Electronic Supplementary Information

Reversible solid to solid transformation in a crystalline state gas-solid reaction at an ambient condition: Fe–N(pyridine) bond formation at the expense of Fe–OH_2 bond breaking and vice versa

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Crystallographic characterization of $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5N)_3]ClO_4$ (4)

Even though the quality of the relevant crystals of compound $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5N)_3]ClO_4$ (**4**) are never good, we solved the structure. The best R factor we could get is 23 % (even after removing some reflections). The highest peak, is also nearly 3.0 which is due to the scattered electron density of heavy atom Iron. The anion (ClO_4^-) is highly disordered in the crystal, thus we refined the oxygen atoms of the anion isotropically.

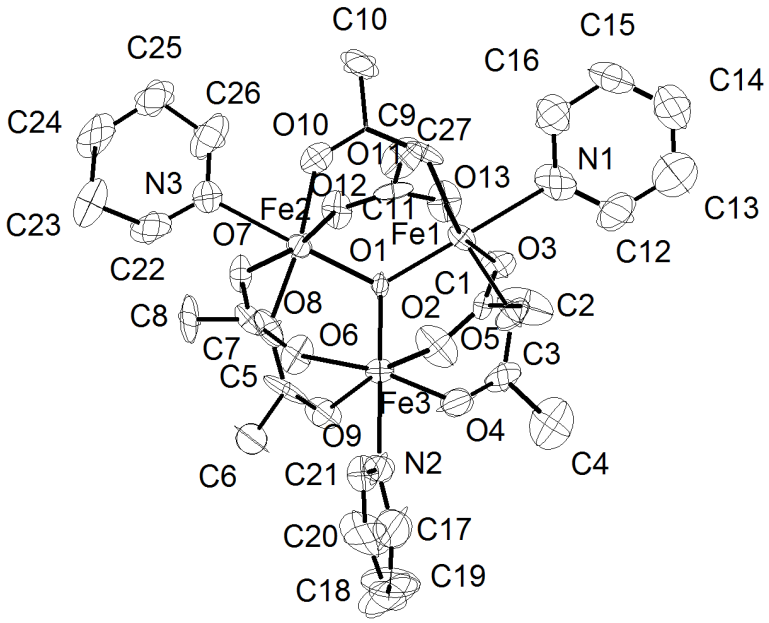


Fig. S1. Thermal ellipsoidal plot of $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5N)_3]^+$ in compound $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5N)_3]ClO_4$ (**4**).

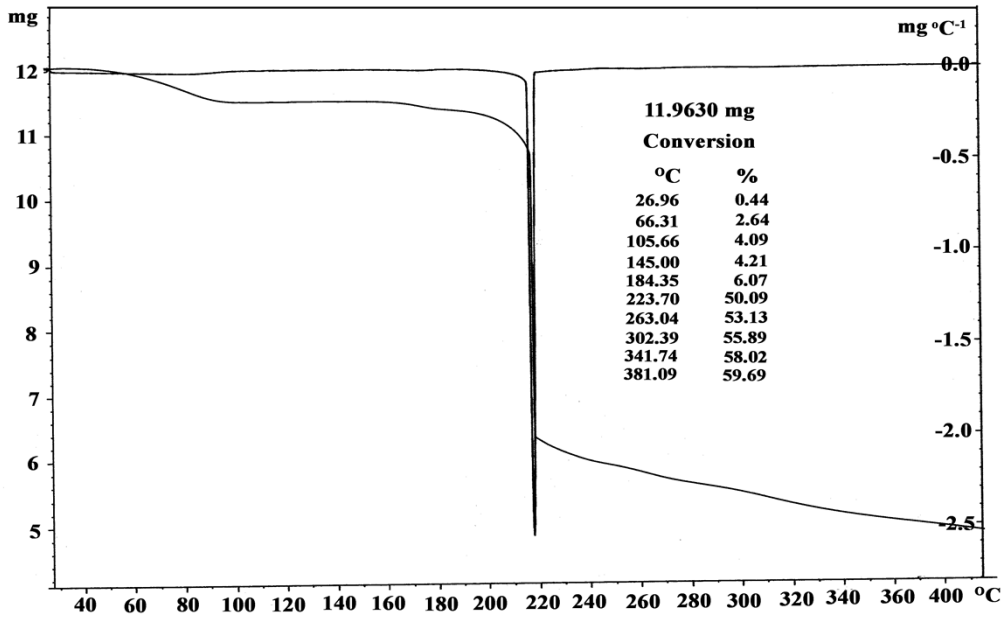


Fig. S2. TGA plot of parent compound $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]ClO_4 \cdot 3H_2O$ (**1**)

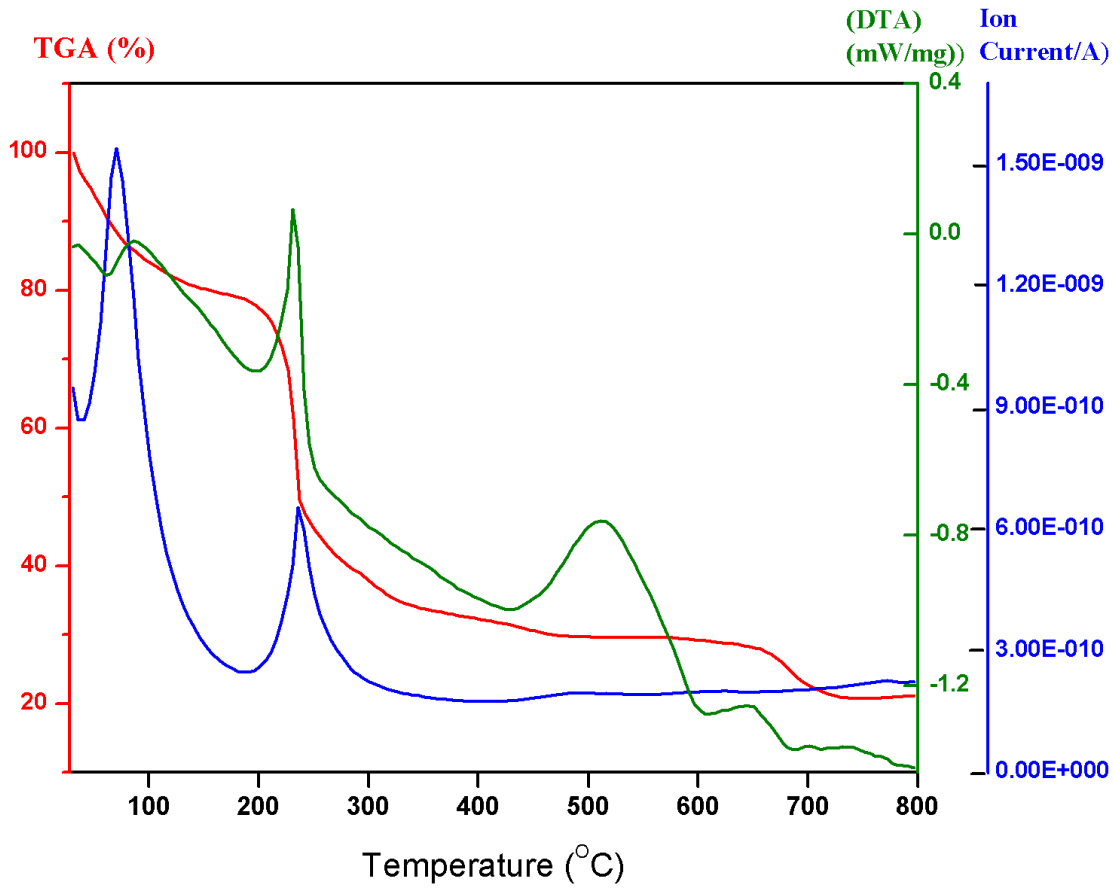
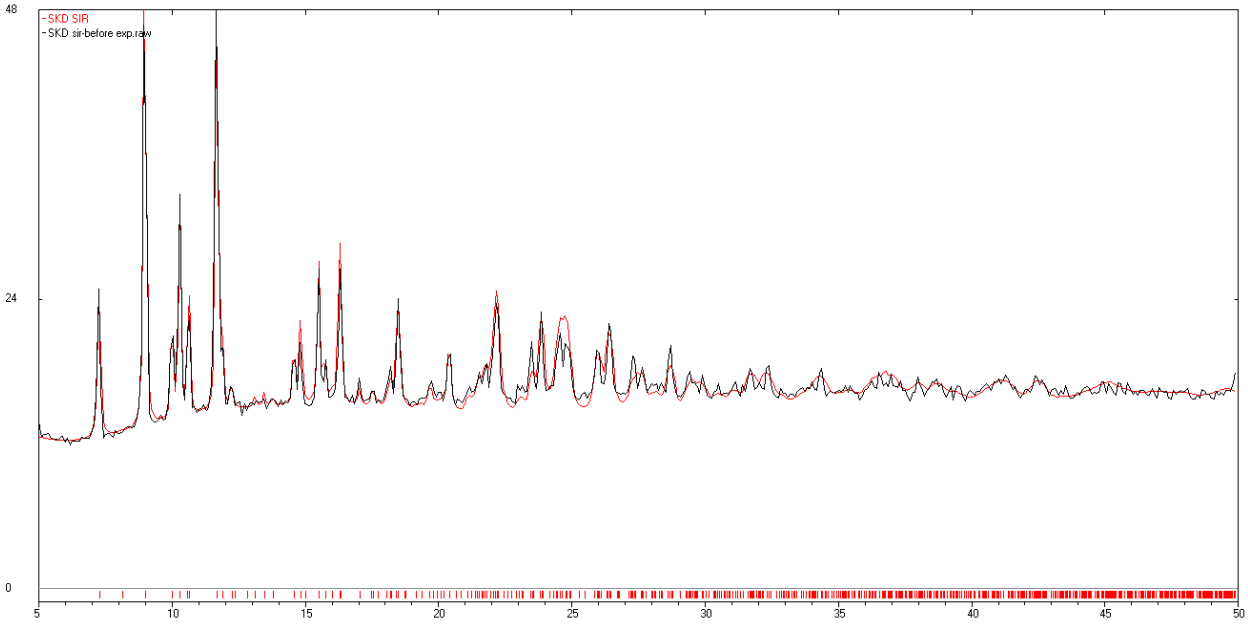
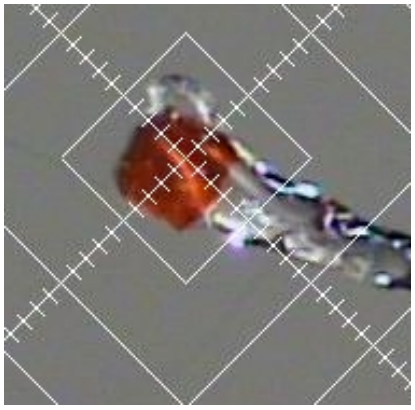


Fig. S3. TGA-MS plot of regenerated compound $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5NO)_2(H_2O)]ClO_4 \cdot 3H_2O$ (**1**). Color code: TGA, Red; DTA, green; MS(18, water), blue.

Fig. S4. PXRD patterns of parent compound **1**: black, observed and red, simulated from single crystal data.



(a)



(b)

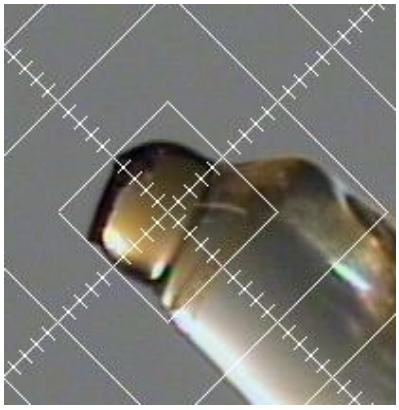


Fig. S5. (a) single crystal of compound 1. (b) Same crystal after exposure to pyridine vapour (which loses its single crystallinity).

Table S1. Crystal data and structure refinement for compound Compound $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5N)_3]\ ClO_4$ (**4**)

Identification code	skd175 (compound **4**)
Empirical formula	$C_{27}H_{33}ClFe_3N_3O_{17}$
Formula weight	874.56
Temperature	298 (2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
space group	P2(1)/n
Unit cell dimensions	
a	7.9670(16) Å
b	27.574(6) Å
c	19.131(4) Å
β	90.23(3)°
V	4202.7(15)Å^3
Z	4
D_{calc}	1.382 Mg/m^3
μ	1.151 mm^{-1}
F(000)	1788
Crystal size	0.18 × 0.08 × 0.04 mm^3
θ range for Data collection	1.30 to 26.36°
Reflections collected / unique	41094 / 8362
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8362 / 24 / 411

Goodness-of-fit on F^2	1.722
R_1/wR_2 [$I > 2\sigma(I)$]	0.2369 / 0.5238
R_1/wR_2 (all data)	0.2802 / 0.5415
Largest diff. Peak/hole	3.113 / -1.668 e.A^{-3}
CCDC	1052815

Table 2. Bond lengths [Å] and angles [°] for compound $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(C_5H_5N)_3]ClO_4$ (**4**)

C(1)-O(2)	1.25(2)
C(1)-O(3)	1.27(2)
C(1)-C(2)	1.59(2)
C(3)-O(4)	1.23(2)
C(3)-O(5)	1.27(2)
C(3)-C(4)	1.58(3)
C(5)-O(9)	1.25(3)
C(5)-O(8)	1.28(3)
C(5)-C(6)	1.61(3)
C(7)-O(6)	1.20(2)
C(7)-O(7)	1.30(2)
C(7)-C(8)	1.58(3)
C(9)-O(10)	1.25(2)
C(9)-O(11)	1.292(19)
C(9)-C(10)	1.40(3)
C(11)-O(12)	1.26(2)
C(11)-O(13)	1.28(2)
C(11)-C(27)	1.43(3)
N(1)-C(12)	1.3900
N(1)-C(16)	1.3900
N(1)-Fe(1)	2.188(9)
C(12)-C(13)	1.3900
C(13)-C(14)	1.3900
C(14)-C(15)	1.3900
C(15)-C(16)	1.3900
N(2)-C(21)	1.4127
N(2)-C(17)	1.4201
N(2)-Fe(3)	2.181(9)
C(17)-C(18)	1.2497
C(18)-C(19)	1.4011
C(19)-C(20)	1.4988
C(20)-C(21)	1.3656
C(22)-N(3)	1.29(3)

C(22)-C(23)	1.41(3)
C(23)-C(24)	1.41(4)
C(24)-C(25)	1.40(4)
C(25)-C(26)	1.41(3)
C(26)-N(3)	1.26(3)
Cl(1)-O(17)	1.27(5)
Cl(1)-O(16)	1.36(7)
Cl(1)-O(14)	1.37(5)
Cl(1)-O(15)	1.90(6)
Fe(1)-O(1)	1.915(10)
Fe(1)-O(13)	1.992(12)
Fe(1)-O(3)	1.996(12)
Fe(1)-O(11)	2.014(13)
Fe(1)-O(5)	2.020(13)
Fe(2)-O(1)	1.922(10)
Fe(2)-O(12)	2.005(11)
Fe(2)-O(8)	2.009(13)
Fe(2)-O(7)	2.029(12)
Fe(2)-O(10)	2.042(14)
Fe(2)-N(3)	2.202(17)
Fe(3)-O(1)	1.888(10)
Fe(3)-O(4)	1.974(15)
Fe(3)-O(2)	1.977(14)
Fe(3)-O(9)	2.002(14)
Fe(3)-O(6)	2.042(12)

O(2)-C(1)-O(3)	120.3(16)
O(2)-C(1)-C(2)	120.9(16)
O(3)-C(1)-C(2)	118.8(15)
O(4)-C(3)-O(5)	123.4(16)
O(4)-C(3)-C(4)	119.7(19)
O(5)-C(3)-C(4)	116.7(18)
O(9)-C(5)-O(8)	125.3(18)
O(9)-C(5)-C(6)	120(2)
O(8)-C(5)-C(6)	115(2)
O(6)-C(7)-O(7)	126.8(16)
O(6)-C(7)-C(8)	122.8(17)
O(7)-C(7)-C(8)	110.3(17)
O(10)-C(9)-O(11)	119.6(15)
O(10)-C(9)-C(10)	120.5(16)
O(11)-C(9)-C(10)	119.1(17)
O(12)-C(11)-O(13)	119.9(19)
O(12)-C(11)-C(27)	121(2)
O(13)-C(11)-C(27)	119(2)
C(12)-N(1)-C(16)	120.0
C(12)-N(1)-Fe(1)	121.0(2)
C(16)-N(1)-Fe(1)	118.8(2)
N(1)-C(12)-C(13)	120.0
C(14)-C(13)-C(12)	120.0
C(13)-C(14)-C(15)	120.0
C(16)-C(15)-C(14)	120.0
C(15)-C(16)-N(1)	120.0
C(21)-N(2)-C(17)	118.0

C(21)-N(2)-Fe(3)	119.3(4)
C(17)-N(2)-Fe(3)	122.6(4)
C(18)-C(17)-N(2)	117.7
C(17)-C(18)-C(19)	131.6
C(18)-C(19)-C(20)	109.0
C(21)-C(20)-C(19)	120.8
C(20)-C(21)-N(2)	120.9
N(3)-C(22)-C(23)	126(2)
C(24)-C(23)-C(22)	112(3)
C(25)-C(24)-C(23)	123(2)
C(24)-C(25)-C(26)	114(2)
N(3)-C(26)-C(25)	125(3)
O(17)-Cl(1)-O(16)	142(4)
O(17)-Cl(1)-O(14)	86(3)
O(16)-Cl(1)-O(14)	125(4)
O(17)-Cl(1)-O(15)	76(3)
O(16)-Cl(1)-O(15)	85(3)
O(14)-Cl(1)-O(15)	86(3)
O(1)-Fe(1)-O(13)	96.4(5)
O(1)-Fe(1)-O(3)	95.6(5)
O(13)-Fe(1)-O(3)	168.0(5)
O(1)-Fe(1)-O(11)	94.1(5)
O(13)-Fe(1)-O(11)	89.9(6)
O(3)-Fe(1)-O(11)	90.1(5)
O(1)-Fe(1)-O(5)	94.2(5)
O(13)-Fe(1)-O(5)	90.2(6)
O(3)-Fe(1)-O(5)	88.0(5)
O(11)-Fe(1)-O(5)	171.6(5)
O(1)-Fe(1)-N(1)	179.5(4)
O(13)-Fe(1)-N(1)	83.3(5)
O(3)-Fe(1)-N(1)	84.8(4)
O(11)-Fe(1)-N(1)	86.2(4)
O(5)-Fe(1)-N(1)	85.5(5)
O(1)-Fe(2)-O(12)	96.4(5)
O(1)-Fe(2)-O(8)	94.3(5)
O(12)-Fe(2)-O(8)	90.4(6)
O(1)-Fe(2)-O(7)	97.1(5)
O(12)-Fe(2)-O(7)	166.5(5)
O(8)-Fe(2)-O(7)	87.8(6)
O(1)-Fe(2)-O(10)	92.9(5)
O(12)-Fe(2)-O(10)	92.0(6)
O(8)-Fe(2)-O(10)	172.1(6)
O(7)-Fe(2)-O(10)	88.1(6)
O(1)-Fe(2)-N(3)	178.0(6)
O(12)-Fe(2)-N(3)	83.1(6)
O(8)-Fe(2)-N(3)	87.6(6)
O(7)-Fe(2)-N(3)	83.5(6)
O(10)-Fe(2)-N(3)	85.2(6)
O(1)-Fe(3)-O(4)	93.6(5)
O(1)-Fe(3)-O(2)	95.8(5)
O(4)-Fe(3)-O(2)	91.8(7)
O(1)-Fe(3)-O(9)	95.0(5)
O(4)-Fe(3)-O(9)	86.4(7)

O(2)-Fe(3)-O(9)	169.2(6)
O(1)-Fe(3)-O(6)	95.8(5)
O(4)-Fe(3)-O(6)	170.3(6)
O(2)-Fe(3)-O(6)	89.9(7)
O(9)-Fe(3)-O(6)	90.1(7)
O(1)-Fe(3)-N(2)	179.0(5)
O(4)-Fe(3)-N(2)	87.2(5)
O(2)-Fe(3)-N(2)	83.5(5)
O(9)-Fe(3)-N(2)	85.7(5)
O(6)-Fe(3)-N(2)	83.5(4)
C(26)-N(3)-C(22)	119(2)
C(26)-N(3)-Fe(2)	119.4(17)
C(22)-N(3)-Fe(2)	121.4(14)
Fe(3)-O(1)-Fe(1)	120.1(5)
Fe(3)-O(1)-Fe(2)	120.7(5)
Fe(1)-O(1)-Fe(2)	119.2(5)
C(1)-O(2)-Fe(3)	135.0(12)
C(1)-O(3)-Fe(1)	136.6(12)
C(3)-O(4)-Fe(3)	137.1(13)
C(3)-O(5)-Fe(1)	131.2(12)
C(7)-O(6)-Fe(3)	133.1(12)
C(7)-O(7)-Fe(2)	130.5(11)
C(5)-O(8)-Fe(2)	132.1(13)
C(5)-O(9)-Fe(3)	132.9(13)
C(9)-O(10)-Fe(2)	136.8(11)
C(9)-O(11)-Fe(1)	135.4(11)
C(11)-O(12)-Fe(2)	135.3(13)
C(11)-O(13)-Fe(1)	136.8(13)