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Due to their unique properties transition metal porphyrins are widely used in many technological applications such as sensors, solar cells, nonlinear optics and nanomaterials [1]. During the last decade the coordination properties and conformational flexibility of porphyrins were heavily exploited in a search of prospective isomers able to deliver better functionality in specific technological applications [1]. One such important class of porphyrins is the nitrogen-confused porphyrins (NCPs), which are novel and prospective materials with improved properties for use as acid catalysts and anion/cation sensors [2]. These porphyrin isomers differ greatly from the parent porphyrins, particularly in their chemical structure and their physical and coordination properties. The multivalent nature of NCPs as a metal ligand provides a potential strategy for stabilising and studying higher or atypical oxidation states of metals, e.g. Ni(I), Ni(III), Cu(III), Ag(III), or unusual coordination geometries [2]. In addition, the outer nitrogen or carbon atoms of the inverted pyrrole ring can be directly connected resulting in oligomeric porphyrin arrays with interesting applications. Using NCPs in such molecular arrays provides new modes of linking single molecules and different coordination properties of the resulting oligomers [2]. In order to realize their full potential a detailed knowledge of the electronic structure and chemical bonding in porphyrins is required. Such information can be obtained with x-ray absorption spectroscopy (XAS).

Here we apply XAS to study the chemical bonding features in Ni porphyrins. The main goal is to understand in detail how the electronic structure changes in going from Ni porphyrin to Ni N-confused porphyrin by a direct comparison of the corresponding x-ray absorption spectra.

XAS measurements were performed at the D1011 beamline at MAX II storage ring in Lund, Sweden. Thick porphyrin layers (~20 nm) were prepared *in situ* by thermal evaporation of powder material onto a polished polycrystalline copper substrate. The XAS spectra were recorded in the total electron yield detection mode by measuring the sample drain current. The estimated photon-energy resolution at the Ni 2p (~850 eV) and N 1s (~400 eV) absorption thresholds was better than 200 meV and 100 meV, respectively.

The molecular formulas of the Ni porphine (NiP), Ni tetraphenylporphyrin (NiTPP), Ni nitrogen-confused tetraphenylporphyrin (NiNCTPP) and free-base porphine (H_2P) are shown in Fig. 1. The measured Ni 2p x-ray absorption spectra for the Ni compounds under study are shown in Fig. 2. The Ni $2p_{3/2}$ XAS of the NiP and NiTPP have a very similar shape: the main absorption line A at the photon energy of 853.9 eV is accompanied by high-energy lines A_2, C and D. The difference between them and the Ni $2p_{3/2}$ XAS of metallic Ni can be understood within the framework of quasi-molecular approach [3, 4] with inclusion of the covalent mixing between the Ni and ligand (N and C) atoms. The main line A in the Ni $2p_{3/2}$ XAS of Ni porphyrins is associated with transitions of Ni $2p_{3/2}$ electrons to the LUMO, which is the antibonding σ-MO of b_{1g} symmetry with predominantly Ni $3d_{x2-y2}$ character. In turn, the structures A_2, C, C* and D are associated with transitions to empty states with hybridized Ni 3d – ligand 2p character. The high-energy shift of the Ni $2p_{3/2}$ absorption in going from Ni metal to Ni porphyrins (1.2 eV) is a result of the decrease in the effective number of 3d electrons on the Ni atom due to the strong Ni 3d – ligand 2p π-type covalent bonding. This metal-to-ligand charge transfer (back-donation) in the Ni porphyrins occurs from the occupied Ni $3d_{xz,yz}$ π (e_g) orbitals to the unoccupied ligand $2p\pi*$ (e_g) orbitals [3].

Three main differences are observed between the Ni $2p_{3/2}$ XAS (Fig. 2) of the NiNCTPP and NiP (and/or NiTPP): (i) the reliably measured high-energy shift of the main absorption line A by 0.5 eV in the NiNCTPP compared to NiP (NiTPP), (ii) an additional low-energy shoulder A_1 separated in energy by approximately 0.8 eV from the main line A in the XAS of the NiNCTPP and (iii) the presence of the high-energy doublet structure A_2-A_3 in the spectrum of the NiNCTPP compared to the

single absorption line A_2 in the NiP (NiTPP). The first two findings reflect a larger transfer of the 3d electron density from the Ni atom to the ligands and the stronger Ni 3d – ligand 2p covalent bonding in the case of the NiNCTPP compared to the other Ni porphyrins indicating a smaller effective number of 3d electrons on the central Ni atom (higher oxidation state) in this nitrogen-confused porphyrin. The third finding is due to a lowering of the symmetry of the porphyrin macrocycle (Ni atom and its nearest neighbours) from D_{4h} (NiP, NiTPP) to C_{2v} in the NiNCTPP [1, 2].
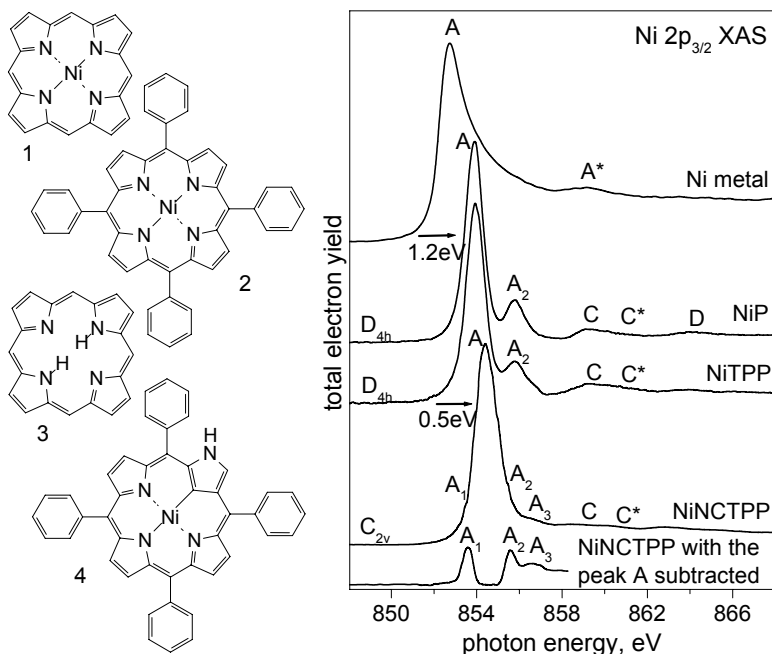
Fig. 1. NiP (1), NiTPP (2), H_2P (3) and NiNCTPP (4).

Fig. 2. Ni $2p_{3/2}$ XAS of the Ni metal and Ni porphyrins under study.
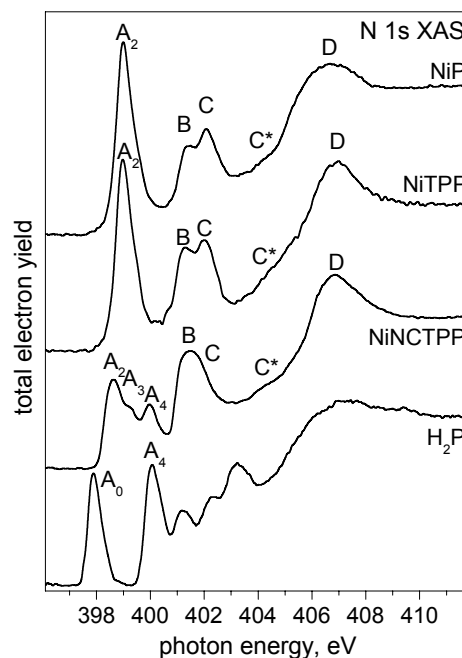
Fig. 3. N 1s XAS of the Ni porphyrins and free-base porphine H_2P.

Comparing the N 1s XAS (Fig. 3) of the Ni porphyrins an interesting shape is observed for the low-energy absorption structures related to the π MOs (structures A_2-A_4) in the spectrum of NiNCTPP. This is associated with (i) the non-equivalence of the confused N atom and the three N atoms bonded to the central Ni atom and (ii) the C_{2v} symmetry of the NiNCTPP macrocycle. In the N 1s XAS of the H_2P, shown in Fig. 3, there are two strong low-energy absorption structures A_0 and A_4 that are related to the π MOs and arise due to the two different N sites in the centre of free-base porphyrin macrocycle. The structure A_0 observed at a photon energy of 397.9 eV is produced by iminic (-C=N-) nitrogens, while the structure A_4 at 400.0 eV results from pyrrolic (-NH-) nitrogens [5]. Thus, in the N 1s spectrum of the NiNCTPP the absorption structure A_4 (400.0 eV) can be associated with the confused N atom, which is of pyrrolic type in this porphyrin (i.e. protonated). In turn, taking into account the C_{2v} symmetry of the NiNCTPP macrocycle and the relative intensities of the A_2-A_4 absorption structures, the structure A_2 is associated with electron transitions to MOs localized on two diagonally opposed N atoms bonded to the central Ni atom, while the structure A_3 is associated with the N atom bonded to the Ni atom and opposite to the inner C atom.

Thus, applying XAS to Ni porphyrins information about their electronic structure can be obtained. Furthermore, the experimentally observed energy shift of band A can be used as a qualitative, and possibly as a quantitative, characterization of back-donation strength (charge-transfer) and the oxidation state of a metal atom in similar Ni compounds.

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