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Multidentate aminophenol ligands prepared with Mannich condensations

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Abstract—Mannich condensations were used to prepare a series of multidentate aminophenol compounds from ethylenediamine, various amounts of paraformaldehyde and 2,4-disubstituted phenols. One of these diaminotetraphenol compounds was reacted with $Zn(OAc)_2{\cdot}2H_2O$ and the resulting solid state structure of the pentacoordinated Zn(II) compound was determined by single crystal X-ray diffraction analysis.

We are reporting the step-wise use of Mannich condensations with substituted phenols, formaldehyde, and ethylenediamine (en) to prepare a series of compounds with multiple amine and alcohol/aminal groups of increasing size and complexity (Scheme 1). Our goal was to build a library of compounds step-wise, in order to have greater control over the number and placement of heteroatoms in these potential ligands. These compounds are of interest as metallochelators and as ligands for bioinorganic modeling, catalysis, and medical imaging. The Mannich reaction is a multi-component condensation between a non-enolizable aldehyde (commonly formaldehyde), an amine (1° or 2°), and an enolizable carbonyl compound. Mannich condensations have been used to make biologically relevant molecules since the early 1900s, and the mechanism has been proposed for the biosynthetic production of alkaloids.[1] In our case, phenols function as the enolizable carbonyl compound and are reactive in the 2-, 4-, or 6-position.[2–4] By using 2,4-disubstituted phenols and varying those substituents, we modulate the electronic and steric properties of the alcohol moieties affecting both how many phenol groups can bind to a transition metal and how strongly those phenols will bind.[5–13]

The amine for all of the Mannich condensations in this letter is ethylenediamine, and it is used toward the goal of preparing a series of multidentate aminoalcohol ligands. Diaminodiphenols **2a**–**c**[15] were prepared by combining 2 equiv of a phenol (**1a**–**c**) with 2 equiv of paraformaldehyde and 1 equiv of ethylenediamine for two days (Scheme 1).[14] These reactions require neither solvent nor inert atmosphere conditions. Each compound was isolated by the addition of methanol to a cooled reaction mixture and filtration of the resulting precipitate in yields ranging from 35% to 61%. Of these, compound **2b** has been reported several times and is more commonly prepared by a two-step process in which 3,5-di-*t*-butyl-2-hydroxybenzaldehyde is condensed with ethylenediamine followed by reduction of the resulting imines.[15–18] The use of a Mannich condensation offers a simple and convenient method for preparing this family of compounds in a one-pot reaction. X-ray diffraction studies of single crystals containing **2b** ligated to several transition metals have been published,[15–18] but to the best of our knowledge, the structure of the free ligand is previously unreported. Clear block crystals of **2b** were grown from the vapor diffusion of CH_2Cl_2 solutions of **2b** and toluene.[19] A thermal ellipsoid diagram of **2b** is presented in Figure 1 and all spectroscopic data are consistent with the structure. Scheme 1 illustrates that the series of compounds **2a**–**c** resemble salen ligands, and one would expect these tetrahydrosalen complexes to be both more flexible and

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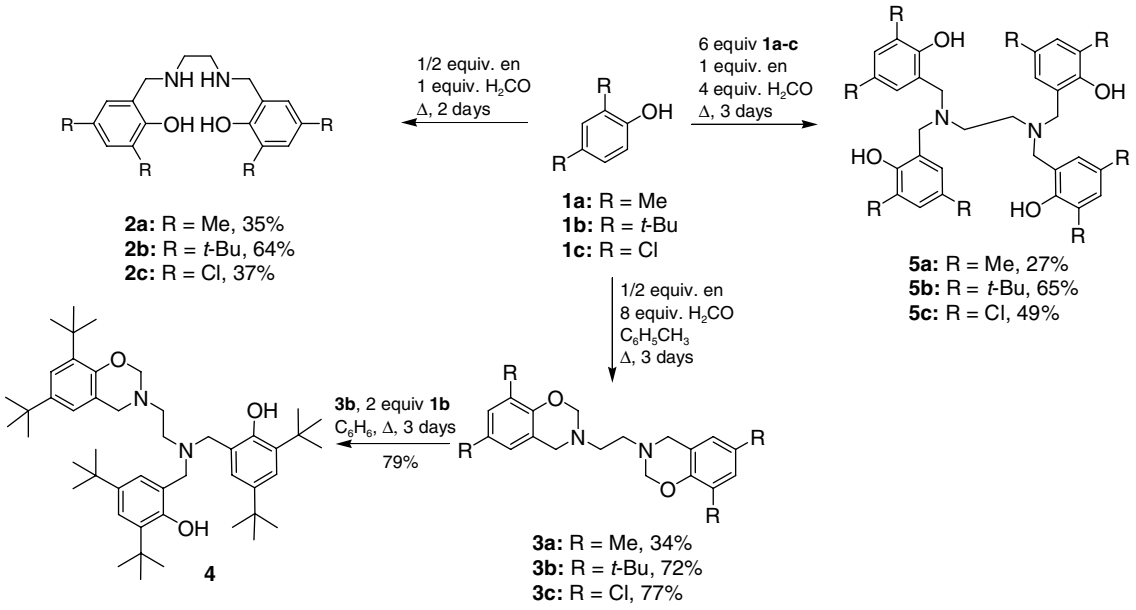

Scheme 1.

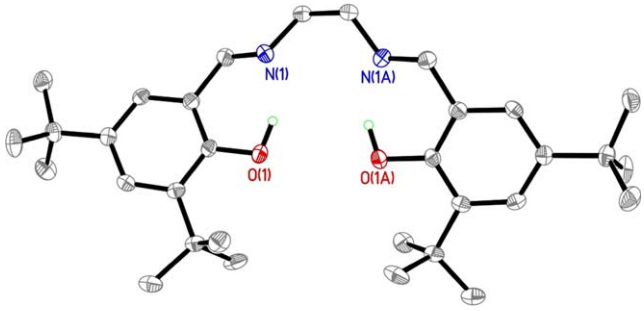

Figure 1. Thermal ellipsoid plot of the single crystal X-ray crystallographic structure of **2b**. Ellipsoids are drawn at 50% and hydrogens are omitted for clarity with the exception of the alcohol hydrogens.

have increased N-basicity compared to the dehydrogenated salen versions.[18,20–22]

The products of Mannich condensations have long been known to be condition dependent.[2–4] By increasing the amount of paraformaldehyde present in the reaction mixture, the reaction conditions favor the formation of dibenzoxazines **3a–c** (Scheme 1).[23] Use of more than two but less than 8 equiv of paraformaldehyde results in mixtures of **2** and **3**, but at 8 equiv and beyond the reactions favor the production of pure **3a–c**.[24] Again, the compounds are isolated by filtration from the chilled solvents in yields ranging from 34% to 77%. These benzoxazines function as a stable surrogate for the putative iminium intermediate of the Mannich condensation. The iminium intermediate is formed under acidic conditions yielding a reactive center for further Mannich and reverse Mannich condensations, and in the future **3a–c** could serve as starting materials for polymers or compounds with two different types of phenols attached to the same amine. This reactivity is demonstrated by combining 1 equiv of the dibenzoxazine **3b** with 2 equiv of **1b** in refluxing benzene for three days followed by removal of the solvent and washing of the crude reaction mixture with methanol, which results in the isolation of **4** in 79% yield, Scheme 1.

The synthesis of **5a–c** was realized by running the reactions neat, in a pressure flask, with an excess of phenol, Scheme 1.[25] A minimal amount of methanol (**5b** and **5c**) or ether (**5a**) was added to the crude reaction mixtures to wash away the unreacted phenol and the product was collected by filtration in 27–65% yield. All of the tetraphenols were more soluble in halogenated organic solvents such as CH_2Cl_2 or $CHCl_3$ than in methanol, with the solubilities decreasing from **5b** to **5a** to **5c**. Compound **5a** has been previously prepared in ~8% yield for use as a ligand to prepare ^{68}Ga diagnostic agents for positron emission topography.[26] A series of similar tetraphenols were also synthesized from 2-naphthol with ethylenediamine and 1,7-diaminoheptane for use in preparing dioxoazaborocines toward the goal of making wood preservatives.[27]

We are interested in using these compounds as potential ligands for bioinorganic modeling chemistry. In order to test the ability of the tetraphenols to bind biologically relevant metals, 1 equiv of **5a** was combined with 1 equiv of $Zn(OAc)_2{\cdot}(H_2O)_2$ and 4 equiv of NaOH in methanol at room temperature for three days. After isolation of the solid by evacuation of the solvent and recrystallization by vapor diffusion of toluene and methanol, we isolated clear block crystals of **6** ($Na[Zn(\mathbf{5a})]{\cdot}CH_3OH$) (Fig. 2). The crystal was subjected to a single crystal X-ray diffraction study and a thermal ellipsoid diagram of the structure is presented in Figure 2 and selected bond angles and distances are given in Table 1. In the solid state structure, three of the phenols of compound **5a** have been deprotonated and are bound to the zinc along with both of the nitrogen atoms in a distorted trigonal planar geometry. One sodium ion and one methanol molecule were found in each asymmetric unit. One nitrogen atom and one oxygen atom

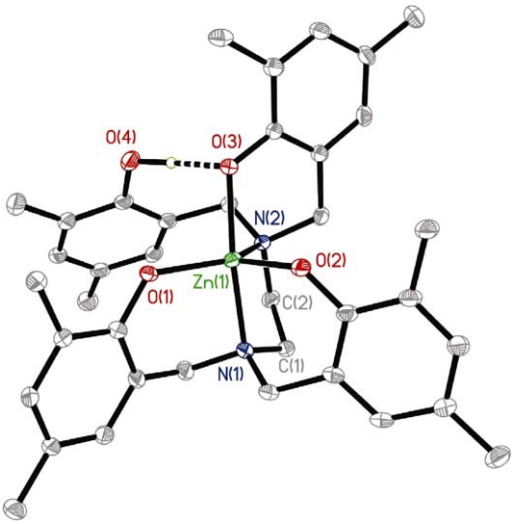

Figure 2. Thermal ellipsoid plot of the single crystal X-ray crystallographic structure of **6**, (Na[Zn(**5a**)]·CH_3OH). Ellipsoids are drawn at 50% and the sodium ion, the methanol, and all hydrogens except for the hydrogen bound to O(4) of the protonated phenol are omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for **6**

Zn(1)–N(1)	2.104(2)
Zn(1)–N(2)	2.180(2)
Zn(1)–O(1)	1.977(2)
Zn(1)–O(2)	2.016(2)
Zn(1)–O(3)	2.030(2)
O(3)–O(4)	2.596(1)
N(1)–Zn(1)–N(2)	83.15(9)
N(1)–Zn(1)–O(1)	94.81(8)
N(1)–Zn(1)–O(2)	91.21(8)
N(1)–Zn(1)–O(3)	166.95(8)
N(2)–Zn(1)–O(1)	133.13(9)
N(2)–Zn(1)–O(2)	116.34(8)
N(2)–Zn(1)–O(3)	83.86(8)
O(1)–Zn(1)–O(2)	110.51(9)
O(1)–Zn(1)–O(3)	94.95(8)
O(2)–Zn(1)–O(3)	93.46(8)

serve as the axial donor atoms, positioned across the zinc at a compressed bond angle of 166.95(8)°. Two oxygen atoms and one nitrogen atom form the equatorial ligands, which are separated by a range of 111–133°. Of note is the fact that O(4) on the fourth phenol ring is still protonated, and is hydrogen bonded to the axial oxygen. This sort of secondary coordination sphere interaction is common in biology and is an example of how proteins and metalloenzymes modulate the reactivities of their active sites. The N_2O_3 binding demonstrated by **6** is similar to the zinc centers in the trinuclear metalloenzymes alkaline phosphatase, phospholipase, and P1 nuclease.[28–30] The structure of **6** was further verified by mass spectroscopy and FTIR.

In conclusion, we were able to prepare a series of diaminophenol compounds using Mannich condensations. By controlling the stoichiometry and reaction conditions, one can build increasingly larger molecules ranging from diaminodiphenols up to diaminotetraphenols. All of the reactions (except for the preparation of **4**) were one pot reactions whose workups involved simple filtrations of highly pure materials. This work should serve as a starting point for building increasingly complex compounds. Our laboratory is now concentrating on preparing hetero-phenol compounds, with the goal of controlling the identity of phenol at each of the four positions of compounds similar to **5a–c** (four different phenols, three different phenols, two different phenols). Furthermore, work has begun on incorporating thiophenols into this reaction scheme in order to open up the possibility of preparing new sulfur containing ligands for bioinorganic modeling of proteins and metalloenzymes that contain cysteine or methionine in their active sites.

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Supplementary data

Selected physical and spectral data for **4** and **6** along with .cif files for **2b** and **6** can be found, in the online version, at doi:10.1016/j.tetlet.2006.04.077.

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14. Typical procedure to make **2a–c**: In a 35 mL pressure flask, 2 equiv of the phenol (30–40 mmol) was combined with 2–3 equiv of 95% paraformaldehyde, and 1 equiv of en. The reaction was heated to ~85 °C and stirred for two days. The reaction, now a yellow-orange oil, was removed from heat and cooled in an ice bath. Methanol (~25 mL) was added to the reaction and the pressure flask was sonicated. The product as a white precipitate formed and was isolated from the yellow filtrate by filtration in 33–64% yield. Characterization for **2a**: ^{1}H NMR ($CDCl_3$) δ 6.76 (s, 2H), 6.64 (s, 2H), 3.79 (s, 4H, Ph–CH_2–N), 2.62 (s, 4H, N–CH_2), 2.13 (6H, s, CH_3), 2.06 (6H, s, CH_3); ^{13}C NMR (DMSO) δ 153.7, 129.6, 126.5, 126.2, 123.5, 122.2, 51.4, 47.2, 20.1, 15.6; FTIR data (ATR of dry film): ν(N–H) 3302 cm^{-1}; HRMS (FAB+) *m/z*: $[M+H]^+$ calcd for $C_{20}H_{29}N_2O_2$, 329.2229; found, 329.2214; mp 104.9–105.8 °C. Characterization for **2b** found in Ref. 20. Characterization for **2c**: ^{1}H NMR (DMSO) δ 7.33 (s, 2H), 7.12 (s, 2H), 3.90 (s, 4H, Ph–CH_2–N), 2.69, (s, 4H, N–CH_2); ^{13}C NMR (DMSO) δ 154.7, 128.0, 127.7, 127.0, 121.4, 121.3, 50.7, 46.9; FTIR data (ATR of dry film): ν(N–H) 3156 cm^{-1}; HRMS (FAB^+) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{17}N_2O_2Cl_4$, 409.0044; found, 409.0043; mp 195.2–196.8 °C.
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19. X-ray crystallography: X-ray intensity data for **2b** and **6** were measured at 100 K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 W power. The crystals were mounted on cryoloops using Paratone N-Exxon oil and placed under a stream of nitrogen. The detector was placed at a distance of 5.009 cm from the crystals. Analysis of the data sets showed negligible decay during data collection. The data sets were corrected for absorption using the SADABS program. The structures were refined using the Bruker SHELXTL Software Package (Version 6.1), and were solved using direct methods until the final anisotropic full-matrix, least squares refinement of F^2 converged (Sheldrick, G. M. SHELXTL, Crystallographic Software Package, version 6.10; Bruker-AXS: Madison, WI, 2000.). In compound **2b**, all atom positions were located and refined. For compound **6**, all hydrogen atoms, with the exception of the phenolic hydroxide, were assigned ideal positions and refined isotropically. A disordered solvent methanol (approximately four per unit cell, one per asymmetric unit) was modeled as a diffuse contributor to the reflection array and not assigned specific atom positions. The density, $F(000)$, and extinction coefficient reflect the full formula. Crystal data for **2b**. Recrystallized from toluene/CH_2Cl_2. $C_{32}H_{52}N_2O_2$; FW = 496.76 g/mol; crystal size $0.40 \times 0.40 \times 0.30$ mm^3; orthorhombic, space group *Pbcn*; $a = 27.507(2)$ Å, $b = 10.7190(9)$ Å, $c = 10.2197(8)$ Å, $V = 3013.3(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.095$ M g/m^3, $\lambda = 0.71073$ Å, $\mu = 0.067$ mm^{-1}, $F(000) = 1096$, $T = 100(2)$ K, $R = 0.0621$, $R_w = 0.1459$. Crystal data for **6**. Recrystallized from toluene/methanol. $C_{45}H_{53}N_2NaO_4Zn$; FW = 774.25 g/mol; crystal size $0.20 \times 0.10 \times 0.05$ mm^3; monoclinic, space group $P2(1)/n$; $a = 14.4659(12)$ Å, $b = 16.7210(14)$ Å, $c = 17.9212(15)$ Å, $\beta = 105.563(2)$, $V = 4175.9(6)$ Å^3, $Z = 4$, $D_{calcd} = 1.282$ Mg/m^3, $\lambda = 0.71073$ Å, $\mu = 0.646$ mm^{-1}, $F(000) = 1712$, $T = 100(2)$ K, $R = 0.0527$, $R_w = 0.1215$. These data have been deposited (**2b**: CCDC 600756, **6**: CCDC 600757) at the Cambridge Crystallographic Data Centre, Cambridge, UK. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ UK [Fax: +44 0 1223 336033 or email deposit@ccdc.cam.ac.uk].
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23. Typical procedure to make **3a–c**: 1 equiv of en, 2 equiv of **1a–c**, 5 equiv of 95% paraformaldehyde and 10 ml of toluene were combined in a round bottomed flask equipped with a condenser and heated at reflux for three days. The round bottomed flask was cooled and a white precipitate and brown oil fell out of the solution. Methanol (10 ml) was added and the flask was sonicated for 30 min. The resulting white precipitate was isolated by filtration in 34–77% yield. Characterization of **3a**: ^{1}H NMR ($CDCl_3$) δ 6.83 (s, 2H), 6.62 (s, 2H), 4.92 (s, 4H, O–CH_2–N), 4.00 (s, 4H, Ph–CH_2–N), 2.98 (s, 4H, N–CH_2), 2.24 (s, 6H, CH_3), 2.17 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 150.2, 129.8, 129.1, 125.4, 125.4, 119.2, 82.85, 50.6, 49.7, 20.7, 15.7; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{28}N_2O_2$, 352.222; found, 352.2159; mp 132.8–133.9 °C. Characterization of **3b**: ^{1}H NMR (C_6D_6) δ 7.38 (d, 2H, $J = 2.4$ Hz), 6.78 (d, 2H, $J = 2.4$ Hz), 4.59 (s, 4H, O–CH_2–N), 3.76 (s, 4H, Ph–CH_2–N), 2.80 (s, 4H, N–CH_2), 1.58 (s, 18H, $C(CH_3)_3$), 1.32 (s, 18H, $C(CH_3)_3$); ^{13}C NMR (C_6D_6) δ 152.0, 142.8, 137.3, 122.9, 122.6, 120.5, 83.0, 52.3, 51.1, 35.8, 35.0, 32.4, 30.6; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{34}H_{53}N_2O_2$, 521.4107; found, 521.4000; mp 153.2–153.8 °C. Characterization of **3c**: ^{1}H NMR ($CDCl_3$) δ 7.23 (d, 2H, $J = 2.54$ Hz), 6.88 (d, 2H, $J = 2.54$ Hz), 5.00 (s, 4H, O–CH_2–N), 4.02 (s, 4H, Ph–CH_2–N), 2.96 (s, 4H, N–CH_2); ^{13}C NMR ($CDCl_3$) δ 148.9, 128.4, 125.9, 125.2, 122.6, 122.1, 84.0, 50.4, 50.0; HRMS (FAB^+) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{17}N_2O_2Cl_4$, 433.0044; found, 433.9930; mp 199.2–200.8 °C.
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25. Typical procedure to make **5a–c**: In a 48 mL pressure flask, 6 equiv (22.5 mmol) of **5a–c**, 4 equiv of 95% paraformaldehyde, and 1 equiv of en were heated to ~80 °C and stirred for three days. The reaction was allowed to cool and approximately 20 mL of ether (**5a**) or methanol (**5b**, **c**) was added to the oily reaction mixture. The flask was sonicated for 10 min and a white precipitate fell out. The precipitate was isolated by vacuum filtration and the product was isolated as a white solid in 27–65% yield. Characterization of **5a**: ^{1}H NMR ($CDCl_3$) δ 6.85 (s, 4H), 6.66 (s, 4H), 3.58 (s, 8H, Ph–CH_2–N), 2.75 (s, 4H, N–CH_2–CH_2–N), 2.21 (s, 12H, CH_3), 2.18 (s, 12H, CH_3); ^{13}C NMR ($CDCl_3$) δ 151.7, 130.9, 128.5, 128.4, 124.3, 121.3, 55.9, 50.2, 20.3, 15.7; FTIR data (ATR of dry film): ν(N–H) 3423 cm^{-1}; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{38}H_{40}N_2O_4$, 596.380; found, 596.3564; mp 186.6–187.4 °C. Characterization of **5b**: ^{1}H NMR ($CDCl_3$) δ 7.87 (s, 4H, O–H), 7.27 (d, 4H, $J = 2$ Hz), 6.90 (d, 4H, $J = 2$ Hz), 3.60 (s, 8H, Ph–CH_2–N), 2.83 (s, 4H, N–CH_2–CH_2–N), 1.39 (s, 18H, $C(CH_3)_3$), 1.28 (s, 18H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 152.1, 141.5, 135.9, 125.0, 123.5,

121.3, 57.1, 50.9, 34.7, 34.1, 31.5, 29.6; FTIR data (ATR of dry film): ν(N–H) 3136 cm^{-1}; HRMS (FAB^+) m/z: $[M+H]^+$ calcd for $C_{62}H_{97}N_2O_4$, 933.7448; found, 933.7771; mp 200.8–201.9 °C. Characterization of **5c**: ^1H NMR (DMSO) δ 10.61 (s, 4 H, O–H), 7.35 (d, 4H, $J = 2$ Hz), 7.13 (d, 4H, $J = 2$ Hz), 3.66 (s, 8H, Ph–CH_2–N), 2.63 (s, 4H, N–CH_2–CH_2–N); ^{13}C NMR (DMSO) δ 151.2, 128.3, 128.1, 126.6, 122.7, 121.0, 54.3, 49.4; FTIR data (ATR of dry film): ν(N–H) 3378 cm^{-1}; HRMS (FAB^+) m/z: $[M+H]^+$ calcd for $C_{30}H_{25}N_2O_4Cl_8$, 756.9323; found, 756.920; mp 201.7–202.9 °C.

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