Preparation and evaluation of 2-azinyl-2H-benzotriazoles as bidentate ligands: Synthesis and characterization of [2-(2-pyridynyl)-2H-benzotriazole](bpy)_2Ru^{2+}

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Abstract

Five 2-azinyl-2H-benzotriazoles (azinyl = 2-pyridinyl, 2-pyrazinyl, 2-pyrimidinyl, 5-methyl-2-pyridinyl) were prepared and characterized as bidentate ligands. The electronic structure of these and related heterocycles was investigated spectroscopically and computationally (TD-DFT). They were tested at the B3LYP/6-31++G(d, p)//B3LYP/6-31G(d, p) level of theory as ligands for MgH2, which permitted the elucidation of trends in complex formation, its geometry as a function of the ring structure, and the number and position of the nitrogen atoms in the azine ring. A Ru^{2+} complex 7a-Ru with 2-pyridinyl-2H-benzotriazole (7a) and two bpy ligands was prepared and characterized structurally, spectroscopically and electrochemically. The results were compared to those for similar complexes and discussed in the context of computational results for MgH2 complexes.

1. Introduction

Heteroaromatic bidentate ligands are important chelates that tune photophysical and electrochemical properties of transition metal complexes. Perhaps the best known and most extensively studied such a ligand is 2,2’-bipyridyl (1), whose ruthenium complexes [1,2] 1-Ru have been explored as components of energy harvesting [3,4] and electroluminescence [5] devices. Replacement of one of the pyridine rings in 1 with fused five-membered heterocycles, such as indole [6,7] or benzimidazole [8,9] in 2 and 3 respectively, leads to anionic ligands and complexes with reduced overall charge. Recently, there has been interest in electrically neutral bidentate ligands based on the fused azole-pyridine structural motif. Such ligands offer different geometry of the coordination site and additional means of controlling red-ox and photophysical properties of the metal complexes [10,11]. Examples of such ligands are 4, 5, and 6 and their complexes 4-M–6-M [12–14]. These and other nitrogen-rich ligands [15,16] are of interest for designing dinuclear complexes [8,17,18] and controlling their supramolecular structures [19–21] and functions [2].

All three ligands 4–6 are based on fused triazole substituted with pyridine, and they differ significantly in their electronic structures. In contrast to 4, derivatives 5 and 6 have a quinoid structure in their non-polar ground states and lower HOMO–LUMO gaps. A similar quinoid structure exists for 2-pyridinyl-2H-benzotriazole (7a), an isomer of 4, but surprisingly, neither 7a nor its close analogs have been investigated to date.

Here we focus on pyridine derivative 7a and its polyazine analogs 7b–7e as new potential bidentate ligands for transition metals. The new ligands are evaluated for their photophysical properties and chelating ability of MgH2 using DFT computational methods. We described the preparation and spectroscopic analysis of the parent ligands 7a–7c and two of their derivatives, 8 and 9. Finally, a ruthenium complex 7a-Ru was prepared and analyzed structurally, spectroscopically, and electrochemically. The experimental data were compared to the computational results.

2. Results and discussion

2.1. Synthesis

The triazoles 7 were prepared from appropriate haloazo derivatives 10 according to a modified general method [22] for substituted 2-phenylnaptho[1,2,3]triazoles (Scheme 1). Thus, a reaction of chloro derivative 10a (Hal = Cl) with excess NaN3 in DMF at 120 °C gave 32% yield of 7a. Addition of catalytic amounts of [Bu4N][Br] improved the yield to 49%. Replacement of the chlorine by fluorine in 10a (Hal = F) increased the yield of 7a further to 79%, which is attributed to a more facile nucleophilic displacement of the F− than Cl− in azobenzenes [23]. Attempts to isolate the transient azide 11 by running the reaction in boiling MeCN were

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A reaction with azopyrazine 10b gave the expected triazole 7b in a good yield. In contrast, a reaction of the pyrimidine derivative 7c under the same conditions gave exclusively the known [24] 1-isomer 12, which was isolated in 56% and identified by comparison of the NMR, UV and IR spectra with the literature data [25]. We speculated that the fluoride anion formed in the reaction attacks the electrophilic C(2) position of the pyrimidine ring (Scheme 2), which results in the formation of electrophilic 2-fluoropyrimidine 7c under the same conditions gave exclusively the known [24] 1-isomer 12 in a good yield. In contrast, a reaction of the pyrimidine derivative 7c with the anion (which results in the formation of electrophilic 2-fluoropyrimidine 7c) was little affected by these precautions, and the approximate ratio of the products 7c:12:14 was 3:2:2 in one run and 2:5:3 in another by 1H NMR. The desired 2-isomer was isolated as the least polar fraction that on TLC appears as a fluorescent spot. The azo derivatives 8 (Scheme 3) and pyridazine 9 (Scheme 4), using appropriately functionalized azo compounds 15 and 16, respectively. In the case of pyridazine 9, the major product (51% yield) was the more polar isomeric compound 17, which was identified on the basis of NMR and IR data. The azo compounds 15 and 16 were obtained using the general procedure [27] by condensing either 2-chloro- or 2-fluoronitrosomethane with appropriate aminozine in aq 50% NaOH/toluene system. The details of the preparation of 10a and 15 will be described elsewhere [28].

The reaction was conducted with 4 equiv. of NaN₃ in the presence of small excess of Ca(OTs)₂ as the fluoride ion scavenger, and [Bu₄N][F] was replaced with [Bu₄N][HSO₄]⁺. The reaction gave a mixture (28% yield) of 7c and 12 in 1:2 ratio and benzotriazole (14) isolated in 56% yield. To avoid the presence of nucleophiles such as traces of water or Me₂NH from decomposing DMF, the reaction was run in freshly dried MeCONMe₂ (DMA) with stoichiometric amounts of rigorously dried NaN₃ and Ca(OTs)₂. The isolated yield of 7c was little affected by these precautions, and the approximate ratio of the products 7c:12:14 was 3:2:2 in one run and 2:5:3 in another by 1H NMR. The desired 2-isomer was isolated as the least polar fraction that on TLC appears as a fluorescent spot. Results for 7c suggest that the preparation of the triazine derivative 7e by this method may be even more challenging considering the electrophilic nature of the C(2) atom in the triazine ring.

Finally, we prepared substituted derivatives, pyridine 8 (Scheme 3) and pyridazine 9 (Scheme 4), using appropriately functionalized azo compounds 15 and 16, respectively. In the case of pyridazine 9, the major product (51% yield) was the more polar isomeric compound 17, which was identified on the basis of NMR and IR data. The origin of the formation of 17 is unclear although similar O- to -N rearrangements were observed before at elevated temperatures for other alkoxyazopyrazines [26]. Heating of product 9 with or without [Bu₄N][Br] in DMF did not give the rearrangement to 17. In contrast, substrate 16 heated with catalytic amounts of [Bu₄N][Br] gave 21% of the rearranged product identified as 18 on the basis of the 1H NMR spectrum and appearance of a signal at 3.97 ppm at the expense of the characteristic signal for the OMe group at 4.25 ppm. A reaction of 16 and NaN₃ conducted without [Bu₄N][Br] gave 8% yield of the expected isomer 9 and 24% yield of the rearranged product 17.

The azo derivatives 10 and 16 were obtained using the general procedure [27] by condensing either 2-chloro- or 2-fluoronitrosobenzene with appropriate aminozine in aq 50% NaOH/toluene system. The details of the preparation of 10a and 15 will be described elsewhere [28].
2.2. Electronic absorption and emission spectra

Experimental absorption and emission spectra for triazoles 7a–7c, 9, 12, and 17 were recorded in MeCN, and the results are presented in Figs. 1–3 and Table 1. All four 2-substituted benzotriazoles exhibit a strong absorption band at about 305 nm and a weaker band around 228 nm, as shown for 7a in Fig. 1. This is consistent with results for other simple 2-aryl-2H-benzotriazoles such as 19 (Table 1) [29,30].

Absorption spectra for 1-substituted benzotriazoles are different from those of the 2-isomers. For instance, the absorption band at about 300 nm recorded for 7c has significantly reduced intensity and is slightly blue-shifted in its 1-isomer 12 (Fig. 2). There are smaller albeit noticeable differences in the absorption spectra of the two isomeric pyridazines (Fig. 3). The N-Me isomer 17 has a broader absorption band around 300 nm than its O-Me isomer 9 containing the aromatic pyridazine ring.

Three of the new triazoles 7a, 7b, and 7c fluoresce. The pyridine derivative 7a exhibits the most efficient photoluminescence with a maximum at 364 nm. For the pyrazine and pyrimidine derivatives 7b and 7c the emission energy is lower by 0.18 and 0.12 eV, respectively, and the emission efficiency is about 20% and 10%, respectively, relative to that observed for 7a (Table 1). In contrast, triazole 12, an isomer of 7c, and the two pyridazines 9 and 17, do not exhibit a detectable fluorescence at ambient temperature.

Absorption spectra were calculated using the TD-DFT method for structures optimized at the B3LYP/6-311G(d, p) level of theory. The heterocycles were found in the Cs symmetry (4 [31], 5, 6, 7a, 7b, 7d, and 9), C2v (1) [32], C2 (7c) [33], and C2h (7e and 19 [34]), which is consistent with their reported experimental solid-state structures.

Computational results demonstrated that the intense low energy absorption bands for 2-substituted benzotriazoles 7 are located around 300 nm, which is in good agreement with the available experimental data (Table 1). The main component of this \(\pi - \pi^*\) excitation typically is the HOMO \(\rightarrow\) LUMO transition with a small contribution from the HOMO \(\rightarrow\) LUMO + 1 transition. The former set of MOs extends over the entire \(\pi\) system, while the MOs involved in the latter transition are localized as shown for 7a in Fig. 4. The exception is the pyridazine 7d for which the HOMO-1 contains the lone pairs of the pyridazine ring and the \(\pi\) orbital participating in the \(\pi - \pi^*\) excitation is the HOMO \(\rightarrow\) LUMO + 2 transition.

The transition energy of the 2-substituted benzotriazole is affected by the number and the position of the nitrogen atoms in the azine ring. Upon substitution of the pyridine ring in 7a for phenyl in 19 the \(\pi - \pi^*\) excitation energy increases by 7 nm (experimental 4 nm) and by an additional 9 nm (experimental 4 nm) in pyrimidine, pyridazine and triazine derivatives. Only in the pyrazine derivative 7b the transition energy decreases markedly. This trend approximately follows the trend in energy of the LUMO in the series from the highest in the phenyl derivative 19 (–2.02 eV) to the lowest in the triazine 7e (–2.69 eV).

A comparison of the results for 2-phenyl and 1-phenyl derivatives 7a and 4, respectively, shows the same type of delocalized MOs (HOMO and LUMO) involved in the \(\pi - \pi^*\) transitions and
little difference in the electronic excitation energy. In the isomeric [1,2,3]triazolo[1,5-a]pyridine derivative 5 and [1,2,4]triazolo[4,3-a]pyridine 6, there are two $\pi-\pi^*$ excitations that are generally lower energy than those calculated for 7a and 4 (Table 1), which result mainly from the HOMO $\rightarrow$ LUMO (low energy) and HOMO $\rightarrow$ LUMO + 1 (high energy) transitions.

The inclusion of the PCM solvation model showed a modest positive solvatochromic effect on the low energy $\pi-\pi^*$ excitation of about 6–13 nm in MeCN, and the calculated energies are closer to those observed experimentally. The only exception are triazolopyridine derivatives 5 and 6 in which the $\pi-\pi^*$ excitations are slightly blue-shifted in the polar solvent.

2.3. Chelation of MgH$_2$

The chelating ability of the triazoles 7 was assessed by examining complexes with MgH$_2$ using computational methods and comparing the results to those for other related ligands. Results in Table 2 indicate that 2-substituted benzotriazoles have enthalpies of complex formation of about $/C_0$ 22 kcal/mol, which are similar to those calculated for bpy (1) and significantly smaller than those for anions 2 and 3. As expected, the introduction of nitrogen atoms to the azine ring diminishes the electron density at the coordinated nitrogen atom and lowers its donating abilities. Consequently, the order of the exotherm follows 7a > 7c > 7d > 7b > 7e. The

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Symm</th>
<th>LUMO/eV</th>
<th>Experimental Absorption (nm (log $\varepsilon$))</th>
<th>Emission (nm)</th>
<th>Theoretical $\pi \rightarrow \pi^*$/nm ($f$)</th>
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<td></td>
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<td></td>
<td>Vacuum $\varepsilon = 1$</td>
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<tr>
<td>1</td>
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<td>283 (4.16)$^b$</td>
<td>365$^i$</td>
<td>267 (0.46)</td>
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<td>412$^c$</td>
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<td></td>
<td></td>
<td>282 (0.59)</td>
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<td></td>
<td>–2.69</td>
<td></td>
<td></td>
<td>282 (0.55)</td>
</tr>
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<td>308 (4.38)$^k$</td>
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<td>300 (4.08)$^j$</td>
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<td>308 (4.38)$^k$</td>
<td>368$^k$</td>
<td>298 (0.62)</td>
</tr>
</tbody>
</table>

*a* TD-B3LYP/6-311G(d, p)//B3LYP/6-311G(d, p).

*b* In MeCN, Ref. [35].

*c* In MeOH, Ref. [36].

*d* In EtOH, Ref. [37].

*e* Not reported.

*f* In MeOH, Ref. [31].

*g* Ref. [38].

*h* In MeCN; this work.

*i* Not detected.

*j* In MeOH, Ref. [30].

**Table 1**

**Experimental and calculated absorption energies and oscillator strength for selected ligands.**
Recrystallization with a mixture of 2-butanol and toluene gave dark-red crystals of 7a-Ru in space group P1 [39]. The unit cell contains two [C$_{14}$H$_{16}$N$_{6}$Ru]$^{2+}$ dications, four [PF$_6$]$^{-}$ anions and one 2-butanol solvent, which replaced the two molecules of MeCN. The structure was not disordered, hence providing a relative chiral anchor for crystal structure refinement. Additionally, the relative positions of the fluorine atoms on the two [PF$_6$]$^{-}$ anions are distinctly non-centrosymmetric [40]. Details for the structure solution and refinement procedures are given in SI.

Both unique dications A and B have similar geometry with the Ru atoms exhibiting the normal octahedral coordination as shown for A in Fig. 5. The pyridine rings are practically coplanar in both 2,2'-bipyridyl (bpy) ligands and the dihedral angles are in a range of 0.8–3.6°. Similar coplanarity of two heterocyclic rings is observed for the benzotriazole ligand in which the dihedral angles is 2.02°(12) in A and 0.1°(12) in B.

Analysis of the bonding to Ru demonstrates that for the benzotriazole ligand the $d_{5}$ distance (2.052(5) Å in A (Fig. 5) and 2.048(5) Å in B) is shorter than the $d_{6}$ (2.089(5) Å in A and 2.075 Å in B), and similar to that found for the Ru–N$_{bpy}$ distances (avg 2.050(5) Å in A and 2.062(5) Å in B).

The Ru–N$_{triaz}$ distance $d_{5}$ observed in 7a-Ru is longer than the analogous Ru–N$_{triaz}$ separation found in 5-Ru by nearly 0.02 Å [13]. In both complexes the Ru–N$_{bpy}$ distance $d_{5}$ is longer by about 0.03 Å than that found for the 2,2'-bipyridyl ligand in 1-Ru [41]. These experimental results followed the trend in calculated $d_{5}$ and $d_{6}$ values for magnesium complexes shown in Table 2 in which the shortest Mg–N distances are calculated for 1-Mg. The bonding between Ru and 2,2'-bipyridyl, Ru–N$_{bpy}$, in 7a-Ru and 5-Ru, remains essentially the same as in the parent complex 1-Ru and is about 2.05 Å.

The benzotriazole ring appears to be little distorted by the coordination to the Ru center and demonstrates significant bond length alternation (bond localization) in accordance with the non-polar Kekule structure for the free ligand 7a. The largest effect of coordination to Ru is observed for the N(2)–N(3) bond, which is longer by about 0.025 Å relative to the analogous N(4)–N(3) bond.

2.5. Characterization of 7a-Ru

To probe the metal–ligand interactions, the ruthenium complex 7a-Ru was characterized by spectroscopic and electrochemical methods and the results are summarized in Table 3. The complex exhibits ligand-centered absorption bands at about 300 nm and two overlapping metal-to-ligand CT bands (MLCT) in the visible range with a maximum at 434 nm (Fig. 6). Deconvoluting of the visible portion of the spectrum revealed a more intense higher energy peak with a maximum at 431 nm, and the second peak with a maximum at 473 nm [42]. The former was attributed to the Ru → bpy excitation, while the low energy peak to the Ru → 7a excitation. This assignment is consistent with spectra of other (bpy)$_{2}$LRu$^{2+}$ complexes in which the band at about 428 nm was ascribed to the Ru → bpy excitation [43]. In complexes of the isomeric [1,2,3]triazole 4-Ru and 5-Ru, the two bands Ru → bpy and Ru → L apparently overlap giving rise to one broad absorption with a maximum at 423 nm for the former and 433 nm for the latter (Table 3). Complex 7a-Ru exhibits a very weak emission at 690 nm ($\lambda_{ex} = 452$ nm), which by comparison to emission of 1-Ru ($\lambda_{ex} = 452$ nm) [44] has a quantum yield of about 0.001 in EtOH at ambient temperature.

A comparison of the lowest energy MLCT bands indicates that the HOMO–LUMO separation in 7a-Ru is smaller than that in 1-Ru ($\lambda_{max} = 452$ nm), which in turn is smaller than that in 5-Ru ($\lambda_{max} = 433$ nm) and in 4-Ru ($\lambda_{max} = 423$ nm). This result is consistent with the significantly lower LUMO in 7a free ligand (−2.12 eV, Table 1) than those in 1, 4, and 5 (about −1.7 eV).
Cyclic voltammetry of 7a-Ru revealed one reversible oxidation and three reversible reduction waves that are shifted to more positive potentials when compared to 1-Ru under the same conditions.\[45\] The Ru2+/Ru3+ half potential for 7a-Ru is more anodic by 0.17 V than that for 1-Ru, which indicates lower electron donating ability of ligand 7a when compared with 2,2'-bipyridyl (1).

Data in Table 3 show that the weakest electron donor is 4, 1-isomer of 7a, as evident from the most anodic potential ($\Delta E_{1/2}^{(ox)} = +0.27$ V) of its complex 4-Ru, while 5 is comparable to 1 ($\Delta E_{1/2}^{(ox)} = -0.03$ V).\[45\] The overall ligand's impact on $E_{1/2}^{(ox)}$ of the complex appears to follow the order $5 < 1 < 7a < 4$. The observed trend in the series does not follow the calculated charge density on the MgH2 fragment in complexes listed in Table 2. This is not unexpected since Mg lacks valence electron pairs and has only one ligand.

Complex 7a-Ru is easier to reduce than 1-Ru by +0.26 V and the reversible process at $E_{1/2}^{(red)} = -1.00$ V is attributed to one-electron reduction of the benzo[1,2,4]triazole ligand. In contrast, the reported $E_{1/2}^{(red)}$ potentials for complexes 4-Ru and 5-Ru are slightly lower than that observed for 1-Ru. This result is consistent with the significantly lower LUMO for 7a ($-2.12$ eV) than for other three free ligands (about $-1.7$ eV).

As a consequence of the higher reduction potential $E_{1/2}^{(red)}$ the cell potential $E_{cell}$ for 7a-Ru is smaller by about 0.1 V than that
measured for its isomers, 4-Ru and 5-Ru, and 1-Ru. This is consistent with the electronic absorption data (Table 3) and indicates the smallest HOMO–LUMO gap for 7a-Ru in the series.

3. Conclusions

Benzotriazoles 7 are new bidentate ligands with tunable electronic properties. A combination of experimental and computational methods allowed for extensive comparison of the triazoles to 2,2’-bipyridyl (1) and to their isomers 4–6 as ligands.

All benzotriazole derivatives 4–9, 12 and 19 have lower HOMO–LUMO gaps than 2,2’-bipyridyl as evident from experimental and calculated excitation energies shown in Table 1. The lowest π–π* excitation for benzotriazoles fall into a range of 4.16–3.91 eV (298–317 nm), which is 0.24–0.49 eV lower energy than that for 1, although some of this difference can be due to solvent effects.

2-Substituted benzotriazoles 7 have significantly lower LUMO energies than the 1 isomers, as evident by 4 and 12, and isomeric

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**Table 3**

Experimental parameters for selected Ru complexes.

<table>
<thead>
<tr>
<th>A</th>
<th>( \lambda_{\text{max}} ) (log ( \epsilon ))/nm</th>
<th>( E_{1/2}^{\text{ox}} )/V</th>
<th>( E_{1/2}^{\text{red1}} )/V</th>
<th>( E_{1/2}^{\text{red2}} )/V</th>
<th>( E_{1/2}^{\text{red3}} )/V</th>
<th>( E_{\text{cell}} )/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Ru</td>
<td>452 (4.13)(^d)</td>
<td>+1.35</td>
<td>−1.26</td>
<td>−1.46</td>
<td>&lt;−1.70</td>
<td>2.61</td>
</tr>
<tr>
<td></td>
<td>450(^e)</td>
<td>+1.26(^d)</td>
<td>−1.33(^d)</td>
<td>−1.51(^d)</td>
<td>−1.77(^d)</td>
<td>2.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+1.35(^f)</td>
<td>1.33(^f)</td>
<td>−1.52(^f)</td>
<td>−1.76(^f)</td>
<td>2.68</td>
</tr>
<tr>
<td>4-Ru</td>
<td>423 (4.21)(^d)</td>
<td>+1.53(^d)</td>
<td>−1.39(^d)</td>
<td>−1.60(^d)</td>
<td>( \approx )</td>
<td>2.92</td>
</tr>
<tr>
<td>5-Ru</td>
<td>433(^e)</td>
<td>+1.23(^e)</td>
<td>−1.42(^e)</td>
<td>−1.65(^e)</td>
<td>( \approx )</td>
<td>2.65</td>
</tr>
<tr>
<td>7a-Ru</td>
<td>473 and 431</td>
<td>+1.52</td>
<td>−1.00</td>
<td>−1.38</td>
<td>−1.81</td>
<td>2.52</td>
</tr>
</tbody>
</table>

\(^a\) Low energy MLCT band recorded in MeCN.

\(^b\) Potentials vs SCE obtained in 0.1 M solution of \([\text{Bu}_4\text{N}]^+\text{[PF}_6^-\] in MeCN and referenced to the Fc/Fc* couple assumed to be +0.46 V vs SCE [46].

\(^c\) \( E_{\text{cell}} = E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}} \).

\(^d\) Ref. [12].

\(^e\) Ref. [13].

\(^f\) Potentials vs SCE obtained in 0.1 M solution of \([\text{Bu}_4\text{N}]^+\text{[BF}_4^-\] in MeCN. Ref. [47].

\(^\approx\) Not reported.
The level of the LUMO in series 7 systematically decreases for each N atom included in the aryl substituent reaching a value of 2.69 eV for the triazinyl derivative 7e. At the same time the ligand’s electron donating ability moderately diminishes. The LUMO energy of the ligands impacts the photophysical and electrochemical behavior of the complexes: the lower the ligand’s LUMO the lower the MLCT energy (smaller HOMO–LUMO gap) and higher reduction potential are expected. This is evident from a comparison of 7a-Ru with their isomeric analogs 4-Ru and 5-Ru.

Theoretical analysis of Mg2+ complexes demonstrated that all 2-substituted benzo[1,2,3]triazoles 7 have tight binding comparable to that of bpy (1) and higher than that for isomeric pyridyl derivatives 4–6. This is supported by experimental molecular structures of Ru2+ complexes shown in Table 3.

Overall, new 2-azinyl-2H-benzotriazoles 7 expand and complement the existing pool of bidentate ligands for designing of mono- and dinuclear metal complexes and deserve further investigation. Functional derivatives such as 8 provide a potential synthetic handle for the preparation of functional materials including surface anchoring of the complex.

4. Computational details

Quantum–mechanical calculations were carried out at the B3LYP/6-31G(d,p) and B3LYP/6-311G(d,p) level of theory using GAUSSIAN 98 and 09 suites of programs [48,49]. Geometry optimizations were undertaken using default convergence limits and with appropriate symmetry constraints. Vibrational frequencies were used to characterize the nature of the stationary points. Zero-point energy (ZPE) corrections were scaled by 0.9806 [50].

Following general recommendations [51], energy for complex formation were derived as the differences of SCF energies of individual species computed using the 6-31G(d,p) basis set (single point calculations). Thermodynamic corrections were obtained using the 6-31G(d,p) basis set.

Electronic excitation energies for the triazoles were obtained at the B3LYP/6-31G(d,p) level using the time-dependent DFT method [52] supplied in the Gaussian package. Solvent effects on electronic spectra were calculated by using solvent models of various hydration and dielectric constants [53].

5. Experimental section

Melting points are uncorrected. 1H NMR spectra were recorded at 300 MHz in CDCl3 and referenced to the solvent (7.27 ppm). The IR spectra were measured in KBr pellet. UV spectra were recorded in UV-grade CH3CN. All compounds were in concentration of 0.6–6 × 10−5 M. Extinction coefficients were obtained by fitting the maximum absorbance against concentration in agreement with Beer’s law.

5.1. Electrochemistry

Electrochemical analysis of 1-Ru and 7a-Ru was conducted under dry argon in MeCN (distilled over CaH2) containing freshly dried [Bu4N][PF6] (50 °C, P2O5, vacuum, overnight) as the supporting electrolyte (0.1 M) and glassy carbon working electrode with Ag/AgNO3 (1 mM in MeCN) electrode as reference. The scan rate was 0.1 V/s. Peak potentials were referenced to the FC/FC’ couple (+0.142 V) by adding small amounts of ferrocene to the solution, which was assumed to be +0.462 V vs SCE (MeCN, 0.1 M [Bu4N][ClO4]). [46] The electrochemical half potentials for 1-Ru and 7a-Ru were identical when less stringent experimental conditions were used.

[(bpy)2Ru2+][PF6]2− (1-Ru) was obtained from commercial [(bpy)2Ru2+2Cl−·H2O by precipitation with [NH4][PF6] and double recrystallization from a MeCN/MeOH mixture.

5.2. Preparation of benzotriazoles 7a, 7b, 7c, and 7d. General procedure

Appropriate 2-(o-halophenyl)azine 10 (1.0 mmol), sodium azide (260 mg, 4.0 mmol), and tetrabutylammonium bromide (64 mg, 0.2 mmol) were dissolved in anhydrous DMF (1.5 ml). The reaction mixture was stirred in 100 °C for 12 h. After cooling, the reaction mixture was diluted with CH2Cl2, and inorganic slats were filtered off. Solvents were evaporated, and the crude product was purified by column chromatography on silica gel. Analytically pure compounds were obtained by crystallization from appropriate solvent.

5.2.1. 2-(2-Pyridinyl)-2H-benzotriazole (7a)

A CH2Cl2/hexanes mixture (9:1) was used as an eluent. Yield: 155 mg (78%); colorless crystals (cyclohexane): mp 104–105 °C; 1H NMR (CDCl3) δ 8.70 (d, J = 4.6 Hz, 1H), 8.37 (d, J = 8.2 Hz, 1H), 7.99–7.94 (m, 3H), 7.48–7.40 (m, 3H) ppm; IR (KBr) ν 1572, 1472, 1433, 1286 cm−1; UV, λmax (log ε) 304 (4.38), 228 (4.25) nm; GC–MS (EI), m/z 197 (M+, 100). Anal. Calc. for C12H15N3: C, 67.34; H, 4.11; N, 28.55. Found: C, 67.36; H, 4.12; N, 28.58%.

5.2.2. 2-(2-Pyrazinyl)-2H-benzotriazole (7b)

CH2Cl2 with increasing amounts of MeCN (0–5%) was used as an eluent. Yield: 159 mg (81%); colorless crystals (cyclohexane): mp 104–105 °C; 1H NMR (CDCl3) δ 8.72 (s, 1H), 8.36 (d, J = 2.3 Hz, 1H), 8.68 (d, J = 1.3 Hz, 1H), 8.02–7.97 (m, 2H), 7.52–7.48 (m, 2H) ppm; IR (KBr) ν 1477, 1400, 1286, 961, 746 cm−1; UV, λmax (log ε) 311 (4.39), 228 (4.25) nm; GC–MS (EI), m/z 197 (M+, 100). Anal. Calc. for C12H13N3: C, 60.91; H, 3.58; N, 35.51. Found: C, 60.96; H, 3.53; N, 35.52%.

5.2.3. 2-(2-Pyrindinyl)-2H-benzotriazole (7c)

2-(2-Fluorophenyl)pyrimidine (10c, 202 mg, 1.0 mmol), sodium azide (65 mg, 1.0 mmol), calcium p-toluenesulfonate (190 mg, 0.556 mmol), and tetrabutylammonium hydrogen sulfate (19 mg, 0.056 mmol) were dissolved in anhydrous DMA (1.5 ml). The reaction mixture was stirred at 110 °C for 6 h. After cooling, the reaction mixture was diluted with CH2Cl2, and inorganic salts were filtered off. Solvents were evaporated under reduced pressure, and the residue was separated by column chromatography on silica gel. Using CH2Cl2 with increasing amounts of MeCN as eluent, benzo[1,2,3]triazole 14 was isolated as the more polar fraction (66 mg, 56% yield). The less polar fraction (54 mg, 28% yield) contained two regioisomeric products 7c and 12 in 1:2 ratio. Further separation (preparative TLC, SiO2, 7% MeCN in CH2Cl2) allowed for isolation of 2-(pyrimidin-2-yl)benzo[1,2,3]triazole (7c) as colorless needles (CH2Cl2/isooctane): mp 117–118 °C; 1H NMR (DMSO-D6) δ 8.16–7.99 (m, 4H), 7.52–7.47 (m, 3H) ppm; IR (KBr) ν 1572, 1420, 1287, 961, 746 cm−1; UV, λmax (log ε) 299 (4.37), 228 (4.36) nm. Anal. Calc. for C10H7N5: C, 60.91; H, 3.58; N, 35.51. Found: C, 60.97; H, 3.47; N, 35.49%.

5.3. 2-(4-Methyl-2-pyridinyl)-2H-benzotriazole (8)

Finally, CH2Cl2 with increasing amounts of MeCN (0–15%) was used as an eluent. Yield: 191 mg (81%); colorless crystals (hexanes/CH2Cl2): mp 179–180 °C; 1H NMR (CDCl3) δ 8.54 (d, J = 4.9 Hz, 1H), 8.21 (s, 1H), 7.96–7.93 (m, 2H), 7.45 (d, J = 8.9 Hz, 1H), 4.86 (d, J = 5.4 Hz, 2H), 2.53 (s, 3H) ppm; IR (KBr) ν 1572 (4.37), 1472, 1433, 1386, 1310, 1266, 746 cm−1; UV, λmax (log ε) 308 (4.40), 229 (4.30) nm. Anal. Calc.
for C$_{12}$H$_{24}$N$_8$RuP$_2$F$_{12}$: calcd for C$_{10}$H$_8$N$_5$: 198.0780; found: 198.0777.

5.5.2. 2-(2-Fluorophenylazo)pyrimidine (5a)

Yield 67%; needles (cyclohexane/CH$_2$Cl$_2$): mp 215–216 °C. 1H NMR (CDCl$_3$) $\delta$ 8.30 (d, $J = 7.5$ Hz, 1H), 7.99 (s, 1H), 7.54–7.40 (m, 2H) ppm. Anal. Calc. for C$_{10}$H$_8$F$_2$N$_4$: C; 53.08; H, 2.61; N, 13.03; F, 12.47. Found: C, 53.12; H, 2.62; N, 13.07; F, 12.49.

5.5.3. 2-(2-Chlorophenylazo)pyrimidine (6a)

Yield 68%; red crystals (cyclohexane/CH$_2$Cl$_2$): mp 204–205 °C. 1H NMR (CDCl$_3$) $\delta$ 8.31 (d, $J = 7.7$ Hz, 1H), 7.97 (s, 1H), 7.63 (d, $J = 8.5$ Hz, 2H) ppm. Anal. Calc. for C$_{10}$H$_8$F$_2$N$_4$: C; 55.64; H, 2.61; N, 13.03. Found: C, 55.58; H, 2.59; N, 13.04.

5.6. Preparation of 2-(2-Halophenylazo)azines 10 and 16. A general procedure [27]

Appropriate aminoazines (2-amino-phenazine, 2-amino-pyrazine, or 3-amino-6-methoxyphenazine, 4.0 mmol) were dissolved in toluene (5.0 mL) and 50% aqueous solution of NaOH (3.4 mL) and 2-halonitrozobenzene (4.5 mmol) were added. The mixture was vigorously stirred with a mechanical stirrer for 25 min at 50 °C. After cooling, water was added, and the mixture was extracted with CH$_2$Cl$_2$. Extracts were dried (Na$_2$SO$_4$) and solvents were evaporated. The residue was purified by column chromatography (silica gel) using hexane with a suitable eluent.

5.6.1. 2-(2-Fluorophenylazo)pyrazine (10b, X = F)

Yield 59%; red crystals (hexanes): mp 107–108 °C. 1H NMR (CDCl$_3$) $\delta$ 8.01–7.98 (m, 2H), 7.51–7.46 (m, 2H), 7.24 (d, $J = 9.5$ Hz, 1H), 4.26 (s, 3H) ppm; UV, $\lambda_{\text{max}}$ (log $\varepsilon$) 304 (4.36), 236sh (4.10), 227 (4.08) nm; MS (FAB), m/z 198 (M$^+$, 100); HRMS, m/z calcld for C$_{10}$H$_7$FN$_4$: 198.0780; found: 198.0777.

5.6.2. 2-(2-Chlorophenylazo)pyrimidine (10c, X = Cl)

Yield 62%; red crystals (hexanes): mp 68–69 °C. 1H NMR (CDCl$_3$) $\delta$ 8.90 (d, $J = 4.8$ Hz, 2H), 7.94 (t, $J = 7.7$ Hz, 1H), 7.57–7.50 (m, 1H), 7.32–7.20 (m, 2H) ppm. Anal. Calc. for C$_{10}$H$_7$F$_2$N$_4$: C; 55.64; H, 2.61; N, 13.03; F, 12.47. Found: C, 55.58; H, 2.60; N, 13.04.

Appendix A. Supplementary data

CCDC 785246 contains the supplementary crystallographic data for 7a-Ru. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.02.023.

References


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A minimum with the C2v symmetry was found at the B3LYP/6-31(d, p) level of theory. The C2v symmetric structure optimized at the B3LYP/6-311(d, p) level of theory has an imaginary frequency of $\omega$.

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**References**

58. Results for 7a-Ru are compared to our data for 1-Ru, while for 4-Ru and 5-Ru the comparison is made with the co-reported data for 1-Ru. The observed difference in results for 1-Ru may be due to the electrolyte and reference.
62. Results for 7a-Ru are compared to our data for 1-Ru, while for 4-Ru and 5-Ru the comparison is made with the co-reported data for 1-Ru. The observed difference in results for 1-Ru may be due to the electrolyte and reference.