Electronic Supplementary Information

Synthesis, Structure, Circular Dichroism of Δ(-)$_{546}$-Di-μ-hydroxo-tetrakis(S-prolinato)dicobalt(III) Complex and NMR Study of its Interaction with Chiral and non-Chiral Probes in Solutions

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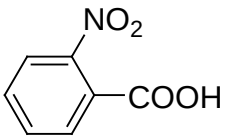
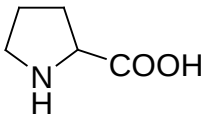
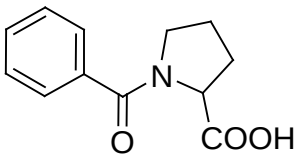
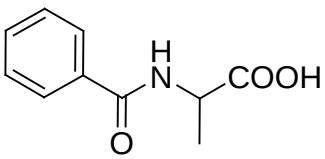
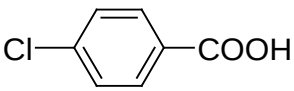
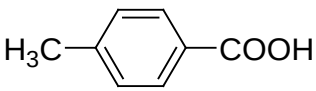
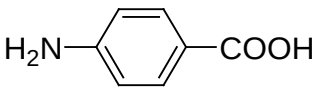
Table S1. pK values and details of concentrations measurement by NMR for the carboxylic acids used in NMR study of solubility of **1** in CD_3OD.

Acid	pK (according to https://scifinder.cas.org/)	Peaks in ^{1}H-NMR spectra used for integration – I(X)
 2-Nitrobenzoic acid	2.19±0.25	7.90-7.67 ppm (m, 4H, C_6H_4)
 S-proline and R-proline	2.35±0.20	4.01-3.95 ppm (m, 1H, α)
 N-Benzoyl-S-proline	3.68±0.20	7.58-7.42 ppm (m, 5H, C_6H_5)
 N-Benzoyl-S-alanine	3.86±0.10	7.87-7.84 ppm (m, 2H, C_6H_5)
 4-Chlorobenzoic acid	3.97±0.10	8.02-7.98 ppm (d, 2H, C_6H_4)
 4-Methylbenzoic acid	4.37±0.10	7.92-7.89 ppm (d, 2H, C_6H_4)
 4-Aminobenzoic acid	4.86±0.10	6.65-6.63 ppm (d, 2H, C_6H_4)

Note: Although pK values, listed in Table S2, were determined for aqueous solutions, we suggest that the tendency for CD_3OD is the same.

Table S2. Selected angles in $Co_2(\mu\text{-}OH)_2(S\text{-}Pro)_4 \cdot 4H_2O$.

Angle	Value, deg	Angle	Value, deg
O(1)–Co(1)–O(2)	80.62(11)	O(2)–Co(2)–O(1)	80.18(10)
O(2)–Co(1)–O(7)	94.01(12)	O(2)–Co(2)–O(5)	88.45(12)
O(1)–Co(1)–O(7)	172.53(13)	O(3)–Co(2)–O(5)	177.30(12)
O(1)–Co(1)–O(9)	94.11(13)	O(2)–Co(2)–O(3)	93.15(12)
O(2)–Co(1)–O(9)	172.12(12)	O(3)–Co(2)–O(1)	89.17(12)
O(7)–Co(1)–O(9)	91.74(12)	O(5)–Co(2)–O(1)	93.25(12)
O(1)–Co(1)–N(2)	88.60(13)	O(2)–Co(2)–N(3)	175.08(14)
O(2)–Co(1)–N(2)	92.47(13)	O(3)–Co(2)–N(3)	86.46(15)
O(7)–Co(1)–N(2)	86.43(13)	O(5)–Co(2)–N(3)	92.12(15)
O(9)–Co(1)–N(2)	93.26(13)	O(1)–Co(2)–N(3)	94.91(14)
O(1)–Co(1)–N(1)	92.44(13)	O(2)–Co(2)–N(4)	92.77(13)
O(2)–Co(1)–N(1)	88.44(12)	O(3)–Co(2)–N(4)	91.91(14)
O(7)–Co(1)–N(1)	92.60(13)	O(5)–Co(2)–N(4)	85.84(13)
O(9)–Co(1)–N(1)	85.92(13)	O(1)–Co(2)–N(4)	172.91(14)
N(2)–Co(1)–N(1)	178.71(13)	N(3)–Co(2)–N(4)	92.15(16)
Co(1)–O(1)–Co(2)	99.11(12)	Co(2)–O(2)–Co(1)	100.09(12)

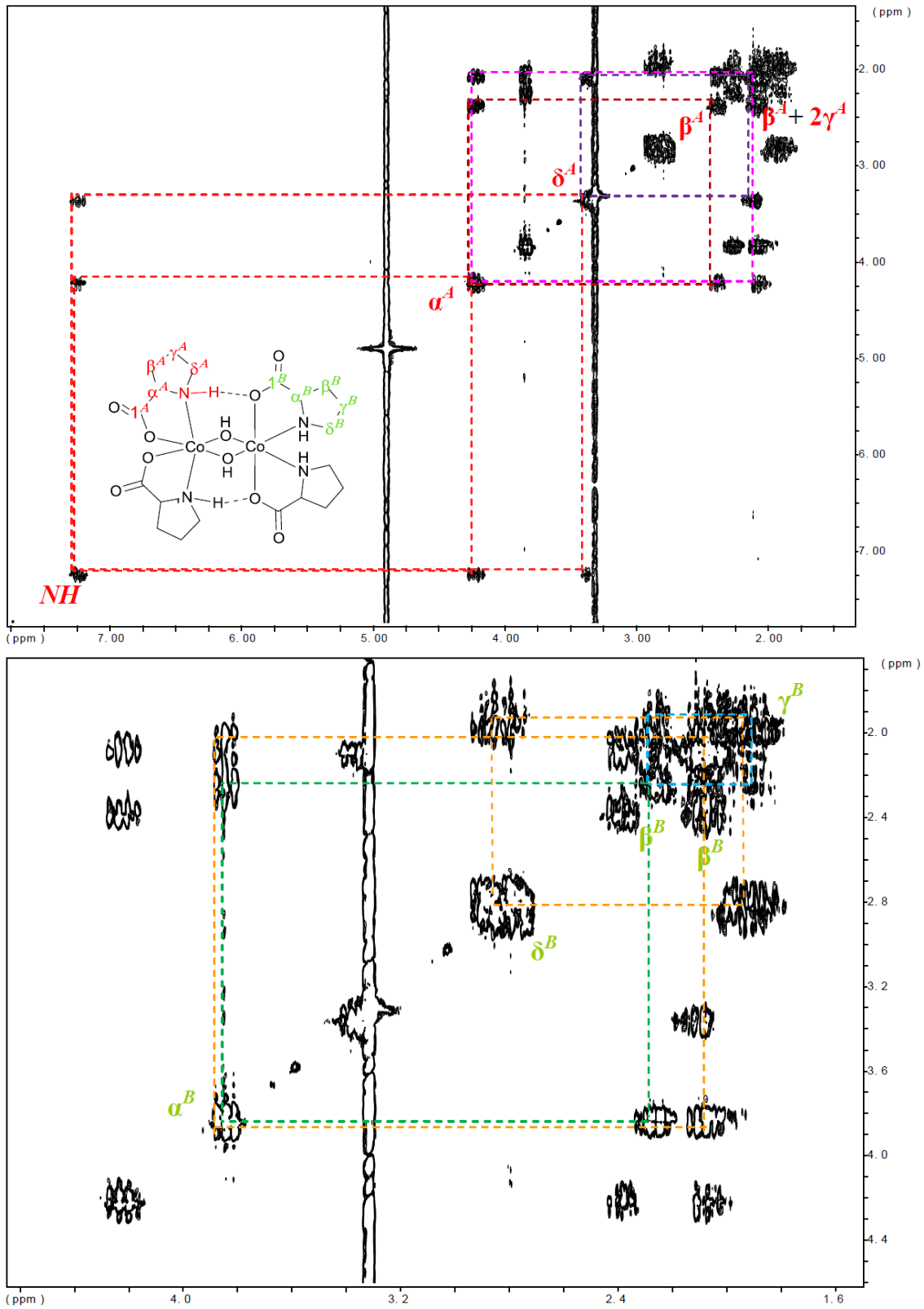


Figure S1. Connectivity of the resonances in HH-COSY spectra of **1** in CD_3OD.

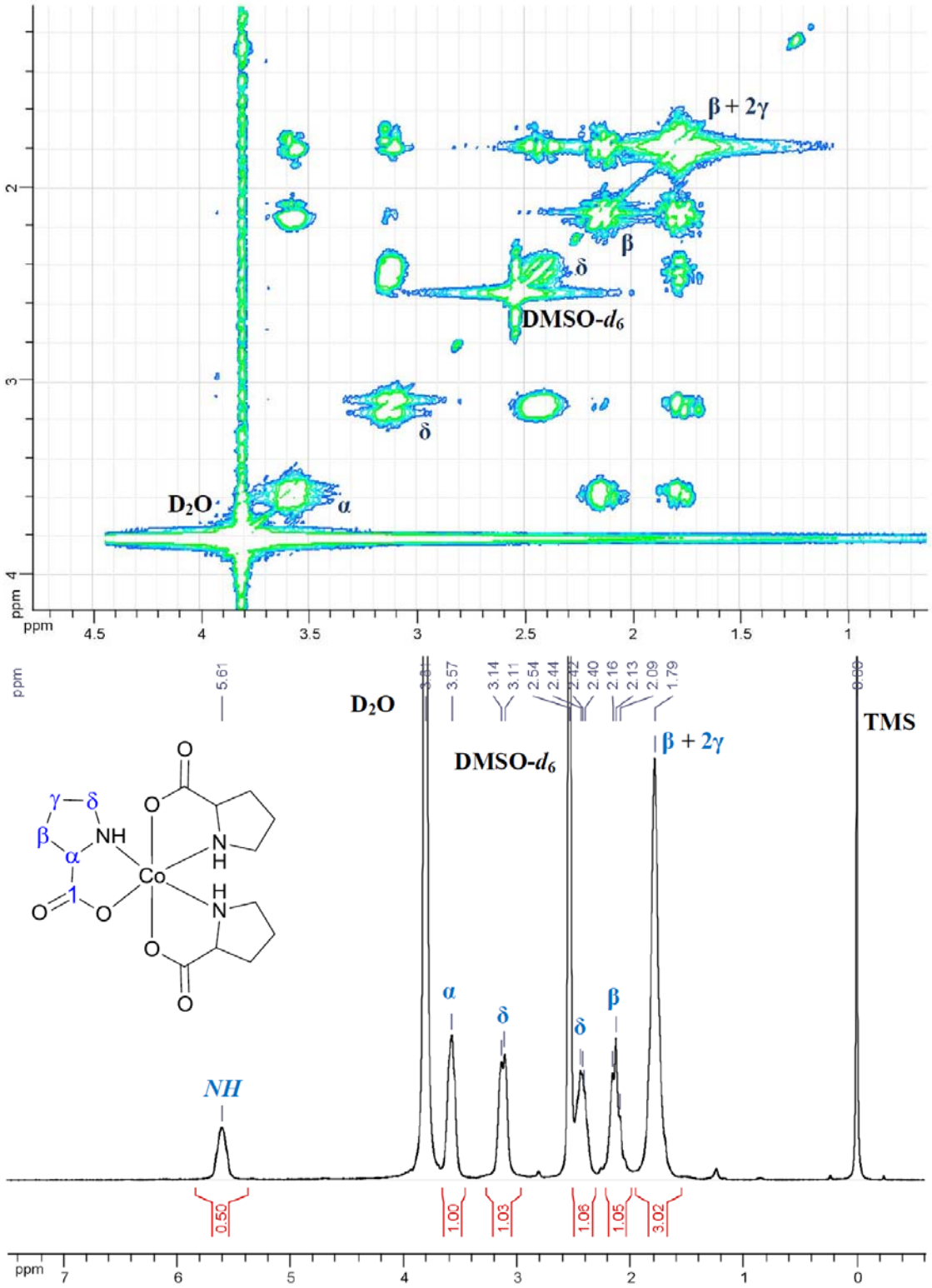


Figure S2. HH-COSY and ^{1}H-NMR spectra of **2** solution in mixture of dimethylsulfoxide-d_6 (80 %) and deuterium oxide (20% by volume).

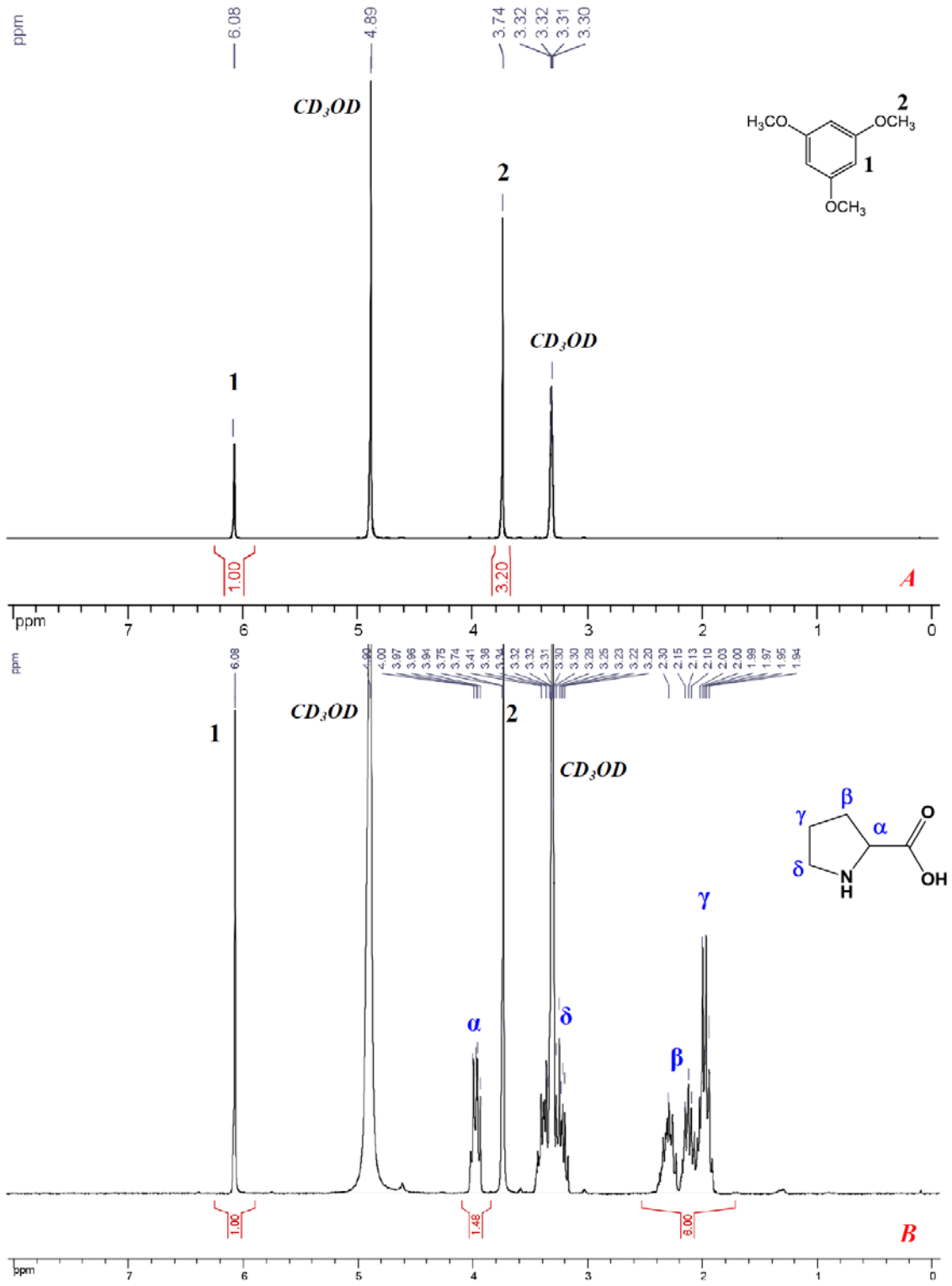


Figure S3. ^{1}H-NMR spectra in methanol-d_4:

A). solution of TMB (0.0094 mol·L^{-1});

B). solution of TMB (0.0094 mol·L^{-1}) and S-proline (0.0425 mol·L^{-1}).

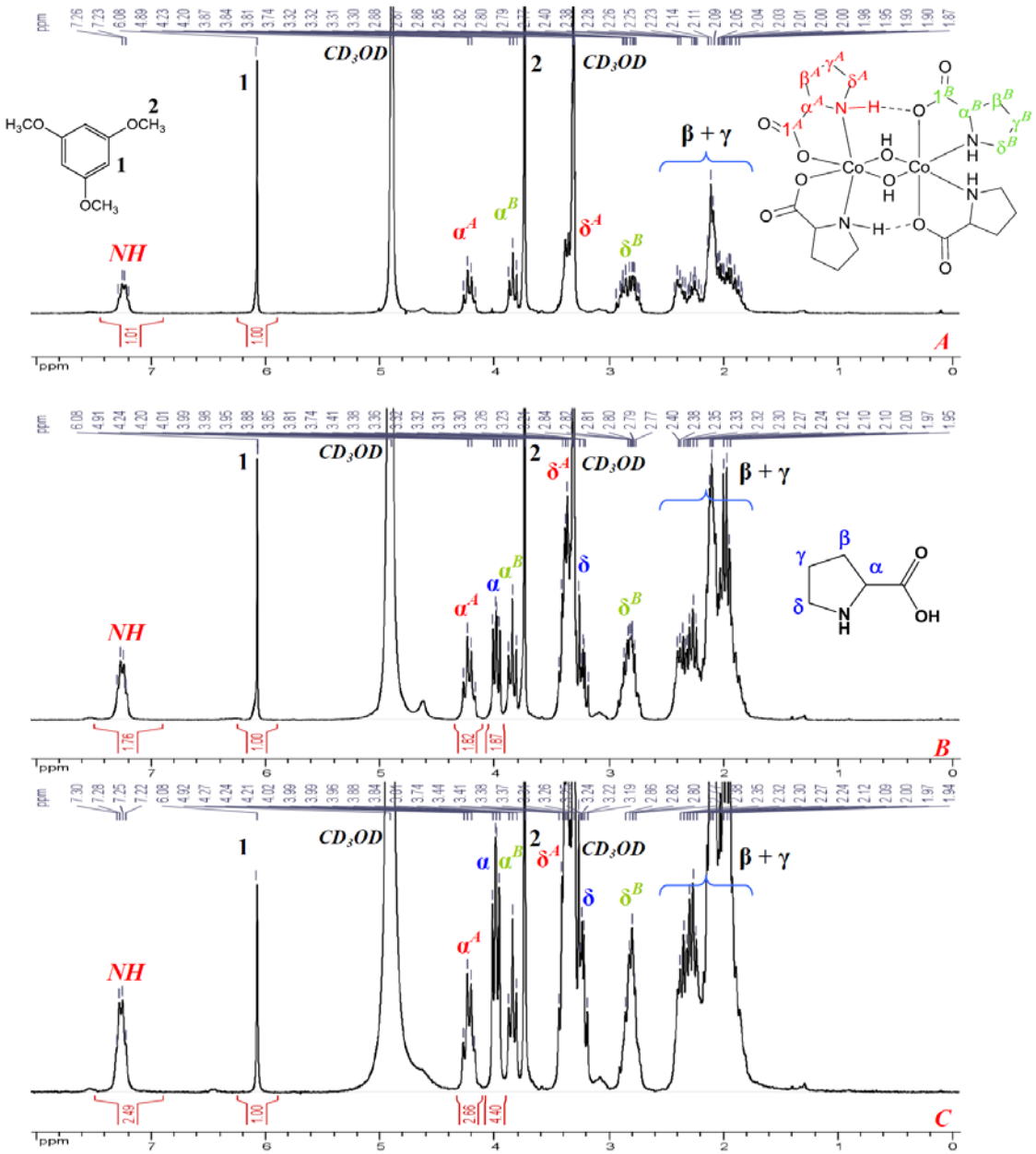


Figure S4. ^{1}H-NMR spectra in methanol-d_4:

A). solution of TMB (0.0094 mol·L^{-1})
and $Co_2(\mu\text{-}OH)_2(S\text{-}prol)_4$ (0.0140 mol·L^{-1}) – saturated at ambient temperature;

B). solution of TMB (0.0094 mol·L^{-1}), S-proline (0.0529 mol·L^{-1})
and $Co_2(\mu\text{-}OH)_2(S\text{-}prol)_4$ (0.0254 mol·L^{-1});

C). solution of TMB (0.0094 mol·L^{-1}), S-proline (0.1247 mol·L^{-1})
and $Co_2(\mu\text{-}OH)_2(S\text{-}prol)_4$ (0.0365 mol·L^{-1}).

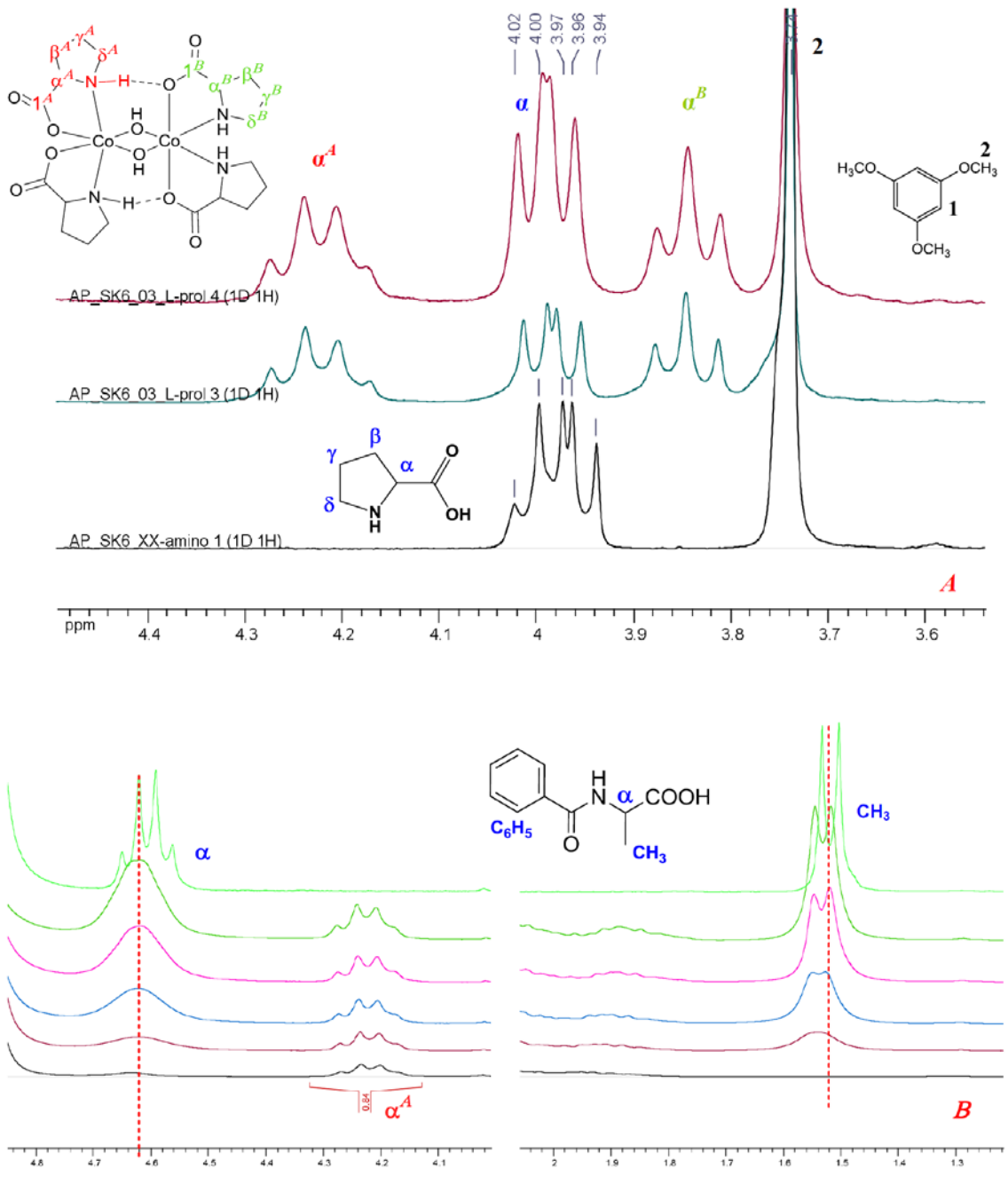


Figure S5. Representative parts of ^{1}H NMR spectra showing: A) changes in peaks of S-proline under increasing concentration of **1**; B) changes of the ^{1}H NMR spectra under increasing concentration of N-benzoyl-S-alanine (the spectrum on the top corresponds to pure N-benzoyl-S-alanine).

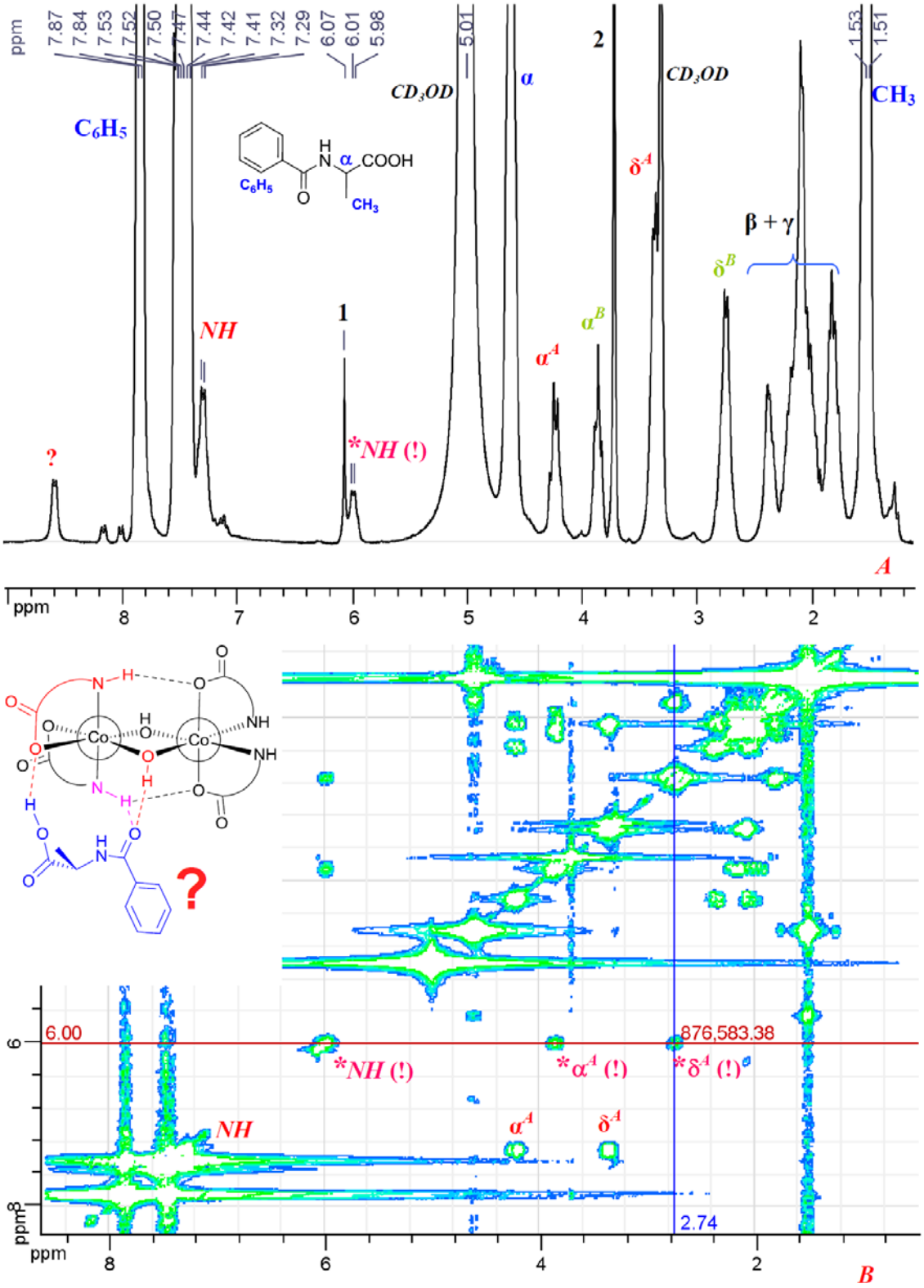


Figure S6. ^{1}H-NMR (A) and HH-COSY (B) spectra showing appearance of additional peaks (presumably belonging to new dinuclear cobalt(III) species); estimated concentrations of the components: c(TMB) = 0.0094 mol·L^{-1}; c(**1**) = 0.07 mol·L^{-1}; c(N-benzoyl-S-alanine) = 0.7 mol·L^{-1}. Inset shows the model of possible interactions.

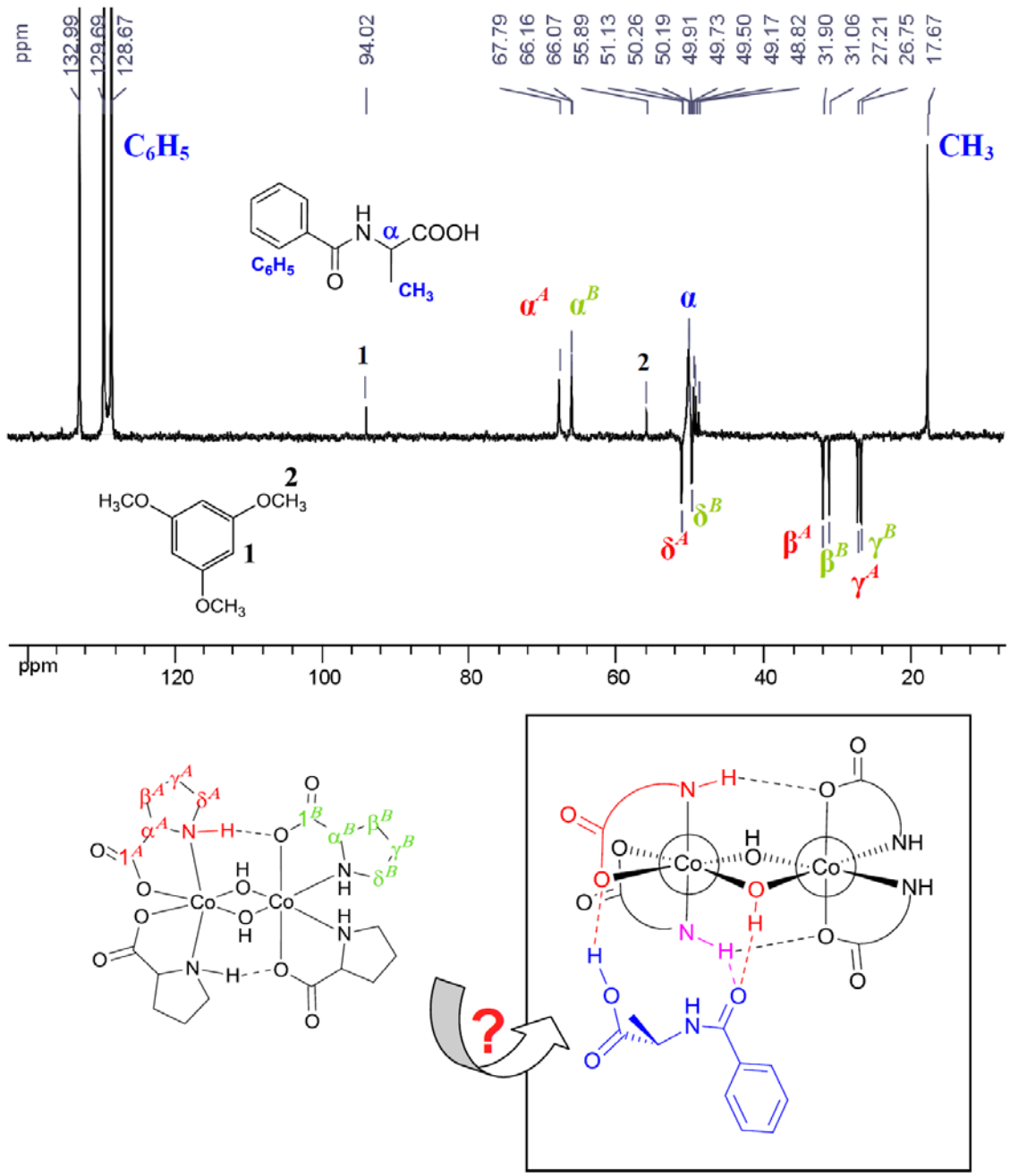


Figure S7. DEPT 135 spectrum, estimated concentrations of the components: c(TMB) = 0.0094 mol·L^{-1}; c(**1**) = 0.07 mol·L^{-1}; c(N-benzoyl-S-alanine) = 0.7 mol·L^{-1}). Inset shows the model of possible interactions.

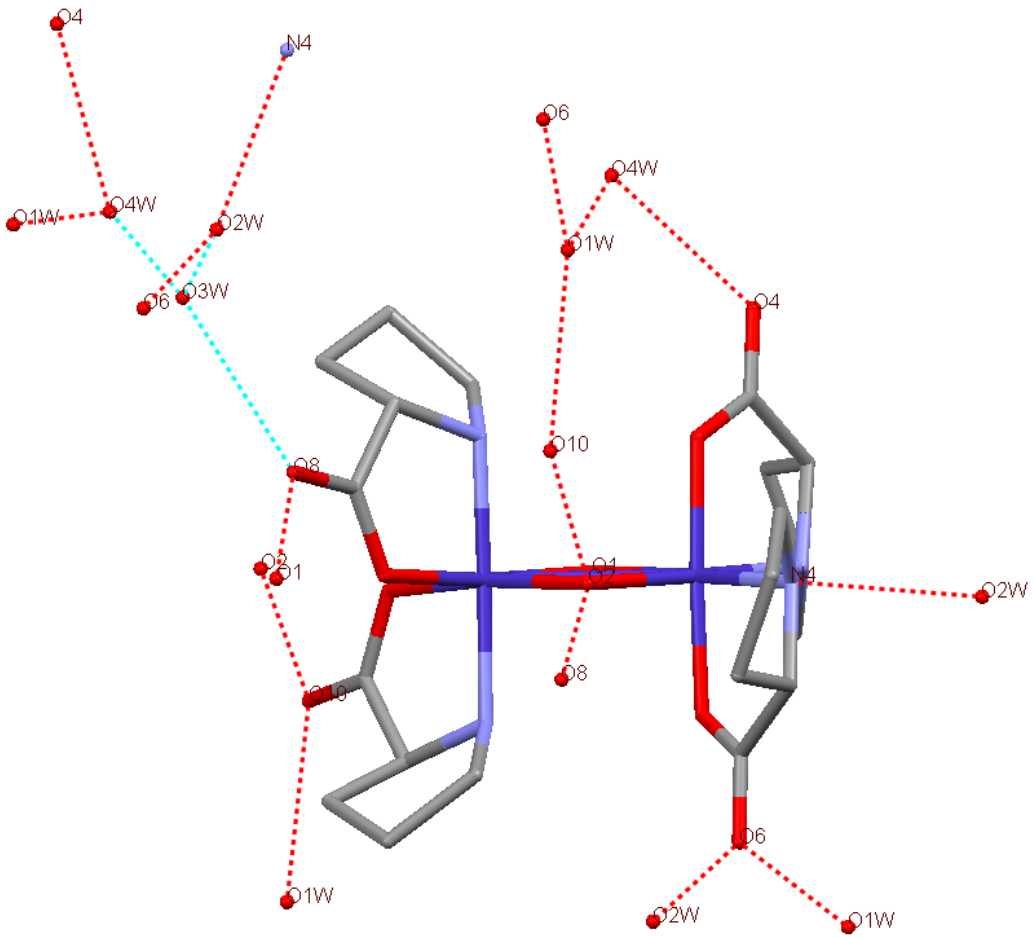


Figure S8. H-bonds in crystal structure of $Co_2(\mu\text{-}OH)_2(S\text{-}Pro)_4$ (**1·4H$_2$O**).