SYNTHESIS AND CHARACTERIZATION OF A SCHIFF BASE OF *p-tert*-BUTYLCALIX[4]ARENE AND ITS COMPLEX WITH COPPER(II)

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Abstract

The synthesis and characterization of a Schiff base of *p-tert*-butylcalix[4]arene (H_2L) and its complex with copper(II) is described. The synthesis of H_2L has been achieved by the condensation of salicylaldehyde with the amine group of upper rim monoamine-*p-tert*-butylcalix[4]arene in ethanol. Attempts for the preparation of metal-ligand (1:2) complexes of this Schiff base with some transition metals failed except for Cu(II), which has been prepared from the copper sulfate, by refluxing in ethanol. The ligand and its complex with copper have been characterized on the basis of elemental analysis and spectral data. Solvatochromisity was observed for the ligand and its copper(II) complex, i.e. in different solvents depending on the solvent polarity, their λ_{max} of absorption in electronic spectra appeared in different wavelengths. Therefore these compounds can be good candidates for nonlinear optical active (NLO) applications. The prepared complex contains two *p-tert*-butylcalix[4]arene moieties, which could be expect to have improved calixarene ability in the fields like molecular recognition, host-guest features and other calixarene related capabilities.

Introduction

Calix[4]arenes can be easily functionalized both at the phenolic OH groups (lower rim) and, after (partial) removal of *tert*-butyl groups, at the para positions of the phenol rings (upper rim).[1-3] The vast majority of this modified calixarenes exist in the cone conformation in which there is a cavity suitable for recepting of different ionic and neutral species.[4] Furthermore, the most significant feature of the chemistry of these molecules is their ability to bind selectively alkali and alkaline earth cations[5,6]. Compared to the number of reports on the binding of alkali metal ions with calxiarenes, reports on the binding of transition metal ions are still limited.[7-9]

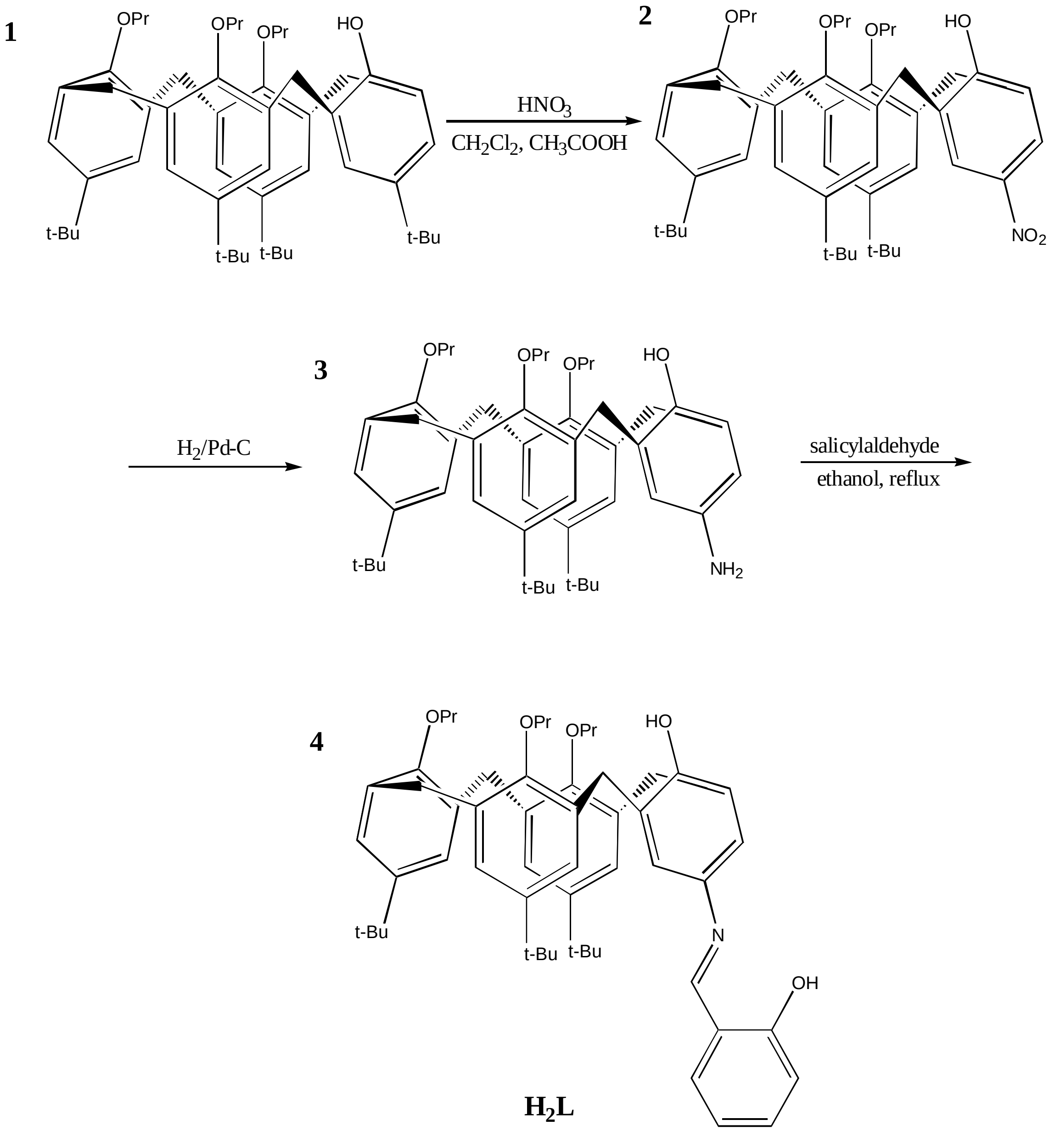
Monofunctionalized calixarenes are potentially excellent starting materials for the selective designing of new materials. Reinhudt et al.[10] reported the *ipso*nitration of *p-tert*-butylcalix[4]arene for the preparation of nitrocalix[4]arene. In the present work the preparation of monoamine functionalized *p-tert*-butylcalix[4]arene at the upper rim and conversion of it to the salicylaldehyde Schiff base and finally complexation with Cu(II) is reported. The attempts for the preparation of complexes with other transition metals such as Co(II) and Ni(II) failed may be because of the steric hindrances. In the case of cobalt and nickel, they often prefer square planar and octahedral complexes but the copper four coordinated tetrahedral complexes are most common.

Results and discussion

Synthesis of the Ligand and it's Complex. Schiff bases are potentially capable of forming stable complexes with metal ions.[9,11] In the present work the synthesis of **4** according to the Scheme 1 is described. The cone mononitro- *p*-*tert*-butylcalix[4]arene, **2**, was obtained form the mono *ipso*nitration of monohydroxycalixarene, **1**,[12]. The mononitro derivative was reduced to corresponding monoamine **3**, by hydrogenation on palladium-charcoal catalyst. The condensation of the compound **3** with salicylaldehyde gave the Schiff base ligand H_2L as a NO donor with a *p*-*tert*-butylcalix[4]arene moiety (Scheme 1). The ^{1}H NMR spectrum of the ligand H_2L inferred the calixarene to be in cone conformation. The conciliation that H_2L exists in a cone conformation was deduced from the presence of two set of characteristic AB systems at 3.19 and 4.33 ppm (J = 13.8 Hz) and 3.25 and 4.38 ppm (J = 12.9 Hz), respectively. On the basis of spectroscopic evidence the transformation of **1** into H_2L occurs with the retention of the cone conformation of the *p*-*tert*-butylcalix[4]arene moiety. The Cu(II) complex of Schiff base ligand, H_2L, was prepared in ethanol in which the metal ligand ratio is 1:2. The analytical results of the isolated solid ligand and the complex with their melting points and colors are compiled in Table 1.

Table 1. The colors, yields, melting points and analytical results of ligand and complex

Compound	Formula Weigh	Color	m.p (°C)	Yield, %	Percents of Elements Calc. (Found)			
					C	H	N	Cu
$H_2L.H_2O$ ($C_{56}H_{73}NO_6$)	856.20	Yellow	192	86	78.56 (79.42)	8.59 (8.69)	1.64 (1.83)	-
$Cu(HL)_2.3H_2O$ ($C_{112}H_{146}CuN_2O_{13}$)	1791.95	Brown	260	80	75.07 (75.31)	8.21 (7.95)	1.56 (1.67)	3.54 (3.78)



Scheme 1. Synthesis of the ligand, H_2L

IR Spectra of the Ligand and Complex. The characteristic IR absorptions are given in Table 2. The observed microanalytical data for C, H, and N atoms of the ligand and complex shows that they contain water molecules, which are, identified by broad O-H absorptions around 3400-3420 cm^{-1} in IR spectra. The most significant differences in the IR spectra of the ligand and complex was the shift of C=N stretching frequencies to lower frequencies due to metal-ligand coordination.[13] Furthermore, a new band has been observed around 554 cm^{-1} which is attributed to ν (M-N=C) and ν (M-O)[14]. All of the IR spectra information supports the suggestion of coordination of the imine nitrogen atom of the calixarene moiety and phenolic oxygen atom of the salicylaldehyde moiety to the metal ion. According to the above discussion, the general structure for the metal complex is proposed as shown in figure 1.

Table 2. Characteristic IR bands of the Ligand and the Complex as KBr Pellets (cm^{-1})

Compound	ν (H_2O)	ν (O-H)	ν (C-H)	ν (M-N=C, M-O)	ν (C=N)
$HL.H_2O$	3420 mbr	3547	2960, 2874 s	-	1620
$Cu(HL)_2.3H_2O$	3410 mbr	3501	2960, 2875 s	554	1610

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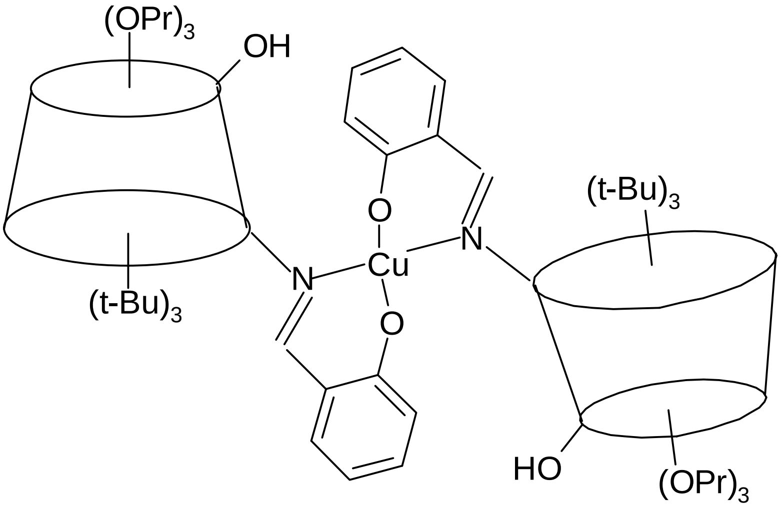

Fig. 1. Structure of the copper complex of H_2L

Electronic Spectra of the ligand and the complex. The electronic spectra were recorded in chloroform and acetonitril (Table 3). The most significant difference in the electronic spectra of the ligand and its complex was the shift of ligand based absorptions to lower frequencies (longer wavelengths) and the appearing newer bands in the complex in longer wavelength region. In complex the longest wave length absorptions have small extinction coefficients and are assigned to metal-ligand charge transfer (MLCT) bands,[15-]

[17] higher energy absorptions immediately adjacent have higher extinction coefficients and can be regarded as intra ligand (IL) transition bands.

A major criterion of potential NLO materials is the existence of solvatochromicity,[18] i.e., the solvent dependent shift of the absorption bands in the UV/vis spectra. The ligand displays strong negative solvatochromicity (-400 cm^{-1}), Table 3. Negative solvatochromicity can be attributed to the stabilization of polar ground states in polar solvents. The data in Table 3 show that the Schiff base and its complex with Cu(II) are good candidates for NLO chromophores due to their strong solvatochromicity.

Table 3. Electronic Spectra of the Ligand and its Complex

Compound	ν_1 (cm^{-1}) x 100		$\Delta\nu_1$ (cm^{-1})	ν_2 (cm^{-1}) x 1000		$\Delta\nu_2$(cm^{-1})
	$CHCl_3$	CH_3CN		$CHCl_3$	CH_3CN	
H_2L	277	281	400	-	-	-
$Cu(HL)_2$	271	265	600	259	250	9000

Conclusions

In this paper we represented the preparation of a Schiff base *p-tert*-buthylcalix[4]arene derivative that could perform complex with Cu^{2+} in which two calix[4]arene moieties are united in one molecule. Therefore because of the presence of two calix[4]arene units in one molecule it will be reliable that we expect the complex has improved inclusion ability and other calix[4]arene related capabilities. Furthermore, the Schiff base ligand and its copper complex, both have solvent dependent UV/vis spectra (solvatochromicity) and then can be suitable NLO materials.

Experimental

Melting points are taken on a Büchi SMP-20 apparatus and are uncorrected. ^{1}HNMR spectra were recorded on a Bruker AM-400MHz in $CDCl_3$ with Me_4Si as an internal standard. Elemental analysis was recorded on Carlo-Erba-Analysor Model 1104. IR spectra were recorded on Bruker IFS 25. UV/vis spectra were recorded on UV/vis. spectrometer 265 FW Shimadzu. *p-tert*-Butylcalix[4]tripropoxyarene, **1**, was prepared according to literature procedure.[19]

Preparation of the Ligand (4). According to the Scheme 1 the mononitro compound[12] was reduced into corresponding monoamine by hydrogenation on palladium-charcoal catalyst and then used for the preparation of the ligand. The ligand H_2L was prepared by treating **3** with salicylaldehyde as described below.

To a solution of 1g (1.36 mmol) of **3** in ethanol (30 mL) was added salicylaldehyde (170 mg, 1.36mmol) and the mixture was refluxed for 24h. After cooling of the reaction mixture, the yellow colored ligand was precipitated by adding of some drops of water. The H_2L was recrystallized in ethanol, yield 1.00 g (86%). ^{1}HNMR ($CDCl_3$) δ 13.85 (1H, s, H-O, sal.), 8.65 (1H, s, H-C=N), 7.44 (2H, d of d Ar-H) 7.35 (4H, m, Ar-H, sal), 7.13 (2H, d of d, Ar-H), 6.55 (4H, d of d Ar-H), 5.95 (1H, s, O-H), 4.38 and 3.25 (4H, d of d, Ar-CH_2-Ar, *J*= 12.9 Hz), 3.85 (2H, t, OCH_2), 3.75 (4H, t, OCH_2), 4.33 and 3.19 (4H, d of d, Ar-CH_2-Ar, *J* = 13.8 Hz), 2.3 (2H, m, CH_2), 1.95 (4H, m, CH_2), 1.35 (9H, s, $C(CH_3)_3$), 1.1 (6H, t, $2CH_3$), 0.95 (3H, t, CH_3), 0.85 (18H, s, $C(CH_3)_3$).

Preparation of the Copper Complex (5). To a solution of **4** (260 mg, 0.3 mmol) in ethanol (20 mL) was added anhydrated $CuSO_4$ (24.7 mg, 0.15 mmol). The mixture was refluxed for 4h and subsequently was allowed to stirring at room temperature for 30 min. The crude product as brown precipitate was filtered and washed with ethanol and dried, yield 215 mg (80%).

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Povzetek

Opisujemo sintezo in karakterizacijo Schiffove baze *p*-*terc*-butilkaliks[4]arena (H_2L) in njegovega kompleksa z bakrom(II). H_2L smo pripravili s kondenzacijo salicilaldehida z aminsko skupino na gornjem robu monoamina-*p*-*terc*-butilkaliks[4]arena v etanolu. Uspelo nam je pripraviti kompleks z bakrom(II), z ostalimi prehodnimi kovinskimi ioni pa ne. Ligand in kompleks smo karakterizirali z elementno analizo in spektroskopskimi podatki. Pri obeh smo opazili solvatokromizem, ki napravi pripravljene spojine za dobre kandidate za uporabo v nelinearni optiki. Pripravljeni kompleks vsebuje dve kaliksarenski skupini, zato predvidevamo, da se bo povečalo molekularno prepoznavanje v host-guest interakcijah.