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Abstract
Investigations of chemical bonding and electronic structure features for
polycrystalline (porphyrinato)nickel (II) (NiP, the simplest Ni porphyrin),
(5,10,15,20-tetraphenylporphyrinato)nickel (II) (NiTPP) and
(2-aza-21-carba-5,10,15,20-tetraphenylporphyrinato)nickel (II) (N-confused NiTPP, NiNCTPP)
have been performed by means of high-resolution soft x-ray absorption and x-ray
photoemission spectroscopy. The Ni $2p_{3/2}$ x-ray absorption spectra show strong
π-back-bonding in these compounds leading to a high-energy shift (1.2 eV for the NiP and
NiTPP) of the entire absorption structure compared to Ni metal. It has been found that the main
absorption line of the Ni $2p_{3/2}$ spectrum of the NiNCTPP is shifted by an additional 0.5 eV to
higher energies in comparison with those for other nickel porphyrins. This shift is evidence of
stronger back-donation (metal-to-ligand charge transfer) and a smaller effective number of 3d
electrons on the central Ni atom in the NiNCTPP as compared to other Ni porphyrins. The
confused N atom in the NiNCTPP is of pyrrolic type (protonated nitrogen), which was
confirmed by the N 1s absorption and core-level photoemission spectra.

1. Introduction

Due to their unique properties 3d transition metal (TM) porphyrins are widely used in many technological applications such as sensors, pigments applications, cancer therapy, artificial photosynthesis, nonlinear optics, and nanomaterials [1]. Such interest is closely related to their biological significance and catalytic importance. During the last decade the coordination properties and conformational flexibility of porphyrins were heavily exploited in a search of prospective porphyrin

isomers able to deliver better functionality in specific technological applications [1, 2]. 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 [3]. These porphyrin isomers differ greatly from the parent porphyrins, particularly in their chemical structure and their physical and coordination properties [3–6]. The multivalent nature of NCPs as a metal ligand provides a potential strategy for stabilizing and studying higher or atypical oxidation states of metals, e.g. Ni(I), Ni(III), Cu(III), Ag(III), or unusual coordination geometries [3, 4]. In addition, the outer nitrogen or carbon

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atoms of the inverted pyrrole ring can be directly connected resulting in oligomeric porphyrin arrays with interesting applications [3, 4, 7]. Using NCPs in such molecular arrays provides new modes of linking single molecules and different coordination properties of the resulting oligomers [3, 4, 7].

The synthesis of novel TM porphyrins has received great attention in the past few years [2, 4, 7–9], while spectroscopic characterization of their electronic structure remains a less well investigated area [10–15]. Experimental studies of TM porphyrins carried out recently have provided useful information about their electronic structure and physical–chemical properties [10–12, 15], but the lack of well reasoned explanations of the results leaves open questions about the nature of the chemical bonding in these compounds. The central part of these complexes (3d atom and its nearest neighbours) is known to define their most important applications and reactivity. Thus it is evident that a detailed knowledge of the electronic structure and chemical bonding in these 3d TM macrocyclic rings is required for the realization of their full potential. Such information can be obtained with high-resolution x-ray absorption (XA) spectroscopy and x-ray photoemission spectroscopy (XPS).

The objective of this work is to reveal the chemical bonding features in Ni porphyrins by studying the unoccupied and occupied electronic states in these compounds with XA and XPS. 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 and photoemission spectra. It is expected that the different structure of the porphyrin macrocycle in these molecules should reflect not only on the characteristic spectral features associated with specific electron transitions within the macrocycle, but also on the metal-to-ligand charge transfer in these complexes.

2. Experimental details

The XA and XPS measurements on the (porphyrinato)nickel (II) (Ni porphine, NiP), (5,10,15,20-tetraphenylporphyrinato) nickel (II) (NiTPP) and (2-aza-21-carba-5,10,15,20-tetraphenylporphyrinato)nickel (II) (N-confused NiTPP, NiNCTPP), as well as the reference compounds Ni metal and free-base porphine (H_2P), were performed at the Russian–German beamline [16] at the BESSY II storage ring (Berlin, Germany). Some of the measurements were repeated under similar experimental conditions at the D1011 beamline [17] at MAX-II storage ring in MAX-Laboratory for Synchrotron Radiation Research (Lund, Sweden). Thick porphyrin layers (∼50 nm) were prepared *in situ* by thermal evaporation of powder material onto a polished polycrystalline copper substrate from a tantalum crucible in a homemade deposition cell operated at a temperature of approximately 600 K. The metal sample was a nickel foil cleaned by scraping with a diamond file in vacuum. The XA 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 (∼853 eV), N 1s (∼400 eV) and C 1s (∼285 eV) absorption thresholds was better than 150 meV, 70 meV and 60 meV, respectively. The
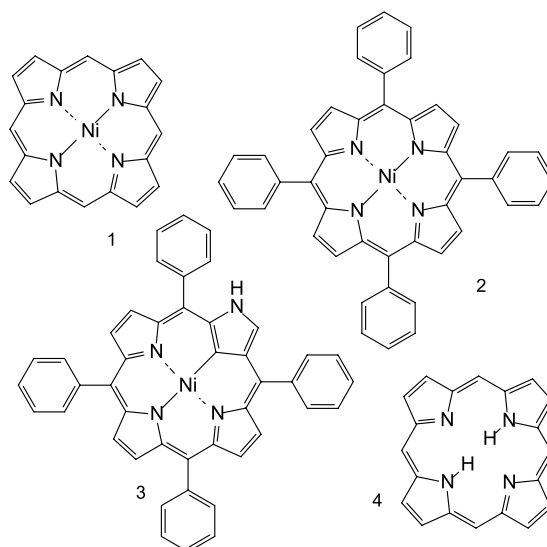

Figure 1. Structural formulae of the NiP (1), NiTPP (2), NiNCTPP (3) and H_2P(4).

spectra were normalized to the incident photon flux monitored by a gold grid. The photon energy at the Ni 2p, N 1s and C 1s edges was calibrated according to a published procedure [9], which allows a direct comparison of the energy positions of structures in different absorption spectra within an accuracy of 0.1 eV. Core-level photoemission spectra were acquired in the angle-integrated mode with a Phoibos 150 electron energy analyzer from SPECS GmbH. The total energy resolution was about 0.2 eV for the N 1s XPS spectra obtained at excitation photon energy of 500 eV. The (porphyrinato)nickel (II) complexes studied in this work were synthesized according to published procedures [3–6, 18, 19].

3. Results and discussion

Ni porphyrins represent a class of flexible molecules with nearly square planar core conformation [1]. The molecular formulae of the compounds under study are shown in figure 1. These square planar molecules have mainly a D_{4h} symmetry of the central part (Ni atom and its nearest neighbours) [1] except for the NiNCTPP, which has a C_{2v} symmetry [4].

The nickel atom formally has the electron configuration of the Ni^{2+} ion $[(3d_{xz,yz}e_g)^4 \ (3d_{z2}a_{1g})^2(3d_{xy}b_{2g})^2]$ in the Ni(II) compounds with D_{4h} symmetry. The chemical bonding of the nickel atom with four pyrrole rings results in the formation of four σ bonds due to in-plane mixing of ligand $2p\sigma$ states with Ni $3d_{z2}$ + 4s, $3d_{x2-y2}$ and $4p_{x,y}$ states, which are described by the a_{1g}, b_{1g} and e_u molecular orbitals (MOs), respectively [10, 20, 21]. In this case the a_{1g} and b_{1g} MOs represent the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively. An additional π bonding of the metal atom with the ligands is fulfilled by a covalent interaction of the Ni $3d_{xz,yz}$ orbitals with the out-of-plane ligand 2p orbitals which is accompanied by a charge transfer from the metal atom into the ligands (π-back-donation) [10, 20–24]. This covalent bonding results in a π-MO of e_g symmetry.
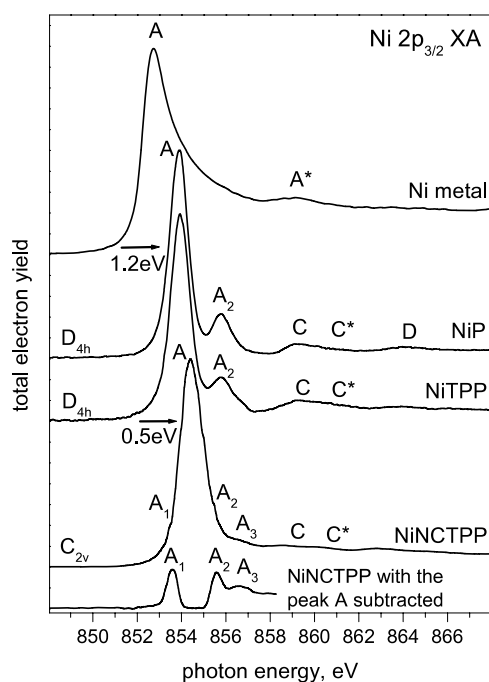
Figure 2. Ni 2p$_{3/2}$ XA spectra of the Ni metal and Ni porphyrins. The bottom spectrum shows the result of subtracting the main peak A from the NiNCTPP spectrum.

The measured Ni 2p x-ray absorption spectra for the Ni compounds under study are shown in figure 2. The intensities of the absorption structures in the spectra have been normalized such that the main absorption lines A have the same intensity. Examining the Ni 2p$_{3/2}$ absorption spectra of the NiP and NiTPP one can see that the spectra are very similar: 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 designations were made taking into account the following comparative analysis of Ni 2p$_{3/2}$, N 1s and C 1s absorption spectra). These structures result from the Ni 2p$_{3/2}$–3d, 4s transitions and are clearly observed over the 10–12 eV energy range above the Ni 2p$_{3/2}$ absorption onset. In turn, the Ni 2p$_{3/2}$ XA spectrum of metallic Ni consists of only one main line A accompanied by the so-called '6-eV' satellite A* assigned to multiple scattering from the environment (neighbouring Ni atoms) at intermediate range [25]. This assignment was based on one-electron real space multiple scattering calculations and the observation that the '6-eV' feature disappears in the case of very thin Ni metal films.

The difference between the absorption spectra of the Ni metal and the Ni(II) porphyrins can be understood within the framework of a quasi-molecular approach [10, 26] with inclusion of covalent mixing between the valence electron states of the Ni and ligand atoms. The covalent bonding between the Ni and ligand (N and C) atoms with participation of the Ni 3d, 4s and ligand 2p electrons is responsible for the appearance of the additional 2p$_{3/2}$ absorption bands in going from Ni metal to the Ni porphyrins. Thus, on the basis of a comparison with the Ni 2p$_{3/2}$ XA spectrum of Ni metal and density functional theory (DFT) calculations [20, 21] the main line A in the Ni 2p$_{3/2}$ XA spectra of Ni porphyrins (figure 2)

can be 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$_{x^2-y^2}$ character (almost pure intra-atomic Ni 2p$_{3/2}$–3d$_{x^2-y^2}$ electron transitions). In turn, the structures A$_2$, C, C* and D are associated with transitions to empty states with hybridized Ni 3d–ligand 2p character (some contribution to the MOs responsible for the XA structures C, C* and D may be due to the Ni 4s, p states). 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 causes a delocalization of the 3d states, decreasing the 3d electron density on the nickel atom and thus a decrease in the screening of the Ni 2p–3d electron transitions and a corresponding increase in their energy (high-energy shift). This metal-to-ligand charge transfer (back-donation) in the Ni porphyrins occurs from the occupied Ni 3d$_{xz,yz}\pi$ (e$_g$) orbitals to the unoccupied ligand 2pπ^*(e$_g$) orbitals, resulting in the corresponding absorption band A$_2$ in the Ni 2p$_{3/2}$ XA spectra [10].

Three main differences are observed between the Ni 2p$_{3/2}$ XA spectra (figure 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) the presence of an additional low-energy shoulder A$_1$ separated in energy by approximately 0.8 eV from the main line A in the XA spectrum of the NiNCTPP and (iii) the presence of the high-energy double structure A$_2$–A$_3$ in the spectrum of the NiNCTPP compared to the single absorption line A$_2$ in the NiP (NiTPP). All of these absorption features are clearly visible on the bottom spectrum of figure 2, which is obtained by subtracting the main peak A from the Ni 2p$_{3/2}$ XA spectrum of the NiNCTPP. 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. This is reasonable in light of the smaller Ni–C bond distance (1.90 Å) in NiNCTPP, leading to a stronger covalent bonding, compared to the Ni–N bond distance (1.96 Å) in the planar Ni porphyrins [4, 27–30]. According to DFT calculations the effective charge on the central Ni atom is equal to +1.68 and +1.8*e* in the Ni(II) porphine and Ni(II) phthalocyanine, respectively [31, 32]. It should be noted that an electron charge of approximately 0.5*e* is transferred from the highest filled ligand 2p MO to the Ni 4s states through σ electron donation [20, 31, 32]. Thus, taking into account the high-energy shifts of the entire Ni 2p absorption structure observed for the Ni(II) porphine (1.2 eV), Ni(II) phthalocyanine (1.4 eV) [10] and the NiNCTPP (1.7 eV) relative to the Ni metal, one can calculate that the effective charge on the central Ni atom is equal to +2.2*e* in the NiNCTPP. In comparison with non-confused Ni(II) porphyrins, this is equivalent to an additional charge transfer of approximately 0.5 of a 3d electron from the central Ni atom to the ligand atoms in the NiNCTPP. This additional charge transfer results in a new unoccupied MO responsible for the low-energy absorption structure A$_1$, which is
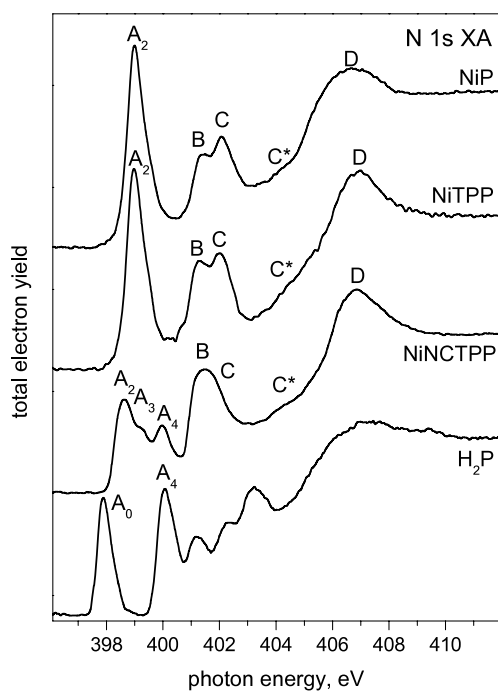
Figure 3. N 1s XA spectra of the Ni porphyrins and free-base porphine H_2P.
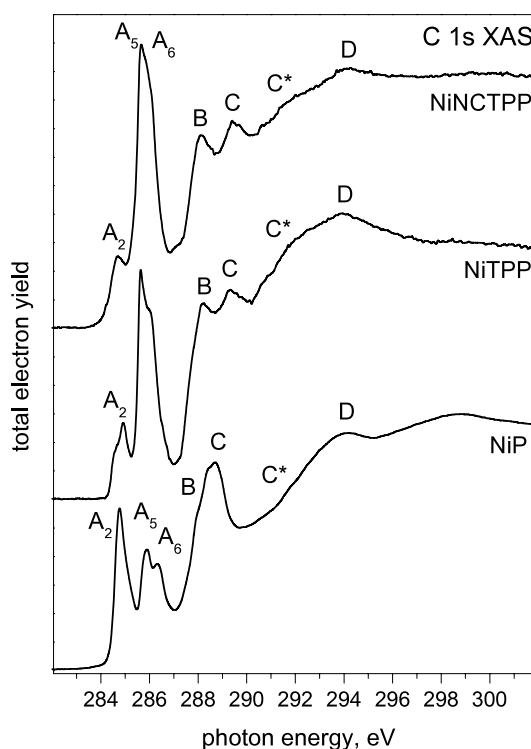

Figure 4. C 1s XA spectra of the Ni porphyrins.

only observed in the Ni $2p_{3/2}$ XA spectrum of the NiNCTPP. Furthermore, a comparative study of the (5,10,15,20-tetra phenylporphyrinato)copper (II)(CuTPP) and (2-aza-21-carba-5,10,15,20-tetraphenylporphyrinato)copper (II) (CuNCTPP), performed by continuous-wave and pulse electron paramagnetic resonance (EPR) methods and DFT calculations, shows much stronger character of the covalent bonding between the Cu atom and the directly coordinating ligand atoms in the N-confused complex [33]. In addition, the analysis of the bonding parameters clearly shows that the Cu–C bond is the strongest among the other metal–ligand bonds in the CuNCTPP [33], which is in good agreement with conclusions stated above for the NiNCTPP. The single absorption structure A_2 observed in the spectra of the NiP and NiTPP appears in the case of the NiNCTPP as a broad, low intensity doublet structure A_2–A_3. This results from a splitting of the doubly degenerated e_g MO, responsible for the A_2 absorption band in the NiP and NiTPP, into b_1 and b_2 MOs with mixed Ni $3d\pi$–ligand $2p\pi$ character. This splitting is due to a lowering of the symmetry of the central part (Ni atom and its nearest neighbours) of the porphyrin molecule from D_{4h} (NiP, NiTPP) to C_{2v} in the NiNCTPP [1, 4].

Comparing the N 1s XA spectra (figure 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 NiN$_3$C quasi-molecule (central part of the NiNCTPP) in this porphyrin. In the N 1s XA spectrum of the free-base porphine H_2P, shown in figure 3 for comparison, 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 [12], which correlates well with the N 1s core-level XPS data presented below. 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 NiN$_3$C quasi-molecule in the NiNCTPP 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 (i.e. N atoms on positions 22 and 24 of the porphyrin macrocycle), while the structure A_3 is associated with the N atom bonded to the Ni atom and opposite to the inner C atom. This conclusion is confirmed by the presence of the doublet structure A_2–A_3 in the Ni $2p_{3/2}$ spectrum of the NiNCTPP, which was assigned to electron transitions into b_1 and b_2 MOs having mixed Ni $3d\pi$–ligand $2p\pi$ character. In the case of the square planar NiP and NiTPP the absorption structure A_2 is due to electron transitions to hybridized Ni $3d\pi$–ligand $2p\pi$ unoccupied states and is observed as a single peak because of the equivalence of all four N atoms bonded to the central Ni atom in these porphyrins. In turn, the structures B and C can be associated with an electron transition to the empty MOs formed by the N and C $2p\pi$ orbitals of the pyrrole rings.

The measured C 1s x-ray absorption spectra for the studied Ni compounds are shown in figure 4. The double absorption structure A_5–A_6 observed only in the C 1s XA spectra is associated with pure C $2p\pi$ states, where the C atoms are in
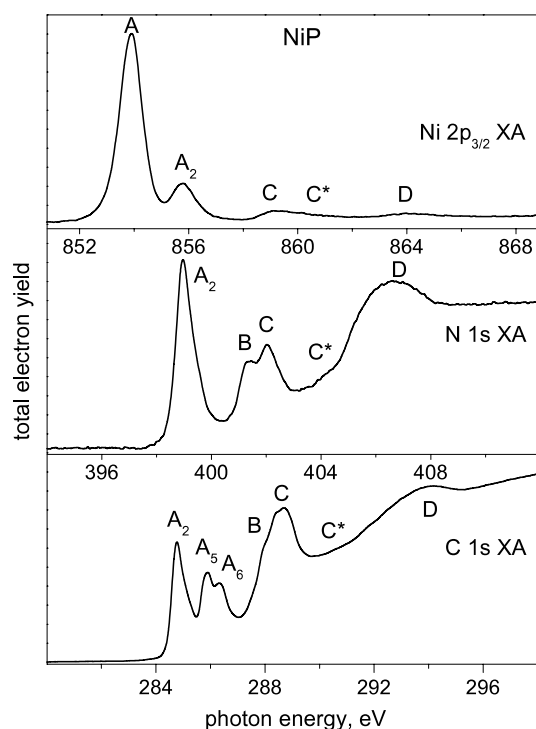
Figure 5. X-ray absorption spectra of NiP. The energy scales of the spectra are aligned using the measured differences between the core levels ΔE (Ni $2p_{3/2}$–C 1s) = 570.8 eV and ΔE (N 1s–C 1s) = 114.3 eV.

the *meso*-positions and its nearest neighbours (C atoms of the pyrrole rings) in the porphyrin macrocycle for the case of Ni porphine. In turn, in the C 1s XA spectra of the NiTPP and NiNCTPP the intensity of the corresponding π resonances A_5–A_6 is much higher than in the NiP spectrum. This is due to the additional contribution from the phenyl rings attached to the *meso*-positions of the porphyrin macrocycle, which is also associated with pure C $2p\pi$ states. As mentioned above, the absorption structure A_2 in the spectrum of the square planar NiP is due to hybridized Ni $3d\pi$–ligand $2p\pi$ unoccupied states, while the structures B and C are associated with the empty MOs formed by the N and C $2p\pi$ orbitals of the pyrrole rings. A complete interpretation of these spectra requires further theoretical calculations.

In figure 5 we compare the Ni $2p_{3/2}$, N 1s and C 1s XA spectra of the NiP. The energy scales of the spectra are aligned using the measured differences between the core levels ΔE (Ni $2p_{3/2}$–C 1s) = 570.8 eV and ΔE (N 1s–C 1s) = 114.3 eV. From figure 5 the correlation in energy positions of absorption bands A_2–D can be clearly seen for all spectra. Comparative analysis of these XA spectra confirms the conclusions stated above about the nature of the observed absorption bands. The small deviations in the energy positions of the bands observed in the XA spectra of the NiP may be attributed naturally to a different effect of the corresponding core holes on the energy positions of unoccupied electron states. This final-state effect occurs due to the Coulomb and exchange interactions between an inner-shell vacancy and an electron excited to an empty state. For different vacancies in the molecule it leads to a different (usually within ∼1 eV)
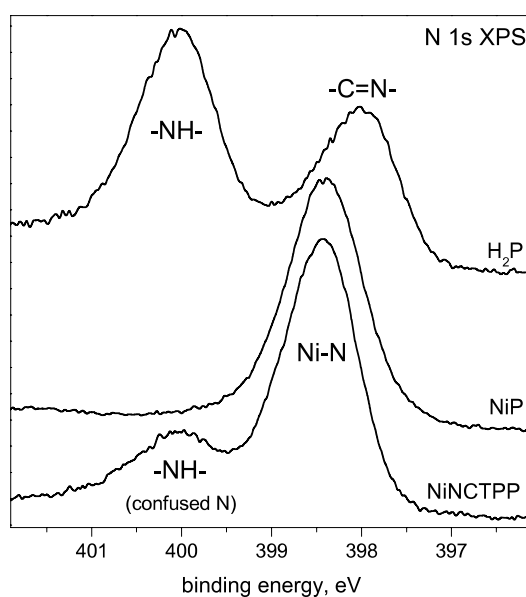
Figure 6. N 1s XPS spectra of the NiP, NiNCTPP and free-base porphine (H_2P).

energy position of the excitation with respect to the vacuum level in the corresponding spectra [26].

Figure 6 shows the N 1s core-level XPS spectra of the compounds under study. In the spectrum of the free-base porphine (H_2P) the two N 1s peaks at 400.0 eV and 398.0 eV represent the two different N sites in the centre of free-base porphyrin macrocycle, pyrrolic (–NH–) and iminic (–C=N–) nitrogens, respectively [34, 35]. In turn, in the NiP all four N atoms are equivalent leading to only one N 1s peak at 398.4 eV (denoted as Ni–N). The N 1s XPS spectrum of the NiNCTPP consists of two peaks at 400.0 and 398.4 eV with a relative intensity ratio of approximately 1:3. This fact confirms the conclusion made from the analysis of the N 1s XA spectra that the confused N atom in the NiNCTPP is of pyrrolic type (i.e. protonated N).

In conclusion, x-ray absorption and x-ray photoemission spectroscopy were used to obtain information about the electronic structure and character of chemical bonding in Ni porphyrins. The x-ray absorption measurements demonstrate a significant role of the Ni 3d–ligand 2p hybridization in Ni porphyrins responsible for the high-energy absorption structures A_2, C–D observed in the Ni $2p_{3/2}$, N 1s and C 1s spectra. The Ni $2p_{3/2}$ XA spectra show strong π-back-bonding in these compounds leading to a high-energy shift (1.2 eV) of the entire absorption structure compared to Ni metal. 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. For the NiNCTPP a further high-energy shift (0.5 eV) of the main line of the Ni $2p_{3/2}$ XA spectrum is observed, which is an evidence of the stronger back-donation and a smaller effective number of 3d electrons on the central Ni atom (higher oxidation state) in this N-confused porphyrin in comparison with other Ni porphyrins. The confused N atom in the NiNCTPP is of pyrrolic type (protonated nitrogen),

which was confirmed by the N 1s absorption and core-level photoemission spectra.

Acknowledgments

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