

Supplementary Information

for

Supramolecular Complex Formation between Tris(1,2-diaminoethane)cobalt(III) and α -Cyclodextrin, $[\text{Co}(\text{en})_3]_2(\text{CO}_3)_3 \cdot 2(\alpha\text{-CDX})$, via Atmospheric Carbon Dioxide Fixation

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Experimental Section

rac, Λ - and Δ - $[\text{Co}(\text{en})_3]\text{X}_3$ (X = Cl or I) were prepared according to the literature¹ and used as starting materials.

$[\text{Co}(\text{en})_3]_2(\text{CO}_3)_3 \cdot 2(\alpha\text{-CDX})$ (1) was synthesized as follows:

Method A: α -CDX (486.4 mg, 0.50 mmol), *rac*- $[\text{Co}(\text{en})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ (199.8 mg, 0.50 mmol) and $\text{LiOH} \cdot \text{H}_2\text{O}$ (62.9 mg, 1.50 mmol) were dissolved in water (7.5 ml) in an open vessel at room temperature and ethanol (9.6 ml) was added to the solution with stirring. The vessel was sealed with film. After one week, orange-yellow crystals of $1 \cdot 3\text{EtOH} \cdot 22\text{H}_2\text{O}$ were obtained. The yield was 35%. Elemental analysis: Found: H, 7.26; C, 35.50; N, 5.38%. Calc for $[\text{Co}(\text{en})_3]_2(\text{CO}_3)_3 \cdot 2(\alpha\text{-CDX}) \cdot 3\text{EtOH} \cdot 22\text{H}_2\text{O} = \text{C}_{93}\text{H}_{230}\text{N}_{12}\text{O}_{94}\text{Co}_2$: H, 7.39; C, 35.59; N, 5.36%. ¹H NMR (600 MHz, D₂O): 5.04 (d, *J* = 3.0 Hz, 6H; α -CDX-1), 3.98 (t, *J* = 9.3 Hz, 6H; α -CDX-3), 3.80-3.92 (m, 18H; α -CDX-5, 6, 6'), 3.60-3.66 (m, 8H; α -CDX-2, EtOH-CH₂), 3.57 (t, *J* = 9.3 Hz, 6H; α -CDX-4), 2.88 (br s, 3H; en), 2.86 (br s, 3H; en), 2.68-2.76 (m, 6H; en), 1.17 ppm (t, *J* = 7.2 Hz, 3H; EtOH-CH₃). ¹³C NMR (150 MHz, D₂O): 168.2 (s; CO₃²⁻), 102.0 (s; α -CDX-1), 81.8 (s; α -CDX-4), 73.9 (s;

α -CDX-3), 72.6 (s; α -CDX-5), 72.3 (s; α -CDX-2), 61.0 (s; α -CDX-6), 58.0 (s; EtOH-CH₂), 45.0 (s; en), 17.5 ppm (s; EtOH-CH₃). UV/Vis (H₂O, 25 °C): λ_{\max} (ϵ) = 464 (87.5), 337 nm (84.0 M⁻¹cm⁻¹). CD (H₂O, 25 °C, pH 10.5): λ_{\max} ($\Delta\epsilon$) = 488 (+0.52), 432 nm (-0.09 M⁻¹cm⁻¹). CD (HCl aq, 25 °C, pH 1.8): λ_{\max} ($\Delta\epsilon$) = 488 (+0.53), 425 nm (-0.04 M⁻¹cm⁻¹).

Method B: Method B is the same as Method A except for the use of K₂CO₃ (103.7 mg, 0.75 mmol) instead of LiOH. After one day, orange-yellow crystals of 1·3EtOH·24H₂O were obtained. The yield was 48%. Elemental analysis: Found: H, 7.32; C, 35.01; N, 5.25%. Calc for [Co(en)₃]₂(CO₃)₃·2(α -CDX)·3EtOH·24H₂O = C₉₃H₂₃₄N₁₂O₉₆Co₂: H, 7.43; C, 35.18; N, 5.29%.

Λ -[Co(en)₃]₂(CO₃)₃·2(α -CDX) (**2**) was synthesized by the same procedure as Method A except for the use of Λ -[Co(en)₃]I₃·H₂O (319.0 mg, 0.50 mmol) instead of the *rac*-[Co(en)₃]Cl₃. After one week, orange-yellow crystals of 2·3EtOH·22H₂O were obtained. The yield was 42%. Elemental analysis: Found: H, 7.21; C, 35.69; N, 5.35%. Calc for [Co(en)₃]₂(CO₃)₃·2(α -CDX)·3EtOH·22H₂O = C₉₃H₂₃₀N₁₂O₉₄Co₂: H, 7.39; C, 35.59; N, 5.36%. ¹H NMR (500 MHz, D₂O): 5.04 (d, *J* = 3.5 Hz, 6H; α -CDX-1), 3.97 (t, *J* = 9.3 Hz, 6H; α -CDX-3), 3.80-3.94 (m, 18H; α -CDX-5, 6, 6'), 3.60-3.67 (m, 9H; α -CDX-2, EtOH-CH₂), 3.58 (t, *J* = 9.1 Hz, 6H; α -CDX-4), 2.87 (br s, 3H; en), 2.86 (br s, 3H; en), 2.68-2.79 (m, 6H; en), 1.17 ppm (t, *J* = 7.1 Hz, 4.5H; EtOH-CH₃). ¹³C NMR (150 MHz, D₂O): 168.5 (s; CO₃²⁻), 102.0 (s; α -CDX-1), 81.8 (s; α -CDX-4), 73.9 (s; α -CDX-3), 72.6 (s; α -CDX-5), 72.3 (s; α -CDX-2), 61.0 (s; α -CDX-6), 58.0 (s; EtOH-CH₂), 45.0 (s; en), 17.5 ppm (s; EtOH-CH₃). UV/Vis (H₂O, 25 °C): λ_{\max} (ϵ) = 464 (87.2), 337 nm (84.4 M⁻¹cm⁻¹). CD (H₂O, 25 °C, pH 10.5): λ_{\max} ($\Delta\epsilon$) = 488 (+1.84), 432 nm (-0.32 M⁻¹cm⁻¹). CD (HCl aq, 25 °C, pH 2.2): λ_{\max} ($\Delta\epsilon$) = 488 (+1.89), 426 nm (-0.13 M⁻¹cm⁻¹).

Δ -[Co(en)₃]₂(CO₃)₃·2(α -CDX) (**3**) was synthesized by the same procedure as Method B except for the use of Δ -[Co(en)₃]Cl₃·H₂O (181.8 mg, 0.50 mmol) instead of the *rac*-[Co(en)₃]Cl₃. The mixture was kept in the refrigerator. After one month, orange-yellow crystals of 3·26H₂O were obtained. The yield was 19%. The crystal **3** easily effloresces in air by losing ethanol molecules. Elemental analysis: Found: H, 7.12; C, 34.13; N, 5.47%. Calc for [Co(en)₃]₂(CO₃)₃·2(α -CDX)·26H₂O = C₈₇H₂₂₀N₁₂O₉₅Co₂: H, 7.22; C, 34.01; N, 5.47%. ¹H NMR (600 MHz,

D₂O): 5.05 (d, $J = 3.6$ Hz, 6H; α -CDX-1), 3.98 (t, $J = 9.3$ Hz, 6H; α -CDX-3), 3.79-3.95 (m, 18H; α -CDX-5, 6, 6'), 3.60-3.67 (m, 8H; α -CDX-2, EtOH-CH₂), 3.58 (t, $J = 9.0$ Hz, 6H; α -CDX-4), 2.88 (br s, 3H; en), 2.87 (br s, 3H; en), 2.67-2.77 (m, 6H; en), 1.18 ppm (t, $J = 6.9$ Hz, 3H; EtOH-CH₃). ¹³C NMR (150 MHz, D₂O): 168.1 (s; CO₃²⁻), 102.1 (s; α -CDX-1), 81.9 (s; α -CDX-4), 73.9 (s; α -CDX-3), 72.7 (s; α -CDX-5), 72.3 (s; α -CDX-2), 61.0 (s; α -CDX-6), 58.0 (s; EtOH-CH₂), 45.0 (s; en), 17.5 ppm (s; EtOH-CH₃). UV/Vis (H₂O, 25 °C): $\lambda_{\max} (\epsilon) = 464 (87.2), 337 \text{ nm} (84.4 \text{ M}^{-1}\text{cm}^{-1})$. CD (H₂O, 25 °C, pH 10.5): $\lambda_{\max} (\Delta\epsilon) = 488 (-1.84), 432 \text{ nm} (+0.33 \text{ M}^{-1}\text{cm}^{-1})$. CD (HCl aq, 25 °C, pH 1.5): $\lambda_{\max} (\Delta\epsilon) = 487 (-1.88), 426 \text{ nm} (+0.14 \text{ M}^{-1}\text{cm}^{-1})$.

X-ray crystallography

The single crystals of **1**~**3** suitable for X-ray analysis were obtained by recrystallization from water-ethanol solution. They all contain some molecules of ethanol as shown by ¹H and ¹³C NMR spectra, but most of the ethanol molecules are disordered and solved as water molecules.

A yellow platelet crystal **1** (CCDC-752015) was mounted in a loop. All measurements were made on a Rigaku Mercury CCD area detector with graphite monochromated Mo-K α radiation. ($\lambda = 0.71070 \text{ \AA}$); C_{43.5}H₁₁₀N₆O_{47.5}Co₁, Mr = 1536.29, 0.35 x 0.20 x 0.10 mm; $T = 200(1) \text{ K}$; triclinic, P1 (#1), $Z = 2$, $a = 13.8755(3) \text{ \AA}$, $b = 17.7282(3) \text{ \AA}$, $c = 17.4932(3) \text{ \AA}$, $\alpha = 77.410(13)^\circ$, $\beta = 66.587(14)^\circ$, $\gamma = 65.518(13)^\circ$, $V = 3586.46(11) \text{ \AA}^3$, $\mu = 3.48 \text{ cm}^{-1}$, $F(000) = 1640$, $\rho_{\text{calcd}} = 1.423 \text{ g cm}^{-3}$, $2\theta_{\text{max}} = 55.2^\circ$. A total of 1800 oscillation images were collected. Of the 34549 reflections collected, 26827 were unique ($R_{\text{int}} = 0.035$). Final $R1 = 0.1368$ for 22063 reflections with $I > 2\sigma(I)$ (850 parameters) and $wR = 0.3981$ for all reflections.

A yellow block crystal **2** (CCDC-752016) was mounted in a loop and all measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with filtered Mo-K α radiation. ($\lambda = 0.71075 \text{ \AA}$); C_{44.5}H₁₁₅N₆O₄₉Co₁, Mr = 1577.34, 0.35 x 0.25 x 0.20 mm; $T = 150(1) \text{ K}$; triclinic, P1 (#1), $Z = 2$, $a = 13.8379(18) \text{ \AA}$, $b = 17.469(2) \text{ \AA}$, $c = 17.772(2) \text{ \AA}$, $\alpha = 83.767(2)^\circ$, $\beta = 65.734(3)^\circ$, $\gamma = 66.892(2)^\circ$, $V = 3595.1(8) \text{ \AA}^3$, $\mu = 3.51 \text{ cm}^{-1}$, $F(000) = 1686$, $\rho_{\text{calcd}} = 1.457 \text{ g cm}^{-3}$, $2\theta_{\text{max}} = 55.2^\circ$. Of the 35652 reflections collected, 26902 were unique ($R_{\text{int}} =$

0.020). Final $R1 = 0.0727$ for 25482 reflections with $I > 2\sigma(I)$ (894 parameters) and $wR = 0.2081$ for all reflections.

A yellow block crystal **3** (CCDC-752017) was mounted in a loop. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with filtered Mo- $K\alpha$ radiation. ($\lambda = 0.71075 \text{ \AA}$); $C_{43.5}H_{105}N_6O_{45}Co_1$, $M_r = 1491.25$, $0.35 \times 0.30 \times 0.25 \text{ mm}$; $T = 200(1) \text{ K}$; triclinic, P1 (#1), $Z = 2$, $a = 13.9205(3) \text{ \AA}$, $b = 17.8065(5) \text{ \AA}$, $c = 17.6812(4) \text{ \AA}$, $\alpha = 83.2080(8)^\circ$, $\beta = 65.3909(8)^\circ$, $\gamma = 66.6668(8)^\circ$, $V = 3653.05(15) \text{ \AA}^3$, $\mu = 3.37 \text{ cm}^{-1}$, $F(000) = 1590$, $\rho_{\text{calcd}} = 1.356 \text{ g cm}^{-3}$, $2\theta_{\text{max}} = 55.2^\circ$. Of the 36196 reflections collected, 27246 were unique ($R_{\text{int}} = 0.014$). Final $R1 = 0.1224$ for 25077 reflections with $I > 2\sigma(I)$ (788 parameters) and $wR = 0.3566$ for all reflections.

All calculations were performed using the CrystalStructure² and SHELX³ software package. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-752015~752017. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Notes and references

- 1 a) *Inorg. Synth.* 1946, vol. II, pp. 221; b) *Inorg. Synth.* 1960, vol. VI, pp. 183.
- 2 CrystalStructure 3.8: Crystal Structure Analysis Package, Rigaku and Rigaku Americas (2000-2007). 9009 New Trails Dr. The Woodlands TX 77381 USA.
- 3 SHELX97: Sheldrick, G.M. (1997).