Electronic Supplementary Material (ESI) for Dalton Transactions

Tetrapodal amidoxime ligands I.
Coordination isomerism due to self-complementary dimerization of an octahedral cobalt(III) complex

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Supporting Information

Content

*Remarks concerning the preparation of methylmalononitrile **7** and its deprotonation*

It is not easy to prepare methylmalononitrile by direct methylation of malononitrile itself because one usually obtains a mixture of the starting material, methylmalononitrile and dimethylmalononitrile which is hard to separate by distillation or chromatography, nevertheless it can be done by using phase transfer catalysts (E. Diez-Barra, A. de la Hoz, A. Moreno and P. Sanchez-Verdu, *Perkin Trans. 1* **1991**, 2589-2592.). We consider the method described in the main text well suited for the preparation of methylmalononitrile on a molar scale. On a smaller scale however, PTC might provide a more convenient access to the material.

From a historic perspective it is interesting to note that methylmalononitrile was first prepared by Arthur Hantzsch more than 100 years ago (*Ber.* **1899**, 32(1), 641–650.) by reacting the silver salt of cyanoform with methyliodide to obtain methylcyanoform which forms methylmalononitrile in an unusual alkaline hydrolysis. In 1933 Strack and Schwaneberg described the preparation of methylmalononitrile from ethyl 2-bromopropionate in a three step procedure (*Ber.* **1933**, 66(9), 1330–1333). Other alkylmalononitriles (e.g. ethylmalononitrile) can be prepared in a single step procedure by the reductive alkylation of malononitrile with aldehydes or ketones in the presence of sodium borohydride (F. Tayyari, D. E. Wood, P. E. Fanwick, R. E. Sammelson, *Synthesis*, **2008**, 279-285.).

Van der Plas et al. (*Tetrahedron* **1988**, 44(10), 2977-2983. *Tetrahedron* **1989**, 45(16), 5151-5162) used sodium hydride to deprotonate 5,5-dicyanopentyne. However, we found the use of lithium hydride more convenient in our studies because commercial LiH can be safely stored and shipped in pure form (unlike sodium hydride with is usually shipping in mineral oil). Commercial lithium hydride is rarely used in organic chemistry due to its low reactivity. As an example its reaction with methanol is very slow even under reflux and it does not react with tert-butanol. It does react with water immediately, but unlike sodium or potassium hydride the nasc. hydrogen does not ignite in air.

We store our LiH in a Schlenk-flask, below you see a powder diffraction pattern of the commercial lithiumhydride we used. The colored lines represent the comparison with a data base.

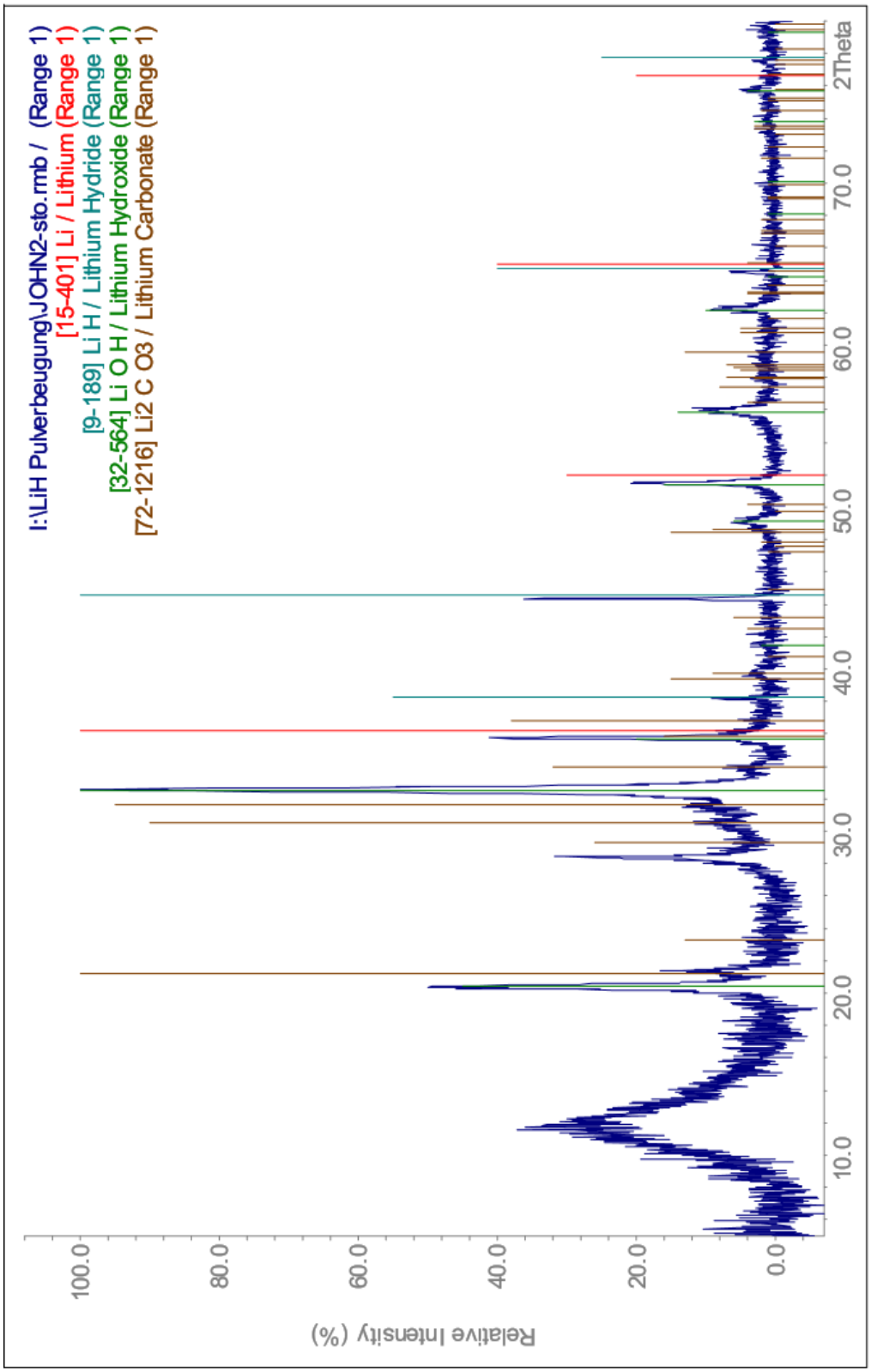


Figure S1: Powder diffraction pattern of the commercial lithium hydride used

It can clearly be seen that commercial lithium hydride contains lithium carbonate and lithium hydroxide. There is another impurity present we could not identify (28°), the compound we used is grey, not colourless.

2,2'-(Pyrimidine-2,4-diyl)bis(2-methylmalononitrile) ***10***

The solid state structure of **10** shows a disorder similar to the one described in the main text, but in this structure stereoisomerism does not complicate the matter further. Bond angles and distances are given in the following table (for general crystallographic information see main text).

Table S2: selected interatomic distances (Å) and angles (°)

C22-N13	1.138(2)	C13-N11	1.141(2)
C21-N14	1.143(2)	C11-N12	1.141(2)
C23-C21	1.480(2)	N14-C21-C23	178.1(1)
C23-C22	1.485(2)	N13-C22-C23	178.6(1)
C12-C13	1.482(2)	N11-C13-C12	176.4(1)
C12-C11	1.481(2)	N12-C11-C12	178.5(1)
C2-C12	1.530(2)	C24-C23-C6-N1	77.8(1)
C6-C23	1.532(2)	C14-C12-C2-N1	74.2(1)

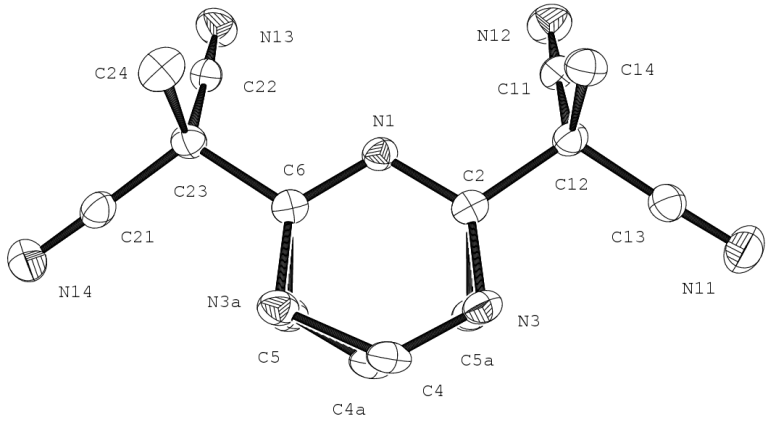


Figure S3: Solid state structure of **10** (ellipsoids drawn at the 50% probability level)

10 was usually used without recrystallization to prepare **4**. The main impurity is presumably one of the two possible monosubstituted pyrimidines (and THF, cf. Figure S4).

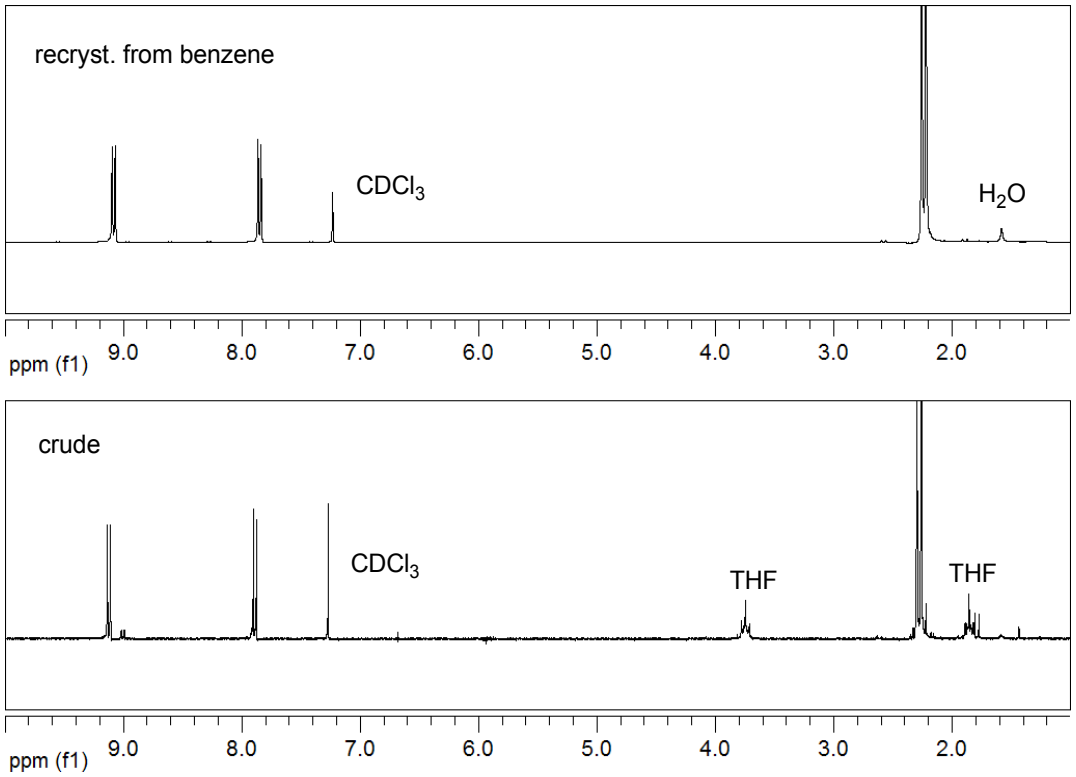


Figure S4: ^{1}H-NMR of crude and recryst. **10**

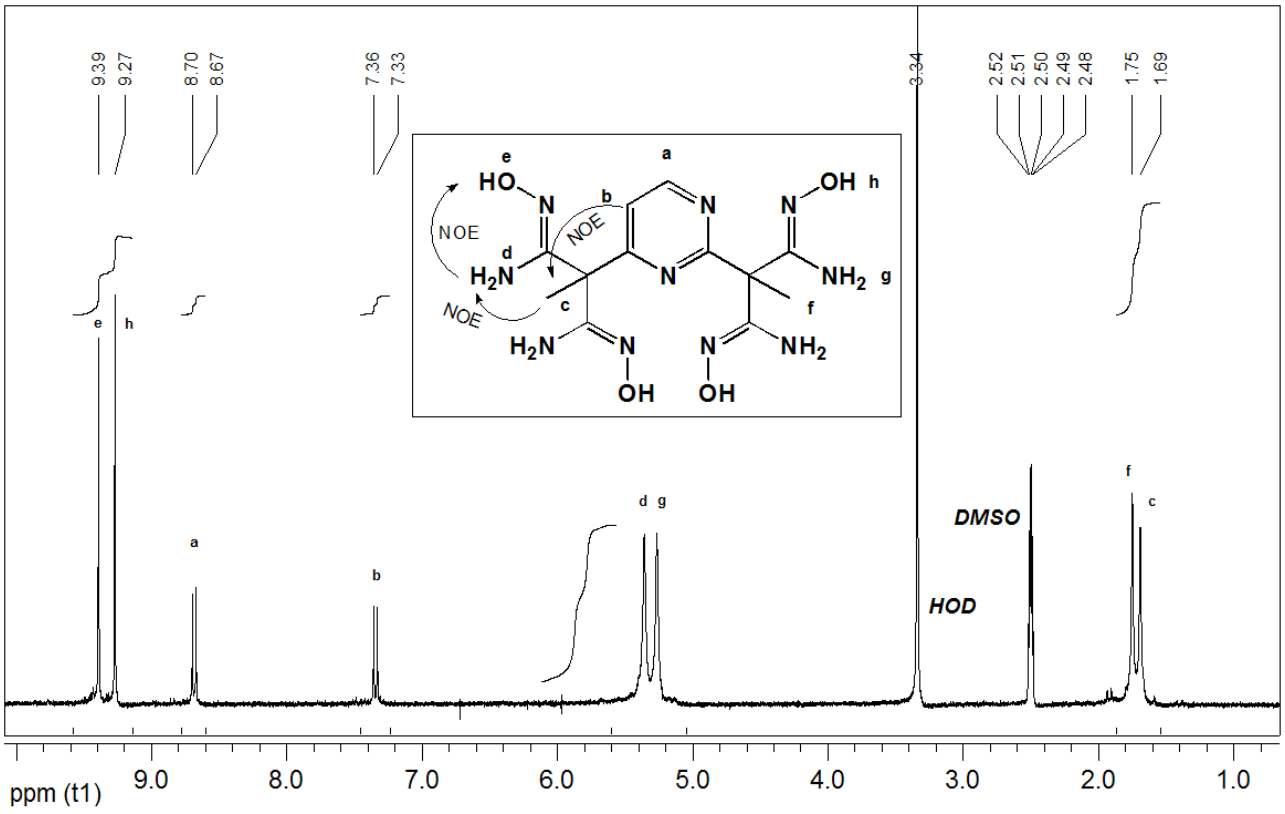


Figure S5: 200 MHz ^{1}H-NMR of ligand **4** with 2D ^{1}H-^{1}H NOESY based assignment (minor impurities are assigned to threefold addition products, cf. main text)

*^{1}H-NMR spectroscopic analysis of **11***

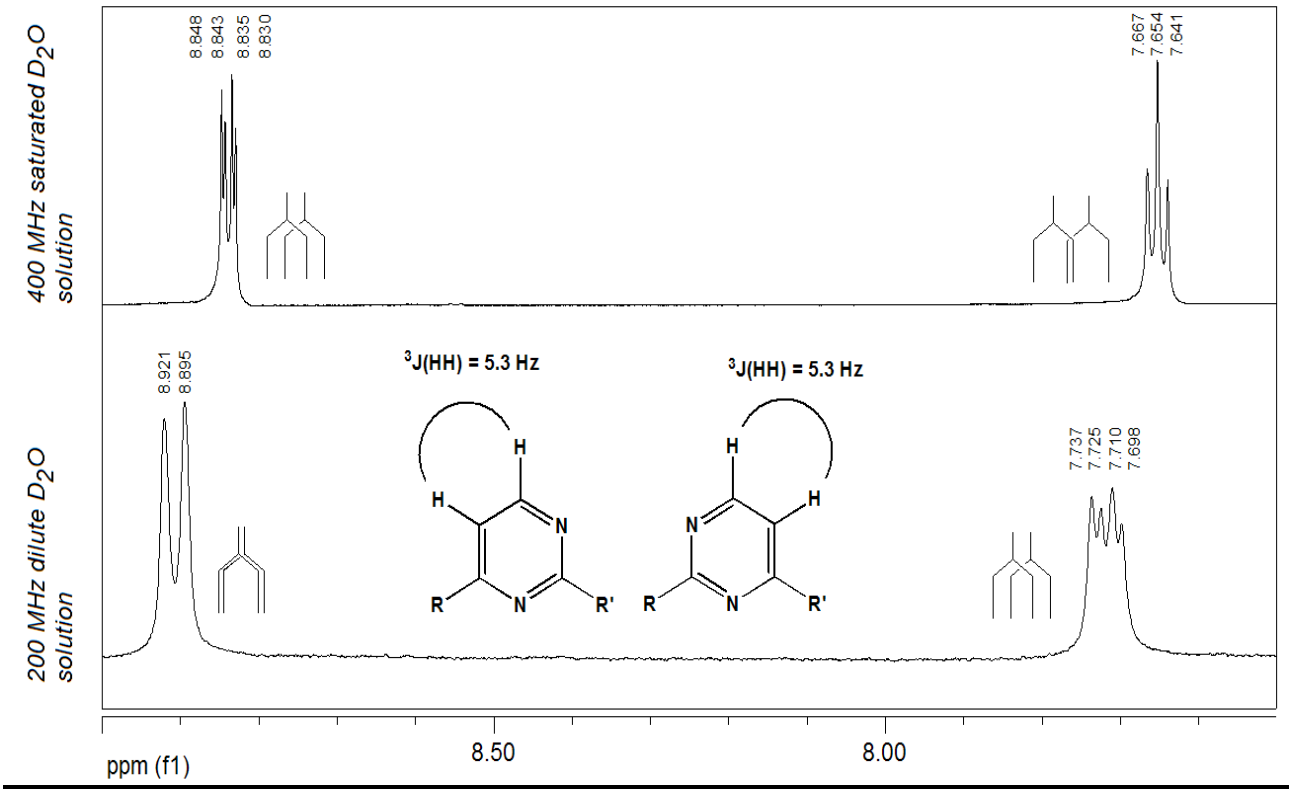


Figure S6: field and concentration dependent ^{1}H-NMR resonances of **11** in D_2O

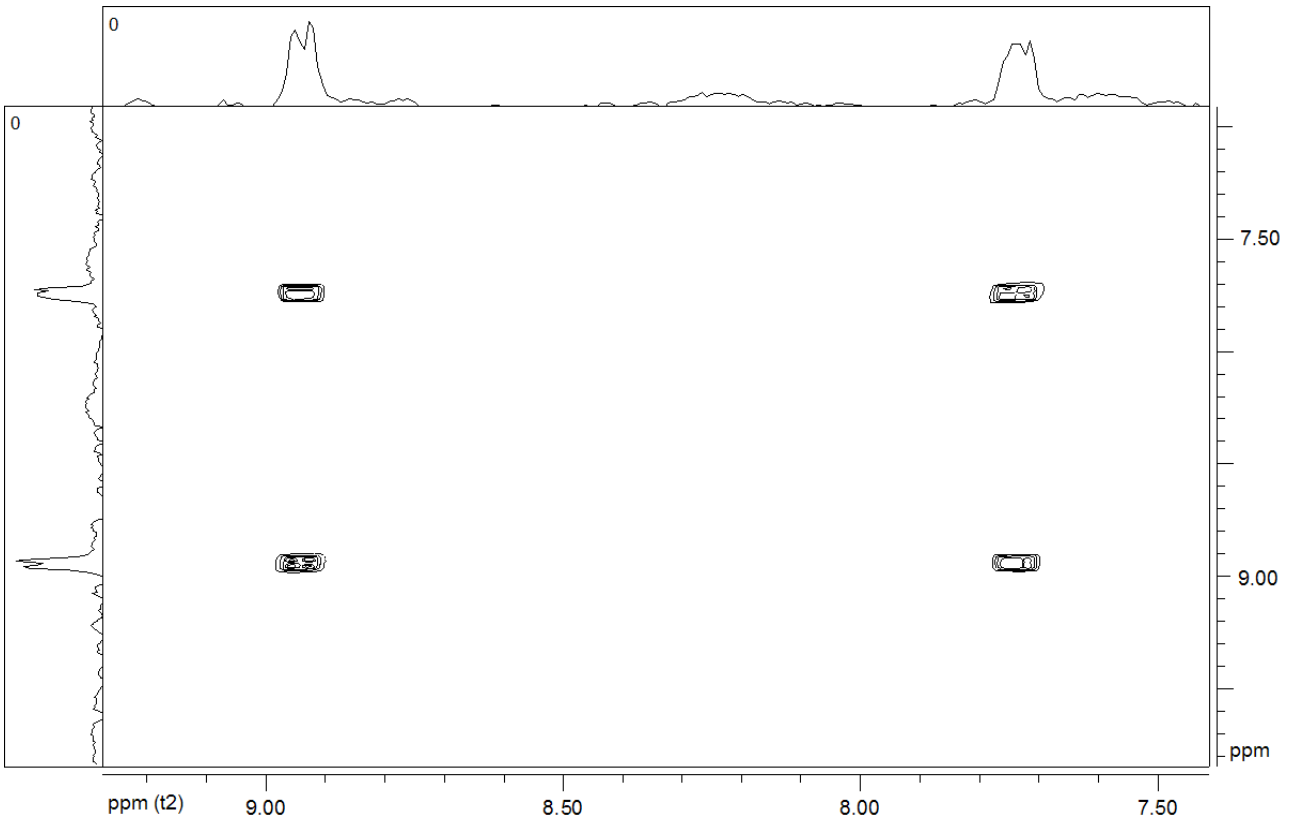


Figure S7: 200 MHz DQF-COSY, coupling of the aromatic CH-protons of **11** in D_2O

^{1}H-NMR-spectroscopy does not yield as conclusive evidence of isomery as 13C{1H}-NMR-spectroscopy, which is presented in the main text. However, field dependent signal analysis (cf. Figure S6) of the aromatic CH-resonances does show consistent behaviour, as the signals can be interpreted as being composed of overlapping doublets with analogous ^{3}J(HH) coupling constants of 5.3 Hz. Within the interpretation presented in the main text, this behaviour is explained by the two possible orientations of the pyrimidine ring, while the isomerism arising upon different combinations of these orientations is not resolved (Figure S7 is supposed to illustrate the coupling between the two signal groups). Comparable behaviour is observed for the singlet signals belonging to the methyl groups when different solvents are compared (DMSO and deueterium oxide, cf. Figure S8) .

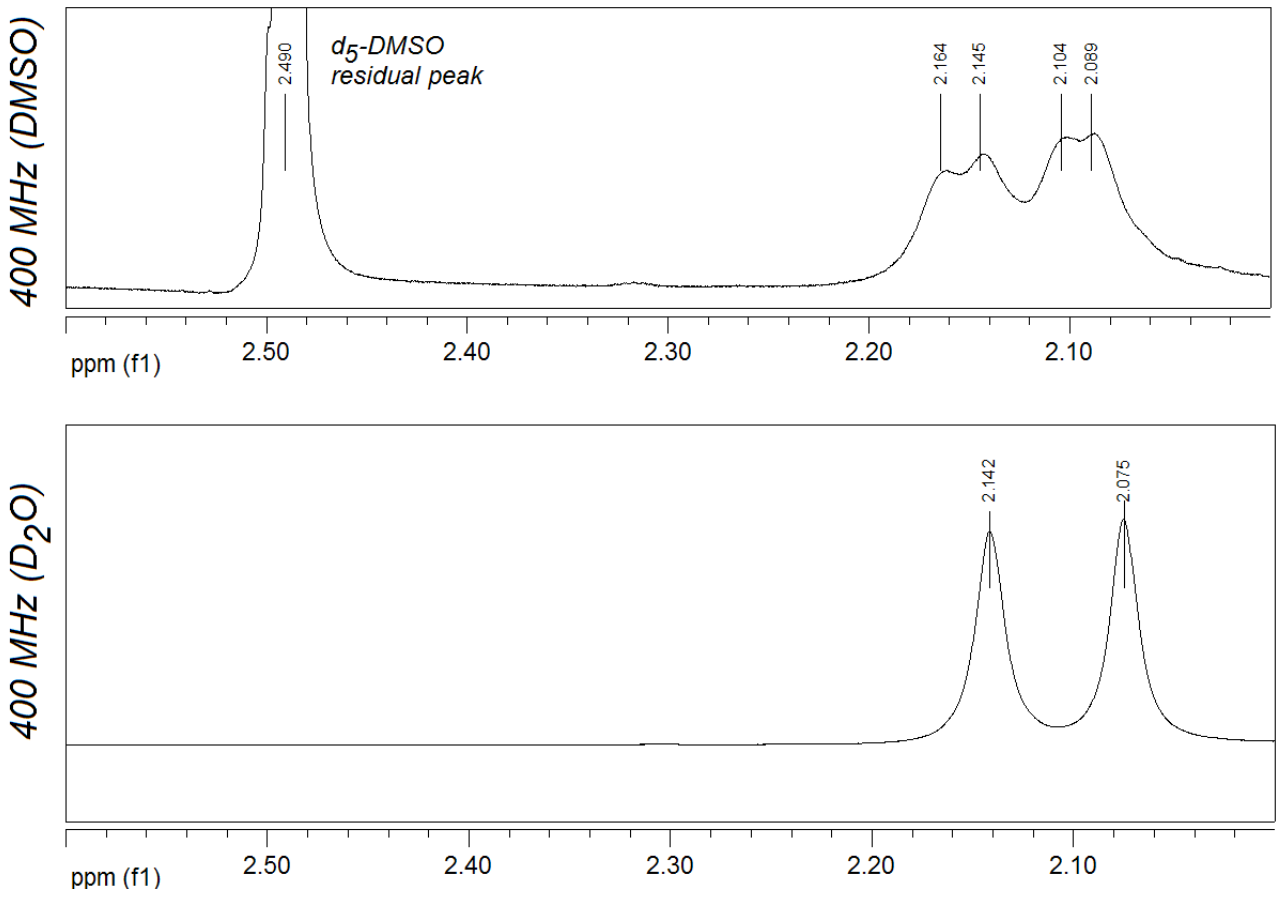
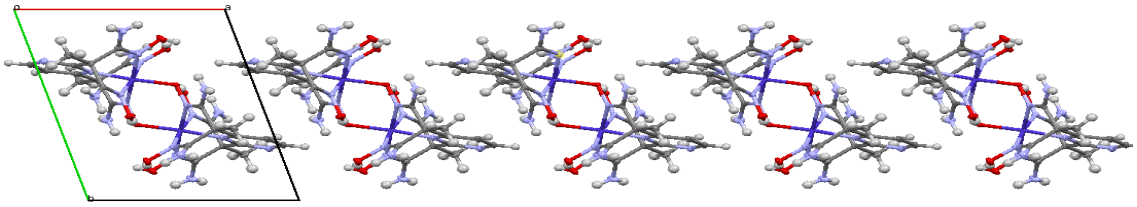


Figure S8: Solvent dependent signal form of the resonances belonging to the methyl groups of **11.**

(Note: In the experimental section of the main text, the 200 MHz 1H-Spectrum of **11** in DMSO is presented. At 200 MHz only two signals are visible in the methyl region due to lower resolution.)

*Additional information on the crystal structure of **11** · 12 H_2O*



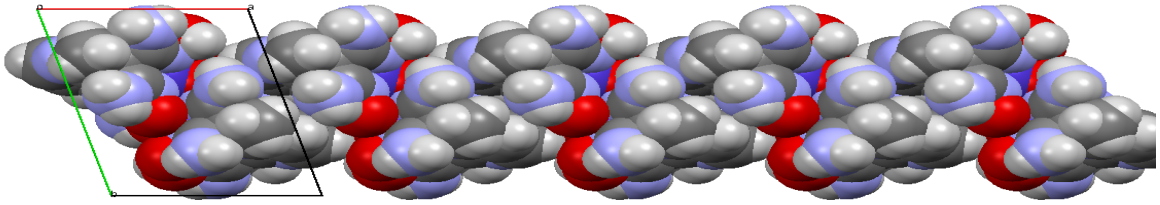


Figure S9: Ellipsoid & spacefill representation of the molecule packing

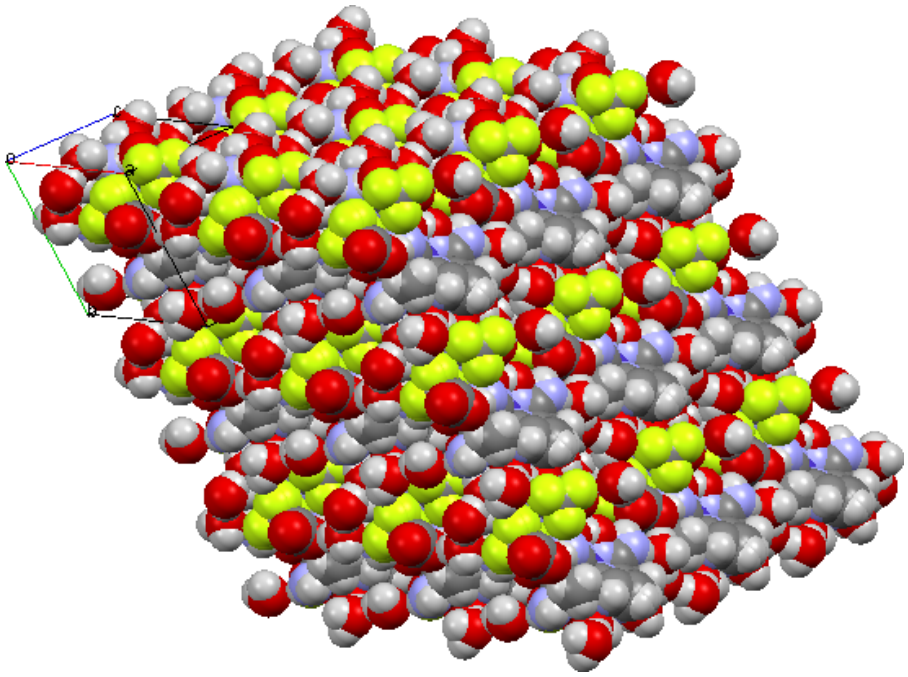


Figure S10: 3 × 3 × 3 unit cells

Table S11. Crystal data and structure refinement for **11**.

Identification code	**11 · 12 H_2O**
Empirical formula	C32 H62 Co2 F12 N20 O28
Formula weight	1520.88
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1

Unit cell dimensions	a = 9.2213(4) Å	α= 69.118(5)°.
	b = 12.9948(6) Å	β= 83.997(4)°.
	c = 13.4621(8) Å	γ = 73.435(4)°.
Volume	1444.63(13) Å^3	
Z	1	
Density (calculated)	1.748 Mg/m^3	
Absorption coefficient	0.716 mm^{-1}	
F(000)	780	
Crystal size	0.40 x 0.22 x 0.11 mm^3	
Theta range for data collection	3.28 to 25.00°.	
Index ranges	-10<=h<=10, -12<=k<=15, -11<=l<=15	
Reflections collected	10144	
Independent reflections	5065 [R(int) = 0.0292]	
Completeness to theta = 25.00°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9254 and 0.7626	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5065 / 110 / 535	
Goodness-of-fit on F^2	0.973	
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0892	
R indices (all data)	R1 = 0.0534, wR2 = 0.0928	
Largest diff. peak and hole	0.555 and -0.327 e.Å^{-3}	

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for boyd30. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(25B)	10260(20)	7100(30)	3887(19)	15(3)
C(26B)	9620(30)	6790(40)	3200(30)	15(3)

N(26B)	9550(30)	7280(40)	4760(20)	18(2)
C(25A)	10150(20)	7220(30)	3659(19)	15(3)
C(26A)	9560(30)	7330(40)	4620(30)	18(2)
N(26A)	9490(20)	6860(30)	3060(20)	15(3)
Co(1)	5661(1)	6332(1)	4760(1)	11(1)
O(8)	6464(2)	4409(2)	6771(2)	18(1)
O(11)	3563(2)	8457(2)	4799(2)	24(1)
O(3)	6299(2)	3953(1)	4967(1)	12(1)
O(10)	3505(2)	7950(2)	3115(2)	19(1)
C(19)	8200(3)	7073(2)	4952(2)	14(1)
C(20)	8199(3)	6621(2)	3424(2)	14(1)
N(4)	7533(2)	6720(2)	4337(2)	13(1)
N(2)	6418(2)	5029(2)	4328(2)	12(1)
N(5)	6524(2)	5521(2)	6152(2)	13(1)
N(12)	7611(3)	4207(2)	3090(2)	19(1)
N(13)	7794(3)	5411(2)	7604(2)	18(1)
N(14)	5295(3)	8870(2)	5982(2)	22(1)
N(15)	5225(3)	7654(2)	1522(2)	20(1)
N(7)	4979(2)	7221(2)	3336(2)	13(1)
N(6)	4960(2)	7659(2)	5164(2)	14(1)
C(22)	7329(3)	6269(2)	2741(2)	14(1)
C(17)	7366(3)	7151(2)	5990(2)	14(1)
C(27)	8203(3)	6240(2)	1719(2)	18(1)
C(28)	8244(3)	7590(2)	6579(2)	20(1)
C(23)	7090(3)	5094(2)	3416(2)	14(1)
C(16)	7201(3)	5958(2)	6633(2)	14(1)
C(21)	5744(3)	7122(2)	2499(2)	14(1)
C(18)	5766(3)	7962(2)	5694(2)	15(1)
C(30)	151(4)	9391(3)	7303(3)	34(1)
C(29)	1418(3)	9237(3)	6516(3)	26(1)
O(32)	2133(2)	9982(2)	6218(2)	33(1)
O(31)	1603(2)	8395(2)	6224(2)	36(1)
F(33)	334(3)	9945(2)	7906(2)	72(1)
F(34)	-114(2)	8414(2)	7944(2)	50(1)
F(35)	-1143(2)	10007(2)	6766(2)	61(1)
C(36)	7569(3)	3690(3)	436(2)	24(1)
C(37)	6222(4)	3228(3)	1002(3)	36(1)
O(38)	7993(3)	3478(2)	-388(2)	36(1)

O(39)	8090(2)	4222(2)	860(2)	25(1)
F(38)	5690(13)	3555(12)	1819(7)	67(3)
F(37)	5061(9)	3608(14)	348(11)	66(3)
F(36)	6609(15)	2088(7)	1383(9)	65(3)
F(38A)	6040(20)	3212(19)	1988(10)	70(5)
F(37A)	4944(14)	3800(20)	485(18)	80(6)
F(36A)	6370(20)	2175(9)	1022(13)	63(4)
O(800)	5887(3)	9680(2)	7630(2)	34(1)
O(400)	8735(2)	6164(2)	9170(2)	22(1)
O(500)	7011(3)	8179(2)	9552(2)	29(1)
O(300)	8371(3)	9300(2)	503(2)	46(1)
O(600)	6943(3)	9129(2)	2421(2)	39(1)
O(700)	1661(3)	8507(2)	873(2)	48(1)

Table S13. Bond lengths [Å] and angles [°] for boyd30.

C(25B)-N(26B)	1.341(14)
C(25B)-C(26B)	1.372(15)
C(25B)-H(25B)	0.9500
C(26B)-C(20)	1.378(16)
C(26B)-H(26B)	0.9500
N(26B)-C(19)	1.325(13)
C(25A)-N(26A)	1.334(13)
C(25A)-C(26A)	1.390(16)
C(25A)-H(25A)	0.9500
C(26A)-C(19)	1.380(16)
C(26A)-H(26A)	0.9500
N(26A)-C(20)	1.317(13)
Co(1)-N(2)	1.907(2)
Co(1)-N(4)	1.909(2)
Co(1)-N(6)	1.911(2)
Co(1)-N(7)	1.913(2)
Co(1)-N(5)	1.919(2)
Co(1)-O(3)#1	1.9196(17)
O(8)-N(5)	1.401(3)
O(8)-H(8)	0.77(3)
O(11)-N(6)	1.408(3)
O(11)-H(11)	0.90(3)

O(3)-N(2)	1.384(3)
O(3)-Co(1)#1	1.9196(17)
O(10)-N(7)	1.408(3)
O(10)-H(10)	0.79(3)
C(19)-N(4)	1.347(3)
C(19)-C(17)	1.545(4)
C(20)-N(4)	1.348(3)
C(20)-C(22)	1.537(4)
N(2)-C(23)	1.302(3)
N(5)-C(16)	1.297(3)
N(12)-C(23)	1.324(4)
N(12)-H(12A)	0.86(3)
N(12)-H(12B)	0.76(3)
N(13)-C(16)	1.333(4)
N(13)-H(13A)	0.87(3)
N(13)-H(13B)	0.85(3)
N(14)-C(18)	1.316(4)
N(14)-H(14A)	0.79(3)
N(14)-H(14B)	0.79(3)
N(15)-C(21)	1.316(4)
N(15)-H(15A)	0.82(3)
N(15)-H(15B)	0.82(3)
N(7)-C(21)	1.293(3)
N(6)-C(18)	1.301(4)
C(22)-C(27)	1.527(4)
C(22)-C(23)	1.538(4)
C(22)-C(21)	1.545(4)
C(17)-C(28)	1.525(4)
C(17)-C(16)	1.525(4)
C(17)-C(18)	1.544(4)
C(27)-H(27A)	0.9650
C(27)-H(27B)	0.9650
C(27)-H(27C)	0.9650
C(28)-H(28A)	0.9957
C(28)-H(28B)	0.9957
C(28)-H(28C)	0.9957
C(30)-F(33)	1.313(4)
C(30)-F(34)	1.329(4)

C(30)-F(35)	1.345(4)
C(30)-C(29)	1.512(4)
C(29)-O(32)	1.251(4)
C(29)-O(31)	1.252(4)
C(36)-O(38)	1.235(4)
C(36)-O(39)	1.250(4)
C(36)-C(37)	1.544(4)
C(37)-F(38A)	1.314(12)
C(37)-F(37A)	1.315(12)
C(37)-F(38)	1.316(8)
C(37)-F(37)	1.323(8)
C(37)-F(36A)	1.327(11)
C(37)-F(36)	1.334(8)
O(800)-H(801)	0.81(4)
O(800)-H(802)	0.99(3)
O(400)-H(401)	0.92(3)
O(400)-H(402)	0.85(3)
O(500)-H(502)	0.82(3)
O(500)-H(501)	0.91(3)
O(300)-H(301)	0.985(10)
O(300)-H(302)	0.962(10)
O(600)-H(601)	1.063(19)
O(600)-H(602)	0.993(19)
O(700)-H(701)	0.90(3)
O(700)-H(702)	0.94(3)

N(26B)-C(25B)-C(26B)	123.2(13)
N(26B)-C(25B)-H(25B)	118.4
C(26B)-C(25B)-H(25B)	118.4
C(25B)-C(26B)-C(20)	118.5(17)
C(25B)-C(26B)-H(26B)	120.7
C(20)-C(26B)-H(26B)	120.7
C(19)-N(26B)-C(25B)	115.8(14)
N(26A)-C(25A)-C(26A)	123.5(12)
N(26A)-C(25A)-H(25A)	118.2
C(26A)-C(25A)-H(25A)	118.2
C(19)-C(26A)-C(25A)	117.6(18)
C(19)-C(26A)-H(26A)	121.2

C(25A)-C(26A)-H(26A)	121.2
C(20)-N(26A)-C(25A)	115.9(14)
N(2)-Co(1)-N(4)	89.35(9)
N(2)-Co(1)-N(6)	177.94(10)
N(4)-Co(1)-N(6)	88.66(9)
N(2)-Co(1)-N(7)	88.95(9)
N(4)-Co(1)-N(7)	87.18(9)
N(6)-Co(1)-N(7)	90.40(9)
N(2)-Co(1)-N(5)	92.63(9)
N(4)-Co(1)-N(5)	86.65(9)
N(6)-Co(1)-N(5)	87.80(9)
N(7)-Co(1)-N(5)	173.62(9)
N(2)-Co(1)-O(3)#1	90.92(8)
N(4)-Co(1)-O(3)#1	173.81(9)
N(6)-Co(1)-O(3)#1	90.99(8)
N(7)-Co(1)-O(3)#1	86.64(8)
N(5)-Co(1)-O(3)#1	99.51(8)
N(5)-O(8)-H(8)	102(3)
N(6)-O(11)-H(11)	105(2)
N(2)-O(3)-Co(1)#1	119.32(14)
N(7)-O(10)-H(10)	98(2)
N(26B)-C(19)-N(4)	124.2(11)
N(26B)-C(19)-C(26A)	7(3)
N(4)-C(19)-C(26A)	118.4(13)
N(26B)-C(19)-C(17)	119.1(11)
N(4)-C(19)-C(17)	116.5(2)
C(26A)-C(19)-C(17)	125.1(13)
N(26A)-C(20)-N(4)	124.6(11)
N(26A)-C(20)-C(26B)	9(3)
N(4)-C(20)-C(26B)	118.0(13)
N(26A)-C(20)-C(22)	118.6(10)
N(4)-C(20)-C(22)	116.7(2)
C(26B)-C(20)-C(22)	125.2(13)
C(19)-N(4)-C(20)	119.9(2)
C(19)-N(4)-Co(1)	120.55(17)
C(20)-N(4)-Co(1)	119.52(18)
C(23)-N(2)-O(3)	115.8(2)
C(23)-N(2)-Co(1)	122.04(19)

O(3)-N(2)-Co(1)	122.16(15)
C(16)-N(5)-O(8)	112.5(2)
C(16)-N(5)-Co(1)	123.31(19)
O(8)-N(5)-Co(1)	124.13(16)
C(23)-N(12)-H(12A)	117(2)
C(23)-N(12)-H(12B)	123(2)
H(12A)-N(12)-H(12B)	118(3)
C(16)-N(13)-H(13A)	119(2)
C(16)-N(13)-H(13B)	121(2)
H(13A)-N(13)-H(13B)	119(3)
C(18)-N(14)-H(14A)	116(2)
C(18)-N(14)-H(14B)	125(2)
H(14A)-N(14)-H(14B)	116(3)
C(21)-N(15)-H(15A)	116(2)
C(21)-N(15)-H(15B)	123(2)
H(15A)-N(15)-H(15B)	120(3)
C(21)-N(7)-O(10)	113.7(2)
C(21)-N(7)-Co(1)	123.92(18)
O(10)-N(7)-Co(1)	121.92(16)
C(18)-N(6)-O(11)	114.7(2)
C(18)-N(6)-Co(1)	123.91(18)
O(11)-N(6)-Co(1)	121.03(17)
C(27)-C(22)-C(20)	110.3(2)
C(27)-C(22)-C(23)	111.9(2)
C(20)-C(22)-C(23)	107.6(2)
C(27)-C(22)-C(21)	111.3(2)
C(20)-C(22)-C(21)	108.6(2)
C(23)-C(22)-C(21)	107.0(2)
C(28)-C(17)-C(16)	112.9(2)
C(28)-C(17)-C(18)	111.1(2)
C(16)-C(17)-C(18)	108.0(2)
C(28)-C(17)-C(19)	110.0(2)
C(16)-C(17)-C(19)	106.6(2)
C(18)-C(17)-C(19)	108.0(2)
C(22)-C(27)-H(27A)	109.5
C(22)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(22)-C(27)-H(27C)	109.5

H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(17)-C(28)-H(28A)	109.5
C(17)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(17)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
N(2)-C(23)-N(12)	123.4(3)
N(2)-C(23)-C(22)	115.9(2)
N(12)-C(23)-C(22)	120.7(2)
N(5)-C(16)-N(13)	124.1(3)
N(5)-C(16)-C(17)	115.5(2)
N(13)-C(16)-C(17)	120.3(2)
N(7)-C(21)-N(15)	124.1(3)
N(7)-C(21)-C(22)	114.0(2)
N(15)-C(21)-C(22)	121.8(2)
N(6)-C(18)-N(14)	124.5(3)
N(6)-C(18)-C(17)	114.7(2)
N(14)-C(18)-C(17)	120.8(3)
F(33)-C(30)-F(34)	107.2(3)
F(33)-C(30)-F(35)	106.0(3)
F(34)-C(30)-F(35)	105.9(3)
F(33)-C(30)-C(29)	114.6(3)
F(34)-C(30)-C(29)	113.6(3)
F(35)-C(30)-C(29)	109.0(3)
O(32)-C(29)-O(31)	127.8(3)
O(32)-C(29)-C(30)	116.0(3)
O(31)-C(29)-C(30)	116.1(3)
O(38)-C(36)-O(39)	128.4(3)
O(38)-C(36)-C(37)	114.7(3)
O(39)-C(36)-C(37)	116.9(3)
F(38A)-C(37)-F(37A)	109.0(14)
F(38A)-C(37)-F(38)	20.4(15)
F(37A)-C(37)-F(38)	90.9(13)
F(38A)-C(37)-F(37)	121.5(11)
F(37A)-C(37)-F(37)	15.3(19)
F(38)-C(37)-F(37)	104.9(9)

F(38A)-C(37)-F(36A)	107.5(13)
F(37A)-C(37)-F(36A)	102.5(14)
F(38)-C(37)-F(36A)	122.2(10)
F(37)-C(37)-F(36A)	89.7(11)
F(38A)-C(37)-F(36)	88.2(12)
F(37A)-C(37)-F(36)	120.6(12)
F(38)-C(37)-F(36)	105.9(9)
F(37)-C(37)-F(36)	109.8(9)
F(36A)-C(37)-F(36)	22.4(11)
F(38A)-C(37)-C(36)	113.0(9)
F(37A)-C(37)-C(36)	112.3(9)
F(38)-C(37)-C(36)	113.9(7)
F(37)-C(37)-C(36)	110.7(7)
F(36A)-C(37)-C(36)	111.9(8)
F(36)-C(37)-C(36)	111.3(6)
H(801)-O(800)-H(802)	101(3)
H(401)-O(400)-H(402)	103(3)
H(502)-O(500)-H(501)	109(3)
H(301)-O(300)-H(302)	82(3)
H(601)-O(600)-H(602)	99(3)
H(701)-O(700)-H(702)	96(3)

Symmetry transformations used to generate equivalent atoms:

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

Table S14. Anisotropic displacement parameters ($Å^2$ x 10^3)for boyd30. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(25B)	10(2)	17(6)	15(8)	0(8)	-2(4)	-4(4)
C(26B)	10(3)	17(4)	15(6)	-3(5)	-2(4)	-1(4)
N(26B)	16(2)	18(4)	20(6)	-6(5)	-3(2)	-5(1)
C(25A)	10(2)	17(6)	15(8)	0(8)	-2(4)	-4(4)
C(26A)	16(2)	18(4)	20(6)	-6(5)	-3(2)	-5(1)
N(26A)	10(3)	17(4)	15(6)	-3(5)	-2(4)	-1(4)
Co(1)	9(1)	14(1)	11(1)	-6(1)	-1(1)	-3(1)
O(8)	24(1)	16(1)	16(1)	-4(1)	-3(1)	-8(1)

O(11)	16(1)	24(1)	29(1)	-13(1)	-7(1)	5(1)
O(3)	11(1)	11(1)	14(1)	-4(1)	-1(1)	-3(1)
O(10)	13(1)	22(1)	20(1)	-9(1)	-4(1)	1(1)
C(19)	12(1)	12(1)	16(2)	-5(1)	-2(1)	-2(1)
C(20)	12(1)	13(1)	17(2)	-4(1)	-1(1)	-2(1)
N(4)	11(1)	14(1)	14(1)	-5(1)	-1(1)	-2(1)
N(2)	10(1)	14(1)	13(1)	-5(1)	0(1)	-4(1)
N(5)	14(1)	13(1)	14(1)	-4(1)	-1(1)	-5(1)
N(12)	27(1)	19(1)	13(1)	-8(1)	5(1)	-6(1)
N(13)	23(1)	17(1)	16(2)	-5(1)	-8(1)	-6(1)
N(14)	21(1)	20(1)	26(2)	-14(1)	-8(1)	0(1)
N(15)	17(1)	28(2)	13(1)	-7(1)	-2(1)	0(1)
N(7)	9(1)	14(1)	17(1)	-6(1)	-1(1)	-1(1)
N(6)	11(1)	15(1)	16(1)	-6(1)	-3(1)	1(1)
C(22)	12(1)	16(1)	14(2)	-7(1)	1(1)	-3(1)
C(17)	11(1)	17(2)	16(2)	-8(1)	-1(1)	-4(1)
C(27)	19(2)	21(2)	14(2)	-7(1)	2(1)	-3(1)
C(28)	22(2)	21(2)	22(2)	-10(1)	-5(1)	-8(1)
C(23)	8(1)	19(2)	14(2)	-8(1)	-2(1)	-2(1)
C(16)	8(1)	18(2)	16(2)	-10(1)	1(1)	-1(1)
C(21)	14(1)	14(1)	15(2)	-5(1)	-2(1)	-5(1)
C(18)	17(2)	15(2)	13(2)	-5(1)	1(1)	-4(1)
C(30)	32(2)	35(2)	44(2)	-23(2)	1(2)	-12(2)
C(29)	23(2)	26(2)	33(2)	-18(2)	0(1)	-3(1)
O(32)	31(1)	29(1)	42(2)	-15(1)	5(1)	-11(1)
O(31)	33(1)	31(1)	51(2)	-22(1)	9(1)	-10(1)
F(33)	68(2)	112(2)	90(2)	-84(2)	43(2)	-56(2)
F(34)	52(1)	56(2)	44(1)	-18(1)	16(1)	-24(1)
F(35)	29(1)	58(2)	80(2)	-22(1)	5(1)	6(1)
C(36)	29(2)	20(2)	20(2)	-3(1)	-2(1)	-7(1)
C(37)	32(2)	42(2)	41(2)	-17(2)	-2(2)	-16(2)
O(38)	54(2)	34(1)	24(1)	-13(1)	4(1)	-18(1)
O(39)	27(1)	27(1)	27(1)	-13(1)	4(1)	-12(1)
F(38)	42(5)	128(8)	68(5)	-67(6)	32(4)	-47(5)
F(37)	44(4)	97(6)	75(4)	-29(3)	-24(3)	-36(4)
F(36)	71(4)	46(3)	69(7)	3(3)	5(4)	-31(2)
F(38A)	62(8)	139(11)	31(4)	-24(5)	14(4)	-75(8)
F(37A)	37(5)	92(8)	86(8)	-4(7)	-6(5)	-12(4)

F(36A)	69(7)	41(4)	91(10)	-26(5)	28(7)	-36(4)
O(800)	38(2)	35(1)	33(2)	-13(1)	-1(1)	-11(1)
O(400)	24(1)	25(1)	18(1)	-7(1)	-2(1)	-9(1)
O(500)	34(1)	28(1)	24(1)	-13(1)	0(1)	-4(1)
O(300)	58(2)	42(2)	47(2)	-21(1)	-2(1)	-19(1)
O(600)	34(1)	37(1)	52(2)	-21(1)	2(1)	-12(1)
O(700)	61(2)	36(2)	47(2)	-24(1)	-4(1)	-1(1)

Table S15: Specified hydrogen bonds (with esds except fixed and riding H)

D-H	H...A	D...A	<(DHA)	(Å)
H-bonds in a single unit				
0.79(3)	1.80(3)	2.585(3)	169(3)	**O10**-H10...**O11**
0.77(3)	1.98(3)	2.725(3)	162(4)	**O8**-H8...**O3**
bifurcated H-bonds between the units				
0.79(3)	2.69(3)	2.848(3)	93(2)	**O10**-H10...**O3_$1**
** No suitable H-bond found for O11...O3_$1 = 3.001(3) A **				
0.77(3)	2.54(3)	3.006(3)	120(3)	**O8**-H8...**O10_$1**
** No suitable H-bond found for O8...O11_$1 = 4.900(3) A **				
H-bonds to the first trifluoroacetate				
0.90(3)	1.61(3)	2.491(3)	164(3)	**O11**-H11...**O31**
0.79(3)	2.14(3)	2.902(3)	161(3)	**N14**-H14A...**O32**
H-bond to the second trifluoroacetate				
0.76(3)	2.23(3)	2.981(3)	170(3)	**N12**-H12B...**O39**
H-bond in the "arch" linking amino functions				
0.79(3)	2.19(3)	2.928(4)	155(3)	**N14**-H14B...**O800**_b
0.91(3)	1.81(3)	2.717(3)	172(3)	**O500**_b-H501_b...**O800**_b
0.82(3)	2.02(3)	2.840(3)	178(3)	**O500**_b-H502_b...**O400**_b
0.85(3)	2.10(3)	2.914(3)	161(3)	**N13**-H13B...**O400**_b

Table S16: Full HTAB analysis

Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	(Å)
O8-H8	0.772	1.979	162.46	2.725	O3
O8-H8	0.772	2.402	118.65	2.854	N7 [-x+1, -y+1, -z+1]
O8-H8	0.772	2.540	130.31	3.096	N2

O8-H8	0.772	2.543	120.19	3.006	O10 [-x+1, -y+1, -z+1]
O10-H10	0.793	1.802	169.14	2.585	O11
O10-H10	0.793	2.441	134.33	3.049	N6
N12-H12A	0.865	2.342	139.83	3.054	O31 [-x+1, -y+1, -z+1]
N12-H12B	0.756	2.233	170.45	2.981	O39
N13-H13A	0.873	2.234	138.12	2.942	O38 [x, y, z+1]
N13-H13B	0.849	2.098	161.05	2.914	O400_b
N14-H14A	0.790	2.142	161.45	2.902	O32
N14-H14B	0.789	2.194	154.76	2.928	O800_b
N15-H15A	0.821	2.513	151.65	3.259	O700_b
N15-H15B	0.820	2.132	169.22	2.941	O500_b [x, y, z-1]
O11-H11	0.898	1.615	164.17	2.491	O31
O800-H801_b	0.809	2.302	160.73	3.077	O10 [-x+1, -y+2, -z+1]
O800-H801_b	0.809	2.436	121.97	2.946	F35 [x+1, y, z]
O800-H802_b	0.990	1.661	162.00	2.621	O600_b [-x+1, -y+2, -z+1]
O400-H401_b	0.915	1.914	173.26	2.825	O39 [-x+2, -y+1, -z+1]
O400-H402_b	0.845	2.052	175.20	2.895	O39 [x, y, z+1]
O500-H502_b	0.823	2.017	178.17	2.840	O400_b
O500-H501_b	0.913	1.811	171.75	2.717	O800_b
O300-H301_b	0.985	2.042	130.40	2.784	O700_b [-x+1, -y+2, -z]
O300-H302_b	0.962	1.886	168.55	2.835	O500_b [x, y, z-1]
O600-H601_b	1.063	1.744	169.77	2.796	O32 [-x+1, -y+2, -z+1]
O600-H601_b	1.063	2.446	112.02	3.011	F33 [-x+1, -y+2, -z+1]
O600-H602_b	0.993	1.794	157.66	2.738	O300_b
O600-H602_b	0.993	2.508	111.08	3.011	F33 [-x+1, -y+2, -z+1]
O700-H701_b	0.903	1.919	166.44	2.805	O38 [-x+1, -y+1, -z]
O700-H702_b	0.944	2.124	144.88	2.946	O300_b [x-1, y, z]

End of electronic supporting information