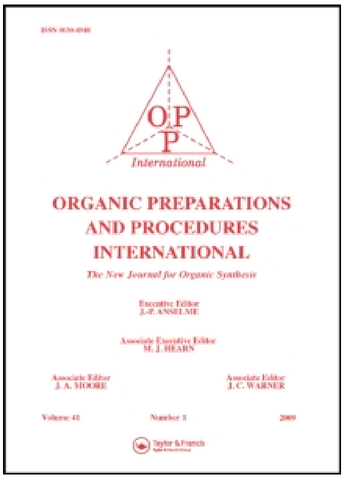

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SYNTHESIS OF NEW *vic*-DIOXIME DERIVATIVES OF *p*-(*tert*-BUTYL) CALIXARENE AND SOME METAL COMPLEXES

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SYNTHESIS OF NEW *vic*-DIOXIME DERIVATIVES OF *p*-(*tert*-BUTYL)CALIXARENE AND SOME METAL COMPLEXES

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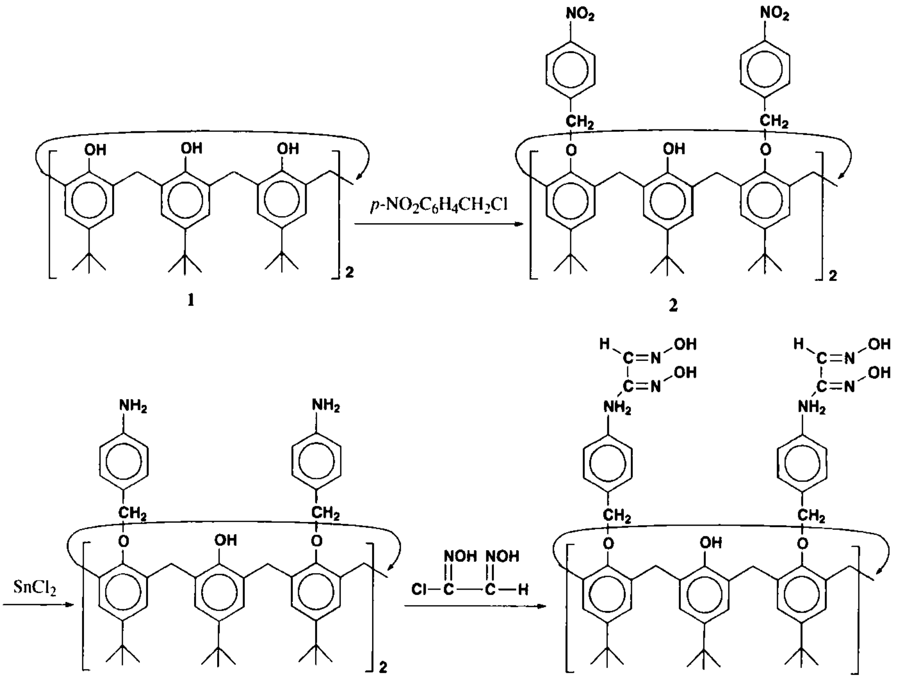
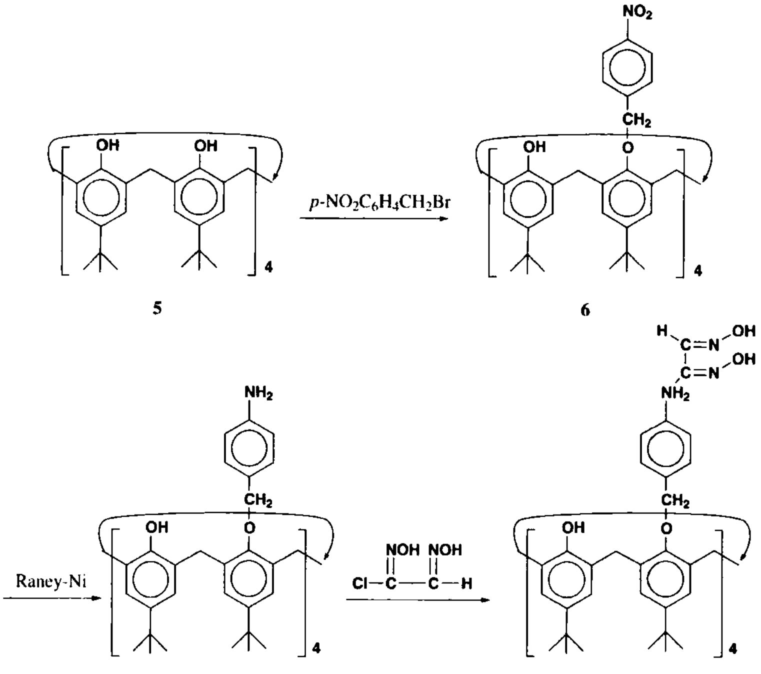
Calixarenes have received increased attention in supramolecular chemistry in the past two decades.[1-3] Various methods for functionalization of calixarenes have been developed.[4] Over the past ten years, much effort has been expended in adorning the calixarene framework[5-7] with various functional groups. Attention has been focused primarily on attachments to the *p*-carbons of aryl groups at the upper rim and the oxygen at the lower rim; only a few attempts have been reported concerning the replacement of the hydroxy groups with other groups. Most of these have dealt with replacement of one to four of the hydroxy groups with hydrogen in the calix[4]arene system. Replacement of one to two of the hydroxy groups with amino and mercapto groups was accomplished recently.[8-13] *vic*-Dioxime derivatives of calixarenes have been of recent interest for organic synthesis and the preparation of calix[6]arenes containing six *vic*-dioxime groups was described recently and the preparation of their complexes with Ni^{2+}, Cu^{2+} and Co^{2+} cations was discussed in detail.[14-24] The present paper describes the synthesis of two new *vic*-dioxime derivatives of *p*-(*tert*-butyl)calix[n]arene (***4*** and ***8***) and their complexes with Ni(II), Cu(II) and Co(II) ions. The structure of these new compounds was elucidated by ^{1}H NMR, IR and elemental analyses.

Four of the six hydroxy groups of ***1*** were benzylated with p-nitrobenzyl chloride according to a literature procedure.[27] Reduction of ***2*** with $SnCl_2.2H_2O$ to give ***3*** (*Scheme 1*) which upon treatment with monochloroglyoxime [25,26] afforded the corresponding *vic*-dioxime derivative ***4***. Similarly, four of the eight hydroxy groups of *p*-(*tert*-butyl)calix[8]arene ***5*** were benzylated with *p*-nitrobenzyl bromide in the presence of K_2CO_3.[28] The nitro groups of compound ***6*** were reduced with Raney-Ni to give ***7*** which was than reacted with monochloroglyoxime [25,26] to yield the corresponding *vic*-dioxime derivative ***8*** (*Scheme 2*).

The ^{1}H NMR spectra of ***4*** and ***8*** showed two peaks (δ 12.50-11.42) arising from the OH protons of the oxime groups (deuterium exchangeable), since the protons of the oxime groups are not equivalent. Consequently, the first peak (δ 11.42) is assigned to be hydroxy proton of the amidoxime and the latter (δ 12.50) to the hydroxy proton of aldoxime since the effect of various substituents is expected to be different. N-H Protons adjacent to neighboring to oxime groups and the O-H protons are observed at δ 7.98-7.82 and δ 7.70-6.78, respectively. Additional evidence for both O-H and N-H protons is also provided by the disappearance of these resonances upon deuterium exchange. Since the solubility of the complexes in organic solvents is very low, ^{1}H NMR spectra could not be obtained.



Scheme 1



Scheme 2

Table 1. Colors, Yields, mp. and Elemental Analyses of Ligands and Complexes

Cmpd	Formulas	mp. (°C) (dec.)	Yield (%)	Calcd (Found) C	H	N	M
$3.H_2O^a$	$C_{94}H_{114}N_4O_7$	293	75	79.95 (79.87)	8.14 (8.19)	3.97 (3.90)	-
$4.3H_2O^b$	$C_{102}H_{126}N_{12}O_{17}$	137	96	68.34 (68.29)	7.09 (7.16)	9.38 (9.29)	-
$4\text{-}Ni.2H_2O^c$	$[C_{102}H_{116}N_{12}O_{14}]Ni_2{\bullet}2H_2O$	>360	93	64.56 (64.51)	6.96 (7.05)	8.86 (8.78)	6.11 (6.07)
$4\text{-}Cu.H_2O^d$	$[C_{102}H_{116}N_{12}O_{14}]Cu_2{\bullet}H_2O$	>360	89	64.87 (64.80)	6.84 (6.92)	8.91 (8.86)	6.67 (6.71)
$4\text{-}Co.5H_2O^d$	$[C_{102}H_{116}N_{12}O_{14}]Co_2{\bullet}5H_2O$	>360	94	62.29 (62.21)	6.98 (7.03)	9.26 (9.21)	6.00 (5.93)
$7.H_2O^a$	$C_{116}H_{142}N_4O_9$	318	96	80.23 (80.14)	8.25 (8.32)	3.23 (3.18)	-
$8.4H_2O^b$	$C_{124}H_{156}N_{12}O_{20}$	144	92	69.76 (69.70)	7.37 (7.44)	7.88 (7.80)	-
$8\text{-}Ni.H_2O^c$	$[C_{124}H_{148}N_{12}O_{16}]Ni_2{\bullet}H_2O$	>360	85	65.64 (65.61)	7.02 (7.11)	7.41 (7.36)	5.11 (5.04)
$8\text{-}Cu.3H_2O^d$	$[C_{124}H_{148}N_{12}O_{16}]Cu_2{\bullet}3H_2O$	>360	82	64.33 (64.28)	7.06 (7.13)	7.26 (7.21)	5.44 (5.63)
$8\text{-}Co.7H_2O^d$	$[C_{124}H_{148}N_{12}O_{16}]Co_2{\bullet}7H_2O$	>360	87	62.60 (62.56)	7.21 (7.23)	7.07 (7.01)	4.96 (5.07)

a) Brownish b) White c) Dark red d) Brown

The Ni(II), Cu(II) and Co(II) complexes of two new ligands were prepared in THF-ethanol (4:1) mixture by the addition (at room temperature) of 1% NaOH solution to raise the pH 4.5-5.0. The characteristic IR bands of the ligands and their complexes are summarized in Table 2. Bands at 3440-

Table 2. Characteristic IR Bands of Ligands and Complexes as KBr Pellets (cm^{-1})

Compounds	$\nu_{(N\text{-}H)}$	$\nu_{(O\text{-}H)}$	$\nu_{(C\text{-}H)(alph)}$	$\nu_{(H2O)}$	$\nu_{(N\text{-}O)}$	$\nu_{(N\text{-}O)}$
$3{\bullet}H_2O$	3420	3300-3200	2910	-	1600	-
$4{\bullet}3H_2O$	3380	3250	2935	-	1640	960
$4\text{-}Ni{\bullet}2H_2O$	3370	-	2940	1710	1610	980
$4\text{-}Cu{\bullet}H_2O$	3390	-	2930	1715	1600	995
$4\text{-}Co{\bullet}5H_2O$	-	3390-3450	-	1730	1620	990
$7{\bullet}H_2O$	3430	3300-3200	2915	-	1610	-
$8{\bullet}4H_2O$	3380	3230	2900	-	1650	970
$8\text{-}Ni{\bullet}H_2O$	3400	-	2885	1715	1620	985
$8\text{-}Cu{\bullet}3H_2O$	3390	-	2900	1710	1615	990
$8\text{-}Co{\bullet}7H_2O$	-	3380	-	1720	1600	995

3380 cm^{-1}, 3280-3180 cm^{-1}, 1680-1610 cm^{-1} and 990-940 cm^{-1} are assigned to N-H, O-H, C=N and N-O stretching bands, respectively, in the IR spectra of the ligands and these values are in accordance with those of the previously reported oximated calixarenes.[14,15]

In order to explain the structure of the complexes, elemental analyses and IR data were used; the absence of the band (O-H···O) in the IR spectra of the ligands with Ni(II), Cu(II) and Co(II) suggested that the complexes obtained have octahedral and square-planar structures as depicted in Fig. 1.

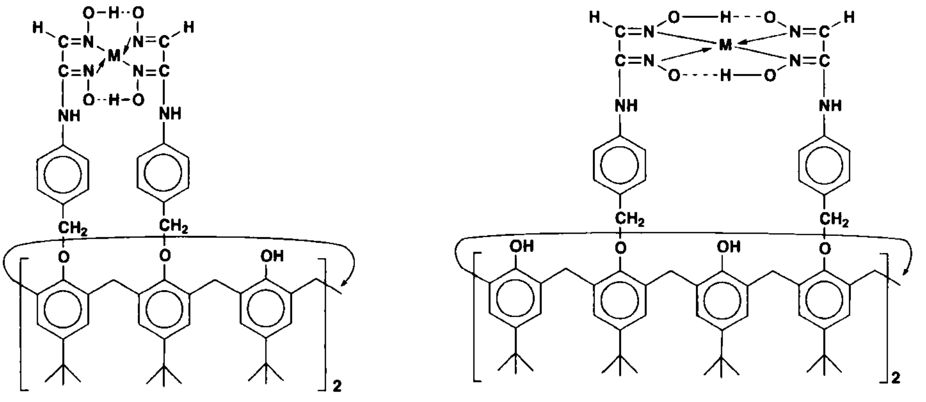


Fig. 1. Octahedral and square-planar Metal Complexes of *4* and *8*.

In the IR spectra of the complexes, the shift of C=N stretching frequency leads to lower frequency and vibration band between metal and the nitrogen atom of the ligands. The metal-ligand ratios in all complexes are 2:1. Consequently, an octahedral structure for Co(II), square-planar coordination for Ni(II) and Cu(II) compounds are proposed.[29]

EXPERIMENTAL SECTION

Melting points were determined on a Electrothermal IA 9100 digital melting point apparatus and are uncorrected. IR spectra were recorded on a Mattson 1000 FTIR spectrometer as KBr pellets, ^{1}H-NMR spectra were recorded on a Bruker 200 MHz spectrometer with deuterium dimethyl sulfoxide as solvent and TMS as internal standard. The elemental analyses were performed in the TUBITAK laboratory. (Center of Science and Technology Research of Turkey).

The preparation of *amphi*-chloroglyoxime [25,26] has been described previously. 5,11,17,23,29,35-Hexa-(*tert*-butyl)-39,42-dihydroxy-37,38,40,41-tetrakis[(4-nitrobenzyl)oxy]calix[6]arene was synthesized according to the method described by Gutsche.[28] 5,11,17,23,29,35,41,47-Octa-(*tert*-butyl)-49,51,53,55-tetrahydroxy-50,52,54,56-tetrakis[(4-nitrobenzyl)oxy]calix[8]arene was synthesized according to the reported procedures.[29] The solvents and reagents were purified by drying over suitable dehydrating agents followed by distillation.

5,11,17,23,29,35-Hexa-(*tert*-butyl)-39,42-dihydroxy-37,38,40,41-tetrakis[(4-aminobenzyl)oxy]-calix[6]arene (3).- A solution of 5.72 g (3.78 mmol) of 5,11,17,23,29,35-hexa-(*tert*-butyl)-39,42-tetrahydroxy-37,38,40,41-tetrakis[(4-nitrobenzyl)-oxy]calix[6]arene (**2**) and 15.00 g (66.37) mmol) of

$SnCl_2$. $2H_2O$ in 100 mL MeOH was refluxed 4 h. The solution was cooled, poured onto ice, neutralized (pH 7-8) by the addition of 1% NaOH solution and extracted twice with CH_2Cl_2. The organic phase was separated, washed with brine and dried (NaS_2O_4) and evaporated to leave a brownish solid. Trituration with 75 mL of CH_3OH followed by crystallization of the insoluble material from *i*-PrOH gave 1.77 g (75%) of **3**, mp. 293°, ^1H NMR ($CDCl_3$): δ 8.12 (8H, s, $-NH_2$), 7.38 (2H, s, -OH), 6.90 (28H, d, ArH), 4.71 (8H, s, $ArCH_2O$), 4.60-4.10 (12H, broad, $ArCH_2Ar$), 1.44 (18H, s, CMe_3, 0.70 (36H, s, CMe_3).

5,11,17,23,29,35-Hexa-(*tert*-butyl)-39,42-dihydroxy-37,38,40,41-tetrakis[(4-oximinobenzyl)oxy]-calix[6]arene (4).- To a solution of 1.04 g (0.76 mmol) 5,11,17,23,29,35-hexa-(*tert*-butyl)-39,42-dihydroxy-37,38,40,41-tetrakis[(4-aminobenzyl)oxy]calix[6]arene **(3)** in 50 mL of methanol-THF (1:4) was added 1.20 g (9.80 mmol) *amphi*-chloroglyoxime in 10 mL of methanol with stirring. KOH (1% in methanol) was added to raise the pH to 5. The mixture was stirred for 12 h at room temperature under a nitrogen stream. The solvent was then removed under vacuum and the residue was washed with diethyl ether and then distilled water and then recrystallized from methanol-chloroform gave 1.16 g (96%) of **4**, mp. 137° (dec.), ^1H NMR ($CDCl_3$): δ 12.50 (4H, s, OH), 11.70 (4H, s, OH), 7.98 (4H, s, -NH), 7.40 (2H, s, -OH), 7.25-6.80 (28H, d, ArH), 6.70 (4H, s, =C-H), 4.75 (8H, s, $ArCH_2O$), 4.50-3.90 (12H, broad, $ArCH_2Ar$), 1.50-0.82 (54H, s, CMe_3).

5,11,17,23,29,35,41,47-Octa-(*tert*-butyl)-49,51,53,55-tetrahydroxy-50,52,54,56-tetrakis[(4-aminobenzyl)oxy]calix[8]arene (7).- A solution of 1.10 g (0.30 mmol) of 5,11,17,23, 29,35,41,47-octa-(*tert*-butyl)-49,51,53,55-tetrahydroxy-50,52,54,56-tetrakis[(4-nitrobenzyl)-oxy]calix[8]arene **(6)** was dissolved with 5 mL (82 mmol) of hydrazine hydrate (80%) in 20 mL THF. Then 2 g (34 mmol) of dried Raney-Ni was added. This reaction mixture was stirred until the gases depart from the solution. The mixture was allowed to warm to room temperature and stirred for additional two hours and set aside until the following day. The mixture was filtered. The solution was concentrated under vacuum to a volume of 5-10 mL and treated with petroleum ether and resulting pale brownish powder was filtered, washed with petroleum ether gave 0.29 g (96%) of **7**, mp. 318° (dec.), ^1H NMR ($CDCl_3$): δ 8.11 (8H, s, $-NH_2$), 7.55 (4H, s, -OH), 7.90-6.96 (32H, d, ArH), 4.92 (8H, s, $ArCH_2O$), 4.15-3.88 (16H, broad, $ArCH_2Ar$), 1.22-1.08 (72H, s, CMe_3).

5,11,17,23,29,35,41,47-Octa-(*tert*-butyl)-49,51,53,55-tetrahydroxy-50,52,54,56-tetrakis [(4-oximinobenzyl)oxy]calix[8]arene (8).- Compound **8** was synthesized from **7** and *amphi*-monochloroglyoxime in a manner similar to that described for **4** using 0.40 g (0.23 mmol) of **7** and 0.12 g (0.98 mmol) of *amphi*-monochloroglyoxime gave 0.29 g (92%) of **8**, mp. 144° (dec.), ^1H NMR ($CDCl_3$): δ 12.34 (4H, s, OH), 11.42 (4H, s, OH), 7.82 (4H, s, -NH), 7.39 (4H, s, -OH), 7.30-6.75 (32H, d, ArH), 6.78 (4H, s, =C-H), 4.84 (8H, s, $ArCH_2O$), 4.20-3.60 (16H, s, $ArCH_2Ar$), 1.30-0.85 (72H, s, CMe_3).

Synthesis of The Ni(II), Cu(II) and Co(II) Complexes.- A solution of 0.40 mmol of metal salt [$NiCl_2.6H_2O$ (95.2 mg), $CuCl_2.2H_2O$ (68.8 mg), or $CoCl_2.6H_2O$ (95.2 mg)] in 20 mL ethanol was added to a solution of 0.20 mmol of the ligand [0.185 g of **4** or 0.353 g of *(8)*] in 10 mL THF-ethanol

(4:1). After addition of 1% NaOH solution in ethanol to adjust the pH at 4.5-5.0, the mixture was stirred on a water bath at 35-45° for 10 min. The precipitated complex was collected, washed with water, ethanol and dried in vacuum. Yields, melting points, colors, elemental analytical results and spectral data of the complexes are given in Tables 1 and 2.

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