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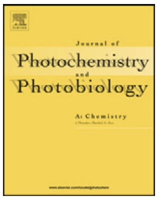

Electronic spectra and photochemical reactivity of bismuth corrole complexes

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ABSTRACT

The first examples of bismuth complexes with meso-substituted corrole ligands are presented. Complexation of 5,10,15-triphenylcorrole with bismuth(III) salts leads to the formation of a neutral low-valent species Bi-tpc, which is characterized by various spectroscopic techniques. In addition to the intense intraligand (IL) absorption bands of the corrole macrocycle, this bismuth(III) complex displays metal-centered (MC) *sp*-transitions and metal-to-ligand charge transfer (MLCT) transitions which show a substantial mixing with the intraligand absorption bands, thus resulting in an irregular *hyper*-type electronic spectrum. Excitation of Bi-tpc in the spectral region of the MC-bands under ambient conditions leads to dioxygen activation and concomitant photochemical formation of the high-valent species (O═)Bi^{V}(tpc), an unprecedented example of a bismuth(V) tetrapyrrole complex. As a potential reaction intermediate of this photoredox process, a labile hydroperoxo species (HOO)Bi^{V}(tpc)$^{+}$ is also identified. First results on the spectroscopic features and the chemical reactivity of (O═)Bi^{V}(tpc) are reported. In solution this neutral bismuth(V) species is in equilibrium with the corresponding protonated form (HO)Bi^{V}(tpc)$^{+}$ carrying an axial hydroxo ligand. Axial ligand exchange processes and the formation of adducts with solvent derived photoproducts are also identified in high-resolution mass spectra of irradiated samples. The molecular and electronic structures of the novel bismuth corrole systems are discussed in terms of supporting density functional theory (DFT) calculations, which suggest an out-of-plane structure of the Bi-tpc and (O═)Bi^{V}(tpc) species. Time-dependent DFT results are supporting the proposed assignment of electronic transitions observed in low- and high-valent bismuth tpc derivatives.

1. Introduction

Light sensitive coordination compounds of the main group metals are attractive candidates for the development of photocatalytic systems based on cheap and abundant materials [1]. Due to their specific electron configuration, redox-active *p*-block elements favour an overall two-electron transfer reactivity in chemical substrate transformations [2]. This behaviour facilitates the efficient formation of new bonds and helps to avoid uncontrolled free radical side-reactions. While the potential of such compounds in homogeneous solution remains widely unexplored, it is therefore not surprising that in the active sites of many heterogeneous catalyst systems the involvement of *p*-block elements seems to play a crucial role for the mechanistic key-steps. In the case of the group 15 element bismuth, some of the most remarkable examples include the presence of Bi^{III} and Bi^{V} centers in catalysts for the allylic oxidation of propene [3], and the photogeneration of O_2 from water involving ternary bismuth oxide species such as $BiVO_4$ [4]. In general, compounds containing a Bi(=O) structural motif are regarded as versatile oxidants for synthetic applications [5] and the rapidly emerging field of photocatalysis with visible-light responsive bismuth oxides also reflects the quite unique properties of these materials [6].

In this context it is highly desirable to study the role of individual metal-oxo centers in photocatalytic processes and to expand the visible-light sensitivity of such systems to longer wavelengths for the purpose of a more efficient solar energy utilization [1c,2]. Since tetrapyrroles such as porphyrins and related macrocyclic ligands are the most versatile photosensitizers available, and at the same time they are able to stabilize high oxidation states of their central metals, we decided to investigate the potential of bismuth corrole complexes for photocatalytic applications.

Available information about bismuth tetrapyrrole complexes remains rather limited [7]. Some of their porphyrin derivatives have found a certain interest as therapeutic drugs against gastric diseases and are potential candidates for cancer- and radiotherapy [8]. To the best of our knowledge, there is only one publication available in the literature that provides some information about bismuth corrole complexes [9]. While other group 15 derivatives with arsenic and antimony derivatives in +III and +V oxidation states of

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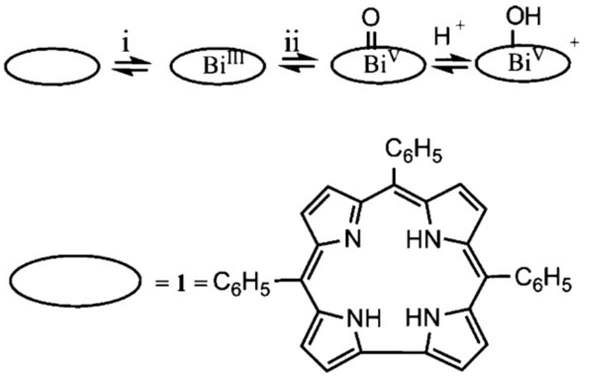


Scheme 1. Synthesis of Bi^{III}(tpc). Reagents and conditions: (i) H_3(tpc) and Bi(Ac)$_3$ mixed in DMF, 70 °C for 12 h under nitrogen and (ii) subsequent irradiation for 5 min in MeOH/DMF solution.

the complexed metal have been investigated [9,10], their Bi counterparts were only accessible as low-valent species. All previous efforts of chemical oxidization were reported to be unsuccessful, and electrochemical oxidation only led to a π-radical cation and a Bi(IV)-species [9]. However, no high-valent Bi(V) tetrapyrrole complex had ever been described. Herein we present the synthesis of the first example of a meso-substituted 5,10,15-triphenylcorrole bismuth(III) complex, Bi-tpc, and report a simple route for the photochemical oxidation of the compound to the corresponding high-valent bismuth(V)-oxo species (Scheme 1).

2. Experimental

2.1. Instrumentation

High-resolution MS measurements were performed with a 6510 quadrupole/time-of-flight (Q-TOF) instrument (Agilent, Palo Alto, CA, USA) using direct infusion of the sample solution at a flow rate of 40 μL/min by means of a Model 22 syringe pump (Harvard Apparatus, South Natick, MA, USA). All MS-Data presented were measured in positive ion-mode. NMR-measurements were performed on a Bruker DRX 500 MHz instrument, equipped with a cryogenically cooled probe. The corresponding deuterated solvent was used as reference for the ^{1}H - and ^{13}C-chemical shift. Irradiation experiments were performed under ambient conditions in fused silica cuvettes with a HBO 100 W high-pressure mercury-arc lamp using a 320 nm cutoff-filter or a 1 kW Hg/Xe lamp equipped with a Schoeffel GM 250-1 high-intensity monochromator. The incident monochromatic light flux density (18 mW/cm^2 at 320 nm) was measured with a calibrated Luzchem SPR-01 spectroradiometer system.

2.2. DFT calculations

Calculations were performed by using the Gaussian 03 package of programs [11]. The electronic structure calculations were based on the Kohn–Sham density functional theory (KS-DFT) with Becke's three-parameter hybrid functional (B3LYP) and at DFT/mPW1PW91 level [12]. Los Alamos National Laboratory 2 (LANL2) relativistic effective core potentials (RECPs) [13] were used to describe the core electrons of Bi atoms and split-valence (double-ζ) basis sets were used to describe s- and p-valence electrons of Bi. The LANL2DZ basis set was augmented by adding one set of polarization functions on all atoms and one set of diffuse functions on all non-hydrogen atoms. For C and H atoms all-electron split-valence 6-311+G(d,p) basis sets supplemented with a single set of diffuse functions on carbon atoms were employed. Analysis of hybridization was performed with natural bond order (NBO) methods. To gain insight into the vertical singlet electronic states, time-dependent density functional theory [14] (TD-PBE0 method) calculations were performed. Energies reported herein were evaluated by using the fourth-order Møller–Plesset perturbation theory [MP4(SDQ)] in combination with PBE0 parameterization. Compositions of molecular orbitals, overlap populations between molecular fragments, bond orders and density-of-states spectra were calculated using the AOMix program [15].

2.3. Syntheses

2.3.1. 5,10,15-Triphenylcorrole (*1*)

The synthesis of the free base corrole ligand H_3(tpc) **1** was carried out by using the acidic condensation conditions described by Gryko [16]. The crude products were purified by column chromatography on silica gel. The purification of corroles can be very tedious due to its similar elution characteristics with normal porphyrin and is hampered by the lack of stability of free-base corroles in solution towards light and air [17]. In part, this lack of stability results from the reduced aromaticity of corrole and the deformation of the macrocycle from planarity due to the steric bulk of the three inner hydrogens [18]. Corroles in aerobic solution under ambient light tend to break down to open chain structures. Therefore a subsequent HPLC purification was performed and the samples were stored in the dark and at −20 °C before the complexation reactions were performed.

2.3.2. Bismuth(III) complex of 5,10,15-triphenylcorrole (*2*)

Metallation of the corrole ligand to form the neutral complex Bi^{III}(tpc) **2** was achieved in DMF under an Ar atmosphere: after addition of a 5-fold excess of Bi(Ac)$_3$ and a 10-fold excess of NaAc, the mixture was heated and stirred overnight at 70 °C (Scheme 1) and turned dark-green. Alternatively, metallation also proceeded smoothly with a 5-fold excess of $BiCl_3$ in pyridine after addition of 10 equiv. of sodium acetate.

^{1}H NMR (500 MHz, Pyridine, 25 °C, δ): 9.15 (d, J = 3.7 Hz, 2H) H2 + H18; 8.99 (d, J = 4.6 Hz, 2H) H7 + H13; 8.65–8.68 (br s, 4H) H3 + H17 and H8 + H12; 8.53 (d, J = 7.3 Hz, 4H) phenyl; 8.35 (d, J = 6.9 Hz, 2H) phenyl; 7.86–7.90 (dd(t), J = 7.4 Hz, 4H) phenyl; 7.74–7.85 (overlapping m, 5H) phenyl. ^{13}C NMR (500 MHz, Pyridine, 25 °C, δ): 116.64 (CH, C2/C18), 122.96 (CH, C3/C17), 126.31 (CH, C8/C12), 127.35 (CH, C7/C13), 133.3 (quart., C1/C19 or C4/C16), 137.2 (quart., C1/C19 or C4, C16), 116.5 (quart., C5/C15), 116.5 (quart., C10), 140.2 (quart., C9/C11 or C6, C14), 141.9 (quart., C9/C11 or C6, C14), 135.9 (CH, phenyl), 135.6 (CH, phenyl), 140.9 (quart., 1-phenyl), 142.7 (quart., 1-phenyl), 128.1 (CH, phenyl), 128.9 (CH, phenyl).

High-resolution mass spectrum after the metallation reaction of free base corrole ($m/z = 732.1731 \equiv$ Bi^{III}(tpc)$^{+\bullet}$; $m/z = 749.1760 \equiv$ (HO)Bi^{V}(tpc)$^{+}$; $m/z = 755.1629 \equiv$ Bi^{III}(tpc)-Na^{+}; $m/z = 765.1710 \equiv$ (HOO)Bi^{V}(tpc)$^{+}$; $m/z = 791.1869 \equiv$ (CH_3COO)Bi^{V}(tpc)$^{+}$).

2.4. Chemicals

All commercially available chemicals were used as received unless otherwise stated. Solvents like methanol, DMF, dichloromethane and pyridine were purified and distilled by standard procedures. NMR solvents were used as received. The metal salts $BiCl_3$ and Bi(Ac)$_3$ were obtained from ACROS and Ventron, respectively.

3. Results and discussion

To approach the unprecedented bismuth(V) oxidation level inside a tetrapyrrole complex, we have chosen corroles as lig-

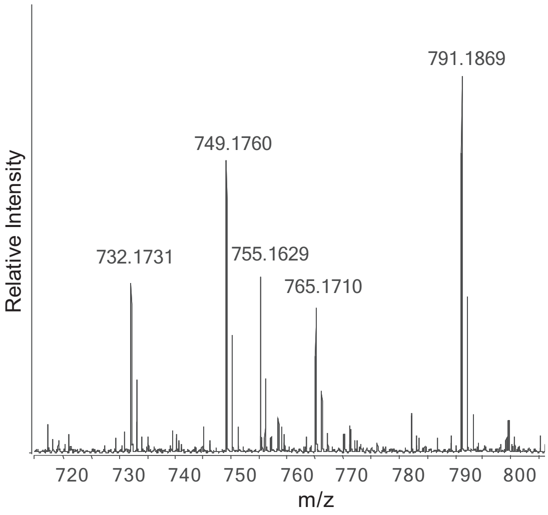


Fig. 1. High-resolution mass spectrum after the metallation reaction of free base corrole with bismuth acetate ($m/z = 732.1731 \equiv$ Bi^{III}(tpc)$^{+\bullet}$, $m/z = 749.1760 \equiv$ (HO)Bi^{V}(tpc)$^{+}$, $m/z = 755.1629 \equiv$ Bi^{III}(tpc)-Na^{+}, $m/z = 765.1710 \equiv$ (HOO)Bi^{V}(tpc)$^{+}$, $m/z = 791.1869 \equiv$ (CH$_3$COO)Bi^{V}(tpc)$^{+}$.

ands, which tend to stabilize high formal oxidation states of their coordinated central metals. From the synthetic point of view, meso-substituted A$_3$- and A$_2$B corroles, where A and B represent different substituents at the methine bridges of the macrocyclic core, are readily accessible since direct one-pot synthetic procedures have been established [16,19,20] starting from pyrrole or the respective dipyrromethanes and the desired aldehydes. Synthesis of the free base H$_3$tpc was performed employing the method introduced by Koszarna and Gryko [16], which allows isolation of meso-triaryl-corroles in good yields. Analytical data obtained for H$_3$tpc are in accordance to those described previously in the literature [21,22]. We herein present the first meso substituted 5,10,15-triphenylcorrole bismuth(III) complex Bi-tpc and also describe a photo-oxidation route to the corresponding bismuth(V) corrole complexes.

3.1. Metal insertion and characterization

Metallation of the free base corrole H$_3$tpc was achieved with bismuth chloride or bismuth acetate as described in more detail in Section 2 (Scheme 1). The progress of the reaction was followed by UV–vis spectroscopy. High resolution ESI-MS of the reaction mixture unequivocally corroborates the formation of Bi-tpc with m/z 732.17 (Fig. 1).

Since an excess of sodium acetate is used for the synthesis of the bismuth(III) corrole, the sodium adduct Bi^{III}(tpc)-Na^{+} of the neutral Bi^{III}(tpc) complex with $m/z = 755.16$ is also detected in the mass spectra. Interestingly, in the reaction mixture several additional strong signals are present, which can be attributed to positively charged bismuth complexes with different anionic axial ligands. This clearly indicates the possibility of an oxidation to the bismuth(V) state within the tpc ligand under ambient conditions (Fig. 1 and Table 1) and thus resembles the properties of low-valent metalloporphyrins with other group 15 elements [23a]. In the latter case, the established oxidation pathways from low-valent to high valent species involve dioxygen activation, formation of peroxide and exchange equilibria of axial ligands in the high-valent state. The peroxo species (HOO)Bi^{V}(tpc)$^{+}$ with $m/z = 765.17$ is found as a key-intermediate of such a redox transformation, which however is no longer present in photolyzed samples (see below).

For the NMR-assignment of the Bi(III)-complex (Figs. 2 and 3), a separate micropreparation in deuterated pyridine was performed and the macrocycle signals were assigned with the help of two-dimensional ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC experiments. Proton and carbon chemical shifts for the four pyrrole subunits are in good agreement with those reported by Balazs et al. [22] for other meso-substituted metallocorroles.

Two of the four characteristic pyrrole–hydrogen doublets with small coupling constants (about 4 Hz) are found at 9.15 and 8.99 ppm and two overlapping signals are observable at 8.67 ppm (but distinguishable with the heteronuclear correlation experiments). The Bi^{III}(tpc) complex shows a strong tendency for demetallation and is unstable in most solvents like hexane, dioxane, chloroform and diethylether, but fairly stable in pyridine and extractable with methylene-chloride.

Table 1
Positively charged bismuth corrole species detected by high-resolution ESI-MS.

Ion	Formula	Observed m/z	Calc. m/z	Δ (ppm)
Bi^{III}(tpc)$^{+\bullet}$	$C_{37}H_{23}BiN_4$	732.1731	732.1721	1.27
(HO)Bi^{V}(tpc)$^{+}$	$C_{37}H_{24}BiN_4O$	749.1758	749.1748	1.58
Bi^{III}(tpc)-Na^{+}	$C_{37}H_{23}BiN_4Na$	755.1629	755.1619	1.44
(HOO)Bi^{V}(tpc)$^{+}$	$C_{37}H_{24}BiN_4O_2$	765.171	765.1698	1.62
(HO)(HCHO)Bi^{V}(tpc)$^{+}$	$C_{38}H_{26}BiN_4O_2$	779.1859	779.1854	0.59
(CH$_3$COO)Bi^{V}(tpc)$^{+}$	$C_{39}H_{26}BiN_4O_2$	791.1869	791.1854	−1.85

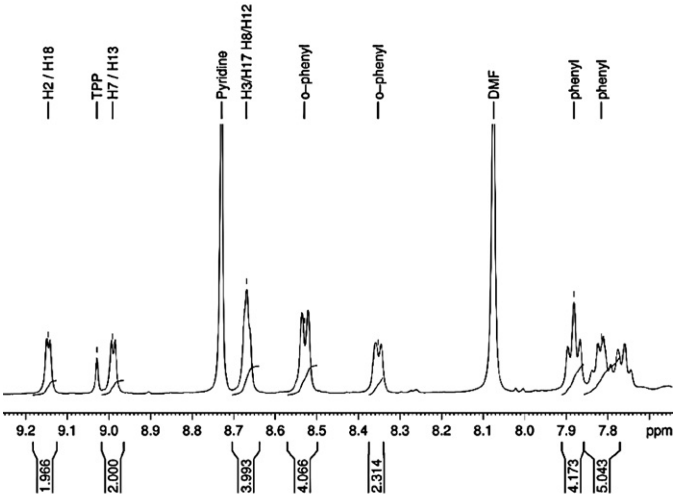


Fig. 2. ^{1}H NMR spectrum of Bi^{III}(tpc) recorded at 298 K in deuterated pyridine.

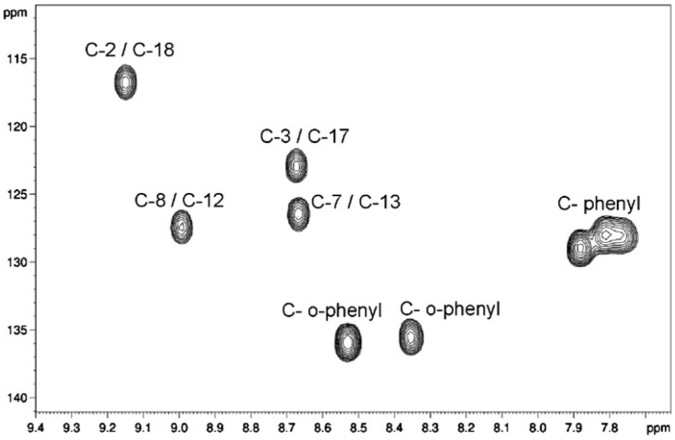


Fig. 3. ^{1}H–^{13}C HSQC-spectrum of Bi^{III}(tpc) at 298 K in deuterated pyridine.

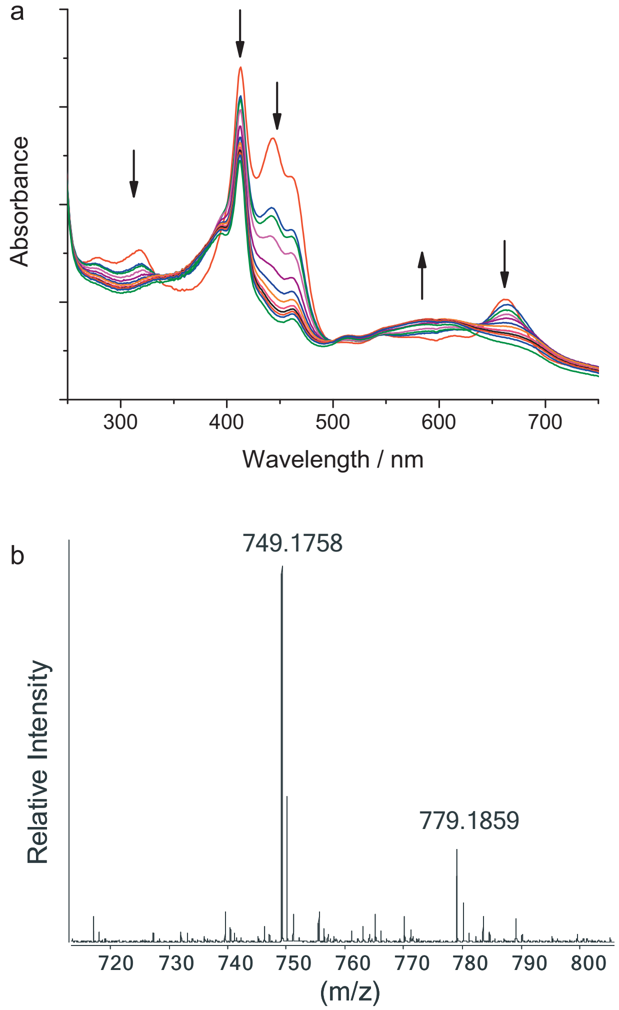
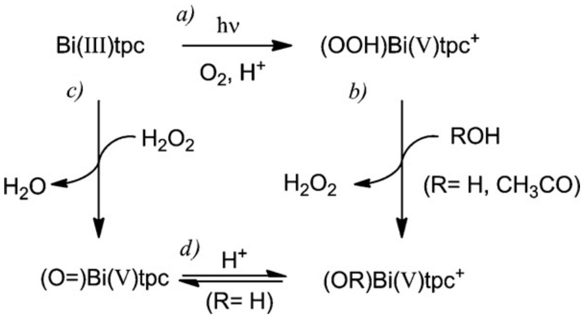


Fig. 4. (a) UV spectral changes during the photolysis of Bi^{III}(tpc) in methanol at 0, 1, 2, 3, 5, 7, 9, 11, 13, 15, 17 and 20 min reaction times (1 cm quartz cell, 298 K, aerobic conditions, full output of a 100 W Hg-lamp passed through a 320 nm Schott cutoff filter). (b) High-resolution ESI-MS spectrum of the protonated bismuth-oxo reaction product $(HO)Bi^{V}(tpc)^{+}$ and the corresponding formaldehyde adduct obtained after the photolysis reaction in MeOH/DMF.

3.2. Formation and reactivity of high-valent species

Chemical oxidation of the low-valent complex Bi^{III}(tpc) with an excess of H_2O_2, iodosobenzene-diacetate and several other oxidizing agents was hampered by a partial demetallation or destruction of the macrocycle. Thus, in order to achieve a clean and complete conversion of the complex to form a bismuth(V) species, the reaction mixture was diluted with methanol and irradiated under aerobic conditions. This photochemical approach was motivated by the fact that several other main group metal tetrapyrrole complexes with an s^2-electron configuration at the central metal are light-sensitive and have been successfully oxidized to the corresponding s^0-systems without any demetallation occurring [23]. Indeed, upon photolysis the Bi^{III}(tpc) absorption maxima at 320, 441 and 663 nm disappear and a full consumption of the bismuth(III) compound is observed (Fig. 4), resulting in the formation of the high-valent species $(HO)Bi^{V}(tpc)^{+}$ (m/z 749.18) as the main reaction product. This compound can be interpreted as the mono-protonated form of a neutral bismuth(V)-oxo complex of triphenylcorrole.

Photolysis of the free base corrole, which was also studied under similar conditions (see supplementary material), led to open-chain species with spectral features resembling the enzymatic degradation products of corroles recently described in the literature [24]. No such indication, however, was found in the case of the bismuth complexes.

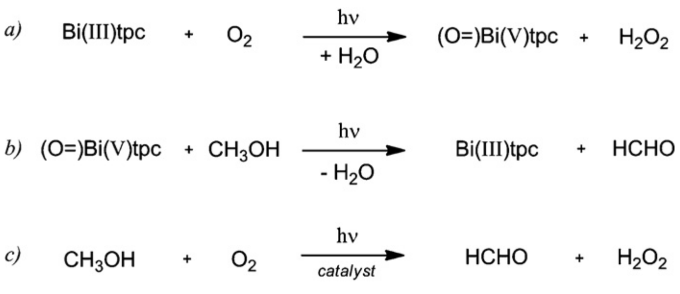


Scheme 2. Proposed reaction pathways in the course of the interconversion between low- and high-valent bismuth triphenylcorrole complexes. (a) Photooxidation of Bi^{III}(tpc) and two-electron activation of dioxygen to form an intermediate hydroperoxo bismuth(V) complex, (b) axial ligand exchange and H_2O_2 release, (c) direct formation of the high-valent oxo-species $(O{=})Bi^{V}$(tpc) in a “peroxide shunt pathway” and (d) pH-dependent equilibrium between oxo- and hydroxo bismuth(V) species.

The formation of high-valent bismuth species in the photoredox process shown in Fig. 4 is tentatively interpreted in terms of the reactivity patterns established for group 15 metalloporphyrin chemistry [25] and briefly summarized in Scheme 2.

The reaction steps summarized in Scheme 2 can easily serve to explain the formation of all bismuth triphenylcorrole species observed in this study (Table 1). However, the presence of a second permanent photoproduct in the irradiated samples with $m/z = 779.19$ still has to be rationalized (Fig. 4b). Since it is well documented that group 15 metal-oxo species are able to photo-oxidize primary alcohols to the corresponding aldehydes [25], we propose the generation of formaldehyde in methanol containing samples of Bi^{III}(tpc) upon photolysis. NMR-spectroscopic results obtained with irradiated samples also suggest such a possibility. Therefore, the cationic species with $m/z = 779.19$ is tentatively assigned to the formaldehyde adduct $(HO)(HCHO)Bi^{V}(tpc)^{+}$ of the high-valent bismuth complex. This indicates the interesting combination of redox reactions to a photocatalytic multielectron transfer process involving bismuth corroles according to Scheme 3.

In a side reaction, the low-valent compound Bi^{III}(tpc) and the H_2O_2 present in such a process should be at least partially consumed following the “peroxide-shunt” pathway described in Scheme 2c. This can serve to explain the dominant photostationary concentration of a bismuth(V) formaldehyde adduct $(HO)(HCHO)Bi^{V}(tpc)^{+}$ and a lack of signals from bismuth(III) species in the mass spectra of irradiated methanolic samples. Further mechanistic studies on the potential photocatalytic reactivity of bismuth corroles, however, are necessary to confirm and expand these first promising results.



Scheme 3. Possible two-electron methanol oxidation involving bismuth corrole photocatalysis. (a) Light-induced dioxygen activation, (b) photochemical substrate transformation and (c) net two-electron redox process catalyzed.

3.3. *Electronic structure and calculated properties*

The electronic absorption spectra of low- and high-valent bismuth triphenylcorrole complexes can be interpreted in terms of Gouterman's classification of regular and irregular metalloporphyrin spectra [7a,23], which is adopted in a modified form in the simplified molecular orbital diagram given in Fig. 5.

In the low-valent species $\mathrm{Bi^{III}}$(tpc), the s^2-valence electron configuration at the central metal induces a perturbation of the four-orbital (π–π^*) transitions of the tetrapyrrole macrocycle. Besides the intraligand (IL) absorptions, the bismuth(III) triphenylcorrole complex also displays a metal-to-ligand charge transfer (MLCT) band in close proximity to the Soret band. This dipole-allowed charge transfer transition shows significant mixing with the IL absorptions, thus resulting in an irregular *hyper*-type electronic spectrum with a typical "split" Soret band in the 300–500 nm spectral region and a red-shifted Q-band. In contrast to the situation in metalloporphyrin derivatives, the lowest unoccupied π^*-orbitals of the tpc-macrocycle are expected to be non-degenerate. The electronic spectra of the metallocorrole derivative are therefore further complicated by the presence of a double structure of the corresponding transitions with two weakly separated peaks reflecting the lower symmetry of the ligand (Fig. 4a). Additional metal-centered (MC) transitions involving the *s* and *p* orbitals of the bismuth(III) central ion should also be possible (Fig. 5a).

This general picture is supported by the results of time-dependent DFT (TD-DFT) calculations, which confirm the presence of a significantly Bi(6*s*)-localized HOMO in the π–π^* frontier orbital region of the corrole ligand and also correctly describe the occurrence of an additional metal-centered (MC) *sp*-transition in the UV-region (Fig. 6a).

In analogy to other low-valent main group metal complexes [1,23], excitation in the spectral region of the singlet MC state absorption band region is thought to be responsible for the observed photoreactivity of the bismuth(III) complex towards dioxygen and the subsequent formation of peroxide species (Scheme 2a). The corresponding *sp*-triplet states can be statically sensitized by the macrocyclic ligand which also gives rise to photosensitivity of such compounds in the visible-light region [23a]. In methanol solution the singlet *sp*-transition of Bi(III)tpc occurs at 315–320 nm (31,750–30,300 $\mathrm{cm^{-1}}$). The corresponding "metal centered" excitations obtained by TD-DFT occur from HOMO-3, -2 and HOMO (+6*s*-orbital contribution) to LUMO+2, +3, +4, +5 exhibiting a high $p_{x,y}$-orbital character. The predicted energy of these transitions can be calculated by NBO analysis giving a value for the MC transition energy of 0.14 hartrees (=3.8 eV, 326 nm or 30,650 $\mathrm{cm^{-1}}$) which is reasonably close to the experimental value. The calculated charge (Q_{NPA}) on the bismuth atom (valence electron configuration $6s^{1.78}6p^{0.69}$) in Bi(III)tpc, obtained by natural bond population analysis (NPA) at the MP2(full) level, is +2.517e. Overall, the electronic structure and absorption properties of the low-valent bismuth complex show typical characteristics for meso-aryl-substituted group 15 metallocorroles with the +III oxidation state [9,26].

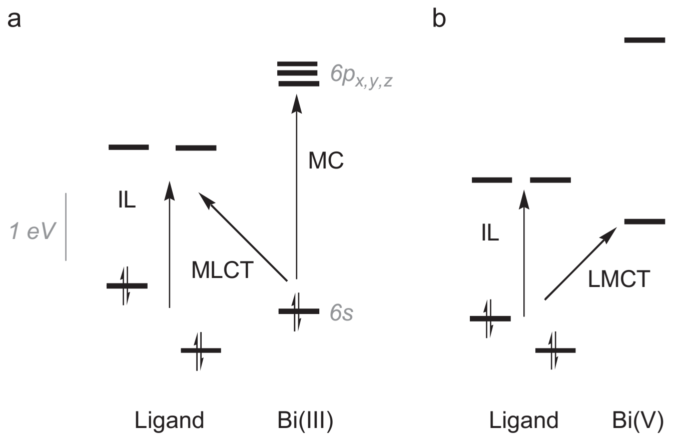


Fig. 5. Qualitative MO-diagram of (a) low-valent and (b) high-valent bismuth corrole complexes. IL: Intraligand (π–π^*) transitions involving electrons localized at the macrocyclic ring; MC: metal centered *sp*-excitation; MLCT: metal-to-ligand charge transfer-; and LMCT: ligand-to-metal charge transfer transitions.

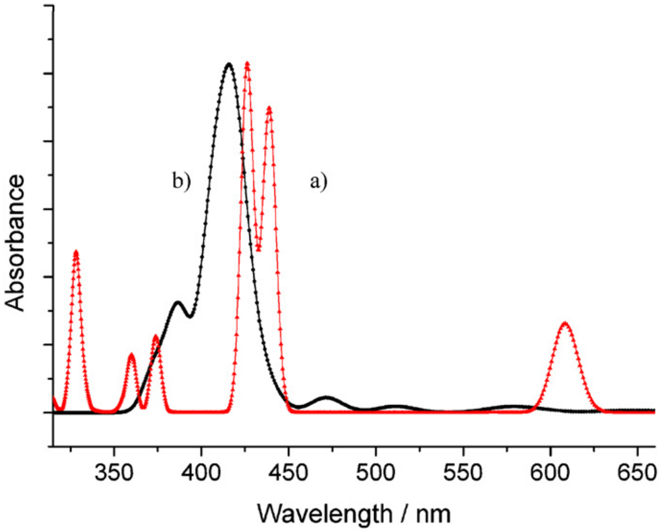


Fig. 6. Calculated UV–vis absorption spectra of (a) the low-valent metallocorrole complex $\mathrm{Bi^{III}}$(tpc) (solid triangles) and (b) the high-valent oxo species (O=)$\mathrm{Bi^{V}}$(tpc) (black solid circles) obtained by time-dependent DFT calculation methods. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

When the central metal of $\mathrm{Bi^{III}}$(tpc) is oxidized to reach the s^0-valence electron configuration of bismuth(V), low-lying MLCT and MC transitions are no longer possible (Fig. 5b). Therefore the irregular *hyper*-type electronic spectrum with a split Soret band and a red-shifted Q-band is no longer observed (Fig. 4a), and the spectra of high-valent bismuth complexes of triphenylcorrole are dominated by the regular π–π^* transitions of the macrocyclic ring with a strong Soret band at around 400 nm and Q-bands in the 500–600 nm region. This is in excellent agreement with the predicted UV–vis spectrum of (O=)$\mathrm{Bi^{V}}$(tpc) obtained by TD-DFT calculations (Fig. 6b), where the splitting of the Soret-band has vanished resulting in a regular metallocorrole-like spectrum. As observed before in other high-valent main group metallocorroles with strongly oxidizing central ions [23b], a low-lying ligand-to-metal charge transfer (LMCT) transition band may also be observed in the visible spectral range due to the presence of an empty metal centered orbital situated in the frontier orbital region of the macrocyclic ligand (Fig. 5b). In the bismuth(V) corrole systems this band seems to occur in the 450–550 nm region (Figs. 4a and 6b). In a simple radical pair model, excitation of such a LMCT state should facilitate the back-reaction of species such as (O=)$\mathrm{Bi^{V}}$(tpc) to finally re-generate Bi(III)tpc via a Bi(IV) s^1-valence electron intermediate. The reversible interconversion of low- and high-valent species is an important pre-requisite for potential catalytic redox cycles involving bismuth corroles. Generally for such kind of tetrapyrrole systems, the possibility of a redox-isomerism between complexes in a formal bismuth(V)-state and bismuth(IV)-species with ligand radical character has to be taken into consideration and further studies have to be carried out to elucidate such electron transfer pathways in more detail. In this context it is important to note that

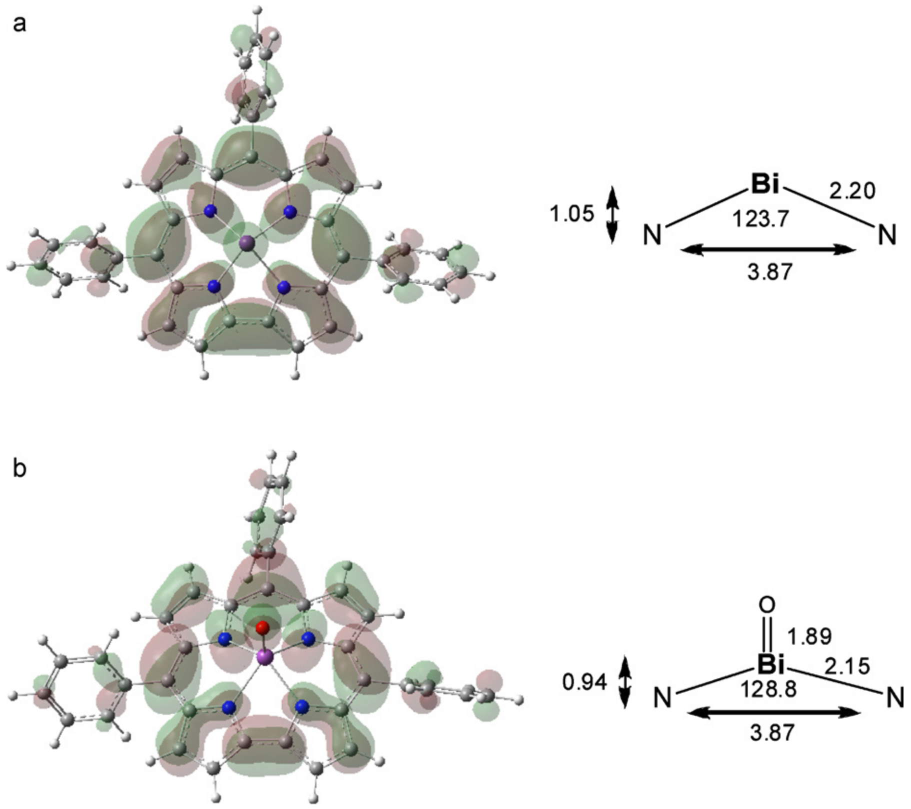


Fig. 7. Structural parameters of the optimum geometry of (a) the low-valent complex Bi^{III}(tpc) and (b) the high-valent species (O=)Bi^{V}(tpc) obtained by DFT-calculations. The bond lengths and the bond angles are indicated in the units of Ångstroms and degrees, respectively. The shaded MO-maps indicate localized electronic Bi(6*s*)-contribution to the HOMO-level.

bismuth(IV) corrole species have been discussed in electrochemical studies before [9], and that our DFT-calculated charges (Q_{NPA}) on the bismuth atom in (O=)Bi^{V}(tpc), which has a natural valence electron configuration of $6s^{0.75}6p^{0.38}$, predicted a natural charge of Q_{NPA} = 3.825e in the electronic ground state.

Due to the large size of bismuth ions [27] a considerable out-of-plane displacement of the main group metal is expected for bismuth corrole complexes and the compounds should exhibit a non-planar square pyramidal structure. The geometry optimized molecular structures of low- and high-valent bismuth triphenylcorrole complexes obtained by DFT calculations are shown in Fig. 7a and b, respectively. In the low-valent complex Bi^{III}(tpc) the bismuth atom is predicted to be 1.05 Å out-of-plane of the four corrole nitrogen atoms and a distance of 0.94 Å is determined for the neutral (O=)Bi^{V}(tpc) species. Compared to mononuclear bismuth(III) porphyrins with an experimental out-of plane distance of about 1.15 Å [8], the calculated value of 1.05 Å for Bi^{III}(tpc) appears to be quite small. Since we succeeded to prepare the first bismuth(V) tetrapyrrole complexes, no reference data on the typical out-of-plane displacements for such high-valent species are available in the literature yet. Attempts to obtain crystals suitable for an X-ray diffraction study of the novel compounds are currently underway.

4. Conclusion

In summary, we presented the synthesis of a new Bi(III)-corrole complex and have shown indications for the oxidation to the corresponding Bi(V) species, which were characterized by high resolution ESI-MS and electronic-spectroscopy. First results on the photochemical reactivity of these compounds were reported and discussed. DFT-calculations of the Bi(III)- and Bi(V)-species suggest an out of plane displacement of the bismuth atom from the macrocyclic ligand and indicate the presence of low-lying electronic transitions involving the central metal, which is in agreement with the presented spectroscopic features such as the characteristic splitting of the Soret-band upon complexation with Bi(III). Future investigations will focus on potential photocatalytic multielectron redox processes and oxygen atom transfer reactions that are expected to be mediated by these novel main group metallocorrole species.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2011.01.008.

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