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The inside and outside protonation of a 15-membered O_2N_2-macrocycle. Synthesis and structural characterization of the protonated ligand salts

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Abstract

Reactions of a mixed dioxa-diaza macrocycle 5,6,14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene (**L**) and various sodium salts NaX (X = picrate, ClO_4, BF_4, PF_6, SCN and BPh_4) in methanol afford the ion-pair compounds containing the protonated macrocyclic ligand as the cation, with the anion from the sodium salt as a counterion. The new compounds were identified and characterized on the basis of elemental analysis, spectroscopic studies (IR, ^{1}H NMR and MS), conductivity data and X-ray structure analysis. The mode of ligand protonation, as well as the hydrogen bond network which stabilizes the binding site of the proton in the protonated macrocyclic species, depend on the sodium salt used. It was found that the proton-to-ligand ratio is 1:1 in the picrate salt (**1**), 1:2 in the perchlorate (**2**), tetrafluoroborate (**3**), hexafluorophosphate (**4**) and thiocyanate (**5**) salts, and 2:3 in the tetraphenylborate salt (**6**), which was converted by recrystallization in acetonitrile into the 1:1 salt (**7**). In the 1:1 proton:ligand compounds, [H(**L**)]X, the intraligand monoprotonation occurs in two modes: the proton is either bound to one of the nitrogen atoms (**1**) or is disordered between two nitrogen atoms (**7**). In the compounds with 1:2, $[H(\mathbf{L})_2]X$, and 2:3, $[H_2(\mathbf{L})_3](X)_2$, proton-to-ligand ratios, there is interligand protonation where one proton is located between nitrogen atoms from two macrocyclic molecules (**2**–**5**) or two protons are shared between nitrogens from three ligand moieties (**6**). Crystallographic and infrared spectroscopic data indicate some differences in location of the proton between the nitrogen atoms in the monoprotonated ligand salts **2**–**5**.

Keywords: Dioxa-diaza macrocycle; Protonation; Spectroscopy; Crystal structures; Hydrogen bonding

1. Introduction

The chemistry of oxygen–nitrogen mixed-donor macrocycles has attracted continuous attention due to their ability to bind selectively different chemical species. With an appropriate combination of the macrocyclic cavity size, shape and topology, substituent effects as well as the number, type and arrangement of donor atoms, these polydentate ligands are able to bind a wider variety of both cations and anions than single heteroatom ligands such as oxygen-containing or nitrogen-containing macrocycles [1,2]. Although these ligands favour transition and post-transition metal ions [3–7], the selected derivatives also form complexes with alkali [8], alkaline earth [9] and lanthanide cations [10], as well as with ammonium [2,11] and oxonium [12]

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ions. In the case of the interaction with some anionic and neutral organic and biological substrates, supramolecular compounds of specific properties and applications were prepared [12,13]. The presence of basic amino sites in the macrocyclic molecule also enables diffusion of a proton inside the molecular cavity, followed by ligand protonation and formation of the protonated derivatives [14–16]. In general, the proton transfer reaction is of great importance in chemistry and biology. It plays a fundamental role in numerous processes including acid–base neutralization and electrophilic addition, and it is involved in transport phenomena, photosynthesis, enzyme reactions, etc. [17]. In general, the problem of proton transfer is important but very complex and far from resolution although there is significant progress due to the application of new theoretical methods using powerful computers [18] and experimental findings on ultrafast reactions involving proton transfers that are induced by lasers [19]. The proton transfer properties of macrocyclic compounds are connected with the number of amino groups in the molecular skeleton, their type (secondary and tertiary) and nature (aliphatic and aromatic), the length of the linkers, the presence of different donor groups in the ligand frame as well as the flexibility/rigidity and the overall structure of the macrocyclic molecule [15]. In addition, the protonated macrocycles can interact with simple as well as with more complex inorganic and organic anions, and their complexation properties are based on the solvation and hydrogen bonding capabilities of both the protonated moiety and the accompanying anion.

In the present work, we investigate the protonation behaviour of 5,6,14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene (**L**) in the interaction with various sodium salts in methanol solution, since it was shown that this dioxa-diaza macrocycle forms the protonated species and does not bind the sodium ion in these reactions. In general, protonation of aza macrocycles would be expected in acidic medium. Thus, the dihydronitrate salt $[H_2(\mathbf{L})](NO_3)_2$ was obtained by the hydrogenation with sodium tetrahydroborate of the structurally related macrocyclic diimine, which was used as a precursor for the synthesis of **L**, and the successive reaction with HNO_3 in a methanol–water solution [16]. In previous studies, it was demonstrated that this mixed-donor ligand binds some transition metal ions in reactions with the corresponding metal salts in methanol solution. Complexes of the type $M(\mathbf{L})X_2$, where M = Ni, Co, Zn or Cd; X = Cl, Br, I or NCS, were synthesized and examined [4,5,20,21]. Interactions between **L** and alkali metal ions have not been studied yet. We report here the preparation and structural characterization of the protonated ligand salts obtained by reactions of this 15-membered macrocycle with a series of sodium salts.

2. Experimental

2.1. Materials and instrumentation

5,6,14,15-Dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene (**L**) was used directly as supplied (Aldrich). Sodium perchlorate, tetrafluoroborate, hexafluorophosphate, tetraphenylborate and thiocyanate salts were commercial chemicals of the highest purity available and used without further purification except for vacuum drying over P_4O_{10} and storing in a dry-box prior to use. Sodium picrate was prepared and purified as described. Solvents used (AR grade) were purified and dried by standard procedures.

Melting points were determined on a hot stage microscope and are uncorrected. FTIR spectra were recorded on an ABB Bomen MB102 spectrometer using KBr pellets. ESI mass measurements were performed on a Finnigan LCQ DECA instrument (ThermoFinnigan, Palo Alto, CA) operating in the positive ion mode. Compounds were dissolved in methanol or acetonitrile (10^{-6} M solutions) and directly injected by a syringe pump at a flow of 5 μL min^{-1}. LDI mass spectra were performed on a Voyager-DE PRO instrument (Applied Biosystems, Foster City, CA), operating in the linear positive ion mode. External mass calibration was done using the Calibration Mixture 1 of Sequazyme Peptide Mass Standards Kit, based on the monoisotopic values of $[M + H]^+$ of des-arg-bradykinin, angiotensin, glu-fibrinopeptide B and neurotensin at *m/z* 905, 1297, 1571 and 1673, respectively. The ^1H NMR spectra were recorded with Varian 300 Gemini and Bruker XWIN-600 Fourier-transform spectrometers in DMSO-d_6 at 300 K. Chemical shifts were referred to the residual solvent signal at 2.51 ppm. The two-dimensional experiments were performed by standard pulse sequences, using Gemini Data System software Version 6.3 Revision A and Bruker XWIN-NMR software Version 3.5. Conductance measurements were carried out at room temperature using a CD 7A Tacussel conductance bridge for 10^{-3} mol^{-1} solutions in DMF. Elemental analyses (CHNS) were performed on a Perkin–Elmer Analyser PE 2400 Series 2 and thermogravimetric analyses with a Cahn RG electromicrobalance in air atmosphere.

2.2. Preparations of the compounds

2.2.1. *[H(**L**)](picrate) (**1**)*

A mixture of 5,6,14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene (**L**) (0.110 g, 0.35 mmol) and sodium picrate (0.108 g, 0.40 mmol) in dry MeOH (10 cm^3) was refluxed for 1–2 h with continuous stirring. The yellow-orange microcrystalline product, which precipitated immediately after cooling to room temperature was collected by filtration, washed with cold MeOH,