XPS and IR Spectroscopic Studies of Titanyl and Vanadyl Complexes with Etioporphyrin II

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The study is devoted to search for organometallic complexes with considerable dipole moments suitable for the creation of new electret materials. The latter are formed by intercalation of organometallic molecules with a high dipole moment into a polymeric matrix. Titanyl and vanadyl complexes with etioporphyrin II were synthesized. The obtained compounds were identified with the use of electronic spectroscopy, NMR spectroscopy, mass spectrometry and liquid chromatography, and studied by vibrational spectroscopy and X-ray photoelectron spectroscopy. Quantum chemical calculations for the optimization of the geometry of etioporphyrin II complexes with vanadyl and titanyl cations were performed. Their vibration spectra, dipole moments and distribution of charge and spin densities were calculated. Mulliken population analysis was carried out. It was shown that the “apix” bond between the metal in the vanadyl complex with etioporphyrin II is of more pronounced covalent nature. In contrast, in case of titanyl a structure with some redistribution of electron density onto the oxygen atom is implemented. This increases the polarity of the “apix” Ti–O bond and the dipole moment of the titanyl macrocomplex in general. The calculated dipole moment of the titanyl complex is higher (2.94 D) than that of the vanadyl complex (2.32 D).

Keywords: Titanyl, vanadyl, etioporphyrin II, metal complexes, IR spectroscopy, X-ray photoelectron spectroscopy, dipole moment.
Introduction

In the previous study[1] we have shown the possibility of creating a new design of an electret material. The idea consisted in the intercalation of organometallic macromolecules of bismuth(III) iodide complexes with porphyrins having high dipole moments[2,3] into PVA upon polymerization in a constant electric field. The latter allows fixing the preset direction of dipole moment vectors in the material, while the use of the macroligand guarantees time stability of the surface potential preventing relaxation processes. This work is aimed at searching new organometallic complexes with considerable dipole moments suitable for implementing the suggested electret material model. On the basis of literature data analysis, we suggested to consider titanyl or vanadyl complexes with porphyrins as such objects. The previous studies demonstrated that the maximum dipole moment can be obtained for compounds with etioporphyrin II.

With the use of vibrational spectroscopy and X-ray photoelectron spectroscopy supported by quantum chemical calculations the bismuth iodide complex with this porphyrin was shown to have the highest dipole moment among all the compounds studied by us before.[1] It is admissible to expect that the strong “apix” M–O bonds in titanyl and vanadyl complexes directed normally to the ligand plane will provide a high contribution to the dipole moment of the macromolecule in general.

The synthesis of VO EP II (Figure 1) was described earlier.[4,5] TiO EP II was prepared by our group and characterized for the first time. The vibrational spectra of a number of EP II metal complexes were published several years ago,[6] however, the assignment of vibration frequencies was limited to the high-frequency area. No analysis of vibrations of the porphyrin cycle atoms bonded to the transition element was carried out.

Experimental

Synthesis

Etioporphyrin II (1, EP II) was obtained by H. Fischer method[7] from 4,4’-dimethyl-3,3’-ditiethyl-5,5’-diethoxycarbonyldipyrromethane. VO EP II complex was synthesized by two methods: by refluxing EP II with vanadyl sulphate in DMF[8] or with VO(IV) acetylacetonate prepared according to the method[9] by refluxing in phenol.[10] The reaction durations in both methods and also the final complex yields had the close values. Titanyl was inserted into the macrocycle with TiO(IV) acetylacetonate (Aldrich), also in phenol.[10] Phenol, chloroform, benzene, methanol, isopropanol (Chimmed) and silica gel 60 (0.040–0.063 mm, Merck) were used in the work.

VO EP II (2a). Yield: 58 %. UV-Vis (CHCl3) $\lambda_{\text{max}}$ (lgε) nm: 408 (5.43), 534 (4.12), 572 (4.45), m/z 543.218 (50V), 544.262 (50V) [M+1$^+$]. Calculated for C32H36N4VO: 543.614. HPLC: RT, 10.618 min; complex content: 99.40 %. Found, %: C 70.70, H 6.68, N 10.31. TiO EP II (2b). Yield 63 %. UV-Vis (DMSO) $\lambda_{\text{max}}$ (lgε) nm: 404 (5.59), 535 (4.11), 573 (4.37), m/z 539.217, 541.240, 543.257 – Ti isotopes [M+1$^+$]. Calculated for C32H36N4TiO: 540.628. $^1$H NMR δH ppm: 10.47 (4H, s, meso-H), 4.22 (8H, q, CH3–C–), 3.75 (12H, s, CH2–), 1.97 (12H, m, CH2–, CH3–). HPLC: RT, 9.210 min; complex content: 99.43 %. Found, %: C 71.39, H 6.92, N 9.95. C32H36N4TiO. Calculated, %: C 71.09, H 6.71, N 10.36.

Equipment and Reagents

Electron absorption spectra were recorded with the UV-Vis Helios Alpha Local Control System spectrophotometer (Ter-
Results and Discussion

The obtained samples of titanyl and vanadyl complexes with etioporphyrin II were identified with the use of a number of physical methods: electronic spectroscopy, NMR spectroscopy, mass spectrometry and liquid chromatography.

Our studies\textsuperscript{[1,2]} showed that the values of the dipole moments of porphyrins metal complexes were essentially influenced by interactions in the metal-nitrogen core. Bismuth(III) in iodide complexes with porphyrins acts a translator of electron density from the porphyrin cycle atoms to the iodine atom.

X-Ray photoelectron spectra of titanyl and vanadyl acetylacetonates and the synthesized titanyl and vanadyl complexes with etioporphyrin II are presented in Figures 2 and 3, respectively. Survey XPS spectra contain the lines of all the elements that are a part of the compounds: C1s, N1s, O1s, and also those of transition elements: Ti2p\(_{1/2}\), Ti2p\(_{3/2}\) and V2p\(_{1/2}\), V2p\(_{3/2}\) and V3p\(_{1/2}\). The binding energies of the core electrons of nitrogen, carbon, oxygen and transition elements are summarized in Table 1.

As in the case of bismuth iodide complexes, the spectra of the titanyl and vanadyl complex compounds with etioporphyrin II were identified with the use of a number of physical methods: electronic spectroscopy, NMR spectroscopy, mass spectrometry and liquid chromatography.
etiolorphyrin II show degenerate bands corresponding to nitrogen 1s electrons. The binding energy of the 1s electron of nitrogen atoms in the complexes takes on an average value as compared to etiolorphyrin II. However, it is slightly lower than in its complex with bismuth(III) iodide. This indicates that all the nitrogen atoms equally participate in the formation of the bonds with the transition element. As for the binding energy of 1s electrons of carbon, its value for the titanyl complex is significantly higher than for etiolorphyrin II, its complexes with bismuth(III) iodide and vanadyl, and it is comparable with the binding energy in titanyl acetylacetonate. On the contrary, the maximum value of the binding energy of oxygen 1s electrons was obtained for the vanadyl etiolorphyrin II complex. It should be noted that, while the “apix” O1s oxygen binding energy in the porphyrin vanadyl complex is lower than in acetylacetonate, in the case of titanyl, on the contrary, the O1s binding energy in the porphyrin complex (531.25/53/529.3 eV) is noticeably higher as compared to the acetylacetonate (531.47/530 eV).

According to the literature data the band of titanium (Ti2p3/2 458.5 eV and 457.5 eV for TiO(acac), and TiO EP II, respectively) and vanadium (V2p3/2 516.6 eV and 515.8 eV for VO(acac), and VO EP II, respectively) correspond to the (IV)-valence state of the metal in these compounds. For both titanyl and vanadyl the binding energy of the p-electrons of the transition elements in the complexes is slightly lower than in the corresponding acetylacetonates. All this together makes it possible to assume that the polarity of the central core of the complex is higher in the case of titanyl.

The above features of X-ray photoelectronic spectra are in general consistent with the obtained values of vibrational frequencies from the absorption IR spectra (Figure 4). The vibrational frequencies of the bismuth(III) iodide, titanyl and vanadyl etiolorphyrin II complexes are summarized in Table 2. The frequencies were assigned on the basis of comparing the experimental data and the performed calculation results.

The assignment of the frequencies of the M–O bond valence vibration does not raise any doubt (993 cm⁻¹ for the vanadyl and 961 cm⁻¹ for the titanyl). These vibrations have the aspect of very intense absorption bands in the regions where nonplanar deformation vibrations of the porphyrin cycle 6(CH) bond also take place.

The frequencies of the valence vibrations of the M–O bonds of titanyl acetylacetonate (1024 cm⁻¹) and vanadyl acetylacetonate (998 cm⁻¹) measured by us for comparison

| Core levels | TiO(acac)₂ | VO(acac)₂ | EP II | TiO EP II | VO EP II |
|-------------|------------|----------|-------|-----------|---------|
| O1s         | 531.5      | 536.6    | –     | 533.3     | 534     |
|             | 530        | 531.7    | –     | 532       | 532.3   |
|             | –          | –        | –     | 529.3     | 530.2   |
| C1s         | 288.5      | 286.7    | 287.5 | 288.6     | 284.8   |
|             | 286.5      | 284.4    | 284.7 | 286.5     | 284.7   |
|             | 284.5      | –        | –     | –         | –       |
| N1s         | –          | –        | 399.4 | 397.9     | 398.3   |
|             | –          | –        | –     | 397.4     | –       |
| Ti2p        | 464.1      | –        | –     | 463.4     | –       |
|             | 458.5      | –        | –     | 457.5     | –       |
| Ti3s/       | 61         | –        | –     | –         | –       |
| Ti3p        | 36         | –        | –     | –         | –       |
| V2p         | –          | –        | 524   | –         | 523.6   |
|             | –          | –        | 516.6 | –         | 515.8   |
| V3s/        | –          | –        | 68.8  | –         | –       |
| V3p         | –          | –        | 40.6  | –         | –       |

Figure 4. IR spectra of VO (red line) and TiO EP II (blue line) in the middle region (A) and in the far region (B).
with the use of their IR spectra are in agreement with the known values. It is obvious that, while the nature of the vanadium–oxygen bond in case of the vanadyl complexes does not undergo considerable changes, the transition from titanium acetylacetonate to its porphyrin complex leads to essential loss of the titanium–oxygen bond strength. The shift of the group of bands related to the valent symmetric and asymmetric C–N vibrations confirms the existence of coordination of the VO and TiO group to the nitrogen atoms of the porphyrin cycle.

The frequencies of the porphyrin cycle vibrations are not characteristic. They are considerably mixed in shape, which is quite natural for such condensed systems. The frequencies of the vibrations with the participation of metal–nitrogen bonds for titanyl (308, 356 cm⁻¹) and vanadyl (306, 360 cm⁻¹) are practically twice higher than the frequencies of the vibrations with the participation of bismuth–nitrogen bonds. This is understandable, if one takes into account that the atomic mass of bismuth is five times higher than that of titanium and vanadium. Moreover, one can assume some decrease in the metal–nitrogen binding energy for transition element atoms. This is in agreement with the XPS data. The frequencies of the deformation vibrations of the nitrogen–carbon cycle in the complexes with the participation of transition element atoms are also considerably higher than the frequencies of the corresponding vibrations of the bismuth(III) iodide complex.

The results of the quantum-chemical calculations are in complete agreement with the above considerations. Thus, for the titanyl complex the Mulliken charges of the titanium and oxygen atoms are equal to 1.41 and –0.43, respectively. The charges of all four nitrogen atoms are equivalent and equal to –0.50, and for the carbon atoms bonded with the nitrogen atoms the charges are equal to –0.15. The residual covalences of Ti–N and Ti–O bonds are respectively 0.49 and 2.32. In the case of the vanadyl complex the corresponding values are: 1.25 for V, –0.38 for O, –0.48 for N, and 0.15 for C. The residual covalences of the V–N and V–O bonds are 0.52 and 2.33. The calculated dipole moment of the titanyl complex is higher (2.94 D) than in case of vanadyl (2.32 D).

Table 2. The experimental vibrational frequencies of bismuth, vanadyl and titanyl etioporphyrin complexes in the region of porphyrin cycle oscillations (cm⁻¹).

| BiI-EP II \ ν, cm⁻¹ | Assignment | VO EP II \ ν, cm⁻¹ | TiO EP II \ ν, cm⁻¹ | Assignment \ \ M = V/Ti |
|---------------------|------------|-------------------|---------------------|------------------------|
| 101                 | v(BiI) + v(\nu(BiN)) | 217               | 218                 | v(MN) + δ_{ring}        |
|                     |            | 231               | 235                 |                        |
| 125                 | δ(BiN) + v(BiN) + v(BiI) | 257               | 260                 | δ(NMO) + δ_{ring}       |
|                     |            | 268               | 271                 |                        |
| 156                 | v(BiI) + v(BiN) + δ(BiNC) | 283               | 285                 | δ(NMN) + δ_{ring} + δ(MNC) |
|                     |            | 293               | 294                 | δ(NMO) + δ_{ring}       |
| 173                 | v(BiN) + δ(BiNC) + δ(BiN) | 306               | 308                 | v_{as}(MN) + δ(NMN) + (CNC) |
|                     |            | 317               | 318 shoulder        |                        |
| 228                 | δ(BiNC) + δ(BiN) | 330               | 331                 | v(MN) + δ(MNC)         |
| 277                 | δ(BiNC) | 360               | 356                 | v_{as}(MN) + δ(CNC)    |
| 301                 | δ_{ring} + δ(NBiN) | 389               | 390                 | δ_{ring} + δ(NMN)      |
|                     |            | 400               | 402                 |                        |
| 346                 | v(BiN) + δ(BiNC) | 423               | 425 shoulder        | δ(NMN) + δ_{ring}      |
| 373                 |            | 446               | 448                 |                        |
| 418                 | δ(CNC) + δ_{ring} + δ(NBiN) | 503               | 496                 | δ(CNC) + δ_{ring} + δ(NMN) |
| 461                 | 510               | 511 shoulder      | δ(CNC) + δ_{ring} + δ(NMN) |
| 492                 | 579               | 576               | δ(CNC) + δ_{ring}   |
| 624                 | δ(CNC) + δ_{ring} | 710               | 711                 | δ(CNC) + δ_{ring}      |
| 662                 |            | 720               | 724                 |                        |
| 679                 |            | 738               | 736                 |                        |
| 757                 |            | 843               | 843                 | δ_{exp}(CCH)           |
| 993                 |            | 961               | v(MO)               |                        |

In the framework of theoretical investigation, we executed quantum-chemical calculations for the optimization of the geometry of the etioporphyrin II complexes with vanadyl and titanyl cations, a calculation of their vibration spectra, dipole moments, as well as the distribution of charge and spin densities and Mulliken population analysis.

The results of the quantum-chemical calculations are in complete agreement with the above considerations. Thus, for the titanyl complex the Mulliken charges of the titanium and oxygen atoms are equal to 1.41 and –0.43, respectively. The charges of all four nitrogen atoms are equivalent and equal to –0.50, and for the carbon atoms bonded with the nitrogen atoms the charges are equal to –0.15. The residual covalences of Ti–N and Ti–O bonds are respectively 0.49 and 2.32. In the case of the vanadyl complex the corresponding values are: 1.25 for V, –0.38 for O, –0.48 for N, and 0.15 for C. The residual covalences of the V–N and V–O bonds are 0.52 and 2.33. The calculated dipole moment of the titanyl complex is higher (2.94 D) than in case of vanadyl (2.32 D).
Conclusion

Summarizing the obtained results, we can conclude that the “apix” bond of the metals in the vanadyl etioporphyrin II complex has more pronounced covalent nature. In contrast, in the case of titanyl a structure with some redistribution of the electron density to the oxygen atom is implemented. This increases the “apix” Ti–O bond polarity and the dipole moment of the titanyl macrocomplex in general.

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