Journal of Optoelectronics and Advanced Materials Vol. 6, No. 2, June 2004, p. 471 - 476

POSSIBLE HYBRIDES BETWEEN POLYOXOMETALATES AND CALIXARENES

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Based on the calixarenes known ability to host anionic species, the preparation of some hybrid materials with polyoxometalates ions is aimed. The work presents our first attempts to evaluate the interaction between calixarenes (Cx) and polyoxometalates (POM) at the interface between two dispersion mediums as well as in the same solvent. The Cx-containing extracting solution was analysed with UV-Vis spectroscopy whereas the crystalline materials isolated from Cx-containing solutions were investigated by FTIR spectra. The experimental measurements suggest a possible Cx-POM interaction.

(Received September 17, 2003; accepted June 3, 2004)

Keywords: Calixarene, Polyoxometalates, Hybrid crystals

1. Introduction

The most recent researches in chemistry and physics are oriented toward the synthesis and characterisation of new materials with either complicated architectures or high utilisation potential. In this respect, a very promising and important class of compounds is represented by calixarenes, cyclic oligomers resulting from the polycondensation of p-tertbutylphenol with formaldehyde [1-3]. Due to their basket-shaped intramolecular cavities, calixarenes are known-hosts for neutral or electrically charged guest species. Consequently, the utilisation domain of calixarene based-materials is extremely variable, from the reception of cations [4], anions [5] or neutral molecules [6] to the catalytic processes [7].

Based on the calixarenes known ability to "bind" anionic species, we attempt to synthesise some hybrid materials with polyoxometalates, macromolecular coordination compounds resulting from the polycondensation of metallic oxoanions with anions of the same or different species [8]. The work presents our first attempts to evaluate the interaction between calixarenes and polyoxometalates. This interaction was studied either at the interface between different dispersion mediums i.e. extraction procedure, or inside the same dispersion medium i.e. con-crystallisation method. In this purpose, polyoxometalates and calixarene derivatives were selected (and prepared), based on solubility criterion. No mention in the literature was found about the possible interaction calixarenes-polyoxometalates.

2. Experimental

The starting p-tertbutylcalix[6]arene, nominated **C6A** and p-tertbutylcalix[8]arene, nominated **C8A** were prepared by the condensation, in KOH presence, of-p-tert-butyl-phenol with

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formaldehyde, in medium of tetralin (C6A) and xylene (C8A), respectively. The products were re-crystallised from chloroform [9,10]. The calixarene derivatives i.e. hexa (etiloxycarbonilmetoxy)-p-tertbutylcalix[6]arene, nominated **C6E** and octa(etiloxycarbonilmetoxy)-p-tertbutylcalix[8]arene, nominated **C8E,** were obtained by the treatment, in the presence of K_2CO_3, of C6A and C8A with equivalent amounts of ethyl-bromoacetate. The products were purified by re-crystallisation from chloroform/methanol mixture [11,12].

The guanidinium silicotungstate (nominated **GuSiW**) was precipitated in aqueous medium, from hydrated silicotungstic acid and equivalent amounts of guanidinium carbonate. The product was re-crystallised from acetonitrile-acetic acid mixture [13].

The interaction calixarene-polyoxometalates was studied either at the interface between different dispersion mediums i.e. extraction procedure, or inside the same dispersion medium i.e. con-crystallisation method. Extraction procedure was performed with chloroform solutions of C6A or C8A and aqueous solution of silicotungstic acid. Equal volumes of equal concentrations (10^{-3}M or 2.10^{-3}M) were vigorously shaken or ultrasound treated. The interaction was evaluated by analysing the organic phase either by UV-Vis spectroscopy, or by FTIR spectroscopy, the latter one being applied to the evaporation residuum. In this purpose, the separated organic phase was divided in two parts, one part being diluted for the UV-Vis absorption measurement, and the other one being left for the slowly solvent evaporation. Con-crystallisation method was performed from equal amounts of 10^{-4}M acetonitrile solutions of GuSiW and C6E or C8E. The solutions were intimately mixed in ultra-sound field and then left to crystallise, by the slow evaporation of the solvent. 1-3 crystalline fractions were collected and FTIR analysed.

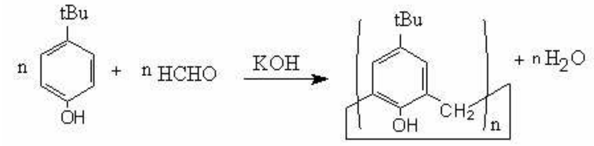
Materials were characterised by FT-IR spectroscopy (JASCO-615; KBr pellets), ^{1}H-NMR spectroscopy (80MHz Brucker Spectrometer; $CDCl_3$; tetramethylsilane as reference) and thermal analysis (Paulik-Erdely OD-102 Derivatograff).

3. Results and disscusion

In order to study the possible interaction between calixarene (Cx) and polyoxometalates (POM), some calixarene derivatives and guanidinium salt of the silicotungstic acid were prepared. The selection of Cx and POM compounds was based both on criterions of atomic arrangements and solubility.

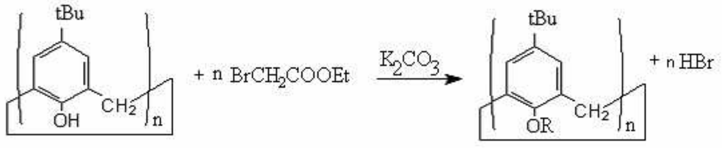
a) Synthesis of calixarenes derivatives

The starting p-tert-butyl calix[6]arene (nominated **C6A)** and p-tert-butyl calix[8]arene (nominated **C8A**) were prepared by condensation of-p-tertbutylphenol with formaldehyde (**reaction 1**). The modified calixarenes i.e. hexa (etiloxycarbonilmetoxy)-p-tertbutylcalix[6]arene (nominated **C6E**) and octa(etiloxycarbonilmetoxy)-p-tertbutylcalix[8]arene (nominated **C8E)** were obtained by the treatment of **C6A** and **C8A** with equivalents amounts of ethyl-bromoacetate (**reaction 2**).



(1)

Where n=6 (**C6A**) and n=8 (**C8A)**



(2)

where R=CH_2COOEt and n=6 (**C6E**) or n=8, (**C8E**)

FT-IR spectra and 1H-NMR spectra proved the calixarene purity as follows:

- p-tertbutylcalix[6]arene (**C6A**): *^{1}H-RMN ($CDCl_{3.,}$ δ_{ppm}):* 1.27(s, 54H, $C(CH_3)_3$); 3.9(m, 12H, Ar-CH_2-Ar); 7.16(s, 12H, ArH); 10.55(s, 6H, OH); *FTIR (KBr):* ν_{OH} = 3120 cm^{-1}.
- p-tertbutylcalix[8]arene (**C8A**): *^{1}H-RMN ($CDCl_{3,,}$ δ_{ppm}):* 1.24(s, 72H, $C(CH_3)_3$); 3.4(d, 4H,$CH_{ec.}$); 4.3(d, 4H,$CH_{ax.}$) 7.14(s, 16H, ArH); 9.66(s, 8H, OH); *FTIR (KBr):* ν_{OH} = 3231,15 cm^{-1}.

- hexa(etiloxycarbonilmetoxy)-p-tertbutylcalix[6]arene (**C6E**): ^{1}*H-RMN (CDCl$_3$, δ_{ppm}):* 1.02(s, 54H, C(C*H*$_3$)$_3$; 1.25(t, 18H, C*H*$_3$); 3.81-4.23(m, 24H, Ar-CH$_2$-Ar and OC*H*$_2$); 4.50(br s, 12H, C(O)C*H*$_2$), 6.98(s, 12H, ArH); *FTIR (KBr):* $\nu_{C=O}$ = 1760 and 1730 cm^{-1}.
- octa(etiloxycarbonilmetoxy)-p-tertbutylcalix[8]arene (**C8E**): ^{1}*H-RMN (CDCl$_3$, δ_{ppm}):* 1.12(br s, 96H, C(C*H*$_3$)$_3$ and C*H*$_3$); 3.81-4.23(m, 48H, Ar-CH$_2$-Ar, OC*H*$_2$ and C(O)C*H*$_2$), 6.95(br s, 16H, ArH); *FTIR (KBr):* $\nu_{C=O}$ = 1760 and 1738 cm^{-1}.

b) Synthesis of guanidinium silicotungstate

The guanidinium silicotungstate (nominated **GuSiW**) was prepared by treating silicotungstic acid [$H_4SiW_{12}O_{40}\cdot xH_2O$ nominated **HSiW**] with equivalent amounts of guanidinium carbonate (**reaction 3**).

$$H_4[SiW_{12}O_{40}] + 2\ [NH_2{=}C(NH)_2]\ _2CO_3 \rightarrow [NH_2{=}C(NH_2)_2]_4\ [SiW_{12}O_{40}] + 2\ CO_2 + 2\ H_2O \qquad (3)$$

The purity of as prepared material was checked out by FT-IR spectroscopy and thermal analysis:

- guanidinium silicotungstate (nominated **GuSiW**): *FTIR (KBr):* $\nu_{Si\text{-}O}^{(1)}$ =1015.8 cm^{-1}; $\nu_{W\text{-}O}^{(2)}$ =972.9 cm^{-1}; $\nu_{W\text{-}O}^{(3)}$ =922.3 cm^{-1} ; $\nu_{W\text{-}O}^{(4)}$ =794.5 cm^{-1} ; $\nu_{NH2\ (sim)}$ =3453.9 cm^{-1}; $\nu_{NH2\ (asim)}$ =3203.2 cm^{-1}; $\nu_{C=N}$ 1664.7 cm^{-1}; $\delta_{NH2}{}^{+}$= 1570.7 cm^{-1}; *Thermal analysis*: firing residuum 88, 9% (theor. 91.1 %).

c) Computational evaluation of Cx-POM interaction

In order to evaluate the possibility of Cx-POM interaction, some computational studies were performed. The molecular modelling (MM$^+$) was applied to the assembly of p-tertbutylcalix[6]arene or p-tertbutylcalix[8]arene with silicotungstate [$SiW_{12}O_{40}$]$^{4-}$ ion [14]. The study revealed that p-tertbutylcalix[8]arenes possesses an intramolecular cavity large enough to guest large anions such as silicotungstate species with Keggin structure (Fig. 1).

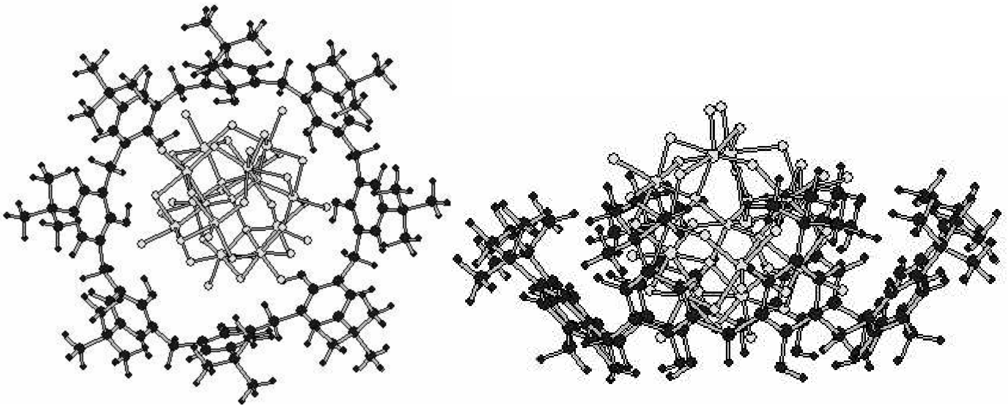


Fig. 1. Silicotungstate - calix [8]arene aggregate, in upper view (left) and side-view (right) image.

d) Possible interaction of calixarenes and polyoxometalates from two different dispersion mediums

The possible interaction Cx-POM was first evaluated by the extraction method. In this purpose, solutions of **C6A** and **C8A** (10^{-3} M and 2.10^{-3} M in CHCl$_3$) and solutions of **HSiW** (10^{-3}M and 2.10^{-3}M, in water) were prepared. Equal volumes of solutions were mechanically shaken and ultrasound treated. Different Cx-POM ratios were used in extraction experiments.

The interaction was evaluated by analysing the organic phase either by UV-Vis spectroscopy, or by FTIR spectroscopy, the latter one being applied to the evaporation residuum.

UV-Vis and FTIR investigation revealed no interaction between [$SiW_{12}O_{40}$]$^{4-}$ and C6A but suggested a possible interaction with C8A. The UV absorption spectrum of the organic-phase containing C8A species shows a small modification of the characteristic absorption bands at 284 nm and 291 nm (Fig. 2). The specific absorption band (at ~ 263 nm) of [$SiW_{12}O_{40}$]$^{4-}$ could not be noticed.

The change of the band ratio (that is well illustrated by the normalised spectra) could be the result of a possible interaction with the polianion species. The FTIR spectra are irrelevant. With the exception of a slight modification in the region of OH vibration, the spectrum of the material containing C8A species did not suffered any significant modifications as compared with the starting compound.

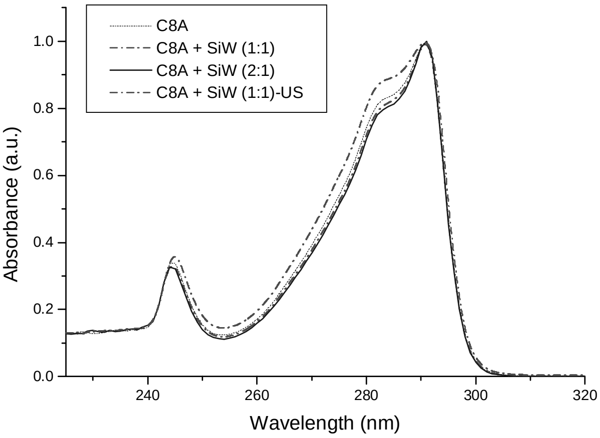


Fig. 2. UV – Vis normalised spectra of calix[8]arene before and after the extraction (8.10^{-5} M in $CHCl_3$)

e) Possible interaction between calixarenes and polyoxometalates from the same dispersion medium

The possible interaction Cx-POM was evaluated by the con-crystallisation method. In this purpose, solutions of **C6E** and **C8E** in acetonitrile (10^{-3} M and 2.10^{-3} M) and solutions of **GuSiW** in acetonitrile (10^{-4} M) were prepared, mixed and ultra-sound treated. The step-wise evaporation of the solvent was performed in order to isolate different crystalline fractions that were investigated by FTIR spectroscopy. The as isolated crystals are nominated as **C6E-GuSiW** and **C8E-GuSiW**. The infrared absorption spectra illustrates the presence of specific bands of both calixarene and guanidinium containing compounds i.e. at ~3200 cm^{-1}, ~1660 cm^{-1} and ~520 cm^{-1} (Figs. 3 and 4).

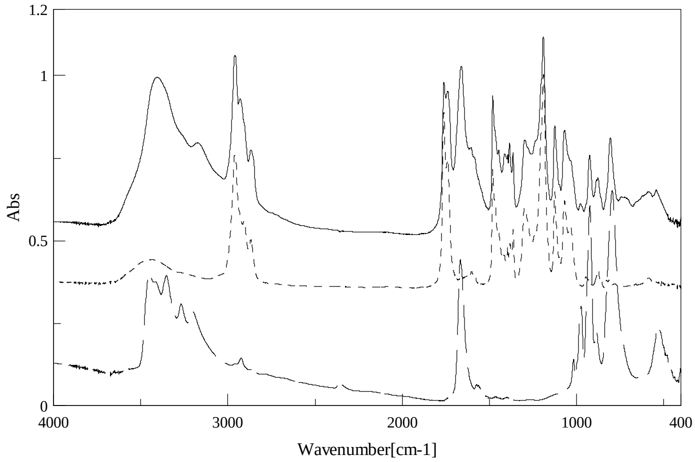


Fig. 3. FTIR spectra of C6E-GuSiW (—) ; GuSiW (---) and C6E(·····) crystals.

The probability to "grow" GuSiW- C6E aggregate increases as the solvent is evaporated from the system (Fig. 5). Different materials resulting from the fractionated crystallisation contain variable amounts of guanidinium compound.

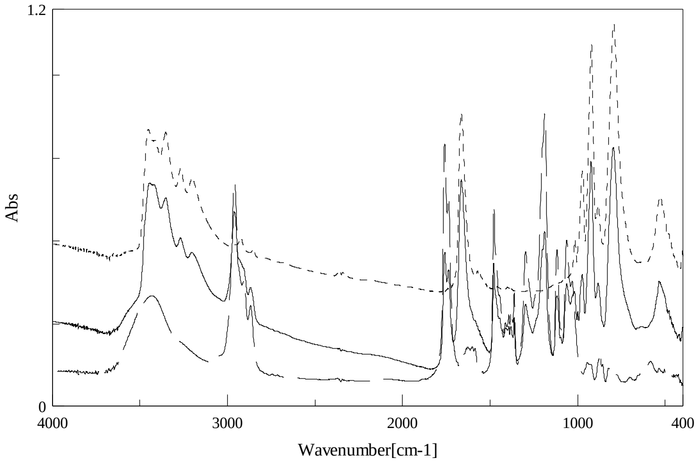


Fig. 4. FTIR spectra of C8E-GuSiW (—), GuSiW (---) and C8E (-·-·-·) crystals.

The experimental registered spectra could not be simulated by the mathematical addition of the individual spectra of GuSiW and C8E or C6E, respectively (Fig. 6). This suggests that, the separated crystalline samples of C6E-GuSiW and C8E-GuSiW are not simply physical mixtures but some interaction material.

Further experiments are to support the supposition of the Cx-POM interaction and to elucidate the nature of the mutual interaction of species under investigation. The work is in progress.

4. Conclusions

FTIR and UV-Vis investigations performed on the materials “elaborated” by both the extraction method and the con-crystallisation procedure suggest a possible interaction between calixarenes and polyoxometalates. This is in agreement with the results of the mathematical modelling applied to the investigated compounds.

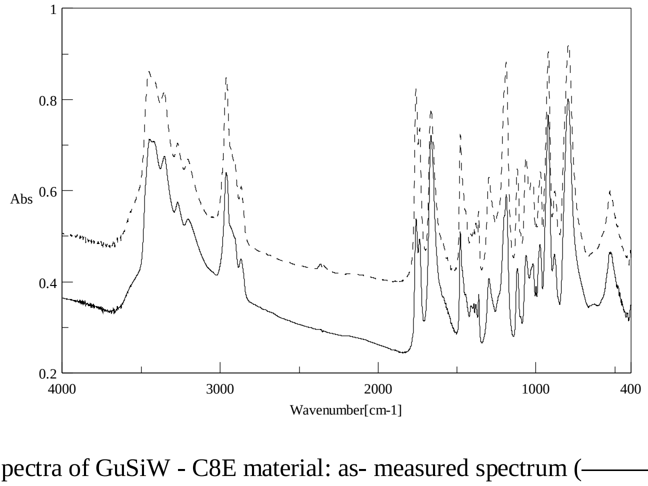


Fig. 6. FTIR spectra of GuSiW - C8E material: as- measured spectrum (———); simulated spectrum (- - - -) , for 1:1 ratio.

Acknowledgements

The work was supported by CERES National Research Program, under contract no. 42/2001.

References

[1] V. Böhmer, Angev. Chem. **107**, 785 (1995).

[2] A. Arduini, A. Pochini, A. Rizzi, A. R. Sicuri, R. Ungaro, Tetrahedron Letters **31**, 4653 (1990).

[3] V. Kovalev, E. Shokova, A. Khomich, Y. Luzikov, New J. Chem. **20**, 483 (1996).

[4] V. W. Yam, K. K. W. Lo, Coordination Chemistry Reviews **184**, 157 (1999).

[5] E. M. Georgiev, N. Wolf, D. M. Roundhill, Polyhedron **16**, 1581 (1997).

[6] L. J. Bauer, C. D. Gutsche, J. Am. Chem. Soc. **107**, 6063 (1985).

[7] S. Steyer, C. Jeunesse, D. Matt, R. Welter, M. Wesolek, Journal of the Chemical Society, Dalton Transactions, 4264 (2002).

[8] G. Marcu, M. Rusu, Chimia polioxometalaților, Ed. Tehnică, Bucureşti (1997).

[9] C. D. Gutsche, B. Dhawan, M. Iqbal, Organic Synthesis **68**, 243 (1989).

[10] C. D. Gutsche, B. Dhawan, M. Leonis, Organic Synthesis **68**, 238 (1989).

[11] F. Arnaud-Neu, E. M. Collins, M. Deasy, G. Ferguson, S. J. Harris, B. Kaitner, A. J. Lough, M. A. McKervey, E. Marrques, B. L. Ruhl, M. J. Schwing-Weill, E. M. Seward, J. Am. Chem. Soc. **111**, 8681 (1989).

[12] S. Y. Han, M. H. Kang, Y. E. Jung, S. K. Chang, J. Chem. Soc. Perkin Trans. **2**, 835 (1994).

[13] M. Cozic, N. Casan-Pastor, M. Hammer, L. Baker **-** Inorg. Chem. **35**, 2403 (1996).

[14] T. N. Ursaleş, E. J. Popovici, I. Silaghi-Dumitrescu, Revista de Chimie, (in press).