Electronic Supplementary Material (ESI) for ChemComm.

Mimicking the Active Site of Aldehyde Dehydrogenases: Stabilization of Carbonyl Hydrates through Hydrogen Bonds

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Supporting Information

Contents

1. General information

All chemicals were purchased and used as received. NMR spectra were recorded on a 300 MHz spectrometer. Chemical shifts (δ) are reported in parts per million with tetramethylsilane as internal standard.

2. NMR experiments with NMO/chloral

Hydration equilibrium of chloral 1

Chloral **1** (22 mg, 0.15 mmol) was dissolved in 0.6 mL MeCN-d_3 (c = 0.25 M) followed by addition of either H_2O (2.7 mg, 0.15 mmol) or NMO·H_2O (20 mg, 0.15 mmol). NMR spectra were recorded immediately.

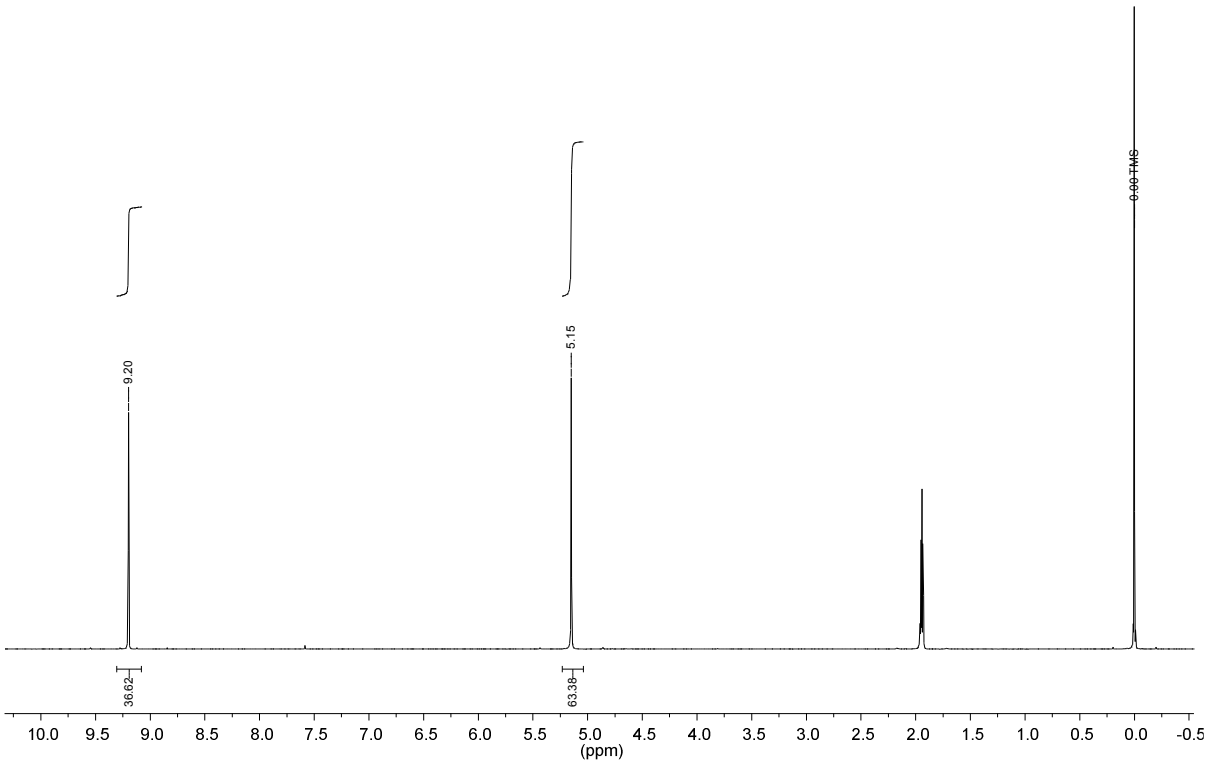

Figure S1. ^{1}H NMR spectrum of chloral **1** in presence of 1.0 equiv of H_2O in MeCN-d_3.

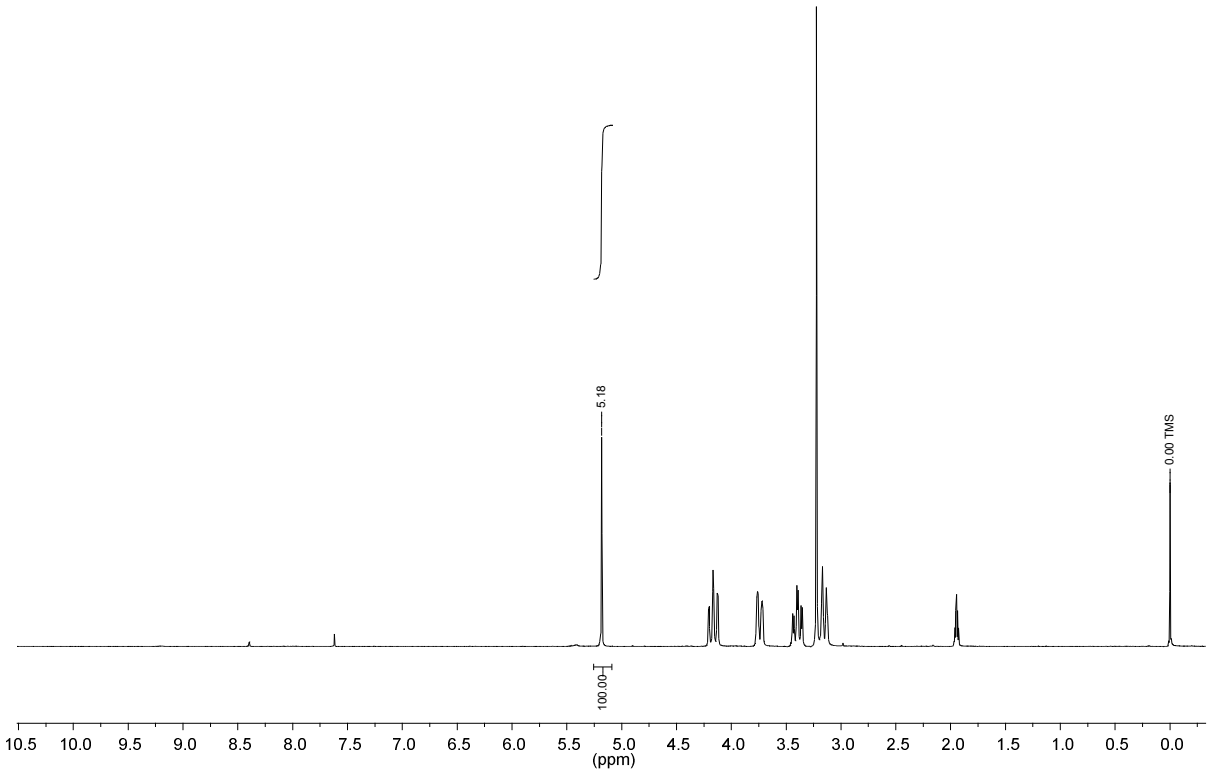

Figure S2. ^{1}H NMR spectrum of chloral **1** in presence of 1.0 equiv of NMO·H_2O in MeCN-d_3.

Job-Plot experiment of the NMO/chloral system

Stock solutions of anhydrous NMO (0.3 M in DMSO-d_6) and chloral hydrate **3** (0.3 M in DMSO-d_6) were prepared. Then, a series of ten NMR samples starting with 10% NMO and 90% chloral hydrate solution and ending with 100% NMO and 0% chloral hydrate solution (10% steps) was prepared and measured immediately.

Table S1. Data for the Job-Plot of the NMO/chloral system

χ_{NMO}	δ_{CH_3} [ppm]
0.1	3.289
0.2	3.292
0.3	3.296
0.4	3.297
0.5	3.311
0.6	3.252
0.7	3.225
0.8	3.159
0.9	3.104
1.0	3.051

3. Crystal structure of the NMO/chloral hydrate complex I (CCDC 1019891)

Preparation of crystals: Co-crystallization of NMO·H_2O and chloral hydrate was carried out by recrystallization of equimolar mixtures of both compounds (0.75 mmol each) from DCM (starting with 0.2 mL of the solvent). After cooling down the solution from 40 °C to room temperature, appropriate crystals formed almost immediately.

Data collection: A colorless crystal block with approximate dimensions 0.12 x 0.22 x 0.22 mm was selected under oil at ambient conditions and attached to the tip of a X-ray capillary. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a three-circle diffractometer BRUKER AXS SMART APEX (released: 2000) with Mo-K_α radiation (λ = 0.71073 Å) and CCD-detector APEX I. There were no detailed records of the data collection parameters especially for UNIT cell (# reflections, # scan width [°], # exposure time [sec]) and DATA collection (# ω-runs, # φ-runs, # scan width [°], exposure time [sec]). The reflections were successfully indexed by an automated indexing routine built in the APEX program suite. The final cell constants were calculated from a set of 9934 strong reflections from the actual data collection. The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.64 Å. A total of 52627 reflection data with I/σ = 18.35 were harvested by collection. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. **Structure solution and refinement:** The systematic absences in the diffraction data were consistent for the monoclinic space groups 2_1/n. The *E*-statistics strongly suggested the centrosymmetric space group 2_1/n that yielded chemically reasonable and computationally stable results of refinement. A successful solution by the direct methods using SHELX-2014[2] and Olex[3] provided most non-hydrogen atoms from the *E*-map. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

Table S2. Crystal data collection and structure solution refinement for complex **I**

Parameter	Complex I	Parameter	Complex I
empiric formula	$C_7H_{14}Cl_3NO_4$	$\rho_{calc.}$ [g · cm^{-1}]	1.27
MW [g · mol^{-1}]	282.54	crystal size [mm]	0.22 x 0.22 x 0.12
X-ray lab code	Roth1 [AJR1a]	T [K]	100.0(15)
a [Å]	12.6911(2)	radiation type / λ [nm]	Mo K_α / 0.71072
b [Å]	12.4710(2)	μ [mm^{-1}]	0.770
c [Å]	14.9357(2)	F(000)	1168.0
α [°]	90.000(0)°	Reflections collected	51329
β [°]	91.68(0)°	Independent reflections	8934 [R(int) = 0.0219]
γ [°]	90.000(0)°	Data/restraints/parameters	8934/0/275
V [Å^3]	2362.86(6)	GooF on F^2	1.028
Z	8	Largest diff. peak/hole [eÅ^{-3}]	0.54/ -0.31
crystal system	monoclinic	2Θ range for data collection	4.152 to 67.126 °
crystal color	colorless	Final R_1[a]/ wR_2[b] all data	0.0335/ 0.0644
space group	$P2_1/n$	Final R_1[a]/ wR_2[b] I>2s(I)	0.0259/ 0.0604

[a] $R_1 = \sum \left| F_o \right| - \left| F_c \right| / \left| F_o \right|$;[b] $wR_2 = [\sum\{w(F_o^2 - F_o^2)^2\} / \sum\{w(F_o^2)^2\}]^{1/2}$

The final least-squares refinement of 275 parameters against 8934 data resulted in R = 0.0259 (based on F^2 for I>2s) and wR2 = 0.0644 (based on F^2 for all data), respectively. The final structure was visualized using Interactive Molecular Graphics and Olex2.[1,2]

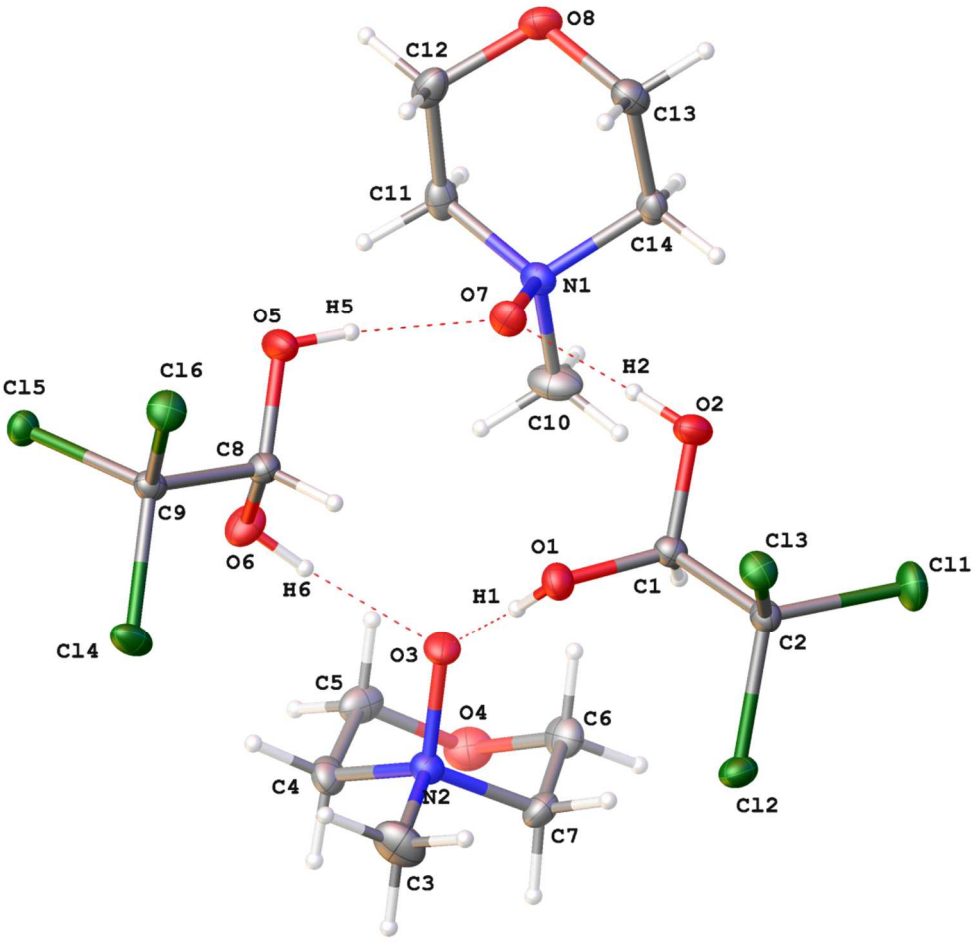

Figure S3. Thermal-ellipsoid of complex **I** is set with 50% probability.

Table S3: Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for complex **I**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	8383.8(2)	2355.8(2)	4255.4(2)	23.91(6)
Cl2	7636.2(2)	4227.0(2)	5188.0(2)	19.23(5)
Cl3	6441.1(2)	2253.0(2)	5200.2(2)	18.31(5)
O1	7852.6(6)	2902.3(6)	6821.3(5)	17.60(13)
O2	8434.8(6)	1382.8(6)	6107.0(5)	19.47(14)
C1	8361.3(7)	2491.3(7)	6086.6(6)	14.76(16)
C2	7724.9(7)	2805.6(8)	5221.9(6)	14.85(16)
Cl4	8136.2(2)	9087.6(2)	5216.7(2)	21.33(5)
Cl5	7163.3(2)	7532.4(2)	4002.3(2)	16.08(5)
Cl6	8855.0(2)	6894.9(2)	5221.9(2)	19.65(5)
O5	6664.0(6)	6387.2(6)	5728.3(5)	20.75(14)
O6	6038.1(6)	8129.3(6)	5664.9(5)	21.39(15)
C8	6911.5(7)	7469.5(7)	5811.7(6)	15.46(16)
C9	7724.5(7)	7732.3(7)	5088.0(6)	13.99(16)
O3	5651.6(6)	-1090.0(5)	7257.7(5)	17.41(13)
O4	3198.0(6)	65.5(7)	7329.5(5)	24.34(16)
N2	5465.7(6)	15.8(6)	7300.4(5)	14.84(14)
C3	6488.6(9)	605.1(10)	7314.0(9)	28.4(2)
C4	4788.1(8)	355.5(8)	6504.5(6)	19.41(18)
C5	3730.9(8)	-196.6(9)	6530.1(7)	22.4(2)
C6	3806.9(8)	-294.9(9)	8087.9(7)	22.16(19)
C7	4871.8(8)	250.9(8)	8133.0(6)	18.60(18)
O7	5866.2(5)	5824.8(6)	7287.1(5)	16.72(13)
O8	4842.1(6)	3280.1(6)	6985.3(5)	21.10(14)
N1	4799.8(6)	5548.6(6)	7335.9(5)	14.96(14)
C10	4175.0(9)	6523.8(9)	7545.0(9)	27.1(2)
C11	4415.0(8)	5069.0(9)	6460.6(6)	19.09(18)
C12	4991.1(8)	4037.2(9)	6279.8(7)	20.80(19)
C13	5262.7(8)	3710.3(8)	7804.6(7)	19.01(18)
C14	4674.4(8)	4716.1(8)	8058.4(6)	16.79(17)

Table S4: Anisotropic displacement parameters ($Å^2 \times 10^3$) for complex **I**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	22.98(11)	31.72(13)	17.37(10)	-5.85(9)	6.51(8)	-0.95(10)
Cl2	23.87(11)	14.73(10)	18.96(10)	3.36(8)	-1.42(8)	-1.62(8)
Cl3	14.17(9)	19.88(10)	20.84(10)	-2.75(8)	-0.21(8)	-3.13(8)
O1	19.7(3)	18.2(3)	14.9(3)	-2.4(2)	0.3(2)	-2.0(3)
O2	24.3(4)	13.5(3)	20.4(3)	-0.3(3)	-3.0(3)	2.2(3)
C1	14.5(4)	13.7(4)	16.1(4)	-0.9(3)	-0.3(3)	0.0(3)
C2	15.1(4)	15.0(4)	14.5(4)	-1.4(3)	1.8(3)	-1.2(3)
Cl4	25.56(12)	14.66(10)	23.23(11)	3.20(8)	-8.39(9)	-6.20(8)
Cl5	16.66(10)	18.23(10)	13.21(9)	0.14(7)	-1.99(7)	-1.08(8)
Cl6	14.87(10)	22.71(11)	21.22(11)	1.04(9)	-1.72(8)	4.08(8)
O5	27.4(4)	14.7(3)	20.7(3)	-0.4(3)	9.0(3)	-3.7(3)
O6	19.1(3)	24.6(4)	20.5(3)	-4.6(3)	0.5(3)	7.0(3)
C8	17.2(4)	14.0(4)	15.3(4)	-0.8(3)	1.7(3)	0.6(3)
C9	14.2(4)	12.9(4)	14.7(4)	0.9(3)	-2.1(3)	-0.1(3)
O3	20.1(3)	13.4(3)	18.8(3)	0.7(2)	1.1(3)	6.2(2)
O4	14.7(3)	25.9(4)	32.4(4)	-2.1(3)	0.0(3)	3.8(3)
N2	13.8(3)	13.8(3)	17.0(3)	1.1(3)	0.8(3)	1.2(3)
C3	17.4(5)	26.9(5)	40.9(6)	6.4(5)	1.1(4)	-5.6(4)
C4	23.0(5)	18.6(4)	16.6(4)	3.8(3)	-0.2(3)	5.2(4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C5	22.6(5)	20.9(5)	23.2(5)	-3.2(4)	-8.6(4)	4.6(4)
C6	19.6(4)	24.5(5)	22.8(5)	-0.8(4)	7.5(4)	0.9(4)
C7	21.2(4)	19.3(4)	15.3(4)	-4.9(3)	0.1(3)	1.4(4)
O7	11.6(3)	19.2(3)	19.4(3)	-0.2(3)	2.5(2)	-5.6(2)
O8	21.3(3)	16.9(3)	25.0(4)	-4.2(3)	-0.2(3)	-3.8(3)
N1	12.1(3)	14.4(3)	18.6(4)	1.0(3)	2.5(3)	-1.0(3)
C10	21.1(5)	17.0(4)	43.3(6)	-1.5(4)	6.1(4)	3.9(4)
C11	15.7(4)	26.0(5)	15.4(4)	3.7(4)	-2.7(3)	-3.6(4)
C12	18.8(4)	26.5(5)	17.3(4)	-5.4(4)	2.6(3)	-6.0(4)
C13	18.6(4)	16.9(4)	21.4(4)	3.2(4)	-2.2(3)	-1.7(3)
C14	17.5(4)	18.6(4)	14.4(4)	1.2(3)	2.8(3)	-3.8(3)

Table S5: Bond lengths for complex **I**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C2	1.7801(9)	O4	C6	1.4250(13)
Cl2	C2	1.7768(10)	N2	C3	1.4913(13)
Cl3	C2	1.7684(9)	N2	C4	1.5072(12)
O1	C1	1.3875(11)	N2	C7	1.5019(12)
O2	C1	1.3858(11)	C4	C5	1.5096(15)
C1	C2	1.5533(13)	C6	C7	1.5129(14)
Cl4	C9	1.7779(9)	O7	N1	1.4004(10)
Cl5	C9	1.7695(9)	O8	C12	1.4316(13)
Cl6	C9	1.7811(9)	O8	C13	1.4254(12)
O5	C8	1.3906(12)	N1	C10	1.4900(13)
O6	C8	1.3926(12)	N1	C11	1.5059(12)
C8	C9	1.5511(13)	N1	C14	1.5093(12)
O3	N2	1.4008(10)	C11	C12	1.5082(15)
O4	C5	1.4273(13)	C13	C14	1.5136(14)

Table S6: Bond angles for complex **I**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O1	C1	C2	108.76(7)	O3	N2	C4	109.50(7)
O2	C1	O1	112.57(8)	O3	N2	C7	108.61(7)
O2	C1	C2	107.64(7)	C3	N2	C4	110.40(8)
Cl2	C2	Cl1	108.79(5)	C3	N2	C7	110.51(8)
Cl3	C2	Cl1	108.47(5)	C7	N2	C4	108.03(7)
Cl3	C2	Cl2	109.31(5)	N2	C4	C5	109.81(8)
C1	C2	Cl1	110.46(6)	O4	C5	C4	111.10(8)
C1	C2	Cl2	107.84(6)	O4	C6	C7	110.87(8)
C1	C2	Cl3	111.91(6)	N2	C7	C6	110.16(8)
O5	C8	O6	112.50(8)	C13	O8	C12	109.23(7)
O5	C8	C9	107.21(7)	O7	N1	C10	109.34(7)
O6	C8	C9	107.94(7)	O7	N1	C11	109.99(7)
Cl4	C9	Cl6	108.18(5)	O7	N1	C14	109.19(7)
Cl5	C9	Cl4	110.01(5)	C10	N1	C11	110.19(8)
Cl5	C9	Cl6	108.75(5)	C10	N1	C14	110.10(8)
C8	C9	Cl4	108.96(6)	C11	N1	C14	108.00(7)
C8	C9	Cl5	110.54(6)	N1	C11	C12	110.35(8)
C8	C9	Cl6	110.37(6)	O8	C12	C11	110.84(8)
C6	O4	C5	109.49(7)	O8	C13	C14	110.60(8)
O3	N2	C3	109.76(8)	N1	C14	C13	109.13(7)

Table S7: Torsion angles for complex **I**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
O1	C1	C2	Cl1	176.96(6)	C3	N2	C4	C5	-176.58(9)
O1	C1	C2	Cl2	58.19(8)	C3	N2	C7	C6	176.52(8)
O1	C1	C2	Cl3	-62.07(9)	C4	N2	C7	C6	55.66(10)
O2	C1	C2	Cl1	-60.82(9)	C5	O4	C6	C7	61.29(11)
O2	C1	C2	Cl2	-179.59(6)	C6	O4	C5	C4	-61.64(11)
O2	C1	C2	Cl3	60.15(9)	C7	N2	C4	C5	-55.65(10)
O5	C8	C9	Cl4	-176.02(6)	O7	N1	C11	C12	63.54(10)
O5	C8	C9	Cl5	62.98(8)	O7	N1	C14	C13	-63.25(9)
O5	C8	C9	Cl6	-57.37(9)	O8	C13	C14	N1	-61.24(10)
O6	C8	C9	Cl4	62.56(8)	N1	C11	C12	O8	58.78(10)
O6	C8	C9	Cl5	-58.44(9)	C10	N1	C11	C12	-175.84(8)
O6	C8	C9	Cl6	-178.79(6)	C10	N1	C14	C13	176.69(8)
O3	N2	C4	C5	62.47(10)	C11	N1	C14	C13	56.33(10)
O3	N2	C7	C6	-63.02(10)	C12	O8	C13	C14	63.00(10)
O4	C6	C7	N2	-59.45(11)	C13	O8	C12	C11	-61.52(10)
N2	C4	C5	O4	59.61(11)	C14	N1	C11	C12	-55.54(10)

Table S8: Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for complex **I**.

Atom	*x*	*y*	*z*	U(eq)
H1	8278	3274	7131	26
H2	8641	1184	6620	29
H1A	9085	2805	6065	18
H5	6389	6172	6201	31
H6	5875	8418	6149	32
H8	7230	7611	6421	19
H3A	6355	1378	7344	43
H3B	6916	384	7839	43
H3C	6867	441	6768	43
H4A	5142	165	5944	23
H4B	4688	1143	6515	23
H5A	3292	24	6003	27
H5B	3833	-983	6499	27
H6A	3906	-1081	8050	27
H6B	3424	-138	8641	27
H7A	4775	1035	8194	22
H7B	5281	-8	8664	22
H10A	3428	6332	7579	41
H10B	4424	6821	8121	41
H10C	4262	7059	7073	41
H11A	4533	5583	5968	23
H11B	3649	4927	6483	23
H12A	4727	3729	5705	25
H12B	5753	4187	6227	25
H13A	6018	3880	7738	23
H13B	5205	3170	8286	23
H14A	3918	4550	8126	20
H14B	4959	4995	8637	20

Table S9: Hydrogen bonds with H...A < r(A) + 2.000 Angstroms and <DHA > 110° for complex **I**.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
O1-H1	0.840	1.799	170.49	2.631	O3
O2-H2	0.840	1.788	176.65	2.627	O7
O5-H5	0.840	1.823	173.78	2.660	O7
O6-H6	0.840	1.795	172.10	2.630	O3
O2-H2	0.840	2.606	147.83	3.347	N1
O6-H6	0.840	2.692	157.68	3.483	N2

4. Crystal structure of the pyridine-*N*-oxide/chloral hydrate complex II (CCDC 1019897)

Preparation of crystals: Co-crystallization of pyridine-*N*-oxide and chloral hydrate was carried out by recrystallization of equimolar mixtures of both compounds (0.75 mmol each) from DCM (starting with 0.2 mL of the solvent). After cooling down the solution from 40 °C to room temperature, appropriate crystals formed almost immediately.

Data collection: A colorless crystal block with approximate dimensions 0.16 x 0.16 x 0.26 mm was selected under oil at ambient conditions and attached to the tip of an X-ray capillary. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a three-circle diffractometer BRUKER AXS SMART APEX (released: 2000) with Mo-K_α radiation (λ = 0.71073 Å) and CCD-detector APEX I. There were no detailed records of the Data collection parameters especially for UNIT cell (# reflections, # scan width [°], # exposure time [sec]) and DATA collection (# ω-runs, # φ-runs, # scan width [°], exposure time [sec]). The reflections were successfully indexed by an automated indexing routine built in the APEX program suite. The final cell constants were calculated from a set of 9979 strong reflections from the actual data collection. The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.64 Å. A total of 24151 reflection data with I/σ = 28.27 were harvested by collection. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.

Structure solution and refinement: The systematic absences in the diffraction data were consistent for the monoclinic space groups $2_1/c$. The *E*-statistics strongly suggested the centrosymmetric space group $2_1/c$ that yielded chemically reasonable and computationally stable results of refinement. A successful solution by the direct methods using SHELX-2014[2] and Olex2[3] provided most non-hydrogen atoms from the *E*-map. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients

Table S10. Crystal data collection and structure solution refinement for complex **II**

Parameter	**Complex II**	**Parameter**	**Complex II**
empiric formula	$C_7H_8Cl_3NO_3$	$\rho_{calc.}$ [g · cm^{-1}]	1.667
MW [g · mol^{-1}]	260.49	crystal size [mm]	0.16 x 0.16 x 0.26
X-ray lab code	Roth2 [AJR130d]	T [K]	100.0(15)
a [Å]	6.15940(10)	radiation type / λ [nm]	Mo K_α / 0.71072
b [Å]	12.8396(2)	μ [mm^{-1}]	0.862
c [Å]	13.3985(2)	F(000)	528.0
α [°]	90.000(0)°	Reflections collected	2617
β [°]	101.56(0)°	Independent reflections	3873[R(int) = 0.0146]
γ [°]	90.000(0)°	Data/restraints/parameters	3873/0/139
V [Å^3]	1038.13(3)	GooF on F^2	1.074
Z	4	Largest diff. peak/hole [eÅ^{-3}]	0.54/ -0.31
crystal system	Monoclinic	2Θ range for data collection	4.438 to 67.096 °
crystal color	Colorless	Final R_1[a]/ wR_2[b] all data	0.0235/ 0.0588
space group	$P2_1/c$	Final R_1[a]/ wR_2[b] I>2s(I)	0.0235/ 0.0576

[a] $R_1 = \sum \left| F_o \right| - \left| F_c \right| / \left| F_o \right|$;[b] $wR_2 = [\sum\{w(F_o^2 - F_o^2)^2\}/ \sum\{w(F_o^2)^2\}]^{1/2}$

The final least-squares refinement of 139 parameters against 3873 data resulted in R = 0.0235 (based on F^2 for I>2s) and wR2 = 0.0588 (based on F^2 for all data), respectively. The final structure was visualized using Interactive Molecular Graphics and Olex2.[1,2]

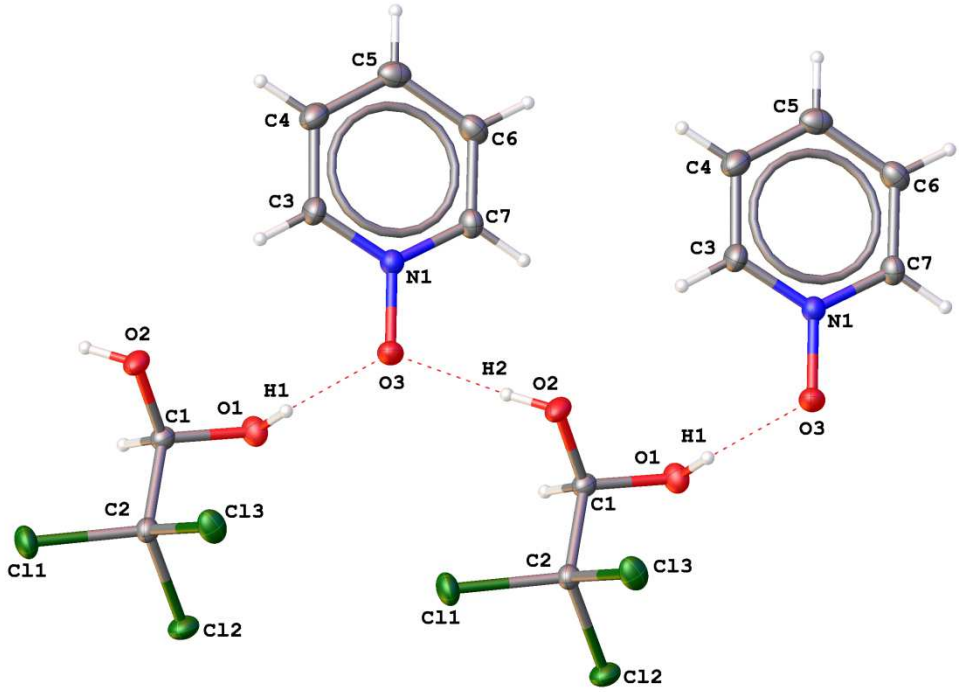

Figure S4. Thermal-ellipsoid of complex **II** is set with 50% probability.

Table S11. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for complex **II**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	1320.1(3)	1396.3(2)	4592.0(2)	21.67(5)
Cl2	4129.0(3)	1868.5(2)	3174.3(2)	20.93(5)
Cl3	6105.7(3)	1269.9(2)	5239.4(2)	20.52(5)
O1	5809.6(11)	3608.4(5)	4620.5(5)	17.96(11)
O2	3808.6(10)	3164.2(5)	5829.6(4)	18.21(11)
C1	3932.6(12)	3119.0(6)	4805.2(6)	14.11(13)
C2	3893.9(12)	1953.1(6)	4472.1(6)	14.42(13)
O3	9703.2(10)	3632.4(5)	5969.0(5)	18.23(11)
N1	9681.1(11)	4474.0(5)	6554.4(5)	14.13(11)
C3	8069.5(14)	4564.0(7)	7101.6(6)	18.26(14)
C4	8025.1(14)	5418.7(7)	7725.5(6)	20.62(15)
C5	9633.6(15)	6186.8(7)	7788.4(6)	20.15(15)
C6	11256.2(14)	6077.4(7)	7207.8(7)	19.73(15)
C7	11256.5(13)	5215.5(6)	6590.9(6)	16.76(13)

Table S12. Anisotropic displacement parameters ($Å^2×10^3$) for complex **II**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka×b×U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	14.36(9)	26.68(10)	23.78(10)	-1.35(7)	3.40(7)	-6.73(7)
Cl2	21.46(10)	26.82(10)	15.36(9)	-6.60(6)	5.71(7)	0.60(7)
Cl3	15.92(9)	17.09(9)	26.41(10)	2.64(6)	-0.92(7)	2.14(6)
O1	17.3(3)	19.0(3)	17.7(3)	1.8(2)	3.9(2)	-3.8(2)
O2	14.8(3)	27.4(3)	12.8(2)	-4.4(2)	4.0(2)	1.2(2)
C1	13.5(3)	15.9(3)	12.9(3)	-0.9(2)	2.6(2)	1.1(2)
C2	11.8(3)	17.2(3)	14.2(3)	-0.9(2)	2.5(2)	-0.3(2)
O3	16.1(3)	17.8(3)	21.4(3)	-6.7(2)	5.2(2)	-1.62(19)
N1	12.9(3)	15.3(3)	14.1(3)	-0.1(2)	2.7(2)	-0.3(2)
C3	15.5(3)	22.1(4)	18.5(3)	-1.6(3)	6.5(3)	-2.5(3)
C4	19.1(4)	26.5(4)	16.9(3)	-3.3(3)	4.9(3)	2.1(3)
C5	21.6(4)	19.4(4)	17.6(3)	-2.9(3)	-0.8(3)	3.7(3)
C6	19.0(4)	15.9(3)	23.1(4)	-0.6(3)	1.3(3)	-1.6(3)
C7	14.7(3)	16.7(3)	19.2(3)	1.4(3)	4.3(3)	-1.7(2)

Table S13. Bond lengths for complex **II.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C2	1.7754(8)	N1	C3	1.3521(10)
Cl2	C2	1.7770(8)	N1	C7	1.3532(10)
Cl3	C2	1.7667(8)	C3	C4	1.3832(12)
O1	C1	1.3810(10)	C4	C5	1.3884(13)
O2	C1	1.3912(9)	C5	C6	1.3911(13)
C1	C2	1.5609(11)	C6	C7	1.3813(12)
O3	N1	1.3369(9)			

Table S14. Bond angles for complex **II**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O1	C1	O2	111.79(6)	O3	N1	C3	118.82(7)
O1	C1	C2	110.52(6)	O3	N1	C7	119.89(6)
O2	C1	C2	108.74(6)	C3	N1	C7	121.29(7)
Cl1	C2	Cl2	108.26(4)	N1	C3	C4	120.07(8)
Cl3	C2	Cl1	110.23(4)	C3	C4	C5	120.00(8)
Cl3	C2	Cl2	109.55(4)	C4	C5	C6	118.57(8)
C1	C2	Cl1	108.85(5)	C7	C6	C5	120.12(8)
C1	C2	Cl2	109.80(5)	N1	C7	C6	119.94(7)
C1	C2	Cl3	110.12(5)				

Table S15. Torsion angles for complex **II**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
O1	C1	C2	Cl1	-173.65(5)	O3	N1	C7	C6	-178.97(7)
O1	C1	C2	Cl2	-55.30(7)	N1	C3	C4	C5	0.16(13)
O1	C1	C2	Cl3	65.40(7)	C3	N1	C7	C6	0.98(12)
O2	C1	C2	Cl1	63.29(7)	C3	C4	C5	C6	0.51(13)
O2	C1	C2	Cl2	-178.37(5)	C4	C5	C6	C7	-0.46(13)
O2	C1	C2	Cl3	-57.66(7)	C5	C6	C7	N1	-0.28(12)
O3	N1	C3	C4	179.03(7)	C7	N1	C3	C4	-0.92(12)

Table S16. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for complex **II**.

Atom	*x*	*Y*	*z*	U(eq)
H1	6840(30)	3483(12)	5080(12)	35(4)
H2	2560(30)	3282(12)	5863(12)	37(4)
H1A	2640(20)	3433(9)	4366(9)	15(3)
H3	6990	4051	7059	22
H4	6918	5479	8103	25
H5	9626	6762	8210	24
H6	12343	6585	7235	24
H7	12339	5145	6201	20

Table S17: Hydrogen bonds with H...A < r(A) + 2.000 Angstroms and <DHA > 110° for complex **II**.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
O1-H1	0.807	1.929	158.86	2.698	O3
O1-H1	0.807	2.683	139.86	3.341	N1
O2-H2	0.793	1.850	176.68	2.642	O3
O2-H2	0.793	2.647	148.73	3.350	N1

(1) Sheldrick, G.M. *Acta Crystallogr. Sect. A.* **2008,** *A64*, 112–122

(2) SHELX, released 2014/6

(3) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K. Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339–341.