The New Tetrafunctional π Acceptor Ligand
3,6-Bis(2’-pyrimidyl)-1,2,4,5-tetrazine (bmtz): Diruthenium Complexes of bmtz and of its 1,4-Dihydro Form

Wolfgang Kaim*, Jörg Fees
Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart
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Synthesis, physical properties and the coordination with two [Ru(bpy)2]2+ complex fragments are described for 3,6-bis(2’-pyrimidyl)-1,2,4,5-tetrazine (bmtz), the first compact ligand which offers four equivalent α-diamine chelate sites. Spectroelectrochemistry of intensely blue {(a-bmtz)[Ru(bpy)2]2}n+, n = 4, reveals a very facile reduction (n = 3) at −0.40 V vs. FeCp2+/o and a metal oxidation (n = 5) at +1.18 V to a diruthenium(II/III) mixed-valent form which exhibits an intervalence transfer absorption at 1490 nm. The corresponding complex [(µ-H2bmtz)[Ru(bpy)2]2]n+ with the 1,4-dihydro form H2bmtz of the tetrafunctional ligand is oxidized in two steps at 0.58 and 1.07 V vs. FeCp2+/o.

Introduction
New unsaturated chelate ligands with multiple functionalities e.g. for supramolecular structuring

Results and Discussion
Ligands
Bmtz was obtained as a reactive purple solid by oxidation of the more stable 1,4-dihydro form, H2bmtz (1), which in turn resulted from the coupling between hydrazine and 2-cyanopyrimidine. Bmtz and the intermediates of reaction sequence (1) analyzed correctly and showed the expected spectroscopic characteristics (1H and 13C NMR, MS, UV/VIS; see Exp. Section).

The facile one-electron reduction of bmtz is illustrated by the reduction potential of −1.12 V vs. FeCp2+/o in aprotic acetonitrile/0.1 M Bu4NPF6. In comparison to the more persistent 3,6-bis(2’-pyridyl)-1,2,4,5-tetrazine (bptz), an increasingly used bis(α-diamine) chelate ligand [4], the particular ease of the reduction back to the 1,4-dihydro species, especially in protic solvents [1], promoted metal–metal interaction in molecular bridged arrangements [2], or pH control of physical properties involving charge transfer excited states [3] are sought-after materials. In this report we describe the synthesis, the electrochemical and spectroscopic properties, and the metal coordination of 3,6-bis(2’-pyrimidyl)-1,2,4,5-tetrazine (bmtz), a first compact ligand with four equivalent α-diamine coordination sites.

* Reprint requests to Prof. Dr. Wolfgang Kaim.

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such as ethanol, is due to the additional nitrogen atoms in the peripheral six-membered rings of bmtz. The additional N centers do not only facilitate the reduction by about 0.1 V, they also serve as basic (chelate) sites for protons or other electrophiles.

The EPR spectrum of chemically or electro-generated bmtz−• at g = 2.0040 shows the typical [4a–c] nonet splitting for four equivalent nitrogen centers with a coupling constant $a(14N) = 0.52 \text{ mT}$ which confirms the occupation of a tetrazine-centered MO ($a_u$), similarly as in bptz [4a, b]. This result could not necessarily be expected since Hückel MO perturbation calculations reveal the presence of two close lying unoccupied MOs, the tetrazine-localized $a_u$ and a more delocalized $b_{1u}$ orbital.

As is typical for 1,2,4,5-tetrazines [4, 5], there is an enormous difference of more than 1 V between the potentials of the first and the second reduction step, bmtz−• is reduced only irreversibly at a cathodic peak potential of −2.17 V vs. FeCp$_2^+$/°.

**Dinuclear complexes**

In view of the rich data base for "polypyridine" ruthenium coordination chemistry with $\alpha$-diimine $\pi$ acceptor ligands [6], we have obtained the dinuclear bis(2,2′-bipyridine)ruthenium(II) complexes of bmtz (complex 1) and H$_2$bmtz (complex 2) according to established procedures [4a, c, 6]. Tetranuclear complexes of bmtz with [Ru(bpy)$_2$]$_2^{2+}$ or other complex fragments with approximately octahedral metal configuration could not be obtained due to the steric interference of neighbouring ancillary equatorial ligands; tetra-

hedrally coordinated metal ions such as Cu(I) [1a] will be necessary to achieve such an arrangement.

The dinuclear complexes can exist as diastereomers (meso and D/L forms [4d]). However, the overlapping of the very many resonances in the $^1$H NMR spectra did not allow us to identify such isomers. Electrochemical and UV/VIS absorption features are known to be only marginally different for diastereomeric ruthenium "polypyridine" complexes [7].

**Electrochemistry of the complexes**

Cyclic voltammetry of [(μ-bmtz)[Ru(bpy)$_2$]$_2$]$^{4+}$ (1) in acetonitrile reveals a considerably facilitated reduction in comparison to the free ligand at −0.40 V and a one-electron oxidation at +1.18 V vs. FeCp$_2^+$/°. The latter is a metal-centered process which leads to the corresponding diruthenium(II/III) mixed-valent species; full oxidation of both metal centers to the trivalent state does not occur until the oxidation limit of the electrolyte (Fig. 1). In the case of the corresponding dinuclear complex with the related bptz ligand, the second oxidation wave has been observed at about +1.85 V vs. FeCp$_2^+$/° [4d, e]; replacement of two pyridyl by two less basic pyrimidyl groups causes the expected increase in the potentials for metal-centered oxidation processes. The second reduction step remains irreversible in the complex 1 at about −1.45 V.

![Cyclic voltammogram](image-url)
The cyclic voltammogram of [(μ-H-bmtz)[Ru(bpy)_2]_2]^{4+} (2) shows only ill-defined reduction waves beyond −1 V vs. FeCp_2^{+/0}, most probably due to rapid chemical processes involving the N−H functions. Two one-electron oxidation waves occur at +0.58 and +1.07 V, illustrating the stronger σ donor effect but weaker capacity for metal−metal coupling of H_2bmtz relative to bmtz; like bptz [4b, d], the latter is distinguished by very low-lying π* orbitals and strong interaction with d_σ(Ru) orbitals.

Absorption spectroscopy of the complexes

As expected, both dinuclear complexes exhibit intense MLCT bands d(Ru) → π* in the visible region. Whereas 2 displays a single intense band at 460 nm which probably comprises transitions to the π* orbitals of bpy and less π accepting H_2bmtz, the low-lying π* levels of the much more potent π acceptor ligand bmtz give rise to long-wavelength transitions at 795 (sh), 672 (ε = 21800 M\(^{-1}\) cm\(^{-1}\)), 600 (sh), 450 (sh) and 377 nm (ε = 13500 M\(^{-1}\) cm\(^{-1}\)). Fig. 2 shows the absorption spectrum of the diruthenium(II) complex 1 and of its neighbouring oxidation states.

The assignment of transitions is similar to that of [(μ-bptz)[Ru(bpy)_2]_2]^{4+} [4c]: The intense long-wavelength band at 672 nm (685 nm for the bptz complex [4c]) is due to the singlet d_{πy}(Ru) → π*(bmtz) (a_u MO) transition, the long-wavelength shoulder probably representing the corresponding triplet transition. Less overlap-allowed MLCT transitions occur as shoulders while the d(Ru) → π*(bpy) transition is hypsochromically shifted to 380 nm, reflecting the poor σ donor effect of the bmtz ligand; neither s-tetrazine nor pyrimidine groups are basic in comparison to pyridyl functions. MLCT transitions to the low-lying unoccupied b_{1u} orbital are not discernible as prominent bands. The energy of 1.84 eV corresponding to the optical absorption maximum at 672 nm agrees well with the electrochemical separation of 1.58 V between the one-electron redox waves of this (4+) state; the difference of 0.26 (e)V is characteristic for ruthenium(II) polypyridine complexes [4c, 8].

Spectroelectrochemistry of the tetracation 1 (Fig. 2) reveals a decrease of the long-wavelength MLCT band both on reduction and oxidation because the participating frontier orbitals are partially populated (reduction) or depopulated (oxidation). The one-electron reduced form displays various bands at 835 (sh), 654, 535, 447 and 372 nm which may be attributed to shifted MLCT and intra-ligand transitions; this (3+) state does not show an EPR signal at room temperature, presumably due to rapid spin relaxation involving the closing unoccupied b_{1u} orbital [4g]. The one-electron oxidized (5+) form, on the other hand, is distinguished by slightly shifted MLCT features at 800 (sh), 655 (ε = 17900 M\(^{-1}\) cm\(^{-1}\)) and 600 (sh) nm, and by a conspicuous symmetrical band at 1490 nm (ε = 970 M\(^{-1}\) cm\(^{-1}\); Δν_{1/2} = 1100 cm\(^{-1}\)) which represents the expected intervacency (IT) or metal-to-metal charge transfer (MMCT) transition of a 4d^5/4d^6 mixed-valent dinuclear complex [4f, g, 9, 10]. The position of this band is similar to that of the prototypical Creutz-Taube ion [(NH_3)_5Ru(μ,η^2-pz)Ru(NH_3)_5]^{3+}, pz = pyrazine [9], or of the more related species [(NH_3)_4Ru(μ,η^4-bptz)Ru(NH_3)_4]^{3+} [4g]; the low intensity has been similarly observed and interpreted for bis(chelate) ligand-bridged d^5/d^6 mixed-valent dimers [4g, 10b].

Summarizing, we have presented a new tetrafunctional π acceptor ligand system by example of dinuclear ruthenium complexes of two different forms. In addition to the possible formation of tetrakis(α-dimine) chelate complexes with sterically less demanding metal complex fragments, the bmtz/H_2bmtz system offers the opportunity to combine dimetal coordination via a π conjugated bridging ligand and two additional sites for interaction with an electrophile. We shall now explore such directions with regard to the development of “supramolecular” structures and devices.

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Fig. 2. UV/VIS/NIR absorption spectra of [(μ-bmtz)[Ru(bpy)_2]_2]^{4+} from spectroelectrochemistry in CH_3CN/0.1 M Bu_4NPF_6.
**Experimental Section**

**Syntheses**

2-Cyanopyrimidine was synthesized according to an established procedure [11] and was characterized by elemental analysis (C, H, N) and $^{13}$C NMR.

$^{13}$C NMR (CDCl$_3$): $\delta = 115.4$ (CN), 123.6 (C$^5$), 142.3 (C$^2$), 158.0 (C$^{4,6}$).

1,4-Dihydro-3,6-bis(2'-pyrimidyl)-1,2,4,5-tetrazine (H$_2$bmtz): A solution of 1.5 g (14 mmol) 2-cyanopyrimidine in 20 ml of THF was treated with 2 ml of conc. hydrochloric acid and stirred for 5 min. An amount of 4 ml (80 mmol) hydrazine hydrate was added dropwise and the mixture was heated to reflux for 4 h. After hydrolysis of the orange solution with 20 ml of water and removal of THF by distillation the product could be extracted with dichloromethane to yield 2.5 g (10 mmol, 73%) of the orange dihydrate.

$C_{10}H_8N_8 \cdot 2 H_2O$ (276.2 g/mol)

Calculated: C 43.47 H 4.38 N 40.58%.

Found: C 44.02 H 4.31 N 41.10%.

UV/VIS (CH$_3$CN): $\lambda_{max} = 240, 295, 371$ nm. – $^1$H NMR (CDCl$_3$): $\delta = 7.37$ (t, J = 4.9 Hz, 2H, H$^6$), 8.49 (s, 2H, NH), 8.83 (d, J = 4.9 Hz, 4H, H$^{5,8}$). – $^{13}$C NMR (CDCl$_3$): $\delta = 121.6$ (C$^5$), 145.0 (C$^2$), 155.9 (C$^{4,6}$), 157.4 (C$^{4,6}$). – MS (20 eV): $m/z = 240$ (100%) [M$^+$].

3,6-Bis(2'-pyrimidyl)-1,2,4,5-tetrazine (bmtz): 2.5 g (10 mmol) of H$_2$bmtz were dissolved in a mixture of 0.01 M sulfuric acid and THF (2/1, v/v), cooled to 275 K and treated slowly with 5 ml of a concentrated aqueous solution of NaNO$_2$ (4.1 g, 60 mmol). After completed oxidation as evident from the colour change to red, the product was immediately extracted from the aqueous phase with dichloromethane. Reduction of the volume and cooling to 250 K produced 1.0 g (4 mmol, 40%) of a purple microcrystalline solid.

$C_{10}H_8N_8$ (238.2 g/mol)

Calculated: C 47.54 H 2.54 N 47.04%.

Found: C 49.70 H 2.43 N 45.01%.

UV/VIS (CH$_3$CN): $\lambda_{max} = 243, 260, 531$ nm. – $^1$H NMR (CDCl$_3$): $\delta = 7.55$ (t, J = 4.9 Hz, 2H, H$^6$), 9.13 (d, J = 4.9 Hz, 4H, H$^{5,8}$). – $^{13}$C NMR (CDCl$_3$): $\delta = 122.7$ (C$^5$), 158.5 (C$^{4,6}$), 159.4 (C$^2$), 163.7 (C$^{4,6}$). – MS (20 eV): $m/z = 238$ (12%) [M$^+$].

$\{\mu$-bmtz$\}[\text{Ru(bpy)}_2]^2/2^+ (1)$: A mixture of 97 mg (0.2 mmol) cis-Ru(bpy)$_2$Cl$_2$, 24 mg (0.1 mmol) bmtz and 320 mg NH$_4$PF$_6$ was heated to reflux for 1 h in 60 ml of dry 1,2-dichloroethane. After cooling and filtration, the volume was reduced to 10 ml and the dark-blue product precipitated with THF. Recrystallization from dichloromethane/heptane (5/1) yielded 120 mg (73%) of dark microcrystals.

$C_{50}H_{38}F_{24}N_{16}P_{12}Ru_2Cl_2 \cdot CH_2Cl_2$ (1730.1 g/mol)

Calculated: C 35.41 H 2.33 N 12.96%.

Found: C 35.08 H 3.52 N 12.93%.

$\{\mu$-bmtz$\}[\text{Ru(bpy)}_2]^2/2^+ (2)$: 242 mg (0.5 mmol) of cis-Ru(bpy)$_2$Cl$_2$ and 120 mg (0.25 mmol) of H$_2$bmtz were heated under refluxing ethanol for 1 h during which 1.0 g (5.4 mmol) of solid KPF$_6$ were added. After cooling, the solvent was removed and the residue redissolved in about 5 ml of acetone. Excess KPF$_6$ was precipitated with about 50 ml of dichloromethane. After filtration the brownish-red product was finally precipitated in 250 mg (61%) yield from the solution with heptane.

$C_{50}H_{40}F_{24}N_{16}P_{12}Ru_2Cl_2 \cdot CH_2Cl_2$ (1747.2 g/mol)

Calculated: C 39.18 H 3.23 N 12.83%.

Found: C 39.61 H 3.04 N 12.80%.

$^1$H NMR spectra of the complexes could not be analyzed due to the large number of overlapping resonances between 7 and 9 ppm, possibly indicating the presence of meso and D/L diastereomers [4d].

**Instrumentation**

$^1$H and $^{13}$C NMR spectra were taken on a Bruker AC 250 spectrometer, $^{13}$C NMR assignments were based on $^1$H–$^1$H coupling patterns. EPR spectra were recorded in the X band on a Bruker System ESP 300 equipped with a Bruker ER 035 M gaussmeter and a HP 5350 B microwave counter. UV/VIS/NIR absorption spectra were recorded on Shimadzu UV 160 and Bruins Instruments Omega 10 spectrophotometers. Mass spectra were obtained with an MT 292 system. Cyclic voltammetry was carried out at 100 mV/s scan rate in acetonitrile/0.1 M Bu$_4$NPF$_6$ using a three-electrode configuration (glassy carbon electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentialstat and function generator. The ferrocene/ferrocenium couple FeC$_2$P$_2$ served as internal reference. Spectroelectrochemical measurements were performed using an optically transparent thin-layer electrode (OTTLE) cell [12] for UV/VIS spectra and a two-electrode capillary for EPR studies [13].

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