New oligo-α-pyridylamino ligands and their metal complexes

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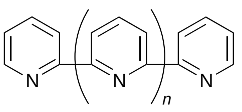
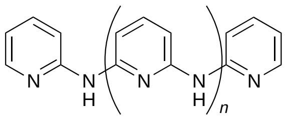
Three novel oligo-α-pyridylamino ligands, tripyridyldiamine (H_2tpda), tetrapyridyltriamine (H_3teptra), pentapyridyltetramine (H_4peptea) are synthesized; the crystal structures of their metal complexes with the all-*anti* configuration of the chelating ligands are reported.

Oligo-α-pyridines **I** exhibit an α-diimine functionality and chelating ability, they bind metal ions strongly and are used as building blocks for the self-assembly of metallosupramolecules.[1–3] We are interested in developing a new type of ligand which might bind oligonuclear metal ions chain; the oligo-α-pyridylamino ligands **II**.[4–6]



I

n = 0, bipyridine
n = 1, terpyridine
n = 2, quaterpyridine
n = 3, quinquepyridine
n = 4, sexipyridine

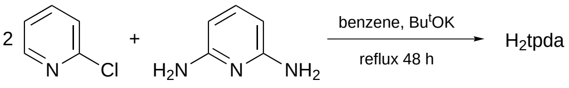


II

n = 0, dipyridylamine(Hdpa)
n = 1, tripyridyldiamine(H_2tpda)
n = 2, tetrapyridyltriamine(H_3teptra)
n = 3, pentapyridyltetramine(H_4peptea)

Here, we report the synthesis of three novel oligo-α-pyridylamino ligands, tripyridyldiamine (H_2tpda), tetrapyridyltriamine (H_3teptra), and pentapyridyltetramine (H_4peptea). The crystal structure of their metal complexes with the all-*anti* conformation of the chelating ligands are presented.

The tripyridyldiamine ligand was synthesized by treating 2.2 equiv. of chloropyridine with 1 equiv. of 2,6-diaminopyridine under basic conditions [eqn. (1)]. The crude product was rinsed with water and recrystallized from propan-2-ol.[7] The iron complex of the ligand was synthesized by treating iron(II) chloride with 2 mol equiv. of H_2tpda in methanol [eqn. (2)]. The electronic spectrum (MeOH solution), shows maxima at 240 nm (3.04×10^4 dm^3 mol^{-1} cm^{-1}), 262 (3.67×10^4), 278 (3.81×10^4) and 334 (3.72×10^4).



(1)

$$\text{H}_2\text{tpda} + \text{FeCl}_2 \xrightarrow{\text{methanol}} [\text{Fe}^{\text{II}}(\text{H}_2\text{tpda})_2]\text{Cl}_2 \quad (2)$$

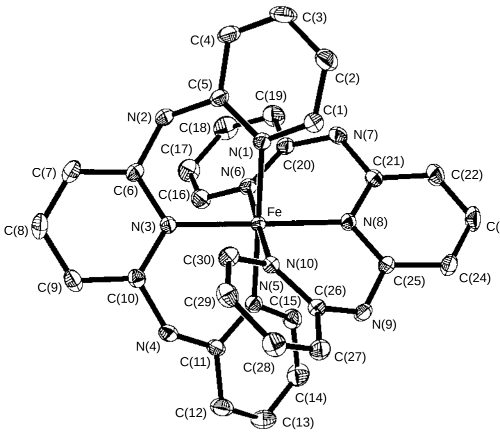
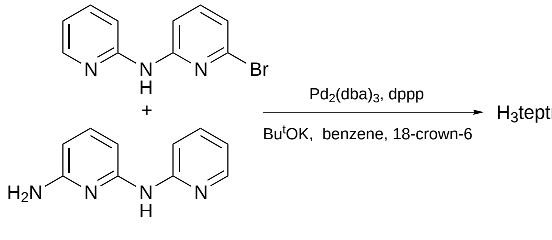


Fig. 1 ORTEP view of $[Fe(H_2tpda)_2]^{2+}$. Selected bond lengths (Å) and angles (°): Fe–N 1.981(2)–2.005(2), av. 1.995; *cis*-N–Fe–N 88.68(9)–91.85(9), av. 90.0, N(1)–Fe–N(5) 179.2(1), N(3)–Fe–N(8), 179.2(1), N(6)–Fe–N(10), 178.6(1); dihedral angles between interpyridyl planes, Py(N1)–Py(N3), 40.8(1), Py(N3)–Py(N5), 34.4(1), Py(N6)–Py(N8), 40.2(1), Py(N8)–Py(N10), 37.6(1).

The molecular structure of $[Fe^{II}(H_2tpda)]^{2+}$ (Fig. 1)‡ reveals that the coordination geometry around Fe^{II} is octahedral with two tridentate H_2tpda ligands arranged in a *mer*-configuration. The H_2tpda ligands coordinate to the iron(II) in an *anti–anti–anti–anti* conformation. The three pyridyl groups of the H_2tpda ligand are essentially planar and are twisted. The dihedral angle between each pair of neighboring pyridyl planes is 38°. The short Fe–N distances, ranging from 1.981(2) to 2.005(2) Å, are consistent with the low spin state of Fe^{II}.

The tetrapyridyltriamine ligand was synthesized by the palladium-catalyzed cross-coupling[8] of (6-bromo-2-pyridyl)(2′-pyridyl)amine and (6-amino-2-pyridyl)(2′-pyridyl)amine in the presence of catalyst [$Pd_2(dba)_3$, dppp, BuᵗOK, and 18-crown-6] in refluxing benzene [eqn. (3)]. The crude product was recrystallized from propan-2-ol. H_3teptra was characterized on the basis of ^1H and ^{13}C NMR spectroscopy, and mass spectrometry. ^1H NMR in $(CD_3)_2SO$ clearly shows two singlets (δ 9.33, 9.07), four doublets (δ 8.19, 7.88, 7.72, 7.10) and three triplets (δ 7.62, 7.50, 6.84) which are consistent with the structural assignment.

The Cu^{II} complex of the ligand was synthesized by treating an equimolar amount of $Cu(ClO_4)_2$ and the H_3teptra in acetonitrile [eqn. (4)]. The electronic spectrum (MeCN solution), shows maxima at 239 nm (2.70×10^4 dm^3 mol^{-1} cm^{-1}), 270(sh) (1.59×10^4), 328 (3.77×10^4) and 368 (9.71×10^3).



(3)

$$\text{H}_3\text{teptra} + \text{Cu(ClO}_4)_2 \xrightarrow{\text{MeCN}} [\text{Cu}^{\text{II}}(\text{H}_3\text{teptra})][\text{ClO}_4]_2 \quad (4)$$

The molecular structure of $[Cu^{II}(H_3teptra)]^{2+}$ (Fig. 2)‡ reveals that the coordination geometry around Cu^{II} is between planar and tetrahedral with the monohelical H_3teptra ligand having an all-*anti* comformation. The four pyridyl groups of the H_3teptra ligand are planar and the dihedral angle between each

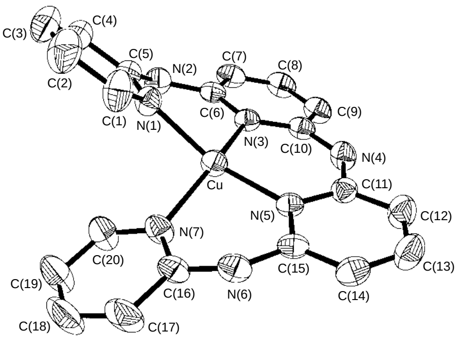
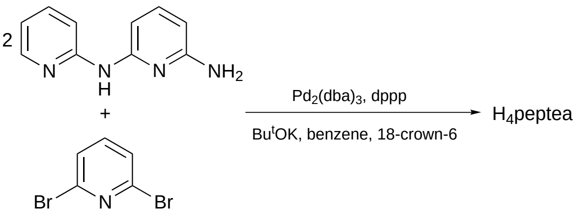


Fig. 2 ORTEP view of $[Cu(H_3teptra)]^{2+}$. Selected bond lengths (Å) and angles (°): Cu–N 1.954(5)–1.982(5), av. 1.967; N(1)–Cu–N(3), 91.9(2), N(1)–Cu–N(5), 151.0(2), N(1)–Cu–N(7) 90.9(2), N(3)–Cu–N(5), 98.2(2) N(3)–Cu–N(7), 150.0(2), N(5)–Cu–N(7), 93.0(2); dihedral angles between interpyridyl planes, Py(N1)–Py(N3), 25.3(3), Py(N3)–Py(N5), 15.0(1), Py(N5)–Py(N7), 20.4(2).

pair of neighboring pyridyl planes is 25.3(3), 15.0(3), 20.4(3)°, respectively. The short Cu–N distances, ranging from 1.954(5) to 1.982(5) indicate a strong binding of the chelating ligand.

The synthesis of pentapyridyltetramine was similar to H_3teptra [eqn. (5)]. H_4peptea was characterized on the basis of its ^1H and ^{13}C NMR and mass spectrometry data. Although the ^1H NMR spectrum of H_4peptea [in $(CD_3)_2SO$] only shows two singlets (δ 9.33, 9.06), five doublets (δ 8.19, 7.90, 7.28, 7.19, 7.08) and three triplets (δ 7.62, 7.50, 6.84), the intergrated area of the triplet at δ 7.50 is equivalent to that originating from three protons when compared to the area of the other triplet, indicating the existence of two independent triplets with an identical chemical shift at δ 7.50.

The Cu^{II} complex of the ligand was synthesized by treating an equimolar solution of $Cu(ClO_4)_2$ and H_4peptea in acetonitrile and precipitated by adding diethyl ether [eqn. (6)]. The electronic spectrum (MeCN solution), shows maxima at 254 nm (1.87×10^4 dm^3 mol^{-1} cm^{-1}), 324 (1.97×10^4), 344 (1.65×10^4) and 378(sh) (6.21×10^3).



(5)

$$H_4peptea + Cu(ClO_4)_2 \xrightarrow{MeCN} [Cu^{II}(H_4peptea)][ClO_4]_2 \quad (6)$$

The crystal structure of $[Cu^{II}(H_4peptea)]^{2+}$ (Fig. 3)‡ reveals that the coordination geometry around Cu^{II} is trigonal bipyramidal with the monohelical H_4peptea ligand existing in an all-*anti* configuration. A crystallographic C_2 axis runs through the C(13)–N(5)–Cu chain. The three independent crystallographic pyridyl groups are planar and the dihedral angle between neighboring pyridine planes is *ca.* 21°.

In summary, the modified Buchwald's procedure[8] leads to the synthesis of new types of oligo-α-pyridylamino ligands. Their metal complexes were studied. The complexes demonstrate the chelating ability of the ligands. Attempts to isolate the metal complexes with different coordination modes of the ligands, *e.g.* the all-*syn* configuration of the ligands which bind metal ions in a chain are being undertaken.

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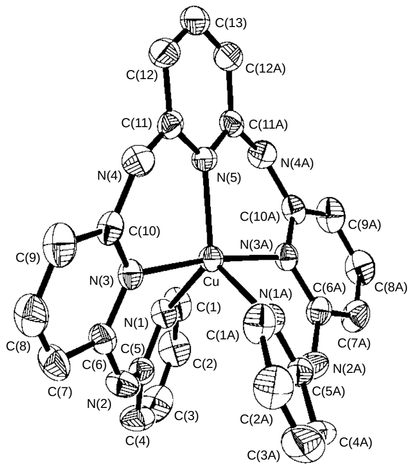

Fig. 3 ORTEP view of $[Cu(H_4peptea)]^{2+}$. Selected bond length (Å) and angles (°): Cu–N(1) 2.102(5), Cu–N(3) 1.972(4), Cu–N(5) 2.017(6); N(1)–Cu–N(1A), 112.2(3), N(1)–Cu–N(3) 87.3(2), N(1)–Cu–N(3A), 88.4(2), N(1)–Cu–N(5), 123.9(1), N(3)–Cu–N(3A), 172.3(3), N(3)–Cu–N(5), 93.8(1); dihedral angles between interpyridyl planes, Py(N1)–Py(N3), 22.2(3), Py(N3)–Py(N5), 19.0(3).

Footnotes and References

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‡ *Crystal data*: for $[Fe(H_2tpda)_2]Cl_2 \cdot 2MeOH$: monoclinic, space group $P2_1/n$, a = 15.0179(2), b = 11.1499(2), c = 20.2308(1) Å, β = 98.864(1)°, U = 3347.15(8) $Å^3$, D_c = 1.424 g cm^{-3}, Z = 4; T_{min} = 0.236, T_{max} = 0.296, 21 345 reflections were measured and 7613 unique reflections ($2\theta < 55°$, R_{int} = 0.046) were used in the refinement. Full-matrix least-squares refinement on F^2 (457 variables) converged to R_F = 0.0506 R_{wF2} = 0.1026 for 5168 reflections with $I > 2\sigma(I)$.

$[Cu(H_3teptra)][ClO_4]_2 \cdot MeCN$: monoclinic, space group $P2_1/c$, a = 12.0470(2), b = 14.4324(1), c = 15.4744(2) Å, β = 92.883(1)°, U = 2687.08(6) $Å^3$, D_c = 1.629 g cm^{-3}, Z = 4; T_{min} = 0.2226, T_{max} = 0.2830, 14 676 reflections were measured and 4721 unique reflections ($2\theta < 50°$, R_{int} = 0.0304) were used in the refinement. Full-matrix least-squares refinement on F^2 (354 variables) converged to R_F = 0.0782 R_{wF2} = 0.2134 for 3877 reflections with $I > 2\sigma(I)$.

$[Cu(H_4peptea)][ClO_4]_2 \cdot 2H_2O$: monoclinic, space group $C2/c$, a = 11.2720(4), b = 36.0332(14), c = 7.7793(2) Å, β = 108.732(1)°, U = 2998.6(2) $Å^3$, D_c = 1.652 g cm^{-3}, Z = 4; T_{min} = 0.318, T_{max} = 0.377), 8685 reflections were measured and 2652 unique reflections ($2\theta < 50°$, R_{int} = 0.056) were used in the refinement. Full-matrix least-squares refinement on F^2 (218 variables) converged to R_F = 0.0723, R_{wF2} = 0.1843 for 1858 reflections with $I > 2\sigma(I)$. For all structures SMART diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å), SADABS absorption correction. CCDC 182/638.

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