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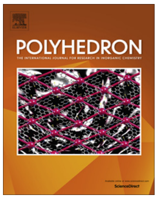

Effects of substituents and phosphine auxiliaries on the structures of Cu (I) clusters with functionalized 2,2′-bipyridyl tetrazole ligands

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Six new Cu(I) clusters have been synthesized via the successive reaction of $[Cu(MeCN)_4](ClO_4)$ with phosphine ancillary and functionalized 2,2′-bipyridyl tetrazole. It is revealed that these Cu(I) cluster complexes respectively display tri-, di- and tetranuclear Cu(I) structures with diverse coordination geometries and various tridentate and tetradentate coordination modes induced by distinct ligand modifications and phosphine auxiliaries. It is demonstrated that the methylation of the 2,2′-bipyridyl ring, the alkylation of the tetrazolyl-NH and the alteration of phosphine ancillary markedly influence the coordination environments of the Cu(I) atoms and the binding modes of the 2,2′-bipyridyl tetrazole ligands, whereas the variation of the alkyl groups on the tetrazolyl ring has no obvious effects on the coordination manners of the resultant 2,2′-bipyridyl tetrazole chelates and the structures of the resulting Cu(I) clusters.

1. Introduction

The study of Cu(I) complexes has attracted rapidly increasing attention not only because of their potential applications in organic light-emitting devices (OLEDs), light-emitting electrochemical cells (LEECs), luminescence sensors/probes, biological labeling, and so on [1–28], but also for their intriguing structures involving metal cluster complexes and metal–organic frameworks (MOFs) [29–31]. Among the Cu(I) system, discrete Cu(I) complexes have been paid much more attention owing to the excellent solubility, feasible theoretical analysis and promising applications [32–48]. Based on diverse starting ligands, a wide variety of Cu(I) clusters have been successfully obtained, showing the crucial role of organic ligands in molecular self-assembly [49–51]. Hence, sophisticated selection of the appropriate ligands can be considered as one of the most effective methods to achieve the targeted assembly structures and properties of Cu(I) clusters [52–54]. It is well known that N-heterocycle ligands can be readily modified by introducing various substituents that exhibit different electronic, steric and conformational effects, which can efficiently influence the final structures including the coordination numbers and geometries of metal atoms and the coordination modes of ligands [55–63]. It is shown that Cu(I) ions with d^{10} close-shell electronic configurations exhibit strong affinity to N donors and irregular coordination geometry with coordination numbers 2–5, which may be the key to the self-assembly of novel structural motifs [63–67].

Polydentate N-heterocyclic ligands are excellent candidates for assembling various coordination architectures with fascinating structures [68–73]. Multi-pyridine heterocyclic ligands, as a typical class of polydentate N-donor ligands, have been widely employed due to the versatile coordination conformations and good binding ability, allowing for various structural topologies [74–76]. Nevertheless, the 2,2′-bipyridyl tetrazole ligands, which contain one tetrazolyl moiety readily undergoing the N–H bond cleavage and NH-alkylation, have never been used hitherto for the construction of Cu(I) cluster complexes. Moreover, the introduction of auxiliary ligands such as phosphine and halogen has been proved to be capable of providing greater flexibility in tuning the structural geometries and properties of Cu(I) clusters *via* the synergistic effect between primary and auxiliary ligands [77–79].

Herein, four functionalized 2,2′-bipyridyl tetrazole ligands (tbpyH, tmbpyH, etbpy and htbpy denote 6-(1*H*-tetrazol-5-yl)-2,2′-bipyridine, 6-(1*H*-tetrazol-5-yl)-4,4′-dimethyl-2,2′-bipyridine, 6-(1-ethyl-tetrazol-5-yl)-2,2′-bipyridine and 6-(1-hexyl-tetrazol-5-yl)-2,2′-bipyridine, respectively) and two phosphine ligands (PPh_3 = triphenylphosphine, dppm = bis(diphenylphosphino) methane) are used (Scheme 1) to construct six new Cu(I) clusters including $[Cu_3(tbpy)_2(PPh_3)_3)](ClO_4)\cdot H_2O\cdot ClCH_2CH_2Cl$ (**1**), $[Cu_3(tmbpy)_2(PPh_3)_3](ClO_4)\cdot CH_3OCH_3\cdot CH_3COCH_3$ (**2**), $[Cu_2(etbpy)_2(PPh_3)_2](ClO_4)_2\cdot DMF$ (**3**), $[Cu_2(htbpy)_2(PPh_3)_2](ClO_4)_2\cdot DMF$ (**4**),

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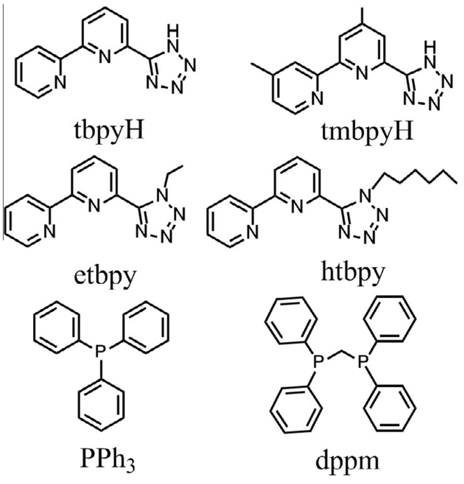

Scheme 1. Structures of ligands used in this work.

$[Cu_4(tbpy)_2(dppm)_4](ClO_4)_2{\cdot}CH_3OCH_3$ (**5**) and $[Cu_4(tmbpy)_2(dppm)_4](ClO_4)_2$ (**6**). It is shown that the methylation of the 2,2′-bipyridyl ring, the alkylation of the tetrazolyl-NH and the variation of phosphine auxiliary ligand bring about distinct Cu(I) cluster complexes, whereas the alteration of the alkyl group on the tetrazolyl ring has no obvious effects on the structures of the resulting Cu(I) clusters. Moreover, it is also noted that polydentate 2,2′-bipyridyl tetrazole ligands exhibit two kinds of tridentate and two kinds of tetradentate coordination modes in Cu(I) clusters.

2. Experimental

2.1. Materials and instrumentation

All reactions were performed under a N_2 atmosphere using anhydrous solvents or solvents treated with an appropriate drying reagent. Commercially available reagents were used without further purification. $[Cu(MeCN)_4](ClO_4)$ was prepared using previously reported procedure [79]. The tbpyH, tmbpyH, etbpy and htbpy ligands were synthesized according to the literature methods with minor modification [80–83]. The ^1H and ^{31}P NMR spectra (Figs. S1–S10) were recorded on Bruker Avance III (400 MHz) spectrometer. Elemental analyses (C, H, and N) were conducted on a Perkin–Elmer mode 240C elemental analyser. UV–Vis absorption spectra in CH_2Cl_2 solution were measured on a Shimadzu UV-2550 spectrometer. Infrared (IR) spectra (Fig. S11) were recorded on a Bruker Optics ALPHA FT-IR spectrometer using KBr pellets. X-ray powder diffraction (XRPD) spectra were recorded on an Empyrean (PANalytical B.V.) diffractometer for a Cu-target tube and a graphite monochromator. Simulation of the XRPD pattern was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program version 3.0 available free of charge via the Internet at http://www.iucr.org.

Caution! The perchlorate salts are potentially explosive and should be handled carefully in small amount.

2.2. Synthesis of complexes **1**–**6**

2.2.1. Synthesis of **1**

A mixture of $[Cu(MeCN)_4](ClO_4)$ (15 mg, 0.045 mmol) and PPh_3 (24 mg, 0.092 mmol) was dissolved in CH_2Cl_2 (3 mL) and stirred for about 30 min and a colorless solution was obtained. Then a solution of tbpyH (11 mg, 0.045 mmol) in CH_2Cl_2 (1.5 mL) was added and the mixture was stirred for another 2 h and a light yellow solution was afforded. The reaction mixture was then evaporated to dryness under reduced pressure to remove CH_2Cl_2 and the yellow residue was acquired. Petroleum ether (about 7.5 mL) was slowly layered over a mixture solution (1.5 mL, CH_2Cl_2:CH_3COCH_3:$ClCH_2CH_2Cl$ = 20:1:1 (v/v/v)) of the above yellow residue. Yellow block-shaped crystals were grown and collected with ~54% yield based on $[Cu(MeCN)_4](ClO_4)$. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.3 MHz): δ 3.58 (s, 1P, PPh_3), 1.33 (s, 2P, PPh_3). IR (KBr pellets, cm^{-1}): 3733m, 3443vs, 3062m, 2924vs, 2856s, 1737m, 1645m, 1470w, 1430s, 1261s, 1163w, 1095vs, 1029m, 803vs, 748s, 696s, 623m, 516s. *Anal.* Calc. for $C_{76}H_{59}ClCu_3N_{12}O_4P_3$: C, 59.92; H, 3.90; N, 11.03. Found: C, 59.97; H, 3.94; N, 11.05%.

2.2.2. Synthesis of **2**

The similar procedure to **1** was used for preparation of **2** except that tbpyH (11 mg, 0.045 mmol) was replaced by tmbpyH (11 mg, 0.045 mmol). Yellow crystals were obtained and collected with ~39% yield based on $[Cu(MeCN)_4](ClO_4)$. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.3 MHz): δ 2.47 (s, 1P, PPh_3), 0.84 (s, 2P, PPh_3). IR (KBr pellets, cm^{-1}): 3732m, 3448vs, 3059m, 2962m, 2925m, 1614s, 1563m, 1477m, 1435m, 1398m, 1260s, 1099vs, 1032m, 867s, 804s, 749s, 697s, 626s, 517vs. *Anal.* Calc. for $C_{80}H_{67}ClCu_3N_{12}O_4P_3$: C, 60.83; H, 4.28; N, 10.64. Found: C, 60.87; H, 4.26; N, 10.61%.

2.2.3. Synthesis of **3**

The similar procedure to **1** was used for preparation of **3** except that tbpyH (11 mg, 0.045 mmol) was replaced by etbpy (11 mg, 0.045 mmol), and the resulting yellow residue was dissolved in N,N′-dimethylformamide (DMF). Orange block-shaped crystals were grown and collected with ~79% yield based on $[Cu(MeCN)_4](ClO_4)$. ^1H NMR (CD_2Cl_2, 400 MHz): δ 8.37 (d, J = 8 Hz, 2H), 8.28 (d, J = 8 Hz, 2H), 8.00 (t, J = 8 Hz, 5H), 7.85 (s, 2H), 7.42 (t, J = 6 Hz, 6H), 7.30 (d, J = 8 Hz, 12H), 7.10 (d, J = 8 Hz, 4H), 6.92 (t, J = 10 Hz, 12H), 4.32 (q, J = 6.7 Hz, 2H, CH_2CH_3), 3.72 (q, J = 6.7 Hz, 2H, CH_2CH_3), 1.33 (t, J = 6 Hz, 2H, CH_2CH_3), 1.09 (t, J = 6 Hz, 4H, CH_2CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.3 MHz): δ 1.06 (s, PPh_3). IR (KBr pellets, cm^{-1}): 3729w, 3440vs, 3065m, 1630s, 1437m, 1314m, 1255m, 1101vs, 750s, 698s, 626s, 517s. *Anal.* Calc. for $C_{62}H_{54}Cl_2Cu_2N_{12}O_8P_2$: C, 54.95; H, 4.02; N, 12.40. Found: C, 54.99; H, 4.05; N, 12.43%.

2.2.4. Synthesis of **4**

The similar procedure to **1** was used for preparation of **4** except that tbpyH (11 mg, 0.045 mmol) was replaced by htbpy (14 mg, 0.045 mmol). Orange block-shaped crystals were afforded and collected with ~76% yield based on $[Cu(MeCN)_4](ClO_4)$. ^1H NMR (CD_2Cl_2, 400 MHz): δ 8.44 (d, J = 8 Hz, 2H), 8.34 (d, J = 8 Hz, 2H), 8.04–7.88 (m, 8H), 7.43 (t, J = 6 Hz, 6H), 7.31 (s, 12H), 7.11 (s, 2H), 6.96 (t, J = 8 Hz, 12H), 3.41 (s, 2H, $CH_2(CH_2)_4CH_3$), 3.01 (s, 2H, $CH_2(CH_2)_4CH_3$), 1.65 (s, 2H, $CH_2CH_2(CH_2)_3CH_3$), 1.37 (s, 2H, $CH_2CH_2(CH_2)_3CH_3$), 1.24–1.15 (m, 6H, $(CH_2)_5CH_3$), 1.02 (s, 6H, $(CH_2)_5CH_3$), 0.82 (t, J = 8 Hz, 6H, $(CH_2)_5CH_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.3 MHz): δ 1.25 (s, PPh_3). IR (KBr pellets, cm^{-1}): 3728m, 3434vs, 2926s, 2858s, 2017w, 1632s, 1436s, 1390m, 1260s, 1105vs, 793m, 749s, 697s, 626s, 517s. *Anal.* Calc. for $C_{70}H_{70}Cl_2Cu_2N_{12}O_8P_2$: C, 57.30; H, 4.81; N, 11.45. Found: C, 57.35; H, 4.84; N, 11.48%.

2.2.5. Synthesis of **5**

The similar procedure to **1** was used for preparation of **5** except that PPh_3 (24 mg, 0.092 mmol) was replaced by dppm (17 mg, 0.045 mmol) and the resulting yellow residue was dissolved in DMF. Yellow block-shaped crystals were obtained and collected with ~42% yield based on $[Cu(MeCN)_4](ClO_4)$. ^1H NMR (CD_2Cl_2, 400 MHz): δ 8.23–8.18 (m, 6H), 7.92 (d, J = 8 Hz, 2H), 7.74 (s, 7H), 7.61 (s, 4H), 7.45 (s, 12H), 7.25 (t, J = 6 Hz, 10H), 6.97 (t, J = 8 Hz, 2H), 6.85–6.77 (m, 15H), 6.63 (s, 9H), 6.44 (s, 19H), 6.27 (s, 8H), 3.34 (s, 8H, $PPh_2CH_2PPh_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.3 MHz): δ −12.40 (s, dppm), −17.96 (s, dppm). IR (KBr pellets, cm^{-1}): 3799w, 3728m, 3439s, 3059m, 2960m, 2924m, 2857m, 1639m,