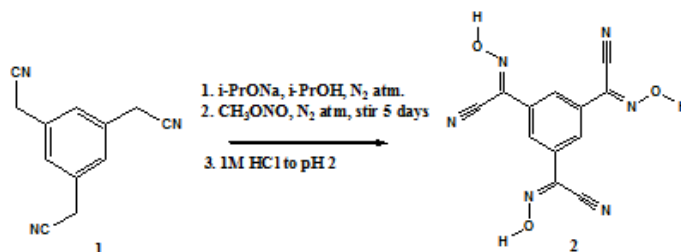


Scheme 1



Synthesis of **1**: To a solution of 1,3,5-tris(bromomethyl)benzene (3.02 g, 8.50 mmol) in THF (25 ml) was added sodium bicarbonate (saturated solution, 30 mL) and sodium cyanide (4.17 g, 85.0 mmol), followed by 30 mL water. The solution was left to stir for 48 h after which it was acidified with 1 M HCl, the THF was removed *via* rotary evaporation to leave behind an off-white solid. Yield: 1.53 g (92%); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 3.81 (s, 6H), 7.31 (s, 3H); IR: ν 2253 cm<sup>-1</sup> (C≡N); MP: 110-115 °C.

Synthesis of **2**: The synthesis of **2** was carried out following a slightly modified procedure as that previously reported in the literature<sup>1</sup>: Na metal (0.540 g, 23.5 mmol) was dissolved in 540 mL 2-propanol. **1** (0.80 g, 4.10 mmol) was dissolved in ~100 mL 2-propanol and added to the sodium solution. Methyl nitrite gas was generated *in situ* as follows: A separate 500-mL three-necked flask was equipped with a stir bar, 10 g of NaNO<sub>2</sub>, 100 mL of distilled H<sub>2</sub>O, and 50 mL of methanol. The NaNO<sub>2</sub> was allowed to dissolve with stirring. A greased septum was introduced into one neck, and a greased one-hole rubber stopper was placed firmly into the central neck. A dropper funnel (125 mL) was greased and attached to the third neck with a Keck clip. A solution of 2:1 H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub> (50 mL) was prepared and kept in an ice bath (~4 °C). After a glass U-tube apparatus was assembled between the *i*-PrONa/acetonitrile solution in the Erlenmeyer flask and the NaNO<sub>2</sub>/H<sub>2</sub>O/MeOH solution in the three-necked flask, the acid/water solution was placed into the dropper funnel, and the acid/water solution was slowly added dropwise to the NaNO<sub>2</sub>/H<sub>2</sub>O/MeOH solution inside the flask. Small bubbles of the evolving CH<sub>3</sub>ONO gas were immediately seen upon the reaction of the acid with the sodium nitrite.

The methyl nitrite gas was then passed through the solution, which caused it to turn yellow. The solution was left to stir for 5 days, after which a precipitate emerged. This solid, the sodium salt of **2**, was filtered off and dried. It was then dissolved in water which was acidified to ~pH 2 whereupon a brown precipitate appeared. In addition, 2-propanol was removed from the first filtrate producing a small amount of solid which was re-dissolved in water, acidified to ~pH 2, resulting in a brown precipitate. Both solids were combined, dissolved in methylene chloride and a small amount of methanol, and purified by column chromatography. (3:1 hexanes/ethyl acetate) to yield a colorless solid. Yield: 0.822 g (71 %); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 8.11 (s, 3H), 14.24 (s, 3H); <sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 110.34, 124.29, 130.49, 132.17; IR: ν 2248 cm<sup>-1</sup> (C≡N), ν 1040 cm<sup>-1</sup> (N-O), ν 3395 cm<sup>-1</sup> (O-H); MP: 240-245 °C (decomp.). M/Z: 305.06 (M+Na)<sup>+</sup>.

Synthesis of Co-Crystal of  $\alpha,\alpha',\alpha''$ -tris(hydroxyimino)-1,3,5-benzenetriacetonitrile 1,2-di(4-pyridyl)ethane, **2:3**: **2**: (5 mg, 0.0177 mmol) was dissolved in ethyl acetate and added to a solution of **3** in ethyl acetate (5.0 mg, 0.0266 mmol), and the resulting solution was left to evaporate at ambient conditions. This produced an off-white powder that was recrystallized from acetonitrile to yield pale yellow plates, mp: 246-248 °C. Crystallizations of **2** proved unsuccessful.

### X-ray crystallography

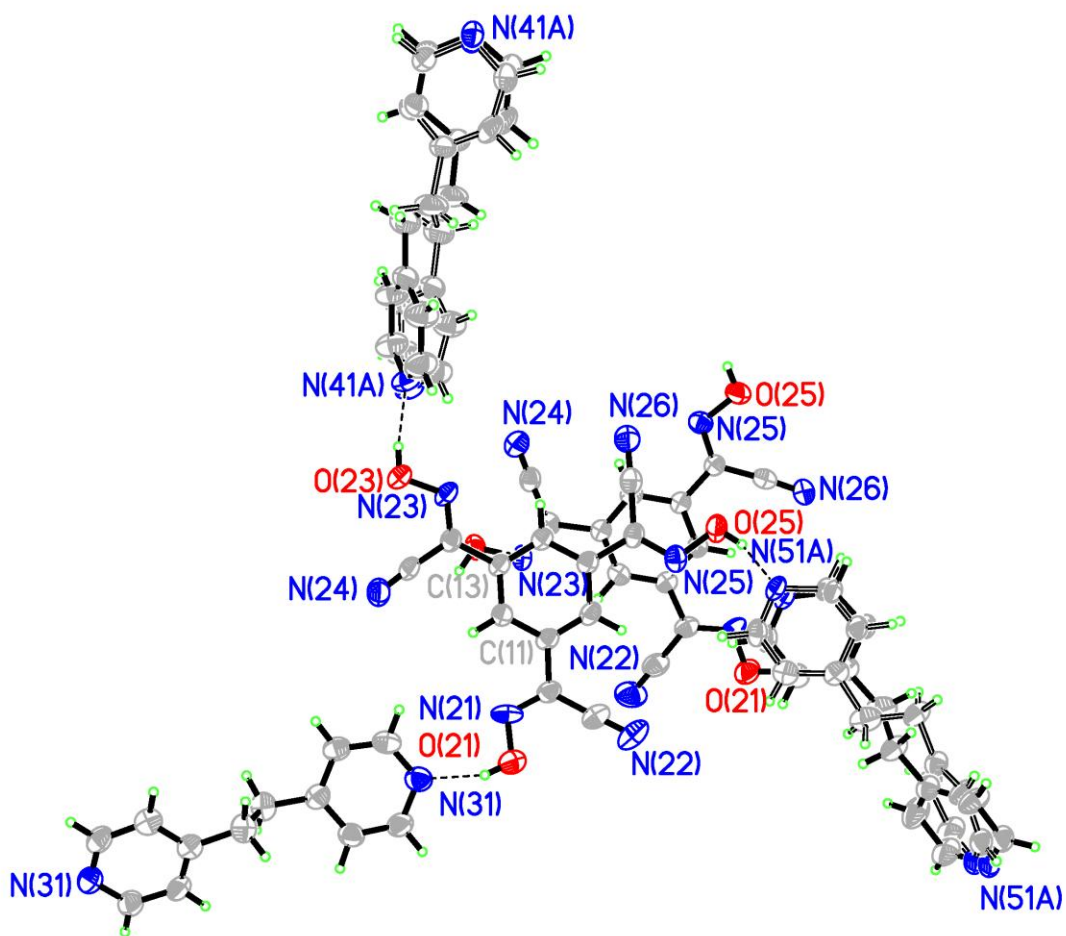
X-ray data were collected on a Bruker Kappa Apex II four-circle CCD diffractometer at 120 K using a fine-focus molybdenum  $K\alpha$  tube. Data were collected using APEX2<sup>(a)</sup> software. Initial cell constants were found by small widely separated “matrix” runs. An entire hemisphere of reciprocal space was collected. Scan speed and scan width were chosen based on scattering power and peak rocking curves.

Unit cell constants and orientation matrix were improved by least-squares refinement of reflections thresholded from the entire dataset. Integration was performed with SAINT,<sup>(a)</sup> using this improved unit cell as a starting point. Precise unit cell constants were calculated in SAINT from the final merged dataset. Lorentz and polarization corrections were applied. Laué symmetry, space group, and unit cell contents were found with XPREP.

(a) SAINT v7.46a, © 1997 - 2007, Bruker AXS, Madison, WI.

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<sup>1</sup> (a) D. Robertson, J. F. Cannon, and N. Gerasimchuk, *Inorg. Chem.*, 2005, **44**, 8326; (b) C. B. Aakeröy, J. Desper, D. J. Salmon and M. M. Smith, *Cryst. Growth Des.*, 2006, **6**, 1033



Caption : Labelled thermal ellipsoid plot of 2:3