Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Synthesis and Characterization of *cyclo*-Pentazolate Salts of Iron(III) and aluminum(III)

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1. Experimental section

General methods

All chemicals from commercial sources were analytical grade and used as received without further purification. Thermal property measurements were obtained on DSC (NETZSCH STA 449F5) at a scan rate of 5 °C min^{-1} in closed Al containers with an argon flow of 50 mL min^{-1}. FT-IR spectra were recorded on a Thermo Nicolet IS10 instrument. Electrospray ionization (ESI) mass spectra were recorded on a Finnigan TSQ Quantum ultra AM mass spectrometer. Elemental analyses were performed on a vario EL III CHNOS elemental analyzer.

2. Crystal structure data

The crystal data of **1** and **2** were collected with a Bruker APEX-II CCD single-crystal diffractometer and a Bruker D8 VENTURE single-crystal diffractometer at 150−193 K. The crystals were irradiated using MoKα radiation (λ = 0.71073 nm). The structures were solved by intrinsic using SHELXT2014 and refinement was carried out by a full-matrix least-squares technique using SHELXT2018 program contained in OLEX2 suite.[1-3] The non-hydrogen atoms were identified by SHELXT program directly and refined anisotropically. The hydrogen atoms were located from difference Fourier map inspection and freely refined with Uiso(H) = 1.5Ueq (N, O). The Relevant crystal data and refinement results are summarized in **Table S1-S9**.

Table S1. Crystal data and structure refinement for compounds **1** and **2**.

Compound	**1**	**2**
CCDC No.	2207237	2207238
Empirical formula	$Fe(H_2O)_6(N_5)_3 \cdot 9H_2O$	$Al(H_2O)_6(N_5)_3 \cdot 9H_2O$
Formula weight	536.24	507.37
Temperature (K)	193	150
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	16.8316(4)	16.7321(8)
b (Å)	14.7115(4)	14.5671(6)
c (Å)	20.1791(6)	20.0005(7)
α (°)	90	90
β (°)	93.400(1)	92.771(2)
γ (°)	90	90
Volume ($Å^3$)	4987.9(2)	4869.2(4)
Z	8	8
Density ($g \cdot cm^{-3}$)	1.428	1.384
μ (mm^{-1})	0.688	0.169
F(000)	2248.0	2144.0
Crystal size (mm^3)	0.12 x 0.13 x 0.15	0.13 × 0.12 × 0.11
Theta range for data collection	2.065 to 27.496	4.176 to 50.014
Index ranges	-21<=h<=20 -19<=k<=16 -25<=l<=26	-19<=h<=19 -17<=k<=17 -23<=l<=22
Reflections collected	56395	75466
Independent reflections	11374 [R(int) = 0.045]	8507 [R(int) = 0.068]
Data/restraints/parameters	11374/10/645	8507/0/559
Goodness-of-fit on F^2	1.019	1.080
Final R indices [I>2sigma(I)]	R1 = 0.0420 wR2 = 0.1167	R1 = 0.0599 wR2 = 0.1426
R indices (all data)	R1 = 0.0700 wR2 = 0.1375	R1 = 0.0904 wR2 = 0.1611
Largest diff. peak and hole (e. $Å^{-3}$)	0.571 and -0.543	0.428 and -0.334

Table S2. Bond lengths for **1**.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
Fe1-O1	1.9790(2)	N1-N2	1.317(3)
Fe1-O2	1.9819(2)	N1-N5	1.314(4)
Fe1-O3	2.0134(2)	N3-N2	1.308(4)
Fe1-O4	1.9895(2)	N3-N4	1.318(4)
Fe1-O5	1.963(2)	N4-N5	1.312(4)
Fe1-O6	1.986(2)	N14-N15	1.306(3)
Fe2-O10	1.9933(2)	N11-N15	1.330(2)
Fe2-O11	1.9835(2)	N11-N12	1.317(3)
Fe2-O12	1.9836(2)	N13-N12	1.317(3)
Fe2-O8	1.983(2)	N13-N14	1.320(3)
Fe2-O9	1.9627(2)	O14-H14A	0.8700
Fe2-O7	2.0190(2)	O14-H14B	0.8700

Table S3. Bond angles for **1**.

Parameter	Bond angle (°)	Parameter	Bond angle (°)
O1-Fe1-O2	90.32(8)	N2-N1-N5	108.0(2)
O1-Fe1-O3	178.65(8)	N1-N2-N3	108.0(2)
O1-Fe1-O4	92.33(8)	N2-N3-N4	108.0(2)
O1-Fe1-O5	89.18(8)	N3-N4-N5	107.8(3)
O1-Fe1-O6	88.41(7)	N1-N5-N4	108.1(2)
O7-Fe2-O8	90.57(7)	N11-N15-N14	108.37(18)
O7-Fe2-O9	91.48(8)	N13-N14-N15	107.8(2)
O7-Fe2-O10	88.85(7)	N12-N13-N14	108.4(2)
O7-Fe2-O11	178.55(8)	N11-N12-N13	107.86(16)
O7-Fe2-O12	88.94(7)	N12-N11-N15	107.56(17)
H12A-O12-H12B	105.00	N22-N21-N25	107.4(3)
H11A-O11-H11B	104.00	N21-N22-N23	108.0(2)

Fe2-O12-H12B	128.00	N22-N23-N24	108.2(2)

Table S4. Torsion angles for **1**.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
N5-N1-N2-N3	-0.3(3)	N11-N12-N13-N14	0.6(3)
N2-N1-N5-N4	0.2(3)	N12-N13-N14-N15	-0.4(3)
N1-N2-N3-N4	0.2(3)	N25-N21-N22-N23	-0.3(3)
N2-N3-N4-N5	-0.1(3)	N22-N21-N25-N24	0.2(4)
N15-N11-N12-N13	-0.5(2)	N21-N22-N23-N24	0.3(3)
N12-N11-N15-N14	0.3(3)	N22-N23-N24-N25	-0.2(3)

Table S5. Hydrogen bonds for **1**.

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
O1-H1A...O15	0.8700	1.7200	2.559(3)	161
O1-H1B...N26	0.8700	1.8800	2.727(3)	163
O2-H2A...O16	0.8700	1.7500	2.615(3)	175
O2-H2B...O23	0.8700	1.7600	2.625(3)	178
O3-H3A...N15	0.8700	1.9300	2.742(2)	155
O3-H3B...N29	0.8700	1.9500	2.760(3)	154
O20-H20B...N23	0.8700	1.9900	2.847(3)	170
O21-H21A...N5	0.8700	1.9500	2.817(3)	178
O23-H23B...N20	0.8700	1.9900	2.850(3)	172
O28-H28A...N24	0.8700	2.0500	2.830(4)	149
O28-H28B...N6	0.8700	2.0600	2.883(4)	159
O29-H29A...N16	0.8700	2.0000	2.841(4)	161
O30-H30B...N25	0.8700	1.9900	2.855(3)	174

Table S6. Bond lengths for **2**.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
Al1-O1W	1.878(2)	N1-N2	1.315(4)

Al1-O2W	1.881(2)	N1-N5	1.313(4)
Al1-O3W	1.856(2)	N3-N2	1.308(4)
Al1-O4W	1.899(2)	N3-N4	1.316(4)
Al1-O5W	1.881(2)	N4-N5	1.315(4)
Al1-O6W	1.871(2)	N6-N7	1.326(3)
Al2-O10W	1.890(2)	N6-N10	1.329(4)
Al2-O11W	1.851(2)	N7-N8	1.318(3)
Al2-O12W	1.877(2)	N8-N9	1.313(3)
Al2-O8W	1.877(2)	N9-N10	1.320(3)
Al2-O9W	1.868(2)	O13W-H13B	0.8500
Al2-O7W	1.898(2)	O13W-H13A	0.8600

Table S7. Bond angles for **2**.

Parameter	Bond angle (°)	Parameter	Bond angle (°)
O1W-Al1-O2W	91.30(9)	N2-N1-N5	107.6(2)
O1W- Al1-O3W	89.66(10)	N1-N2-N3	108.4(2)
O1W- Al1-O4W	178.92(10)	N2-N3-N4	108.0(3)
O1W- Al1-O5W	88.88(9)	N3-N4-N5	107.8(3)
O1W- Al1-O6W	90.09(10)	N1-N5-N4	108.2(3)
O7W- Al2-O8W	90.34(9)	N11-N15-N14	107.5(3)
O7W- Al2-O9W	89.42(10)	N13-N14-N15	108.7(3)
O7W- Al2-O10W	89.24(9)	N12-N13-N14	107.7(3)
O7W- Al2-O11W	91.06(10)	N11-N12-N13	108.9(3)
O7W- Al2-O12W	178.70(10)	N12-N11-N15	107.2(3)
H12A-O12W-H12B	110.00	N22-N21-N25	108.0(2)
H11A-O11W-H11B	108.00	N21-N22-N23	107.9(2)
Al2-O12W-H12B	124.00	N22-N23-N24	108.3(2)

Table S8. Torsion angles for **2**.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)

N5-N1-N2-N3	0.5(4)	N11-N12-N13-N14	0.4(4)
N2-N1-N5-N4	-0.5(4)	N12-N13-N14-N15	0.0(4)
N1-N2-N3-N4	-0.4(4)	N25-N21-N22-N23	-0.3(3)
N2-N3-N4-N5	0.0(4)	N22-N21-N25-N24	0.5(3)
N15-N11-N12-N13	-0.6(4)	N21-N22-N23-N24	0.1(3)
N12-N11-N15-N14	0.6(4)	N22-N23-N24-N25	0.3(3)

Table S9. Hydrogen bonds for **2**.

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
O1W-H1WB...O30W	0.8600	1.7200	2.572(3)	175
O1W-H1WA...N10	0.8700	1.8900	2.735(3)	164
O2W-H2WA...O18W	0.8700	1.8500	2.675(3)	156
O2W-H2WB...O24W	0.8700	1.8800	2.691(3)	154
O3W-H3WA...O20W	0.8600	1.8100	2.643(3)	160
O3W-H3WB...O15W	0.8600	1.6800	2.514(4)	162
O20W-H20B...N1	0.8600	1.9600	2.820(3)	177
O21W-H21B...N2	0.8500	2.0000	2.819(3)	162
O23W-H23B...N15	0.8500	1.9800	2.814(4)	164
O28W-H28B...O19W	0.8400	1.9000	2.753(3)	175
O28W-H28B...O19W	0.8400	1.9000	2.740(3)	176
O29W-H29A...N3	0.8700	1.9500	2.808(4)	165
O30W-H30B...O21W	0.8800	1.9500	2.826(4)	170

3. IR Spectra

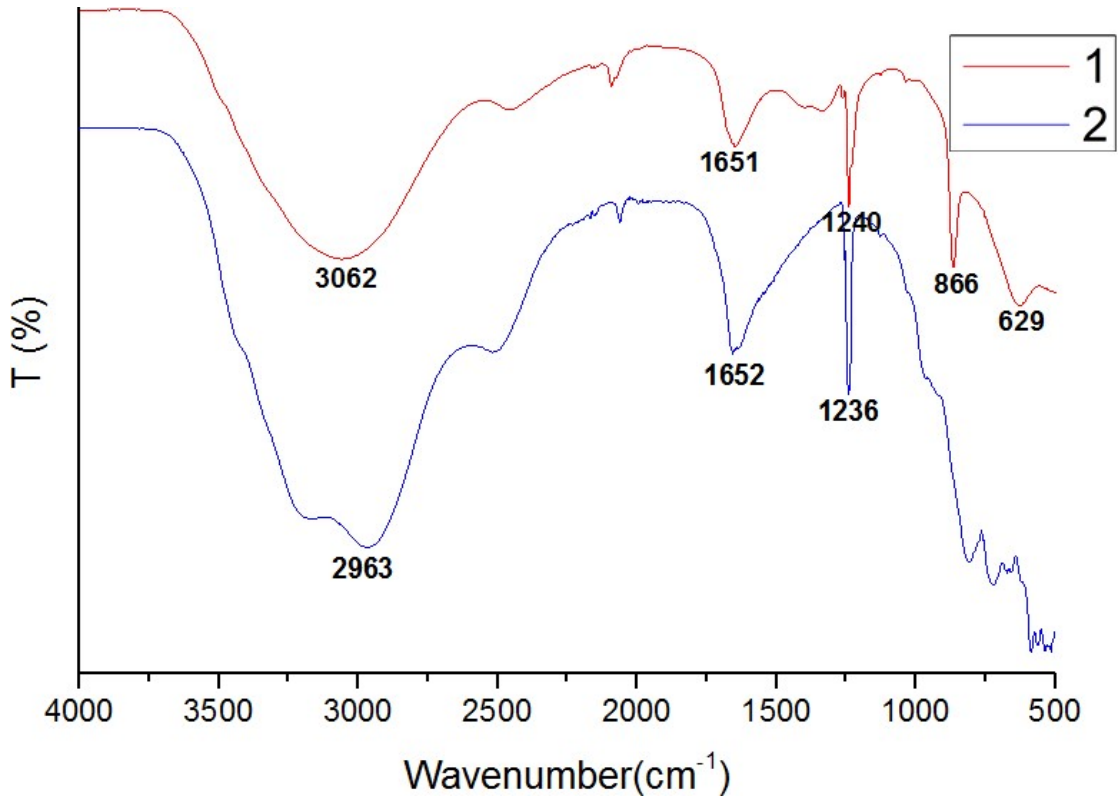
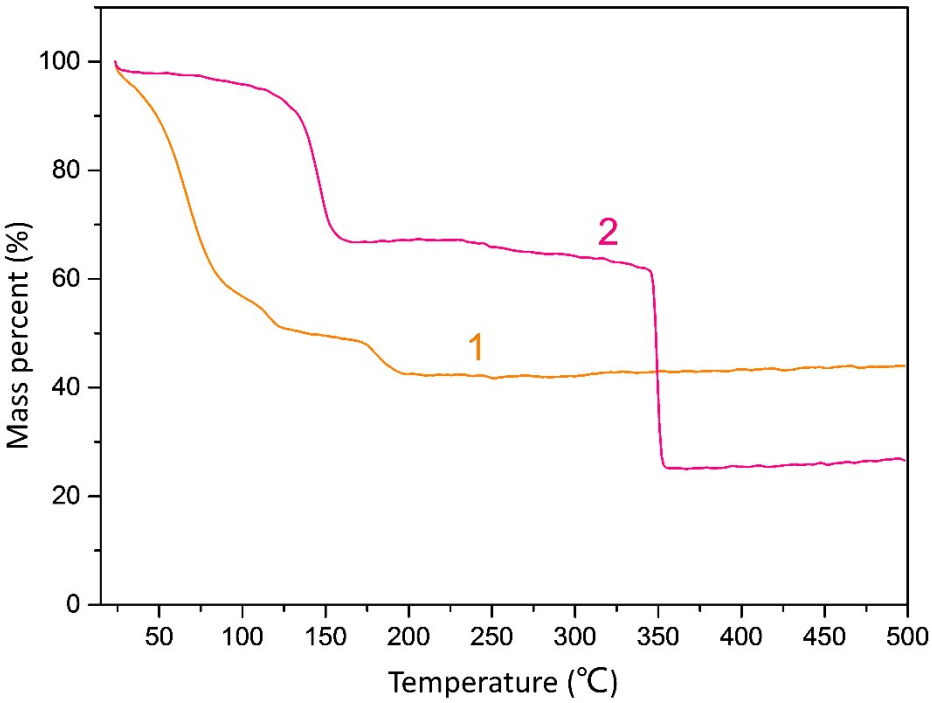


Figure S1. IR spectra for **1** and **2**.



4. Thermal analysis

Figure S2. TG curves of **1** and **2**. The plots were recorded with a heating rate of 5 °C min^{-1}.

5. Mass spectra

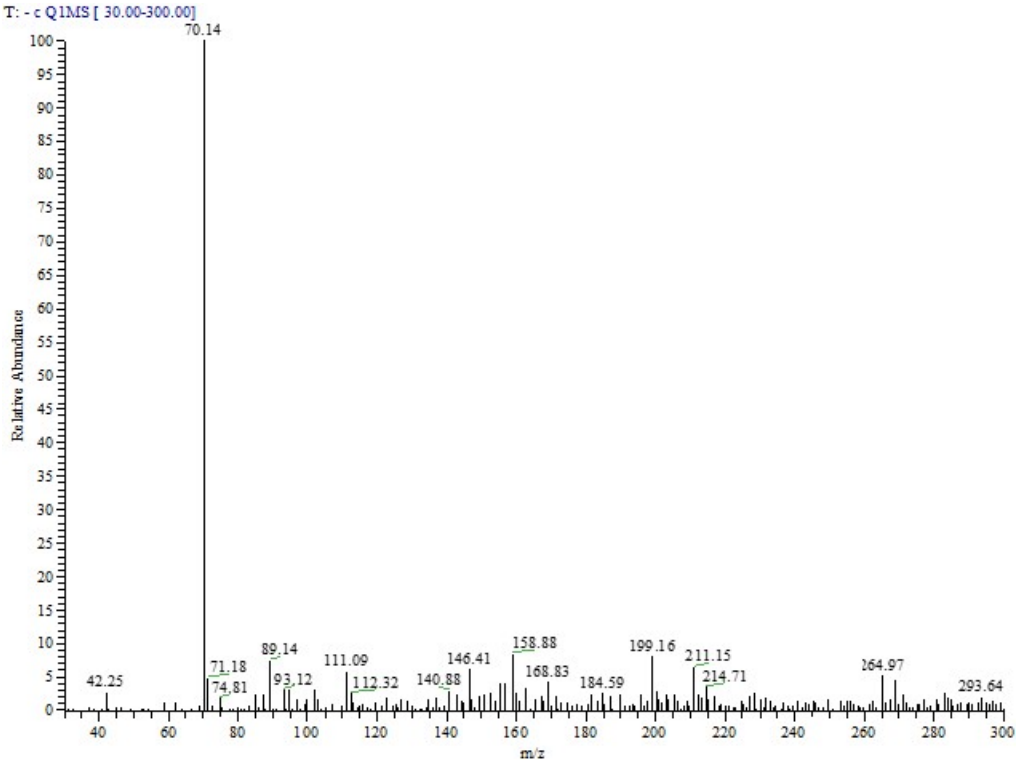


Figure S3. Mass spectra of **1**.

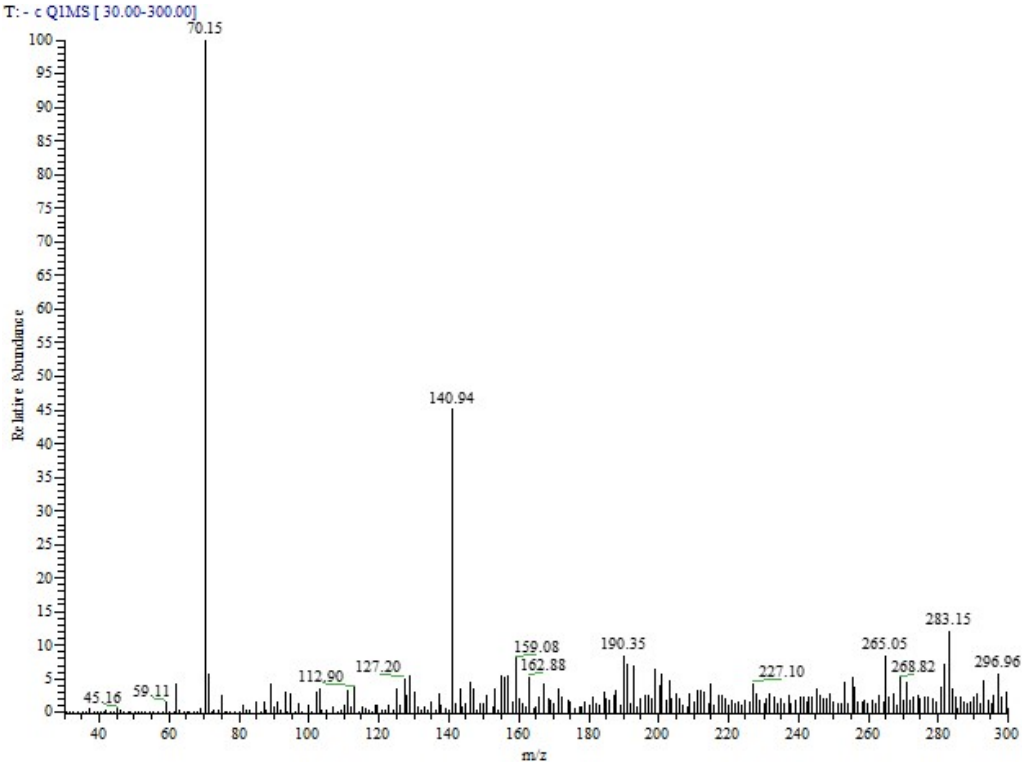


Figure S4. Mass spectra of **2**.

References

1. Sheldrick, G., Crystal structure refinement with SHELXL. *Acta Crystallographica Section C* **2015,** *71* (1), 3-8.

2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009,** *42* (2), 339-341.

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