Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Mode of iron(III) chelation by hexadentate hydroxypyridinones

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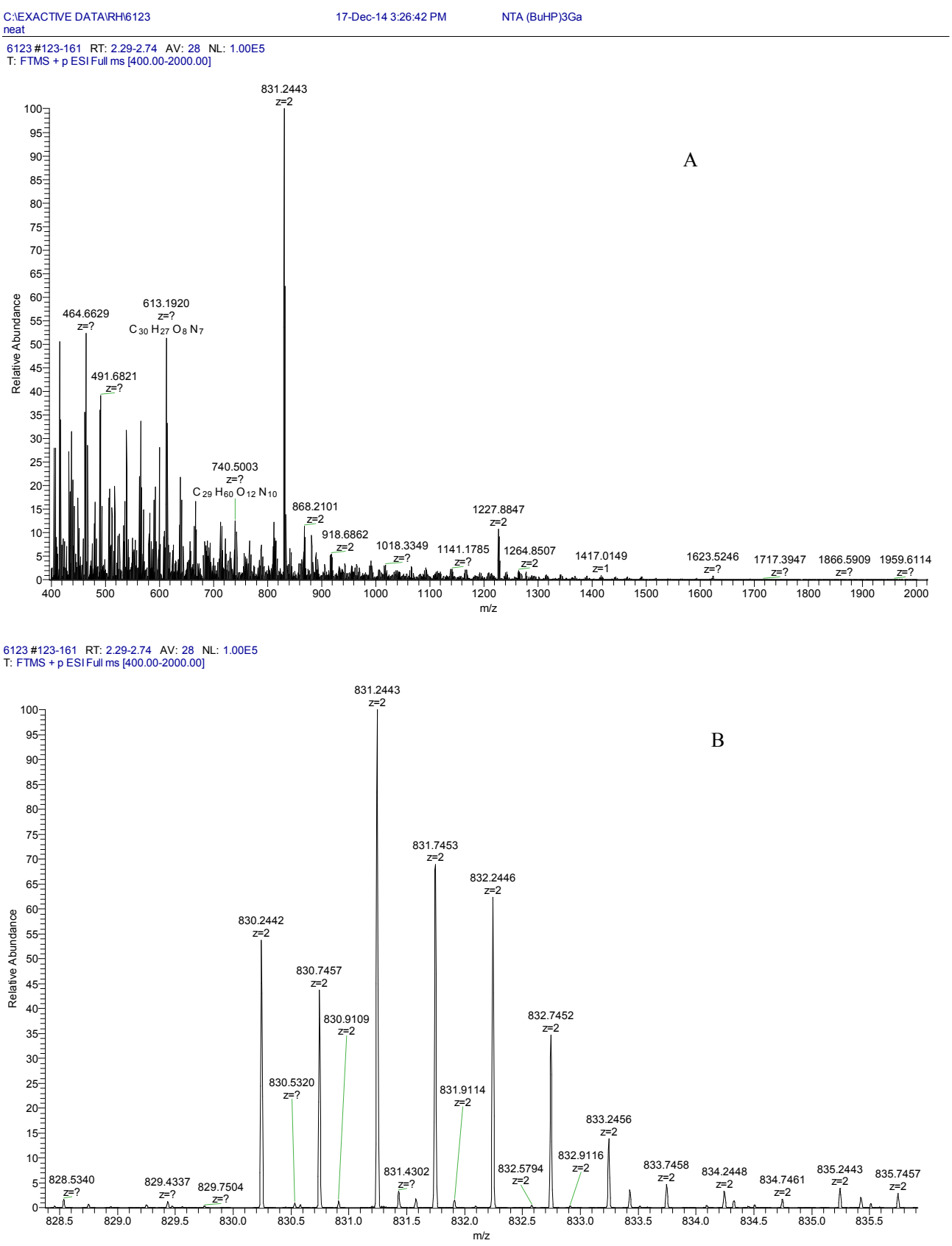

Figure S1. High resolution mass spectrum of peak 779 provides evidence of doubly charged complex $[Ga_2^{III}(L\text{-}3H)+2K]^{2+.}$ The complex was prepared from a 1:1 molar ratio of gallium chloride and $NTA(BuHP)_3$ (**4**) (100µM) in water with stepwise addition of KOH(0.1M) to pH7.0. Sample was then diluted 10 fold in 1% formic acid and inject into the instrument.

Synthesis of NTA(BuHP)$_3$ (4): A mixture of nitrilotriacetic acid (0.191g, 1mmol), dihydrochloric salt of 1-(4-aminobutyl)-3-(benzyloxy)-2-methylpyridin-4(1*H*)-one (1.292g, 3.6mmol), 1-hydroxybenzotriazole (0.551g, 3.6mmol), 1,3-dicyclohexylcarbodiimide (0.742g, 3.6mmol) and N-methyl morpholine (0.79mL) in DMF (15mL) was stirred at room temperature for 2 days. After filtration, the filtrate was concentrated and the residue was purified by silica column chromatography using CH_2Cl_2/MeOH (6:1 to 2:1) as an eluent to provide benzyl protected NTA(BuHP)$_3$ as a pale yellow solid (0.52g, 52% yield). To a suspension of the protected NTA(BuHP)$_3$ (0.18g) and concentrated hydrochloric acid (0.15 mL) in MeOH (20 mL) was added 5 % Pd/C (0.09 g). Hydrogenation was carried out at 30 psi H_2 for 3 h. After filtration to remove the catalyst, the filtrate was concentrated to dryness. The residue was purified by crystallization from methanol/acetone. The hydrochloride of NTA(BuHP)$_3$ was obtained as a white solid (0.138g, 88% yield). ^{1}H NMR (DMSO-d_6, 400MHz) δ 1.48 (m, 6H, CH_2), 1.74 (m, 6H, CH_2), 2.54 (s, 9H, CH_3), 3.12 (m, 6H, CH_2), 3.55 (br, 6H, CH_2), 4.35 (t, *J*=7.6Hz, 6H, CH_2), 7.35 (d, J=7.2Hz, 3H, C5-H in pyridinone), 8.32 (d, *J*=7.2Hz, 3H, C6-H in pyridinone), 8.81 (t, *J*=6.0Hz, 3H, NH); ^{13}C NMR (DMSO-d_6, 100MHz) δ 12.44 (*C*H_3), 25.57 (*C*H_2), 26.97 (*C*H_2), 30.68 (*C*H_2), 37.58 (*C*H_2), 55.43 (N*C*H_2CO), 110.71 (*C*-5H in pyridinone), 137.97 (*C*-2 in pyridinone), 141.34 (*C*-3 in pyridinone), 142.93 (*C*-6 in pyridinone), 158.47 (*C*-4 in pyridinone), 206.47 (CONH). ESI-MS: *m/z* 726 $[M+H]^+$.

MS Instruments:

High resolution mass spectrometry Thermo Exactive Benchtop Orbitrap with Instrument settings: Sheath Gas flow rate: 10; Aux gas flow rate: 0; Sweep gas flow rate: 0; Sprayvoltage: 4 kV; Capillary temp 250 °C; Capillary voltage: 60 V; Tube lens voltage: 120 V; Skimmer voltage: 25 V; Heater temp: 30 °C; Ion source: ESI positive mode; Resolution: Ultra High; Fragmentation: HCD Gas on.

Electrospray ionization mass spectrometry Samples were directly infused into a LCQ Deca XP ion trap mass spectrometer (ThermoFinnigan, San Jose, USA) using a 250 µl syringe at a flow rate of 5.0 µl/min. The instrument was operated in positive ion mode employing the following conditions:

source voltage 4.5 kV; capillary voltage 25 V; capillary temperature 100 to 300 °C and tube lens voltage 10 V.

ESI-MS of the Gallium complex of NTA(BuHP)$_3$:

The MS displays a major peak at 831.2 (Figure S1A) which corresponds to complex consisting of a 1:1 molar ratio of gallium and NTA(BuHP)$_3$ (**4**), namely $[Ga^{III}(L\text{-}3H)+K]^+$. With high resolution MS (Figure S1B), the peak was found to display a typical gallium isotope distribution, namely 830.24, 830.75, 831.24,831.75, 832.24, 832.75, 833.24, where the peaks are separated by half mass units. This confirms that the peak 831.2 corresponds to a doubly charged dimer of mass 1662.4 corresponding to the complex $[Ga_2^{III}(L\text{-}3H)_2+2K]^{2+}$.