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Cu(I) or Cu(I)–Cu(II) Mixed-Valence Complexes of 2,4,6-Tri(2-pyridyl)-1,3,5-triazine: Syntheses, Structures, and Theoretical Study of the Hydrolytic Reaction Mechanism

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The reactions of 2,4,6-tri(2-pyridyl)-1,3,5-triazine (tpt) with copper(I) halides under solvothermal or traditional conditions yielded two polymeric Cu(I) complexes $[Cu_2I_2(tpt)]_n$ (**1**) and $[Cu_3I_3(tpt)]_n$ (**2**), one mixed-valence Cu(I)–Cu(II) complex $[Cu_4Cl_2I_4(tpt)_2]$ (**3**), and two Cu(II) complexes [CuBr(bpca)] (**4**) and [CuI(bpca)] (**5**) (bpca = bis(2-pyridylcarbonyl)-amine). Complex **1** is a zigzag chain with tpt in a bis-bipyridine-like coordination mode, whereas complex **2** with tpt chelating three Cu(I) cations is a ladderlike coordination polymer. Complex **3** is mixed-valence, with Cu(I) in a distorted tetrahedral geometry and Cu(II) in a distorted square pyramidal geometry, forming a ladderlike supramolecular chain. Complexes **4** and **5** are the products of in situ hydrolysis of tpt involving the oxidation of Cu(I). The synthesis and characterization of complex **1**, **2**, and **5** indicated that Cu(I) cannot promote the hydrolysis of tpt. The theoretical study shows that the main effect for hydrolysis of tpt is the electron-withdrawing effect of metal ions.

Introduction

The compound 2,4,6-tri(2-pyridyl)-1,3,5-triazine (tpt) with transition-metal salts has been studied, first as an analytical reagent for various metals[1] and recently as a ligand for designing metal complexes.[2−6] Several interesting chemical phenomena have been observed of the tpt ligand in the synthetic process of its metal complexes, such as methoxylation,[4,7] hydroxylation,[8] and hydrolysis.[9−13] The hydrolysis of aryl-substituted triazine requires vigorous conditions,[14] whereas it becomes easier when metal cations such as Cu(II) or Rh(III) are complexed. The promotion of tpt hydrolysis by Cu(II) in aqueous media has been found for the first time by Lerner and Lippard,[9] and a metal-induced angular strain mechanism was suggested. About 20 years later, Paul and co-workers proposed that the main reason for the promotion should be the electron-withdrawing effect of metal cations, when they observed a similar hydrolysis reaction in the presence of Rh(III).[12,13]

As a versatile ligand, tpt may adopt different coordination modes (Scheme 1), possibly coordinating metals in terpyridine-like sites, bipyridine-like sites, or a mix of both sites to yield a variety of coordination complexes, such as tridentate terpyridine-like (**I**),[15,16] bidentate bipyridine-like (**II**),[17] mixed tridentate and bidentate type (in one terpyridine-

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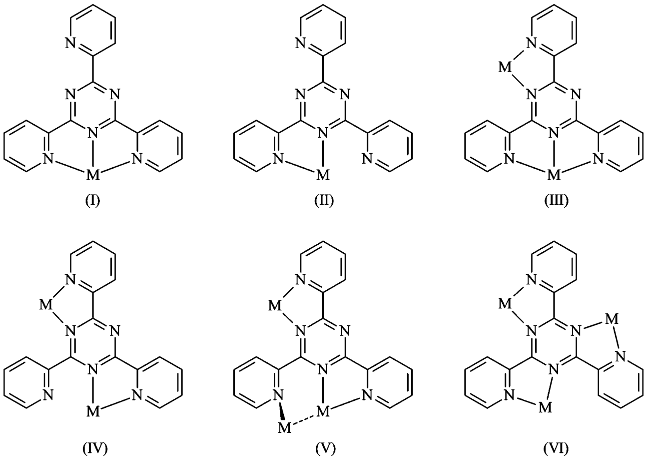
Scheme 1. Possible Coordination Modes of tpt



like and one bipyridine-like) (**III**), [2,3,6] and bis-bipyridine-like (**IV**). [4,7] Although tpt has the potential to coordinate three metal ions (**V** and **VI** in Scheme 1), no structures of tpt coordinating three metals can be found in the latest version of the CCDC database. Metal complexes of tpt chelating three metals are really rare. [18] It has been found that the coordination of a second metal to tpt is difficult because of the deactivation of the triazine ring by the inductive effect of the first metal, a consequence of steric interactions between the hydrogen atoms and the metal ions.[19] The difficulty of further coordination of a third metal to tpt would be expectable.

We are interested in exploring the coordination chemistry of d^{10} metal halides or pseudohalides because of their favorable photoluminescence properties and intriguing coordination architectures.[20−23] The reactions of ligand tpt with Cu(II) have been extensively studied, and the hydrolysis of tpt has been developed as a method for synthesizing new Cu(II) complexes of bis(2-pyridylcarbonyl)amine (bpca), although the mechanism for hydrolysis of tpt remains controversial. [24,25] Little investigation has been focused on the coordination chemistry of Cu(I) or mixed-valence Cu(I)−Cu(II) complexes of tpt. In this paper, we report the syntheses of a series of Cu(I) or mixed-valence Cu(I)−Cu(II) complexes of tpt, and its Cu(II) hydrolytic product bpca by solvothermal and traditional reactions. The experiments proved that Cu(I) cannot promote the hydrolysis of tpt like Cu(II) does. Discussions and theoretical studies are performed to gain insight to the mechanistic aspects of the hydrolysis of tpt.

Experimental Section

General. All reagents were commercially available and used as received. Solvents acetonitrile and *n*-hexane were of analytical grade and used without further purification. Infrared spectra were obtained in KBr disks on a Nicolet Avatar 360 FTIR spectrometer in the range of 4000−400 cm^{-1}. Elemental analyses of C, H, and N were determined with a Perkin−Elmer 2400C elemental analyzer.

Synthesis of Complexes. $[Cu_2I_2(tpt)]_n$ 1. Method A: A mixture of CuI (0.0190 g, 0.10 mmol), tpt (0.0156 g, 0.05 mmol), triphenylphosphine (PPh_3, 0.0266 g, 0.10 mmol), and acetonitrile (8.0 mL) was sealed in a 15 mL Teflon-lined reactor and heated in an oven at 180 °C for 60 h; it was then slowly cooled to room temperature. Black diamond-like crystals were collected and dried in air. (yield: ~60%). Method B: A solution of tpt in acetonitrile was carefully layered on the solution of CuI in the KI saturated aqua solution; black diamond-like crystals were collected after 1 day (yield: 51%). Anal. Calcd for $C_{18}H_{12}Cu_2I_2N_6$: C, 31.15; H, 1.73; N, 12.11. Found: C, 31.13; H, 1.71; N, 12.14. IR (ν, cm^{-1}): 3051w, 2917w, 1527s, 1466w, 1364s, 1258m, 1151w, 1090w, 1041w, 1008w, 853w, 767s, 665m, 612w.

$[Cu_3I_3(tpt)]_n$ 2. A mixture of CuI (0.0190 g, 0.10 mmol), tpt (0.0156 g, 0.05 mmol), 1,2-bis(diphenylphosphino)ethane (dppe) (0.0398 g, 0.10 mmol), and acetonitrile (8.0 mL) was sealed in a 15 mL Teflon-lined reactor and heated in an oven at 180 °C for 60 h; it was then slowly cooled to room temperature. Black sticklike crystals were collected and dried in air (yield: 51−62%). Anal. Calcd for $C_{18}H_{12}Cu_3I_3N_6$: C, 24.44; H, 1.36; N, 9.50. Found: C, 24.46; H, 1.35; N, 9.58. IR (ν, cm^{-1}): 2925w, 2847w, 1601m, 1527s, 1470m, 1397m, 1258w, 1160w, 1045w, 1021w, 841s, 763m, 661w, 620w, 559m.

$[Cu_4Cl_2I_4(tpt)_2]$ 3. A mixture of CuI (0.0190 g, 0.10 mmol), $CuCl_2$ (0.0134 g, 0.10 mmol), tpt (0.0156 g, 0.05 mmol), dppe (0.0400 g, 0.10 mmol), and acetonitrile/*n*-hexane (v, 1:1, 8.0 mL) was sealed in a 15 mL Teflon-lined reactor and heated in an oven at 140 °C for 60 h; it was then slowly cooled to room temperature. Black block crystals were collected and dried in air (yield: 40%). Anal. Calcd for $C_{36}H_{24}Cl_2Cu_4I_4N_{12}$: C, 29.67; H, 1.65; N, 11.52. Found: C, 29.65.13; H, 1.66; N, 11.53. IR (ν, cm^{-1}): 3047w, 2917w, 2847w, 1642w, 1519s, 1462w, 1356m, 1262w, 1147m, 1086w, 104w, 1004w, 767s, 743w, 661w, 612w.

[CuBr(bpca)] 4. A mixture of CuBr (0.0144 g, 0.10 mmol), tpt (0.0156 g, 0.05 mmol), and acetonitrile (8.0 mL) was sealed in a 15 mL Teflon-lined reactor and heated in an oven at 140 °C for 60 h; it was then slowly cooled to room temperature. Blue stick crystals were collected and dried in air (yield: 29%). Anal. Calcd for $C_{12}H_8CuBrN_3O_2$: C, 38.95; H, 2.16; N, 11.45. Found: C, 38.96; H, 2.18; N, 11.48. IR (ν, cm^{-1}): 2913w, 2847w, 1705s, 1621m, 1597m, 1462w, 1351s, 1094w, 1045w, 1021w, 853w, 763m, 698w, 630w, 545w.

[CuI(bpca)] 5. Method A: A mixture of CuI (0.0190 g, 0.10 mmol), tpt (0.0156 g, 0.05 mmol), and acetonitrile (8.0 mL) was sealed in a 15 mL Teflon-lined reactor and heated in an oven at 180 °C for 60 h; it was then slowly cooled to the room temperature. Green needle crystals were collected and dried in air (yield: 35%). Method B: The mixture of CuI and tpt in acetonitrile or acetonitrile/(KI aqua saturated solution) was stirred for 3 days to give a clear green solution. Green needle crystals were obtained by slow evaporation of the solution at room temperature for 4 days (yield:

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Table 1. Summary of the Crystal Data and Structure Refinement Parameters for **1**−**5**

	1	**2**	**3**	**4**	**5**
formula	$C_{18}H_{12}Cu_2I_2N_6$	$C_{18}H_{12}Cu_3I_3N_6$	$C_{36}H_{24}Cl_2Cu_4I_4N_{12}$	$C_{12}H_8BrCuN_3O_2$	$C_{12}H_8CuIN_3O_2$
M_r	693.22	883.66	1457.33	369.66	416.65
cryst syst	monoclinic	triclinic	triclinic	orthorhombic	orthorhombic
space group	*C*2/c	$P\bar{1}$	$P\bar{1}$	*Pbcn*	*Pbcn*
a (Å)	11.5230(15)	7.0620(7)	8.8716(6)	12.3074(15)	12.4730(11)
b (Å)	14.7026(18)	12.5728(12)	10.2789(7)	14.3586(17)	14.4913(13)
c (Å)	12.0369(15)	13.6359(13)	12.7502(9)	6.8007(9)	6.9476(6)
α (deg)	90	68.4990(10)	68.6270(10)	90	90
β (deg)	93.025(2)	80.147(2)	77.3570(10)	90	90
γ (deg)	90	82.043(2)	80.0040(10)	90	90
V (Å^3)	2036.4(4)	1106.06(19)	1050.83(13)	1201.8(3)	1255.78(19)
Z	4	2	1	4	4
D_c (g cm^{-3})	2.261	2.653	2.303	2.043	2.204
μ (mm^{-1})	5.137	7.063	5.106	5.141	4.197
no. of reflns collected	5987	9563	9087	6886	7293
no. of unique reflns	2194	4921	4692	1379	1489
R_{int}	0.0178	0.0287	0.0156	0.0309	0.0213
GOF	1.030	1.014	1.076	1.067	1.194
R1 [$I > 2\sigma(I)$]^a	0.0340	0.0654	0.0289	0.0428	0.0358
wR2 [$I > 2\sigma(I)$]^b	0.0774	0.1598	0.0749	0.1113	0.0773
R1 [all data]	0.0414	0.0868	0.0335	0.0730	0.0432
wR2 [all data]	0.0814	0.1730	0.0846	0.1302	0.0811

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = [\sum_w(F_o^2 - F_c^2)^2/\sum_w(F_0^2)^2]^{1/2}$.

40%). Method C: A solution of tpt in acetonitrile was carefully layered on a KI saturated aqua solution of CuI. Black crystals were observed after 1 day that had been characterized as complex **1**. When the solution was allowed to stand, black crystals disappeared and green needle crystals were formed after 7 days (yield: 15%). Anal. Calcd for $C_{12}H_8CuIN_3O_2$: C, 34.56; H, 1.92; N, 10.08. Found: C, 34.54; H, 1.93; N, 10.07. IR (ν, cm^{-1}): 2917w, 2847m, 1707s, 1625m, 1597m, 1450w, 1352s, 1286m, 1098w, 1045w, 1021w, 759m, 694m, 628m, 543w.

X-ray Structure Determination. Suitable crystals of **1**−**5** were mounted with glue at the end of a glass fiber. Data collections were performed on a Bruker-AXS SMART CCD area detector diffractometer at 293(2) K using ω rotation scans with a scan width of 0.3° and Mo Kα radiation ($\lambda = 0.71073$ Å). The crystal parameters and experimental details of the data collection are summarized in Table 1. Empirical absorption corrections were carried out utilizing the SADABS routine. The structures were solved by direct methods and refined by full-matrix least squares refinements on the basis of F^2. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were added geometrically and refined with a riding model; structure solutions, refinements, and graphics were performed with the SHELXL-97 package (see the Supporting Information).[26] Selected bond lengths and angles for the complexes are given in Table 2.

Calculation Details. Density functional calculations were performed, employing the Gaussian03 suite of programs, [27] at the B3LYP level. The basis set used for C, O, N, and H atoms was 6-31G**, whereas effective core potentials with a LanL2DZ basis set were employed for transition metals. Molecular graphics have been made with programs and MOLEKEL.[28]

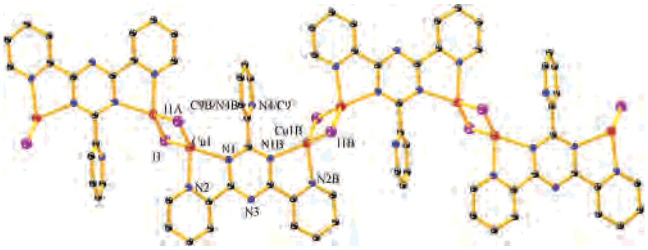

Figure 1. View of zigzag chain of **1**. Symmetric code: A, $-x + {}^1/_2$, $-y + {}^1/_2$, $-z + 2$, B, $-x$, y, $-z + {}^3/_2$.

Results and Discussion

Description of Crystal Structures. Complex 1. X-ray diffraction determination revealed that ligand tpt in **1** adopts the bis-bipyridine-like mode (**IV**, Scheme 1), chelating two Cu(I). The N(3) atom resides on a 2-fold symmetry axis, and the uncoordinated pyridyl is site occupancy disordered, as shown in Figure 1. Each Cu(I) atom coordinates two N-donors of ligand tpt and two symmetrical I$^-$ anions to complete a distorted tetrahedral coordination sphere. The Cu(I)-donor bond distances are all within normal values (Cu(1)−N(1) = 2.144(3) Å, Cu(1)−N(2) = 2.086(3) Å, Cu(1)−I(1) = 2.5667(6) Å, Cu(1)−I(1A) = 2.5468(10) Å). The copper (I) centers bridged by two I$^-$ anions are separated by a relatively short distance of 2.5468(10) Å, indicating Cu(I)−Cu(I) interaction. The $[Cu_2tpt]^{2+}$ building block is bridged by I$^-$ anions to form a zigzag chain (Figure 1).

Complex 2. As illustrated in Figure 2a, ligand tpt in **2** adopts the coordinate mode **V**, in which tpt chelates three

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1**−**5**[a]

Complex 1			
Cu1−N1	2.144(3)	Cu1−N2	2.086(3)
Cu1−I1	2.5667(6)	Cu1−I1A	2.5468(10)
N1−Cu1−N2	78.71(11)	N1−Cu1−I1	127.19(8)
N1−Cu1−I1A	104.24(8)	N2−Cu1−I1	109.30(9)
N2−Cu1−I1A	106.81(10)	I1−Cu1−I1A	121.12(2)
Complex 2			
Cu1−N1	2.059(9)	Cu1−N2	2.212(8)
Cu1−I1	2.6276(17)	Cu1−I2	2.5819(18)
Cu2−N3	2.029(9)	Cu2−I2	2.5447(17)
Cu2−I1A	2.5195(17)	Cu3−N4	2.216(8)
Cu3−N5	2.072(9)	Cu3−I3	2.5859(16)
Cu3−I3B	2.5671(17)		
N1−Cu1−N2	77.6(3)	N1−Cu1−I1	121.3(3)
N1−Cu1−I2	110.9(3)	N2−Cu1−I1	98.2(2)
N2−Cu1−I2	120.8(2)	I1−Cu1−I2	120.05(6)
N3−Cu2−I2	111.6(3)	N3−Cu2−I1A	116.0(3)
I2−Cu2−I1A	131.34(7)	N4−Cu3−N5	77.7(3)
N4−Cu3−I3	127.3(2)	N4−Cu3−I3A	103.5(2)
N5−Cu3−I3	105.2(3)	N5−Cu3−I3A	125.5(3)
I3−Cu3−I3A	114.67(5)		
Complex 3			
Cu1−N1	2.052(3)	Cu1−N2	1.927(3)
Cu1−N3	2.053(3)	Cu1−Cl1	2.1866(10)
Cu1−I1A	3.0498(6)	Cu2−N4	2.222(3)
Cu2−N5	2.5432(5)	Cu2−I1	2.5432(5)
Cu2−I2	2.5537(6)		
N1−Cu1−N2	79.01(12)	N1−Cu1−N3	157.25(12)
N1−Cu1−Cl1	100.45(9)	N1−Cu1−I1A	90.20(9)
N2−Cu1−N3	78.25(12)	N2−Cu1−Cl1	169.94(10)
N2−Cu1−I1A	87.37(9)	N3−Cu1−Cl1	101.80(9)
N3−Cu1−I1A	89.51(9)	Cl1−Cu1−I1A	102.69(4)
N4−Cu2−N5	77.57(11)	N4−Cu2−I1	128.13(8)
N4−Cu2−I2	100.11(8)	N5−Cu2−I1	112.42(9)
N5−Cu2−I2	120.78(9)	I1−Cu2−I2	113.94(2)
Complex 4			
Cu1−N1	2.011(3)	Cu1−N1A	2.011(3)
Cu1−N2	1.927(6)	Cu1−Br1	2.3718(10)
N1−Cu1−N1A	164.2(2)	N1−Cu1−N2	82.10(11)
N1−Cu1−Br1	97.90(11)	N1A−Cu1−N2	82.10(11)
N1A−Cu1−Br1	97.90(11)	N2−Cu1−Br1	180.000(1)
Complex 5			
Cu1−N1	2.020(3)	Cu1−N1A	2.020(3)
Cu1−N2	1.936(5)	Cu1−I1	2.5659(7)
N1−Cu1−N1A	164.46(18)	N1−Cu1−N2	82.23(9)
N1−Cu1−I1	97.77(9)	N1A-Cu1−N2	82.23(9)
N1A−Cu1−I1	97.77(9)	N2−Cu1−I1	180.0

[a] Symmetry transformations for **1**: A, $-x + {}^1/_2$, $-y + {}^1/_2$, $-z + 2$; B, $-x$, y, $-z + {}^3/_2$. For **2**: A, $x + 1$, y, z; B, $-x + 1$, $-y$, $-z$; C, $x - 1$, y, z. For **3**: A, $-x + 2$, $-y$, $-z + 1$. For **4**: A, $-x$, y, $-z + {}^1/_2$. For **5**: A, $-x + 1$, y, $-z + {}^3/_2$.

copper(I) cations. As far as we are aware, this is the first structure with ligand tpt chelating three metal cations with mode **V**. In complex **2**, three independent Cu(I) atoms bear two different coordination geometries. Both Cu(1) and Cu(3) adopt a distorted tetrahedral coordination sphere, coordinating two N-donors of ligand tpt and two iodine anions. Cu(2) adopts an approximately planar trigonal coordination sphere, coordinating one N-donor and two I$^-$ anions with N(3)−Cu(2)−I(1A) = 116.0(3)°, N(3)−Cu(2)−I(2) = 111.6(3)°, I(1A)−Cu(2)−I(2) = 131.34(7)°, and the sum of angles about Cu(2) is 358.9°. CuI and tpt assemble a novel molecular ladderlike coordination polymer, in which the neutral infinite ladder features two CuI chains as supports and two tpt ligands with two CuI as rungs (Figure 2b). The coordination sphere of two copper atoms of the rung in complex **2** is similar to those in complex **1**; however, the distance of two Cu(I) centers (2.781(3) Å) is obviously longer than that in complex **1** (2.5468(10) Å). Interestingly, both CuI ladder supports (CuI chains) in complex **2** are helical: one is right-handed and the other is left-handed (Figure 2c). Single CuI helical chains are really rare.[29] The interannular torsions between the pyridyl rings and triazine rings (43.7°) play a key role in forming the helical CuI chain, which allowed two copper atoms to coordinate two nitrogen donors of two pyridyls and one nitrogen donor of triazine (Figure 2a). Such phenomena have been observed in several complexes of 2,2′:6′,2″-terpyridine derivatives, which form polynuclear double helical cations that result from the partitioning of terpyridine into monodentate and bidentate domains upon coordination to Cu(I) or Ag(I) centers.[20, 30−33]

Complex 3. Ligand tpt in **3** has a coordination mode of **III**, chelating two copper atoms, as shown in Figure 3. The necessity to charge balance indicates that the metals have a mixed-valence Cu(I)−Cu(II) fashion. In view of the preference of Cu(I) for a tetrahedral coordination geometry and Cu(II) for a square pyramidal geometry, as illustrated in Figure 3, the Cu(1) should be divalent and Cu(2) should be monovalent. Mixed-valence Cu(I)−Cu(II) compounds with a geometry similar to that of **3** have been proven in our recent work by the study of the temperature-dependent magnetic susceptibility.[34] Divalent Cu(1) has a distorted square pyramidal geometry, which was coordinated by three nitrogen donors of ligand tpt, one additional chloride donor, and one bridging iodine donor. The distances of Cu−N bonds range from 1.927(3) to 2.053(3) Å, in good agreement with those found in $[\{CuCl_2\}(tpt)\{CuCl_2(MeOH)\}]$.[6] The monovalent Cu(2) coordinates two nitrogen donors of ligand tpt and two iodine donors, completing a distorted tetrahedral geometry. The Cu(2)−N bond distances (2.053(3)−2.222(3) Å) are slightly longer than the Cu(1)−N bond distances (1.927(3)−2.053(3) Å), and the Cu(2)−I bond distances (2.5432(5)−2.5537(6) Å) are obviously shorter than the Cu(1)−I bond distances (3.0498(6) Å), showing the difference between divalent and monovalent copper atoms. The I(1) and symmetrical I(1A) bridge four copper atoms (Cu(1), Cu(2), Cu(1A), Cu(2A)), forming a tetranuclear gridlike structure (Figure 3). The tetranuclear entities are further linked by longer semicoordinate Cu···I bonds (3.548(1) Å) to construct a ladderlike supramolecular chain, as shown in Figure 3.

Complexes 4 and 5. The crystal structure of **4** is shown in Figure 4a. The copper with a planar four-coordinated geometry is coordinated by three nitrogens of ligand bpca and one Br$^-$ anion. The Cu−N bonds in **4**, ranging from

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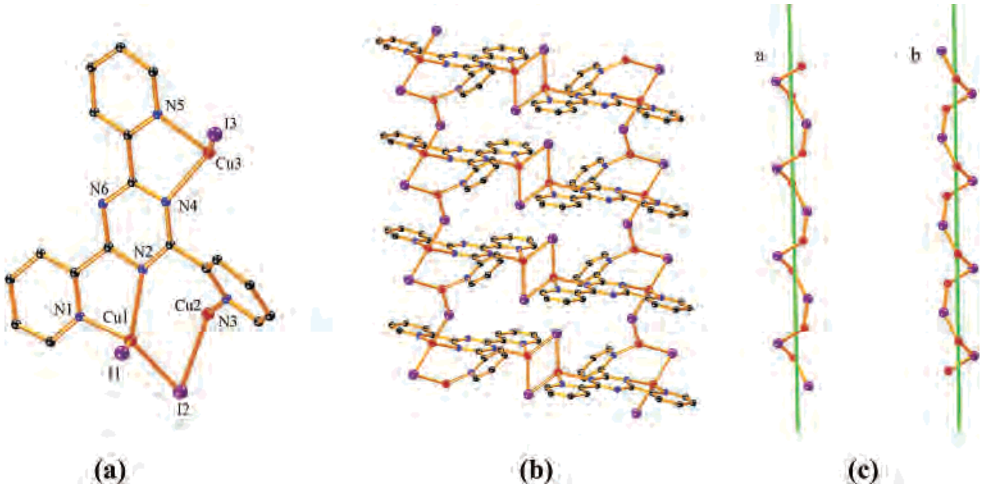


Figure 2. (a) Asymmetrical unit of **2**. (b) Ladderlike structure of **2**. (c) Helical CuI chains in **2**, right-handed and left-handed helices.

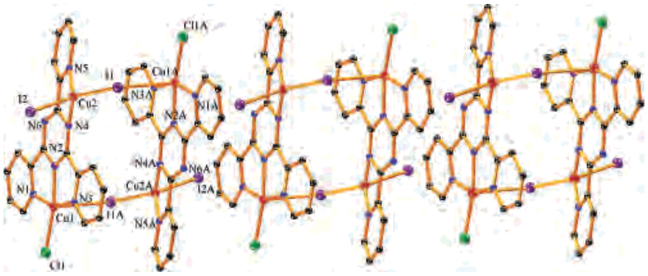


Figure 3. Ladderlike supramolecular chain in **3**. Symmetric code: A, $-x + 2, -y, -z + 1$.

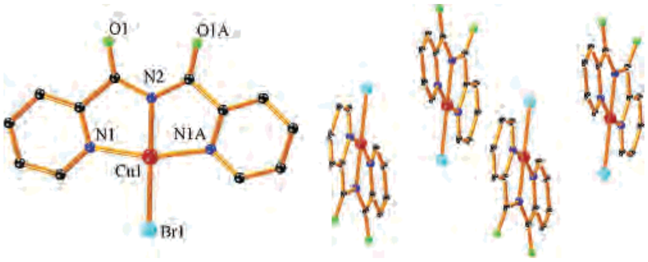
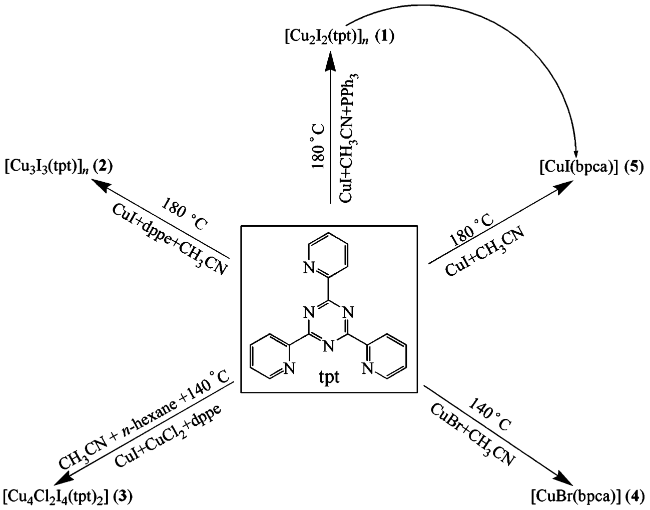


Figure 4. View of the mononuclear structure of **4** (left) and the ladderlike supramolecular chain (right). Symmetric code: $-x, y, -z + {}^{1}/_{2}$.

1.927(6) to 2.011(3) Å, are similar to those found in $[Cu(bpca)]^+$.[9−11] It is noteworthy that complex **4** is a supramolecular isomer of the coordination polymer $[CuBr(bpca)]_n$.[24] Unlike in the polymer $[CuBr(bpca)]_n$, where the $[Cu(bpca)]^+$ cations are bridged by Br^- anions in a zigzag fashion, the $[Cu(bpca)]^+$ cations in **4** are linked by the longer semicoordinate Cu⋯Br bonds of 3.427 Å to form a ladderlike supramolecular chain (Figure 4b). Complexes **5** and **4** are isostructural with the same space group, *Pbcn*, and similar unit-cell dimensions (see crystal data in Table 1, selected bond lengths and angles in Table 2).

Syntheses and Mechanism of Hydrolysis. Solvothermal treatments of ligand tpt and copper(I) or copper(II) halides under different conditions afford corresponding Cu(I) and mixed-valence Cu(I)−Cu(II) complexes of tpt, and Cu(II) complexes of bpca by in situ hydrolysis of tpt and oxidation of Cu(I) (Scheme 2).

Scheme 2. Synthesis of Complex **1**−**5**



The presence of triphenylphosphine or 1,2-bis(diphenylphosphino)ethane, which prevents the oxidation of Cu(I), is crucial in the synthesis of complexes **1** and **2** with nonhydrolyzed tpt under solvothermal conditions. Notably, different phosphines (PPh_3 and dppe) result in distinctly different complexes **1** and **2**. The process of supramolecular self-assembly is so complicated that crystal structures of produced supramolecules are unexpected and uncontrollable.[35] It is clear that phosphines play not only the role of avoiding the oxidation of Cu(I) but also of affecting the supramolecular self-assembly, even though it does not exist in the final product. Similar observations were recently reported by Chen's group[36] and ours.[37] We propose that an auxiliary complexing agent, phosphine in this work, that possesses a suitable coordination ability to form an intermediate with metals during the reactions may effectively influence the coordination mode of metals and ligands.

Under solvothermal conditions similar to those for the synthesis of **1** and **2**, the absence of PPh_3 or dppe led to the hydrolysis of tpt, yielding Cu(II)−bpca complex **5** (Method A). Another route to attaining **5** (Method B) was the direct

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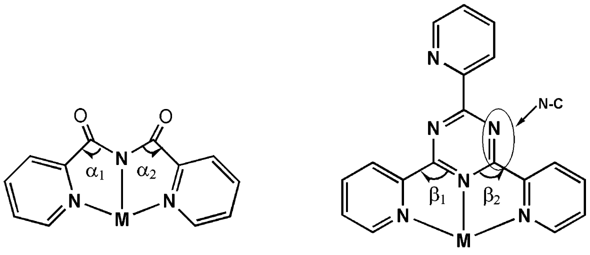
Scheme 3



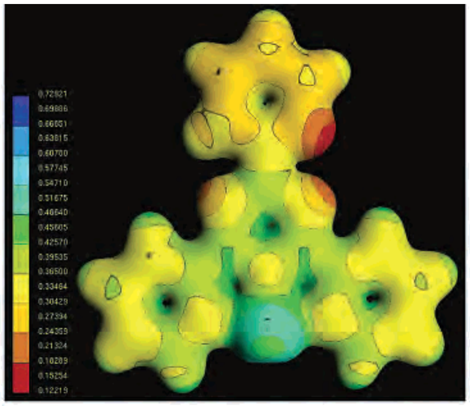
(I) (II)

synthesis by stirring the suspension of CuI with ligand tpt in acetonitrile in atmospheric conditions. The synthesis of **5** from CuI and tpt should be accompanied by the oxidation of Cu(I) and hydrolysis of ligand tpt. Two questions raised here are which step is the priority and whether Cu(I) can promote the hydrolysis of tpt as Cu(II). It is well-known that phosphine can reduce Cu(II) to Cu(I) in mild conditions. In the absence of phosphine, solvothermal (Method A) and direct (Method B) synthesis of **5** indicate that Cu(II) is essential to the hydrolysis of tpt, in agreement with the conclusion that Cu(II) catalyzes the hydrolysis of tpt and that Cu(I) cannot promote the hydrolysis. Method C for the synthesis of **5** used the layering technique. During the slow diffusion, the primary product complex **1** was obtained; it would be further transferred to **5**. The fact proves that the oxidation of Cu(I) is preferential in the hydrolysis process.

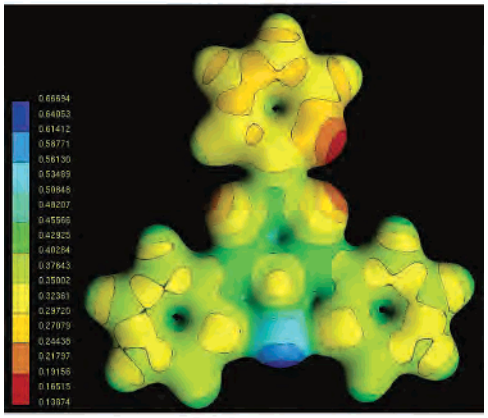
To have an insight about the role of oxygen in this reaction, we carried out comparative experiments following methods A−C for syntheses of complex **5** under an inert atmosphere (argon). For method A, small black crystals were obtained, and no green crystals like **5** were observed. For method B, the color of the solvent did not change to green after the solution was stirred for 1 week. For method C, the black crystals of **1** could not transferred to **5** after standing for 1 week. All these experiments indicated that copper(I) cannot be oxidized and tpt cannot hydrolyze under an inert atmosphere. The dissolved oxygen plays a critical role for oxidizing copper(I) to copper(II) and then promote the hydrolysis of tpt.

The mechanism of the Cu(II) promoting hydrolysis of tpt has been suggested to be metal-induced angular strain on the basis of the crystal structure data of the Cu(II)−bpca complex, which was the main product of hydrolysis of tpt in the presence of Cu(II).[9] However, the nucleophilic attack actually occurs at the carbon atoms of the triazine ring of unhydrolyzed tpt. The structure data of complex [{$CuCl_2$}(tpt){$CuCl_2$(MeOH)}] [6] and **3** show that the angle values of β_1 and β_2 (112.4 and 113.8° for [{$CuCl_2$}(tpt){$CuCl_2$(MeOH)}], 112.6(3) and 113.4(3)° for **3**, Scheme 3, compound II) are close to the α_1 and α_2 values of complexes **4** and **5** (α_1−α_2, range from 111.2(4)−111.6(3)°, Scheme 3, compound I). The large offsets from the ideal value of 120° indicate that the angular strain truly occurs on ligand tpt after the coordination of Cu(II). The literature also reported that the unhydrolyzed complexes [Cu(tpt)X_2]·$n$$H_2O$ (X = Cl or Br) can hydrolyze to $[Cu(bpca)X]_n$,[24] and the complex [Cu(tpt)(bpca)]·CF_3SO_3 [14] cannot further hydrolyze where angular strain did not occur. It seems reasonable that the main reason for Cu(II) promoting the hydrolysis of tpt is metal-induced angular strain. However, even though the metal-introduced angular strain occurred, tpt ligands in Ru(II)−tpt complexes did not hydrolyze to bpca.[12, 13] On the basis of the structural data and NMR results of Rh(III) and Ru(II) complexes, Paul and co-workers concluded that tpt hydrolysis promoted by Rh(III) ions is due to the electron-withdrawing effect of metal ions rather than metal-induced angular strain.

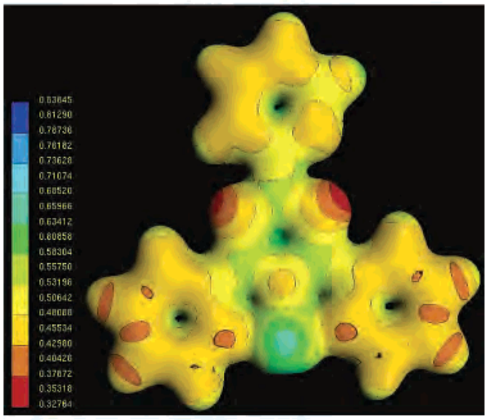
To gain insight into the mechanistic aspects of the hydrolytic reaction of these complexes, we performed



(a) Ru-tpt



(b) Cu-tpt



(c) Rh-tpt

Figure 5. Electrostatic potential (color coded as shown) mapped on the 0.02 au density isosurface in the M−N from G03/B3LYP.

Table 3. Calculation Results for M(tpt)

M	Ru(II)	Cu(II)	Rh(III)
Mayer bond order of N−C	1.18	1.15	1.09
Mulliken atomic charges of C	0.48645	0.50276	0.51946
	0.48976	0.50360	0.52225
N−C (Å)	1.30878	1.31296	1.32949
	1.31239	1.31744	1.32995
β_1 (deg)	113.325	112.512	114.239
β_2 (deg)	113.081	112.169	114.253

molecular orbital calculations of M(tpt) (M = Ru(II), Cu(II), and Rh(III)) with the related optimized X-ray geometry. The electrostatic potential mapped on the 0.02 au density isosurface in the M−N (M = Ru, Cu, or Rh) is illustrated in Figure 5. The Mayer bond order[38] of the N−C in the tpt ligand (Scheme 3), calculated as being 1.18, 1.15, and 1.09 for the Ru(II), Cu(II), and Rh(III) compounds, respectively, is much weaker than that of neutral tpt (1.36). A further analysis (Table 3) shows that either the N−C bond lengths or the Mulliken charges of C in the tpt ligand increase orderly. All of these suggest that the trend of hydrolysis of metal-bound tpt should be Ru(II) < Cu(II) < Rh(III), in good agreement with the experimental results and in favor of the hypothesis of an “electron-withdrawing effect of the metal ion” presented by P. Paul. The slight violation of the stained angle $\beta_1$or β_2 found in the Cu(II) compound can be attributed to the fact that the van der Waals radii of Cu (1.28 Å) is much smaller than that of Ru (1.32 Å) or Rh (1.34 Å).

Conclusion

In summary, we successfully synthesized and characterized two CuI complexes of tpt, a mixed-valence Cu(II)−Cu(I) complex of tpt, and two Cu(II) complexes of bpca by in situ hydrolysis of tpt and oxidation of Cu(I). It has been proven that the presence of PPh_3 or dppe not only prevented the oxidation of Cu(I) but also affected the self-assembly in the formation of complexes **1** and **2**. The experiments proved that the copper(I) cannot promote the hydrolysis of tpt and provided structure data of the precursor of the hydrolysis of tpt. The theoretical study supports that the main hydrolytic effect is the electron-withdrawing effect of metal ions.

Acknowledgment. This study was financially supported by the National Natural Science Foundation of China (20571050 and 20271031) and the Natural Science Foundation of Guangdong Province (No. 021240).

Supporting Information Available: Crystallographic data in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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