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Supporting information for article:

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Electronic Supporting Information

Solvent Exchange in a Metal-organic Framework Single Crystal Monitored by Dynamic *in situ* X-ray diffraction

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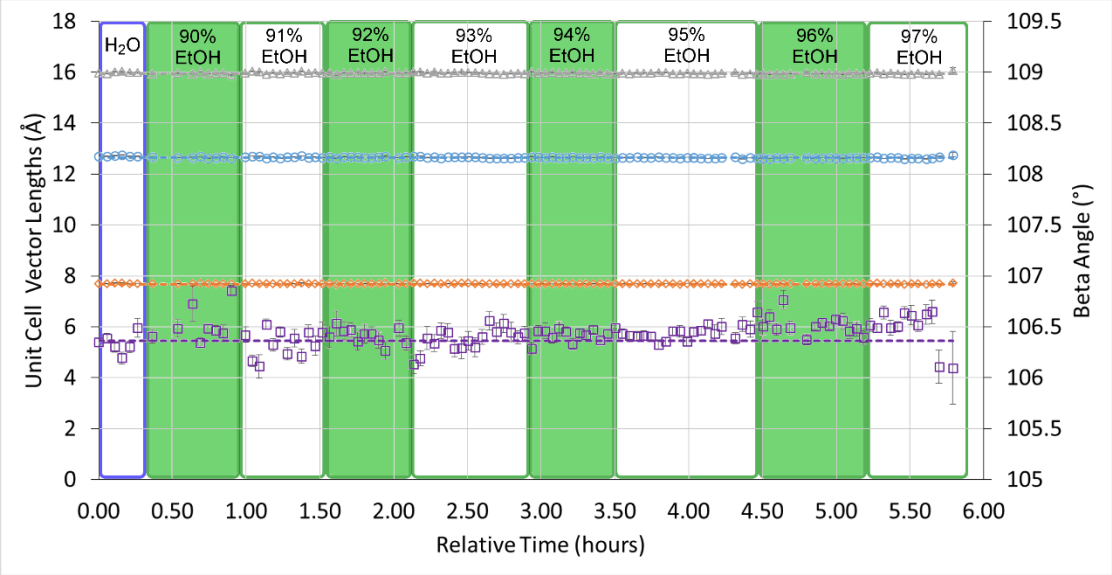

Figure S1. Time resolved unit cell parameters (*a* (blue circles), *b* (orange diamonds), *c* (grey triangles), and β (purple squares)) determined from rs-DIX measurements demonstrating that **1** is stable in ethanol/water solutions up to concentrations of 96% ethanol. Alternating shaded regions show the percentage of ethanol in the ECC. Dashed lines correspond to the unit cell of **1** (same color scheme as noted above).

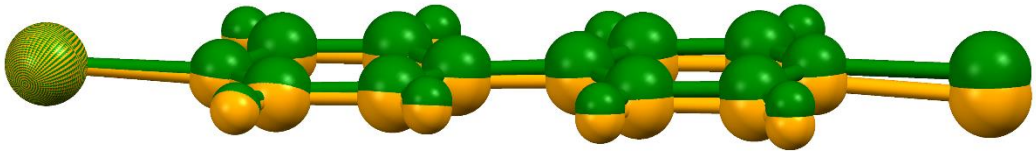

Figure S2. Side view of the overlay of 4,4'-bipyridine ligands from structures 1 (green) and 2 (orange) showing the rotation of the ligand around the cobalt metal center (left).

Crystal Structure Refinement Details

Indexing, data integration and reduction were performed using SaintPlus.(*SMART and SAINTPLUS - Area Detector Control and Integration Software, version 6.01*, 1999) Absorption correction was performed by multi-scan method implemented in SADABS.(Sheldrick, 2004) Space groups were determined using XPREP implemented in APEX2.(Sheldrick, 2014) Using Olex2,(Dolomanov *et al.*, 2009) the structure was solved with the ShelXS structure solution program(Sheldrick, 2008) using direct methods and refined with the ShelXL refinement package using least-squares.(Sheldrick, 2015) The structure was refined by full-matrix least squares against F^2. Hydrogen atoms were placed in geometrically calculated positions or found in the Fourier difference map and included in the refinement process using riding model. In each structure, DFIX restraints were applied to hydrogen atoms of water molecules to ensure chemically reasonable positions based on the distances to nearby hydrogen bond acceptors. These restraints were applied to hydrogen atoms on O7 in **1**, O5 and O6 in **2**, and O5 in **3**.

Structure 1

Table S1 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Structure1. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Co1	8040.4(6)	5084.7(11)	1779.5(3)	19.1(2)
O1	8304(3)	4437(5)	3034.3(19)	28.3(10)
O2	8734(3)	1641(6)	3301(2)	32(1)
O3	7954(3)	8376(5)	5472(2)	31.6(10)
O4	8707(3)	7466(5)	6812.1(19)	26.0(9)
O5	6656(3)	6589(6)	2042(2)	38.8(11)
N1	9516(3)	1114(6)	6620(2)	19.1(10)
N2	6853(4)	3284(7)	1105(2)	24.9(11)
C1	8598(4)	3143(8)	3537(3)	19.8(12)
C2	8755(4)	3517(7)	4502(3)	15.6(11)
C3	8537(4)	5157(8)	4772(3)	20.5(11)
C4	8695(4)	5491(7)	5665(3)	18.4(12)
C5	8439(4)	7188(7)	5985(3)	19.2(12)
C6	9072(4)	4138(7)	6266(3)	16.2(11)
C7	9267(4)	2495(7)	5989(3)	16.3(11)
C8	9113(4)	2176(7)	5105(3)	17.1(11)

C9	6266(7)	3461(11)	282(4)	72(3)
C10	5541(7)	2206(12)	-155(4)	86(4)
C11	5374(5)	686(8)	233(3)	30.9(14)
C12	6024(6)	475(10)	1072(4)	53(2)
C13	6729(6)	1817(10)	1483(3)	49(2)
O6	7325(4)	-1012(7)	3607(3)	50.4(13)
O7	4876(7)	4654(19)	2131(5)	209(7)

Table S2 Anisotropic Displacement Parameters ($Å^2×10^3$) for Structure1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co1	30.5(4)	14.9(4)	10.6(3)	0.2(3)	3.7(2)	-5.0(4)
O1	48(2)	24(3)	11.4(15)	4.9(14)	6.8(15)	6.0(18)
O2	55(3)	27(3)	13.4(16)	-3.3(16)	8.8(16)	9(2)
O3	49(2)	17(2)	24.3(17)	-0.2(16)	3.9(17)	8.2(19)
O4	43(2)	21(3)	14.8(16)	-4.6(14)	9.1(15)	4.1(19)
O5	41(3)	33(3)	39(2)	-0.6(19)	5.3(18)	4(2)
N1	32(3)	15(3)	8.1(17)	3.7(16)	2.8(16)	7(2)
N2	29(3)	26(3)	17.2(19)	-1.3(19)	2.6(17)	-5(2)
C1	24(3)	28(4)	8(2)	0(2)	4.5(18)	1(2)
C2	24(3)	13(3)	11(2)	-0.1(18)	7.7(18)	0(2)
C3	27(3)	19(3)	16(2)	3(2)	6.1(18)	3(3)
C4	24(3)	13(3)	18(2)	-4.1(18)	6.3(19)	0(2)
C5	27(3)	12(3)	19(2)	-2(2)	7(2)	0(2)
C6	29(3)	11(3)	8.0(19)	-0.3(18)	5.7(19)	0(2)
C7	22(3)	15(3)	12(2)	0.2(19)	4.4(18)	1(2)
C8	31(3)	9(3)	14(2)	-1.2(19)	11(2)	3(2)
C9	104(7)	54(6)	31(3)	16(3)	-23(4)	-52(5)
C10	123(7)	66(7)	30(3)	20(4)	-40(4)	-64(6)

C11	36(3)	21(4)	30(3)	4(2)	-1(2)	-8(3)
C12	69(5)	47(6)	29(3)	11(3)	-12(3)	-32(4)
C13	67(5)	46(5)	20(3)	11(3)	-11(3)	-23(4)
O6	61(3)	46(4)	37(2)	6(2)	3(2)	-11(3)
O7	107(6)	420(20)	107(6)	-13(8)	48(5)	-133(10)

Table S3 Bond Lengths for Structure1.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Co1	O1	1.993(3)		N2	C13	1.307(8)
Co1	O3[1]	2.370(4)		C1	C2	1.521(6)
Co1	O4[1]	2.054(4)		C2	C3	1.383(7)
Co1	O5	2.235(4)		C2	C8	1.392(7)
Co1	N1[2]	2.161(4)		C3	C4	1.402(6)
Co1	N2	2.097(4)		C4	C5	1.467(7)
O1	C1	1.263(6)		C4	C6	1.400(7)
O2	C1	1.239(7)		C6	C7	1.381(7)
O3	Co1[3]	2.370(4)		C7	C8	1.388(6)
O3	C5	1.259(6)		C9	C10	1.374(9)
O4	Co1[3]	2.054(4)		C10	C11	1.364(9)
O4	C5	1.282(5)		C11	C11[5]	1.468(11)
N1	Co1[4]	2.161(4)		C11	C12	1.364(7)
N1	C7	1.432(6)		C12	C13	1.396(9)
N2	C9	1.316(7)				

[1]+X,3/2-Y,-1/2+Z; [2]+X,1/2-Y,-1/2+Z; [3]+X,3/2-Y,1/2+Z; [4]+X,1/2-Y,1/2+Z; [5]1-X,-Y,-Z

Table S4 Bond Angles for Structure1.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O1	Co1	O3[1]	163.39(15)		O2	C1	C2	119.5(4)
O1	Co1	O4[1]	104.65(14)		C3	C2	C1	120.4(4)
O1	Co1	O5	81.71(15)		C3	C2	C8	120.8(4)
O1	Co1	N1[2]	96.28(15)		C8	C2	C1	118.7(5)
O1	Co1	N2	103.88(17)		C2	C3	C4	119.9(5)
O4[1]	Co1	O3[1]	58.79(13)		C3	C4	C5	122.2(5)
O4[1]	Co1	O5	82.02(17)		C6	C4	C3	118.7(5)
O4[1]	Co1	N1[2]	91.71(16)		C6	C4	C5	119.1(4)
O4[1]	Co1	N2	147.58(15)		O3	C5	O4	118.9(5)
O5	Co1	O3[1]	93.81(15)		O3	C5	C4	122.1(4)
N1[2]	Co1	O3[1]	86.14(15)		O4	C5	C4	119.0(4)
N1[2]	Co1	O5	172.66(16)		C7	C6	C4	121.0(4)
N2	Co1	O3[1]	91.79(14)		C6	C7	N1	118.2(4)
N2	Co1	O5	87.19(18)		C6	C7	C8	120.0(4)
N2	Co1	N1[2]	100.14(17)		C8	C7	N1	121.5(5)
C1	O1	Co1	140.0(3)		C7	C8	C2	119.6(5)
C5	O3	Co1[3]	84.2(3)		N2	C9	C10	122.5(7)
C5	O4	Co1[3]	98.0(3)		C11	C10	C9	122.4(6)
C7	N1	Co1[4]	111.9(3)		C10	C11	C11[5]	122.9(6)
C9	N2	Co1	124.0(4)		C12	C11	C10	114.7(6)
C13	N2	Co1	119.5(3)		C12	C11	C11[5]	122.1(7)
C13	N2	C9	116.2(5)		C11	C12	C13	119.8(6)
O1	C1	C2	115.0(5)		N2	C13	C12	124.3(5)
O2	C1	O1	125.5(4)					

[1]+X,3/2-Y,-1/2+Z; [2]+X,1/2-Y,-1/2+Z; [3]+X,3/2-Y,1/2+Z; [4]+X,1/2-Y,1/2+Z; [5]1-X,-Y,-Z

Table S5 Torsion Angles for Structure1.

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Co1	O1	C1	O2	-7.4(10)		C2	C3	C4	C6	-0.2(7)
Co1	O1	C1	C2	174.4(4)		C3	C2	C8	C7	-0.9(8)
Co1[1]	O3	C5	O4	-2.2(5)		C3	C4	C5	O3	7.8(8)
Co1[1]	O3	C5	C4	177.0(5)		C3	C4	C5	O4	-172.9(5)
Co1[1]	O4	C5	O3	2.6(5)		C3	C4	C6	C7	-1.1(7)
Co1[1]	O4	C5	C4	-176.7(4)		C4	C6	C7	N1	-172.2(4)
Co1[2]	N1	C7	C6	85.4(5)		C4	C6	C7	C8	1.4(8)
Co1[2]	N1	C7	C8	-88.2(5)		C5	C4	C6	C7	176.6(5)
Co1	N2	C9	C10	176.1(8)		C6	C4	C5	O3	-169.8(5)
Co1	N2	C13	C12	-175.1(6)		C6	C4	C5	O4	9.4(7)
O1	C1	C2	C3	2.6(7)		C6	C7	C8	C2	-0.4(8)
O1	C1	C2	C8	-177.9(5)		C8	C2	C3	C4	1.2(7)
O2	C1	C2	C3	-175.7(5)		C9	N2	C13	C12	-0.4(12)
O2	C1	C2	C8	3.7(7)		C9	C10	C11	C11[3]	-178.2(9)
N1	C7	C8	C2	173.0(5)		C9	C10	C11	C12	-3.2(14)
N2	C9	C10	C11	0.2(17)		C10	C11	C12	C13	4.4(12)
C1	C2	C3	C4	-179.4(4)		C11[3]	C11	C12	C13	179.4(8)
C1	C2	C8	C7	179.7(5)		C11	C12	C13	N2	-2.8(13)
C2	C3	C4	C5	-177.8(5)		C13	N2	C9	C10	1.7(13)

[1]+X,3/2-Y,1/2+Z; [2]+X,1/2-Y,1/2+Z; [3]1-X,-Y,-Z

Table S6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Structure1.

Atom	*x*	*y*	*z*	U(eq)
H5A	6900	7288	2490	58
H5B	6177	5878	2161	58
H1A	9915	1537	7134	23
H1B	9919	309	6451	23
H3	8285	6038	4362	25
H6	9192	4349	6861	19
H8	9249	1073	4916	21
H9	6346	4475	-15	86
H10	5150	2399	-738	103
H12	5998	-560	1370	64
H13	7138	1656	2064	59
H6A	7803	-295	3532	76
H6B	7476	-1277	4146	76
H7A	4179	4645	1918	313
H7B	5065	3909	2541	313

Crystal structure determination of [Structure1]

Crystal Data for $C_{13}H_{15}CoN_2O_7$ (*M* =370.20 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 12.655(3) Å, *b* = 7.6693(19) Å, *c* = 15.934(4) Å, *β* = 106.636(5)°, *V* = 1481.7(6) Å^3, *Z* = 4, *T* = 296.15 K, μ(synchrotron) = 1.197 mm^{-1}, *Dcalc* = 1.660 g/cm^3, 13840 reflections measured ($5.336° \leq 2\Theta \leq 52.878°$), 2948 unique ($R_{int}$ = 0.1180, R_{sigma} = 0.0982) which were used in all calculations. The final R_1 was 0.0579 ($I > 2\sigma(I)$) and wR_2 was 0.1418 (all data).

Refinement model description

Number of restraints - 2, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All N(H,H) groups
 At 1.5 times of:
  All O(H,H) groups
```

```
2. Restrained distances
 H7A-O6_$1
 1.9 with sigma of 0.02
 H7B-O7_$2
 3.3 with sigma of 0.02
3.a Free rotating group:
 O6(H6A,H6B), O7(H7A,H7B)
3.b Rotating group:
 O5(H5A,H5B)
3.c Secondary CH2 refined with riding coordinates:
 N1(H1A,H1B)
3.d Aromatic/amide H refined with riding coordinates:
 C3(H3), C6(H6), C8(H8), C9(H9), C10(H10), C12(H12), C13(H13)
```

Structure 2

Table S7 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Structure2. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Co1	1908.9(7)	4957.8(13)	8197.8(5)	19.8(3)
O1	1616(5)	5436(7)	6947(3)	42.8(16)
O2	1067(5)	8176(8)	6675(3)	36.2(14)
O3	2059(5)	1580(7)	4536(4)	50.6(17)
O4	1431(5)	2583(7)	3192(3)	35.4(13)
O5	3331(7)	3481(9)	7796(5)	71(2)
N1	481(5)	8901(8)	3385(3)	22.1(13)
N2	3125(5)	6720(8)	8872(3)	25.4(14)
C1	1285(6)	6731(10)	6438(4)	24.1(16)
C2	1205(6)	6412(9)	5492(4)	21.0(15)
C3	1469(5)	4774(9)	5217(4)	21.5(14)
C4	1352(6)	4504(8)	4329(4)	20.5(15)
C5	1633(6)	2801(9)	4015(5)	26.9(16)
C6	979(6)	5861(9)	3738(4)	19.9(14)
C7	762(5)	7487(8)	4006(3)	16.2(13)
C8	866(6)	7777(9)	4885(4)	20.3(14)
C9	3712(8)	6543(12)	9709(5)	54(3)

C10	4453(9)	7786(14)	10148(5)	70(4)
C11	4613(6)	9316(10)	9760(4)	27.4(16)
C12	3951(7)	9544(11)	8914(5)	41(2)
C13	3231(7)	8228(12)	8491(4)	44(2)
C14	3931(9)	4430(20)	7305(8)	107(6)
C15	5029(11)	4980(20)	7923(9)	109(5)
O6	7571(9)	8931(11)	3523(5)	97(3)

Table S8 Anisotropic Displacement Parameters ($Å^2×10^3$) for Structure2. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co1	34.6(5)	14.2(4)	8.7(4)	0.2(4)	4.1(3)	-8.5(5)
O1	91(5)	27(3)	13(2)	2(2)	19(3)	-11(3)
O2	57(4)	41(4)	13(2)	-10(2)	15(2)	3(3)
O3	61(4)	22(3)	48(3)	-10(3)	-13(3)	16(3)
O4	72(4)	18(3)	27(2)	-9(2)	31(3)	-2(3)
O5	93(6)	44(5)	73(5)	2(4)	20(4)	-9(4)
N1	38(4)	18(3)	12(2)	3(2)	10(2)	3(3)
N2	34(3)	23(3)	15(2)	-1(2)	3(2)	-11(3)
C1	36(4)	30(4)	9(3)	-3(3)	10(3)	-17(3)
C2	35(4)	19(4)	10(3)	-2(2)	6(3)	-4(3)
C3	37(4)	11(4)	15(3)	4(3)	7(3)	-1(3)
C4	38(4)	9(3)	17(3)	-3(2)	13(3)	-1(3)
C5	37(4)	9(4)	35(4)	-8(3)	12(3)	1(3)
C6	42(4)	12(3)	8(3)	-2(2)	10(3)	-2(3)
C7	29(4)	15(3)	7(2)	3(2)	8(2)	1(3)
C8	35(4)	13(4)	16(3)	1(2)	13(3)	3(3)
C9	74(7)	41(6)	28(4)	12(4)	-11(4)	-39(5)
C10	95(8)	65(7)	18(4)	13(4)	-28(4)	-48(6)

C11	34(4)	24(4)	22(3)	-5(3)	4(3)	-14(3)
C12	55(5)	38(6)	23(3)	6(3)	1(3)	-25(4)
C13	61(6)	44(5)	16(3)	3(3)	-3(3)	-26(5)
C14	52(7)	186(18)	84(9)	34(10)	24(6)	-18(9)
C15	87(9)	134(14)	113(11)	-28(11)	43(8)	-23(11)
O6	169(9)	53(5)	72(5)	1(4)	41(6)	-26(6)

Table S9 Bond Lengths for Structure2.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Co1	O1	1.962(5)		N2	C13	1.332(10)
Co1	O3[1]	2.406(6)		C1	C2	1.512(8)
Co1	O4[1]	2.036(6)		C2	C3	1.404(9)
Co1	O5	2.408(8)		C2	C8	1.401(9)
Co1	N1[2]	2.142(6)		C3	C4	1.404(8)
Co1	N2	2.093(6)		C4	C5	1.482(9)
O1	C1	1.269(9)		C4	C6	1.387(9)
O2	C1	1.228(9)		C6	C7	1.373(9)
O3	Co1[3]	2.406(6)		C7	C8	1.395(8)
O3	C5	1.259(9)		C9	C10	1.375(11)
O4	Co1[3]	2.036(5)		C10	C11	1.370(12)
O4	C5	1.276(8)		C11	C11[5]	1.483(13)
O5	C14	1.462(13)		C11	C12	1.372(10)
N1	Co1[4]	2.142(6)		C12	C13	1.393(11)
N1	C7	1.438(8)		C14	C15	1.511(17)
N2	C9	1.326(9)				

[1]+X,1/2-Y,1/2+Z; [2]+X,3/2-Y,1/2+Z; [3]+X,1/2-Y,-1/2+Z; [4]+X,3/2-Y,-1/2+Z; [5]1-X,2-Y,2-Z

Table S10 Bond Angles for Structure2.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O1	Co1	O3[1]	160.7(2)		O2	C1	C2	120.5(6)
O1	Co1	O4[1]	102.3(2)		C3	C2	C1	120.9(6)
O1	Co1	O5	74.3(3)		C8	C2	C1	119.3(6)
O1	Co1	N1[2]	99.9(2)		C8	C2	C3	119.8(5)
O1	Co1	N2	106.5(2)		C4	C3	C2	119.5(6)
O3[1]	Co1	O5	99.1(2)		C3	C4	C5	121.2(6)
O4[1]	Co1	O3[1]	58.49(19)		C6	C4	C3	119.4(6)
O4[1]	Co1	O5	78.9(2)		C6	C4	C5	119.4(6)
O4[1]	Co1	N1[2]	96.7(2)		O3	C5	O4	119.9(6)
O4[1]	Co1	N2	142.4(2)		O3	C5	C4	121.7(6)
N1[2]	Co1	O3[1]	84.5(2)		O4	C5	C4	118.4(6)
N1[2]	Co1	O5	171.5(2)		C7	C6	C4	121.4(5)
N2	Co1	O3[1]	90.8(2)		C6	C7	N1	119.5(5)
N2	Co1	O5	86.0(3)		C6	C7	C8	119.9(6)
N2	Co1	N1[2]	101.7(2)		C8	C7	N1	120.5(6)
C1	O1	Co1	136.3(5)		C7	C8	C2	119.8(6)
C5	O3	Co1[3]	82.5(4)		N2	C9	C10	122.2(7)
C5	O4	Co1[3]	99.0(4)		C11	C10	C9	122.3(7)
C14	O5	Co1	119.3(8)		C10	C11	C11[5]	122.5(8)
C7	N1	Co1[4]	111.3(4)		C10	C11	C12	115.1(7)
C9	N2	Co1	123.7(5)		C12	C11	C11[5]	122.3(9)
C9	N2	C13	116.6(6)		C11	C12	C13	120.3(7)
C13	N2	Co1	119.1(4)		N2	C13	C12	123.3(6)
O1	C1	C2	115.2(6)		O5	C14	C15	109.2(11)
O2	C1	O1	124.3(6)					

[1]+X,1/2-Y,1/2+Z; [2]+X,3/2-Y,1/2+Z; [3]+X,1/2-Y,-1/2+Z; [4]+X,3/2-Y,-1/2+Z; [5]1-X,2-Y,2-Z

Table S11 Torsion Angles for Structure2.

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Co1	O1	C1	O2	1.5(13)		C2	C3	C4	C6	0.2(10)
Co1	O1	C1	C2	179.5(5)		C3	C2	C8	C7	1.9(10)
Co1[1]	O3	C5	O4	-2.3(7)		C3	C4	C5	O3	-5.2(11)
Co1[1]	O3	C5	C4	177.4(7)		C3	C4	C5	O4	174.6(7)
Co1[1]	O4	C5	O3	2.8(8)		C3	C4	C6	C7	2.5(11)
Co1[1]	O4	C5	C4	-177.0(6)		C4	C6	C7	N1	173.8(6)
Co1	O5	C14	C15	101.8(12)		C4	C6	C7	C8	-3.0(11)
Co1[2]	N1	C7	C6	-81.1(7)		C5	C4	C6	C7	-176.7(7)
Co1[2]	N1	C7	C8	95.8(6)		C6	C4	C5	O3	174.0(7)
Co1	N2	C9	C10	-175.5(9)		C6	C4	C5	O4	-6.2(11)
Co1	N2	C13	C12	174.3(7)		C6	C7	C8	C2	0.8(10)
O1	C1	C2	C3	0.9(10)		C8	C2	C3	C4	-2.3(10)
O1	C1	C2	C8	-178.9(7)		C9	N2	C13	C12	3.0(14)
O2	C1	C2	C3	178.9(7)		C9	C10	C11	C11[3]	178.1(11)
O2	C1	C2	C8	-0.8(10)		C9	C10	C11	C12	2.4(17)
N1	C7	C8	C2	-176.1(6)		C10	C11	C12	C13	-3.9(14)
N2	C9	C10	C11	2.0(19)		C11[3]	C11	C12	C13	-179.6(10)
C1	C2	C3	C4	177.9(6)		C11	C12	C13	N2	1.3(15)
C1	C2	C8	C7	-178.4(6)		C13	N2	C9	C10	-4.6(15)
C2	C3	C4	C5	179.3(7)						

[1]+X,1/2-Y,-1/2+Z; [2]+X,3/2-Y,-1/2+Z; [3]1-X,2-Y,2-Z

Table S12 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Structure2.

Atom	*x*	*y*	*z*	U(eq)
H5	3260(20)	2430(20)	7567(19)	107
H1A	119	9718	3576	27
H1B	45	8503	2875	27
H3	1720	3876	5621	26
H6	875	5665	3146	24
H8	710	8873	5067	24
H9	3619	5543	10008	65
H10	4860	7582	10729	84
H12	3983	10583	8621	49
H13	2803	8410	7913	52
H14A	3521	5459	7032	128
H14B	4032	3691	6847	128
H15A	5287	5990	7691	163
H15B	5541	4038	7987	163
H15C	4958	5262	8485	163
H6A	7566	8954	4049	146
H6B	7803	9905	3395	146

Crystal structure determination of [Structure2]

Crystal Data for $C_{15}H_{17}CoN_2O_6$ (*M* =380.23 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 12.899(9) Å, *b* = 7.638(7) Å, *c* = 16.085(11) Å, *β* = 108.337(11)°, *V* = 1504(2) Å^3, *Z* = 4, *T* = 296.15 K, μ(synchrotron) = 1.177 mm^{-1}, *Dcalc* = 1.679 g/cm^3, 21276 reflections measured ($5.326° \leq 2\Theta \leq 53.85°$), 3213 unique ($R_{int}$ = 0.1363, R_{sigma} = 0.0899) which were used in all calculations. The final R_1 was 0.0857 ($I > 2\sigma(I)$) and wR_2 was 0.1983 (all data).

Refinement model description

Number of restraints - 6, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups, All N(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups, All O(H) groups, All O(H,H) groups
2. Restrained distances
 O5-H5
 0.85 with sigma of 0.01
 H6B-O2_$1
 2.1 with sigma of 0.02
 H6A-O3_$2
 2.2 with sigma of 0.02
 H5-O6_$2
 2 with sigma of 0.02
 C14-H5
 1.910219 with sigma of 0.02
 Co1-H5
 3.024124 with sigma of 0.02
3.a Free rotating group:
 O6(H6A,H6B)
3.b Secondary CH2 refined with riding coordinates:
 N1(H1A,H1B), C14(H14A,H14B)
3.c Aromatic/amide H refined with riding coordinates:
 C3(H3), C6(H6), C8(H8), C9(H9), C10(H10), C12(H12), C13(H13)
3.d Idealised Me refined as rotating group:
 C15(H15A,H15B,H15C)
```

Structure 3

Table S13 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Structure3. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Co1	1804.3(7)	5029.2(11)	3201.9(4)	19.8(2)
O1	1766(3)	5318(5)	1982(2)	23.9(10)
O2	979(4)	-2951(6)	6689(2)	29.1(10)
O3	1950(4)	3535(6)	4518(3)	33.0(11)
O4	1535(4)	2424(5)	3200(2)	25.5(10)
N1	388(4)	-3851(6)	3403(3)	18.2(10)
N2	3131(4)	6630(7)	3885(3)	26.3(12)
C1	1328(5)	-1577(7)	6462(3)	16.7(12)

C2	1237(4)	-1319(7)	5510(3)	14.9(11)
C3	1506(5)	291(7)	5220(3)	17.4(12)
C4	1377(5)	529(7)	4337(3)	16.6(11)
C5	1641(5)	2259(8)	4011(3)	18.8(12)
C6	979(5)	-833(8)	3742(3)	17.0(11)
C7	723(5)	-2450(7)	4028(3)	17.1(12)
C8	850(5)	-2701(7)	4912(3)	15.7(11)
C9	3631(8)	6596(11)	4751(4)	62(3)
C10	4375(9)	7860(13)	5196(4)	74(3)
C11	4613(5)	9278(9)	4766(4)	28.8(14)
C12	4058(7)	9343(11)	3893(4)	53(2)
C13	3345(7)	8009(12)	3477(4)	54(2)
O5	3948(15)	1670(20)	7339(11)	241(8)
C14	3948(13)	3120(20)	6763(10)	126(5)
C15	3003(12)	4130(20)	6679(9)	122(5)

Table S14 Anisotropic Displacement Parameters ($Å^2×10^3$) for Structure3. The Anisotropic displacement factor exponent takes the form: -$2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co1	36.8(4)	13.7(4)	8.7(3)	-1.1(3)	7.3(3)	-7.2(4)
O1	43(2)	20(2)	11.6(17)	3.5(15)	11.7(16)	3.1(19)
O2	53(3)	24(2)	11.6(18)	1.1(16)	13.4(18)	-10(2)
O3	57(3)	15(2)	20(2)	1.9(17)	3.9(19)	-12(2)
O4	52(3)	13(2)	15.0(18)	2.7(16)	15.7(18)	-3.9(19)
N1	34(3)	13(2)	7.1(19)	-3.0(17)	6.2(18)	-6(2)
N2	34(3)	29(3)	15(2)	-3(2)	7(2)	-7(2)
C1	25(3)	18(3)	8(2)	1(2)	6(2)	2(2)
C2	21(3)	13(3)	10(2)	1(2)	4(2)	-2(2)
C3	27(3)	13(3)	11(2)	-3(2)	6(2)	2(2)
C4	28(3)	9(3)	14(2)	2.3(19)	7(2)	-2(2)
C5	28(3)	13(3)	15(2)	2(2)	6(2)	-1(2)
C6	29(3)	16(3)	6(2)	1(2)	6(2)	2(2)
C7	25(3)	16(3)	10(2)	-1(2)	6(2)	-1(2)
C8	27(3)	9(3)	12(2)	-1(2)	8(2)	-1(2)
C9	96(7)	51(6)	21(3)	9(3)	-4(4)	-47(5)
C10	113(8)	65(6)	15(3)	9(4)	-17(4)	-56(6)
C11	34(3)	30(4)	20(3)	0(3)	7(2)	-12(3)
C12	75(6)	52(5)	24(3)	5(3)	7(3)	-43(5)
C13	73(6)	63(6)	19(3)	0(3)	7(3)	-45(5)

Table S15 Bond Lengths for Structure3.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Co1	O1	1.963(3)		C1	C2	1.512(6)
Co1	O3	2.359(4)		C2	C3	1.391(7)
Co1	O4	2.009(4)		C2	C8	1.400(7)
Co1	N1[1]	2.100(5)		C3	C4	1.390(7)
Co1	N2	2.070(5)		C4	C5	1.493(7)
Co1	C5	2.520(6)		C4	C6	1.387(8)
O1	C1[2]	1.272(6)		C6	C7	1.387(8)
O2	C1	1.235(7)		C7	C8	1.392(7)
O3	C5	1.245(7)		C9	C10	1.370(10)
O4	C5	1.275(6)		C10	C11	1.367(10)
N1	Co1[3]	2.100(5)		C11	C11[5]	1.498(12)
N1	C7	1.431(7)		C11	C12	1.350(9)
N2	C9	1.329(8)		C12	C13	1.375(10)
N2	C13	1.312(9)		O5	C14	1.437(19)
C1	O1[4]	1.272(7)		C14	C15	1.389(18)

[1]+X,1+Y,+Z; [2]+X,1/2-Y,-1/2+Z; [3]+X,-1+Y,+Z; [4]+X,1/2-Y,1/2+Z; [5]1-X,2-Y,1-Z

Table S16 Bond Angles for Structure3.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O1	Co1	O3	157.40(16)		C3	C2	C8	119.8(4)
O1	Co1	O4	99.24(16)		C8	C2	C1	119.5(5)
O1	Co1	N1[1]	111.60(17)		C4	C3	C2	119.9(5)
O1	Co1	N2	102.44(18)		C3	C4	C5	120.7(5)
O1	Co1	C5	129.22(17)		C6	C4	C3	120.2(5)
O3	Co1	C5	29.34(15)		C6	C4	C5	119.1(4)
O4	Co1	O3	59.32(15)		O3	C5	Co1	68.1(3)
O4	Co1	N1[1]	104.28(18)		O3	C5	O4	120.0(5)
O4	Co1	N2	133.4(2)		O3	C5	C4	120.9(5)
O4	Co1	C5	30.08(16)		O4	C5	Co1	52.2(3)
N1[1]	Co1	O3	82.78(17)		O4	C5	C4	119.1(5)
N1[1]	Co1	C5	92.25(18)		C4	C5	Co1	169.4(4)
N2	Co1	O3	89.71(17)		C4	C6	C7	120.2(4)
N2	Co1	N1[1]	105.16(19)		C6	C7	N1	118.2(4)
N2	Co1	C5	113.94(19)		C6	C7	C8	120.0(5)
C1[2]	O1	Co1	127.2(4)		C8	C7	N1	121.7(5)
C5	O3	Co1	82.5(3)		C7	C8	C2	119.8(5)
C5	O4	Co1	97.7(3)		N2	C9	C10	122.9(7)
C7	N1	Co1[3]	109.9(3)		C11	C10	C9	121.0(6)
C9	N2	Co1	124.7(5)		C10	C11	C11[5]	122.6(7)
C13	N2	Co1	117.9(4)		C12	C11	C10	115.6(6)
C13	N2	C9	115.9(6)		C12	C11	C11[5]	121.7(7)
O1[4]	C1	C2	116.2(5)		C11	C12	C13	120.9(7)
O2	C1	O1[4]	124.1(5)		N2	C13	C12	123.7(6)
O2	C1	C2	119.7(5)		C15	C14	O5	107.7(15)
C3	C2	C1	120.6(5)					

[1]+X,1+Y,+Z; [2]+X,1/2-Y,-1/2+Z; [3]+X,-1+Y,+Z; [4]+X,1/2-Y,1/2+Z; [5]1-X,2-Y,1-Z

Table S17 Torsion Angles for Structure3.

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Co1	O3	C5	O4	5.5(5)		C3	C4	C5	Co1	-149(2)
Co1	O3	C5	C4	-173.8(5)		C3	C4	C5	O3	-2.0(9)
Co1	O4	C5	O3	-6.5(6)		C3	C4	C5	O4	178.6(5)
Co1	O4	C5	C4	172.9(4)		C3	C4	C6	C7	-0.9(9)
Co1[1]	N1	C7	C6	79.0(5)		C4	C6	C7	N1	-175.8(5)
Co1[1]	N1	C7	C8	-97.6(5)		C4	C6	C7	C8	0.9(8)
Co1	N2	C9	C10	-168.7(9)		C5	C4	C6	C7	-179.6(5)
Co1	N2	C13	C12	167.8(8)		C6	C4	C5	Co1	30(3)
O1[2]	C1	C2	C3	-6.9(8)		C6	C4	C5	O3	176.6(6)
O1[2]	C1	C2	C8	174.7(5)		C6	C4	C5	O4	-2.7(8)
O2	C1	C2	C3	172.7(5)		C6	C7	C8	C2	0.0(8)
O2	C1	C2	C8	-5.7(8)		C8	C2	C3	C4	0.8(8)
N1	C7	C8	C2	176.6(5)		C9	N2	C13	C12	1.5(14)
N2	C9	C10	C11	2.4(18)		C9	C10	C11	C11[3]	177.6(10)
C1	C2	C3	C4	-177.6(5)		C9	C10	C11	C12	0.9(15)
C1	C2	C8	C7	177.5(5)		C10	C11	C12	C13	-2.8(14)
C2	C3	C4	C5	178.7(5)		C11[3]	C11	C12	C13	-179.5(9)
C2	C3	C4	C6	0.1(8)		C11	C12	C13	N2	1.7(16)
C3	C2	C8	C7	-0.9(8)		C13	N2	C9	C10	-3.5(15)

[1]+X,-1+Y,+Z; [2]+X,1/2-Y,1/2+Z; [3]1-X,2-Y,1-Z

Table S18 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Structure3.

Atom	*x*	*y*	*z*	U(eq)
H1A	-75	-3440	2896	22
H1B	25	-4669	3600	22
H3	1773	1207	5617	21
H6	884	-662	3150	20
H8	678	-3785	5104	19
H9	3468	5674	5069	75
H10	4723	7752	5800	89
H12	4160	10302	3569	63
H13	2996	8089	2872	64
H5	3338	1177	7167	361
H14A	4621	3819	7006	151
H14B	3928	2680	6192	151
H15A	2417	3816	6147	183
H15B	3184	5355	6658	183
H15C	2755	3927	7173	183

Crystal structure determination of [Structure3]

Crystal Data for $C_{15}H_{15}CoN_2O_5$ (*M* =362.22 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 12.631(2) Å, *b* = 7.5996(14) Å, *c* = 16.109(3) Å, *β* = 109.223(3)°, *V* = 1460.1(5) Å^3, *Z* = 4, *T* = 296.15 K, μ(synchrotron) = 1.204 mm^{-1}, *Dcalc* = 1.648 g/cm^3, 23515 reflections measured (5.32° ≤ 2Θ ≤ 52.816°), 2988 unique (R_{int} = 0.1090, R_{sigma} = 0.0633) which were used in all calculations. The final R_1 was 0.0720 (I > 2σ(I)) and wR_2 was 0.1787 (all data).

Refinement model description

Number of restraints - 1, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups, All N(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups, All O(H) groups
2. Restrained distances
 H5-O1_$1
 2.2 with sigma of 0.02
3.a Secondary CH2 refined with riding coordinates:
 N1(H1A,H1B), C14(H14A,H14B)
3.b Aromatic/amide H refined with riding coordinates:
 C3(H3), C6(H6), C8(H8), C9(H9), C10(H10), C12(H12), C13(H13)
3.c Idealised Me refined as rotating group:
 C15(H15A,H15B,H15C)
3.d Idealised tetrahedral OH refined as rotating group:
 O5(H5)
```

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