

COMPLEXATION OF METAL CATIONS WITH THIOAMIDE CALIX[4]ARENE DERIVATIVE

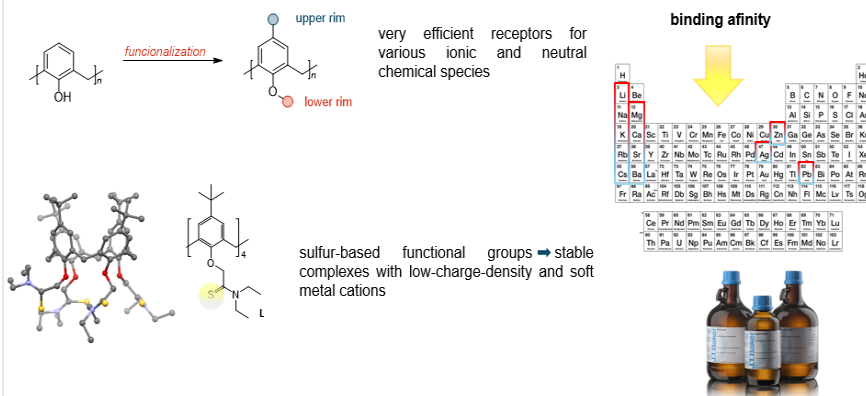
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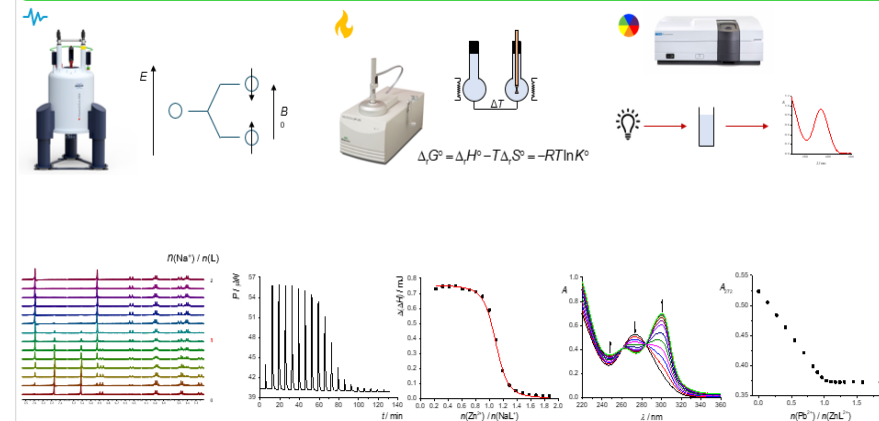


Introduction & Aim

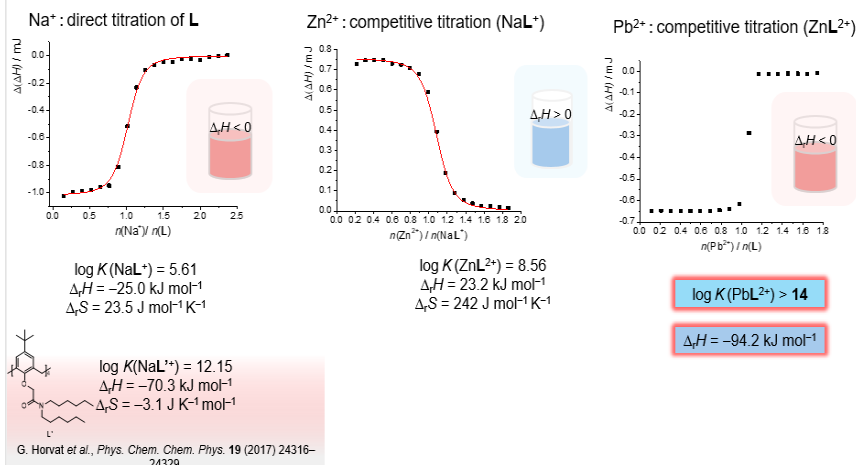


¹ Gutsche, C. D.; Calixarenes: An Introduction, 2nd edition, The Royal Society of Chemistry, Cambridge, 2008.
² a) Modrušan, M.; Cindro, N.; Usenik, A.; Leko, K.; Glaser, L.; Tomišić, V.; Horvat, G.; Potaž, J.; Tomišić, V. *Croat. Chem. Acta* **2024**, *97*, 1-15; b) Potaž, J.; Čvetošić, M.; Usenik, A.; Cindro, N.; Horvat, G.; Leko, K.; Modrušan, M.; Tomišić, V. *Molecules* **2022**, *27*, 470; c) Leko, K.; Usenik, A.; Cindro, N.; Modrušan, M.; Potaž, J.; Horvat, G.; Stilinović, V.; Hensar, T.; Tomišić, V. *ACS Omega* **2023**, *8*, 43074-43087; d) Čvetošić, M.; Cindro, N.; Bregović, N.; Tomišić, V. *ACS Phys. Chem. Au* **2024**, *4*, 6, 773-786.
³ a) Delgado, X.; Harwood, J. M.; Hosseini, M. W.; De Can, A.; Fischer, J.; Kyriakos, N. J. *Chem. Soc., Chem. Commun.* **1994**, 1979; b) Danil de Namor, A. F.; Pawlikowski, T. S.; New J. Chem. **2011**, *35*, 375-384; c) Shiao, W. J. *J. Incl. Phenom. Microscop. Chem.* **2005**, *52*, 13-37.

Experimental



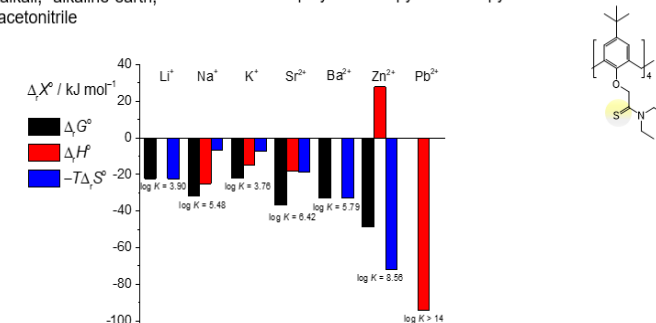
Results and discussion



Conclusions

stable complexes with alkali, alkaline-earth, and soft metal cations in acetonitrile

interplay of enthalpy and entropy contributions

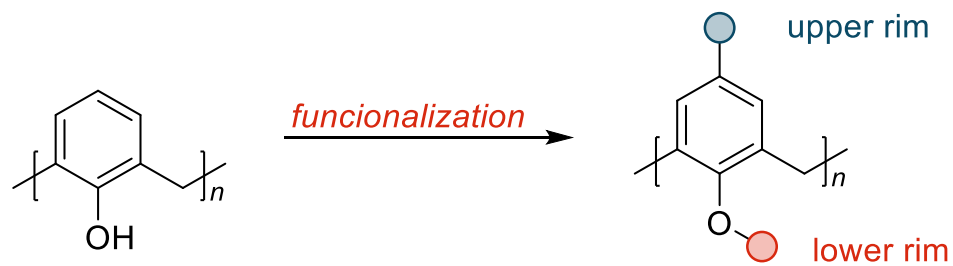


model compound for the development of calixarene-based receptors for soft metal cations

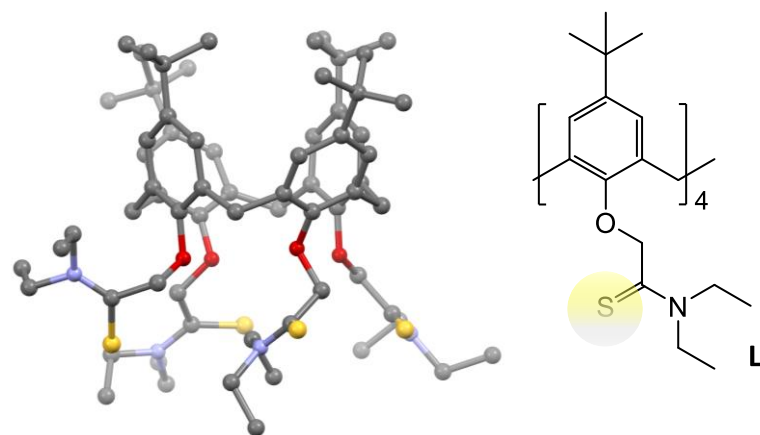


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Introduction & Aim



very efficient receptors for various ionic and neutral chemical species



sulfur-based functional groups → stable complexes with low-charge-density and soft metal cations

binding affinity

1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium																
11 Na Sodium	12 Mg Magnesium																
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Cesium	56 Ba Barium	57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	89 Ac Actinium	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Nh Nihonium	114 Fl Flerovium	115 Mc Moscovium	116 Lv Livermorium	117 Ts Tennessine	118 Og Oganesson

58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium

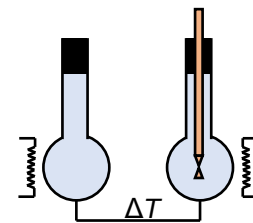
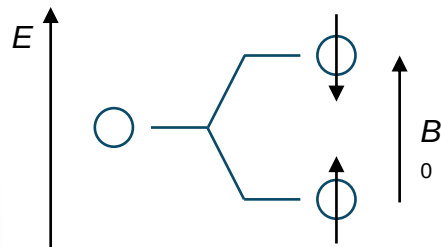


¹ Gutsche, C. D.; *Calixarenes: An Introduction*, 2nd edition, The Royal Society of Chemistry, Cambridge, **2008**.

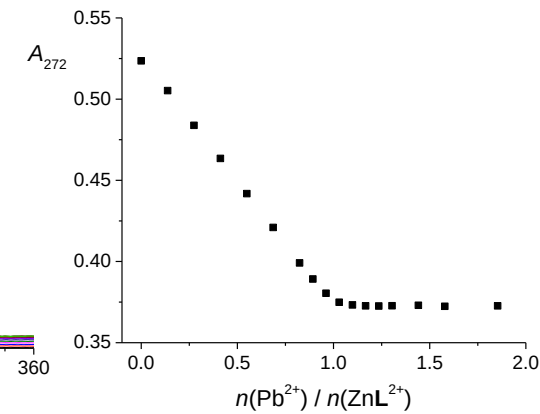
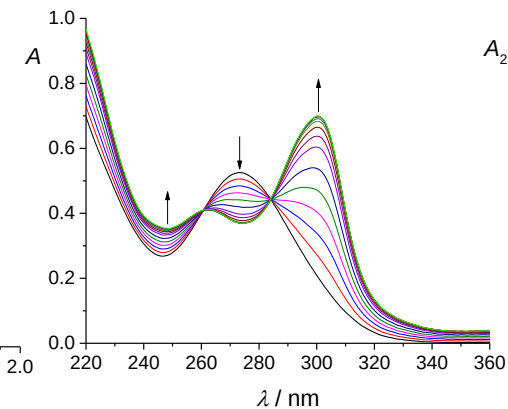
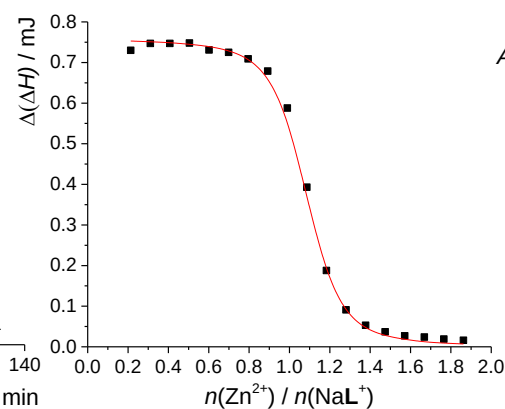
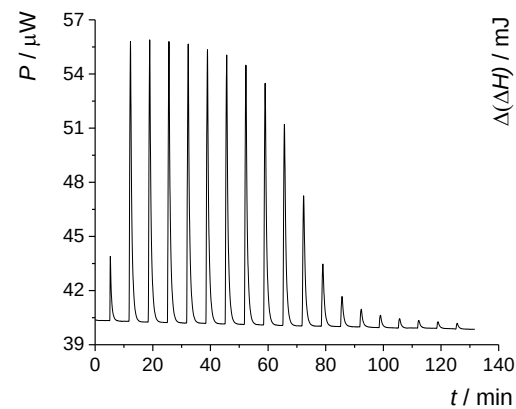
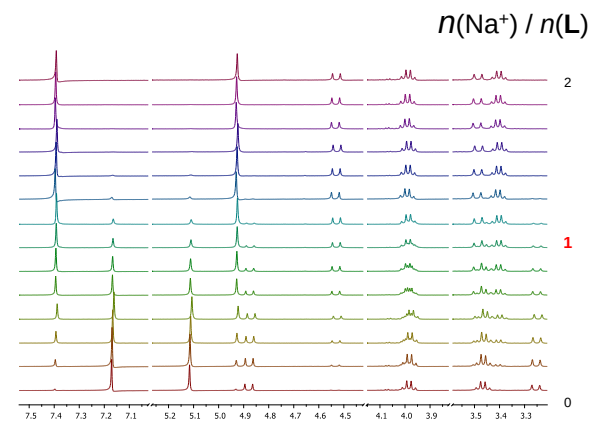
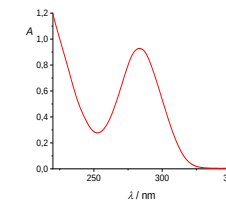
² a) Modrušan, M.; Cindro, N.; Usenik, A.; Leko, K.; Glazer, L.; Tomaš, R.; Horvat, G.; Požar, J.; Tomišić, V. *Croat. Chem. Acta*, **2024**, 97, 1–15; b) Požar, J.; Cvetnić, M.; Usenik, A.; Cindro, N.; Horvat, G.; Leko, K.; Modrušan, M.; Tomišić, V. *Molecules* **2022**, 27, 470; c) Leko, K.; Usenik, A.; Cindro, N.; Modrušan, M.; Požar, J.; Horvat, G.; Stilić, V.; Hrenar, T.; Tomišić, V. *ACS Omega*, **2023**, 8, 43074–43087; d) Cvetnić, M.; Cindro, N.; Bregović, N.; Tomišić, V. *ACS Phys. Chem Au*, **2024**, 4, 6, 773–786.

³ a) Delaigue, X.; Harrowfield, J. McB.; Hosseini, M. W.; De Cian, A.; Fischer, J.; Kyritsakas, N. *J. Chem. Soc., Chem. Commun.* **1994**, 1579; b) Danil de Namor, A. F.; Pawłowski, T. S.; *New J. Chem.* **2011**, 35, 375–384; c) Śliwa, W. *J. Incl. Phenom. Macrocycl. Chem.* **2005**, 52, 13–37.

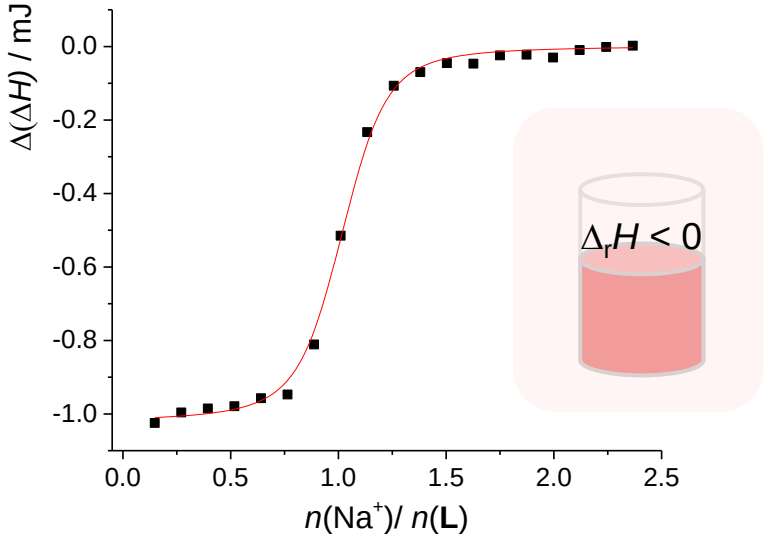
Experimental



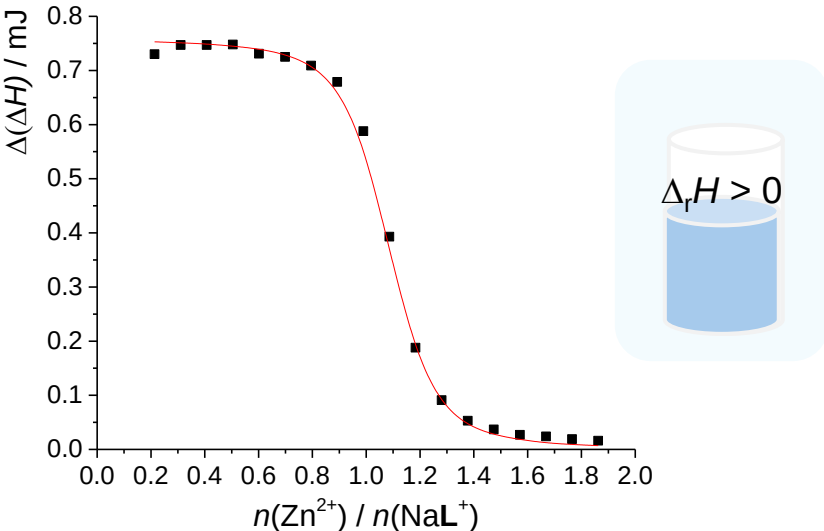
$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ = -RT \ln K^\circ$$



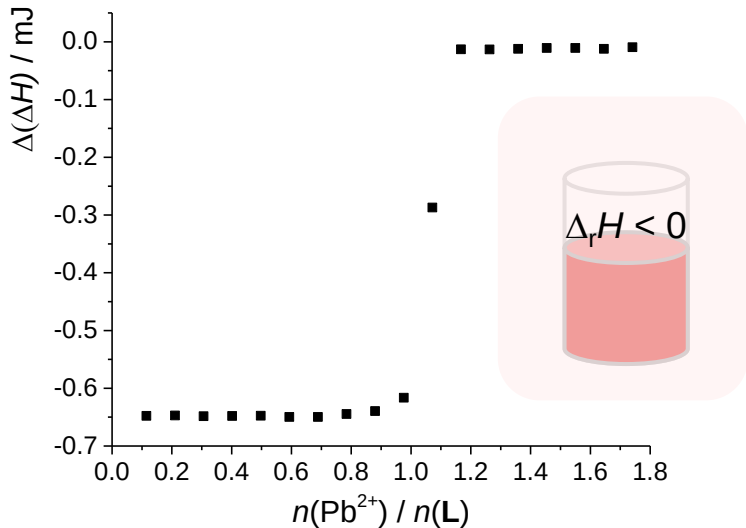
Na⁺ : direct titration of L


$$\begin{aligned}\log K(\text{NaL}^+) &= 5.61 \\ \Delta_r H &= -25.0 \text{ kJ mol}^{-1} \\ \Delta_r S &= 23.5 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

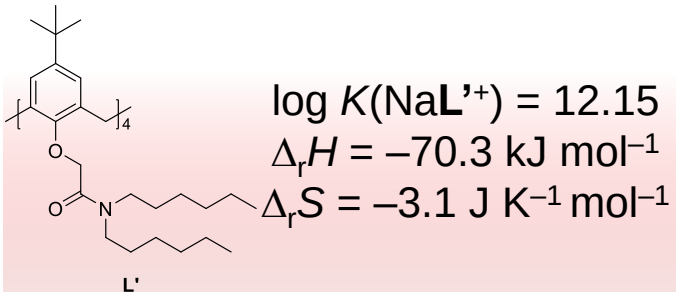
Zn²⁺ : competitive titration (NaL⁺)


$$\begin{aligned}\log K(\text{ZnL}^{2+}) &= 8.56 \\ \Delta_r H &= 23.2 \text{ kJ mol}^{-1} \\ \Delta_r S &= 242 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

Pb²⁺ : competitive titration (ZnL²⁺)



$\log K(\text{PbL}^{2+}) > 14$

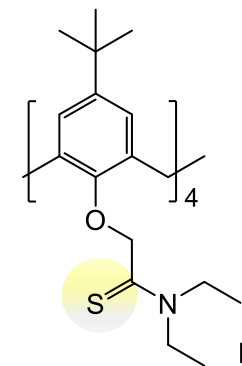
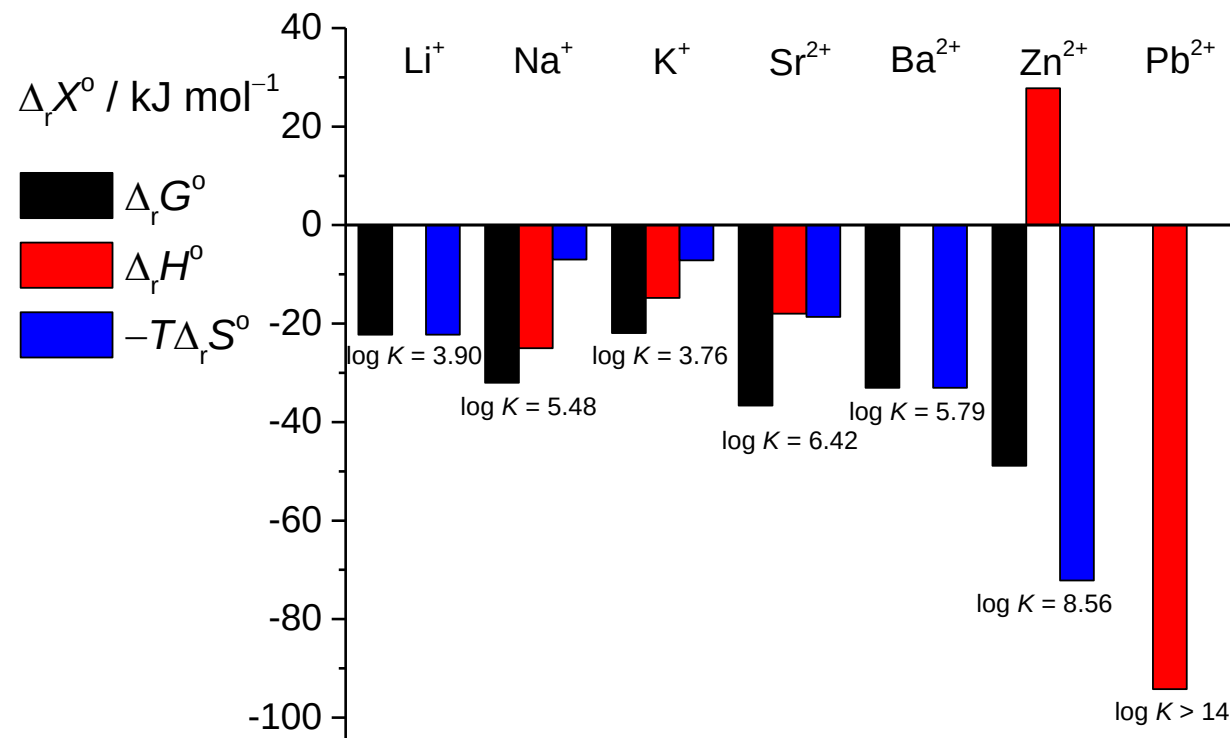
$$\Delta_r H = -94.2 \text{ kJ mol}^{-1}$$


G. Horvat et al., *Phys. Chem. Chem. Phys.* **19** (2017) 24316–24329.

Conclusions

stable complexes with alkali, alkaline-earth, and soft metal cations in acetonitrile

interplay of enthalpy and entropy contributions



model compound for the development of calixarene-based receptors for soft metal cations



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