Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

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To cite this article: Hasalettin Deligöz & Mustafa Yilmaz (1997) Synthesis and Metal Complexation of Two vic-Dioxime Derivatives of Calix[4]Arenes, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 27:3, 391-400, DOI: 10.1080/00945719708000196

To link to this article: http://dx.doi.org/10.1080/00945719708000196

SYNTH. REACT. INORG. MET.-ORG. CHEM., 27(3), 391-400 (1997)

SYNTHESIS AND METAL COMPLEXATION OF TWO vic-DIOXIME DERIVATIVES OF CALIX[4]ARENES

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ABSTRACT

Two new vic-dioxime compounds of calix[4]arene and their transition metal complexes were synthesized from 28-[(4-aminobenzyl)oxy]-25,26,27-tribenzoyloxycalix[4]arene and amphi-chloroglyoxime or amphi-dichloroglyoxime. The complexes of these compounds with Ni(II), Cu(II) and Co(II) ions were investigated. All of the complexes of these ligands are tetrahedral with a metal-ligand ratio of 1:2. The prepared compounds were characterised based on ^{1}H NMR and IR spectra as well as elemental analyses.

INTRODUCTION

Calixarenes, which are accessible from the base-catalysed condensation of para-substituted phenols with formaldehyde, are a new class of host molecules[1-3]. These compounds serve as host in inclusion compounds[1], selective complexing agents for metal ions[4-11], and catalysts for chemical reactions[12].

Contrary to a number of reports on the binding of alkali metal ions[13], and lanthanide ions[14], reports on the binding of transition metal ions[15] are still limited.

In the present work, we report the synthesis of two novel calix[4]arenes substituted with vic-dioximes (Fig. 1) and their complexes with Ni(II), Cu(II), and Co(II) ions.

RESULTS AND DISCUSSION

Synthesis of Ligands and Complexes

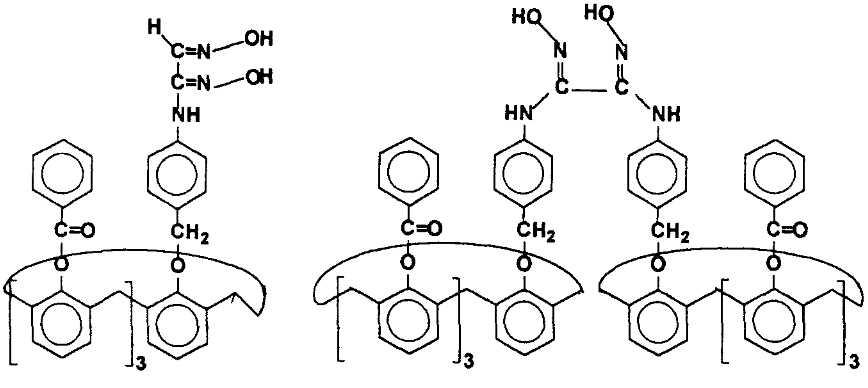
vic-Dioxime derivatives of calixarenes have been the subject of recent interest. In one of our previous articles[16,17], the synthesis of calix[6]arenes containing six vic-dioxime groups was described, and the preparation of their complexes with Ni^{2+}, Cu^{2+}, and Co^{2+} cations was discussed.

In this paper, the preparation of compounds *(1)* and *(2)* is described. Three phenolic groups of calix[4]arene were first benzoyllated by a procedure described in the literature[18]. This compound was than reacted with p-nitrobenzylbromide in the presence of K_2CO_3 to yield compound *(3)*. The nitro group of compound *(3)* was reduced to the amino group with $SnCl_2.2H_2O$ to give *(4)* (Scheme 1). Compound *(4)* was then reacted with either monochloroglyoxime or dichloroglyoxime to yield the corresponding vic-dioxime derivatives *(1)* and *(2)*.

While compound *(1)* was unsymmetrical, compound *(2)* was a symmetrical dioxime. This was detected based on the NMR signals of the OH protons of the oxime groups. Since the protons of the oxime groups of compound *(2)* are identical, a single signal appeared at $\delta = 11.5$ ppm, while two signals were observed for the OH groups of compound *(1)*, at 11.6 ppm and 12.4 ppm, respectively. The first signal belongs to the amidoxime proton, while the second to the aldoxime proton.

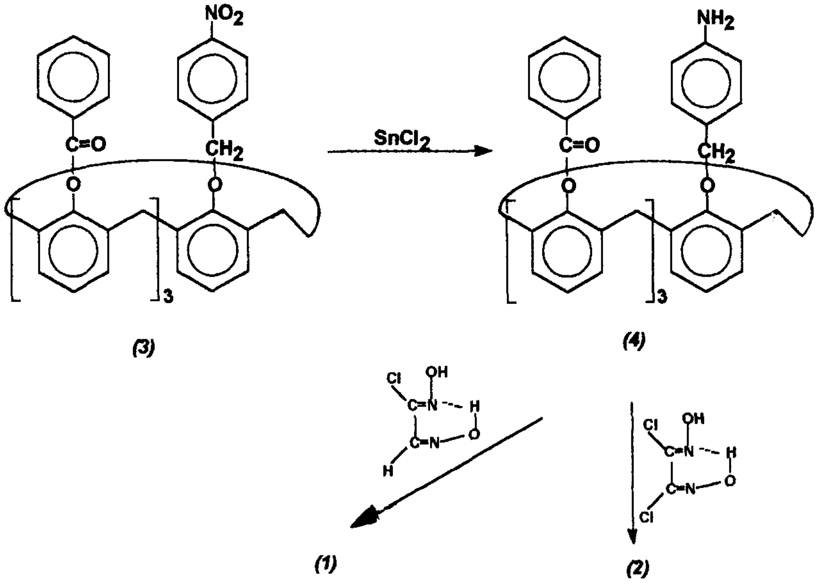
IR Spectra of Ligands and Complexes

The Ni(II), Cu(II), and Co(II) complexes of the ligand were prepared in THF-ethanol (1:4) by the addition of base (NaOH). The elemental analytical results



(1) (2)

Fig. 1. Structures of the two vic-Dioxime Derivative of Calix[4]arenes Studied, *(1)* contains 2 H_2O molecules and *(2)* contains 3 H_2O molecules.



Scheme 1

and characteristic IR absorptions are given in Tables I and II. The observed micro analytical data for C, H, and N atoms of the complexes show that all the complexes are hyrates. The water molecules are identified by broad O-H absorptions around 3400-3550 cm^{-1} in the IR spectra of the complexes, and this band disappeared after heating at 110 °C for 6 h. Thus, the water molecules are not directly coordinated to the central metal atom but held in the crystal lattice of the complexes.

In the IR spectra of the ligands, the broad band near 3550-3400 cm^{-1} has been assigned to O-H of the lattice water molecules which probably are held in the crystal lattice of the ligands. The bands at 3250-3270 cm^{-1} and 1650-1670 cm^{-1}, in the ligands, are assigned to O-H and C=N stretches appear at frequencies expected for substituted aminoglyoximes[19].

The most significant differences in the IR spectra of the ligands and their complexes was the shift of the C=N stretches which have shifted to lower frequency by about 30-50 cm^{-1} due to metal-ligand coordination. The appearance of the OH stretching band around 3270-3220 cm^{-1} indicates the presence of free OH groups in the ligand and complexes. The weak stretching band at around 2360-2200 cm^{-1} in both ligands is assigned to the OH···O frequency of the enol, both of these bands are absent in the spectra of the complexes[20,21]. Consequently, amphi-complexes were obtained and a N,O-chelated tetrahedral structure is proposed for these complexes (Fig. 2a and 2b). The reaction of ***1*** and ***2*** with Ni(II), Cu(II), and Co(II) salts gave the products with a metal/ligand ratio of 1:2. The structures of these complexes are non-planar. It is known from the literature[22], that vic-dioximes form two different complexes, which are in the anti- and amphi-forms.

The distinct colors of the anti- and amphi-complexes with Ni(II) (brick-red or yellow-green, respectively) make the identification of these complexes straightforward[22]. The color of the Ni(II) complexes of ***(1)*** or ***(2)*** is yellow-green, thus amphi-complexes are formed.

Table I. The Color, Yields, Melting Points and Elemental Analytical Results of the Ligands and the Complexes

Compounds [Formulas]	MW (Calc.)	Color	M.p.(dec.) (°C)	Yield %	Calcd. (Found) % C	H	N	M
(1) $\cdot 2H_2O$		White	115	49	72.26	5.12	4.36	-
$C_{58}H_{49}N_3O_{10}$	(948.04)				(72.35)	(5.32)	(4.02)	
(1)-Ni$\cdot H_2O$		Yellow-	(240)	63	72.77	4.74	4.39	3.07
$NiC_{116}H_{90}N_3O_{19}$	(1888.69)	green			(73.05)	(5.02)	(4.69)	(3.01)
(1)-Cu$\cdot 4H_2O$		Green	(230)	74	70.03	4.86	4.22	3.19
$CuC_{116}H_{96}N_3O_{22}$	(1947.59)				(69.85)	(5.05)	(4.38)	(3.22)
(1)-Co$\cdot 5H_2O$		Pale-	(245)	82	69.56	4.93	4.20	2.94
$CoC_{116}H_{98}N_3O_{23}$	(1960.99)	brown			(70.01)	(5.10)	(4.35)	(3.01)
(2)$\cdot 3H_2O$		White	120	33	75.15	5.07	3.08	-
$C_{114}H_{92}N_4O_{19}$	(1822.00)				(75.72)	(5.28)	(3.25)	
(2)-Ni$\cdot 2H_2O$		Yellow-	(250)	55	75.47	4.83	3.09	1.62
$NiC_{228}H_{174}N_4O_{34}$	(3572.59)	green			(75.85)	(5.00)	(3.15)	(1.59)
(2)-Cu$\cdot 3H_2O$		Green	(265)	67	75.00	4.86	3.07	1.74
$CuC_{228}H_{176}N_4O_{35}$	(3595.46)				(75.35)	(5.02)	(3.11)	(1.65)
(2)-Co$\cdot 5H_2O$		Pale-	(270)	72	74.36	4.93	3.04	1.60
$CoC_{228}H_{180}N_4O_{37}$	(3626.88)	brown			(74.01)	(5.22)	(3.25)	(1.69)

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

Compound	$\nu_{(H2O)}$	$\nu_{(O\text{-}H)}$	$\nu_{(C=O)}$	$\nu_{(C=N)}$
(1) $\cdot 2H_2O$	3430	3250	1755	1670
(1)-Co $\cdot 5H_2O$	3420	3220	1750	1640
(1)-Ni $\cdot H_2O$	3430	3230	1755	1620
(1)-Cu $\cdot 4H_2O$	3420	3230	1755	1640
(2) $\cdot 3H_2O$	3400	3270	1740	1650
(2)-Co $\cdot 5H_2O$	3400	3230	1710	1620
(2)-Ni $\cdot 2H_2O$	3450-3400	3230	1740	1620
(2)-Cu $\cdot 3H_2O$	3550	3240	1750	1610

EXPERIMENTAL

The preparation of amphi-chloroglyoxime[23,24] and amphi-dichloroglyoxime[25] was described previously. 25,26,27-Tribenzoyloxy-28-hydroxycalix[4]-arene was synthesized according to a reported procedure[18]. ^1H NMR spectra were recorded on a Bruker 200 MHz spectrometer, IR spectra were recorded on a Pye Unicam SP 1025 spectrophotometer as KBr pellets. The elemental analyses were performed in the TUBITAK Laboratory. (Center of Science and Technology Research of Turkey).

Synthesis of 28-[(4-Nitrobenzyl)oxy]-25,26,27-tribenzoyloxycalix[4]arene (3)

A 2.00 g (2.72 mmol) sample of 25,26,27-tribenzoyloxy-28-hydroxycalix[4]arene in 50 mL THF was stirred at 40 °C until a clear solution was obtained, then 4.00 g of anhydrous K_2CO_3 were added and stirring was continued under nitrogen. A solution of p-nitrobenzylbromide (1.20 g, 5.56 mmol) in 10 mL THF was added. The mixture was stirred at 60 °C for 20 h. At the end of the period the mixture was filtered and washed with THF. The solvent (THF) was evaporated

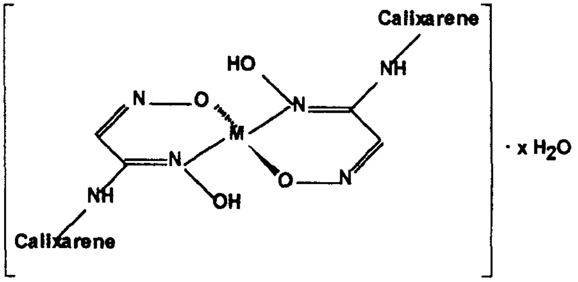


Fig. 2a. Metal Complexes of *(1)*; HL = *(1)*; $[L_2M](H_2O) = [L_2Ni(II)]\cdot(H_2O)$, $[L_2Cu(II)]\cdot(4H_2O)$ and $[L_2Co(II)]\cdot(5H_2O)$.

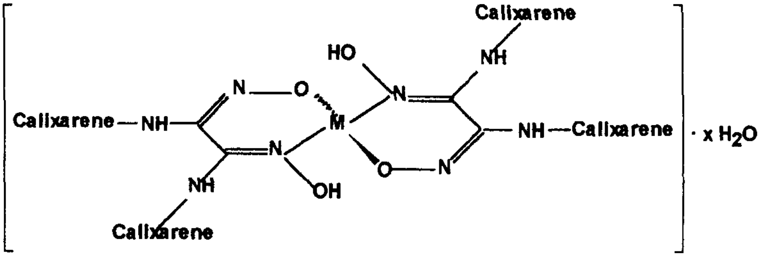


Fig. 2b. Metal Complexes of *(2)*; HL'= *(2)*; $[L_2M](H_2O) = [L'_2Ni(II)]\cdot(2H_2O)$, $[L'_2Cu(II)]\cdot(3H_2O)$ and $[L'_2Co(II)]\cdot(5H_2O)$.

under reduced pressure and 0.1 N HCl acid was added. The resulting yellow precipitate was collected by filtration, washed with methanol and dried. After crystallisation from CH_2Cl_2/hexane (10:3), 1.73 g (73%) of *(3)* was obtained as a yellow powder. M.p.118 °C. ^1H NMR ($CDCl_3$): δ = 8.3-7.9 (9H, s, ArH of nitrobenzyl and benzoyl groups), 7.5-6.6 (22H, m, ArH of calix[4]arene), 3.4-4.1 (10H, broad, $-CH_2-$). Anal. Calcd. for $C_{56}H_{41}NO_9\cdot5H_2O$ (MW:962.02); C, 69.92; H, 5.34; N, 1.46. Found: C, 69.75; H, 5.48; N, 1.42.

Synthesis of 28-[(4-Aminobenzyl)oxy]-25,26,27-tribenzoyloxycalix[4]arene (4)

A solution of 3.50 g (4.00 mmol) of *(3)* and 16 g (7.71 mmol) of $SnCl_2.2H_2O$ in 150 mL of EtOH was refluxed for 24 h. The solution was cooled, poured on ice, neutralised by addition of NaOH, and extracted two times with CH_2Cl_2. The organic phase was separated, washed with brine, dried with Na_2SO_4 and evaporated to a brownish solid. This was treated with 75 mL of MeOH, and the insoluble material was crystallised from i-PrOH. Yield: 2.77 g (82%), light brown solid, m.p. 135 °C. ^1H NMR ($CDCl_3$): δ = 7.3-6.7 (27H, m, ArH of calix[4]arene and benzoyl groups), 6.3 (4H, s, ArH of aminobenzyl group), 3.3-4.2 (10H, broad, $-CH_2-$), 3.0-2.3 (2H, broad, NH_2). Anal. Calcd. for $C_{56}H_{43}NO_7 3H_2O$ (MW:896.01); C, 75.07; H, 5.51; N, 1.56. Found: C, 75.31; H, 5.68; N, 1.59.

Preparation of The Ligands (1) and (2)

To a solution of 4.20 g (5.00 mmol) 28-[(4-aminobenzyl)oxy]-25,26,27-tribenzoyloxycalix[4]arene *(4)* in 50 mL of methanol-THF (1:4) was added 0.62 g (5.00 mmol) amphi-chloroglyoxime in 10 mL methanol with stirring. KOH solution (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 than removed under vacuum, and the residue was washed first with diethyl ether and then with distilled water and then crystallised from methanol. Finally, product *(1)* was recrystallized from methanol/chloroform (3:1). Yield: 2.26 g (49%), m.p. 115 °C (dec.). ^1H NMR ($CDCl_3$): δ= 12.4 (1H, s, OH), 11.6 (1H, s, OH), 7.8-6.6 (33H, m, ArH of calix[4]arene, benzoyl and iminobenzyl groups, C-NH, and =CH), 3.5-4.1 (10H, broad, CH_2). The IR and elemental analyses of *(1)* are given in Tables I and II.

(2) was synthesized from *(4)* and amphi-dichloroglyoxime in a manner similar to that described for *(1)* using 4.2 g (5.00 mmol) of *(4)* and 0.32 g (2.00 mmol) of amphi-dichloroglyoxime. Yield: 0.35 g (33%), m.p. 110 °C(dec.). ^1H

NMR ($CDCl_3$): δ = 11.5 (2H, s, OH), 6.6-7.8 (64H, m, ArH of calix[4]arene, benzoyl and iminobenzyl groups, C-NH), 3.5-4.1(20H, broad, $-CH_2$). The IR and elemental analyses of ***(2)*** are given in Tables I and II.

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 ***(1)*** or 0.353 g of ***(2)***)] in 10 mL of THF-ethanol (4:1). After adding 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 °C for 10 min. The precipitated complex was filtered off, washed with water, ethanol and dried in vacuo. Yields, melting points, elemental analytical results, and spectral data of the complexes are given in Tables I and II.

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