Supplementary Material (ESI) for New Journal of Chemistry

Supplementary Information

Enthalpy driven nitrate complexation by guanidinium-based macrocycles

Pascal Blondeau, Jordi Benet-Buchholz, and Javier de Mendoza*

General

All commercially available reagents (Aldrich, Fluka, Acros, NovaBiochem, Panreac) were used without any further purification. The Dowex ion-exchange resin (PF_6^-) was prepared from the commercially available Dowex 1×8-200 ion exchange resin (Cl^-) by eluting with an aq. solution of HPF_6 (1M) until no chloride was detected (negative test with $AgNO_3$) and with distilled water until neutral pH.

Melting points were measured with a Büchi B-540 apparatus. The optical rotations $[\alpha]^{20}_D$ were determined on a Perkin-Elmer 241 MC polarimeter using a cell (1 dm) at 20 °C (Na_D 589 nm). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 500 Ultrashield NMR spectrometer, using the residual solvent peak as internal standard. Mass spectra were recorded on a Waters LCT Premier spectrometer using ESI technique.

Chrystallographic Studies

For crystal growth, a solution of **4** (3 mg) in CH_3CN (1 mL) was slowly allowed to evaporate at room temperature. For **5** a solution (3 mg) in CH_2Cl_2 (1 mL) was prepared and then left to evaporate in a saturated atmosphere of hexane for 2 days. For **6**, a solution in DMF (3 mg, 0.5 mL) was left to air-evaporate for 5 days at 80 ºC in a fume hood. The measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.

Data for **4**-**6** were collected on a Bruker-Nonius diffractometer equipped with a APPEX 2 4K CCD area detector, a FR591 rotating anode with $Mo_{K\alpha}$ radiation, Montel mirrors as monochromator and a Kryoflex low temperature device (T = -173 ^{o}C).[†] Full-sphere data collection was used with ω and φ scans. Programs used: Data collection Apex2 V. 1.0-22 (Bruker-Nonius 2004), data reduction Saint + Version 6.22 (Bruker-Nonius

2001) and absorption correction SADABS V. 2.10 (2003). Structure Solution and Refinement: SHELXTL Version 6.10 (Sheldrick, 2000) was used.[1]

ITC Titrations

ITC titrations were performed using an isothermal titration microcalorimeter Microcal VP-ITC. All measurements were performed at 303 K. The host solution was filled into the cell of the ITC instrument and guest solutions were added with the syringe. In each case control experiments with dilution of guest in the solvent were performed and were found to be negligible. Concentration of host (PF_6^-) (c = 1 mM in acetonitrile) and concentration of guest, tetrabutylammonium salts (c = 14 mM in acetonitrile) were similar for all titrations. The volume of injection was 5 µL and the stirring speed was 300 rpm. Samples were weight with a microbalance Mettler Toledo MX5. Tetrabutylammonium salts of acetate, benzoate and chloride were weight in a dry box. The solvent was previously degassed by sonication during 15 min. Titrations were made 3 times in order to be reproducible. Analysis and curve fitting were done using the software Origin 7.

^{1}H-NMR Titrations

Two standard solutions were prepared in acetonitrile, one with the receptor ($[R]_0$ = 0.005 M) and the other one with the substrate and receptor together ([S] = 0.05 M and $[R]_0$ = 0.005 M), in order to keep constant the concentration of receptor during the titration. All titrations were performed using an initial amount of 0.5 mL of receptor solution. To this solution increasing amounts of standard solution of the substrate (0.4 mL, 0 up to 5 equivalents) were added. After each addition, the ^{1}H-NMR spectrum was registered and the variation in the chemical shifts of the protons affected was plotted *versus* guest concentration. Association constants (K_a), measured from the guanidinium NH chemical shift, were obtained by using a non-linear square curve fitting program.[2]

[1] G. M. Sheldrick (1998) *SHELXTL Crystallographic System Ver. 5.10*, Bruker AXS, Inc.: Madison, Wisconsin.

[2] Software available on Prof. C. A. Hunter's web page: http://chris-hunter.staff.shef.ac.uk/soft.html.