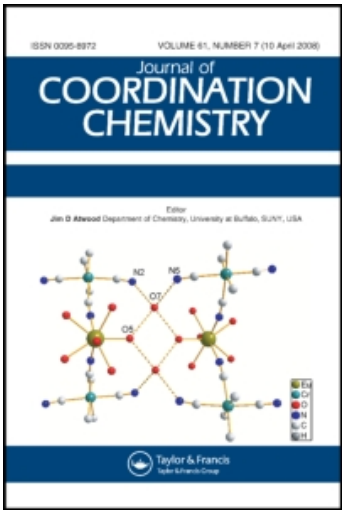

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Dicopper complex of p-tert -butylcalix8arene bearing acylhydrazone pendant domains

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Dicopper complex of *p-tert*-butylcalix[8]arene bearing acylhydrazone pendant domains

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A dicopper complex of *p-tert*-butylcalix[8]arene bearing eight salicylaldehyde acylhydrazone domains was prepared and its single crystal structure determined, in which only four acylhydrazone domains act as monoanionic tridentate planar chelators to coordinate to two copper ions.

Keywords: Calixarene; Multimetallic complex; Polydentate ligand; Conformation; Crystal structure

1. Introduction

The assembly of highly organized multimetallic architectures is important for catalysis, magnetism, new materials, medicine, molecular electronic devices and associated nano-technologies. Developing methods for tailoring properties and tuning the stoichiometries in multimetallic complexes is a considerable challenge, and for this purpose various synthetic methodologies have been established. The organic backbone of calix[n]arenes provides a platform for assembly of several metal centers in close proximity [1, 2]. Calix[4]arenes are the lowest oligomers in the series and are readily available; numerous metal complexes have been prepared and structurally authenticated. The vast majority of these metallocalix[4]arene derivatives exist as either mono or binuclear complexes, retaining a cone-like conformation for the parent ligands [3]. By contrast, metal compounds containing the larger ring systems such as calix[6]arene and calix[8]arene are still quite rare despite conformational variations offered by the increased flexibility of the larger number of polyphenolic rings [4–8]. An additional attractive feature of the latter is their ability to simultaneously coordinate more than one metal. Recently, the coordination chemistry of calix[8]arenes towards transition metal centers has attracted much attention [9–11]. Owing to the large size and flexibility, calix[8]arenes appear to be more suitable for encapsulation of metal centers. Due to the presence of a large number of potential binding sites, such ligands offer interesting

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possibilities for preparation of multinuclear species [12]. As part of an ongoing program investigating coordination environments of larger calix[n]arenes ($n = 6, 8$), herein we report preliminarily results of design of polydentate Schiff-base ligands of calix[8]arene as a platform for construction of multimetallic complexes.

2. Experimental

2.1. *Reagents and instruments*

All reagents and solvents were commercial available of analytical grade and used as received. Evaporation of organic solvents was carried out with a rotary evaporator in conjunction with a water aspirator. *p-tert*-butylcalix[8]arene **1** was prepared according to published methods.

Melting points were taken on a hot-plate microscope apparatus and are uncorrected. ^{1}H NMR spectra were recorded with a Bruker AV-600 spectrophotometer (600 MHz for ^{1}H NMR). IR spectra were obtained on a Bruker Tensor27 spectrometer (KBr disc). X-ray data were collected on a Bruker Smart APEX-2 diffractometer.

2.2. *Synthesis of ethyl* p-tert-*butylcalix[8]arylacetate (2)*

A suspension of **1** (3.0 mmol, 3.90 g), anhydrous potassium carbonate (36.0 mmol, 4.0 g) and potassium iodide (0.5 g, 3.0 mmol) in dry acetone (100 mL) was heated to reflux under nitrogen for at least 0.5 h. Then ethyl α-chloroacetate (24.0 mmol, 2.60 mL) was added. The reaction mixture was refluxed for 24 h; the second portion of ethyl α-chloroacetate (24.0 mmol, 2.60 mL) was added and the mixture was refluxed for an additional 5 days. After removal of acetone, the residue was dissolved in water and acidified with hydrochloric acid, then extracted with $CHCl_3$. The yellow organic layers were separated and dried with $MgSO_4$. Red oil was yielded after evaporation of the solvent, which was triturated with alcohol to give white product, and recrystallized from ethanol to give pure **2**. Yield: 87.2%, m.p. 226–228°C, IR (KBr) υ: 2957(s), 2893(m), 2858(m), 1745(vs), 1470(s), 1365(m), 1190(s), 1048(m) cm^{-1}; ^{1}H NMR ($CDCl_3$), δ: 6.90 (s, 16H, ArH), 4.60 (s, 16H, CH_2), 4.30 (m, 16H, OCH_2), 3.80–4.10 (m, 16H, CH_2), 1.10–1.30 (m, 96H, CH_3). Anal. Calcd for $C_{120}H_{160}O_{24}$: C, 72.55; H, 8.12. Found: C, 72.79; H, 7.85.

2.3. *Synthesis of* p-tert-*butylcalix[8]aryl acyl hydrazine (3)*

A mixture of ethyl *p-tert*-butylcalix[8]arylacetate (**2**) (0.50 mmol, 0.998 g) and hydrated hydrazine (10 mL, 80%) in 15 mL of ethanol was refluxed for 24 h. After cooling to room temperature, the resulting precipitate was collected by filtration and washed with absolute alcohol to give the white solid **3**. 95.2%, mp: 290°C (decomp.). IR(KBr) υ: 3316(m), 3041(m), 2957(s), 2893(m), 2858(m), 1668(vs), 1604(m), 1470(vs), 1280(m), 1182(s), 1104(m) cm^{-1}. Anal. Calcd for $C_{104}H_{144}N_{16}O_{16}$: C, 66.64; H, 7.74; N, 11.96. Found: C, 66.81; H, 8.23; N, 11.73.

2.4. *Synthesis of salicylaldehyde* p-tert-*butylcalix[8]aryl acyl hydrazone (4)*

To a suspension of *p-tert*-butylcalix[8]aryl acyl hydrazine **3** (0.50 mmol, 0.937 g) in ethanol (30 mL) was added salicylaldehyde (5.0 mmol, 0.61 g) in ethanol (10 mL). The mixture was then refluxed overnight to give light yellow precipitate. After cooling to room temperature, the precipitate was collected by filtration and washed with absolute alcohol to give **4**, light yellow solid, 90.0%, m.p. 256–258°C. IR(KBr) υ: 3408(s), 3217(m), 3048(m), 2964(s), 2893(m), 2858(m), 1689(vs), 1611(s), 1470(vs), 1266(s) cm^{-1}. UV ($CHCl_3$) λ: 320(0.96), 279(2.16), 239(2.04) nm. Anal. Calcd for $C_{160}H_{176}N_{16}O_{24}$: C, 70.99; H, 6.55; N, 8.28. Found: C, 71.25; H, 6.31; N, 7.70.

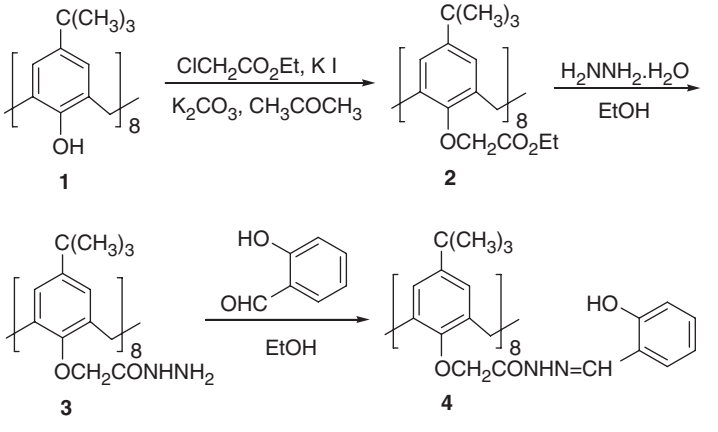
2.5. *Synthesis of copper complex of* p-tert-*butylcalix[8]aryl acyl hydrazone (5)*

To a solution of *p-tert*-butylcalix[8]aryl acyl hydrazone **4** (0.10 mmol, 0.270 g) in methanol (20 mL) was added copper acetate tetrahydrate (0.40 mmol, 0.102 g). Then the mixture was stirred at room temperature for 12 h to give a clear solution. Methanol was removed by evaporation and the residue was triturated with a mixture of chloroform and petroleum ether to give dark greenish-yellow solid, 28%. UV ($CHCl_3$) λ: 360(0.67), 273(1.70), 241(2.60) nm. IR(KBr) υ: 3410(m), 2959(m), 1666(s), 1624(vs), 1539(s), 1471(m), 1448(m), 1196(s) cm^{-1}. Anal. Calcd for $C_{160}H_{172}N_{16}O_{24}Cu_2$: C, 67.90; H, 6.13; N, 7.92. Found: C, 67.53; H, 6.347; N, 7.58.

3. Results and discussion

3.1. *Synthesis*

The *p-tert*-butylcalix[8]arene acylhydrazone was prepared in three steps (scheme 1). *p-tert*-butylcalix[8]arene **1** is completely *O*-alkylated according to the published procedure [13], with a little deviation, by ethyl α-chloroacetate in the system of K_2CO_3/KI/acetone for refluxing about 5 days to give ethyl *p-tert*-butylcalix[8]aryl



Scheme 1. Synthesis of *p-tert*-butylcalix[8]arene acylhydrazone.

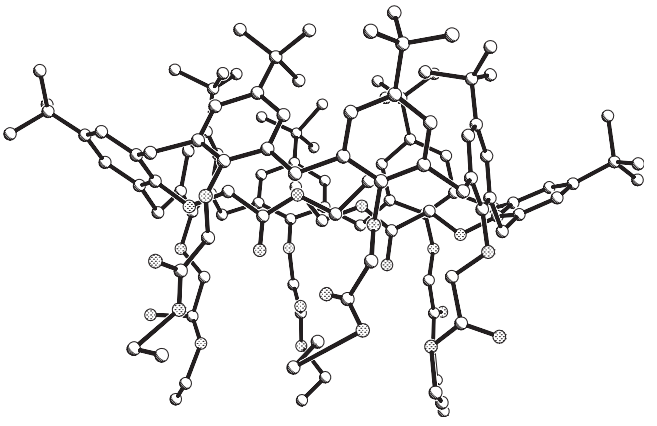


Figure 1. ORTEP drawing of ethyl *p-tert*-butylcalix[8]aryl acetate **2**; hydrogen atoms are omitted for clarity.

acetate **2** in 87% yield. This activated ester provides an excellent chance for chemical modification on the lower rim of calix[n]arene. Refluxing **2** with excess of hydrated hydrazine in ethanol gave the corresponding calixaryl acylhydrazine derivative **3** [14]. The acylhydrazine derivative **3** has very poor solubility in most organic solvents with eight hydrophilic hydrazine groups, making characterization difficult. In the IR spectra of **3**, the C=O group of acylhydrazine shows stronger absorption at 1680 cm^{-1}, while C=O group of ester **2** appears at 1750 cm^{-1}, indicating that all ethyl ester groups in **2** are transformed into acylhydrazine groups. Even with limited solubility in ethanol, **3** reacts smoothly with salicylaldehyde in hot ethanol. When the suspension of **3** and salicylaldehyde in ethanol was refluxed overnight, the white solid disappeared at first and then the expected yellow precipitates of Schiff-base were formed. After workup, the salicylideneimine derivative **4** was obtained in moderate yields (71%). **4** has eight functional salicylaldehyde acylhydrazone groups and has good solubility in common organic solvents. In their UV–Vis spectrum, the new C=N groups have λ_{max} in $CHCl_3$ at about 315~317 nm. In IR spectrum the C=O group of amide shows a very strong absorption at 1654 cm^{-1}, while the C=N group of hydrazone shows a strong peak at 1625 cm^{-1}.

3.2. *Structure*

From the crystal structure of **2** (figure 1 and table 1), it can be clearly seen that the molecule exists in nearly cone configuration with the presence of a C_2 axis perpendicular to the molecular plane [12]. The eight phenolic units in the ring were divided into two groups with two phenolic rings (1- and 5-phenolic units), almost perpendicular to the other six phenolic units. The eight *p-t*-butylphenol units stand in nearly one direction. The six *O*-acetate groups stretch to the lower rim of calixarene, and the other two *O*-acetate groups on 1- and 5-phenolic rings stretch to the center of the cavity. Thus, the eight ethoxycarbonylmethoxy groups in the calixarene are close, good for coordination to metal ions.

Complexation of copper by calix[8]arene acylhydrazone ligand **4** was performed in methanol solution by reacting 4 : 1 stoichiometric amounts of copper acetate with

Table 1. Crystal data and structure refinement details of **2** and **5**.

	2	**5**
Empirical formula	$C_{120}H_{160}O_{24}$	$C_{160}H_{169}Cu_2N_{16}O_{24.50}$
Formula weight	1986.48	2835.19
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2(1)/n$	Monoclinic, Pn
Unit cell dimensions (Å, °)		
a	21.731(2)	16.729(5)
b	23.820(2)	16.088(5)
c	24.545(2)	33.359(10)
α	5.916(2)	90
β	105.509(2)	106.309(13)
γ	108.823(2)	90
Volume (Å^3)	12645(2)	8617(5)
Z, D_{Calcd} (g cm^{-3})	4, 1.043	2, 1.093
Absorption coefficient (mm^{-1})	0.071	0.311
$F(000)$	4288	2990
Crystal size (mm^3)		$0.20 \times 0.16 \times 0.12$
θ range for data collection	2.02–25.00	1.27–25.5
h, k, l ranges	$-25 \le h \le 25$, $-27 \le k \le 28$, $-22 \le l \le 29$	$-19 \le h \le 17$, $-18 \le k \le 19$, $-25 \le l \le 39$
Reflections collected/unique	65001/22186 [R(int) = 0.0834]	40743/15147 [R(int) = 0.2113]
Completeness to $\theta = 27.50$	99.6%	99.7%
Absorption correction	None	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	22186/0/1298	15147/78/916
Goodness-of-fit on F^2	1.246	0.947
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1733$, $wR_2 = 0.4176$	$R_1 = 0.1273$, $wR_2 = 0.2890$
R indices (all data)	$R_1 = 0.2948$, $wR_2 = 0.4649$	$R_1 = 0.3191$, $wR_2 = 0.4235$
Largest diff. peak and hole (e Å^{-3})	1.544 and −0.449	1.095 and −1.137

the ligand. Under these conditions, the dark green complex was isolated in 28% yield. X-ray quality crystals of copper complex were grown by slow diffusion of light petroleum into chloroform solution of the complex. The crystal structure of **5** is displayed in figure 2. The structure looks very complicated because there are 160 carbon atoms, 16 nitrogen atoms and 24 oxygen atoms, as well as two copper atoms in the molecule. We can divide the eight acylhydrazone arms connecting to each phenolic ring of calix[8]arene into two groups. The four inner-stretching acylhydrazone arms coordinate to copper, while the other four are outside and did not coordinate to copper. The coordination motif around two copper ions in **5** is represented in figure 3. Two acylhydrazone arms connecting to 1- and 5-phenolic rings coordinate to $Cu(1)^{2+}$, while two acylhydrazones arms connecting to 3- and 7-phenolic rings coordinate to $Cu(2)^{2+}$. Each coordinated acylhydrazone is a monoanionic tridentate planar chelator. The phenolic proton is ionized, while the amide proton is not removed. The slightly twisted octahedral coordination geometry around copper was established through two phenolic oxygens, two imine nitrogens and two carbonyl oxygens. Several copper complexes of simple salicylaldehyde acylhydrazone have been prepared, in which this class of diprotic ligand typically is tridentate donor with ionization state dependent on the conditions and the metal employed [15]. The two Cu–O distances of phenolic groups are in the range of 1.964(8), [Cu1–O3], 1.990(8) [Cu2–O9] Å, shorter than the two Cu–O distances of carbonyl groups, 2.254(8) Å, [Cu1–O2] and 2.234(8) Å, [Cu2–O8]. The two

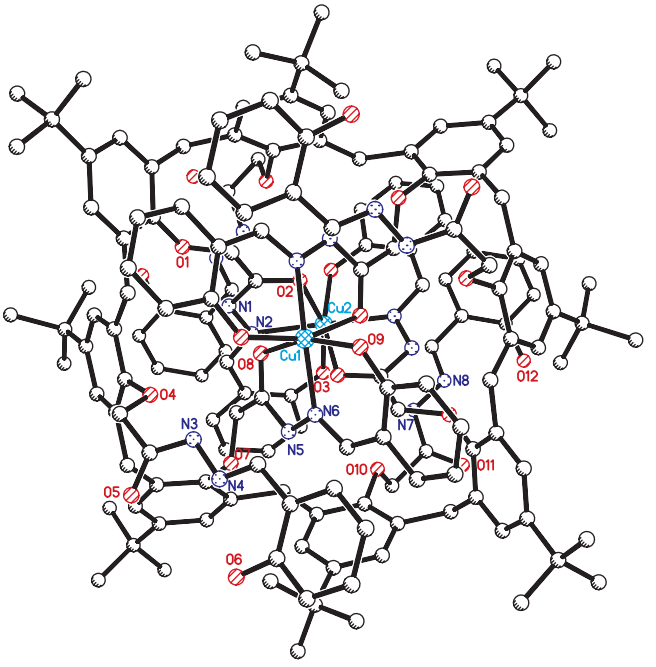


Figure 2. ORTEP drawing of **5**; hydrogen atoms are omitted for clarity.

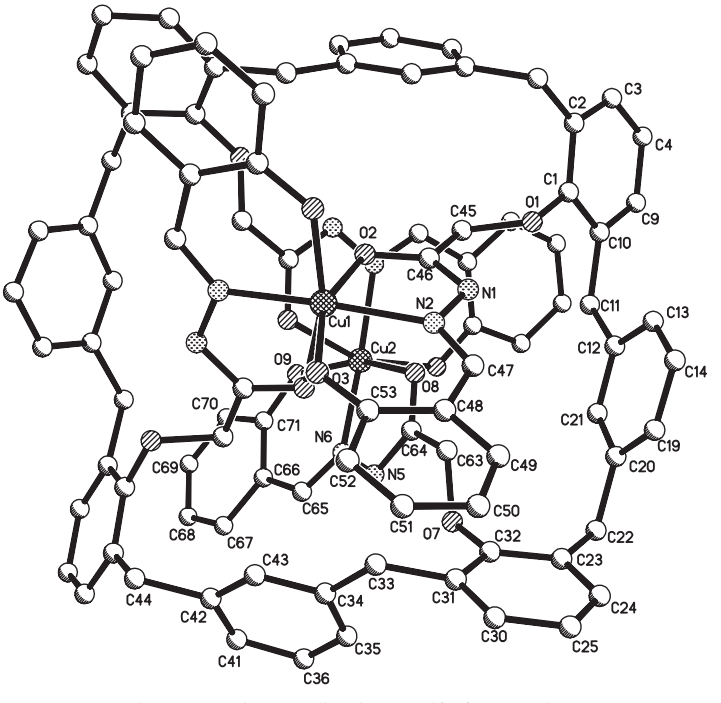


Figure 3. The coordination motif of copper in **5**.

Cu–N band lengths are 2.111(10) Å [Cu1–N2] and 2.079(10) Å [Cu2–N6]. Because the oxygen atom of carbonyl group is coordinated to copper ion, the C=O distance 1.262(12) Å [C(46)–O(2)] in the coordinated acylhydrazone is longer than in the non-coordinated acylhydrazone (1.197(17) Å [C(55)–O(5)]. Similar phenomenon was observed in the N=CH bond distances (N2–C47, 1.290(13) Å via N4–C56, 1.24(2) Å). The C–O bond distance (O6–C62, 1.309(16) Å) is also slightly longer after coordination (O3–C53, 1.320(14) Å).

To the best of our knowledge, there are few reported copper complexes of calixarene in the literature. J.L. Atwood first reported a water-soluble copper complex with calix[4]arenesulfonate as ligand [16]. Reinaud prepared a two-coordinate copper complex with bidentate imidazolyl pendant arms on calix[4]arene. Using calix[6]arene as platform [17], Reinaud and Le Mest prepared trispyridine-Cu and trisimidazole-Cu funnel-type complexes as metalloredox models to study the properties of a monocopper center embedded in a biomimetic cavity [18]. Very recently, a nano-capsule copper complex of pyrogallol[4]arene was preliminarily determined [19]. The dicopper complex **5** is the first copper complex with calix[8]arene as platform. Thus, the preparation and crystal determination of transition metal complexes of larger calyx[6]arene ($n = 6, 8$) are worth further study.

Supplementary material

Single crystal X-ray diffraction data are deposited with CCDC (Deposition numbers **2**: CCDC 678019; **5**: 678020).

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