Electronic Supplementary Information

The first structurally characterized coordination compounds with homocysteine

Masahiro Kouno,*[a,b] Takumi Konno,*[a,c] Naoto Kuwamura,[d] Tatsuhiro Kojima,[e] Shota Takamuku,[f] Soichiro Nishio[f] and Nobuto Yoshinari*[a]

[a] The University of Osaka, 1-1 Machikaneyama-cho, Toyonaka, Osaka, Japan 560-0043

[b] Hyogo Prefectural Institute of Technology, 3-1-12 Yukihira-cho, Suma, Hyogo, Japan 654-0037.

[c] Department of Chemistry, College of Science, National Taiwan Normal University, Taipei 11677, Taiwan

[d] Kogakuin University, 2665-1 Nakano-cho, Hachioji, Tokyo, Japan 192-0015.

[e] Kobe City College of Technology, 8-3 Gakuenhigashimachi, Nishi-ku, Kobe, Hyogo, Japan 651-2102

[f] QunaSys Inc., Aqua Hakusan Building 9F, 1-13-7 Hakusan, Bunkyo-ku, Tokyo, Japan 113-0001

Experimental Section.

Materials. Homocysteine and its precursors were prepared according to the methods in the literature. [26,27] All other chemicals were commercially available and used without purification.

Physical measurements.

The elemental analyses (C, H, N) were performed with a YANACO CHN coder MT-6 at The University of Osaka. The IR spectra were recorded on a JASCO FT/IR-4100 infrared spectrometer using KBr disks at room temperature. The NMR spectra were recorded in D_2O with a JEOL ECA500 (500 MHz) spectrometer at room temperature, using 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) as the internal standard. The electronic absorption spectra were recorded on a JASCO V-670 spectrophotometer at room temperature. The diffuse reflectance spectra were recorded on a JASCO V-670 spectrophotometer at room temperature.

Preparation of compounds.

(a) **Preparation of D-homocysteine thiolactone·D-mandelic acid**

This compound was prepared by referring to the procedure described in a patent.[26] Triethylamine (30 ml, 0.22 mol) was added to a solution containing D/L-homocysteine thiolactone hydrochloride (30 g, 0.20 mol) in acetone (500 ml). After stirring the mixture at room temperature for 1 h, the resulting white suspension was filtered. D-Mandelic acid (23 g) was added to the colorless filtrate, followed by stirring at room temperature for 1 h. A white powder which appeared was filtered and washed with acetone. Yield: 19 g (71%). IR spectrum (cm^{-1}, KBr disk): 3404 (ν_{OH}), 3152 (ν_{NH2}), 2884 (ν_{CH2}), 1710 (ν_{COOH}), 1556 (δ_{NH3}). ^1H NMR spectrum (ppm from DSS, D_2O): 7.44-7.35 (5H, m), 4.97 (1H, s), 4.29 (1H, dd, J = 13.0 Hz, 7.2 Hz), 3.55-3.43 (2H, m), 2.86-2.79 (1H, m), 2.30-2.21 (1H, m).

(b) **Preparation of D-homocysteine thiolactone hydrochloride**

This compound was prepared according to the procedure described in the literature.[27] Concentrated hydrochloric acid (5 ml) was added to a solution containing D-homocysteine thiolactone· D-mandelic acid (13 g, 48 mmol) in acetone (165 ml). When the mixture was stirred at room temperature for 1.5 h, a white powder precipitated, which was fileted and washed with acetone. Yield: 6 g (81%). 93% e.e. (based on CD spectrum) IR spectrum (cm^{-1}, KBr disk): 3430 (ν_{OH}), 2923(ν_{CH2}), 1692 (ν_{COOH}), 1503 (δ_{NH3}). ^1H NMR spectrum (ppm from DSS, D_2O): 4.31 (1H, dd, J = 13.0 Hz, 7.2 Hz), 3.55-3.44 (2H,

m), 2.86-2.80 (1H, m), 2.31-2.22 (1H, m).

(c) **Preparation of D-homocysteine (D-H_2hcys)**

This compound was prepared according to the procedure for synthesizing L-homocysteine.[27] An aqueous solution (160 ml) of D-Homocysteine thiolactone hydrochloride (7.0 g, 0.046 mol) was dropwise added to an aqueous solution of 6 M NaOH (60 ml) in an ice bath. To the resulting colorless solution, 12 M HCl (60 ml) was dropwise added. Then, the mixture solution was evaporated to dryness. The residue was dissolved in ethanol (50 ml), followed by filtering NaCl through Celite. Trimethylamine (31 ml) was added to the filtrate, which resulted in the precipitation of a white crystalline solid. The white solid was filtered and washed with ethanol. Yield: 3.7 g (59%) Anal. Calcd for $C_4H_8N_1O_2S_1 \cdot 0.5H_2O$ = C, 33.55; H, 6.34; N, 9.78 %. Found: C, 33.76; H, 6.18; N, 9.80%. IR spectrum (cm^{-1}, KBr disk): 3434 (ν_{OH}), 3169 (ν_{NH2}), 2940 (ν_{CH2}), 1617 (ν_{COOH}), 1587 (δ_{NH2}). ^{1}H NMR spectrum (ppm from DSS, D_2O): 3.87 (1H, dd, J = 7.2 Hz, 5.7 Hz), 2.70-2.59 (2H, m), 2.21-2.08 (2H, m).

(d) **Preparation of Na[Co(D-hcys)$_2$] (Na[1])**

To an aqueous solution (50 ml) of $Co(ClO_4)_2 \cdot 6H_2O$ (50 mg, 0.14 mmol) were added D-H_2hcys$\cdot 0.5H_2O$ (56 mg, 0.39 mmol) and an aqueous solution of 0.1 M NaOH (4.1 ml). The green mixture was stirred at room temperature for 45 min in air, which gave a brown solution. The brown solution was evaporated to dryness. Then, the residue was washed with ethanol and filtered to collect a brown solid. When the ethanolic filtrate was allowed to stand at room temperature, several dark brown microcrystals suitable for single-crystal X-ray analysis appeared. The brown solid could not be recrystallized to isolate an analytically pure sample because of its very high solubility in water. Given that [**1**]$^-$ was quantitatively formed in the reaction, the ε and Δε values of [**1**]$^-$ in the brown reaction solution were estimated based on the molar concentration of Co^{2+} (Fig. 1). The ^{1}H NMR spectra of the reaction solution, which showed five broad signals due to CH_2 and CH protons of hcys ligands, was illustrated in Figure S14.

(e) **Preparation of [Pd{Co(D-hcys)$_2$}$_2$] ([2])**

To an aqueous solution (200 ml) of $CoCl_2 \cdot 6H_2O$ (100 mg, 0.420 mmol) were added D-H_2hcys$\cdot 0.5H_2O$ (173 mg, 1.21 mmol) and an aqueous solution of 0.1 M NaOH (2.5 ml). The green mixture was stirred at room temperature for 20 min in air, which gave a brown solution. Then, a solid sample of $Na_2[PdCl_4]$ (63 mg, 0.214 mmol) was added to the brown solution, and the mixture was stirred at room temperature for 1 h. The resulting greenish

yellow solution was successively passed through QAE-Sephadex A25 (Cl^- form) and SP-Sephadex C25 (Na^+ form) columns using water as an eluent, which gave a greenish yellow solution. The solution was evaporated to dryness, and the green residue was recrystallized from water by adding ethanol. Yield: 66 mg (59%) Anal. Calcd for [Pd{Co(D-hcys)$_2$}$_2$]·7.5H_2O = $C_{16}H_{43}Co_2N_4O_{15.5}Pd_1S_4$ = C, 21.54; H, 4.86; N, 6.28%. Found: C, 21.30; H, 4.58; N, 6.18%. IR spectrum (cm^{-1}, KBr disk): 3434 (ν_{OH}), 3238 (ν_{NH2}), 3138(ν_{NH2}), 2934 (ν_{CH2}), 1632 (ν_{COOH}), 1587 (δ_{NH2}), 1385 (δ_{CH2}). ^{1}H NMR spectrum (ppm from DSS, D_2O): 6.20 (1H, dd, J_1 = 5.0 Hz, J_2 = 11.7 Hz), 5.45 (1H, d, J = 11.2 Hz), 3.86 (1H, dd, J_1 = 8.1 Hz, J_2 = 5.4 Hz), 2.44-2.36 (1H, m), 2.28-2.19 (1H, m), 2.19-2.11 (1H, m), 1.91-1.85 (1H, m). ^{13}C{^{1}H} NMR spectrum (ppm from DSS, D_2O): δ 185.5, 58.70, 32.06, 24.53. UV-Vis absorption in water (λ_{max}/nm, (ε/$mol^{-1}dm^3cm^{-1}$)): 613(220), 382^{sh}(10500), 323^{sh}(20700), 290(27700), 220^{sh}(32000), 206(36300). (sh denotes the shoulder band) Circular dichroism band in water (λ_{max}/nm, (Dε/$mol^{-1}dm^3cm^{-1}$)): 651(-2.71), 561(+2.22), 456(-5.22), 379(+5.59), 346(+2.42), 312(+7.21), 264(-6.17), 237(+6.89), 205(-27.7). Diffuse reflectance spectrum (λ_{max}/nm): 621, 381^{sh}, 339, 300, 249, 210. (sh denotes the shoulder band)

(f) **Preparation of [Pd{Co(D-hcys)$_2$}{Co(L-hcys)$_2$}] ([3])**

To an aqueous solution (200 ml) containing $CoCl_2$·6H_2O (100 mg, 0.420 mmol) were added D/L-H_2hcys (173 mg, 1.29 mmol) and an aqueous solution of 0.1 M NaOH (2.5 ml). The green mixture was stirred at room temperature for 30 min in air, which gave a brown solution. Then, a solid sample of $Na_2[PdCl_4]$ (64 mg, 0.218 mmol) was added to the brown solution, and the mixture was stirred at room temperature for 6.5 h. The resulting dark green microcrystals were collected by filtration and washed with water and ethanol. Yield: 123 mg (64%) Anal. Calcd for [Pd{Co(D-hcys)$_2$}{Co(L-hcys)$_2$}]·7H_2O = $C_{16}H_{42}Co_2N_4O_{15}Pd_1S_4$ = C, 21.76; H, 4.79; N, 6.34%. Found: C, 21.63; H, 4.54; N, 6.27%. IR spectrum (cm^{-1}, KBr disk): 3435 (ν_{OH}), 3241 (ν_{NH2}), 3136(ν_{NH2}), 2927 (ν_{CH2}), 1626 (ν_{COOH}), 1391 (δ_{CH2}). Diffuse reflectance spectrum (λ_{max}/nm): 615, 373^{sh}, 331, 282, 249, 213. (sh denotes the shoulder band.)

Single-crystal X-ray Analysis.

Single-crystal X-ray diffraction measurements for D-homocysteine thiolactone·D-mandelic acid were performed at 200 K with a Rigaku FR-E Superbright rotating-anode X-ray source with a Mo-target (λ = 0.71075 Å) and a Rigaku RAXIS VII imaging plate detector. The intensity data were collected by using the ω-scan technique and were empirically corrected for absorption. Single-crystal X-ray diffraction measurements for [Pd{Co(D-hcys)$_2$}$_2$] ([**2**]) was performed at 100 K using synchrotron radiation (λ=0.700 Å) at the BL02B1 beamline in SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI); a Rigaku Mercury 2 CCD detector was used as a detector. Single-crystal X-ray diffraction measurement for *trans*(N)-Na[Co(D-hcys)$_2$] (Na[**1**]) and [Pd{Co(D-hcys)$_2$}{Co(L-hcys)$_2$}] ([**3**]) were performed at 100 K using synchrotron radiation (λ = 0.8000 Å for Na[**1**], λ = 0.6300 Å for [**3**]) at 2D beamline in Pohang Accelerator Laboratory (PAL); ADSC Q210 CCD area detector and Rayonix MX225HS CCD area detector were used for Na[**1**] and [**3**], respectively, as a detector. Absorption corrections were applied using PLATON[S1] for Na[**1**] and [**2**] and HKL3000sm for [**3**]. The intensity data were collected by using the ω-scan technique and were empirically corrected for absorption. For D-homocysteine thiolactone·D-mandelic acid and [**2**], the collected diffraction data were processed with the Rapid Auto software program. For Na[**1**] and [**3**], the diffraction images were processed by using HKL3000[S2]. The structures were solved by direct methods using SHELXS-2013 or SHELXS-2014[S3]. Structure refinements were carried out using the full-matrix least squares (SHELXL-2013 or SHELXL-2014) analysis. All calculations were performed using the Yadokari-XG software package. Hydrogen atoms were included in the calculated positions except for those from water molecules. For Na[**1**], all non-hydrogen atoms were refined anisotropically. The distance between H2B and H13A was fixed using DFIX command to optimize a crystal structure. For [**2**], [**3**] and D-homocysteine thiolactone·D-mandelic acid, all non-hydrogen atoms were refined anisotropically.

Theoretical calculations.

All calculations were performed using ORCA 6.0.1.[4] The ωB97X-D3 functional was employed with the def2-TZVPD basis set, and solvent effects were taken into account using the CPCM model with water as the solvent. The def2/J auxiliary basis set was employed, and the RIJCOSX approximation was applied. The computational resources were provided by the supercomputer Fugaku.

References:

[S1] A. L. Spek, *J. Appl. Cryst* **2003**, *36*, 7.

[S2] Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307.

[S3] G. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* **2008**, *64*, 112.

[S4] F. Neese, *WIREs Comput. Molec. Sci.* **2022**, *12*, e1606.

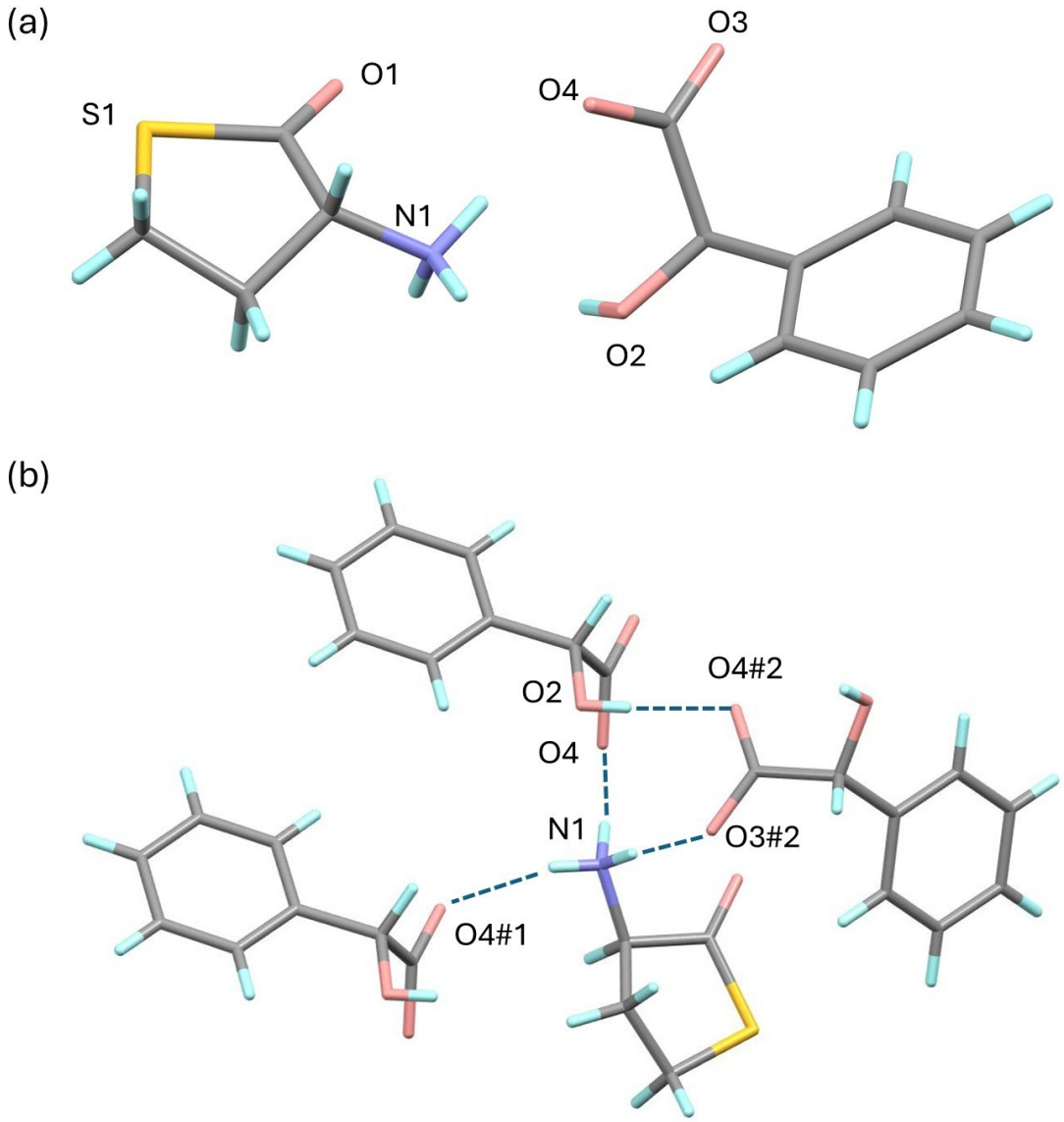


Figure S1. (a) Perspective views of D-homocysteine thiolactone·D-mandelic acid and (b) intermolecular hydrogen bonding interactions. Color codes: S, yellow; O, pink; N, pale blue; C, gray; H, light blue. (#1) x+1, y, z; (#2) -x, y-1/2, -z+1.

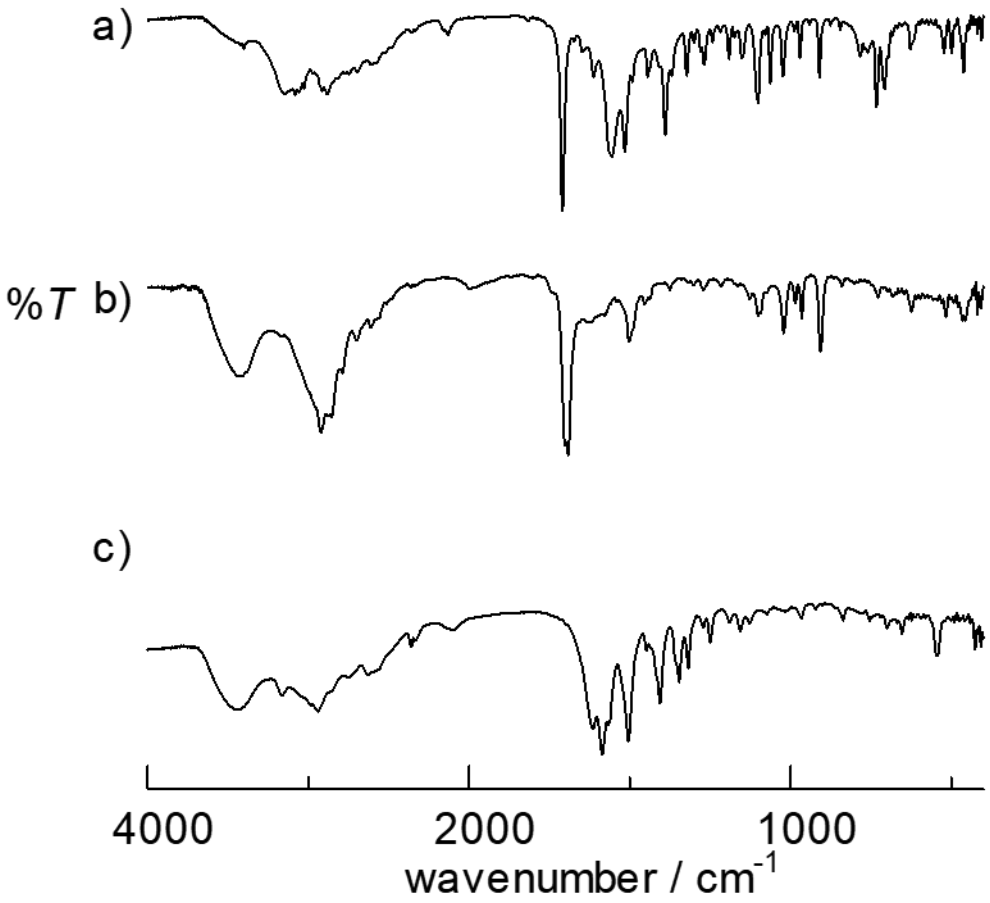


Figure S2. IR spectra of (a) D-homocysteine thiolactone·D-mandelic acid (b) D-homocysteine thiolactone hydrochloride and (c) D-H_2hcys.

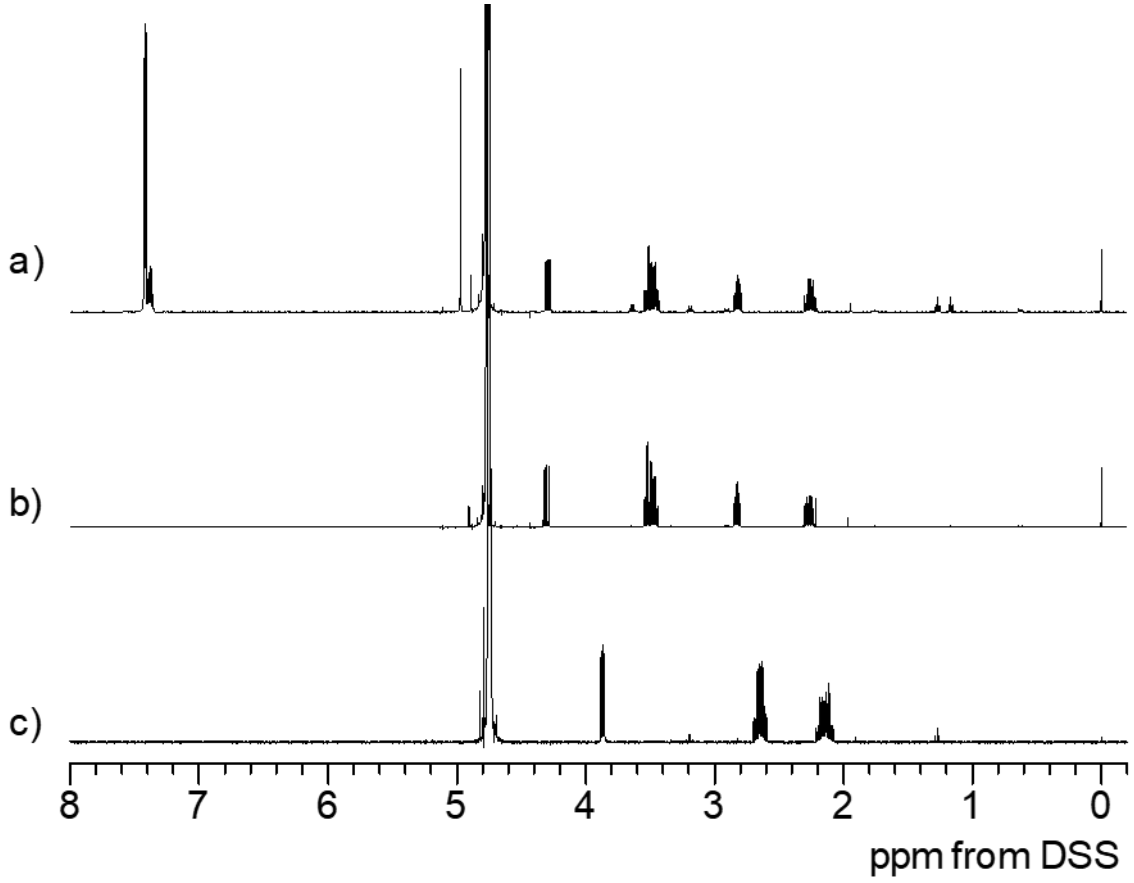


Figure S3. ^{1}H NMR spectra of (a) D-homocysteine thiolactone·D-mandelic acid (b) D-homocysteine thiolactone hydrochloride and (c) D-homocysteine in D_2O.

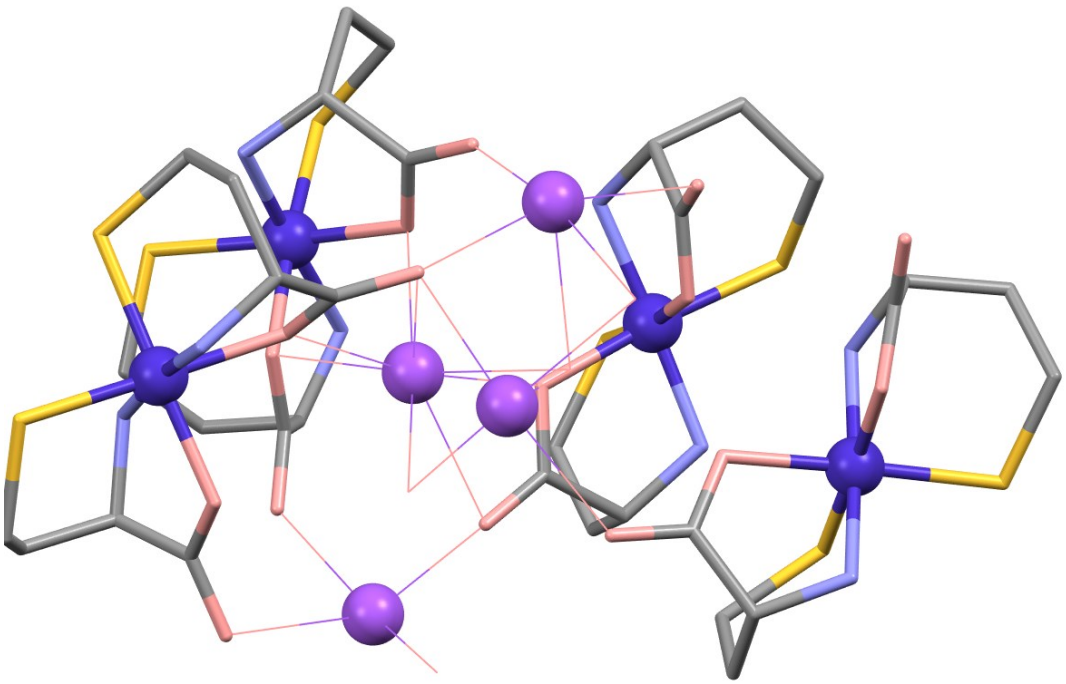


Figure S4. The X-ray structure of Na[**1**] in the asymmetric unit. H atoms are omitted for clarity. Color codes: S, yellow; O, pink; N, pale blue; C, gray.

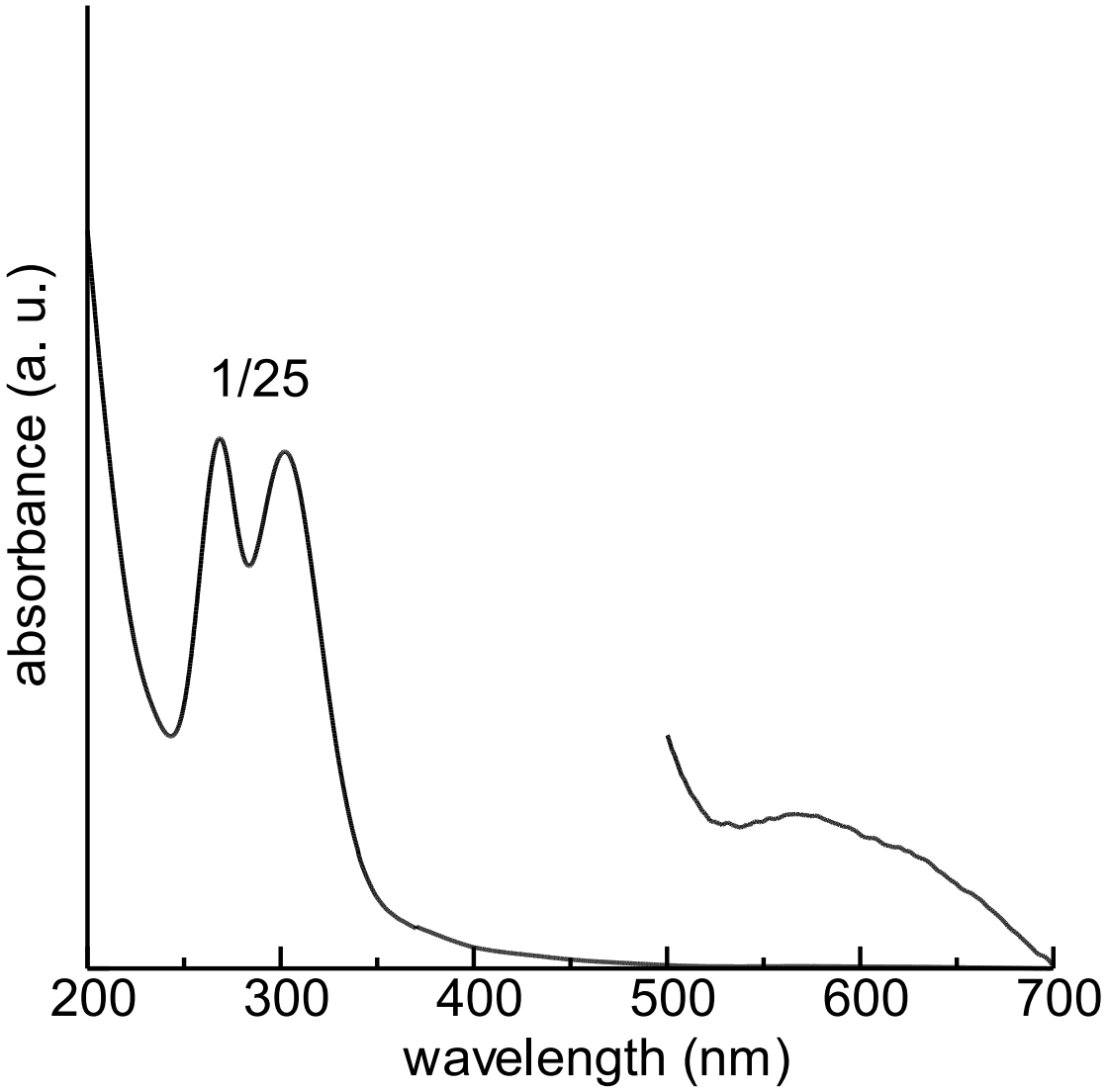


Figure S5. Absorption spectrum of the eluent containing [**1**]$^{-}$ passed through an QAE Sephadex column with 0.05 M aqueous NaCl.

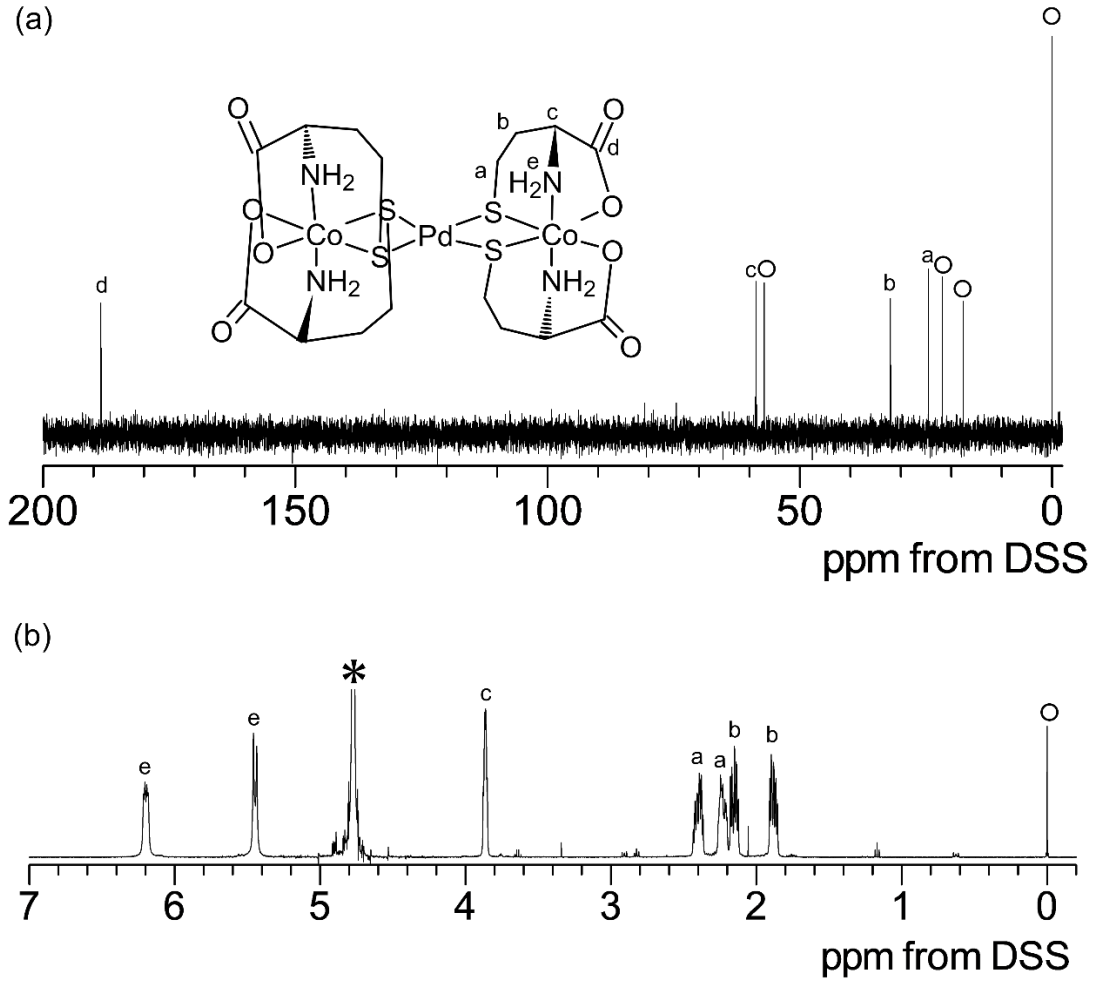
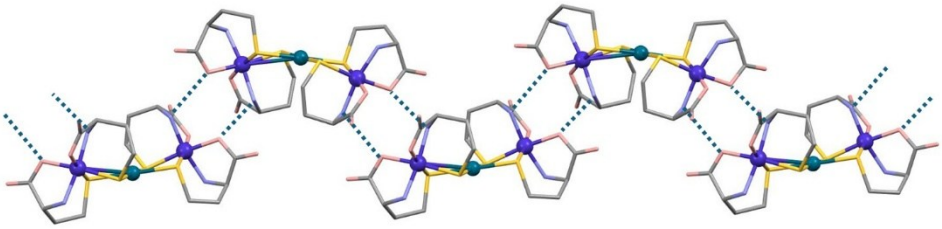


Figure S6. (a) $^{13}C\{^{1}H\}$ NMR and (b) ^{1}H NMR spectra of [**2**] in D_2O. * and ○ denote the signals form water and DSS, respectively.

(a)



(b)

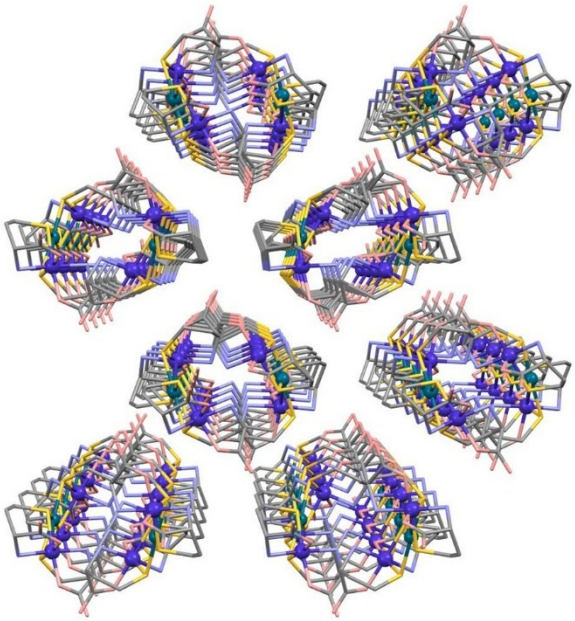


Figure S7. (a) 1 D zigzag chain and (b) packing structures of [**2**]. Color codes: Pd, blue green; Co, purple blue; S, yellow; O, pink; N, pale blue; C, gray. Hydrogen bonds (av. N···O = 2.86 Å) are represented by blue dashed lines in (a).

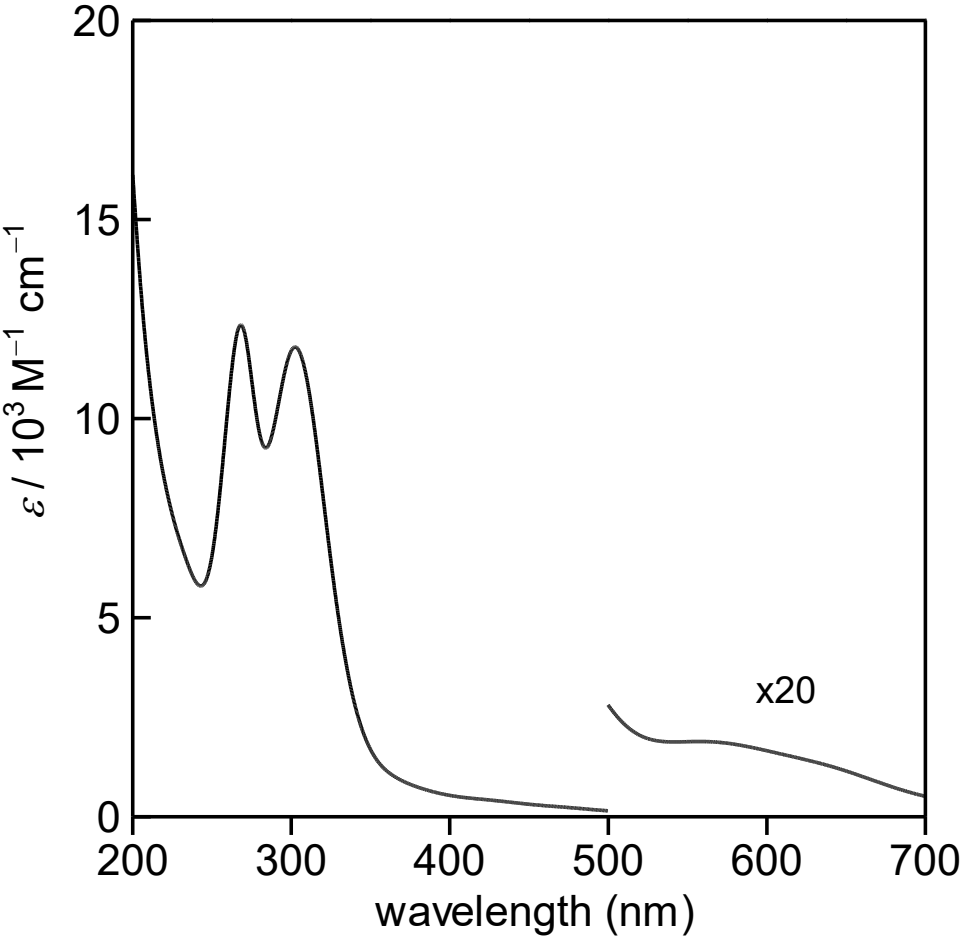


Figure S8. Absorption spectra of the reaction solution of $CoCl_2 \cdot 6H_2O$ with D/L-H_2hcys.

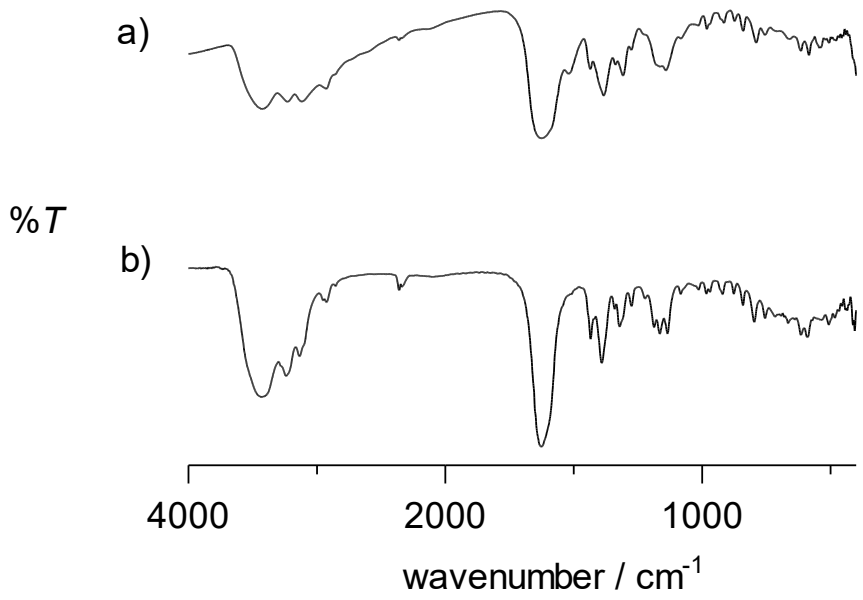


Figure S9. IR spectra of (a) [**2**] and (b) [**3**].

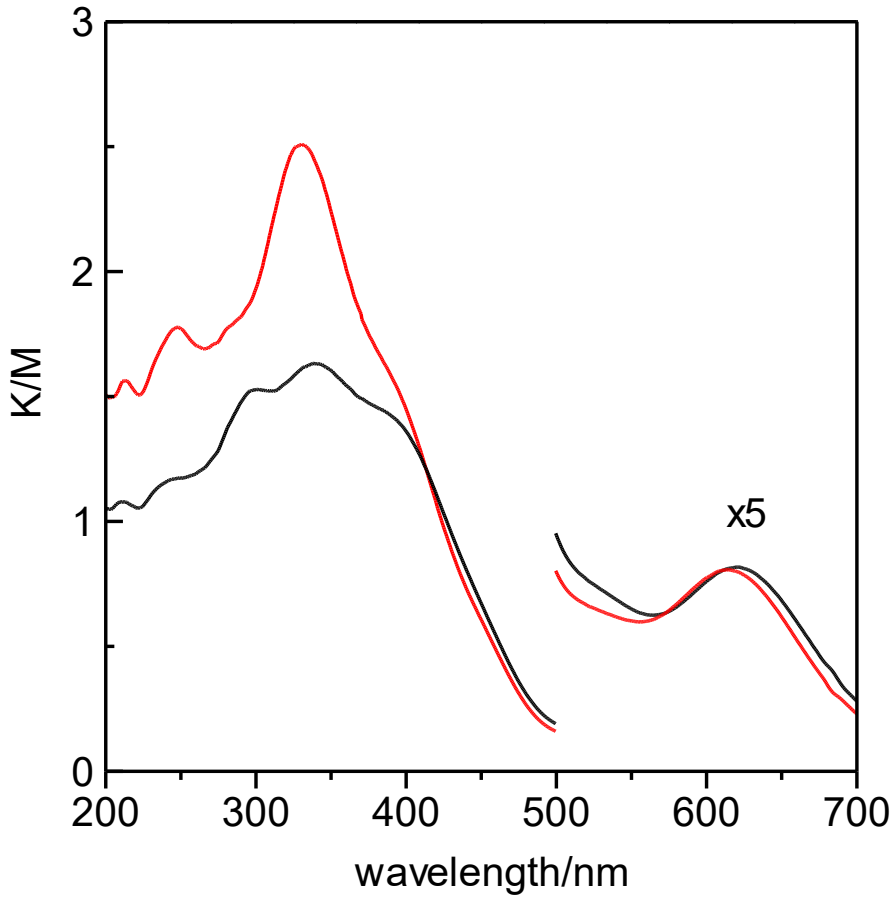


Figure S10. Diffuse reflectance spectra of [**2**] (black) and [**3**] (red).

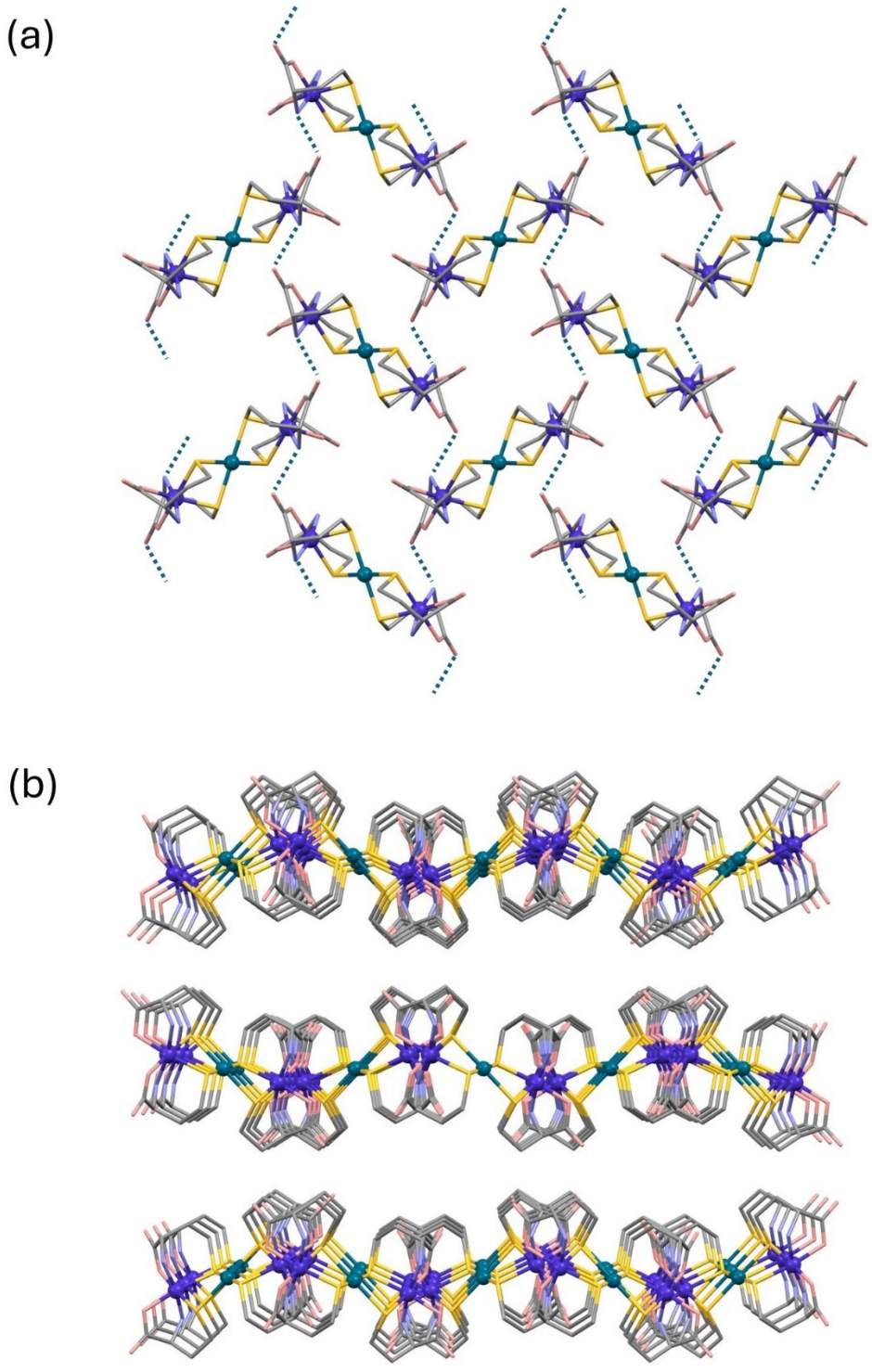


Figure S11. (a) 2D sheet and (b) packing structures of [**3**]. Color codes: Pd, blue green; Co, purple blue; S, yellow; O, pink; N, pale blue; C, gray. Hydrogen bonds (av. N···O = 3.02 Å) are represented by blue dashed lines in (a).

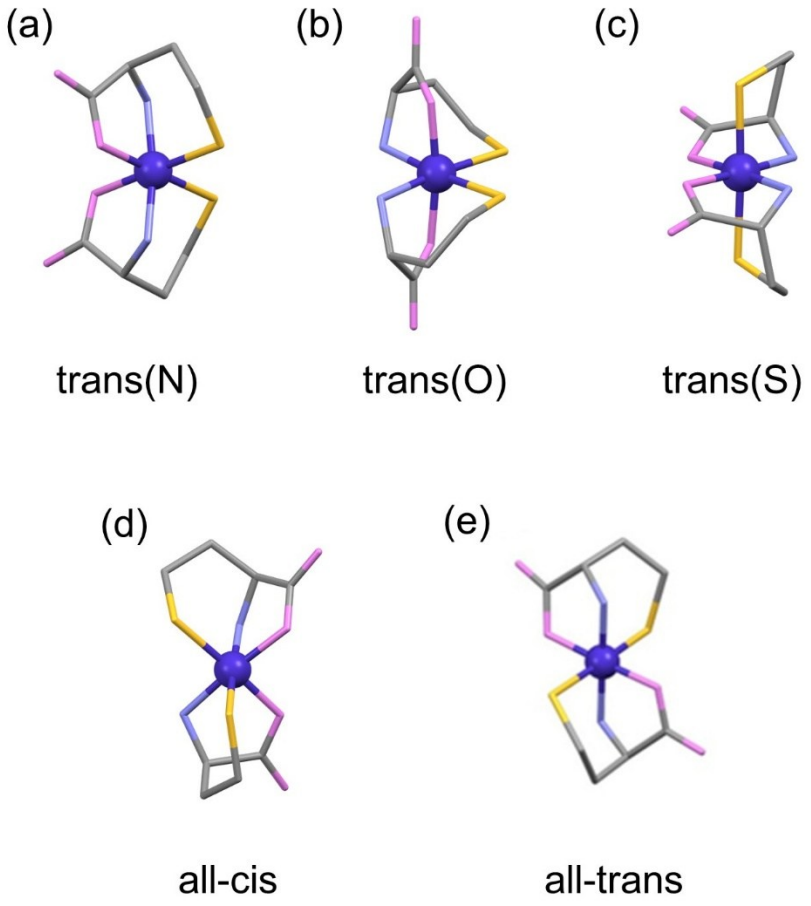


Fig. S12. The optimized structures of (a) trans(N), (b) trans(O), and (c) trans(S) isomers for $[Co(D\text{-hcys})_2]^-$ and (d) all-cis and (e) all-trans isomers for $[Co(D\text{-hcys})(L\text{-hcys})]^-$. Hydrogen atoms are omitted for clarity.

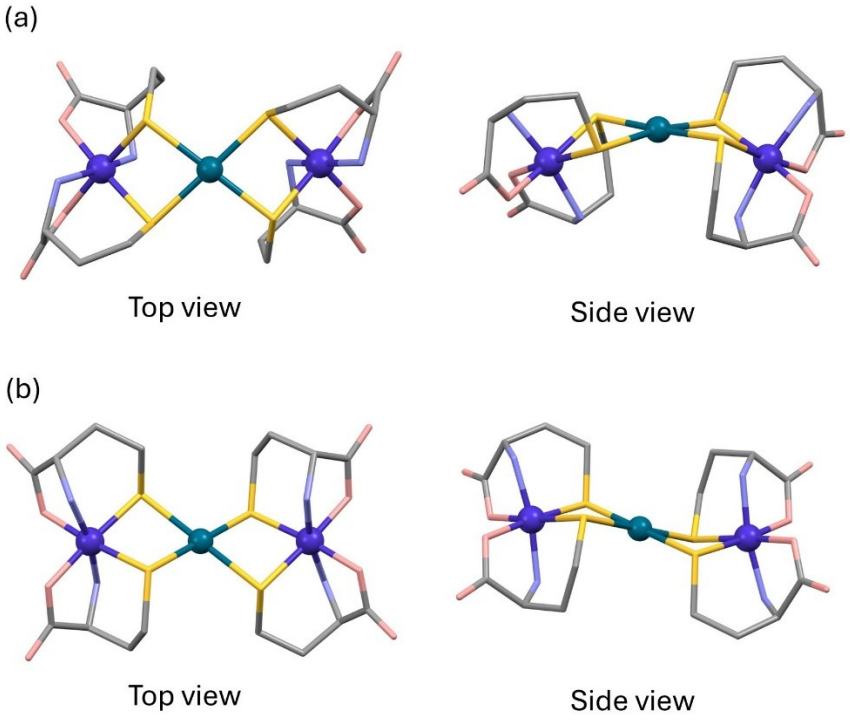


Figure S13. The optimized structures of (a) [**2**] and (b) [**3**]. Hydrogen atoms are omitted for clarity.

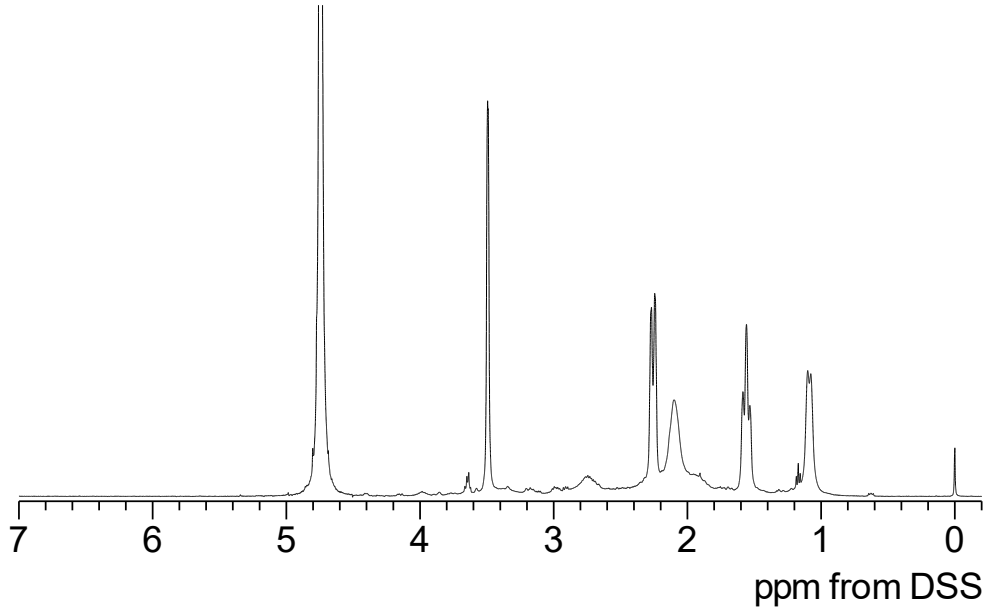


Figure S14. ^{1}H NMR spectrum of the reaction solution containing [**1**]$^{-}$, which was prepared from $Co(ClO_4)_2$, D-H_2hcys and NaOH in D_2O in air.

Table S1. Crystal data of D-homocysteine thiolactone·D-mandelic acid.

Formula	$C_{12}H_{15}NO_4S$
Color, form	Colorless, block
Mw	269.31
Crystal system	Monoclinic
Space group	$P2_1$
a/ Å	6.43350(10)
b/ Å	7.6836(2)
c/ Å	12.6869(3)
β/ °	93.801(7)
V/ Å^3	625.76(2)
Z	2
T/ K	200(2)
F(000)	284
ρ calcd / g· cm^{-3}	1.429
μ / mm^{-1}	0.265
Crystal size/ mm^3	0.22×0.07×0.07
Limiting indices	$-7 \le h \le 8$,
	$-9 \le k \le 9$,
	$-16 \le l \le 16$,
*R*1 ($I>2\sigma(I)$[a)]	0.0301
w*R*2 (all data)[b)]	0.0712
GOF	1.086
Flack x	0.04(2)

[a] $R_1 = S||Fo|-|Fc|| / S(|Fo|)$.

[b] $wR_2 = [Sw(Fo^2-Fc^2)^2 / Sw(Fo^2)^2]^{1/2}$.

Table S2. Crystal data of Na[**1**], [**2**] and [**3**].

	Na[**1**]	[**2**]	[**3**]
Formula	$C_{32}H_{56}Co_4N_8Na_4O_{20}S_8$	$C_{16}H_{28}Co_2N_4PdO_8S_4$	$C_{16}H_{28}Co_2N_4O_8PdS_4$
Color, form	Brown, needle	Green, block	Yellow, plate
Mw	1457.00	756.92	756.92
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$C2/c$
a/ Å	9.9442(5)	13.3013(13)	21.324(4)
b/ Å	18.9994(11)	15.1999(15)	13.010(3)
c/ Å	28.1065(16)	17.1485(16)	10.937(2)
α/ °	90	90	90
β/ °	90	90	93.53(3)
γ/ °	90	90	90
V/ Å^3	5310.3(5)	3467.1(6)	3028.4(11)
Z	4	4	4
T/ K	100(2)	100(2)	100(2)
F(000)	2976	1520	1520
ρ calcd / g· cm^{-3}	1.822	1.450	1.660
μ / mm^{-1}	2.279	1.670	1.425
crystal size/ mm^3	0.10×0.02×0.02	0.02×0.02×0.01	0.02×0.02×0.02
Limiting indices	$-10 \le h \le 11$,	$-17 \le h \le 15$,	$-33 \le h \le 33$,
	$-21 \le k \le 21$,	$-19 \le k \le 19$,	$-21 \le k \le 21$,
	$-31 \le l \le 26$	$-22 \le l \le 22$	$-19 \le l \le 19$,
*R*1 ($I>2\sigma(I)$[a)]	0.0623	0.0472	0.0579
w*R*2 (all data)[b)]	0.1798	0.1013	0.1637
GOF	0.968	0.959	1.083
Flack x	0.02(2)	0.036(18)	

[a] $R_1 = S|(|Fo|-|Fc|)| / S(|Fo|)$.

[b] $wR_2 = [Sw(Fo^2-Fc^2)^2 / Sw(Fo^2)^2]^{1/2}$.

Table S3. Selected bond distances and angles for Na[**1**].

Bond distances (Å)			
Co(1)-N(1)	1.911(14)	Co(3)-S(5)	2.229(6)
Co(1)-N(2)	1.917(14)	Co(3)-S(6)	2.222(6)
Co(2)-N(3)	1.936(14)	Co(4)-S(7)	2.231(6)
Co(2)-N(4)	1.919(14)	Co(4)-S(8)	2.223(5)
Co(3)-N(5)	1.937(16)	Co(1)-O(2)	1.998(14)
Co(3)-N(6)	1.934(15)	Co(1)-O(3)	2.014(14)
Co(4)-N(7)	1.943(15)	Co(2)-O(5)	1.990(13)
Co(4)-N(8)	1.950(15)	Co(2)-O(8)	1.986(13)
Co(1)-S(1)	2.221(7)	Co(3)-O(10)	2.007(12)
Co(1)-S(2)	2.220(7)	Co(3)-O(11)	1.992(12)
Co(2)-S(3)	2.225(6)	Co(4)-O(14)	1.998(12)
Co(2)-S(4)	2.218(6)	Co(4)-O(15)	2.021(12)
Angles (°)			
S(1)-Co(1)-N(1)	91.8(5)	N(5)-Co(3)-O(10)	83.1(6)
S(2)-Co(1)-N(2)	92.0(5)	N(6)-Co(3)-O(11)	82.1(6)
S(3)-Co(2)-N(3)	90.5(5)	N(7)-Co(4)-O(14)	82.1(6)
S(4)-Co(2)-N(4)	89.9(5)	N(8)-Co(4)-O(15)	81.9(6)
S(5)-Co(3)-N(5)	91.4(5)	S(1)-Co(1)-O(2)	95.0(5)
S(6)-Co(3)-N(6)	89.5(5)	S(2)-Co(1)-O(3)	95.3(4)
S(7)-Co(4)-N(7)	90.5(5)	S(3)-Co(2)-O(5)	94.9(4)
S(8)-Co(4)-N(8)	92.0(5)	S(4)-Co(2)-O(8)	94.4(4)
N(1)-Co(1)-O(2)	82.4(6)	S(5)-Co(3)-O(10)	92.4(4)
N(2)-Co(1)-O(3)	79.8(6)	S(6)-Co(3)-O(11)	95.5(4)
N(3)-Co(2)-O(5)	82.8(6)	S(7)-Co(4)-O(14)	95.4(4)
N(4)-Co(2)-O(8)	84.2(6)	S(8)-Co(4)-O(15)	93.8(4)

Table S4. Selected bond distances and angles for [**2**].

Bond distances (Å)			
Co(1)-N(1)	1.914(6)	Co(1)-O(2)	1.933(6)
Co(1)-N(2)	1.924(6)	Co(1)-O(4)	1.918(5)
Co(2)-N(3)	1.930(6)	Co(2)-O(6)	1.908(5)
Co(2)-N(4)	1.906(6)	Co(2)-O(8)	1.904(6)
Co(1)-S(1)	2.205(2)	Pd(1)-S(1)	2.269(2)
Co(1)-S(2)	2.219(3)	Pd(1)-S(2)	2.3000(19)
Co(2)-S(3)	2.224(3)	Pd(1)-S(3)	2.304(2)
Co(2)-S(4)	2.220(2)	Pd(1)-S(4)	2.289(2)
Angles (°)			
S(1)-Co(1)-N(1)	95.0(2)	S(1)-Co(1)-O(2)	93.00(17)
S(2)-Co(1)-N(2)	93.9(2)	S(2)-Co(1)-O(4)	89.80(18)
S(3)-Co(2)-N(3)	94.8(2)	S(3)-Co(2)-O(6)	90.12(18)
S(4)-Co(2)-N(4)	92.6(2)	S(4)-Co(2)-O(8)	94.99(17)
N(1)-Co(1)-O(2)	84.0(3)	S(1)-Pd(1)-S(2)	81.70(8)
N(2)-Co(1)-O(4)	81.3(2)	S(1)-Pd(1)-S(3)	97.99(8)
N(3)-Co(2)-O(6)	83.9(3)	S(2)-Pd(2)-S(4)	98.34(8)
N(4)-Co(2)-O(8)	84.2(3)	S(3)-Pd(2)-S(4)	82.01(8)

Table S5. Selected bond distances and angles for [**3**].

Bond distances (Å)			
Co(1)-N(1)	1.951(2)	Co(1)-O(2)	1.945(2)
Co(1)-N(2)	1.956(2)	Co(1)-O(4)	1.963(2)
Co(1)-S(1)	2.2302(8)	Pd(1)-S(1)	2.3091(7)
Co(1)-S(2)	2.2572(9)	Pd(1)-S(2)	2.3356(7)
Angles (°)			
S(1)-Co(1)-N(1)	93.86(7)	S(1)-Co(1)-O(2)	93.85(6)
S(2)-Co(1)-N(2)	94.54(8)	S(2)-Co(1)-O(4)	90.25(7)
N(1)-Co(1)-O(2)	83.02(9)	S(1)-Pd(1)-S(2)	99.31(3)
N(2)-Co(1)-O(4)	82.53(10)	S(1)-Pd(1)-S(2)#1	80.69(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+1/2,-z+1

Table S6. Gibbs energies, ΔG relative to trans(N) isomer, averaged bond distances and angles of the DFT optimized structures of *trans*(N), *trans*(O) and *trans*(S) isomers for $[Co(D\text{-hcys})_2]^-$ and *all-cis* and *all-trans* isomers for $[Co(D\text{-hcys})(L\text{-hcys})]^-$.

Isomer	*trans*(N)	*trans*(O)	*trans*(S)	*all-cis*	*all-trans*
Gibbs energy					
G(hartree)	-2903.1593	-2903.1443	-2903.1458	-2903.1524	-2903.1485
ΔG(kcal/mol)	0	9.38	8.45	4.30	6.78
Bond distances (Å)					
Co-N	1.950	1.998	1.952	1.970	1.955
Co-S	2.256	2.275	2.310	2.262	2.315
Co-O	1.964	1.925	1.927	1.956	1.919
Angles (°)					
S-Co-N (chelate)	90.38	91.65	91.43	91.00	90.00
N-Co-O (chelate)	83.40	82.32	83.42	82.49	84.15
S-Co-O (chelate)	94.24	92.06	90.92	93.85	91.31
S-Co-N (trans)	n/a	174.71	n/a	174.82	n/a
N-Co-O (trans)	n/a	n/a	177.44	173.53	n/a
S-Co-O (trans)	179.34	n/a	n/a	176.33	n/a
O-Co-O	86.02	171.48	94.41	90.81	178.03
N-Co-N	171.34	92.48	98.79	95.60	179.05
S-Co-S	85.52	84.44	177.30	86.26	175.13

Table S7. Gibbs energies, ΔG relative to [**2**], averaged bond distances and angles for DFT optimized structures of [**2**] and [**3**].

Complex	[**2**]	[**3**]
G(hartree)	-5934.0703	-5934.0694
ΔG(kcal/mol)	0	0.57
Co-N	1.950	1.950
Co-S	2.254	2.255
Co-O	1.932	1.932
Pd-S	2.329	2.333
S-Co-N (chelate)	93.60	93.81
N-Co-O (chelate)	86.65	83.04
S-Co-O (chelate)	92.46	92.54
S-Co-O (trans)	175.05	175.19
O-Co-O	90.76	90.76
N-Co-N	170.44	169.88
S-Co-S	84.55	84.38