

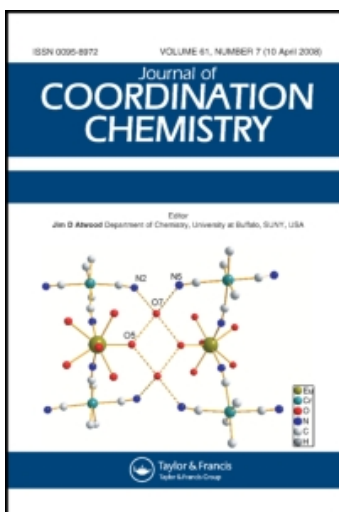
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### Syntheses, structures, and spectroscopic properties of binuclear copper(II) complexes containing *N,N*-bis(2-pyridylmethyl)amine ligands

Jing Qian<sup>a</sup>; Jin-Lei Tian<sup>b</sup>; Li Feng<sup>c</sup>; Wen Gu<sup>b</sup>; Xiao-Jun Zhao<sup>a</sup>; Shi-Ping Yan<sup>b</sup>

<sup>a</sup> College of Chemistry & Life, Tianjin Normal University, Tianjin 300387, P.R. China <sup>b</sup> Department of Chemistry, Nankai University, Tianjin 300071, P.R. China <sup>c</sup> Department of Chemistry, Tianjin Traditional Chinese Medicine University, Tianjin 300193, P.R. China

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## Syntheses, structures, and spectroscopic properties of binuclear copper(II) complexes containing N,N-bis(2-pyridylmethyl)amine ligands

JING QIAN<sup>†</sup>, JIN-LEI TIAN<sup>‡</sup>, LI FENG<sup>§</sup>, WEN GU<sup>‡</sup>,  
XIAO-JUN ZHAO<sup>†</sup> and SHI-PING YAN<sup>\*‡</sup>

<sup>†</sup>College of Chemistry & Life, Tianjin Normal University, Tianjin 300387, P.R. China

<sup>‡</sup>Department of Chemistry, Nankai University, Tianjin 300071, P.R. China

<sup>§</sup>Department of Chemistry, Tianjin Traditional Chinese Medicine University,  
Tianjin 300193, P.R. China

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Two new  $\mu$ -carboxylato-bridged binuclear copper(II) complexes [Cu<sub>2</sub>(bpea)<sub>2</sub>( $\mu$ -C<sub>2</sub>O<sub>4</sub>)](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (**1**) and [Cu<sub>2</sub>(bpma)<sub>2</sub>( $\mu$ -ta)](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (**2**) (bpea = N,N-bis(2-pyridylmethyl)ethylamine; bpma = N,N-bis(2-pyridylmethyl)methylamine; ta = terephthalate dianion) have been synthesized and structurally determined by X-ray diffraction. Complex **1** is crystallized in a monoclinic space group *C2/c* with unit cell parameters  $a = 21.539(17)$  Å,  $b = 12.608(10)$  Å,  $c = 13.117(11)$  Å,  $\beta = 96.788(13)^\circ$ . In **1**, each Cu(II) is five-coordinate, square-pyramidal geometry with a CuN<sub>3</sub>O<sub>2</sub> donor set. Complex **2** is crystallized in a monoclinic space group *P2<sub>1</sub>/n* with unit cell parameters  $a = 11.346(3)$  Å,  $b = 15.418(4)$  Å,  $c = 11.958(3)$  Å,  $\beta = 116.519(4)^\circ$ . In **2**, each Cu(II) also is square-pyramidal CuN<sub>3</sub>O<sub>2</sub> core, where three N- and one O-donors are equatorial and an oxygen of the bridging ligand occupies the axial site with a weak link. Elemental analyses, IR, UV and EPR spectra of the complexes were determined.

**Keywords:** Copper; N,N-bis(2-pyridylmethyl)amine; Crystal structure; Spectroscopic properties

### 1. Introduction

The ligands bpa-R, first reported by Romary *et al.* [1], are classical tridentate nitrogen donors which can bind to the metal both facial and meridional [2] and are more flexible than triazacyclononane (TACN), which is strictly facially coordinating [3–5]. Like *tris*-pyrazolylborates, bpa-R can adopt both  $k^2$  and  $k^3$  coordination modes, but unlike *tris*-pyrazolylborates can coordinate in both facial and meridional  $k^3$  modes [6]. A variety of transition metal complexes with bpa-R have been reported [7–17]. Coordination chemistry of copper is of continuing importance in relation to the structures and reactivity of the active sites in copper metalloproteins [18], but studies on copper(II) complexes with bpa-R are limited [19]. The Cu(II) ion, owing to the well-known

\*Corresponding author. Email: yansp@nankai.edu.cn

“plasticity” of the coordination sphere, forms complexes of coordination number four-six, with a variety of irregular geometries [20, 21]. Herein we report the syntheses, structures, and spectroscopic properties of the Cu(II) complexes  $[\text{Cu}_2(\text{bpea})_2(\mu\text{-C}_2\text{O}_4)](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  (**1**) and  $[\text{Cu}_2(\text{bpma})_2(\mu\text{-ta})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  (**2**).

## 2. Experimental

### 2.1. Materials and instrumentation

Unless stated, reagents were obtained from commercial sources and used without purification. Solvents used in this research were purified by standard procedures.

Elemental analyses (C, H, and N) were performed on a Model 240 Perkin-Elmer instrument. Infrared spectra were recorded as KBr pellets in the range 400–4000  $\text{cm}^{-1}$  on a Bruker Tensor 27 FTIR spectrophotometer. UV-Vis spectra were measured in the solid state using the diffuse-reflectance technique and in DMSO solution on a Jasci V-570 UV-Vis spectrophotometer. X-band EPR measurements were performed in the solid state on a Bruker ELEXSYS electro-spin resonance spectrometer at 120 K. The electrochemical behaviors of **1** and **2** were investigated by cyclic voltammetry (CV) in  $\text{CH}_3\text{CN}$  containing 0.1 M  $(\text{Bu}_4\text{N})\text{PF}_6$  as the supporting electrolyte. A three-electrode system containing a platinum-wire working electrode, a platinum-plate electrode (counter), and an Ag/AgCl reference electrode was used. Voltammetric recordings were performed under high-purity nitrogen at room temperature. The concentrations of the complexes were 0.001 M for each measurement and the voltage scan rate was 100  $\text{mV s}^{-1}$ . Electric conductivities were performed on a DDS-11C conductivity apparatus.

### 2.2. Preparation of complexes

The ligands bpma and bpea were prepared according to literature methods [22, 23].

**2.2.1.  $[\text{Cu}_2(\text{bpea})_2(\mu\text{-C}_2\text{O}_4)](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  (**1**).** To a water solution (5 mL) of  $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$  (0.5 mmol), a methanolic solution (10 mL) of bpea (0.5 mmol) was added dropwise with stirring. The mixture was stirred at room temperature for 0.5 h and added dropwise to a water solution (5 mL) of  $\text{K}_2\text{C}_2\text{O}_4$  (0.4 mmol). After refluxing for 3 h, the green solution was filtered and placed in a refrigerator. Deep blue-green block crystals suitable for X-ray structure analysis were obtained by the slow evaporation of filtrate over 5 months. Crystals were collected by filtration, washed with diethyl ether and dried in air. Yield: 39% (based on the copper salt). Anal. Calcd for  $\text{C}_{30}\text{H}_{36}\text{Cl}_2\text{Cu}_2\text{N}_6\text{O}_{13}$  (%): C, 40.60; H, 4.06; N, 9.47; Found(%): C, 40.21; H, 4.59; N, 9.12.

**2.2.2.  $[\text{Cu}_2(\text{bpma})_2(\mu\text{-ta})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  (**2**).** To a methanolic solution (5 mL) of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (1 mmol), an acetonitrile solution (10 mL) of bpma (1 mmol) was added dropwise with stirring. The deep-blue mixture was stirred at room temperature for 1 h and added dropwise to an acetonitrile solution (5 mL) of  $\text{H}_2\text{ta}$  (1 mmol)/triethylamine (2 mmol). The solution was heated to reflux for 6 h and filtered. Deep blue

block crystals suitable for X-ray analysis were obtained by slow evaporation of the filtrate at room temperature, collected by filtration, washed with diethyl ether and dried in air. Yield: 26% (based on the copper salts). Anal. Calcd for  $C_{34}H_{36}Cl_2Cu_2N_6O_{13}$  (%): C, 43.65; H, 3.85; N, 8.99; Found(%): C, 43.17; H, 4.09; N, 9.32.

*Caution:* Although no problems were encountered in this work, transition-metal perchlorates are potentially explosive and should thus be prepared in small quantities and handled with care.

### 2.3. X-ray structure determination

The blue prismatic crystals of **1** and **2** were mounted on a glass fiber and used for data collection. Crystal data for **1** were collected at 293(2) K, for **2** at 294(2) K using a Bruker Smart 1000 CCD diffractometer. Graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) with the  $\omega$ - $2\theta$  scan technique was used. An empirical absorption correction was applied to raw intensities [24]. The structures were solved by direct methods (SHELX-97) and refined with full-matrix least-squares on  $F^2$  using SHELX-97 [25, 26]. Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. The hydrogens were added theoretically, riding on the concerned atoms and refined with fixed thermal factors. The details of crystallographic data and structure refinement parameters are summarized in table 1.

Table 1. Crystallographic data and structure refinement parameters for **1** and **2**.

	<b>1</b>	<b>2</b>
Empirical formula	$C_{30}H_{36}Cl_2Cu_2N_6O_{13}$	$C_{34}H_{36}Cl_2Cu_2N_6O_{13}$
Formula weight	886.63	934.67
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
Unit cell dimensions (Å, °)		
<i>a</i>	21.539(17)	11.346(3)
<i>b</i>	12.608(10)	15.418(4)
<i>c</i>	13.117(11)	12.271(2)
$\alpha$	90	90
$\beta$	96.788(13)	119.310(2)
$\gamma$	90	90
Volume (Å <sup>3</sup> ), <i>Z</i>	3537(5), 4	1871.7(8), 2
Calculated density (mg m <sup>-3</sup> )	1.665	1.658
Absorption coefficient (mm <sup>-1</sup> )	1.428	1.354
<i>F</i> (000)	1816	956
$\theta$ range for data collection (°)	1.87–26.94	2.06–26.44
Limiting indices	$-26 \leq h \leq 26,$ $-8 \leq k \leq 15,$ $-16 \leq l \leq 15$	$-14 \leq h \leq 7,$ $-19 \leq k \leq 18,$ $-13 \leq l \leq 15$
Reflections collected	9980	10340
Independent reflections	3705 [ $R(\text{int}) = 0.0531$ ]	3802 [ $R(\text{int}) = 0.0704$ ]
Data/restraints/parameters	3705/46/241	3802/0/263
Goodness-of-fit on $F^2$	1.023	1.000
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0595, wR_2 = 0.1554$	$R_1 = 0.0524, wR_2 = 0.1203$
<i>R</i> indices (all data)	$R_1 = 0.1044, wR_2 = 0.1807$	$R_1 = 0.1210, wR_2 = 0.1564$
Largest difference peak and hole (e Å <sup>-3</sup> )	1.085 and -0.662	0.715 and -0.592

Symmetry transformations used to generate equivalent atoms for **1**:  $-x+1, y, -z+1/2$ ; for **2**:  $-x+1, -y+2, -z+1$ .

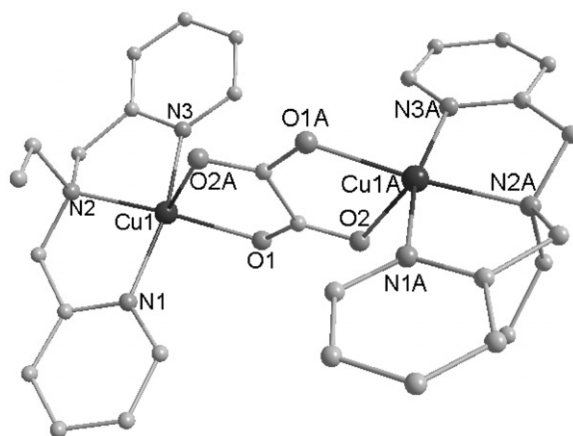


Figure 1. The labeling scheme of  $[\text{Cu}_2(\text{bpea})_2(\mu\text{-C}_2\text{O}_4)]^{2+}$ ; hydrogens,  $\text{ClO}_4^-$ , and  $\text{H}_2\text{O}$  are omitted for clarity.

### 3. Results and discussion

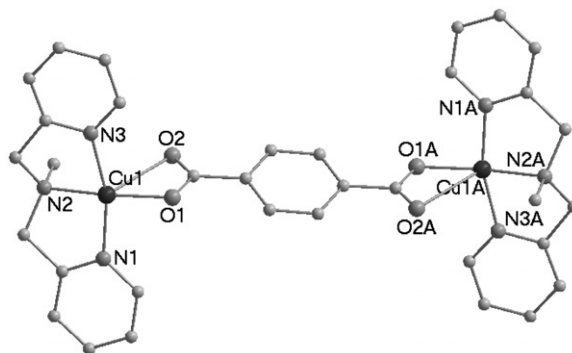
#### 3.1. Crystal structure

The labeled diagram of  $[\text{Cu}_2(\text{bpea})_2(\mu\text{-C}_2\text{O}_4)]^{2+}$  of **1** is shown in figure 1 with noncoordinated  $\text{H}_2\text{O}$  and  $\text{ClO}_4^-$  omitted. Selected bond lengths and angles are listed in table 2. The binuclear complex consists of two  $[\text{Cu}^{\text{II}}(\text{bpea})]$  subunits bridged by a bis-bidentate oxalate, two uncoordinated perchlorates, and one water.  $[\text{Cu}_2(\text{bpea})_2(\mu\text{-C}_2\text{O}_4)]^{2+}$  is centrosymmetric and the geometry around Cu(1) and Cu(1A) is distorted square pyramidal ( $\tau$  parameter is 0.12) [27, 28] with a  $\text{CuN}_3\text{O}\cdots\text{O}$  chromophore (4 + 1). The basal plane is described by the pyridyl N(1), N(2), and the N(3) of the amine of the ligand and O(1) from bridging oxalate. An oxalate oxygen [O(2A)] occupies the axial position. The Cu(1) is 0.1394 Å up from the square plane formed by N(1), N(2), N(3), and O(1). The Cu–O bond length is 2.002 Å and Cu–N average bond lengths 2.001 Å in equatorial plane, similar to those found previously [29]. The apical positions are occupied by bridging oxalate at 2.307 Å, longer than those in the basal plane. In oxalate, the C–O bond lengths range from 1.231 to 1.259 Å and the C–C bond length is 1.562 Å, typical for oxalate-bridged binuclear complexes [30–32]. The oxalate is almost coplanar (maximum deviation, 0.073 Å). Cu1 deviates by 0.023 Å from the plane. The dihedral angle between the mean copper coordination plane and the oxalate plane is 4.5°. The bite angle formed by Cu and the two oxygens of oxalate (O1–Cu1–O2A) is 77.75°, close to those reported for oxalate-bridged copper(II) [31–33]. The Cu(1)  $\cdots$  Cu(1A) distance is 5.552 Å, close to 5.597 Å [29] and 5.528 Å; 5.469 Å [31], slightly shorter than 5.608 Å [30] to 5.631 Å [33], and longer than 5.1–5.4 Å found in dimeric Cu(II) complexes [34–38].

A perspective view of **2** along with the atom-labeling scheme is presented in figure 2. Selected bond lengths and angles are listed in table 2. The structure of **2** consists of centrosymmetrical binuclear units in which the two Cu(II)'s are bridged by an amphimonodentate terephthalate through O(1) and O(1A). The  $[\text{Cu}_2(\text{bpma})_2(\mu\text{-ta})]^{2+}$  is centrosymmetric and the geometry around Cu(1) and Cu(1A) is distorted square pyramidal ( $\tau$  parameter of 0.07) [27, 28] with a  $\text{CuN}_3\text{O}_1\cdots\text{O}$  chromophore (4 + 1).

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

<b>1</b>			
Cu(1)–N(1)	1.982(5)	Cu(1)–O(1)	2.002(4)
Cu(1)–N(2)	2.016(5)	Cu(1)–O(2A)	2.307(4)
Cu(1)–N(3)	2.004(5)	Cu(1)–Cu(1A)	5.552
N(1)–Cu(1)–O(1)	94.53(17)	N(1)–Cu(1)–N(3)	165.0(2)
O(1)–Cu(1)–N(2)	172.23(15)	N(1)–Cu(1)–N(2)	84.2(2)
O(1)–Cu(1)–N(3)	97.40(17)	N(3)–Cu(1)–N(2)	82.8(2)
N(1)–Cu(1)–O(2A)	102.20(16)	O(1)–Cu(1)–O(2A)	77.75(13)
N(2)–Cu(1)–O(2A)	110.02(16)	N(3)–Cu(1)–O(2A)	89.26(16)
<b>2</b>			
Cu(1)–N(1)	1.952(4)	Cu(1)–O(1)	1.944(3)
Cu(1)–N(2)	2.015(4)	Cu(1)–N(3)	1.971(4)
Cu(1)–Cu(1A)	10.815(19)	Cu(1)–O(2)	2.562
O(1)–Cu(1)–N(1)	96.05(15)	N(1)–Cu(1)–N(3)	163.70(16)
O(1)–Cu(1)–N(2)	167.65(15)	N(1)–Cu(1)–N(2)	83.63(16)
O(1)–Cu(1)–N(3)	98.83(15)	N(3)–Cu(1)–N(2)	83.25(16)

Figure 2. The labeling scheme of  $[\text{Cu}_2(\text{bpma})_2(\mu\text{-ta})]^{2+}$ ; hydrogens,  $\text{ClO}_4^-$ , and  $\text{H}_2\text{O}$  are omitted for clarity.

The geometry around Cu is a distorted square planar with three N atoms from terminal-ligand bpma and one O atom from ta. The intramolecular  $\text{Cu1}\cdots\text{Cu1A}$  distance is 10.815 Å. The average Cu–N and Cu–O bond lengths of 1.979 Å and 1.944 Å, respectively, are in the normal range [39–41]. Apical positions are occupied by O2 at the semicoordination length of 2.562 Å, longer than that of **1**. Compared with **1**, the main difference is found in the coordination polyhedron of Cu(II), which has a semicoordinate apical Cu–O bond distance.

### 3.2. IR spectrum studies

The complexes have similar IR spectra. The  $\nu_{(\text{C}-\text{N})}$  of **1** and **2** are a shoulder involving a split sharp peak at  $1600\text{ cm}^{-1}$ , while  $\nu_{(\text{C}-\text{H})}$  for **1** and **2** are a split sharp peak at 2960, 2932 and  $2983\text{ cm}^{-1}$ , respectively. A strong  $\nu(\text{ClO}_4^-)$  at  $1090\text{ cm}^{-1}$  and a medium absorption at  $622\text{ cm}^{-1}$  for **1** ( $1084$  and  $623\text{ cm}^{-1}$  for **2**) indicate uncoordinated  $\text{ClO}_4^-$ . Split sharp peaks about  $1600\text{--}1400\text{ cm}^{-1}$  are assigned to  $\text{C}_2\text{O}_4^{2-}$  for **1** and absorption bands at  $1577$  and  $1440\text{ cm}^{-1}$  ( $\Delta\lambda = 137\text{ cm}^{-1}$ ) are attributed to bidentate carboxylate

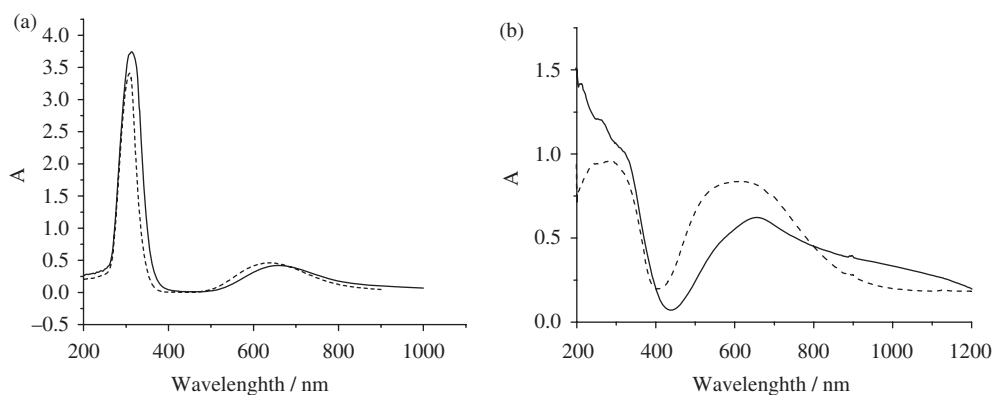


Figure 3. UV-Vis spectra of DMSO solution (a) and of solid state (b) of **1** (solid line) and **2** (dashed line).

for **2**. These data are consistent with the structural analysis of **1** and **2**. Abundant absorption peaks in the region  $620\text{--}770\text{ cm}^{-1}$  argue for the presence of pyridyls.

### 3.3. Electronic spectrum studies

Electronic absorption spectra in DMSO and electronic reflectance spectra in solid state of **1** and **2** suggest that the structure observed in the solid state is retained in DMSO (figure 3). Very strong absorptions of **1** and **2** in the UV region at 312 nm ( $\epsilon = 3.73 \times 10^4$ ) for **1** and 310 nm ( $\epsilon = 3.38 \times 10^4$ ) for **2** can be attributed to  $\pi\text{--}\pi^*$  charger transfer of the ligand. In the visible region the maximum absorptions at 658 nm ( $\epsilon = 4.04 \times 10^3$ ) for **1** and 630 nm ( $\epsilon = 4.73 \times 10^3$ ) for **2** are consistent with square-pyramidal geometry of Cu(II), typical of d–d transitions of Cu(II) in a weak tetragonal ligand. The molar electrical conductivities of **1** and **2** in DMF, 141 and  $154\text{ cm}^2\text{ }\Omega^{-1}\text{ mol}^{-1}$ , respectively, are consistent with structural analysis [42].

### 3.4. EPR spectrum studies

Polycrystalline electron paramagnetic resonance (EPR) spectra of **1** and **2** at 120 K exhibit an unresolved axial signal ( $g_{\parallel} > g_{\perp} > 2.0$ ) with  $g_{\parallel} = 2.21$  and  $g_{\perp} = 2.039$  (**1**)  $g_{\parallel} = 2.17$  and  $g_{\perp} = 2.038$  (**2**), suggesting a  $d_{x^2-y^2}$  ground state (Supplementary material). The absence of hyperfine splitting and the high  $g_{\parallel}$  value indicate that no band corresponding to  $\Delta M_s = \pm 2$  was observed in the spectra, ruling out copper–copper interaction. These results are consistent with the crystal structures.

### 3.5. Electronic chemical behavior studies

Cyclic voltammetric studies to establish the redox behaviors of the Cu(II) complexes (Supplementary material) reveal non-Nernstian, irreversible redox processes for both complexes. For **1**, only a reduction peak is observed near  $-0.8\text{ V}$ , indicating that Cu(I) is unstable in solution. The peak near  $-1.2\text{ V}$  is presumed to be dioxygen in solution.

Redox behavior of **2** indicates almost reversible redox process involving the  $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$  couple near  $-0.474\text{ V}$ . The anodic to cathodic peak current ratio of around 0.27 for **2** suggests poor reversibility of the electron transfer.

### Supplementary material

The CCDC Nos of **1** and **2** are 602625 and 602629, respectively.

### Acknowledgments

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