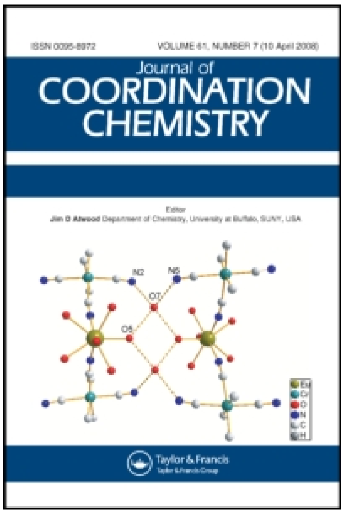

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization and semiempirical calculations of mercury(II) complexes of 3,6-*bis*(2'-pyridyl)-1,2,4,5-tetrazine

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To cite this Article El-Qisairi, Arab K.(2007) 'Synthesis, characterization and semiempirical calculations of mercury(II) complexes of 3,6-*bis*(2'-pyridyl)-1,2,4,5-tetrazine', Journal of Coordination Chemistry, 60: 10, 1069 — 1076
To link to this Article: DOI: 10.1080/00958970601001890
URL: http://dx.doi.org/10.1080/00958970601001890

Journal of Coordination Chemistry
Vol. 60, No. 10, July 2007, 1069–1076

Synthesis, characterization and semiempirical calculations of mercury(II) complexes of 3,6-*bis*(2′-pyridyl)-1,2,4,5-tetrazine

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(*Received 19 June 2006; in final form 16 August 2006*)

The reactions of 3,6-*bis*(2′-pyridyl)-1,2,4,5-tetrazine (bptz) with HgX_2 ($X = Cl$, Br, I) have been investigated. The isolated complexes have been characterized by elemental analysis, conductivity measurements, IR, ^1H, and ^{13}C NMR spectroscopy. PM3 calculations show that the *trans*-conformation is preferred. Thermodynamic calculations and orbital energies are reported.

Keywords: 3,6-*bis*(2′-Pyridyl)-1,2,4,5-tetrazine (bptz); Mercury (II); Semiempirical calculations

1. Introduction

The 3,6-*bis*(2′-pyridyl)-1,2,4,5-tetrazine (hereafter noted bptz) is a *bis* α-diimine chelating ligand, known to form mono- and di-nuclear complexes with transition metal ions [1]. In mononuclear complexes, bptz has two uncoordinated imine nitrogen atoms available for hydrogen bonding [1a]. It has been reported that hydrogen bonding between successive layers may play an important role in shortening interplanar spacing in columnar, one-dimensional complexes [2]. Considerable attention has been paid to the *bis* α-diimine ligands for their possible use as electron propagating components in electron transfer agents, model systems for biological studies and light-capturing antennas via charge transfer transitions [3]. However, bptz may exist in two different conformations as shown in figure 1. X-ray diffraction analysis shows that free bptz exists in *trans* conformation [1c].

Mercury(II) has received special interest for its use as a major constituent of bactericides, diuretics, antiseptics, skin ointments and laxatives [4]. Compounds of Hg(II) have also been used as probes in bioinorganic studies [5], as well as in electron microscopy to help elucidate the structures of macromolecules [6].

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970601001890

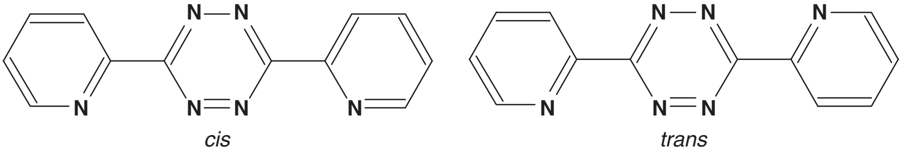


Figure 1. Conformational structures of the free ligand bptz.

These considerations encouraged us to investigate the reactions of bptz with mercury(II) and we report the preparation and characterization of mono-nuclear complexes of mercury(II) with bptz.

2. Experimental

2.1. *Materials*

The solvents used were analytical reagent grade and used as purchased. Mercury salts and all other chemicals were obtained from Aldrich and used as received. The bptz ligand was prepared following literature procedure [7] and checked for purity by FTIR [8], ^{1}H [1a] and ^{13}C NMR. FTIR (KBr): Ring breathing vibration 1638m, 1600m, 1582m, 1443s, 1391vs; β(C–H) 1130s, 1092m; pyridine ring vibrations 993m, 920m; γ(C–H) 799s, 745s cm^{-1}. ^{1}H NMR (200 MHz, DMSO-d_6): $\delta = 8.97$ (d, 2H, $J = 6.1$ Hz); 8.63 (d, 2H, $J = 6.0$ Hz); 8.17 (t, 2H, $J = 8.0$ Hz); 7.75 (t, 2H, $J = 6.0$ Hz) ppm. ^{13}C NMR (50 MHz, DMSO-d_6): $\delta = 164.0$, 151.1, 150.0, 137.0, 126.6, 124.5 ppm.

2.2. *Physical measurements*

Elemental analyses for C, H, and N were carried out by M–H–W Laboratories, Phoenix, Arizona, USA. IR spectra (KBr pellets) were recorded on a Mattson 5000 FT-IR spectrophotometer. Proton and ^{13}C NMR spectra were determined with a Bruker AC-200 NMR spectrometer in DMSO-d_6 using TMS as internal standard. Conductivity measurements were carried out on a Jeneway 4010 conductivity meter at 25°C for 10^{-3} M solutions in dimethylformamide (DMF). Electronic absorption spectra were measured using a Spectronic Genesys 2 spectrophotometer in DMF. Melting points were obtained using an electrothermal melting point apparatus.

2.3. *Preparation of the complexes*

2.3.1. [$HgCl_2$(bptz)]. A hot solution of bptz (0.095 g, 0.40 mmol) in methanol (20 mL) was slowly added to a stirred solution of $HgCl_2$ (0.109 g, 0.40 mmol) in methanol (5 mL). The mixture was refluxed overnight. The greenish-yellow solid formed was filtered off, washed well with water, methanol and diethyl ether, and dried under vacuum to yield 0.165 g (81%). M.p. 256°C (dec.). UV/vis (DMF): λ_{max} ($\log \varepsilon_{max}$) = 268 nm (3.43). Molar conductance (Λ_M) in DMF = 7.0 S cm^2 mol^{-1}.

FTIR (KBr): Ring breathing vibrations 1680s, 1646m, 1616s, 1578m, 1535s, 1507vs, 1470vs, 1433s, 1362vs, 1334m; β(C–H) 1150m; pyridine ring vibrations 980w, 931w; γ(C–H) 779w, 712w cm^{-1}. ^{1}H NMR (200 MHz, DMSO-d$_6$): $\delta = 9.10$ (br s, 1H); 8.90 (br d, 1H); 8.70 (br d, 1H); 8.62 (br s, 1H, $J = 6.0$ Hz); 8.20 (br s, 1H); 8.15–7.90 (br s, 1H); 7.72 (br s, 1H); 7.60 (br s, 1H) ppm. ^{13}C NMR (50 MHz, DMSO-d$_6$): $\delta = 161.9$, 150.0, 148.9, 148.0, 147.2, 144.8, 138.8, 138.2, 128.0, 125.8, 123.4, 122.5 ppm. Anal. Calcd for [HgCl$_2$(bptz)] (%): C, 28.59; H 1.58; N 16.55. Found: C, 28.13; H, 1.52; N, 16.48.

2.3.2. [HgBr$_2$(bptz)]. A solution of bptz (0.095 g, 0.40 mmol) in hot ethanol (20 mL) was slowly added to a suspension of HgBr$_2$ (0.145 g, 0.46 mmol) in water (10 mL). The mixture was refluxed overnight. The greenish-yellow product was filtered off, washed well with water, ethanol and diethyl ether, and dried under vacuum to yield 0.153 g (64%). M.p. 230°C (dec.). UV/Vis (DMF): λ_{max} (log ε_{max}) = 271 nm (4.50). Molar conductance (Λ_M) in DMF = 11.0 S cm^2 mol^{-1}. FTIR (KBr): Ring breathing vibrations 1679vs, 1648m, 1618s, 1586m, 1586m, 1512vs, 1474s, 1437m, 1364s, 1337m; β(C–H) 1152s, 1086m; pyridine ring vibrations 997m; γ(C–H) 775m cm^{-1}. ^{1}H NMR (200 MHz, DMSO-d$_6$): $\delta = 8.91$ (s, 1H); 8.78 (br d, 1H); 8.65 (br. d, 1H); 8.20 (t, 1H, $J = 6.0$ Hz); 8.13–8.05 (d, 1H, $J = 6.5$ Hz); 8.02 (t, 1H, $J = 6.4$ Hz); 7.74 (br. d, 1H); 7.64 (br. t, 1H) ppm. ^{13}C NMR (50 MHz, DMSO-d$_6$): $\delta = 161.1$, 149.6, 149.1, 148.8, 148.4, 147.1, 138.8, 138.4, 127.9, 126.4, 124.4, 123.5 ppm. Anal. Calcd for [HgBr$_2$(bptz)] (%): C, 24.16; H, 1.35; N, 14.10. Found: C, 24.29; H, 1.36; N, 14.00.

2.3.3. [HgI$_2$(bptz)]. A solution of bptz (0.095 g, 0.40 mmol) in hot ethanol (20 mL) was slowly added to a suspension of HgI$_2$ (0.182 g, 0.46 mmol) in water (10 mL). The mixture was refluxed overnight. The yellow solid obtained was filtered off, washed well with water, ethanol and diethyl ether, and dried under vacuum to yield 0.246 g (89%). M.p. 215°C (dec.). UV/Vis (DMF): λ_{max} (log ε_{max}) = 274 nm (4.59). Molar conductance (Λ_M) in DMF = 14.0 S cm^2 mol^{-1}. FTIR (KBr): Ring breathing vibrations 1669s, 1638s, 1618vs, 1588m, 1526m, 1508m, 1470s, 1433m, 1360m, 1310w; β(C–H) 1152m; pyridine ring vibrations 999m; γ(C–H) 774m cm^{-1}. ^{1}H NMR (200 MHz, DMSO-d$_6$): $\delta = 8.82$ (s, 1H); 8.77 (d, 1H, $J = 6.0$ Hz); 8.60 (d, 1H, $J = 6.0$ Hz); 8.18 (t, 1H, $J = 6.0$ Hz); 8.12–8.04 (m, H); 8.00 (s, 1H); 7.73 (t, 1H, $J = 6.3$ Hz); 7.57 (t, 1H, $J = 6.5$ Hz) ppm. ^{13}C NMR (50 MHz, DMSO-d$_6$): $\delta = 159.2$, 149.5, 148.8, 148.6, 147.7, 147.5, 138.7, 138.2, 127.9, 126.2, 125.9, 123.3 ppm. Anal. Calcd for [HgI$_2$(bptz)] (%): C, 20.86; H, 1.17; N, 12.17. Found: C, 20.80; H, 1.22; N, 12.20.

2.4. *PM3 calculations*

Three-dimensional structures of the compounds were obtained by using the program SYBYL [9], and the structures thus obtained were optimized with the Tripos force field. The resulting conformations were used as starting structures for the semi-empirical calculations of conformations, heats of formation, and atomic charges. These calculations were performed by using the semi-empirical quantum mechanical method PM3 [10] of the program MOP AC 7.0 [11]. All structures were optimized without any restriction.

3. Results and discussion

The 3,6-*bis*(2′-pyridyl)-1,2,4,5-tetrazine (bptz) ligand was reacted with HgX_2 (X = Cl, Br, I) using 1 : 1 molar ratios. The analytical and physical data of the complexes are given in the experimental section. The compounds are colored, solid, stable in air, and were isolated in good yields. They are insoluble in water and common organic solvents while they are soluble in DMF and DMSO. The molar conductance values support their non-ionic nature [12].

3.1. *IR spectroscopy*

The important infrared absorption bands for the bptz ligand and its complexes are presented in the experimental section. The bands were assigned by comparison with the reported spectral data for bptz and its complexes [1a, 8] and other related α-diimine ligands and their complexes [13, 14]. The vibrational spectral data have been used to distinguish monometallic from bimetallic complexes [13b, e, f, 14].

In our IR spectra, the bands showing appreciable changes upon complexation are those of ring breathing modes, which doubled in number as compared to the free ligand. The out-of and in-plane deformations as well as the pyridine-ring vibrations undergo an increase in number and/or reduction in intensity. All these changes suggest that upon coordination to Hg(II), the ligand bptz is no more symmetric and thus support the structure shown in figure 2.

Bimetallic complexes of related ligands such as 2,2′-bipyrimidine and 3,6-*bis* (2′-pyridyl)pyridazine have been reported to show a decrease in the number of bands in ring breathing with respect to the monometallic complexes [13b, e, 14].

3.2. *^{1}H and ^{13}C-NMR spectroscopy*

The ^{1}H- and ^{13}C-NMR spectral data of the bptz ligand and its complexes are given in the experimental section. The peaks were assigned on the basis of earlier

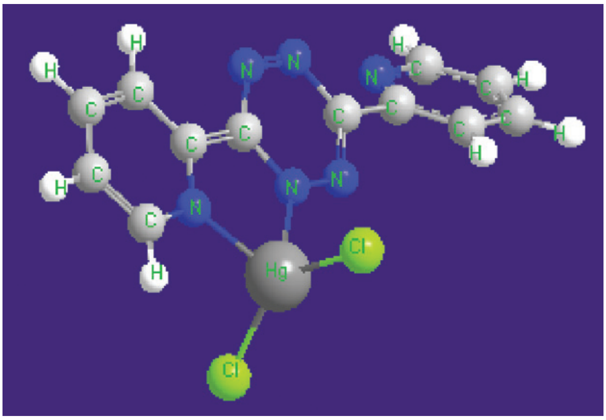


Figure 2. Molecular structure of trans-conformation for $[HgCl_2(bptz)]$.

studies made on coordinated bptz and related α-diimine ligands and their complexes [1a, 13b–f, 15].

The ^{1}H-NMR spectrum of free bptz exhibits four different proton resonances for the two equivalent pyridyl groups [1a] while eight different peaks are assigned for these groups in our complexes. This indicates that the two pyridyl groups are chemically inequivalent upon complexation of bptz to Hg(II) and strongly supports the monometallic rather than bimetallic nature of our complexes. Kaim and Kohlmann [1a] reported that bptz mononuclear complexes showed eight different proton resonances whereas the bimetallic ones gave four peaks [1a] as the free ligand.

Furthermore, the ^{13}C-NMR spectra for the Hg(II) complexes show 12 peaks as expected for the unsymmetrically coordinated ligand while the free symmetrical bptz shows only six peaks.

3.3. *Theoretical calculations*

PM3 calculations [9–11] show that the two rings attached to mercury are coplanar, while the third ring is out of the plane as shown in table 1 (see figure 1). The calculated geometrical parameters around the mercury atom show distorted tetrahedral geometry (table 1). The calculated heats of formation for *cis*- and *trans*-conformations (table 2) show that in all cases, the heat of formation of the *trans* is slightly less than that of *cis*-conformation suggesting that *trans* is slightly preferable. Thermodynamic calculations (table 2) with negative ΔG also suggests that the *trans* is slightly preferable. Bond lengths and angles for the complexes (table 1) were compared with those reported for similar systems [16], and found in good agreement.

The complex [HgI$_2$(bptz)] shows highest calculated $\lambda_{\max}$ (259 nm, table 2) which matches with that obtained experimentally from UV measurements (274 nm). Also, the calculated E_{LUMO}–E_{HOMO} (4.804 eV) of [HgI$_2$(bptz)] is less than the other two complexes (table 2) which agrees with the highest conductivity measurements ($\Lambda_M = 14.0\,\text{S cm}^2\,\text{mol}^{-1}$) relative to other two complexes {$\Lambda_M = 7.0$ for [HgCl$_2$(bptz)] and $11.0\,\text{S cm mol}^{-1}$ for[HgBr$_2$(bptz)]}.

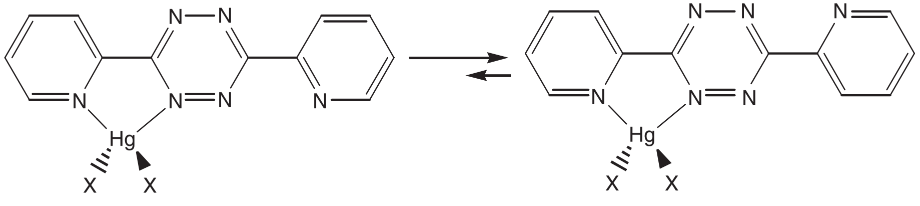
Table 1. The dihedral angles and the calculated geometrical parameters of 3,6-*bis*(2′-pyridyl)-1,2,4,5-tetrazine complexes.

Complex	*Cis*[a]	*Trans*[a]	Bond lengths and angles[b]
[HgCl$_2$(bptz)]	11.3	12.5	N–Hg, 2.165; Hg–Cl, 2.256; ⟨NHgN, 80.5; ⟨NHgCl, 104.5; ⟨ClHgCl, 138.0
[HgBr$_2$(bptz)]	15.0	35.5	N–Hg, 2.150; Hg–Br, 2.343; ⟨NHgN, 80.7; ⟨NHgBr, 103.4; ⟨BrHgBr, 141.6
[HgI$_2$(bptz)]	5.7	2.8	N–Hg, 2.156; Hg–I, 2.598; ⟨NHgN, 80.4; ⟨NHgI, 108.4; ⟨IHgI, 129.5

[a] Comparison of the dihedral angles (in degrees) of 3,6-*bis*(2′-pyridyl)-1,2,4,5-tetrazine complexes for the twisted third pyridine ring (see figure 1).

[b] The calculated geometrical parameters (bond lengths in Angstrom and angles in degrees) of *trans* complexes around the mercury atom.

Table 2. The calculated heat of formation (ΔH_f), orbital energies (HOMO and LUMO), Gibbs free energy (ΔG) and electronic absorption spectra of *cis-trans* conformations of 3,6-*bis*(2′-pyridyl)-1,2,4,5-tetrazine complexes.



X		ΔH_f (kcal mol^{-1})	HOMO (eV)	LUMO (eV)	$E_g{}^a$ (eV)	ΔG (kcal mol^{-1})	Calculated λ_{max} (nm)	Experimental λ_{max} (nm)
Cl	*trans* (cis)	84.023 (84.907)	−9.387 (−9.311)	−2.998 (−3.042)	6.389 (6.269)	−0.871	194	268
Br	*trans* cis	89.421 (90.459)	−10.567 (−10.517)	−2.985 (−3.017)	7.582 (7.500)	−0.140	163	271
I	*trans* cis	121.294 (122.344)	−7.974 (−9.550)	−3.170 (−3.170)	4.804 (6.380)	−1.044	259	274

[a] E_g = LUMO–HOMO.

4. Summary

We have obtained mononuclear mercury(II) bptz complexes. Spectroscopic properties and theoretical calculations of the complexes are consistent with *trans* conformation of bptz and distorted tetrahedral geometry around Hg(II) ion.

Acknowledgments

The author gratefully acknowledges helpful discussions with Professors Salim M. Khalil (Mu'tah University-Jordan), Mukarrum H. Zaghal (Yarmouk University-Jordan), David Crumrine (Loyola University Chicago-USA) and Mr Prakash B Sanjeevaiah (Loyola University Chicago-USA).

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