Influence of the Lewis basicity hardness of recrystallization solvents on the coordination sphere of the complex [Co(3,5-dinitrobenzoate-O,O')$_2$]: Crystallographic and Theoretical Analysis.

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Table S1.Dielectric constants and dipole moments for water (H_2O), methanol (CH_3OH), ethanol (EtOH), dimethyl sulfoxide (DMSO), acetone (Act), and acetonitrile (ACN).

	Dielectric constant*	**Dipole moment (D)***
H_2O	80	1.85
DMSO	47	3.96
ACN	37	3.92
CH_3OH	33	1.70
EtOH	30	1.69
Act	21	2.88

* Li, C.-P.; Du, M. Role of solvents in coordination supramolecular systems. *Chem. Commun*. 2011, 47, 5958–5972. DOI: 10.1039/c1cc10935a

Table S2. Crystallographic data of complex [$Co(DNB)_2$] crystallized in acetone (Act), acetonitrile (ACN), dimethyl sulfoxide (DMSO), and water H_2O.

Crystal Data	**Act**	**ACN**	**DMSO**	**H_2O**
Chemical Formula	$C_{66}H_{74}Co_3N_{12}O_{48}$	$C_{54}H_{38}Co_3N_{18}O_{37}$	$C_{18}H_{22}CoN_4O_{16}S_2$	$C_{14}H_{22}CoN_4O_{20}$
M_r	1980.16	1707.81	673.44	625.28
Solvent for Crystallization	*Acetone*	*Acetonitrile*	*dimethylsulfoxide*	*water*
Crystalline system, space group	Triclinic, *P*-1	Triclinic, *P*-1	Monoclinic, $P2_1/n$	Triclinic, *P*-1
a, b, c (Å)	12.7882 (10), 13.2551 (10), 14.4372 (11)	11.2634 (8), 12.6777 (9), 25.2927 (18)	10.3871 (9), 5.2909 (4), 22.6353 (17)	7.1199 (3), 11.6544 (5), 15.0334 (7)
α, β, γ (°)	67.940 (2), 79.147 (3), 69.028 (3)	99.217 (3), 102.517 (3), 100.460 (3)	90, 91.788 (3) , 90	103.409 (2), 98.950 (2), 92.642 (2)
Volume, (Å^3)	2113.7 (3)	3391.5 (4)	1243.36 (17)	1194.27 (9)
Z	1	2	2	2
Temperature, (K)	100(2)	100(2)	100(2)	100(2)
Radiation type	Mo K_α	Mo K_α	Mo K_α	Mo K_α
μ (mm^{-1})	0.69	0.84	0.95	0.82
Data collection				
Diffractometer	Bruker D8 Venture	Bruker D8 Venture	Bruker D8 Venture	Bruker D8 Venture
Absorption correction	Multi-Scan method (SADABS)	Multi-Scan method (SADABS)	Multi-Scan method (SADABS)	Multi-Scan method (SADABS)
No. of measured, independent and observed reflections [I>2σ(I)]	92160, 12892, 9316	168659, 20677, 16206	20489, 2845, 2536	42405, 5469, 5113
R_{int}	0.060	0.049	0.048	0.037
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.717	0.715	0.650	0.650
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.057, 0.164, 1.14	0.036, 0.102, 1.16	0.025, 0.066, 1.10	0.022, 0.058, 1.06
No. of reflections	12892	20677	2845	5469
Refined parameters	607	1026	189	352
H-atoms treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.77, −0.94	0.54, −0.63	0.37, −0.42	0.38, −0.35

Table S3. Suggested names considering the nomenclature for compounds crystallized in water (H_2O), methanol (CH_3OH), ethanol: acetone (EtOH: Act), dimethyl sulfoxide (DMSO), acetone (Act), and acetonitrile (ACN)

H_2O	Tetraaquabis(3,5-dinitrobenzoato-κ^1O)cobalt(II) tetrahydrate.
CH_3OH	Tetrakis(methanol)bis(3,5-dinitrobenzoato-κ^1O)cobalt(II).
EtOH: Act	Tetrakis(ethanol)bis(3,5-dinitrobenzoato-κ^1O)cobalt(II).
DMSO	Diaquabis(dimethylsulfoxide-κO)bis(3,5-dinitrobenzoato-κ^1O)cobalt(II).
ACN	**1.** Acetonitrileaqua(μ-3,5-dinitrobenzoato-1κ^2O,O′:2κ^1O′)bis(μ-3,5-dinitrobenzoato-1κ^1O:2κ^1O′)-bis(μ-3,5-dinitrobenzoato-2κ^1O:3κ^1O′)-acetonitrileaqua(μ-3,5-dinitrobenzoato-3κ^2O,O′:2κ^1O′)tricobalt(II) **2.** Diacetonitrile(μ-3,5-dinitrobenzoato-1κ^2O,O′:2κ^1O′)bis(μ-3,5-dinitrobenzoato-1κ^1O:2κ^1O′)-bis(μ-3,5-dinitrobenzoato-2κ^1O:3κ^1O′)-diacetonitrile (μ-3,5-dinitrobenzoato-3κ^2O,O′:2κ^1O′)tricobalt(II) acetonitrile trisolvate

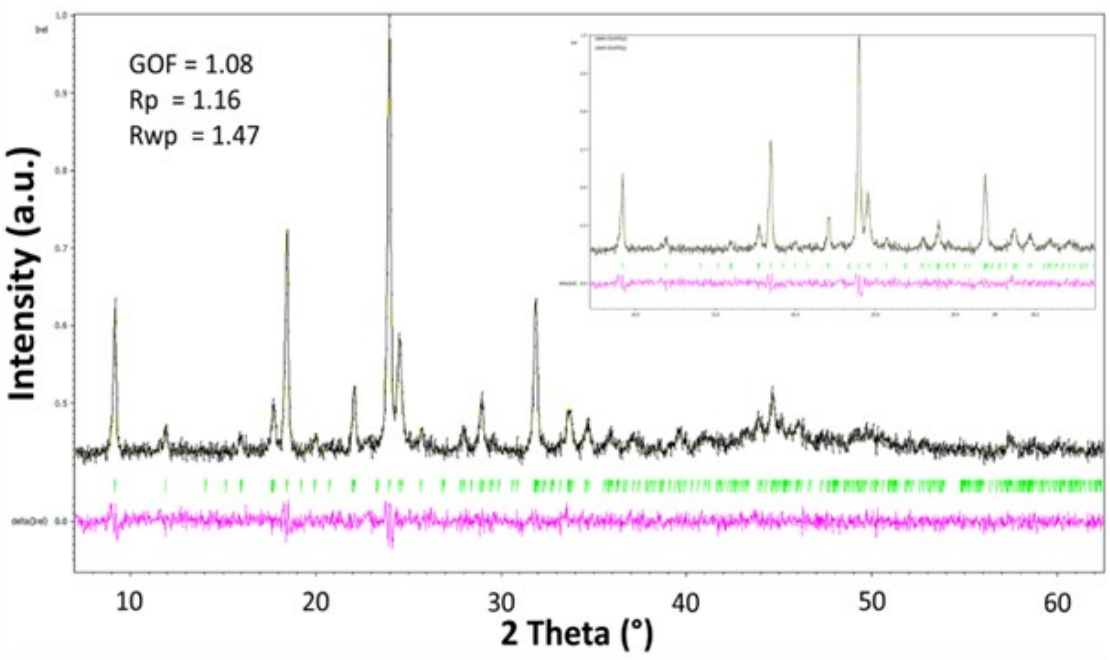

Figure S1. Graphical result of LeBail analysis of complex [Co(DNB)$_2$]. Unit cell a = 9.6586 (17) Å, b = 11.6717 (14) Å, c = 6.3204 (9) Å and β = 96.286 °, with most probably space group $P2_1/m$.

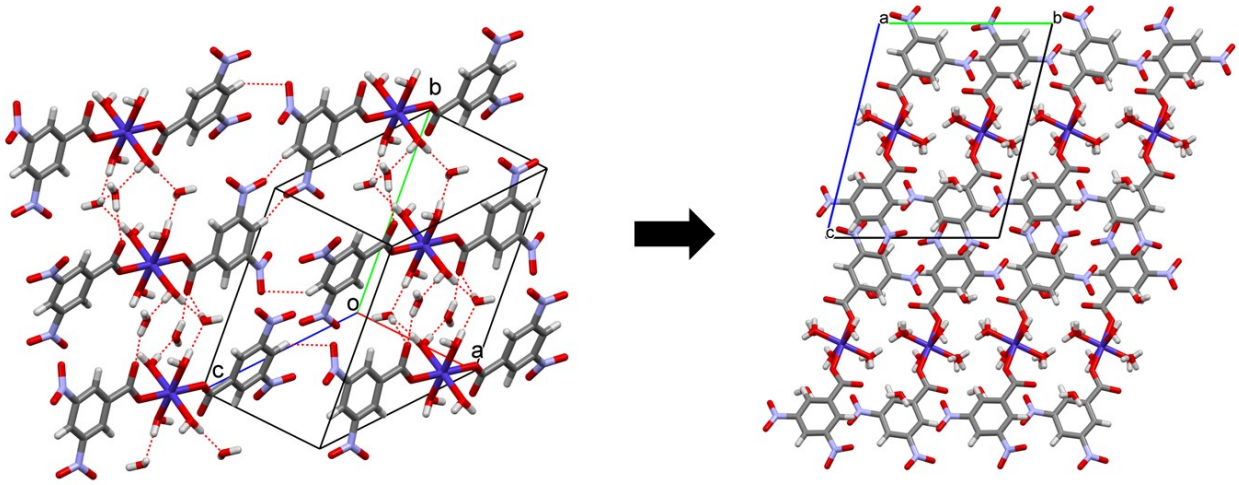

Figure S2. Packing of the complex [Co(DNB)$_2$] recrystallized in H_2O.

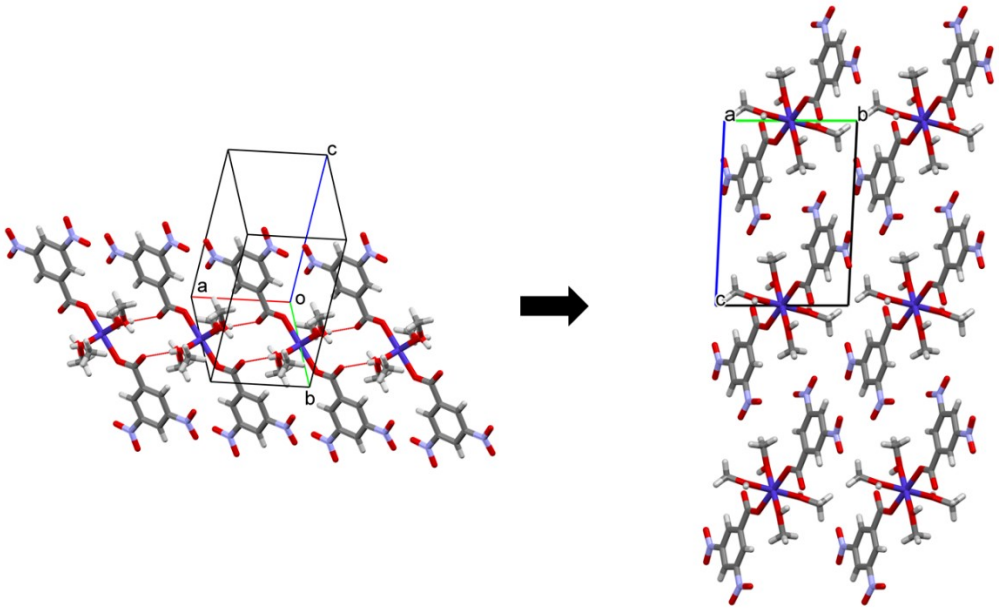

Figure S3. Packing of the complex [Co(DNB)$_2$] recrystallized in MeOH.

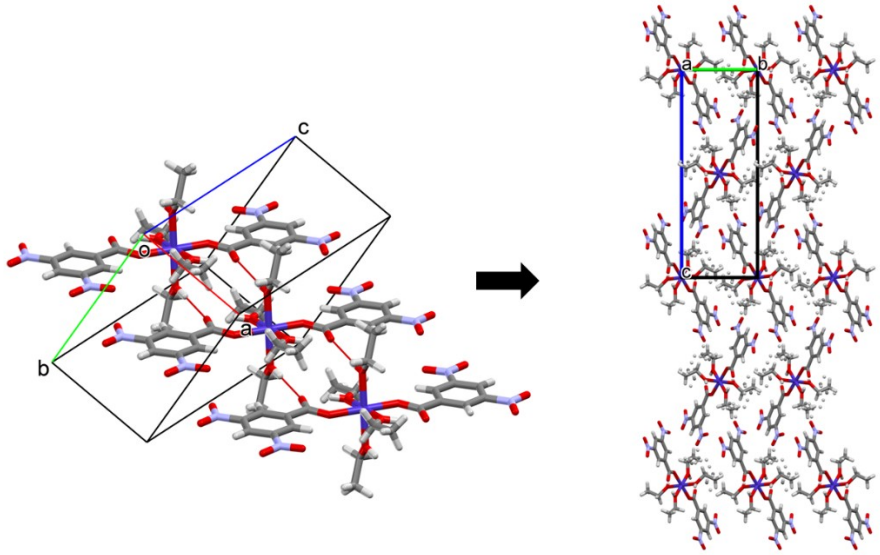

Figure S4. Packing of the complex [Co(DNB)$_2$] recrystallized in EtOH.

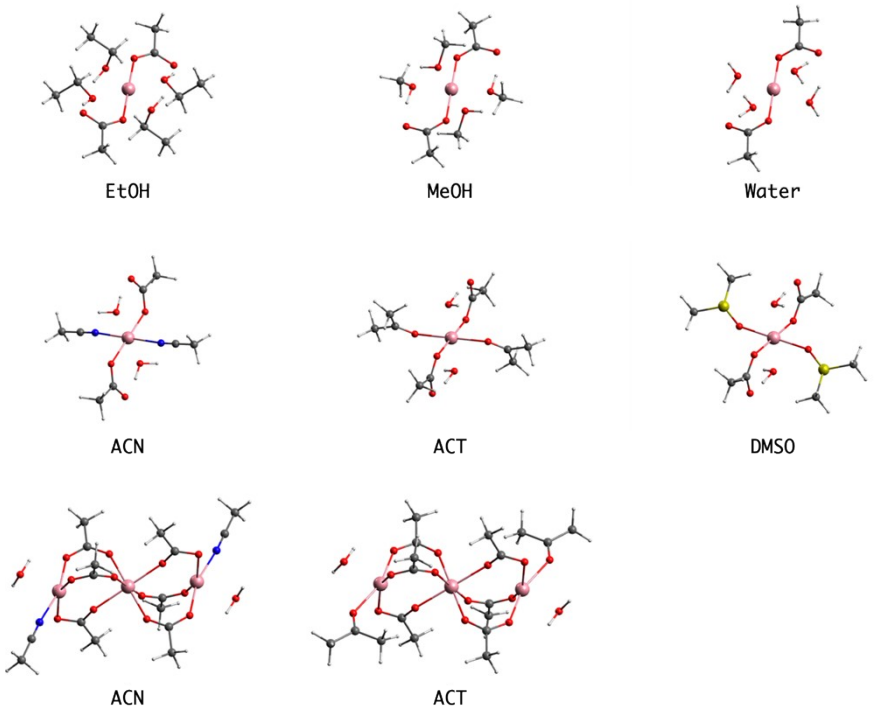

Figure S5. Optimized geometries of models of the [Co(DBN)$_2$] complex recrystallized in the different solvents.

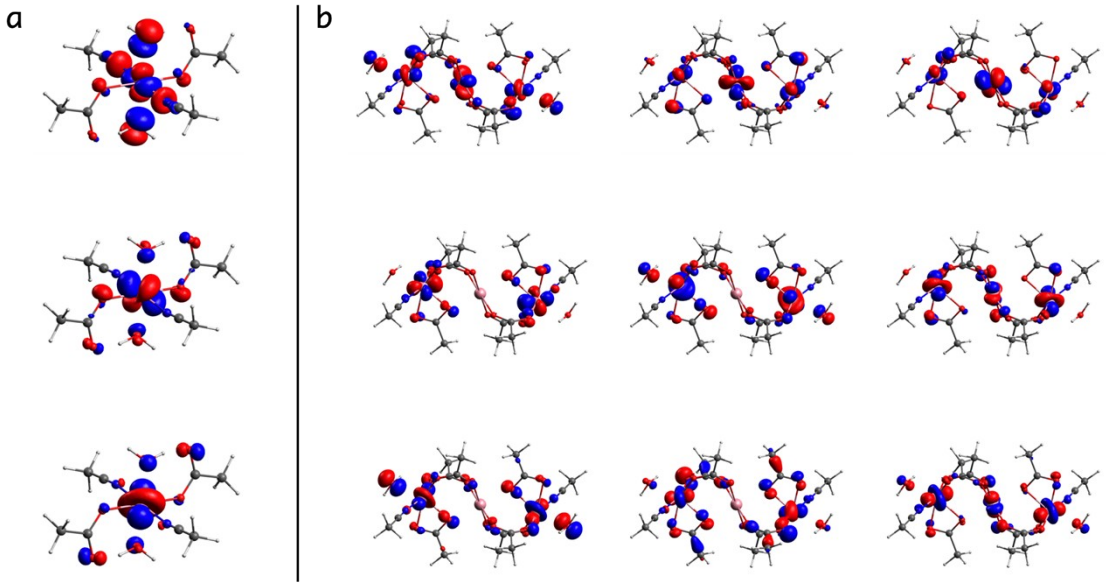

Figure S6. SOMOs of models of the [Co(DBN)$_2$] complex recrystallized in ACN. a) Mononuclear with S=3/2 ground state and b) Trinuclear with S=9/2 ground state.

Table S4. Analysis of Potential Hydrogen Bonds for complex crystallized in H_2O

Analysis of Potential Hydrogen Bonds and Schemes with d(D...A) < R(D)+R(A)+0.50, d(H...A) < R(H)+R(A)-0.12 Ang., D-H...A > 100.0 Deg

Note: - ARU codes in [] are with reference to the Coordinates printed above (Possibly transformed, when MOVE .NE. 1.555)

Nr	Typ	Res	Donor	---	H....Acceptor	[ARU]	D - H	H...A	D...A	D - H...A	A..H..A*	A'..H..A"	Sum(XY,YZ)	Sum(XZ)
1		1	O3	--H3A	..O10	[1555.05]	0.82	1.88	2.6939(13)	179				
2		1	O3	--H3B	..O7	[2766.02]	0.85	1.92	2.7703(12)	175				
3		1	O4	--H4A	..O7	[1555.02]	0.82	1.92	2.7360(12)	179				
4	Intra	1	O4	--H4B	..O11	[ ]	0.83	1.99	2.7535(13)	153				
5		1	O5	--H5A	..O8	[1555.03]	0.84	1.91	2.7552(12)	176				
6		1	O5	--H5B	..O9	[2676.04]	0.84	1.99	2.8201(13)	173				
7		1	O6	--H6A	..O8	[2676.03]	0.82	1.96	2.7760(12)	169				
8	Intra	1	O6	--H6B	..O21	[ ]	0.83	1.91	2.6915(12)	157				
9		2	O7	--H7A	..O4	[2666.01]	0.80	2.58	3.1679(12)	131				
10		2	O7	--H7A	..O5	[2666.01]	0.80	2.21	2.9241(12)	149'	75'		355	
11		2	O7	--H7B	..O11	[2766.01]	0.82	2.06	2.8297(13)	157				
12		3	O8	--H8A	..O9	[1555.04]	0.82	2.07	2.8784(13)	166				
13		3	O8	--H8B	..O3	[1455.01]	0.81	2.20	2.9427(13)	151				
14		3	O8	--H8B	..O6	[1455.01]	0.81	2.50	3.0954(12)	131'	75'		357	
15		4	O9	--H9A	..O21	[1555.01]	0.81	1.93	2.7062(13)	160				
16		4	O9	--H9B	..O1AA	[2677.01]	0.82	2.55	3.2506(12)	144				
17		5	O10	--H10A	..O13	[1556.01]	0.79	2.58	3.1001(13)	124				
18		5	O10	--H10A	..O26	[2776.01]	0.79	2.46	2.9235(14)	119'	117'		360	
19		5	O10	--H10B	..O11	[2766.01]	0.79	2.04	2.7648(13)	152				
20		1	C14	--H14	..O25	[2775.01]	0.95	2.45	3.3714(15)	164				
21		1	C24	--H24	..O14	[1456.01]	0.95	2.54	3.3232(15)	139				

Translation of ARU-Code to CIF and Equivalent Position Code

```
   [  1456.] = [  1_456] =-1+x,y,1+z
   [  1556.] = [  1_556] =x,y,1+z
   [  2677.] = [  2_677] =1-x,2-y,2-z
   [  2766.] = [  2_766] =2-x,1-y,1-z
   [  2666.] = [  2_666] =1-x,1-y,1-z
   [  2676.] = [  2_676] =1-x,2-y,1-z
   [  2776.] = [  2_776] =2-x,2-y,1-z
   [  2775.] = [  2_775] =2-x,2-y,-z
   [  1455.] = [  1_455] =-1+x,y,z
```

For C--H...Acceptor Interactions See: Th. Steiner, Cryst. Rev, (1996), 6, 1-57

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Table S5. Analysis of Potential Hydrogen Bonds for complex crystallized in MeOH

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================================================================================================================================================
Analysis of Potential Hydrogen Bonds and Schemes with d(D...A) < R(D)+R(A)+0.50, d(H...A) < R(H)+R(A)-0.12 Ang., D-H...A > 100.0 Deg
================================================================================================================================================
Note: - ARU codes in [] are with reference to the Coordinates printed above (Possibly transformed, when MOVE .NE. 1.555)
================================================================================================================================================

Nr Typ Res Donor --- H....Acceptor [    ARU  ]      D - H      H...A      D...A  D - H...A    A..H..A* A'..H..A" Sum(XY,YZ)  Sum(XZ)
------------------------------------------------------------------------------------------------------------------------------------------------
 1       1 O(7)  --H(7D)  ..O(2)    [  2665.01]    0.77(3)    1.90(3)   2.663(2)     178(4)
 2 Intra 1 O(8)  --H(8D)  ..O(2)    [         ]    0.80(3)    1.89(2) 2.6498(19)     158(2)

Translation of ARU-Code to CIF and Equivalent Position Code
============================================================
   [  2665.] = [  2_665] =1-x,1-y,-z
```

Table S6. Analysis of Potential Hydrogen Bonds for complex crystallized in EtOH

```
================================================================================================================================================
Analysis of Potential Hydrogen Bonds and Schemes with d(D...A) < R(D)+R(A)+0.50, d(H...A) < R(H)+R(A)-0.12 Ang., D-H...A > 100.0 Deg
================================================================================================================================================
Note: - ARU codes in [] are with reference to the Coordinates printed above (Possibly transformed, when MOVE .NE. 1.555)
================================================================================================================================================

Nr Typ Res Donor --- H....Acceptor [    ARU  ]      D - H      H...A      D...A  D - H...A    A..H..A* A'..H..A" Sum(XY,YZ)  Sum(XZ)
------------------------------------------------------------------------------------------------------------------------------------------------
 1       1 O7    --H7     ..O2     [  1655.01]    0.82(2)    1.90(2)   2.713(3)     169(3)
 2 Intra 1 O8    --H8     ..O2     [         ]    0.81(3)    1.85(3)   2.632(3)     162(3)

Translation of ARU-Code to CIF and Equivalent Position Code
============================================================
   [  1655.] = [  1_655] =1+x,y,z
```

Table S7. Analysis of Potential Hydrogen Bonds for complex crystallized in DMSO

```
================================================================================================================================================
Analysis of Potential Hydrogen Bonds and Schemes with d(D...A) < R(D)+R(A)+0.50, d(H...A) < R(H)+R(A)-0.12 Ang., D-H...A > 100.0 Deg
================================================================================================================================================
Note: - ARU codes in [] are with reference to the Coordinates printed above (Possibly transformed, when MOVE .NE. 1.555)
================================================================================================================================================

Nr Typ Res Donor --- H....Acceptor [    ARU  ]      D - H      H...A      D...A  D - H...A    A..H..A* A'..H..A" Sum(XY,YZ)  Sum(XZ)
------------------------------------------------------------------------------------------------------------------------------------------------
 1 Intra 1 O(3)  --H(3A)  ..O(11)  [  3676.01]       0.83       1.84 2.6311(16)        159
 2       1 O(3)  --H(3B)  ..O(2)   [  1545.01]       0.81       2.27 2.9455(15)        141
 3       1 O(3)  --H(3B)  ..O(1)   [  3666.01]       0.81       2.58 3.2683(15)        144'        72'                357

 4       1 C(21) --H(21C) ..O(15)  [  4464.01]       0.98       2.41   3.215(2)        139
 5       1 C(22) --H(22A) ..O(14)  [  2566.01]       0.98       2.47   3.290(2)        141
 6       1 C(22) --H(22B) ..O(15)  [  2556.01]       0.98       2.52   3.208(2)        127
 7       1 C(22) --H(22C) ..O(3)   [  1565.01]       0.98       2.49   3.318(2)        142

Translation of ARU-Code to CIF and Equivalent Position Code
============================================================
   [  3676.] = [  3_676] =1-x,2-y,1-z
   [  1565.] = [  1_565] =x,1+y,z
   [  3666.] = [  3_666] =1-x,1-y,1-z
   [  1545.] = [  1_545] =x,-1+y,z
   [  2556.] = [  2_556] =1/2-x,1/2+y,3/2-z
   [  4464.] = [  4_575] =-1/2+x,3/2-y,-1/2+z
   [  2566.] = [  2_566] =1/2-x,3/2+y,3/2-z

For C--H...Acceptor Interactions See: Th. Steiner, Cryst. Rev, (1996), 6, 1-57
```

Table S8. Analysis of Potential Hydrogen Bonds for complex crystallized in Acetone

```
================================================================================================================================================
Analysis of Potential Hydrogen Bonds and Schemes with d(D...A) < R(D)+R(A)+0.50, d(H...A) < R(H)+R(A)-0.12 Ang., D-H...A > 100.0 Deg
================================================================================================================================================
Note: - ARU codes in [] are with reference to the Coordinates printed above (Possibly transformed, when MOVE .NE. 1.555)
================================================================================================================================================

Nr Typ Res Donor --- H....Acceptor [    ARU  ]      D - H      H...A      D...A  D - H...A    A..H..A* A'..H..A" Sum(XY,YZ)  Sum(XZ)
------------------------------------------------------------------------------------------------------------------------------------------------
 1       1 O12   --H12A   ..O17    [  2666.03]    0.87(5)    1.85(5)   2.710(3)     168(6)
 2       1 O12   --H12B   ..O18    [  2666.04]    0.82(6)    1.92(6)   2.702(4)     159(5)
 3       1 O13   --H13A   ..O16    [  2566.02]    0.80(5)    1.91(5)   2.709(4)     170(4)
 4       1 O13   --H13B   ..O19    [  1555.05]    0.85(5)    1.93(6)   2.767(3)     169(5)

 5 Intra 1 C4    --H4     ..O11    [  2666.01]       0.95       2.40   3.306(4)        159
 6       1 C7    --H7     ..O1     [  2657.01]       0.95       2.55   3.446(4)        158
 7       1 C11   --H11    ..O16    [  1555.02]       0.95       2.51   3.423(4)        162
 8       1 C16   --H16    ..O5     [  1554.01]       0.95       2.56   3.502(4)        174
 9       2 C30   --H30A   ..O4     [  2566.01]       0.98       2.51   3.386(5)        148
10       2 C30   --H30C   ..O7     [  1555.01]       0.98       2.50   3.460(5)        165
11       3 C33   --H33A   ..O19    [  1655.05]       0.98       2.56   3.460(5)        153
12       4 C36   --H36B   ..O6     [  2656.01]       0.98       2.59   3.338(7)        133

Translation of ARU-Code to CIF and Equivalent Position Code
============================================================
   [  2666.] = [  2_666] =1-x,1-y,1-z
   [  2566.] = [  2_566] =-x,1-y,1-z
   [  2657.] = [  2_657] =1-x,-y,2-z
   [  2656.] = [  2_656] =1-x,-y,1-z
   [  1554.] = [  1_554] =x,y,-1+z
   [  1655.] = [  1_655] =1+x,y,z

For C--H...Acceptor Interactions See: Th. Steiner, Cryst. Rev, (1996), 6, 1-57
```

Table S9. Analysis of Potential Hydrogen Bonds for complex crystallized in Acetonitrile

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================================================================================================================================================
Analysis of Potential Hydrogen Bonds and Schemes with d(D...A) < R(D)+R(A)+0.50, d(H...A) < R(H)+R(A)-0.12 Ang., D-H...A > 100.0 Deg
================================================================================================================================================
Note: - ARU codes in [] are with reference to the Coordinates printed above (Possibly transformed, when MOVE .NE. 1.555)
================================================================================================================================================

Nr Typ Res Donor --- H....Acceptor [    ARU  ]      D - H      H...A      D...A  D - H...A    A..H..A* A'..H..A" Sum(XY,YZ)  Sum(XZ)
------------------------------------------------------------------------------------------------------------------------------------------------
 1       2 O7AA  --H7AA   ..N15    [  2565.04]    0.86(4)    2.10(4)   2.949(2)     173(3)
 2       2 O7AA  --H7AB   ..O22    [  2565.01]    0.82(3)    2.56(3) 2.8959(18)     106(3)
 3       2 O7AA  --H7AB   ..N14    [  2565.03]    0.82(3)    2.29(3)   3.067(3)     158(4)'  84.0(10)'             348(5)

 4       2 C3    --H3A    ..O2     [  2675.02]       0.98       2.47   3.302(3)        142
 5       2 C3    --H3C    ..O12    [  1665.02]       0.98       2.57   3.369(3)        139
 6 Intra 2 C20   --H20    ..O1     [  2565.02]       0.95       2.55   3.448(2)        159
 7       1 C32   --H32B   ..O22    [  1665.01]       0.98       2.40   3.263(3)        146
 8       1 C32   --H32C   ..O13    [  2786.01]       0.98       2.43   3.342(3)        155
 9 Intra 1 C35   --H35    ..O24    [  2676.01]       0.95       2.53 3.4422(19)        161
10       4 C64   --H64B   ..O20    [  1445.01]       0.98       2.39   3.368(2)        177
11       5 C65   --H65B   ..O10    [  2665.02]       0.98       2.43   3.378(3)        164

Translation of ARU-Code to CIF and Equivalent Position Code
============================================================
   [  2565.] = [  2_565] =-x,1-y,-z
   [  2676.] = [  2_676] =1-x,2-y,1-z
   [  1445.] = [  1_445] =-1+x,-1+y,z
   [  2786.] = [  2_786] =2-x,3-y,1-z
   [  1665.] = [  1_665] =1+x,1+y,z
   [  2675.] = [  2_675] =1-x,2-y,-z
   [  2665.] = [  2_665] =1-x,1-y,-z

For C--H...Acceptor Interactions See: Th. Steiner, Cryst. Rev, (1996), 6, 1-57
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