Supporting Information for

A Triple-Stranded Helicate and Mesocate from the Same Metal and Ligand

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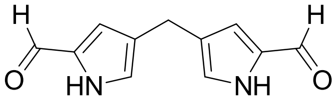
I Experimental Details

General

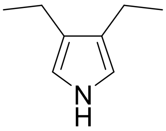
All commercially available chemicals and solvents were purchased from Aldrich, Fisher and other commercial suppliers and used without further purification. TLC analyses were performed on commercial aluminum plates pre-coated with silica gel. Column chromatography was carried out using silica gel (particle size: 0.040-0.063 mm, 230-400 mesh). The mass spectrum and high-resolution mass spectrum (HRMS) of the ligand were taken on a Kratos MS50 (EI). The mass spectra of the metal complexes were taken using MALDI-TOF in the presence of DCTB as matrix on the Bruker Biflex IV. ^{1}HNMR and ^{13}CNMR spectra were recorded with Bruker 300 spectrometers and chemical shifts are reported in ppm using the residual non-deuterated solvent as reference standard (CD_3OD: ^{1}H 3.31 ppm; CD_2Cl_2: ^{1}H 5.32 ppm, ^{13}C 54.00 ppm). X-ray crystallographic analyses were carried out on a Bruker X8 APEX diffractometer with graphite monochromated Mo-K radiation. Data were collected and integrated using the Bruker SAINT software package.[S3] The structures were solved by direct methods.[S5] All refinements were performed using the SHELXTL[S13] crystallographic software package of Bruker-AXS.

4,4'-methylenebis(1H-pyrrole-2-carbaldehyde) (1)



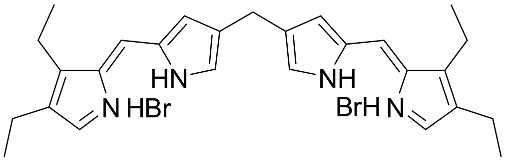
1 was prepared following the procedure reported recently.[S1]

3,4-diethyl pyrrole (2)



2 was prepared according to reported procedure. [S2]

bis(5-((3,4-diethyl-2H-pyrrol-2-ylidene)methyl)-1H-pyrrol-3-yl)methane dihydrobromide (LH_2•2HBr) (3)



To a 2mL THF solution of **1** (0.20g) was added 2.2 eq. of **2** (0.27g). After the mixture was subsequently cooled to -50 °C under argon, HBr (0.25 mL, 33% in acetic acid) was added dropwise and the reaction mixture was stirred at -50 °C for 20 min. before 50mL diethyl ether was added to precipitate the product. The dark red **3** was collected by filtration.

Yield: 94%. ^{1}H NMR* (300 MHz, CD_3OD, 25 °C) δ = 8.02 (s, 2H; CH), 7.88 (s, 2H; CH), 7.85 (s, 2H; CH), 7.77 (s, 2H; CH), 4.00 (s, 2H; *meso*-CH_2), 2.86-2.78 (q, J = 7.6 Hz, 4H; CH_2), 2.61-2.54 (q, J = 7.6 Hz, 4H; CH_2), 1.28-1.21 (m, 12H; CH_3). MS (EI) m/z 412 ($[M - 2HBr]^+$). HRMS (EI, $[M - 2HBr]^+$) Calcd for $C_{27}H_{32}N_4$: 412.2627. Found: 412.2626.

* The lifetime of **3** in solution is not long enough to allow the taking of a ^{13}C NMR spectrum of **3**, although **3** is stable in solid state.

Co_2L_3 (4)

Newly-made **3** from the last step and Co[$(Py)_4Cl_2$]Cl (0.32g, 1eq.) were quickly dissolved in a 50mL solution of $CHCl_3$ and MeOH (1 : 1, v : v). The solution was then added rapidly to a refluxing mixture of $CHCl_3$ and MeOH (1 : 1, v : v), followed by addition of 2 drops of triethylamine. The reaction mixture was stirred under reflux for another 10 min. before the removal of solvents under reduced pressure. Using CH_2Cl_2 as eluant, the mixture was passed through a short column which was filled with silica gel and the red fractions were collected. Subsequently, chromatography was performed on a 1 meter long silica column using CH_2Cl_2 / hexanes (1 : 1, v : v) as eluant. After the removal of solvents, **4** and **5** were obtained as red powders from the first and second fraction, respectively.

Yield: 26%. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C) δ = 7.17 (s, 6H; CH), 6.80 (s, 6H; CH), 5.69 (br s, 6H; CH), 3.51 (s, 6H; *meso*-CH_2), 2.69-2.51 (m,, 12H; CH_2), 2.21-2.38 (m, 12H; CH_2), 1.14 (t, *J* = 7.7 Hz, 18H; CH_3), 0.93 (t, *J* = 7.5 Hz, 18H; CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C) δ = 152.0, 150.0, 145.5, 134.3, 133.8, 133.3, 133.2, 129.4, 127.3, 30.3, 18.9, 18.5, 17.7, 15.0. MS (MALDI-TOF) *m/z* 1348.7 (M^+).

Co_2L_3 (5)

Yield: 16%. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C) δ = 7.17 (s, 6H; CH), 6.83 (s, 6H; CH), 5.76 (s, 6H; CH), 5.68 (s, 6H; CH), 3.36 (d, *J* = 13.9 Hz, 3H; *meso*-CH), 3.25 (d, *J* = 13.9 Hz, 3H; *meso*-CH), 2.61 (m, 12H; CH_2), 2.28 (m, 12H; CH_2), 1.14 (t, *J* = 7.3 Hz, 18H; CH_3), 0.94 (t, *J* = 7.5 Hz, 18H; CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C) δ = 152.4, 150.0, 145.6, 135.8, 134.6, 134.2, 134.1, 127.9, 127.3, 30.3, 18.9, 18.5, 17.7, 15.0. MS (MALDI-TOF) *m/z* 1348.8 (M^+).

Fe_2L_3 (6)

6 and **7** were prepared following the procedure of **4** and **5**, except $FeCl_3$ (0.11g) was added instead of Co[$(Py)_4Cl_2$]Cl. **6** was obtained as dark red powder from the first fraction and **7** from the second fraction.

Yield: 13%. ^{1}H NMR** (300 MHz, CD_2Cl_2) δ = 20.18 (s), 16.66 (s), 11.86 (s), 9.63 (s), 9.25 (s), 7.19 (s), -6.81 (s), -25.09 (br s), -26.51 (br s). MS (MALDI-TOF) *m/z* 1342.6 (M^+).
** The spectrum shows broad peaks due to the paramagnetism of Fe^{3+}.

Fe_2L_3 (7)

Yield: 9%. ^{1}H NMR** (300 MHz, CD_2Cl_2) δ = 19.89 (s), 12.13 (s), 10.16 (s), 9.53 (s), 9.32 (s), 7.46 (s), 5.36, -6.98 (s), -23.93 (br s), -24.73 (br s). MS (MALDI-TOF) *m/z* 1342.7 (M^+).
** The spectrum shows broad peaks due to the paramagnetism of Fe^{3+}.

Ⅱ NMR Spectra

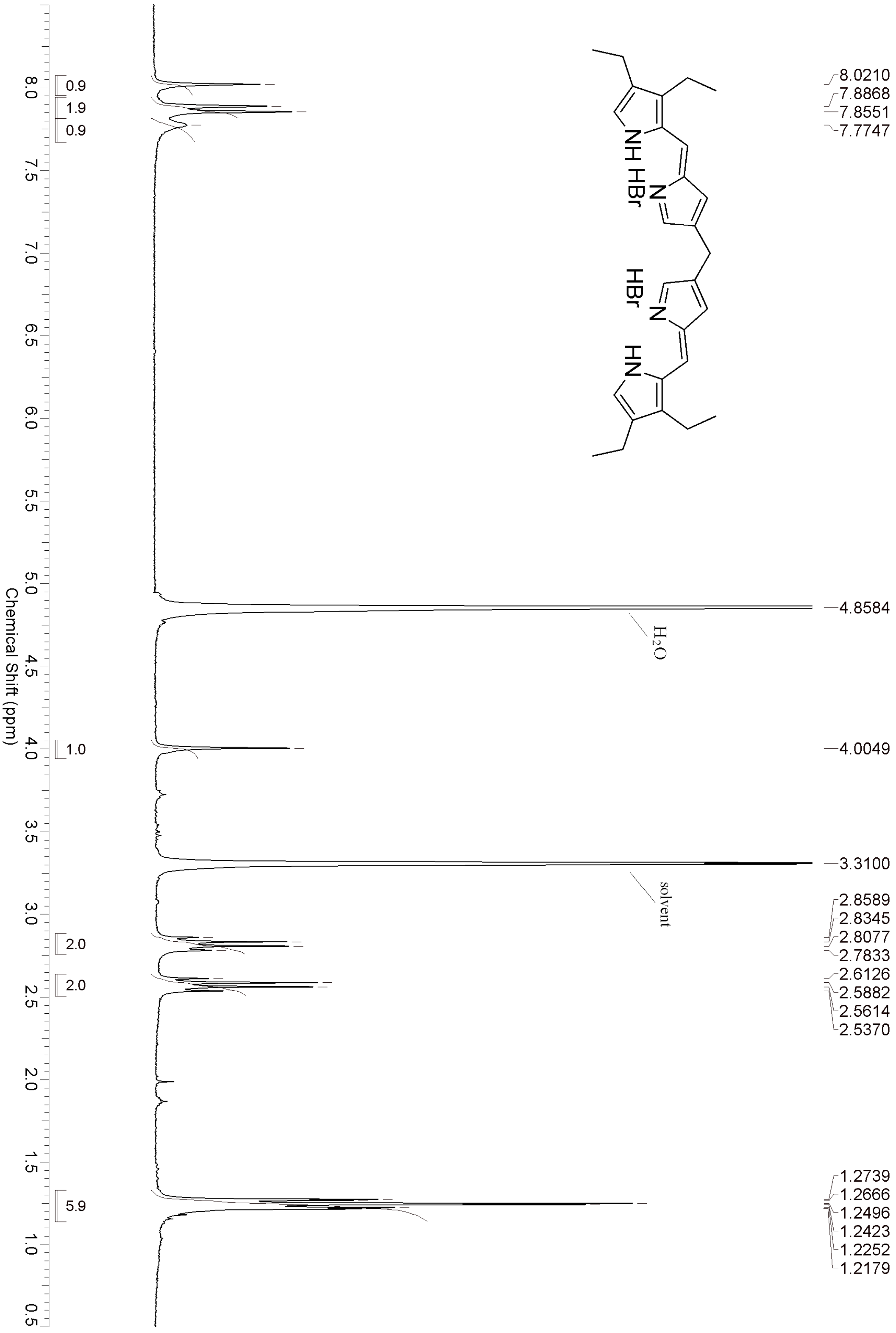


Figure S1. ^{1}H NMR spectrum of **3** in CD_3OD.

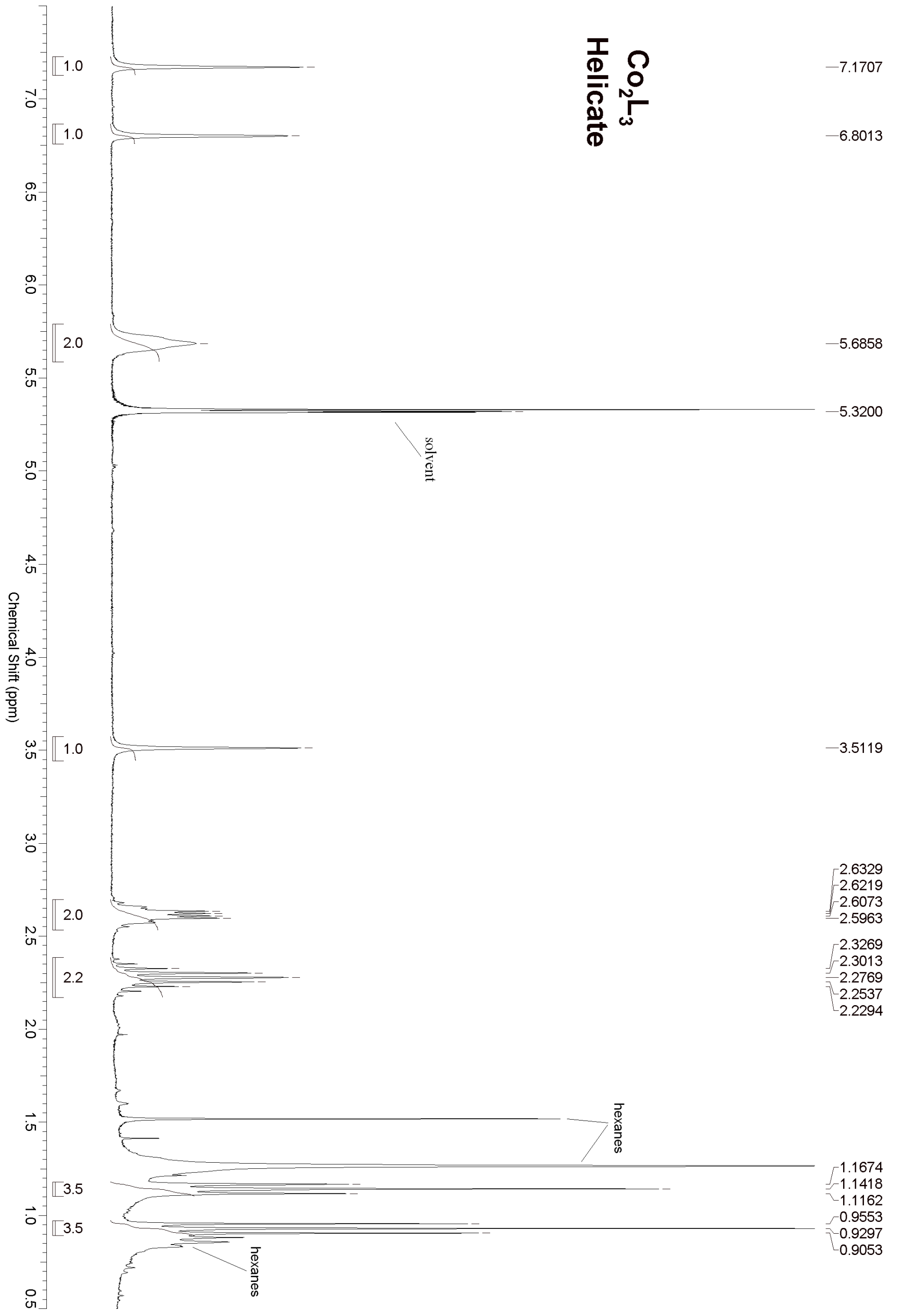


Figure S2. ^{1}H NMR spectrum of **4** in CD_2Cl_2.

Note: Hexanes in the sample was introduced during column chromatography. Heating or pumping cannot remove them. The calculation of yields, however, was done before introducing hexanes and separating the helicates and mesocates.

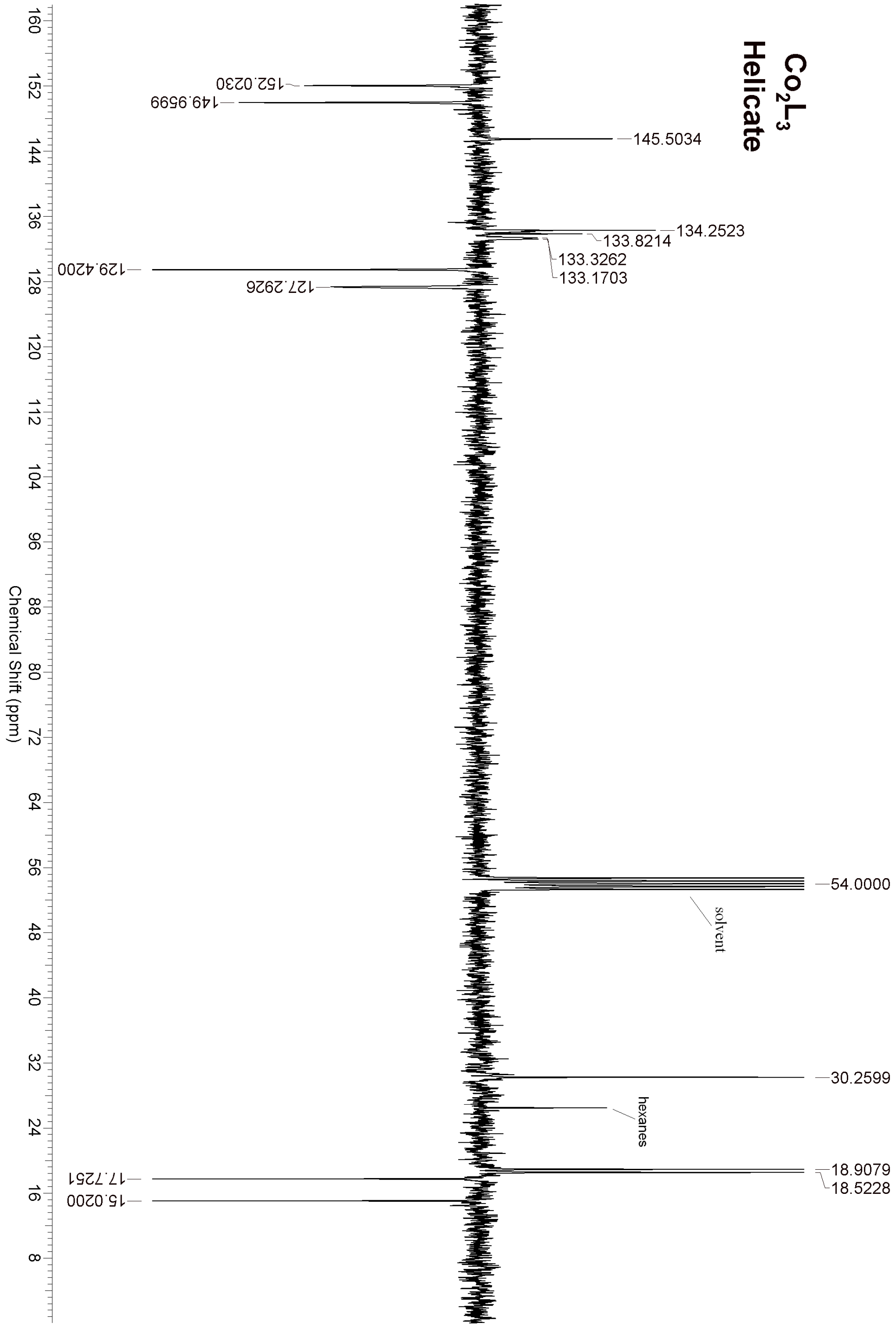


Figure S3. ^{13}C NMR spectrum of **4** in CD_2Cl_2.

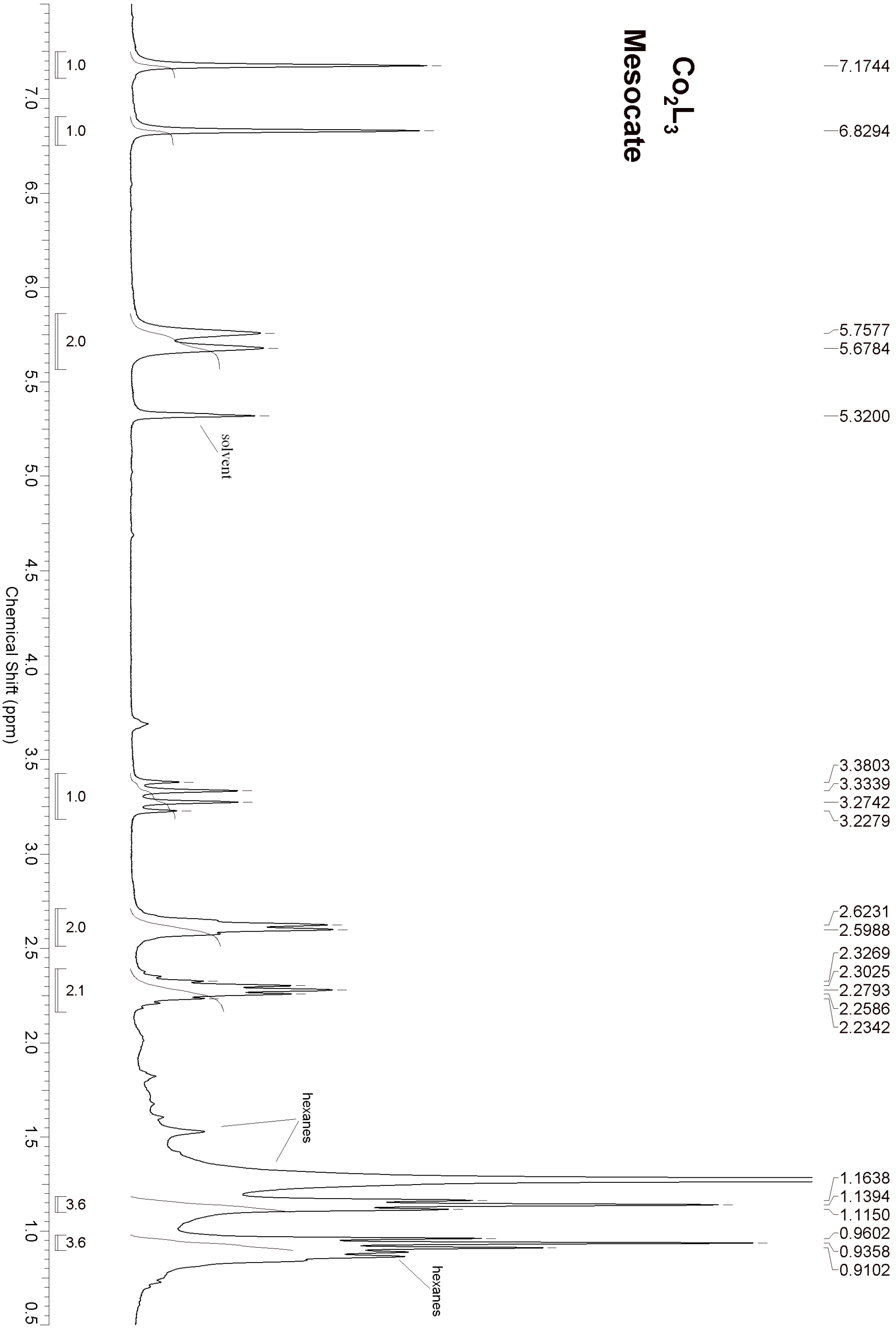


Figure S4. ^{1}H NMR spectrum of **5** in CD_2Cl_2.

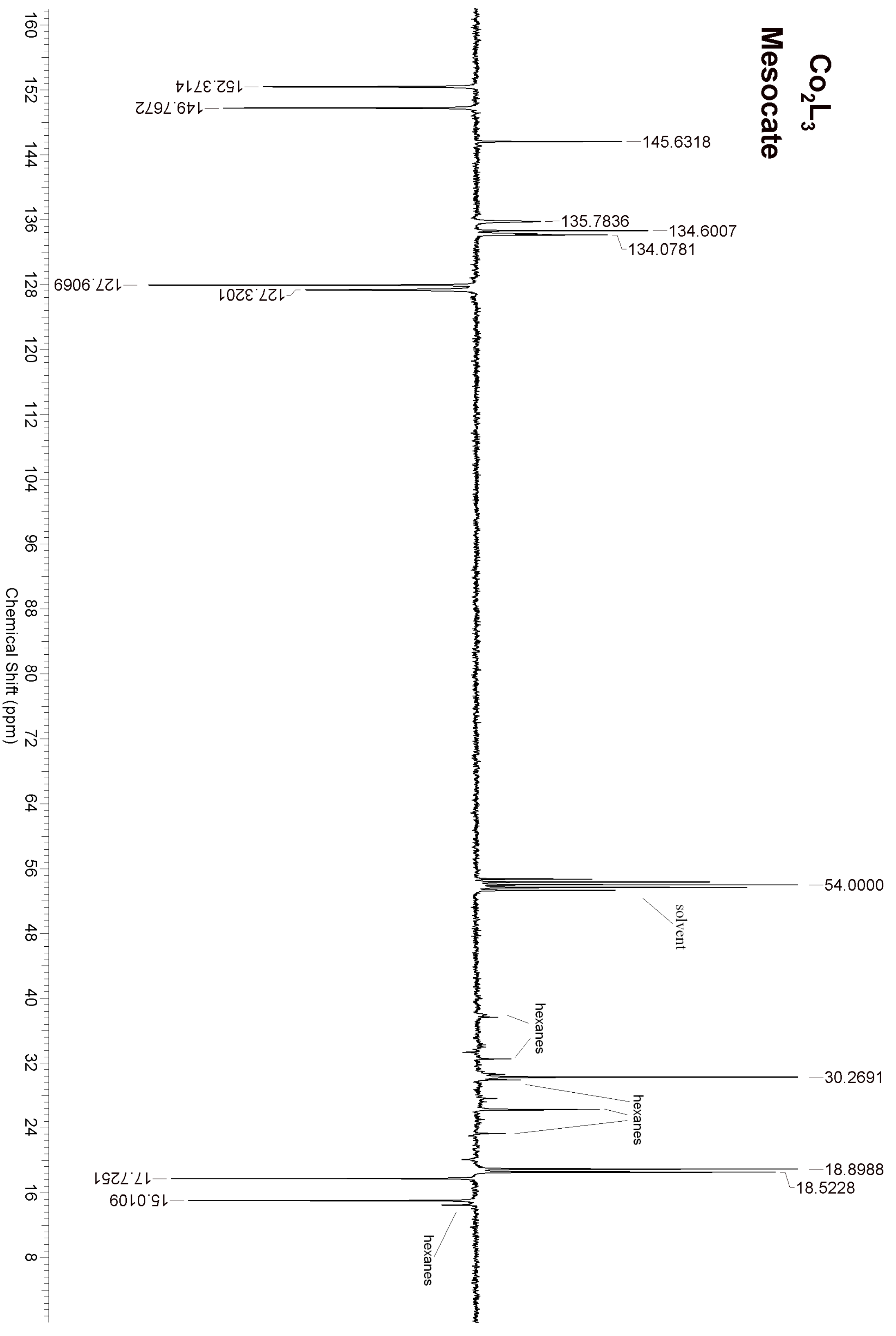


Figure S5. ^{13}C NMR spectrum of **5** in CD_2Cl_2.

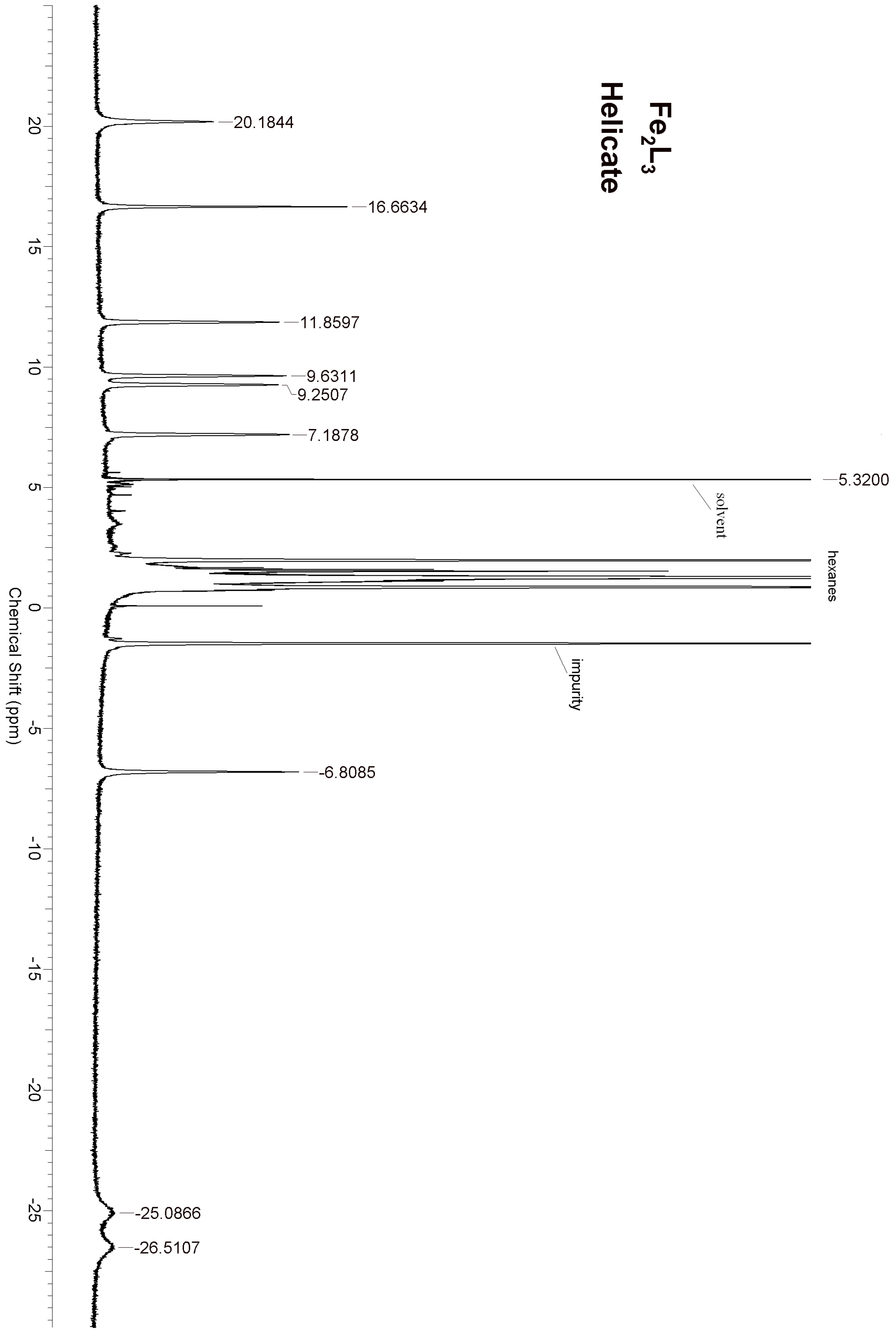


Figure S6. ^{1}H NMR spectrum of **6** in CD_2Cl_2.

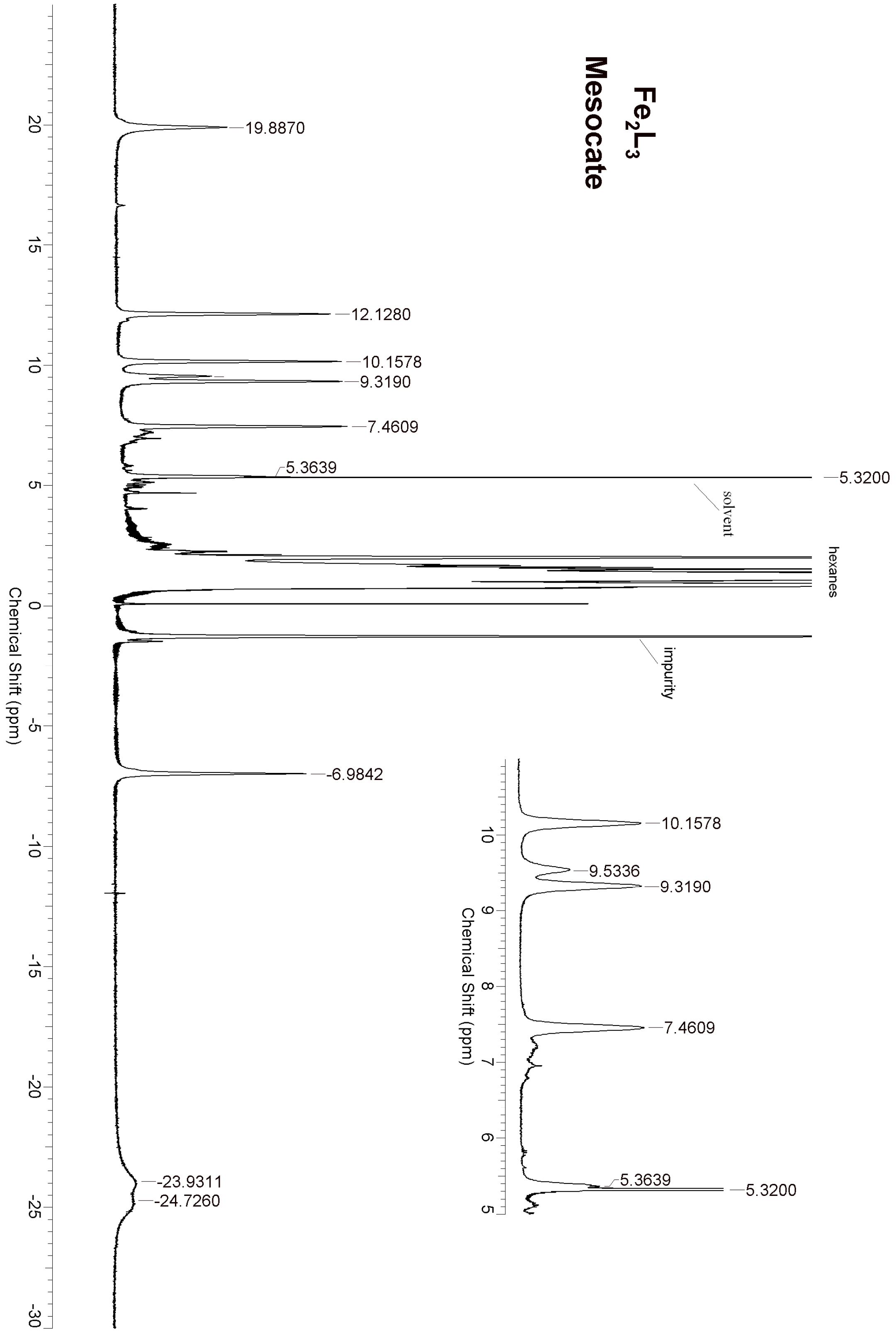


Figure S7. ^{1}H NMR spectrum of **7** in CD_2Cl_2.

Ⅲ Crystallographic Data

Single crystals of **4-7** suitable for X-ray crystallography were grown by vapor diffusion of hexane into a CH_2Cl_2 solution.

Crystallographic data of 4

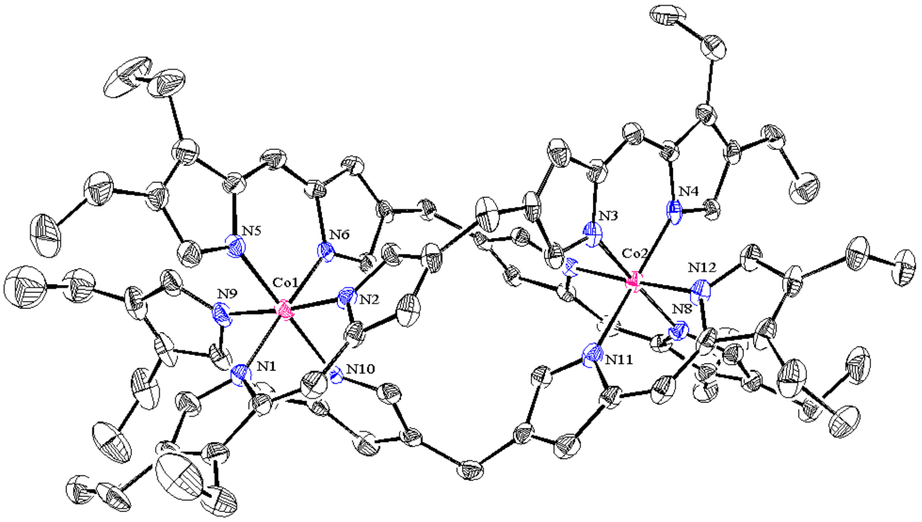


Figure S8. ORTEP structure of **4**.

A red needle crystal of $C_{84}H_{96}Cl_6N_{12}Co_2$ having approximate dimensions 0.10 × 0.12 × 0.50 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of -100.0 ± 0.1°C to a maximum 2θ value of 56.0°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 60.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Of the 44178 reflections that were collected, 12657 were unique (R_{int} = 0.0480); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT[S3] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 6.47 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS[S4]), with minimum and maximum transmission coefficients of 0.867 and 0.937, respectively. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods.[S5] Three molecules of CH_2Cl_2 were located and modeled, however there was residual electron density that could not be resolved. As a result the PLATON/SQUEEZE[S6] program was used to generate a data set free of any solvent in the region of the remaining electron density. The output from SQUEEZE generates a completely merged (i.e., only unique) dataset, and thus the Rint value will be zero. The post-SQUEEZE Rint(=0.00) has been exchanged for the original Rint (pre-SQUEEZE =0.048) to give the reader some feel for the quality of the data. By leaving the Rint=0.00, the reader has no idea whether the agreement for the original dataset was good (i.e. 3%) or bad (30%). The disordered ethyl groups and solvent methylene chloride molecules were modelled using DFIX and SADI commands in order to maintain similar bond lengths and angles. Unrestrained anisotropic refinements resulted in numerous NPD atoms, thus the ISOR command was used to ensure approximate isotropic behaviour of all atoms. The EADP and EXYZ commands were used when refining disordered solvent molecules where only the chloride atoms were in different orientations and the central carbon was common to both fragments. SQUEEZE was employed to resolve any unmodelled lattice solvent. The formula (and any values subsequently derived from it) no longer takes into account any unmodelled solvent. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions but were not refined. The final cycle of full-matrix least-squares refinement[S7] on F^2 was based on 12657 reflections and 993 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors ($R1 = 0.0651$ ($I > 2\sigma(I)$) and $wR2 = 0.1966$ (all data)).

The standard deviation of an observation of unit weight[S8] was 1.085. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.520 and -0.736 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[S9]. Anomalous dispersion effects were included in Fcalc[S10]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[S11]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[S12]. All refinements were performed using the SHELXTL[S13] crystallographic software package of Bruker-AXS.

Crystallographic data of 5

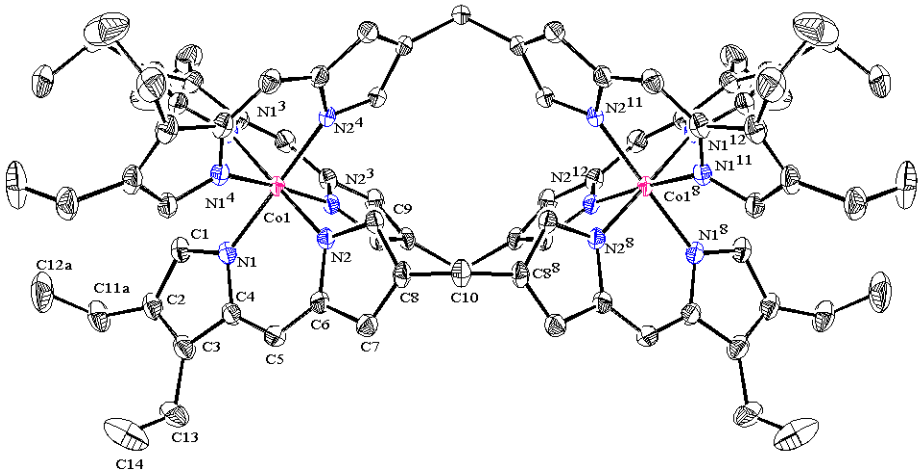


Figure S9. ORTEP structure of **5**; 3 = -y, x-y, z; 4 = -x+y, -x, z; 8 = x, y, -z+1/2; 11 = -x+y, -x, -z+1/2;12 = -y, x-y, =z+1/2

A red prism crystal of $C_{81}H_{90}N_{12}Co_2$ having approximate dimensions 0.12 × 0.27 × 0.54 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of -100.0 ± 0.1ºC to a maximum 2θ value of 55.6º. Data were collected in a series of ϕ and ω scans in 0.50º oscillations with 10.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Of the 45184 reflections that were collected, 3875 were unique ($R_{int} = 0.0315$); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT[S3] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 3.87 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS[S4]), with minimum and maximum transmission coefficients of 0.864 and 0.955, respectively. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods.[S5]All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions but were not refined. The material crystallizes with the unique one-6th of the molecule residing on a 6_3 screw-axis. Additionally, one ethyl substituent is disordered and was modeled in two orientations. The SADI command was used to ensure similar bond distances in the disordered ethyl group. SQUEEZE was employed to resolve any unmodelled lattice solvent. The formula (and any values subsequently derived from it) no longer takes into account any unmodelled solvent. As a result the PLATON/SQUEEZE[S6] program was used to generate a 'solvent-free' data set. The final cycle of full-matrix least-squares refinement[S7] on F^2 was based on 3875 reflections and 158 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors ($R1 = 0.0332$ ($I > 2\sigma(I)$) and $wR2 = 0.0906$ (all data)).

The standard deviation of an observation of unit weight[S8] was 1.087. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.319 and -0.234 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[S9]. Anomalous dispersion effects were included in Fcalc[S10]; the values for Δf' and Δf" were those of Creagh and McAuley[S11]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[S12]. All refinements were performed using the SHELXTL[S13] crystallographic software package of Bruker-AXS.

Crystallographic data of 6

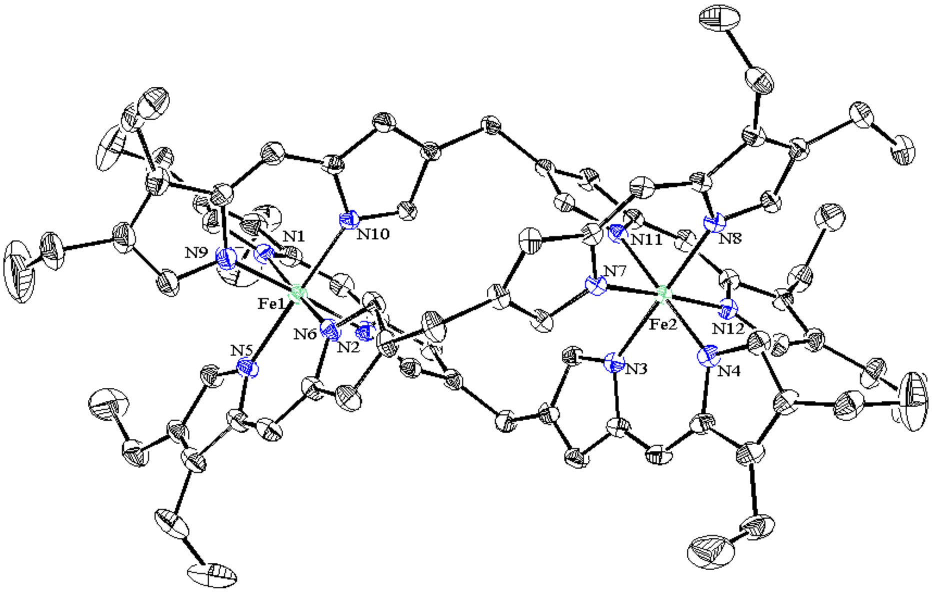


Figure S10. ORTEP structure of **6**.

A black columnar crystal of $C_{84}H_{96.5}Cl_{6.5}N_{12}Fe_2$ having approximate dimensions 0.20 × 0.25 × 0.50 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of -100.0 ± 0.1°C to a maximum 2θ value of 56.2°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 10.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Of the 81561 reflections that were collected, 19584 were unique ($R_{int} = 0.0356$); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT[S3] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 6.10 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS[S4]), with minimum and maximum transmission coefficients of 0.638 and 0.884, respectively. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods.[S5] The disordered ethyl groups were modelled using DFIX and SADI commands in order to maintain similar bond lengths and angles. Unrestrained anisotropic refinements resulted in numerous NPD atoms, thus the ISOR command was used to ensure approximate isotropic behaviour of all atoms. The disordered methylene chloride containing C82 was 'split' such that C82A and C82B occupied the same space with the same anisotropic displacement parameters (EXYZ and EADP commands). The material also crystallizes with methylene chloride in the lattice. There are three solvent molecules free in the asymmetric unit, including one that is disordered in two orientations and were refined using the SADI command to maintain similar C-Cl distances for each fragment. All non-hydrogen atoms except C75B and C85 were refined anisotropically. All hydrogen atoms were placed in calculated positions but were not refined. The final cycle of full-matrix least-squares refinement[S7] on F^2 was based on 19584 reflections and 1020 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors ($R1 = 0.0545$ ($I > 2\sigma(I)$) and $wR2 = 0.1570$ (all data)).

The standard deviation of an observation of unit weight[S8] was 1.044. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.978 and -1.247 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[S9]. Anomalous dispersion effects were included in Fcalc[S10]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[S11]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[S12]. All refinements were performed using the SHELXTL[S13] crystallographic software package of Bruker-AXS.

Crystallographic data of 7

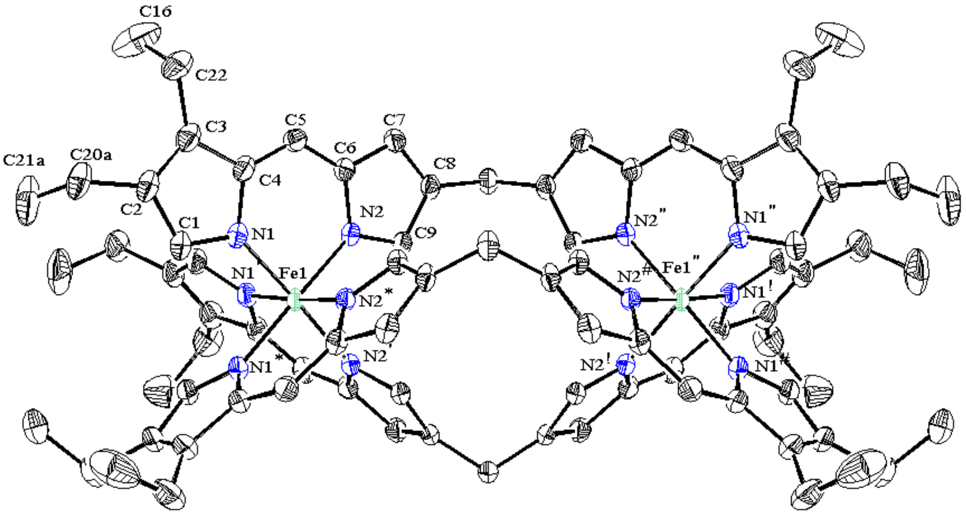


Figure S11. ORTEP structure of **7**; ' = -x+y, -x, z; * = -y, x-y, z ; " = x, y, -z+½; # = -y, x-y, -z+½; ! = -x+y, -x, -z+½.

A black prism crystal of $C_{81}H_{90}N_{12}Fe_2$ having approximate dimensions 0.20 × 0.44 × 0.54 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of -100.0 ± 0.1°C to a maximum 2θ value of 55.4°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 5.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Of the 60586 reflections that were collected, 3788 were unique (R_{int} = 0.0505); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT[S3] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 5.16 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS[S4]), with minimum and maximum transmission coefficients of 0.745 and 0.902, respectively. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods.[S5] The material crystallizes with 1/6th of the molecule in the asymmetric unit. The remainder of the molecule is made up of fragments related by symmetry. Additionally, the crystal forms with solvent in the lattice. The SADI command was used to ensure similar bond distances in the disordered ethyl group. SQUEEZE was employed to resolve any unmodelled lattice solvent. The formula (and any values subsequently derived from it) no longer takes into account any unmodelled solvent. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions but were not refined. The final cycle of full-matrix least-squares refinement[S7] on F^2 was based on 3788 reflections and 157 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors (R1 = 0. 0379 ($I > 2\sigma(I)$) and wR2 = 0.1148 (all data)).

The standard deviation of an observation of unit weight[S8] was 1.167. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.318 and -0.179 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[S9]. Anomalous dispersion effects were included in Fcalc[S10]; the values for Δf' and Δf" were those of Creagh and McAuley[S11]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[S12]. All refinements were performed using the SHELXTL[S13] crystallographic software package of Bruker-AXS.

Table S1. Crystallographic Data of **4**-**7**.

	4	**5**	**6**	**7**
Formula	$C_{84}H_{96}Cl_6N_{12}Co_2$	$C_{81}H_{90}N_{12}Co_2$	$C_{84}H_{96.5}Cl_{6.5}N_{12}Fe_2$	$C_{81}H_{90}N_{12}Fe_2$
Formula weight	1604.29	1349.51	1616.36	1343.35
cryst. syst.	triclinic	trigonal	triclinic	trigonal
Space group	*P*-1 (# 2)	*P* 6$_3$/*m* (#176)	*P*-1 (# 2)	*P* 6$_3$/*m* (# 176)
a/Å	13.7050(9)	15.0431(8)	13.3137(10)	15.0249(11)
b/Å	17.5163(9)	15.0431(8)	17.3134(14)	15.0249(11)
c/Å	17.8828(11)	24.400(2)	18.8476(15)	24.422(2)
α/deg	81.878(3)	90.0	88.243(4)	90.0
β/deg	76.930(3)	90.0	72.590(4)	90.0
γ/deg	83.402(3)	120.0	80.864(4)	120.0
$V/Å^3$	4124.5(4)	4781.8(6)	4092.2(6)	4774.6(6)
Z	2	2	2	2
D_c/g cm^{-3}	1.292	0.937	1.312	1.112
μ(MoKα) cm^{-1}	6.47	3.87	6.18	5.16

No. of obsd data (I>0.00σ(I))	12657	3875	19584	3788
Reflection / Parameter Ratio	12.75	24.53	19.20	24.13
$R1^{a}$; $wR2^{b}$ (all data)	0.0975; 0.1966	0.0408; 0.0906	0.0853; 0.1570	0.0517; 0.1148
GOF	1.085	1.087	1.044	1.167
No. of obsd data (I>2σ(I))	8912	3252	14380	3024
($R1$; $wR2$) [c]	(0.0651; 0.1821)	(0.0332; 0.0880)	(0.0545; 0.1338)	(0.0379; 0.1066)

[a] $R1 = \Sigma\omega||Fo|-|Fc|| / \Sigma\omega|Fo|$, [b] $wR2 = \sqrt{\Sigma^{1}} / \Sigma\omega(Fo^{2})^{2}$ [c] refined on F, $I>2\sigma(I)$

Ⅳ References

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S2 Milgram, B. C.; Eskildsen, K.; Richter, S. M.; Scheidt, W. R.; Scheidt, K. A., *J. Org. Chem.* **2007,** 72, 3941-3944.

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S6 **SQUEEZE.** Sluis, P.; Spek, A. L. *Acta Crystallogr., Sect A* **1990**, *46*, 194-201.

S7. Least Squares function minimized: $\Sigma w(F_o^2 - F_c^2)^2$

S8. Standard deviation of an observation of unit weight: $[\Sigma w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$
Where: N_o = number of observations, N_v = number of variables

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