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Synthesis of 6-Chloro-N,N,N',N'-tetrakis-pyridin-2-ylmethyl-[1,3,5]triazine-2,4-diamine

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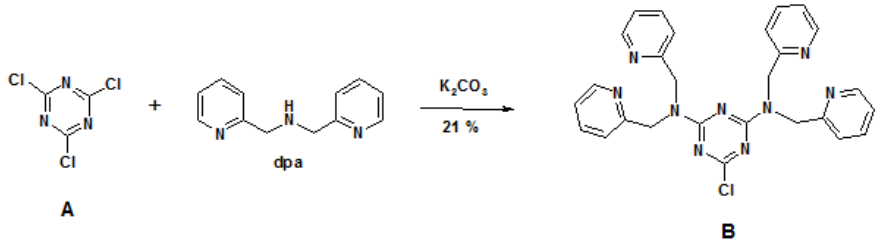
Transition metal complexes of pyridine-containing ligands are widely used in catalysis [1], supramolecular self-assembly [2], and anion recognition [3]. Binuclear Zn^{2+}-2,2'-dipicolylamine (dpa) complexes are particular useful for the binding of phosphorylated peptides in aqueous solution under physiological pH with high affinity and selectivity [4-9]. Similar ligands based on 2,2'-bipyridylamine (bpa) and 2,4,6-tris-chloro-triazine, have been used to form coordination networks with copper(II) ions. In these compounds the bpa moiety is attached directly to the hetero-aromatic core. Combination of 2,4,6-tris-chloro-triazine with dpa moieties leads to a new hybrid compound **B**, which should be used in phosphate binding studies. We describe the versatile short synthesis of the dpa compound **B** starting from 2,4,6-tris-chloro-triazine **A**.



2,4,6-Tris-chloro-triazine (**A**, 3 g, 16.3 mmol) was dissolved in 120 mL of acetone and di-(pyridylmethyl) amine (dpa; 6.49 g, 32.6 mmol) and K_2CO_3 (9 g, 65.2 mmol) were added subsequently. The reaction mixture was refluxed for 24 h and the insoluble parts were filtered off. The mixed was poured onto crushed ice and stirred for 15 min at room temp., water was added and the mixture stirred for an additional 15 min. The product was obtained by filtration as a pale yellow solid (2.9 g, 35%).

Melting point: > 200°C

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.82 (s, 4 H, CH_2), 5.03 (s, 4 H, CH_2), 6.90 (d, ^{3}J = 8.0 Hz, 2 H), 7.04 (t, ^{3}J = 5.8 Hz, 2 H), 7.16 (t, ^{3}J = 5.6 Hz, 2 H), 7.31 (d, ^{3}J = 8.0 Hz, 2 H), 7.38 (t, ^{3}J = 7.7 Hz, 2 H), 7.64 (t, ^{3}J = 7.7 Hz, 2 H), 8.41 (d, ^{3}J = 4.1 Hz, 2 H), 8.51 (d, ^{3}J = 4.9, 2 H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 51.9 (-, 2 C), 52.1 (-, 2 C), 121.3-122.5 (+, 8 C), 136.7 (+, 2 C), 136. 7 (+, 2 C), 149.2 (+, 2 C), 149.3 (+, 2 C), 157.2 (C_{quat}, 2 C), 157.2 (C_{quat}, 2 C), 165.7 (C_{quat}, 2 C), 169.9 (C_{quat}, 1 C).

ES-MS (DCM/MeOH + 10 mmol/l NH_4Ac): *m/z* (%) = 510.3 (100) [MH^+].

Elemental analysis: Calc. C 63.59, H 4.74, N 24.72 found C 63.27, H 4.72, N 24.58; IR (KBr) n (cm^{-1}) = 2927 (w), 2529 (w), 1707 (s), 1571 (s), 1491 (m), 1433 (w), 1410 (w), 1354 (w), 1319 (w), 1237 (w), 1169 (w), 1084 (w), 1048 (w), 972 (w), 947 (w), 889 (w), 863 (w), 804 (w), 756 (m), 683 (w), 617 (w), 554 (w), 458 (w).

Figure 1. ^{1}H-NMR spectrum of compound **B**

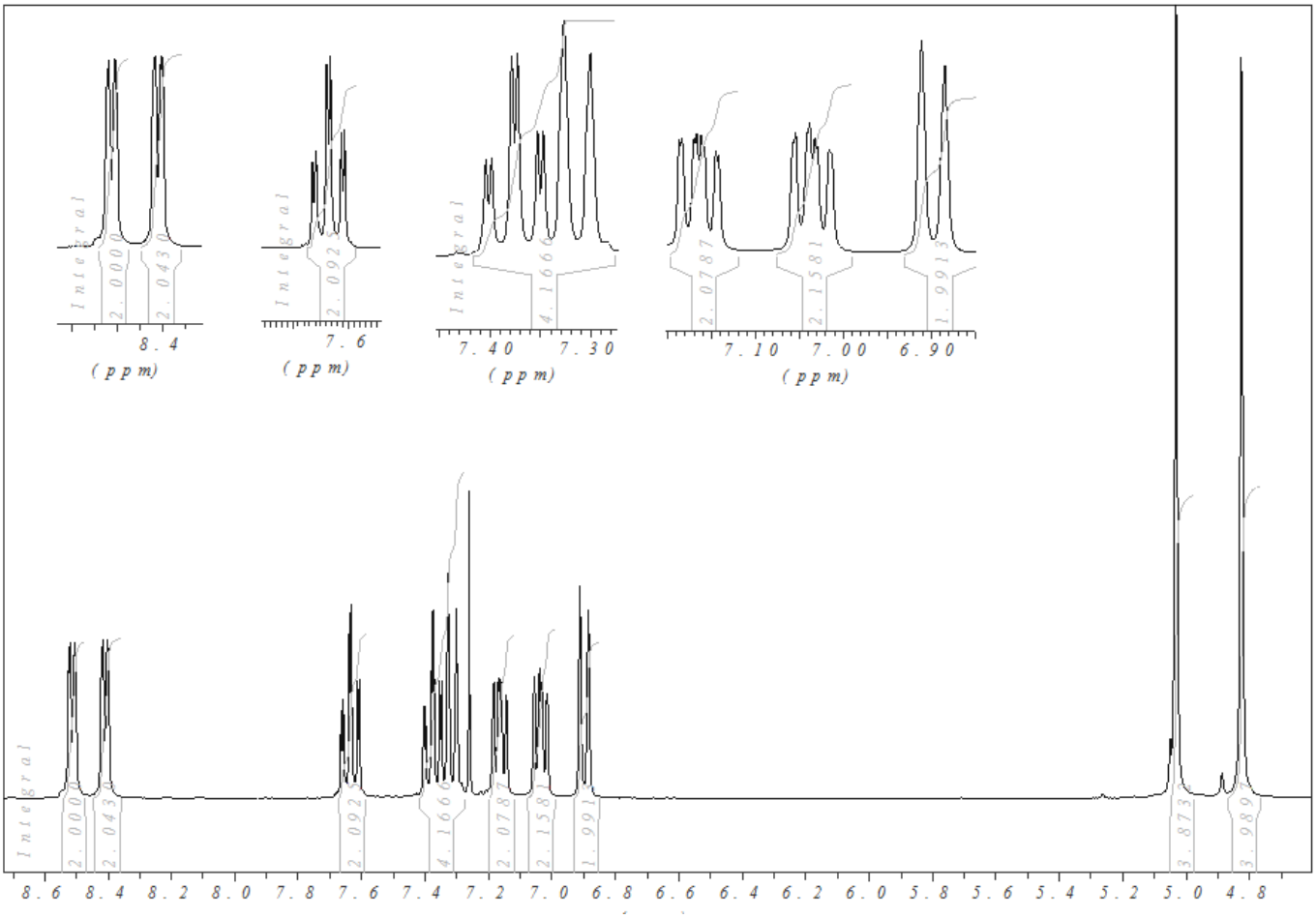
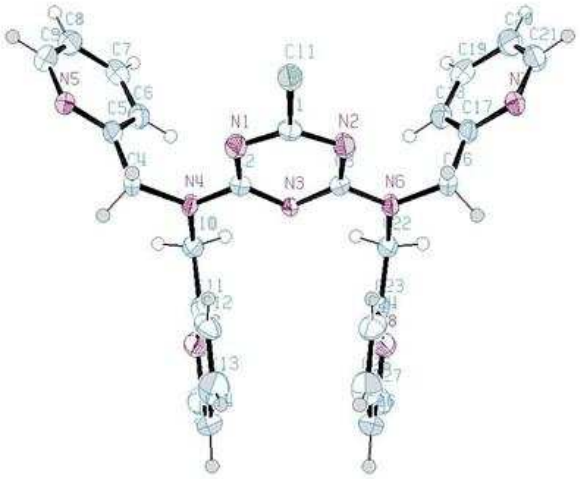


Figure 2. X-ray structure of **B.** Suitable crystals were obtained by recrystallization from DCM/MeOH 5:1.



Conclusion

A new dpa compound **B** was prepared in a one step synthesis. The compound can be prepared from commercially available compounds and is accessible by a simple reaction. Surprisingly, in first attempts this compound did not form spontaneously complexes with Zn^{2+} salts at conditions described for other dpa ligands [4-9].

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