NO Sorption, In-crystal Nitrite and Nitrate Production with Arylamine Oxidation in Gas-Solid Single Crystal to Single Crystal Reactions

Mads Sondrup Møller, Alexander Haag, Vickie McKee, and Christine J. McKenzie*

Instrumentation. Electrospray ionization (ESI) mass spectra were recorded in high-resolution positive-ion mode on a Bruker microTOF-QII mass spectrometer using MeCN as solvent. IR spectra were recorded in the solid state on a Spectrum 65 FT-IR spectrometer (ATR mode, PerkinElmer). Raman spectra were recorded in the solid state using a confocal Raman microscope (Thermo Scientific DXR). Excitation wavelength 532 nm.

Crystallography. All data were collected at 100(2)K on a Synergy, Dualflex, AtlasS2 diffractometer using CuK_α radiation (λ = 1.54184 Å) and the *CrysAlis PRO* 1.171.39.27b suite. The structures were solved by dual space methods (SHELXT) and refined on F^2 using all the reflections (SHELXL-2018/1). For both complexes the high angle data were weak, the intensity of the data dropped off rapidly with θ angle. All full-occupancy non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms were inserted at calculated positions using a riding model. Further details for individual structures are given in the structure descriptions below.

Computing. Data collection: *CrysAlis PRO* 1.171.39.27b (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* 1.171.39.27b (Rigaku OD, 2015); data reduction: *CrysAlis PRO* 1.171.39.27b (Rigaku OD, 2015); program(s) used to solve structure: *ShelXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b), *SQUEEZE* (Spek, 2015); GUI: *ShelXle*, (Hübschle et al, 2011); molecular graphics: *Mercury* (Macrae at al., 2008); software used to prepare material for publication: Olex2 (Dolomanov *et al.* 2009), *publCIF* (Westrip, 2010).

Table S1 *Data Collection and refinement Parameters*

Identification code	**3**	**4**
Empirical formula	$C_{80}H_{83.6}N_{25}O_{36.4}Co_4$	$C_{87.6}H_{95}N_{18}O_{11.4}F_{31}P_5Co_4$
Formula weight	2213.43	2561.98
Temperature/K	100(2)	100.00(10)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	10.2477(6)	12.5820(5)
b/Å	11.0788(5)	15.0550(7)
c/Å	20.5444(8)	16.6109(6)
α/°	93.154(3)	82.568(3)
β/°	98.663(4)	82.672(3)
γ/°	90.411(4)	76.060(4)
Volume/Å^3	2302.07(19)	3012.9(2)
Z	1	1
ρ_{calc} g/cm^3	1.597	1.412
μ/mm^{-1}	6.439	5.807
F(000)	1138.0	1300.0
Crystal size/mm^3	0.322 × 0.121 × 0.06	0.251 × 0.155 × 0.067
Radiation	Cu$K\alpha$ (λ = 1.54184)	Cu$K\alpha$ (λ = 1.54184)
2θ range /°	7.994 to 133.194	7.276 to 117.856
Index ranges	$-10 \leq h \leq 12$, $-13 \leq k \leq 12$, $-24 \leq l \leq 24$	$-14 \leq h \leq 14$, $-16 \leq k \leq 17$, $-19 \leq l \leq 19$
Reflections collected	17673	45519
Independent reflections	8112	8493
R_{int}, R_{sigma}	0.0443, 0.0597	0.0673, 0.0457
Data/restraints/parameters	8112/698/625	10255/690/832
Goodness-of-fit on F^2	1.019	1.336
R1, wR2 [I>=2σ (I)]	0.0751, 0.1959	0.10.56, 0.3078
R1, wR2 [all data]	0.0964, 0.2097	0.1264, 0.3270
Largest diff. peak/hole / e Å^{-3}	0.85/-0.43	1.65/-0.87

Structure Description 3

$\{[(\mathrm{bpbp})\mathrm{Co^{III}}_2(\mu^{1}\text{-}N{:}\mu^{1}\text{-}O)\text{-ONO})]_2(\mathrm{NO_2bdc})\}(\mathrm{NO_3})_6 \cdot [2\mathrm{NO}, 2\mathrm{NO_2}, \mathrm{H_2O}]$

The $\{[\mathrm{Co(III)}_2(\mathrm{bpbp})(\mathrm{ONO})]_2(\mathrm{NO_2bdc})\}^{6+}$ cation (Figures 2a and S3) is disordered across a centre of symmetry. The two independent cobalt ions are 6-coordinate and their bond lengths indicate that they are both in the +III oxidation state (Table S2). As is generally observed in this series, the bpbp ligand provides three facially-coordinated nitrogen donors to each metal ion as well as a bridging phenolate. The nitro group of the $\mathrm{NO_2bdc}$ bridge is necessarily disordered over two symmetry-related positions and is also somewhat less than full occupancy; it has been refined as 0.35 $\mathrm{NO_2}$ and 0.15 $\mathrm{NH_2}$ at each position (so 70% oxidized). The coordination spheres are completed by a *syn-syn* μ-carboxylate bridge and a (μ^{1}-*N*:μ^{1}-*O*)-ONO anion.

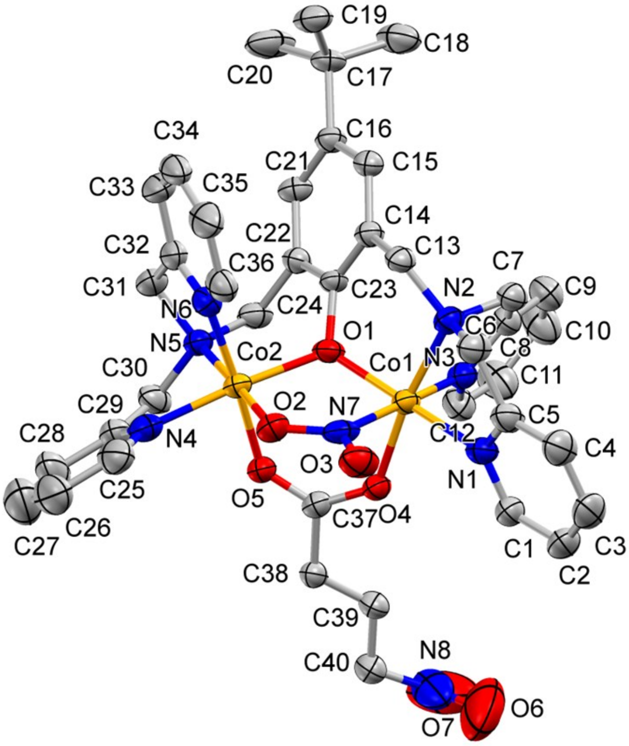


Figure S1. *The independent part of the cation in* ***3*** *shown with 50% probability ellipsoids. H atoms, anions and solvate molecules omitted.*

The cation charge is balanced by three independent nitrate counter ions (six per cell). These are not significantly disordered in terms of position, but the possibility of some nitrate/nitrite disorder cannot be definitively ruled out.

Table S2. *Selected geometric parameters (Å, º) for* ***3***

Co1—O1	1.887 (3)	Co2—O1	1.885 (4)
Co1—N1	1.915 (5)	Co2—N4	1.918 (5)
Co1—N2	1.964 (4)	Co2—N5	1.954 (4)
Co1—N3	1.942 (5)	Co2—N6	1.917 (5)
Co1—N7	1.990 (5)	Co2—O2	1.928 (4)
Co1—O4	1.923 (3)	Co2—O5	1.922 (4)
N7—O2	1.313 (6)	N7—O3	1.209 (6)

In addition to the cation and anions, there is some more diffuse electron density in the cell. Initially this density was modelled by fitting partial-occupancy NO and NO_2 molecules (1.4 and 1.6 molecules respectively per unit cell, distributed over 6 sites) and water molecules (0.6 per cell over 2 sites). This approach was moderately successful ($R1$=0.0908, $wR2$=0.2585, peak/hole +1.517/-0.49 e Å^{-3}), however an improved refinement was obtained when PLATON SQUEEZE was used; the CIF reports the SQUEEZEd refinement. This additional electron density, along with the nitrate counter ions, occupies channels between the cations (Figs 3b and S4).

SQUEEZE detected several voids and recovered significant electron density (Table 3). Based on the electron count and attempts to model the diffuse electron density, 2NO, $2NO_2$ molecules and one water molecule were added to the UNIT instruction and the formula.

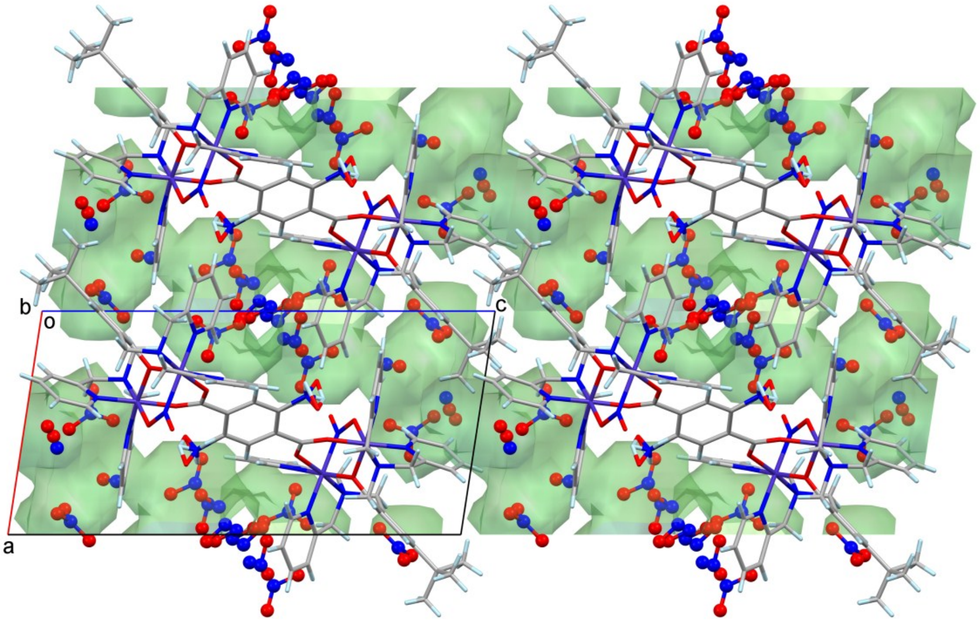


Figure S2. *Superposition of the void space between cations (pale green) and the modelled nitrate anions, NO, NO_2 and water "solvate" molecules in* ***3****. View down the b axis.*

Table S3. *SQUEEZE data for* ***3***

Number	**x**	**y**	**z**	**Volume ($Å^3$)**	**Electron count**
1	0.000	0.500	0.500	150	65
2	0.259	0.506	0.811	14	7
3	0.500	1.000	1.000	65	20
4	0.740	0.494	0.189	15	7

Void probe radius 1.20 Å

$2NO + 2NO_2 + H_2O$ = 86 electrons

The final formula is then $\{[Co(III)_2(bpbp)(ONO)]_2(0.3\ NH_2bdc, 0.7\ NO_2bdc)\}\cdot 6NO_3\ \cdot[NO\cdot\ 2NO_2\cdot\ H_2O]$, however it is recognised that other species, such as NO, N_2O_2 or disordered NO_2^- partly mixed in with NO_3^- are not explicitly ruled out by the structural data.

Structure Description 4

{[(bpbp)Co^{III}_2(μ^1-*N*:μ^1-*O*)-ONO)]$_2$(NO_2bdc)}(PF_6)$_5$(F)[3MeCN, 0.4Et_2O]

The {[Co(III)$_2$(bpbp)(ONO)]$_2$(0.5 NH_2bdc, 0.5 NO_2bdc)}·)}$^{6+}$ cation (Figure S5) is disordered across a centre of symmetry, the conformation is very similar to **3**. The nitro group of the NO_2bdc bridge is necessarily disordered with equal occupancy of two symmetry-related positions. The nitrogen (N40) was refined with 50% site occupancy and O41 and O42 both have 25% occupancy (i.e. 50% the -NH_2 of the precursor has been oxidised). The two independent cobalt ions are both 6-coordinate and their bond lengths indicate that they are both in the +III oxidation state (Table S4). As for **3**, the bpbp ligand provides three facially-coordinated nitrogen donors to each metal ion as well as a bridging phenolate. The coordination spheres are completed by a *syn-syn* μ-carboxylate bridge and a (μ^1-*N*:μ^1-*O*)-ONO anion. The cation charge is balanced by 2 independent PF_6^- anions lying on centres of symmetry, one full-occupancy ion and one 50% occupancy ion which is disordered over two overlapping positions (i.e. 2½PF_6^- anions per asymmetric unit; 5 per unit cell / formula unit). One positive charge per cation remains to be accounted for and has been assigned to a disordered fluoride ion distributed over 3 sites in the asymmetric unit (6 in the cell) with occupancies of 30%, 10%and 10% (i.e. ½F^- per asymmetric unit, one per formula unit). The asymmetric unit also contains one full-occupancy acetonitrile solvate and another with 50% occupancy and a 20% occupancy diethylether molecule, giving a final formula of {[Co(III)$_2$(bpbp)(ONO)]$_2$(0.5 NH_2bdc, 0.5 NO_2bdc)}F(PF_6)$_5$·3MeCN·0.4Et_2O.

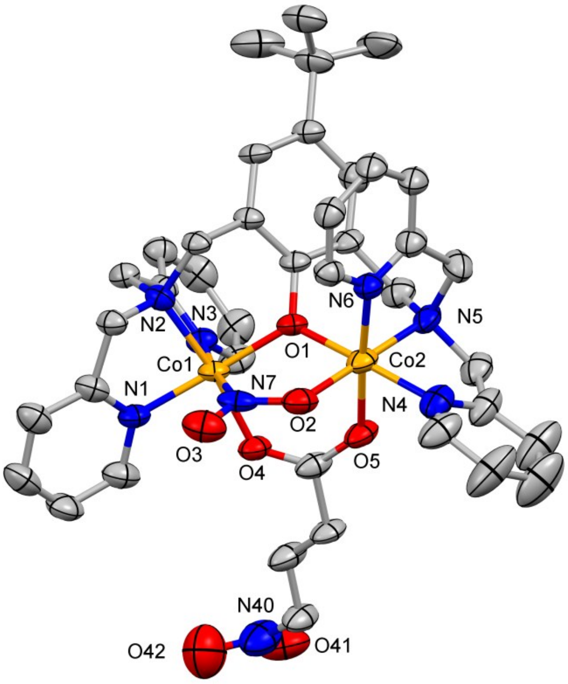


Figure S3. *The independent part of the cation in* ***4*** *shown with 40% ellipsoids. H atoms, anions and solvate molecules omitted.*

Table S4. *Geometric parameters (Å, °) for* ***4***

Co1—O1	1.889 (5)	Co2—O1	1.891 (5)
Co1—O4	1.907 (5)	Co2—O2	1.914 (6)
Co1—N1	1.904 (6)	Co2—O5	1.905 (5)
Co1—N2	1.955 (6)	Co2—N4	1.918 (7)
Co1—N3	1.940 (6)	Co2—N5	1.948 (7)
Co1—N7	1.967 (7)	Co2—N6	1.926 (6)
O2—N7	1.347 (9)	O3—N7	1.173 (8)

All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters, except for the Et_2O (SOF 0.2), the minor PF_6^- component (SOF 0.2) and the disordered F^- anion (SOFs 0.3, 0.1 and 0.1). Hydrogen atoms were inserted at calculated positions using a riding model.

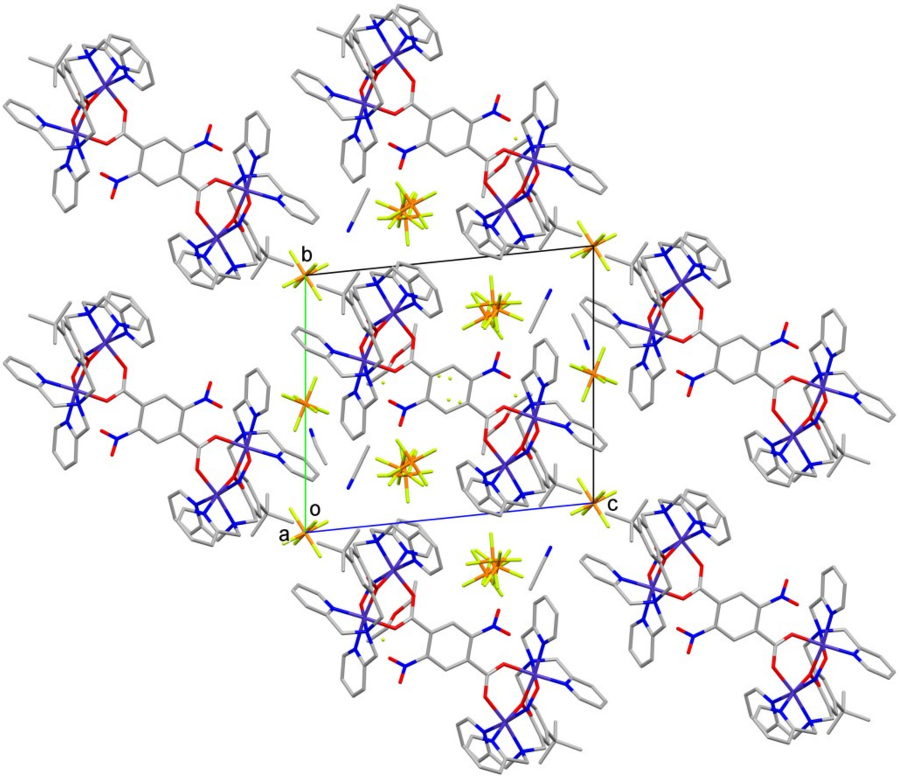
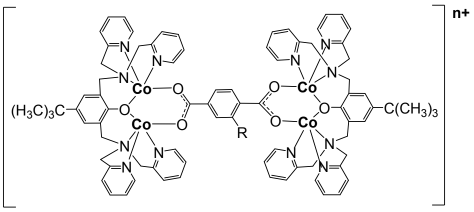


Figure S4. *Unit cell packing of* ***4*** *viewed down the a axis. Hydrogen atoms omitted for clarity.*

Table S5 Comparison of unit cell parameters for the nitrate salts of the tetracobalt dinitrate, diperoxy and dinitrite complexes.



NH_2bdc^{2-} R = NH_2
NO_2bdc^{2-} R = NO_2

	1	**2**	**3**	**4**
	TOQLOC	**LOFMIE**	*Manuscript3*	*Manuscript 4*
counteranion	$(NO_3)_2$	$(NO_3)_4$	$(NO_3)_6$	$F(PF_6)_6$
Co_2 oxidation state	Co(II)Co(II)	Co(III)Co(III)	Co(III)Co(III)	Co(III)Co(III)
Exogenous bridge	NO_3^-	O_2^{2-}	NO_2^-	NO_2^-
Bridging ligand	NH_2bdc^{2-}	NH_2bdc^{2-}	NO_2bdc^{2-}	NO_2bdc^{2-}
Temperature (K)	150.0(2)	150.0(2)	100(2)	100(2)
Crystal System	Triclinic	Triclinic	Triclinic	Triclinic
Space Group	P-1	P-1	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a (Å)	10.1905(13)	10.8710(9)	10.2477(6)	12.5820(5)
b (Å)	21.156(3)	20.7504(19)	11.0788(5)	15.0550(7) Å
c (Å)	22.015(3)	21.3627(15)	20.5444(8)	16.6109(6)
α (°)	115.123(4)	64.984(2)	93.154(3)°	82.568(3)°
β (°)	92.484(5)	86.763(4)	98.663(4)°	82.672(3)°
γ (°)	99.306(5)	79.326(3)	90.411(4)°	76.060(4)°
Volume (Å^3)	4207.3(10)	4290.0(6)	2302.07(19)	3012.9(2)
Z	2	2	1	1
volume per formula unit	2104	2145	2302	3013
Gas accessible void (Å^3) with anions, without solvate[a]	398 (9%)	355 (8%)	208 (9%)	552 (18%)
Gas accessible void (Å^3) without non-coord anions or solvate[a]	635 (15%)	927 (22%)	606 (26%)	1409 (47%)

[a] Solvent Accessible Voids calculated using PLATON. Grid = 0.20 Å, Probe Radius = 1.20 Å, NStep = 6 (neglecting voids too small to contain solvate, i.e. < 40Å^3)

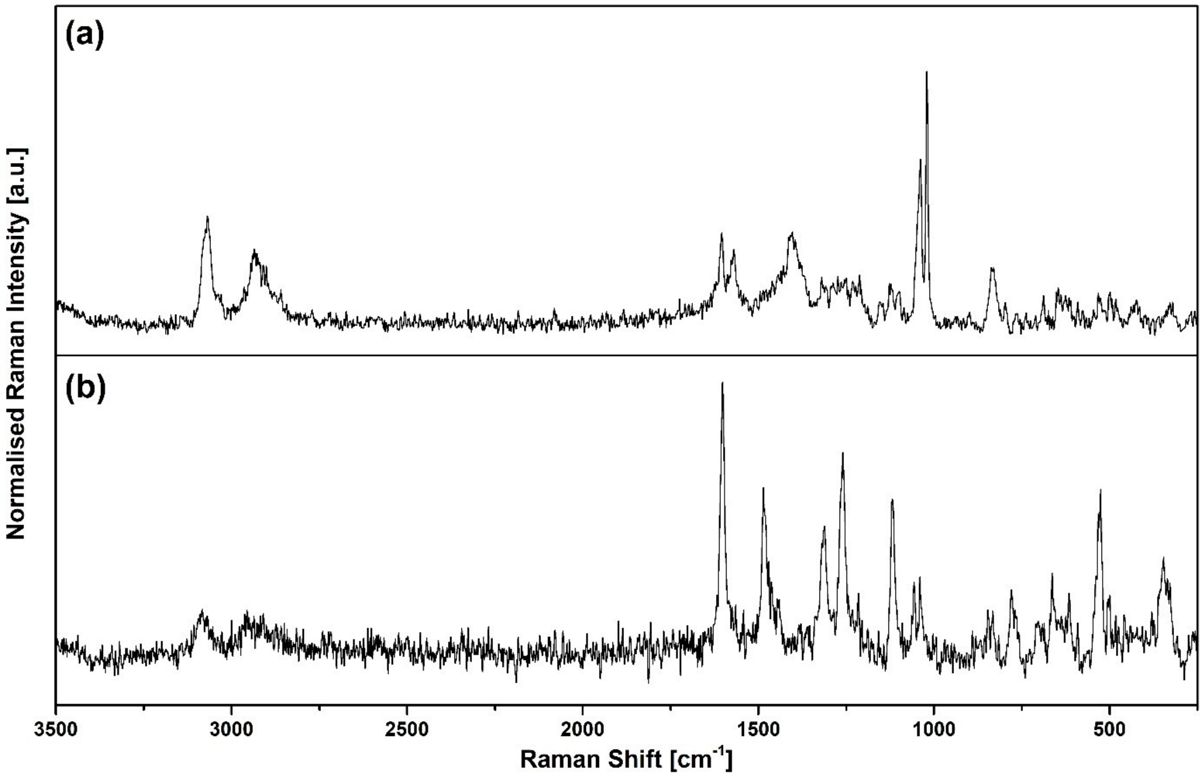


Figure S5. *Solid state Raman spectra of (a)* ***2*** *and (b)* ***3****. The absorption due the peroxide at 831 cm^{-1} is relatively weak due to desorption of O_2 during the experiment because of the heat generated by the laser which triggers its release. Excitation λ = 532nm.*

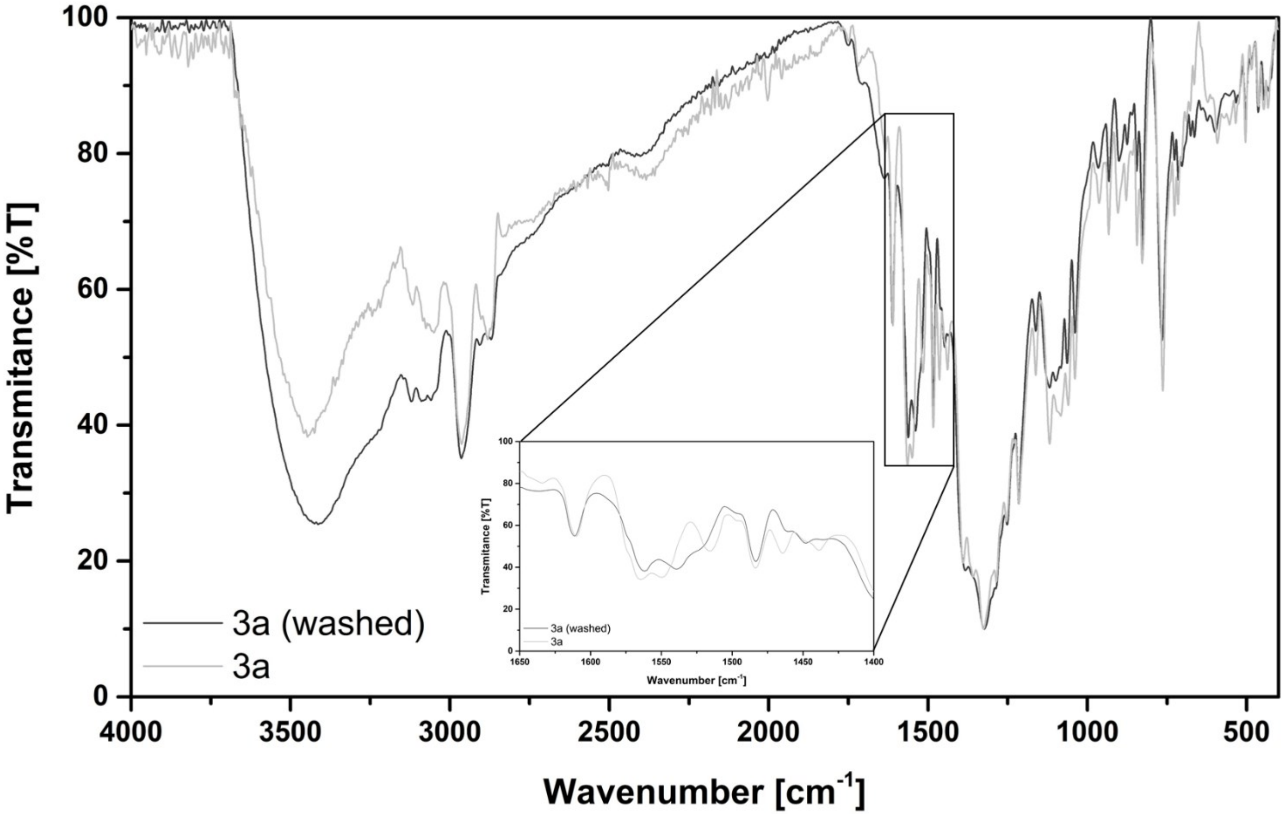


Figure S6. *IR spectra of* ***3****. Fresh, and ground and washed (MeCN).*

References

1. O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, and H. Puschmann. J. Appl. Cryst. 2009, **42**, 339-341.
2. C.B. Hübschle, G.M. Sheldrick and B. Dittrich. J. Appl. Cryst., 2011, **44**, 1281-1284.
3. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van der Streek, *J. Appl. Crystallogr*., 2006, **39**, 453-457
4. Rigaku Oxford Diffraction, (2018), CrysAlisPro Software system, version 1.171.39.27b, Rigaku Corporation, Oxford, UK.
5. G.M. Sheldrick, Acta Cryst., 2015a, **A71**, 3-8.
6. G.M. Sheldrick, Acta Cryst., 2015b, **C71**, 3-8.
7. A.L. Spek, Acta Cryst. ,2015, **C71**, 9–18.
8. S.P. Westrip, *J. Appl. Cryst*., 2010, **43**, 920-925.