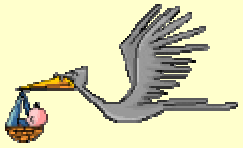
Novosibirsk, Institute of inorganic chemistry SB RAS

G.A.Kostin

Thiacalixarenes for palladium extraction from nitric and alkaline media

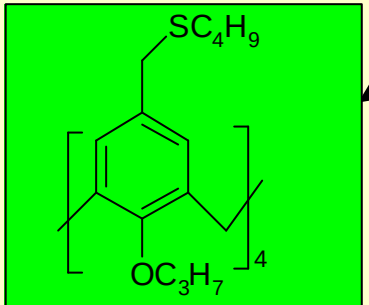


ARCUS

St-Petersburg, July, 2009

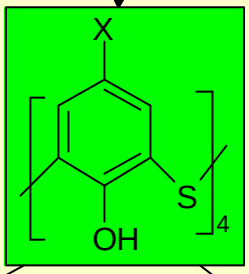
SupraChem

R_2S are very good Pd extractants from acid (HCl or HNO_3) media



Macrocyclic extractants: chelating effect, preorganisation

Some another way



+

X-group is variable

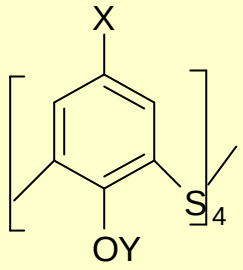
OH can also work in alkaline media

-

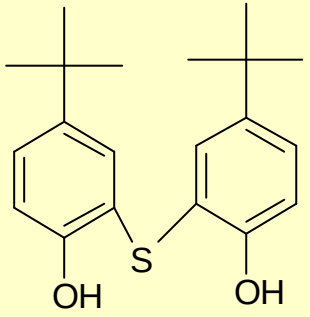
$C_6H_5SC_6H_5$ –

extremely poor extractant of Pd

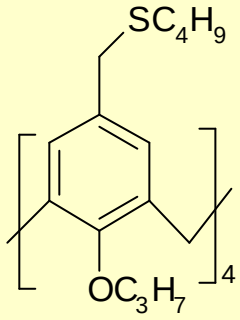
Compounds in action



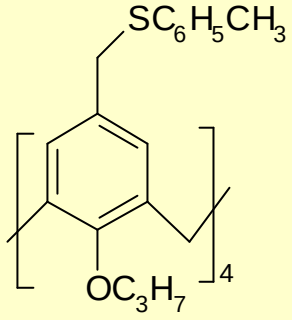
	Y	X	
C74	H	H	cone
C102	H	t-Bu	cone
C104	Me	H	1,3-alt
C103	Bu	H	1,3-alt
C53	H	$CH_2PO(Ph)_2$	cone
C54	H	$CH_2PO(OEt)_2$	cone
C160	H	$CH_2OC_3H_7$	cone
C259	$C_{10}H_{21}$	t-Bu	cone



C165



C7

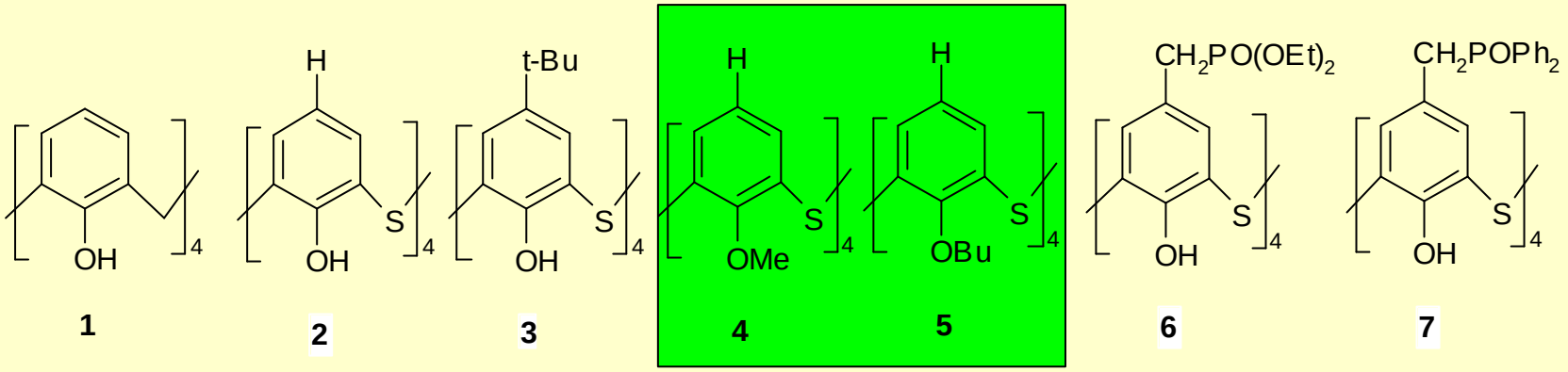


C5

All extractants were prepared in the Institute of Organic Chemistry NAS Ukraine (prof. V. Kalchenko)

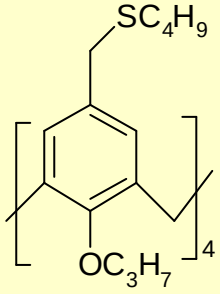
All D values are shown for 0,01 M concentration of extractant if other not shown

Extraction from nitric acid



1,3 - alternate

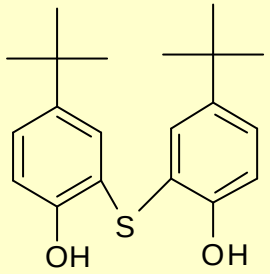
HNO_3, M	D_{Pd} for extractant						
	1	**2**	**3**	**4**	**5**	**6**	**7**
0,3	0,001	370	21,6	0,19	0,12	82	>200
0,5	0,001	373	14,9	0,19	0,1	82	>200
1	0,002	352	8,4	0,20	0,05	57	125
1,5	-	237	6,8	0,23	0,07	36	83
2	-	216	4,8	0,26	0,09	29	62
3	-	63	4,2	0,26	0,10	27	64



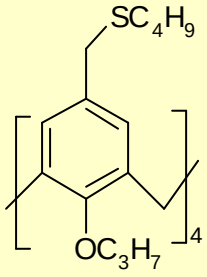
D_{Pd} > 4000

From nitric acid to alkaline solutions

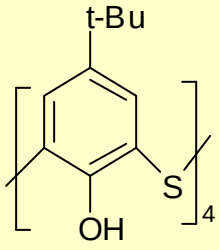
??	Percent of recovery and D (in parenthesis) for extractant							
	C165	C7	C102	C259	C74	C103	C104	C160
1,44	100 (>1000)	100 (>1000)	80 (4,0)	0,5 (0,005)	74,0 (2.8)	15,3 (0,18)	-	-
3,45	100 (>1000)	100 (>1000)	95 (20,2)	0,4 (0,004)	99,8 (550)	-	-	99,7 (370)
4,80	99,8 (550)	100 (>1000)	90,2 (9,2)	0,5 (0,005)	99,6 (240)	14,5 (0,17)	-	99,6 (290)
6,55	23,7 (0,31)	9,5 (0,105)	0,5 (0,005)	0,1 (0,001)	0,3 (0,003)	2,9 (0,03)	-	0,6 (0,006)
8,8	5,7 (0,06)	5,0 (0,053)	0,3 (0,003)	0,08 (0,0008)	-	-	0,2 (0,002)	-
10,0	13,0 (0,15)	4,1 (0,043)	0,3 (0,003)	0,08 (0,0008)	0,7 (0,007)	0,3 (0,003)	-	0,7 (0,007)
12,5	100 (>1000)	2,7 (0,028)	0,2 (0,002)	0,09 (0,0009)	36,3 (0,57)	0,3 (0,003)	0,5 (0,005)	7,8 (0,085)
13,4	98 (40)	1,0 (0,01)	0,1 (0,001)	0,08 (0,0008)	40,0 (0,67)	-	-	6,3 (0,067)



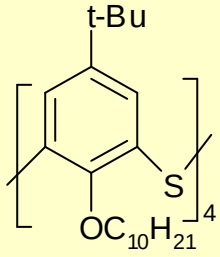
C165



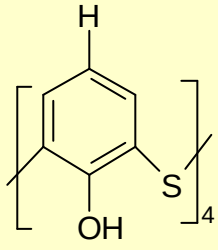
C7



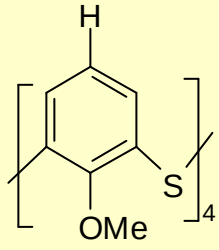
C102



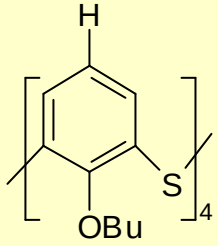
C259



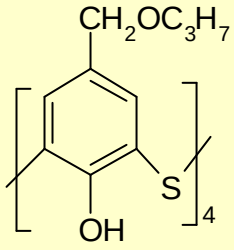
C74



C103

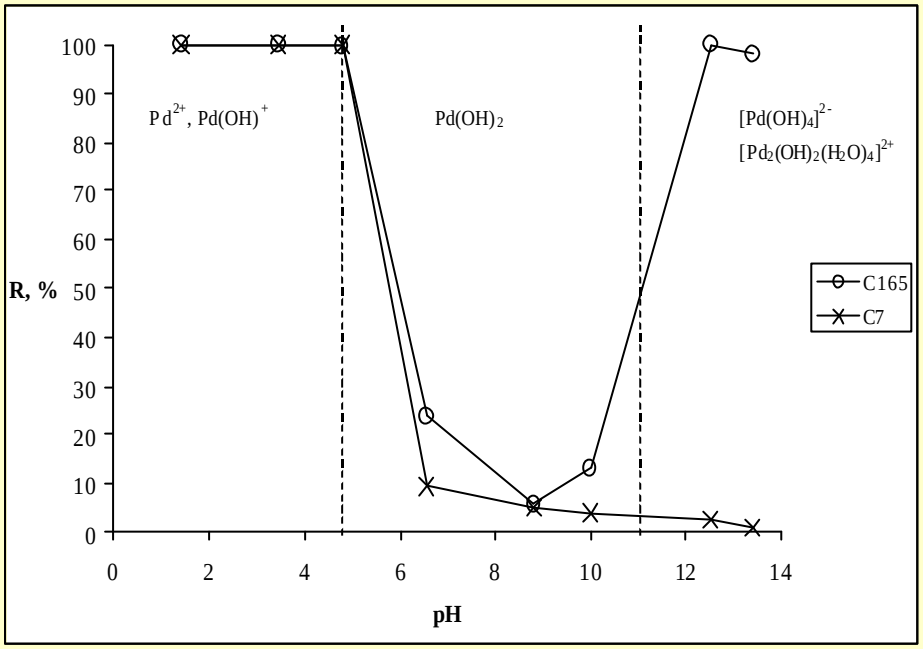


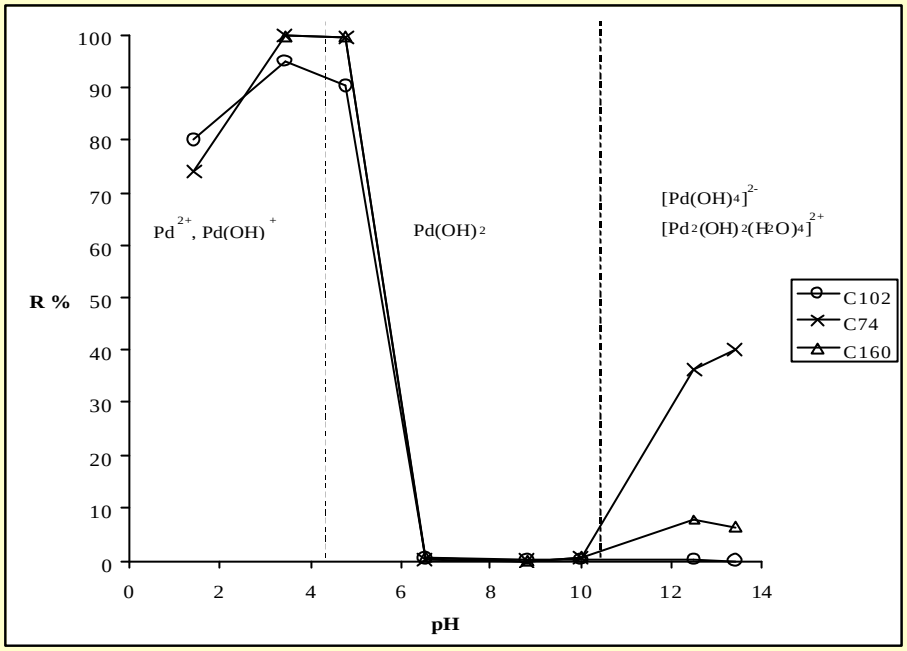
C104



C160

pH dependencies of extraction

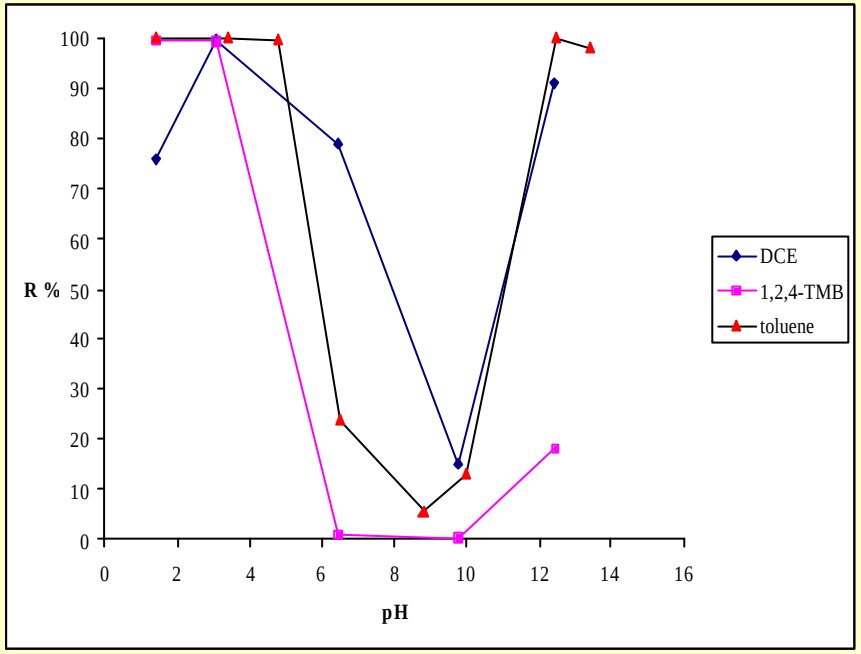


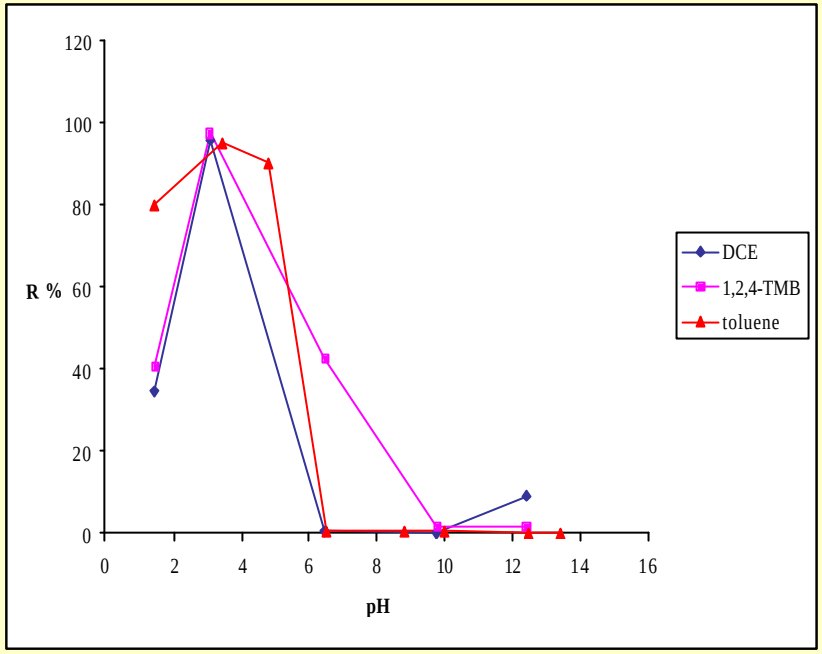


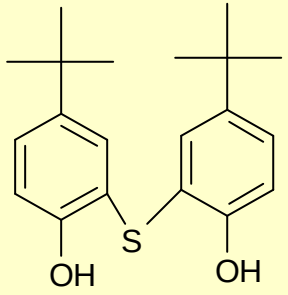
Generally two dependencies of recovery percent (E) on pH can be defined: 1. Strong decrease of R at pH > 5 with further diminution for extractants with alkoxy-groups in low rim (**C7, C103, C104**); 2. Minimum in the pH range pH = 5-10 for thiacalixarenes with OH-groups in low rim (**C74, C160**, except **C102**) and non-cyclic **C165**.

In the second case the dependence of E_{Pd} on pH is similar to the dependence of palladium solubility with distribution of palladium on different complex forms. These regularities are determined by coordination extraction of palladium from weak acid solutions and by chelation in alkaline solutions with participation of sulfur and oxygen atoms after substitution of OH protons to the polymeric palladium forms.

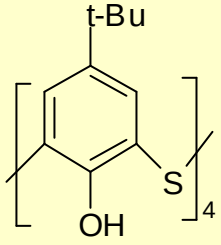
Solvent influence on the extraction







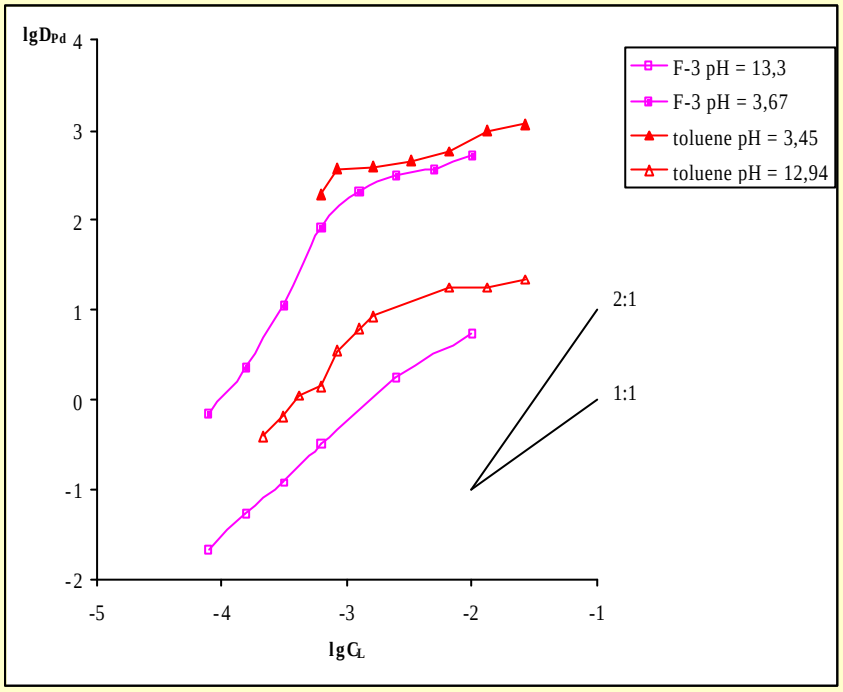
C165



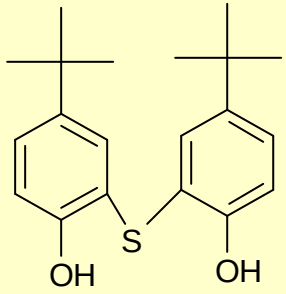
C102

Toluene > DCE > 1,2,4-TMB

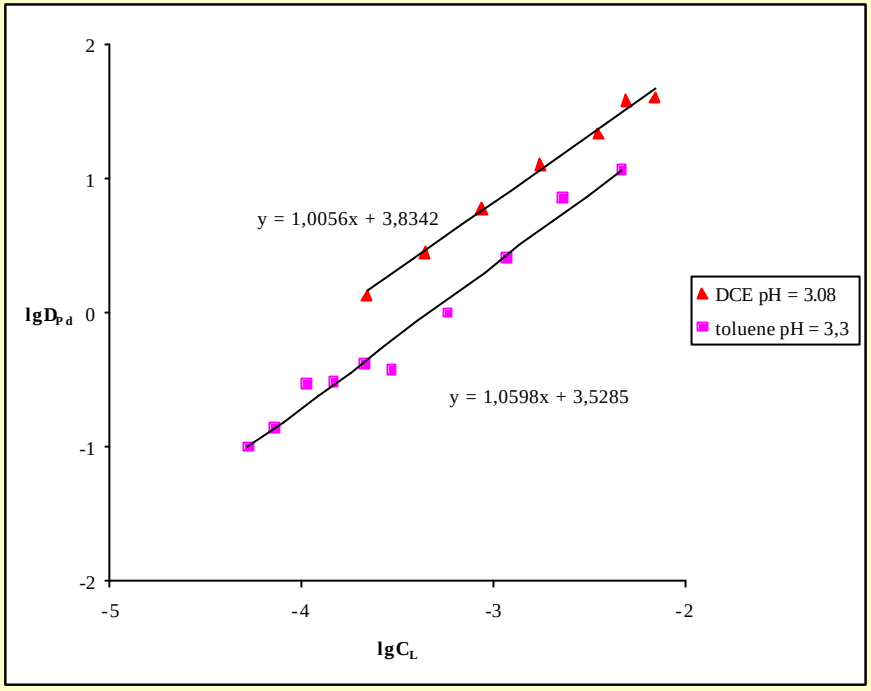
Composition of extracted species



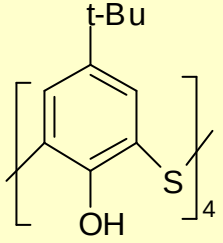
Slopes of log-log dependencies are in the range from 1 to 2



C165

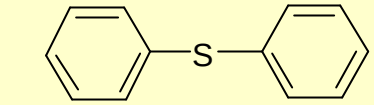


Slopes of log-log dependencies are close to 1

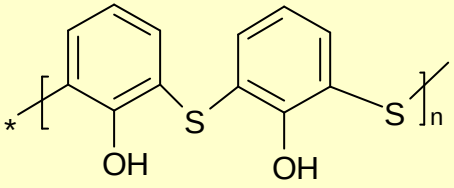


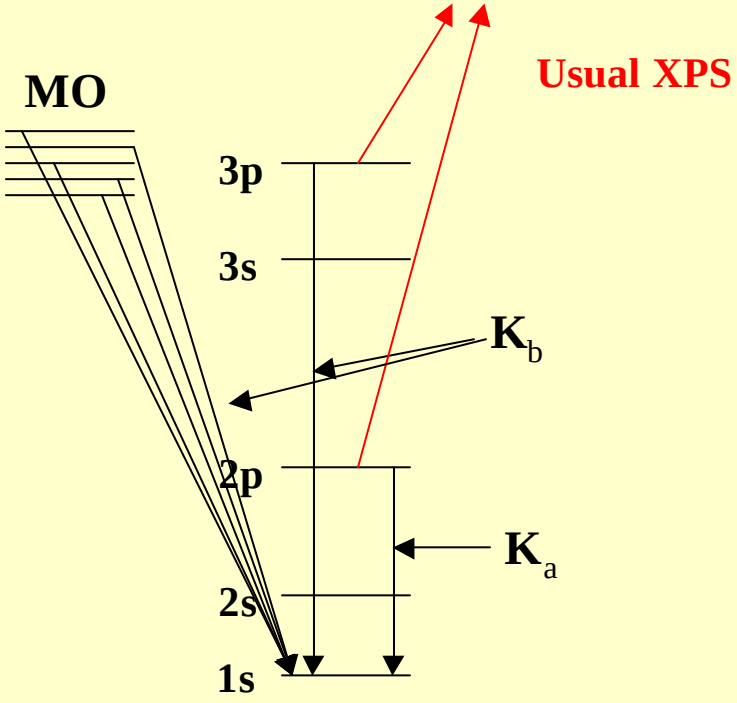
C102

Electronic structure of thiacalixarenes



not equal !!!



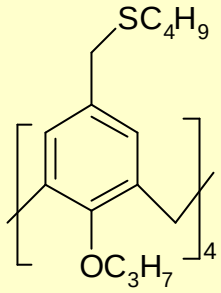


K_a and K_b are emission spectra
More sensible than XPS
K_a spectrum can provide the information about effective charge state of atom
K_b spectrum can provide the information about HOMO with the participation of S_{3p} orbitals.

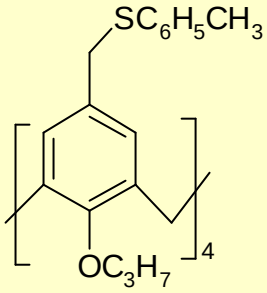
Electronic structure of thiacalixarenes

Substance	Average K_α line position, eV	Shift, eV	Substance	Average K_α line position, eV	Shift, eV
S	2289,984	0	S	2289,984	0
C74	2289,785	-0,199	KSCN	2289,867	-0,117
C102	2289,697	-0,287	$(C_{10}H_{21})_2S$	2289,844	-0,14
C104	2289,809	-0,175	Thiocarbamide	2290,036	+0,052
C103	2289,781	-0,203	$(C_5H_{11})_2SO$	2290,075	+0,091
C54	2289,74	-0,244	$(C_6H_{13})_2SO$	2290,096	+0,112
C53	2289,813	-0,171	$(C_4H_9)_2SO_2$	2290,568	+0,584
C7	2289,665	-0,319	Na_2SO_4	2290,884	+0,9
C7+Pd	2289,758	-0,226			
C5	2289,581	-0,403	$(C_6H_5)_2S$		+0,01
C5+Pd	2289,844	-0,14			

Negative shift means negative charge. Data of K_α and XPS correlates. Quite surprising that for **TCA** negative shift is greater than for **DDS.** For **C7** and **C5** – most negative shift was found.



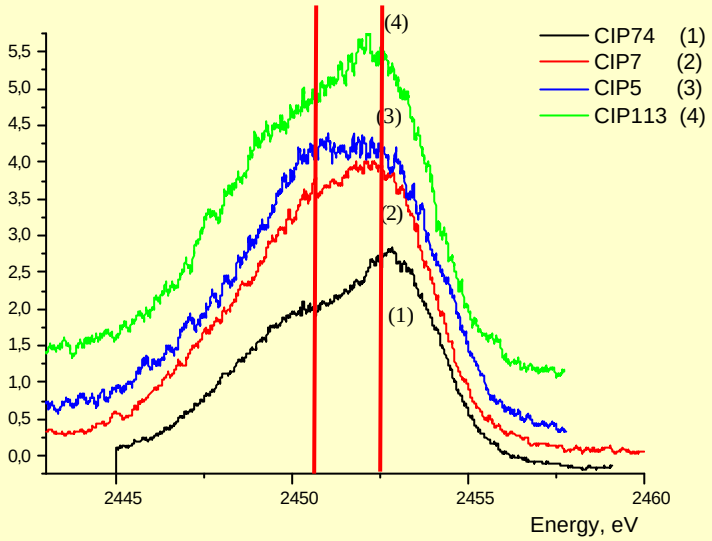
C7

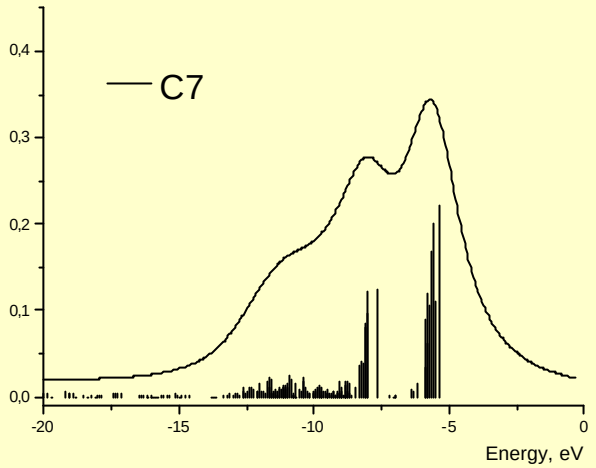


C5

Calixarene	$S2p_{3/2}$, eV	O1s, eV	K_α line shift in respect to elementary sulfur, eV
C74	163.7	533.4	-0,199
C102	163.8	533.5	-0,287
C53	163.7	530.7, 533.2	-0,171
C7	163.2	532.5	-0,319
C7+Pd	163.5	532.5	-0,226
C5+Pd	163.5	532.6	-0,14

Electronic structure of thiacalixarenes



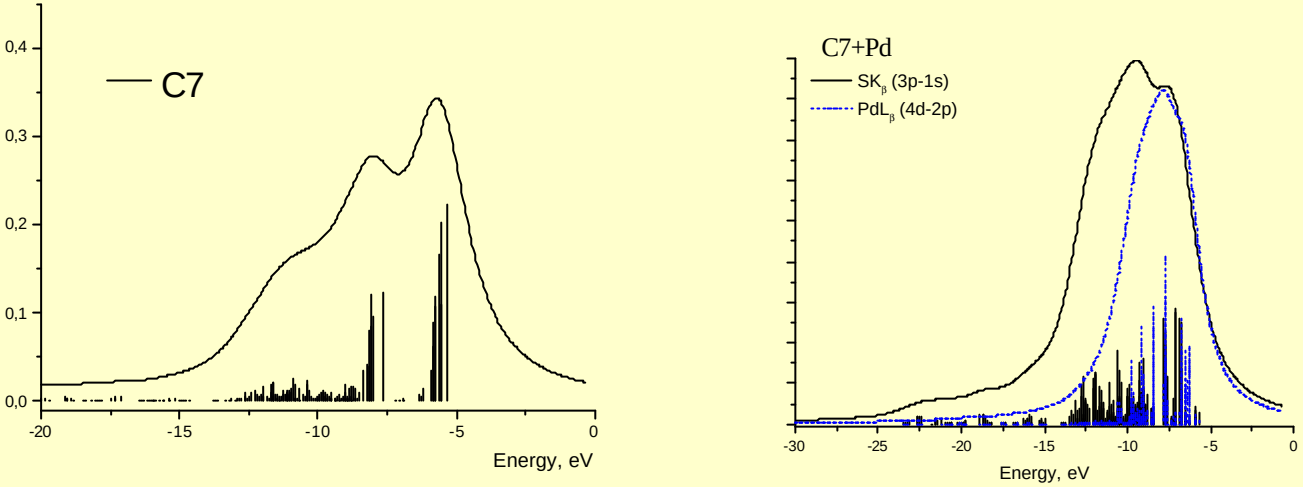


Experimental (left) and calculated (right) K_b spectra of sulfur-containing calixarenes.

There are two band series in all experimental spectra. According to calculations the shoulder in the region 2450 eV is determined by s-bonding MO with the participation of S_{3p}. The maximum in the region 2453 – 2455 eV is determined by MO, localized mainly on sulfur atom that close to unshared 3p orbital.

No p-bonding Ar-S-Ar was found in thiacalixarenes The reason of it is the non-linear structure of bridging fragment.

Electronic structure of thiacalixarenes



K_b spectra of calixarene thioester (left) and complex with Pd (right)

Because of the coordination of Pd electronic density on sulfur decrease (according to both K_a and K_b spectra). And this decrease is mainly related to the unshared 3p orbital.

Acknowledgments

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