
11	1	2.363577	−1.032188	−1.751285
12	6	2.636002	−1.129528	−0.698588
13	6	−3.340158	0.008085	−1.053579
14	30	−0.080123	0.023230	0.192986
15	1	3.470921	0.135441	0.857694
16	6	3.258335	0.176651	−0.213103
17	1	4.234325	0.254311	−0.699207
18	6	−2.419483	1.225480	−1.192773
19	7	−1.647089	1.490924	0.046492
20	1	2.201406	1.388815	−1.636376
21	6	2.493612	1.446585	−0.586440
22	7	1.247631	1.696360	0.197171
23	1	3.151898	2.315133	−0.474514
24	6	−0.983297	2.817616	0.085212
25	1	−0.977321	3.147790	1.123409
26	1	0.415356	2.517943	−1.533599
27	6	0.438029	2.757665	−0.469712
28	1	−1.553976	3.554241	−0.486480
29	1	−1.224330	−3.575414	−0.759757
30	1	0.914123	3.736788	−0.357240
31	1	3.369459	−1.937237	−0.620552
32	1	−2.278766	1.434627	0.840013
33	1	−2.746746	−1.087288	0.730704
34	1	−3.347883	−2.096635	−0.580686
35	1	−3.664172	−0.266113	−2.060418
36	1	−4.240909	0.289008	−0.502805
37	1	−1.705618	1.074222	−2.004094
38	1	−3.022353	2.100417	−1.453631
39	6	1.554586	2.082804	1.610268
40	1	0.884583	2.892671	1.892494
41	1	2.575619	2.466237	1.677838
42	6	1.378025	0.946497	2.602950
43	1	1.387028	1.345861	3.617670
44	1	2.157969	0.189266	2.518004
45	8	0.089616	0.347467	2.331953
46	1	−0.080198	−0.369582	2.956551

```
E(RTPSSh) = −2547.8824995 Hartree
Zero-point correction = 0.422295
Thermal correction to Energy = 0.440813
Thermal correction to Enthalpy = 0.441757
Thermal correction to Gibbs Free Energy = 0.378376
Sum of electronic and zero-point Energies = −2547.460204
Sum of electronic and thermal Energies = −2547.441687
Sum of electronic and thermal Enthalpies = −2547.440742
Sum of electronic and thermal Free Energies = −2547.504124
```

Table S 13. Cartesian coordinates of [Zn(TE1EtOH)]$^{2+}$ (*trans*-III) optimized with DFT calculations (rtpssh/Def2-TZVPP; scrf=(pcm,solvent=water)).

```
---------------------------------------------------------------------
 Center      Atomic              Coordinates (Angstroms)
 Number      Number            X            Y            Z
---------------------------------------------------------------------
    1           1          -1.308451    -3.677217    -0.488759
    2           6           0.646862    -2.808080    -0.226601
    3           1           0.844563    -2.714334    -1.296196
    4           1          -1.077022    -2.904553     1.085302
    5           6          -0.857826    -2.819937     0.018893
    6           1           3.288974    -2.184049     0.069957
    7           1           1.384024    -1.871087     1.427484
    8           7           1.276155    -1.636848     0.442359
    9           6           2.628553    -1.328500    -0.098780
   10           1           2.518752    -1.203000    -1.177643
   11           1          -1.309693    -1.512578    -1.474464
   12           7          -1.422319    -1.541074    -0.462151
   13           1          -2.973550    -1.355126     0.925934
   14           6          -2.859773    -1.330208    -0.159957
   15           1           4.303049    -0.069286     0.201064
   16           6           3.254304    -0.073698     0.508876
   17           1           3.273064    -0.140566     1.600064
   18          30          -0.107669    -0.030447     0.333002
   19           1          -3.218274     0.022671    -1.805945
   20           6          -3.369544    -0.001827    -0.720845
   21           1          -4.451086     0.019175    -0.568628
   22           6           2.666274     1.258297     0.040212
   23           1           2.552923     1.231111    -1.044960
   24           7           1.328064     1.598993     0.607267
   25           1          -2.872689     1.237429     0.993198
   26           6          -2.800066     1.273590    -0.095746
   27           7          -1.368619     1.474460    -0.442401
   28           1          -1.288385     1.453410    -1.457841
   29           1          -3.383491     2.132965    -0.440461
   30           6           0.714585     2.723666    -0.158182
   31           1           0.943557     2.566437    -1.213272
   32           1          -1.063844     2.866529     1.082547
   33           6          -0.798359     2.755573     0.030098
   34           1           1.154473     3.679701     0.140434
   35           1           1.097003    -3.741183     0.117898
   36           1           3.365072     2.067519     0.279819
   37           1          -1.219657     3.604971    -0.513416
   38           1          -3.452483    -2.150754    -0.576502
   39           6           1.416648     1.961590     2.054545
   40           1           2.446466     2.216888     2.316190
   41           1           0.807600     2.849795     2.219026
   42           6           0.914257     0.863871     2.971070
   43           1           0.785160     1.252949     3.981329
   44           1           1.585181     0.004289     3.007224
```

53

```
   45          8                          -0.369756    0.456873    2.443707
   46          1                          -0.771527   -0.203317    3.023725
 -----------------------------------------------------------------------
E(RTPSSh) = -2547.8884707 Hartree
 Zero-point correction = 0.422096
 Thermal correction to Energy = 0.440712
 Thermal correction to Enthalpy = 0.441657
 Thermal correction to Gibbs Free Energy = 0.377894
 Sum of electronic and zero-point Energies = -2547.466375
 Sum of electronic and thermal Energies = -2547.447758
 Sum of electronic and thermal Enthalpies = -2547.446814
 Sum of electronic and thermal Free Energies = -2547.510577
```

Table S 14. Cartesian coordinates of [Zn(TE1EtOH)]$^{2+}$ (*cis*-V) optimized with DFT calculations (rtpssh/Def2-TZVPP; scrf=(pcm,solvent=water)).

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	1	4.064104	0.663398	-1.006960
2	1	3.702931	-1.402805	0.050439
3	1	3.193795	-0.142460	1.167772
4	6	3.008048	0.406149	-0.895126
5	1	2.624128	2.490835	-1.307864
6	6	2.943926	-0.632100	0.225639
7	1	2.380002	2.042817	0.382912
8	1	2.707153	-0.023240	-1.855588
9	6	2.244822	1.706479	-0.646750
10	7	1.626809	-1.313213	0.422922
11	1	1.996964	-3.238164	-0.420103
12	1	1.739213	-1.933718	-1.577983
13	7	0.788546	1.527068	-0.873736
14	1	0.217951	3.085506	0.399790
15	1	0.184290	3.530930	-1.312428
16	1	0.668216	1.292087	-1.857964
17	6	1.398787	-2.345773	-0.627625
18	6	-0.034784	2.730765	-0.601099
19	30	-0.090610	-0.004212	0.253637
20	6	-0.076384	-2.718451	-0.736977
21	1	-0.441213	-3.164059	0.189183
22	6	-1.508646	2.349801	-0.676227
23	1	-0.209374	-3.455988	-1.531922
24	1	-0.725376	-1.210054	-1.951183
25	1	-2.135155	3.223398	-0.483221
26	1	-1.747292	1.985476	-1.675960
27	7	-0.884649	-1.500703	-0.988174

54

28	7	-1.804419	1.263768	0.297302
29	6	-2.348655	-1.709124	-0.823916
30	1	-2.822625	0.032408	-2.010283
31	1	-2.514496	-2.075776	0.191045
32	6	-3.121433	0.599706	0.069930
33	1	-2.686084	-2.484047	-1.518017
34	1	-3.385483	0.105378	1.005942
35	6	-3.137262	-0.422879	-1.066153
36	1	-3.878386	1.365471	-0.125092
37	1	-4.182957	-0.705271	-1.209557
38	1	-1.853336	1.696803	1.216193
39	6	1.591688	-1.935295	1.775325
40	1	0.860311	-2.742628	1.764934
41	1	2.565719	-2.366842	2.025243
42	6	1.179922	-0.927812	2.826848
43	1	1.058706	-1.420810	3.791680
44	1	1.899693	-0.113236	2.926771
45	8	-0.095156	-0.395107	2.393667
46	1	-0.374145	0.302066	3.000555

```
E(RTPSSh) = -2547.8928807 Hartree
Zero-point correction = 0.422505
Thermal correction to Energy = 0.441130
Thermal correction to Enthalpy = 0.442074
Thermal correction to Gibbs Free Energy = 0.377974
Sum of electronic and zero-point Energies = -2547.470376
Sum of electronic and thermal Energies = -2547.451751
Sum of electronic and thermal Enthalpies = -2547.450807
Sum of electronic and thermal Free Energies = -2547.514907
```

Table S 15. Cartesian coordinates of [Cu(TE1EtOH)]$^{2+}$ (*trans*-III) optimized with DFT calculations (utpssh/Def2-TZVPP; scrf=(pcm,solvent=water)).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	1	1.288347	3.606739	-0.753114
2	6	-0.693398	2.755921	-0.616969
3	1	-0.832203	2.676915	-1.696598
4	1	0.926524	2.855153	0.806974
5	6	0.780702	2.768335	-0.270787
6	1	-3.310767	2.197430	-0.281027
7	1	-1.387185	1.734452	1.002173
8	7	-1.318885	1.555327	0.001075
9	6	-2.694226	1.323963	-0.511543
10	1	-2.621220	1.243637	-1.597450
11	1	1.366387	1.469695	-1.726584
12	7	1.362458	1.474720	-0.706570
13	1	2.757461	1.276749	0.839850

14	6	2.762110	1.278657	-0.251366
15	1	-4.374902	0.055078	-0.283033
16	6	-3.338795	0.070191	0.063225
17	1	-3.392713	0.122995	1.153708
18	29	0.027734	0.012222	-0.175551
19	1	3.343698	-0.005511	-1.886843
20	6	3.363198	-0.012422	-0.791864
21	1	4.417125	-0.029824	-0.506415
22	6	-2.701971	-1.233295	-0.402741
23	1	-2.583424	-1.207717	-1.487112
24	7	-1.355087	-1.521529	0.175183
25	1	2.698094	-1.288810	0.826806
26	6	2.723792	-1.290355	-0.264173
27	7	1.324380	-1.459249	-0.734753
28	1	1.331954	-1.447359	-1.754555
29	1	3.311955	-2.154440	-0.586804
30	6	-0.762790	-2.689944	-0.548053
31	1	-0.957789	-2.551327	-1.612167
32	1	0.957169	-2.869749	0.757679
33	6	0.730154	-2.747188	-0.301433
34	1	-1.249398	-3.617317	-0.233605
35	1	-1.185495	3.668956	-0.275352
36	1	-3.361345	-2.073342	-0.160283
37	1	1.176282	-3.585391	-0.841348
38	1	3.364617	2.130347	-0.580827
39	6	-1.448273	-1.842790	1.641000
40	1	-0.826784	-2.716434	1.829857
41	1	-2.477227	-2.114635	1.886633
42	6	-0.985522	-0.726755	2.554442
43	1	-0.933510	-1.107548	3.576400
44	1	-1.665181	0.128178	2.544103
45	8	0.321406	-0.330869	2.102546
46	1	0.675443	0.339855	2.700303

```
E(UTPSSh) = -2409.017898 Hartree
Zero-point correction = 0.423123
Thermal correction to Energy = 0.441475
Thermal correction to Enthalpy = 0.442419
Thermal correction to Gibbs Free Energy = 0.378587
Sum of electronic and zero-point Energies = -2408.594775
Sum of electronic and thermal Energies = -2408.576423
Sum of electronic and thermal Enthalpies = -2408.575479
Sum of electronic and thermal Free Energies = -2408.639311
```

Table S 16. Cartesian coordinates of [Cu(TE3MeEtOH)]$^{2+}$ (*trans*-I) optimized with DFT calculations (utpssh/Def2-TZVPP; scrf=(pcm,solvent=water)).

| Center Number | Atomic Number | Coordinates (Angstroms) | | |
| | | X | Y | Z |

```
-------------------------------------------------------------------
    1          7              1.751368    -1.002387    -0.178869
    2          7              0.757439     1.920788    -0.328345
    3          7             -1.881506     1.069374     0.394579
    4          7             -0.992268    -1.764251    -0.477538
    5          6              2.542850    -0.522450    -1.354329
    6          1              1.974552    -0.782878    -2.248129
    7          1              3.476382    -1.094919    -1.380491
    8          6              2.860913     0.965173    -1.380658
    9          1              3.477818     1.126041    -2.268329
   10          1              3.488611     1.260059    -0.538434
   11          6              1.653185     1.878077    -1.521390
   12          1              1.990254     2.900318    -1.727858
   13          1              1.043411     1.551960    -2.366090
   14          6             -0.432088     2.749386    -0.674494
   15          1             -0.154547     3.807632    -0.706634
   16          1             -0.757310     2.462410    -1.674494
   17          6             -1.528292     2.521366     0.337253
   18          1             -1.206520     2.826311     1.331489
   19          1             -2.415403     3.108495     0.084731
   20          6             -2.880035     0.790188    -0.683327
   21          1             -2.475267     1.183873    -1.616025
   22          1             -3.782542     1.364603    -0.447134
   23          6             -3.247111    -0.673471    -0.871269
   24          1             -3.675858    -1.097918     0.037822
   25          6             -2.126410    -1.540659    -1.421556
   26          1             -2.524527    -2.520044    -1.710289
   27          1             -1.708993    -1.073690    -2.315317
   28          6              0.085343    -2.485473    -1.213168
   29          1              0.200755    -2.003294    -2.184043
   30          1             -0.211798    -3.524050    -1.388633
   31          6              1.375315    -2.426474    -0.430481
   32          1              1.268842    -2.932656     0.526251
   33          1              2.179013    -2.929480    -0.974563
   34          1             -4.051667    -0.696596    -1.610341
   35         29             -0.072621     0.038800     0.071937
   36          6             -1.443297    -2.599556     0.663335
   37          1             -0.625229    -2.760887     1.359296
   38          1             -2.250908    -2.108481     1.196139
   39          1             -1.798234    -3.566109     0.292936
   40          6              1.464284     2.544696     0.818781
   41          1              2.356413     1.979296     1.064997
   42          1              1.752192     3.567154     0.555752
   43          1              0.823928     2.558929     1.695941
   44          6              2.573775    -0.908484     1.060481
   45          1              3.390366    -1.636222     1.016365
   46          1              3.019032     0.082180     1.092717
   47          6             -2.487155     0.797491     1.722755
   48          1             -1.778144     1.064893     2.502643
   49          1             -3.392999     1.398754     1.846043
   50          1             -2.748506    -0.251735     1.818704
   51          6              1.761998    -1.133910     2.319104
```

```
    52              1                    1.447731   -2.173993    2.431125
    53              1                    2.370816   -0.866592    3.184791
    54              8                    0.607712   -0.278932    2.239689
    55              1                    0.057762   -0.417168    3.020359
 ------------------------------------------------------------------
 E(UTPSSh) = -2526.9681769 Hartree
 Zero-point correction = 0.505837 (/Particle)
 Thermal correction to Energy = 0.528201
 Thermal correction to Enthalpy = 0.529145
 Thermal correction to Gibbs Free Energy = 0.458266
 Sum of electronic and zero-point Energies = -2526.462340
 Sum of electronic and thermal Energies = -2526.439976
 Sum of electronic and thermal Enthalpies = -2526.439032
 Sum of electronic and thermal Free Energies = -2526.509910
```

Table S 17. Cartesian coordinates of [Cu(CB-TE1EtOH)]$^{2+}$ (*cis*-V) optimized with DFT calculations (utpssh/Def2-TZVPP; scrf=(pcm,solvent=water)).

```
 ------------------------------------------------------------------
 Center      Atomic                        Coordinates (Angstroms)
 Number      Number                     X           Y           Z
 ------------------------------------------------------------------
    1              6                   -2.897416   -0.115309   -0.671957
    2              1                   -3.842601    0.434601   -0.726613
    3              1                   -2.885281   -0.828773   -1.495792
    4              6                   -2.829110   -0.876773    0.650492
    5              1                   -2.783745   -0.199288    1.505020
    6              6                   -1.749122   -1.949784    0.743192
    7              1                   -1.920299   -2.555177    1.640989
    8              1                   -1.834820   -2.610834   -0.121071
    9              6                    0.580990   -2.544148    0.402279
   10              1                    0.184859   -3.018972   -0.495429
   11              1                    0.621247   -3.300959    1.193709
   12              6                    1.979686   -2.011132    0.135363
   13              1                    2.583094   -2.784787   -0.341248
   14              1                    2.482444   -1.742838    1.061839
   15              6                    3.040121    0.163632   -0.427460
   16              1                    3.983767   -0.388951   -0.420980
   17              1                    3.076829    0.878074   -1.251116
   18              6                    2.872113    0.897706    0.898273
   19              1                    3.809850    1.426792    1.084646
   20              6                    1.770112    1.950386    0.921240
   21              1                    1.914520    2.629292    0.079259
   22              1                    1.850630    2.540894    1.840796
   23              6                   -0.531350    2.537580    0.436777
   24              1                   -0.072455    3.054082   -0.406834
   25              1                   -0.630568    3.259332    1.254789
   26              6                   -1.901239    2.009614    0.053713
   27              1                   -2.447190    1.667283    0.928479
   28              1                   -2.496155    2.808722   -0.394137
```

```
29          6                  -0.082429    0.740483    2.054797
30          1                  -1.117959    1.023834    2.221716
31          1                   0.483088    1.114544    2.912561
32          6                   0.031202   -0.795214    2.039227
33          1                   1.055566   -1.081660    2.262027
34          1                  -0.584442   -1.187032    2.854051
35          7                  -1.790629    0.864972   -0.904381
36          7                   0.383654    1.423165    0.812778
37          7                  -0.354892   -1.441920    0.755489
38          7                   1.935684   -0.794314   -0.731530
39          1                   2.766982    0.197597    1.729855
40         29                   0.073146    0.020708   -0.744539
41          1                  -3.786736   -1.394430    0.748467
42          1                   2.078682   -1.099819   -1.690614
43          6                  -1.842144    1.395839   -2.301237
44          1                  -2.863548    1.700060   -2.547892
45          1                  -1.203587    2.279074   -2.335315
46          6                  -1.341076    0.383254   -3.301788
47          1                  -1.986108   -0.491848   -3.379511
48          1                  -1.244386    0.845086   -4.284525
49          8                  -0.031575   -0.022813   -2.830501
50          1                   0.258114   -0.799438   -3.326929
-------------------------------------------------------------------
E(UTPSSh) = -2486.4296847 Hartree
Zero-point correction = 0.457865
 Thermal correction to Energy = 0.476942
 Thermal correction to Enthalpy = 0.477886
 Thermal correction to Gibbs Free Energy = 0.413335
 Sum of electronic and zero-point Energies = -2485.971819
 Sum of electronic and thermal Energies = -2485.952743
 Sum of electronic and thermal Enthalpies = -2485.951798
 Sum of electronic and thermal Free Energies = -2486.016350
```

Table S 18. Cartesian coordinates of [Cu(CB-TEMeEtOH)]$^{2+}$ (*cis*-V) optimized with DFT calculations (utpssh/Def2-TZVPP; scrf=(pcm,solvent=water)).

```
-------------------------------------------------------------------
Center      Atomic                     Coordinates (Angstroms)
Number      Number                 X           Y           Z
-------------------------------------------------------------------
   1          6                   2.815812    0.157721   -0.822747
   2          1                   3.842044    0.401507   -0.528855
   3          1                   2.850003   -0.772927   -1.389019
   4          6                   2.266641    1.266030   -1.716894
   5          1                   2.171280    2.211398   -1.179065
   6          6                   0.981936    0.929932   -2.464463
   7          1                   0.796900    1.694494   -3.227856
   8          1                   1.107578   -0.025000   -2.977959
   9          6                  -1.300689    0.116916   -2.368541
  10          1                  -0.860988   -0.778628   -2.808774
```

```
11            1                    -1.668133    0.745552   -3.187466
12            6                    -2.454232   -0.252454   -1.456713
13            1                    -3.168742   -0.874186   -2.000285
14            1                    -2.993155    0.634228   -1.134610
15            6                    -2.846354   -0.654526    0.939181
16            1                    -3.878398   -0.898023    0.664539
17            1                    -2.552487   -1.330945    1.744048
18            6                    -2.786728    0.786457    1.432325
19            1                    -3.602470    0.893284    2.151777
20            6                    -1.509693    1.169620    2.164971
21            1                    -1.313845    0.433490    2.946346
22            1                    -1.644958    2.142065    2.651687
23            6                     0.908288    1.232831    2.187383
24            1                     0.790974    0.412679    2.896133
25            1                     0.971032    2.163406    2.762274
26            6                     2.171478    1.051432    1.370310
27            1                     2.394139    1.941390    0.788253
28            1                     3.023969    0.889168    2.033716
29            6                    -0.287928    2.401395    0.391214
30            1                     0.711155    2.827490    0.405466
31            1                    -0.957607    3.172498    0.780720
32            6                    -0.694144    2.107995   -1.066456
33            1                    -1.776949    2.135976   -1.150634
34            1                    -0.317023    2.922488   -1.690770
35            7                     2.038813   -0.102751    0.429028
36            7                    -0.295891    1.225799    1.310291
37            7                    -0.223088    0.802667   -1.606703
38            7                    -1.981604   -0.986921   -0.237906
39            1                    -3.013080    1.499564    0.637160
40           29                     0.021433   -0.488418    0.080273
41            1                     3.031136    1.445906   -2.476846
42            6                     2.555129   -1.329362    1.108485
43            1                     3.646717   -1.290667    1.167737
44            1                     2.157087   -1.333091    2.123486
45            6                     2.107356   -2.578883    0.396352
46            1                     2.538113   -2.678419   -0.599876
47            1                     2.357923   -3.460845    0.985957
48            8                     0.667579   -2.464980    0.292003
49            1                     0.334999   -3.149520   -0.301622
50            6                    -2.125291   -2.446381   -0.487447
51            1                    -1.772502   -3.002491    0.378262
52            1                    -3.179319   -2.685281   -0.653739
53            1                    -1.564684   -2.726484   -1.378865
------------------------------------------------------------------------
 E(UTPSSh) = -2525.7466492 Hartree
 Zero-point correction = 0.485656
 Thermal correction to Energy = 0.506014
 Thermal correction to Enthalpy = 0.506958
 Thermal correction to Gibbs Free Energy = 0.440098
 Sum of electronic and zero-point Energies = -2525.260993
 Sum of electronic and thermal Energies = -2525.240635
 Sum of electronic and thermal Enthalpies = -2525.239691
```

```
   Sum of electronic and thermal Free Energies = -2525.306551
```

Table S 19. NMR calculation for EPR-TPSSh of [Cu(CBTE1EtOH)]$^{2+}$

```
#

#
! uks tpssh tightscf Normalprint grid5 def2-TZVPP def2/JK SOMF(1X) RIJK
cpcm(water)
%pal
  nprocs 12
end
* xyz 2 2
 C                  2.68644300      0.89820800      0.19204400
 H                  3.64878300      0.76128700      0.69594500
 H                  2.89108400      1.06559300     -0.86530500
 C                  1.98326200      2.12671000      0.76622300
 H                  1.70885400      1.98296900      1.81278900
 C                  0.80284900      2.65416400     -0.04293600
 H                  0.50869500      3.63506700      0.34840200
 H                  1.12016400      2.79410300     -1.07783200
 C                 -1.26341000      2.15069300     -1.21596800
 H                 -0.62302500      2.23363700     -2.09419600
 H                 -1.73029200      3.12739400     -1.04619900
 C                 -2.34130500      1.10524100     -1.45444600
 H                 -2.81863100      1.28287600     -2.41902200
 H                 -3.12157000      1.16450200     -0.69894700
 C                 -2.74169200     -1.28124800     -0.89297200
 H                 -3.68398500     -1.16504200     -1.43559400
 H                 -2.33828100     -2.26654100     -1.13096600
 C                 -3.00071000     -1.16695200      0.60519500
 H                 -3.84138300     -1.82806100      0.82929300
 C                 -1.84930300     -1.61425200      1.49808600
 H                 -1.54162900     -2.61760100      1.19921100
 H                 -2.19473700     -1.66900300      2.53656600
 C                  0.51661400     -1.51586700      2.01672600
 H                  0.51512000     -2.49976000      1.54663100
 H                  0.39438700     -1.66229300      3.09539800
 C                  1.82649100     -0.80017000      1.74454400
 H                  1.92142100      0.08970800      2.36063800
 H                  2.66599200     -1.45010600      2.00122900
 C                 -0.80843500      0.55303000      2.13070400
 H                  0.10670900      0.76887200      2.67512700
 H                 -1.60193500      0.47224300      2.87858200
 C                 -1.14290200      1.73631700      1.20362000
 H                 -2.20267600      1.71611200      0.96386600
 H                 -0.96882200      2.66109200      1.76126100
 N                  1.92837600     -0.38689000      0.30955100
 N                 -0.63300600     -0.76001100      1.44437400
 N                 -0.38541600      1.76601800     -0.07724300
 N                 -1.76993900     -0.27540100     -1.41629600
```

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H                       -3.34310400    -0.16538700     0.87420800
Cu                       0.04733500    -0.28399400    -0.50474800
H                        2.73115700     2.92369800     0.77517000
H                       -1.56705400    -0.54631900    -2.37497500
C                        2.61010700    -1.47261700    -0.45994300
H                        3.67939700    -1.47927400    -0.22922600
H                        2.18233800    -2.42002300    -0.13061800
C                        2.39580900    -1.32220300    -1.94619800
H                        2.87495100    -0.43334400    -2.35639700
H                        2.76878200    -2.20329200    -2.46867600
O                        0.96105700    -1.22551600    -2.13040100
H                        0.77508600    -0.94550600    -3.03622400
*
%cpcm smd true # turn on SMD
smdsolvent "water" # specify the name of solvent from the list
end
%method
SpecialGridAtoms 29
SpecialGridIntAcc 7
end
%eprnmr gtensor true ori CenterOfElCharge
Nuclei = all Cu {aiso,adip,fgrad}
end
```

Visible spectra of copper complexes of TE1EtOH, TE3MeEtOH, CB-TE1EtOH and CB-TEMeEtOH
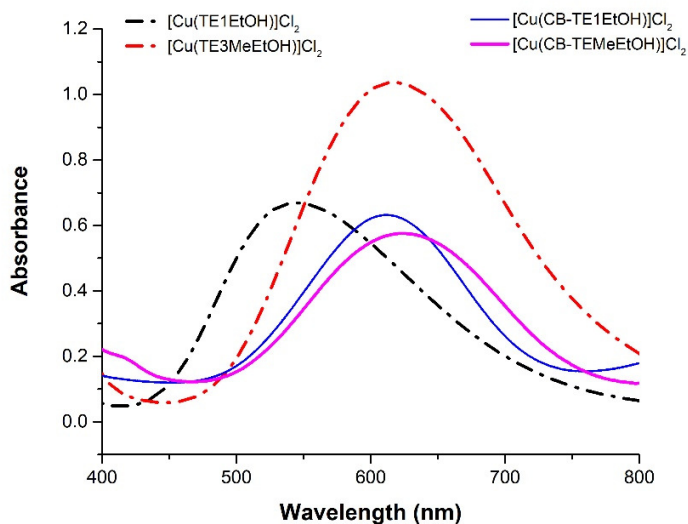
Figure S31. Visible spectra of [Cu(TE1EtOH)Cl₂] (black dashed), [Cu(TE3MeEtOH)Cl₂] (red dashed), [Cu(CB-TE1EtOH)Cl₂] (blue) and [Cu(CB-TE1EtOH)Cl₂] (purple) recorded in ultra-pure water at 6 mM for complexes' concentration.

Experimental and simulated X band EPR spectra of Copper(II) complexes considering the presence of one paramagnetic species in solution.
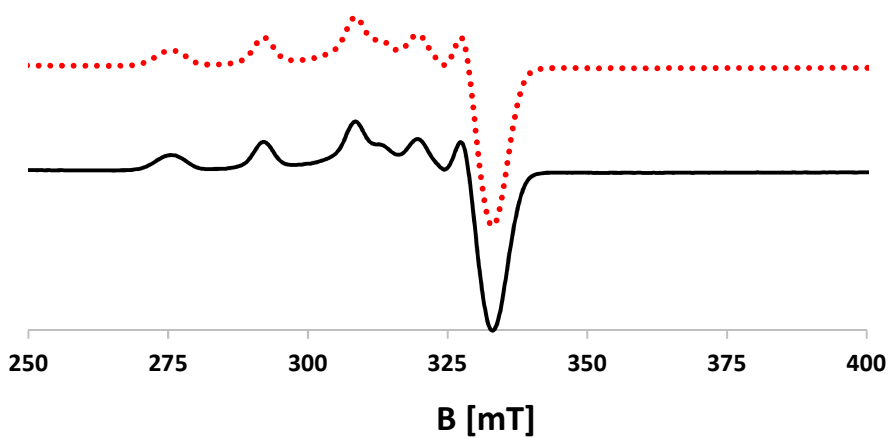
[Cu(TE1EtOH)]Cl$_2$
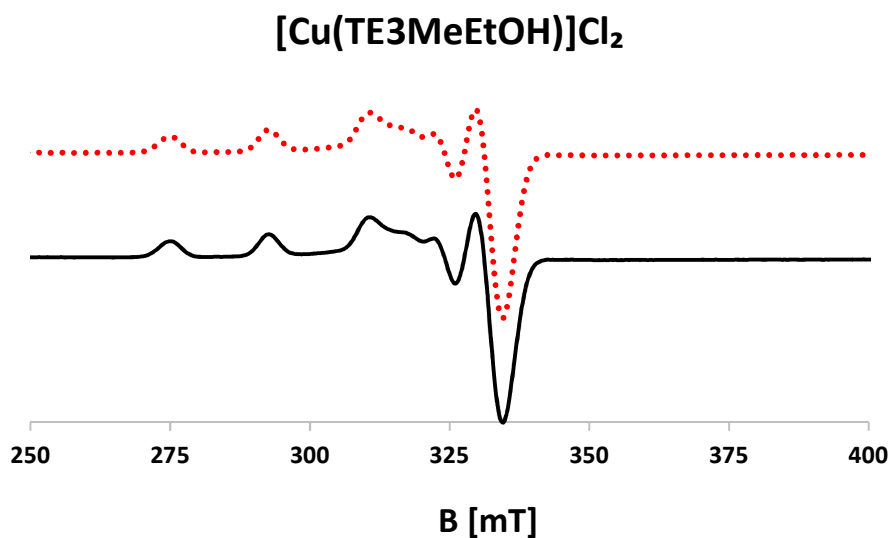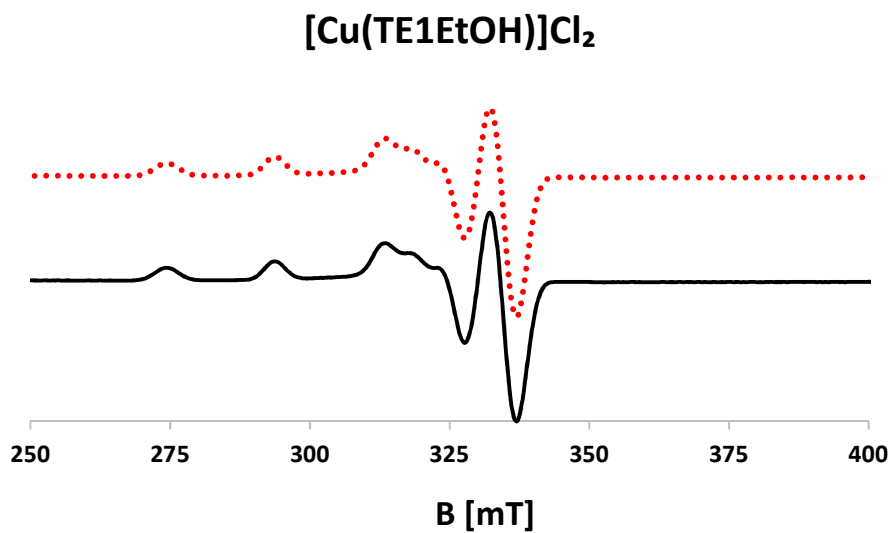
[Cu(TE3MeEtOH)]Cl$_2$

Figure S32. Experimental (plain lines) and simulated (dashed lines) X-band EPR spectra (v = 9.31 GHz) of [Cu(TE1EtOH)]$^{2+}$, [Cu(TE3MeEtOH)]$^{2+}$, recorded at 20 mM in a frozen solution of H$_2$O/DMF (1/1) at a 150-152 K.

[Cu(CB-TE1EtOH)]Cl$_2$
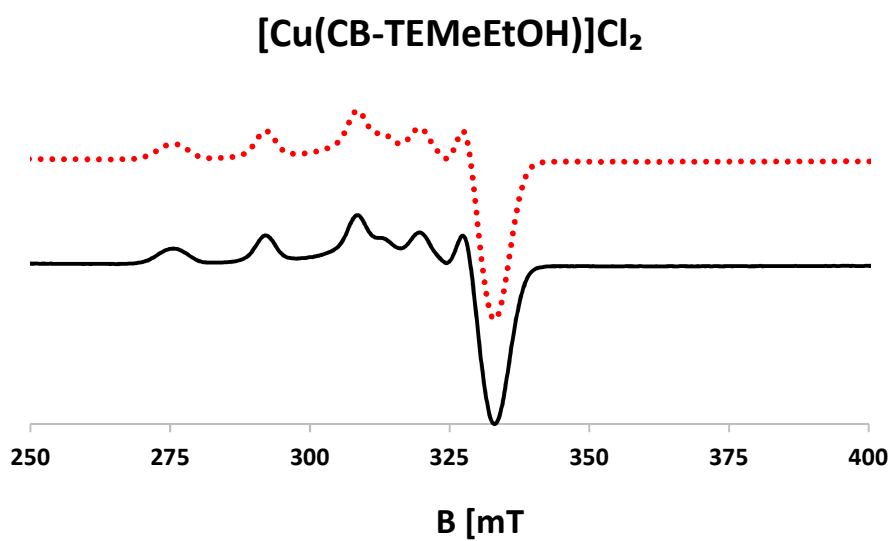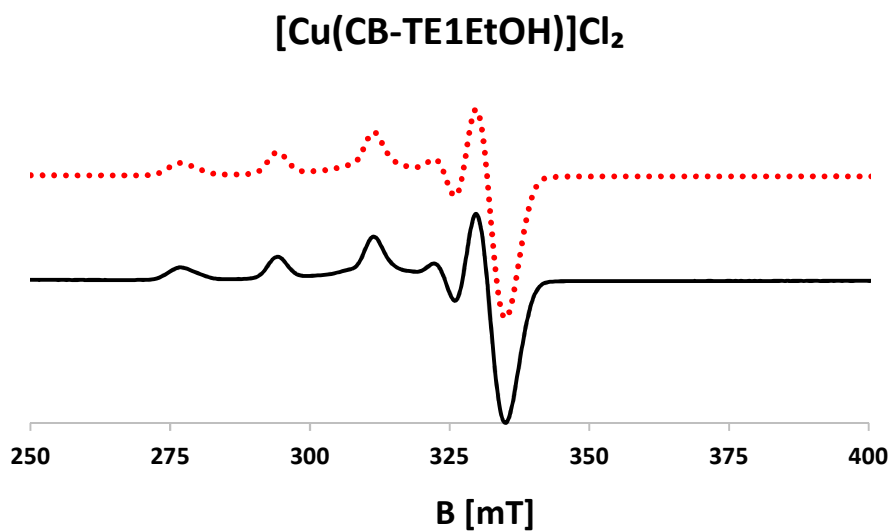
[Cu(CB-TEMeEtOH)]Cl$_2$

Figure S33. Experimental (plain lines) and simulated (dashed lines) X-band EPR spectra (v = 9.31 GHz) of [Cu(CB-TE1EtOH)]$^{2+}$ and [Cu(CB-TEMeEtOH)]$^{2+}$ recorded at 20 mM in a frozen solution of H$_2$O/DMF (1/1) at a 150-152 K.

Experimental and simulated X-band EPR spectra of [Cu(CB-TEMeEtOH)]Cl$_2$ considering the presence of two paramagnetic species in solution.
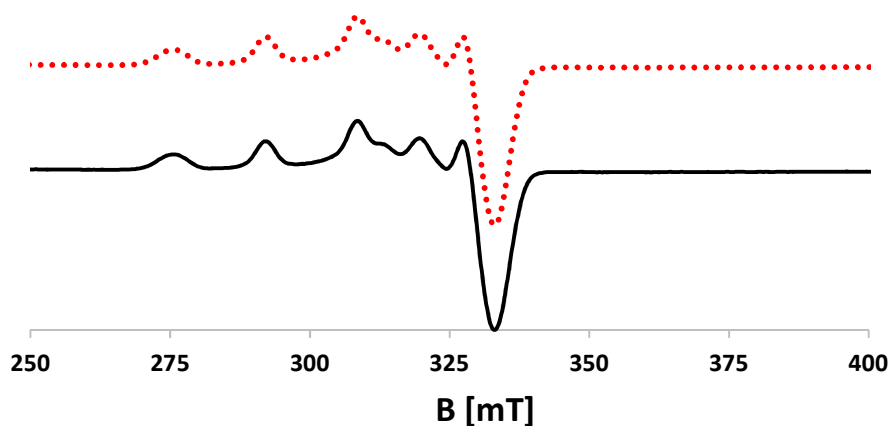
[Cu(CB-TEMeEtOH)]Cl$_2$ - species A
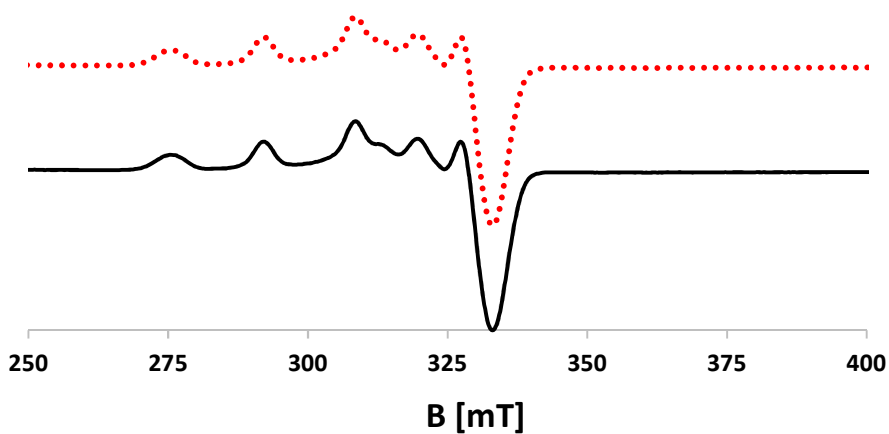
[Cu(CB-TEMeEtOH)]Cl$_2$ - species B

[Cu(CB-TEMeEtOH)]Cl₂ - Full simulation (A & B)

Figure S34. Experimental (plain lines) and simulated (dashed lines) X-band EPR spectra (v = 9.31 GHz) of [Cu(CB-TEMeEtOH)]²⁺ recorded at 20 mM in a frozen solution of H₂O/DMF (1/1) at a 150-152 K, considering the presence of two species in solution (A & B).

Table S20. EPR parameters for [Cu(CB-TEMeEtOH)]Cl₂ reported in this work (Figure S34, 150 K in H2O/DMF (1:1)) considering the presence of two paramagnetic species in solution A & B.

[Cu.CB-TEMeEtOH]Cl₂	g_z	g_y	g_x	A_z	A_y	A_x
A	2.209	2.050	2.050	171.6	-	-
B	2.032	2.085	2.214	38.9	56.9	175.2

Study of Copper(II) complexes dissociation in acidic media
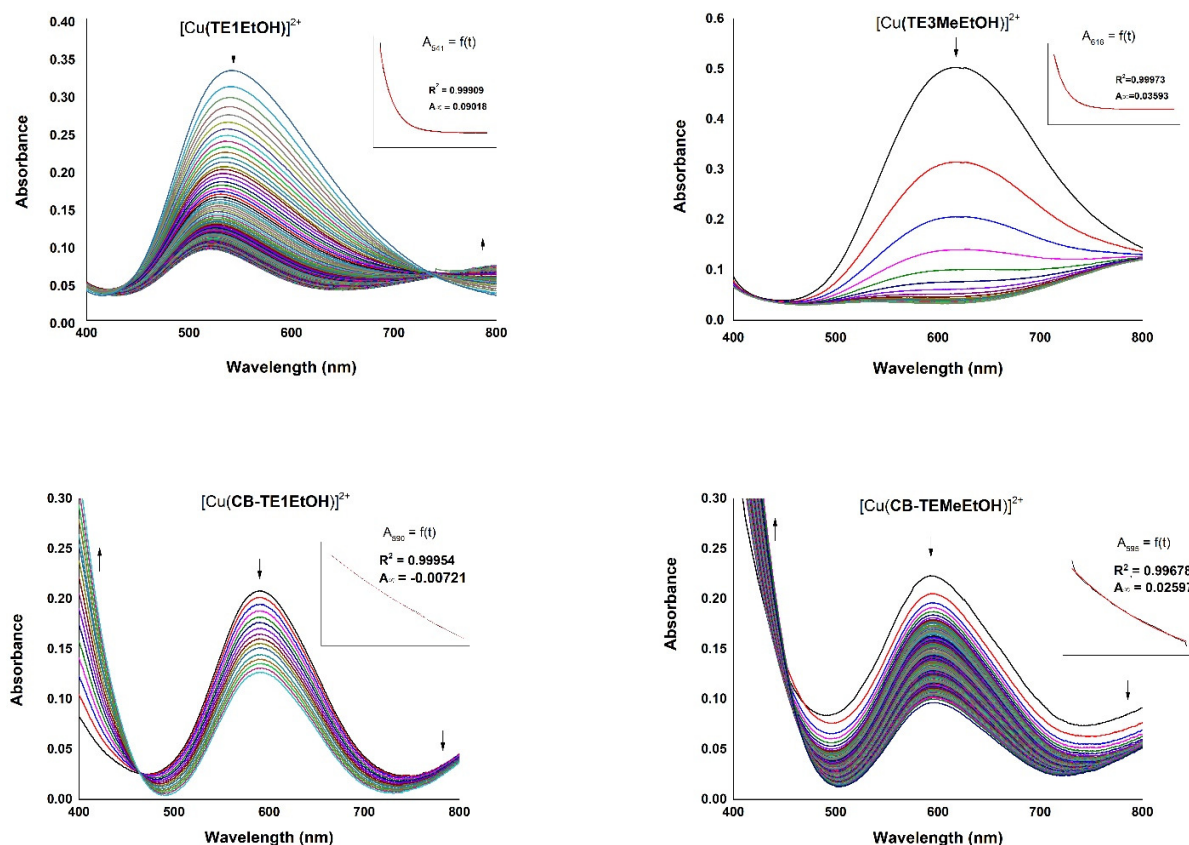
Figure S35. Visible spectra of acid-mediated dissociation of [Cu(TE1EtOH)]$^{2+}$, [Cu(TE3MeEtOH)]$^{2+}$ (3 mM in 3 M HCl at 25 °C), [Cu(CB-TE1EtOH)]$^{2+}$ and [Cu(CB-TEMeEtOH)]$^{2+}$ (3 mM in 5 M HCl at 70 °C) with a gap time ranging from 10 to 30 minutes. Arrows indicate the changes in absorbance during the experiment on both sides of isobestic points. Exponential curves corresponding to experimental/model fitting of the function A$_{\lambda max}$ = f(t) made on OriginPro9. R^2 is the adjusting parameter and A$_\infty$ the asymptote of the exponential model.
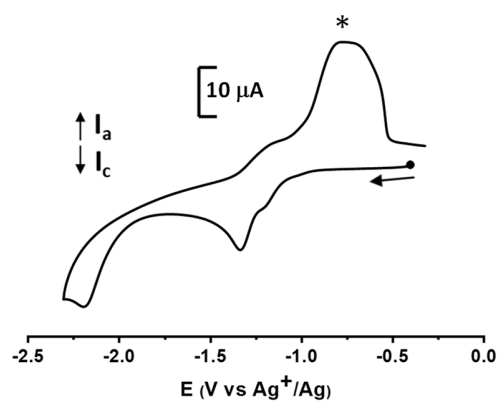
Electrochemical studies of Copper(II) complexes

Figure S 36. Cyclic voltammograms of [Cu(TE1EtOH)]Cl$_2$ in DMF + TBAPF$_6$ (0.1 M). Scan rate 0.1 V.s^{-1}. *Signals are attributed to redissolution peaks.
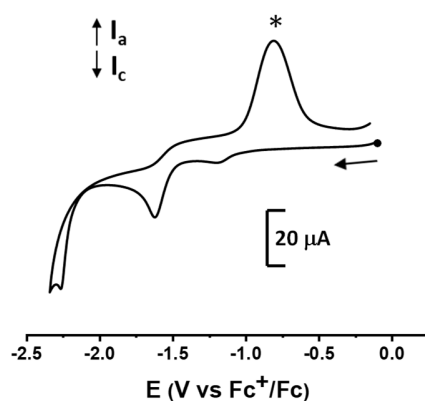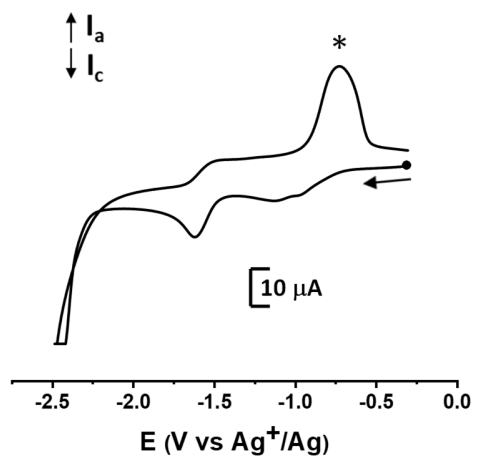

Figure S 37. Cyclic voltammograms of [Cu(CB-TEEtOH)]Cl$_2$ in DMF + TBAPF$_6$ (0.1 M). Scan rate 0.1 V.s^{-1}. *Signals are attributed to redissolution peaks.

Figure S 38. Cyclic voltammograms of [Cu(CB-TEMeEtOH)]Cl$_2$ in DMF + TBAPF$_6$ (0.1 M). Scan rate 0.1 V.s^{-1}. *Signals are attributed to redissolution peaks.