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A Novel Crown Ether. $2C_{60}$ Complex

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The synthesis and characterisation of a novel complex formed by crown ether 2 and 2 molecules of fullerene C_{60} is reported.

INTRODUCTION

In the last few years, fullerene complexes have been one of the most challenging synthetic targets for chemists because of their unique structural features as well as their considerable therapeutic potential [1]. For example, the electron deficient nature of the fullerene allows it to form charge transfer complexes with electron donors. For example, it has been reported a complex as a tridimensional network chains of porphyrazine with a fullerene C_{60} with charge-transfer properties [2]. Recently we described the oligomerization of benzylic alcohols using a bentonite clay catalyst to give linear and cyclic oligomers like cyclotriveratrylene [3], which has been used as a guest for fullerenes [4]. There are several reports concerning the interactions between fullerenes and macrocycles like calixarenes [5-13], cyclotriveratrylenes [14], aza crown ethers [15], and other macrocycles [16], however to the best of our knowledge, this is the first example involving a crown ether. In this paper we report the synthesis and characterisation of a new crown ether **2**, and its complexation with two C_{60} molecules.

RESULTS AND DISCUSSION

In a typical experiment cyclohexene oxide **1**, clay [17] and potassium bromide were stirred in benzene at room temperature to give **2**. Structural assignment of **2** was made on spectroscopic grounds and confirmed by X-ray diffraction analysis. The ORTEP and side view representation (Scheme 1) shows that **2** adopts a cupped hand form.

Crown ether **2** and C_{60} (Mer Corp) dissolved in a 1:1 stoichiometry in benzene after 5 hours reflux yield a brown microcrystalline material **3**.

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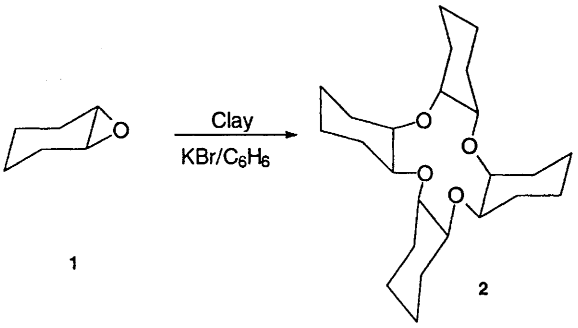
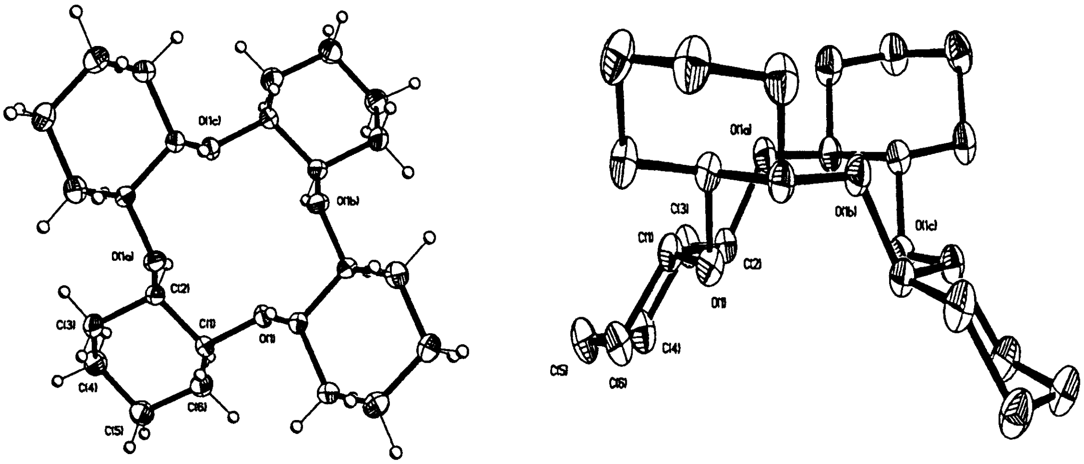




Top view of crown ether

Side view of the crown ether

SCHEME 1

The elemental analysis of **3** is consistent with one molecule of **2** and two molecules of C_{60}, with three molecules of water and three molecules of benzene. The UV-visible spectroscopy of **3** shows an absorption a $\lambda_{max} = 280$, 329 and 405 nm. The appearance of the 280 nm band has been atributed to a charge transfer between the n-orbital on oxygen atom of **2** and π-orbital of C_{60} [2, 5, 13].

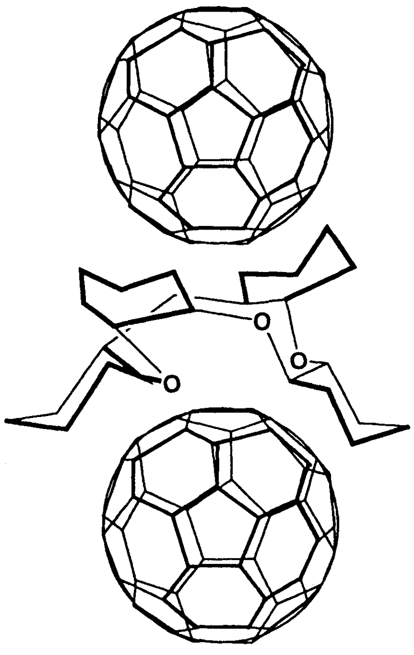
^{13}C CP-MAS NMR spectra of **2** and the complex **3** are shown in Figure 1. The free crown ether **2** shows four signals at δ 23.52, δ 24.50, δ 31.66 and δ 33.59 assigned to $C_{3,4}$ and $C_{2,6}$ methylene carbons, respectively. The signals of methine carbon at positions 1 and 6 are at δ 78.91 and δ 83.50 respectively. The spectra of the free fullerene shows one signal at δ 143.7. On the other hand the spectrum of complex **3**, all the above signals are shifted. Methylene carbons $C_{3,4}$ and $C_{2,6}$ shown only one broad diminished signal at δ 25.13–34.79, and for the methine carbons $C_{1,6}$ a broad signal appared at δ 74.75–85.87. The signal of the fullerene was shifted to δ 143.0. It can also be observed a signal at δ 128.59, assigned to benzene molecules occluded in the crystal structure of **3**. The upfield shift of δ 0.7 of the signal of C_{60} might indicated a complex formation [8] and the significant alteration of chemical shifts of the crown ether carbons suggested a significant conformational change of **1** in the complex **3**.

In summary we describe an attractive route to construct crown ethers such as **2** and the formation of a novel complex with two C_{60} molecules.

EXPERIMENTAL SECTION

General Remarks

Infrared (IR) spectra were recorded on a Nicolet FT-IR Magna 700 Spectrometer. NMR spectra



Complex **3**

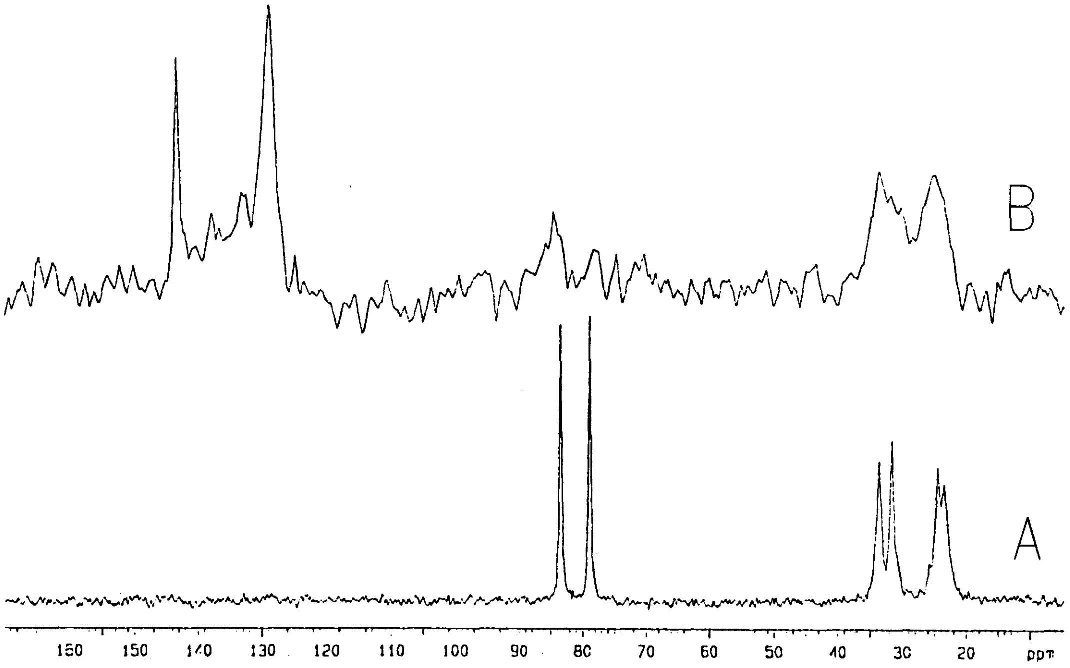


FIGURE 1 ^{13}C CP-MAS NMR spectra of (A) **1** and (B) complex **3**.

were measured on a Varian Unity 500 spectrometer using 500 MHz for protons and 125 MHz for ^{13}C. The chemical shifts are expressed in ppm downfield from tetramethylsilane ($\delta = 0.0$ ppm) as an internal standard. The ^{13}C CP-MAS NMR spectra were measured on a Bruker spectrometer 125 MHz. Elemental analyses were performed at Galbraith Laboratories, INC. Knoxville. FAB$^+$ mass spectra were taken with a JEOL JMS AX505 HA mass spectrometer. X-ray crystalographic data were collected at room temperature on a Siemens P/4 diffractometer.

Tetracyclohexan[b,e,h,k,]-1,4,7,10,-tetraoxacyclododecane 2; To a suspension of clay (0.5 g) and potassium bromide (0.5 g) in dry benzene (25 ml) was added 1.2 g (10 mmoles) of **1** and the mixture was stirred at room temperature for 25 min. After this time the reaction mixture was filtered on celite, washed with benzene, and the filtrated was evaporated to dryness. The residue, an oil was then purified by column chromatography (silica gel, hexane/ethyl acetate, 90/10) to afford **2** (0.6 g 50%). IR (KBr): 2930, 2858, 1727, 1448, 1430, 1367, 1270, 1086, 796, 777, 696, 576, 526, 457 cm^{-1}. UV-Vis 258 nm, ^{1}H NMR (C_6D_6) δ 3.73-3.71 (m, 2H), 1.98-1.95 (m, 2H), 1.49-1.47 (m, 2H), 1.27-1.23 (m, 2H), 1.10-1.03 (m, 2H). ^{13}C NMR (C_6D_6) δ 25.87 ($\underline{C}H_2$), 33.43 ($\underline{C}H_2$), 81.35 ($\underline{C}$H—O). ^{13}C CP-MAS NMR Chemical shifts δ 23.52 ($\underline{C}H_2$), 24.50 ($\underline{C}H_2$), 31.66 ($\underline{C}H_2$), 33.59 ($\underline{C}H_2$), 78.91 ($\underline{C}$H—O), 83.50 ($\underline{C}$H—O). Anal. Calcd for $C_{24}H_{40}O_4$: C, 73.93; H, 10.90. found; C, 73.90; H, 10.92.

TABLE I Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2 × 10^3) for: Tetracyclohexyl-12-crown-4 ether

	x	*y*	*z*	*U(eq)**
O(1)	3492(1)	1669(1)	1402(2)	37(1)
C(1)	2948(1)	816(1)	1441(3)	35(1)
C(2)	1900(1)	1049(1)	1388(2)	34(1)
C(3)	1312(1)	152(1)	1102(3)	46(1)
C(4)	1590(1)	−412(1)	−1108(3)	53(1)
C(5)	2634(1)	−661(1)	−1013(4)	53(1)
C(6)	3228(1)	224(1)	−716(3)	49(1)

*Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE II Bond lengths (Å) for: Tetracyclohexyl-12-crown-4 ether

O(1)—C(1)	1.432 (2)	O(1)—C(2A)	1.432 (2)
C(1)—H(1)	0.962 (20)	C(1)—C(2)	1.519 (2)
C(1)—C(6)	1.519 (2)	C(2)—H(2)	1.009 (17)
C(2)—C(3)	1.524 (2)	C(2)—O(1A)	1.432 (2)
C(3)—H(3A)	0.957 (19)	C(3)—H(3B)	0.998 (19)
C(3)—C(4)	1.521 (2)	C(4)—H(4A)	1.057 (18)
C(4)—H(4B)	0.978 (18)	C(4)—C(5)	1.518 (2)
C(5)—H(5A)	0.958 (19)	C(5)—H(5B)	1.046 (18)
C(5)—C(6)	1.516 (2)	C(6)—H(6A)	0.986 (19)
C(6)—H(6B)	0.993 (18)		

TABLE III Bond angles (°) for: Tetracyclohexyl-12-crown-4 ether

C(1)—O(1)—C(2A)	115.0(1)	O(1)—C(1)—H(1)	109.2(11)
O(1)—C(1)—C(2)	110.0(1)	H(1)—C(1)—C(2)	108.8(10)
O(1)—C(1)—C(6)	108.2(1)	H(1)—C(1)—C(6)	109.7(11)
C(2)—C(1)—C(6)	111.0(1)	C(1)—C(2)—H(2)	106.2(9)
C(1)—C(2)—C(3)	110.7(1)	H(2)—C(2)—C(3)	112.3(10)
C(1)—C(2)—O(1A)	107.7(1)	H(2)—C(2)—O(1A)	109.7(10)
C(3)—C(2)—O(1A)	110.1(1)	C(2)—C(3)—H(3A)	108.4(10)
C(2)—C(3)—H(3B)	108.7(10)	H(3A)—C(3)—H(3B)	108.2(14)
C(2)—C(3)—C(4)	112.4(1)	H(3A)—C(3)—C(4)	111.5(9)
H(3B)—C(3)—C(4)	107.6(11)	C(3)—C(4)—H(4A)	108.9(10)
C(3)—C(4)—H(4B)	110.5(9)	H(4A)—C(4)—H(4B)	107.9(13)
C(3)—C(4)—C(5)	110.1(1)	H(4A)—C(4)—C(5)	108.6(9)
H(4B)—C(4)—C(5)	110.8(10)	C(4)—C(5)—H(5A)	112.1(10)
C(4)—C(5)—H(5B)	107.6(9)	H(5A)—C(5)—H(5B)	107.4(14)
C(4)—C(5)—C(6)	110.6(1)	H(5A)—C(5)—C(6)	109.2(10)
H(5B)—C(5)—C(6)	109.9(10)	C(1)—C(6)—C(5)	113.4(1)
C(1)—C(6)—H(6A)	107.9(11)	C(5)—C(6)—H(6A)	107.2(10)
C(1)—C(6)—H(6B)	105.8(9)	C(5)—C(6)—H(6B)	112.8(9)
H(6A)—C(6)—H(6B)	109.8(14)		

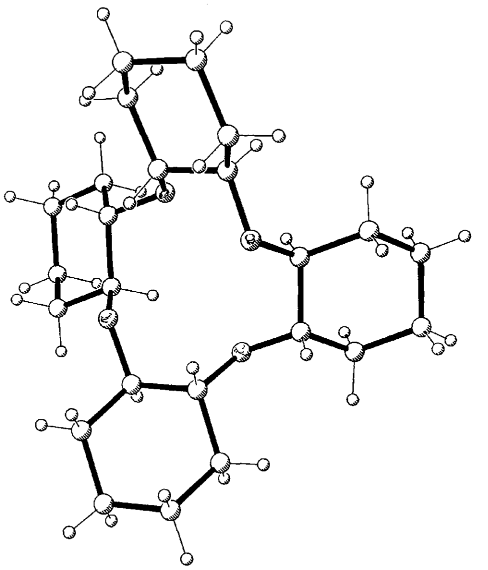
TABLE IV Anisotropic displacement coefficients ($\AA^2 \times 10^3$) for: Tetracyclohexyl-12-crown-4 ether

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	34(1)	33(1)	44(1)	−6(1)	−4(1)	2(1)
C(1)	32(1)	28(1)	44(1)	−3(1)	−2(1)	1(1)
C(2)	31(1)	30(1)	39(1)	2(1)	−2(1)	−3(1)
C(3)	33(1)	40(1)	65(1)	−4(1)	−1(1)	−10(1)
C(4)	50(1)	44(1)	65(1)	−4(1)	−9(1)	−17(1)
C(5)	53(1)	40(1)	67(1)	1(1)	2(1)	−19(1)
C(6)	43(1)	45(1)	58(1)	3(1)	8(1)	−10(1)

The anisotropic displacement factor exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12})$.

TABLE V H-Atom coordinates ($x10^4$) and isotropic displacement coefficients ($\AA^2 \times 10^3$) for: Tetracyclohexyl-12-crown-4 ether

	x	y	z	U
H(1)	3085(12)	474(13)	2890(37)	55(2)
H(2)	1808(12)	1503(12)	14(32)	55(2)
H(3A)	659(13)	325(12)	1065(26)	55(2)
H(3B)	1419(12)	−260(12)	2528(35)	55(2)
H(4A)	1467(12)	6(12)	−2647(34)	55(2)
H(4B)	1203(12)	−983(12)	−1241(27)	55(2)
H(5A)	2836(12)	−993(11)	−2417(36)	55(2)
H(5B)	2736(12)	−1111(12)	451(35)	55(2)
H(6A)	3133(12)	613(12)	−2163(35)	55(2)
H(6B)	3911(13)	84(11)	−511(29)	55(2)

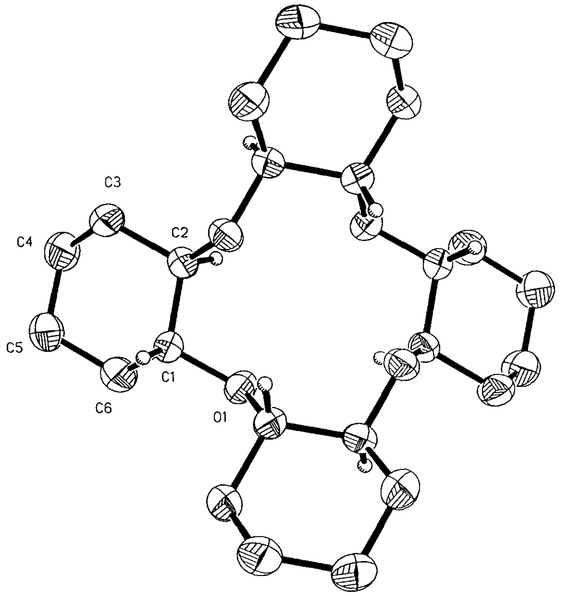


Structure Determination Summary (M469)

Tetracyclohexyl-12-crown-4 ether

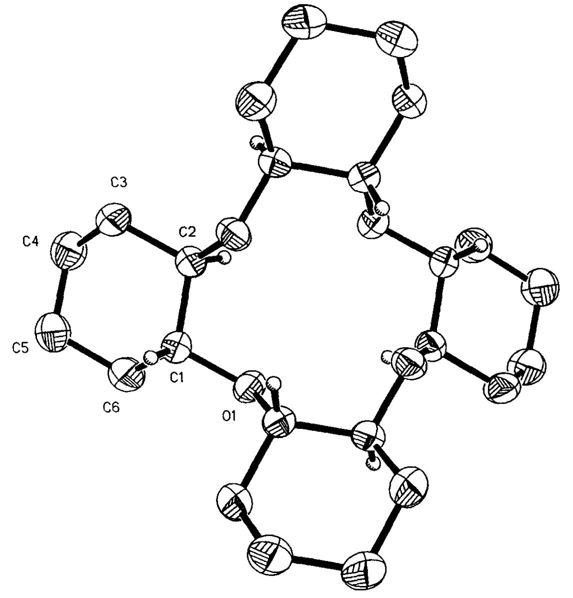
Crystal Data*	
Empirical Formula	$C_{24}H_{40}O_4$
Color; Habit	Colorless, prism
Crystal size (mm)	0.48 × 0.20 × 0.20
Crystal System	Tetragonal
Space Group	$P4_2/n$
Unit Cell Dimensions	a = 14.143(1) Å c = 5.5841(3) Å
Volume	1116.93(6) $\AA^3$
z	2
Formula weight	392.6
Density (calc.)	1.167 Mg/m^3
Absorption Coefficient	0.609 mm^{-1}
F (000)	432

Crystal data for **2**: $C_{24}H_{40}O_4$. $M = 392.56$. Tetragonal, space group $P4_2/n$. $a = 14.143(1)$, $c = 5.5841(3)$ Å, $U = 1116.93$ $\AA^3$. Dc $(Z = 2) = 1.167$ g cm^{-3}. F(000) = 432, μ(Cu-Kα) = 0.609 mm^{-1}. 1633 reflections, 1633 ($R_{int} = 2.77\%$) independent reflections ($2\theta_{max} = 113.5°$). 1418 (F > 4.0 σ(F)): $R = 0.035$, $wR = 0.089$.



Tetracyclohexyl-12-crown-4 ether

Data Collection	
Diffractometer Used	Siemens P4/PC
Radiation	CuKα ($\lambda = 1.54178$ Å)
Temperature (K)	293
Monochromator	Highly oriented graphite crystal
2θ Range	3.0 to 113.5°
Scan Type	ω
Scan Speed	Variable; 4.00 to 60.00°/min. in ω
Scan Range (ω)	1.20°
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard Reflections	3 measured every 97 reflections
Index Ranges	$-15 \leq h \leq 15$, $-15 \leq k \leq 15$ $-6 \leq \ell \leq 6$
Reflections Collected	1633
Independent Reflections	1633 ($R_{int} = 2.77\%$)
Observed Reflections	1418 ($F > 4.0\sigma(F)$)
Absorption Correction	Face-indexed numerical
Min./Max. Transmission	0.8354/0.9285



Tetracyclohexyl-12-crown-4 ether

Solution and Refinement	
System Used	Siemens SHELXTL PLUS (PC Version)
Solution	Direct Methods (SIR92)
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\Sigma w(F_o - F_c)^2$
Absolute Structure	N/A
Extinction Correction	$\chi = 0.027(3)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Hydrogen Atoms	Fractional coordinates refined, common isotropic U
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0024F^2$
Number of Parameters Refined	96
Final R Indices (obs. data)	$R = 4.16\,\%$, $wR = 7.24\,\%$
R Indices (all data)	$R = 4.69\,\%$, $wR = 7.70\,\%$
Goodness-of-Fit	1.17
Largest and Mean Δ/σ	0.000, 0.000
Data-to-Parameter Ratio	14.8:1
Largest Difference Peak	0.32 eÅ^{-3}
Largest Difference Hole	− 0.30 eÅ^{-3}
Solved by: R. A. Toscano	

Complex : Crown ether 1:2 C_{60} (3). A benzene solution of **2** (58 mg, 0.138 mmol) was added to a benzene solution of C_{60} (100 mg, 0.138 mmol), and the mixture stirred vigorously at 80°C for 5 h. After this period, a brown precipitate was formed. The solid was filtered from the colorless solution and washed with benzene affording 129 mg of compound **3**. Elemental analysis results were consistent with a 1:2 stoichiometry. IR (KBr): 3944, 3433, 2926, 2853, 1603, 2598, 2076, 1716, 1618, 1445, 1370, 1255, 1182, 1130, 1093, 806, 526, cm^{-1} UV-Vis: 405, 329, 258 nm. ^{13}C CP-MAS NMR Chemical shifts 25.13 – 34.79 (CH_2), 74.75-85.87 (CH—O), 128.59 (C_6H_6), 143.08 (C_{60}). Anal. Calcd. for $C_{96}H_{40}O_4$, $3H_2O$, $3C_6H_6$: C, 91.69; H, 3.01; Found: C, 92.02; H, 3.02.

Acknowledgments

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[17] Bentonite-Clay. On examination by X-ray fluorescence, the montmorillonite type clay used in this work proved to have the following composition (%); SiO_2, 75.4; Al_2O_3, 9.3; MgO, 0.4; Fe_2O_3, 1.3; CaO, 4.0; K_2O, 0.4; TiO_2, 0.4; H_2O (110°), 9.5 The commercial acid-activated material was obtained from Tonsil Mexicana S.A. and analized with a Phillips Spectrometer using Cr primary radiation. The measured specific surface area was 300 m^2/g (B.E.T. N_2) and the pore volume was 0.4789 cm^3/g. The acidity by NH_3 thermodesorption was 0.099 meq/g. The particle size was 325 mesh.