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Utility of charge-transfer complexation for the assessment of macrocyclic polyethers: Spectroscopic, thermal and surface morphology characteristics of two highly crown ethers complexed with acido acceptors

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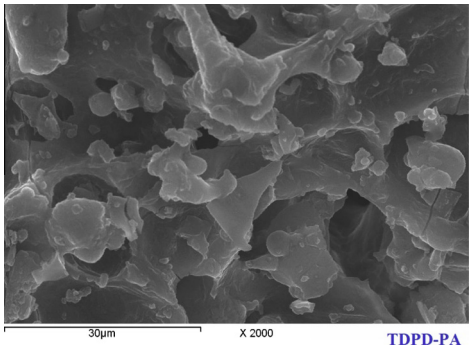
HIGHLIGHTS

- CT complexes of two macrocyclic crown ethers were reported.
- Bonding modes were ascertained from various spectral techniques.
- Complexes were characterized in both solution and solid state.
- Spectroscopic, thermal and kinetic properties were determined.
- Microstructure properties of the reported complexes were observed.

GRAPHICAL ABSTRACT

The morphology of the TDPD–PA complex.



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ABSTRACT

The study of the complexing ability of macrocyclic compounds to organic and inorganic substances is of great interest. The aim of this work is to provide basic data that can be used to the assessment of macrocyclic crown ethers quantitatively based on charge-transfer (CT) complexation. This goal was achieved by preparing CT complexes of two interesting mixed nitrogen–oxygen crown ethers with acido acceptors (chloranilic and picric acid), which were fully structurally characterized. The crown ethers are 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (HDHC) and 1,4,10-trioxa-7,13-diaza-cyclopentadecane (TDPD). The obtained complexes were structurally characterized via elemental analysis, IR, Raman, ^{1}H NMR, and UV–visible spectroscopy. Thermal properties of these complexes were also studied, and their kinetic thermodynamic parameters were calculated. Furthermore, the microstructure properties of these complexes have also been investigated using X-ray diffraction (XRD) and scanning electron microscope (SEM).

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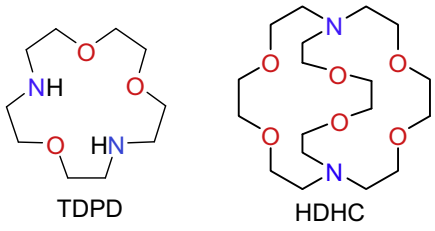
Introduction

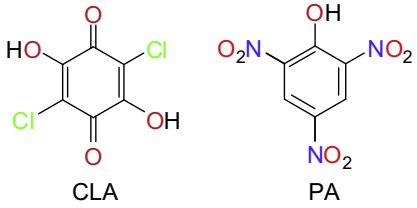
Charge-transfer (CT) or donor–acceptor interactions have attracted considerable interest and growing importance. During the last two decades, a large number of studies have been reported on CT or proton-transfer interactions in solid state and in solution. This is owing to their significant physical and chemical properties [1–9]. CT interaction was first introduced by Mulliken [10–13] and has been widely discussed by Foster [14]. The formation of CT complexes may generally be attributed to a transfer of negative electrical charge from an electron donor molecule to an acceptor molecule and it is natural to classify the process involved as a "charge-transfer" interaction. The organic electron donors with donor atoms such as nitrogen, sulfur and oxygen or of mixed donor atoms are well known to form stable CT complexes with a number of σ- and π-acceptors. CT complexation is of great importance in chemical and photochemical reactions, including addition, substitution, condensation [15], molecular self-assemblies [16,17], biochemical and bioelectrochemical energy-transfer processes [18], biological systems [19], and drug-receptor binding mechanisms [20–23].

CT interactions are in most cases associated with the formation of intensely colored product. Such interactions play important roles in many processes such as understanding the drug-receptor binding and quantitative estimation of drugs. The crystalline drug-acceptor complexes have a vital role in biological systems such as antimicrobial activity and DNA-binding. Also, literature shows that these complexes exhibit potential antimicrobial properties against Gram-positive and Gram-negative bacteria as well as fungi [24–34]. Because of the high electrical conductivities of some CT solid products, this complexation found many significant applications in electronics, optical devices, non-linear optical materials, electrically conductive materials, microemulsions, surface chemistry, photocatalysts, dendrimers, solar energy storage, organic semiconductors, and the investigation of redox processes [35–42].

Since several years we have investigated intensively the CT interactions (synthesis, characterization and application) [43–68]. As part of our continuing interest in this field, this research was performed to describe the complexation chemistry of two crown ethers namely 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane (HDHC) and 1,4,10-trioxa-7,13-diaza-cyclopentadecane (TDPD) (Scheme 1) with acido acceptors; chloranilic acid (CLA) and picric acid (PA) (Scheme 2). The PA possesses one proton donor group, while the CLA possess two equivalent groups. Moreover CLA is interesting from a biological point of view as a benzoquinone derivative being an electron accepting system. The formed complexes were characterized by spectroscopy (UV–vis., IR, Raman and ^{1}H NMR), elemental and thermal analyses. The mechanism of the interactions was discussed based on the obtained spectral data. The microstructure properties of these complexes were determined using X-ray diffraction (XRD) and scanning electron microscope (SEM).



Scheme 1. The structure of crown ethers (donors) (TDPD and HDHC).



Scheme 2. The structure of acido acceptors (CLA and PA).

Experimental methods and calculations

Chemicals and solutions

All chemicals were obtained in analytical purity and were used as purchased. The crown ethers of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (HDHC; $C_{18}H_{36}N_2O_6$; 376.49 g/mol), and 1,4,10-trioxa-7,13-diaza-cyclopentadecane (TDPD; $C_{10}H_{22}N_2O_3$; 218.29 g/mol) (Scheme 1) were obtained from Aldrich Chemical Company (USA) with a stated purity of greater than 98% and were used without further purification. The acido acceptors of chloranilic acid (CLA; $C_6H_2Cl_2O_4$; 208.98 g/mol) and picric acid (PA; $C_6H_3N_3O_7$; 229.10 g/mol) (Scheme 2) were purchased from Merck (Darmstadt, Germany) and were used without modification. Methanol of HPLC grade was also from Merck (Darmstadt, Germany). Standard stock solutions of crown ether donors and each acceptor at a concentration of 5.0×10^{-3} M were freshly prepared prior to each series of measurements by dissolving precisely weighed quantities in a 100 mL volumetric flask using methanol solvent. The stock solutions of donors (HDHC and TDPD) and acceptors (CLA or PA) were protected from light. Solutions for spectroscopic measurements were made by mixing appropriate volumes of donor and acceptor stock solutions with the solvent immediately before running the spectra.

Reaction chemistry

The solid CT complexes of HDHC–CLA, HDHC–PA, TDPD–CLA and TDPD–PA were prepared according to the literature methods reported [14,19,31,67,68]. The synthesis procedure is summarized as follows. Two mmol of each donor (20 ml) was added to 20 ml of methanolic solutions containing CLA or PA (2 mmol) and stirred at room temperature for 1 h. Strong change in colors was observed upon mixing solutions of the donors with the acceptors. These changes in colors represent strong evidence of the CT interactions between the donors and the acceptors. The volume of the solution was reduced to one-half by evaporation on a water bath. The resulting solutions were allowed to stand at room temperature. The formed complexes were isolated, filtered off and washed twice thoroughly with the minimum given solvent to obtain the pure products. The complexes were then collected and dried *in vacuo* for 48 h. The four title complexes were characterized by spectroscopy (UV–vis., IR, Raman and ^{1}H NMR), elemental and thermal analyses.

Stoichiometry determination

In solution-state

To determine the stoichiometry of the donor–acceptor CT interactions in solution-state, various molar ratios were examined by spectrophotometric titration measurements. These titrations monitored the detectable CT bands during the reactions of HDHC and TDPD with CLA or PA. Briefly, 0.25, 0.50, 0.75, 1.00, 1.50, 2.0, 2.50, 3.00, 3.50 or 4.00 mL of a standard solution (5.0×10^{-4} M)