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Dinuclear and polymeric copper(I) ethylene adducts bridged by bis-pyridyl derivatives of 1,2,4-triazole and 1,2,4,5-tetrazine

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A B S T R A C T

The reaction of $[Cu(MeCN)_4]PF_6$ with 3,5-bis(2-pyridyl)-1*H*-1,2,4-triazole (Hbptrz) in MeOH under C_2H_4 afforded the colorless needle crystals of $[Cu_2(bptrz)(C_2H_4)_2]PF_6{\cdot}MeOH$ (**1**). The X-ray crystallographic study showed that there are two $[Cu_2(bptrz)(C_2H_4)_2]^+$ cation moieties, two PF_6^- anions and two solvated MeOH molecules in the unit cell. This result indicates that the central triazole ring was deprotonated to produce the anionic bptrz ligand. Each Cu(I) atom is coordinated by two chelate N atoms of bptrz and the C=C bond of C_2H_4 in the trigonal–planar geometry to produce a notable dinuclear Cu(I)–bptrz/C_2H_4 adduct bearing the anionic bptrz in the transoid conformation. In contrast, the reaction of $Cu(NO_3)_2{\cdot}H_2O$, Cu turnings and 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine (4-bptz) in Me_2CO under C_2H_4 gave black brick crystals of $\{[Cu_4(4,5\text{-}H_2\text{-}4\text{-}bptz)_2(C_2H_4)_2(NO_3)_4]{\cdot}Me_2CO{\cdot}0.5H_2O\}_n$ (**2**). This result indicates that 3,6-bis(4-pyridyl)-4,5-dihydro-1,2,4,5-tetrazine (4,5-H_2-4-bptz) was produced by the two-electron reduction of 4-bptz. Four Cu(I) atoms are bridged by two 4,5-H_2-4-bptz and four NO_3^- anions to form two distinct rectangular $[Cu_4(4,5\text{-}H_2\text{-}4\text{-}bptz)_2(NO_3)_4]$ frameworks. Furthermore, these rectangular $[Cu_4(4,5\text{-}H_2\text{-}4\text{-}bptz)_2(NO_3)_4]$ subunits are linked via the N atom in the central 4,5-dihydrotetrazine ring each other to generate a unique 2-D Cu(I)–4,5-H_2-4-bptz/C_2H_4–NO_3 coordination polymer with a channel structure along the *a*-axis. Thermogravimetric analysis (TG–DTA) showed that complexes **1** and **2** were thermochemically stable to a relatively high temperature.

1. Introduction

1,2,4,5-Tetrazine and its 3,6-bis-pyridyl derivatives are an attractive polydentate N ligands since they can bridge metal ions by a bidentate site for chelation and exo N-donor site for bridging [1]. In particular, 3,6-bis(2-pyridyl)-1,2,4,5-tertazine (bptz) is expected to form bis-chelating metal complexes in the cis/trans (syn/anti) coordination modes with the three redox states of the neutral (bptz), radical anionic ($bptz^{\cdot -}$) and dihydro (H_2bptz) forms. For these reasons, we recently have explored preparations and structural diversity of Cu(I)–C_2H_4 adducts with the related bptz ligands [2a,2b]. In comparison with bptz, 3,5-bis(2-pyridyl)-1*H*-1,2,4-triazole (Hbptrz) is structurally regarded as an analog ligand of bptz. Since the Hbptz ligand can be often deprotonated to form an anionic 3,5-bis(2-pyridyl)-1,2,4-triazolate (bptrz) in the formation process of complexes, it is expected to produce diverse mono- and polynuclear complexes and coordination polymers with bptrz in coordination modes (a)–(c) in Scheme 1. To our knowledge, only one mononuclear Ru(II)–bptrz complex has been structurally characterized in the coordination mode (a) [3], together with mononuclear Fe(III) complex with the neutral Hbptrz ligand in the zwitterionic form [4]. Dinuclear bptrz complexes of Mn(II) [5a,5b], Fe(II) [4,6a–c], Fe(III) [4], Ni(II) [7], Cu(I) [8], Cu(II) [9] and Cu(II)–Ln(III) (Ln = Gd and Dy) [10] have been widely known in the cisoid conformation (b). Several tetra-, penta- and octa-nuclear bptrz complexes of Dy(III) [11a,11b], Fe(II) [12] and Cu(II) [13a,13b] and the coordination polymers of Cu(II) [13a,14] and Mn(II) [15] containing the anionic bptrz ligand have been also reported in the cisoid coordination mode (b). In contrast, it is noteworthy that bptrz complexes have been relatively limited in the transoid conformation (c). Only a few dinuclear bptrz

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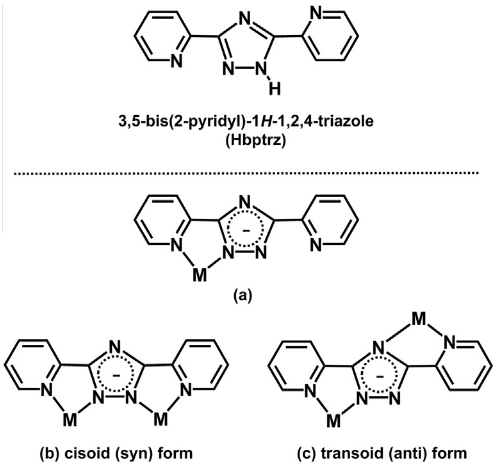
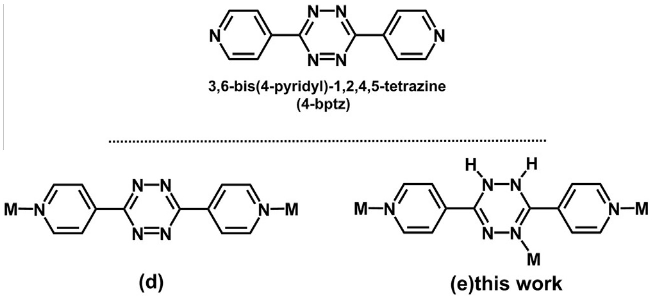
complexes of Ru(II) and Os(II) [16] have been structurally characterized in the transoid conformation (c), together with the binary tetranuclear and polymeric bptrz complexes of Cu(I) [5b,17] and the coordination polymers of Mn(II) [18] and Cu(I/II) [19] containing the anionic bptrz ligand. Tetranuclear bptrz complexes of Cu(I) [20] and Ru(II) [21] containing two cis/trans coordination modes (b) and (c) have been also reported. Thus, previous structural studies suggest that bptrz complexes would prefer the cisoid conformation (b) to the transoid conformation (c), although the related bptz complexes have a greater tendency to prefer the transoid conformation than the cisoid conformation [1]. Recently, the *in situ* metal/organic reactions under hydro/solvothermal conditions have been also described in the one-pot synthesis of bptrz complexes of Mn(II) [5a,5b], Ni(II) [7], Cu(I) [5b,17,20] and Cu(II) [13a,13b].

In comparison with bptz and bptrz ligands, 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine (4-bptz) possesses an exo N-donor site for bridging in 4-pyridyl group in addition to potentially coordinative four N atoms in the tetrazine ring (Scheme 2). Therefore, 4-bptz is structurally considered as a family of linearly bridging ligands such as pyrazine, 4,4′-bipyridine and bis(4-pyridyl)ethylene. It is predicted that 4-bptz can link between several metal ions to form diverse coordination polymers ranging from 1-D to 3-D structures. To our knowledge, tetranuclear Re(I) complex which were formed by the combinations of two dinuclear Re(I)–bibzim units and two 4-bptz ligands has been reported [22]. Several 1-D, 2-D and 3-D coordination polymers of Cu(I) [23a,23b], Ag(I) [24], Mn(II) [25] and Cd(II) [26] which were formed by the connections of 4-bptz complex units and counter anions have been characterized, together ternary coordination polymers of Ni(II) [27], Mn(II) [28], Cu(II) [29] and Cd(II) [30] containing 4-bptz ligand as a supporting ligand. Recently, 3-D porous coordination polymers (Metal–Organic Frameworks) were constructed by the combinations of Cu(II) [31] and Zn(II) [32a–h] complex units or $[WS_4Cu_x]^{x-2}$ cluster units [33a,33b] and 4-bptz, and their adsorption property of small gaseous molecules have been investigated. However, it is remarkable that the bridging of metal ions by any of N atoms in the central tetrazine ring has not yet been observed in all cases of the related 4-bptz complexes [1]. As part of our going investigation, we herein isolated two novel dinuclear and polymeric Cu(I)–C_2H_4 adducts $[Cu_2(bptrz)(C_2H_4)_2]PF_6{\cdot}MeOH$ (**1**) and $\{[Cu_4(4,5\text{-}H_2\text{-}4\text{-}bptz)_2(C_2H_4)_2(NO_3)_4]{\cdot}Me_2CO{\cdot}0.5H_2O\}_n$ (4,5-H_2-4-bptz = 3,6-bis(4-pyridyl)-4,5-dihydro-1,2,4,5-tetrazine) (**2**), and their structures and properties have been characterized by IR, X-ray, ^1H NMR and TG–DTA analyses.



Scheme 1. The known coordination modes (a)–(c) of bptrz.



Scheme 2. The known coordination modes of 4-bptz (d) and 4,5-H_2-4-bptz (e).

2. Experimental

2.1. General procedures and reagents

All procedures were carried out using standard Schlenk techniques under C_2H_4. $Cu(NO_3)_2{\cdot}H_2O$, Cu turnings and 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine (4-bptz) were purchased from Wako Pure Chemical Industries, Mitsuwa Chemicals and Sigma–Aldrich, and these chemicals were used without further purification. $[Cu(MeCN)_4]PF_6$ [35] and 3,5-bis(2-pyridyl)-1*H*-1,2,4-triazole (Hbptrz) [36] were prepared by modifications of the literature method. Pure C_2H_4 gas (> 99.9%) was purchased from Sumitomo Seika Chemicals. All organic solvents were dried and distilled by usual methods before use. The IR spectra were recorded with a Jasco FT–IR 430 spectrometer using KBr pellets. Thermogravimetric analysis (TG–DTA) was carried out with a Rigaku Thermo Plus 8120 under flowing N_2 gas. ^1H NMR spectrum was measured on a JEOL JNM-AL 400 FT NMR spectrometer at room temperature.

2.2. Preparation of Cu(I)–{bptrz, 4,5-H_2-4-bptz}/C_2H_4 complexes

2.2.1. $[Cu_2(bptrz)(C_2H_4)_2]PF_6{\cdot}MeOH$ (*1*)

$[Cu(MeCN)_4]PF_6$ (37.4 mg, 0.10 mmol) and Hbptrz (11.4 mg, 0.05 mmol) were reacted in MeOH (10 mL) under C_2H_4 for half an hour at room temperature. The resultant yellow reaction solution was filtered, and the filtrates were sealed in 7 mmϕ glass tubes under C_2H_4. The reaction solution was allowed to stand for three days at −30 °C, and colorless needle crystals of air-sensitive Cu(I)–bptrz/C_2H_4 complex **1** were obtained. After complex **1** was dried by flowing C_2H_4 gas, it was immediately subjected to elementary analysis, IR and TG–DTA. Complex **1** is practically insoluble in common deuterated solvents such as $CDCl_3$, CD_3OD and $(CD_3)_2CO$. We are currently unable to obtain appropriate ^1H NMR spectra. Yield 5.3 mg (18%). *Anal.* Calc. for $Cu_2C_{17}N_5H_{20}OPF_6$: C, 35.06; H, 3.46; N,12.02. Found: C, 35.43; H, 3.01; N, 12.35%. IR (KBr, cm^{-1}): 3097(w), 1608(m), 1526(w, C_2H_4), 1418(m), 842(s, PF_6).

2.2.2. $\{[Cu_4(4,5\text{-}H_2\text{-}4\text{-}bptz)_2(C_2H_4)_2(NO_3)_4]{\cdot}Me_2CO{\cdot}0.5H_2O\}_n$ (*2*)

The precursor Cu(I)–C_2H_4 complex $[Cu(C_2H_4)_n]NO_3$ was prepared by the reductive reaction of $Cu(NO_3)_2{\cdot}H_2O$ (12.1 mg, 0.05 mmol) with Cu turnings in Me_2CO (5 mL) under C_2H_4. A 5 mL solution of 4-bptz (4.7 mg, 0.02 mmol) was added to the above Cu(I)–C_2H_4 solution. The reddish-brown solution was stirred for half an hour and the reaction solution was filtered. The resultant yellowish-brown filtrates were introduced to 7 mmϕ glass tubes under C_2H_4 and they were layered with pentane. The glass tubes were sealed and they were allowed to stand at −10 °C for