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Theoretical Study of Oxozirconium Porphyrin, Octamethylporphyrin, Porphyrazine and Phthalocyanine Complexes

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The molecular structures, vibrational spectra and electronic spectra of oxozirconium porphyrin, octamethylporphyrin, porphyrazine and phthalocyanine have been studied by density functional theory and time-dependent density functional theory calculations utilizing B3LYP method and triple-ζ valence basis sets.

Keywords: Zirconium, porphyrin, phthalocyanine, porphyrazine, density functional theory, molecular structure, vibrational spectra.

Introduction

Among porphyrin and phthalocyanine complexes of IV period metals the titanium complexes are most widely studied. Oxotitanum phthalocyanine (TiOPc) is a well-known near-IR photoconductor which is applied in GaAsAl laser printers, and it was studied extensively. Its structures in crystals[1] as well as in the gas phase[2] were investigated experimentally, by X-ray crystallography and gas-phase electron diffraction, respectively. Electronic spectra, photoconductivity and optical properties of the solid state TiOPc were also intensively studied (for detailed list of references see[2,3]).

Until recently, the information about the structure of oxotitanium porphyrins was absent. In 2006 Sakurai *et al.*[4] investigated a discoloration reaction of oxotitanium porphyrin (TiOP) by density functional theory calculations. According to the data of the study,[4] geometry optimization yielded a structure of C_{4v} symmetry for TiOP. In 2008 a study of molecular structures, vibrational spectra and electronic spectra of oxotitanium complexes of porphyrin (TiOP), octamethylporphyrin (TiO(OMP)), porphyrazine (TiOPz) and phthalocyanine (TiOPc) by density functional theory computations was carried out.[3] All four molecules were found to possess the equilibrium structures of C_{4v} symmetry with convex macrocycles.[3]

On the other hand, information about structures of zirconium porphyrin and phthalocyanine complexes is scant. Structural studies of oxozirconium complexes are absent. X-ray crystallographic studies of other zirconium complexes with axial substituents exist, namely of chloro-*cis*-bis(trimethylsilyl)amido(5,10,15,20-tetraphenyl-porphyrinato)zirconium(IV),[5] dichloro-octaethylporphyrinato-zirconium(IV),[6] bis(*tert*-butoxy)octaethylporphyrinatozirconium(IV),[6] dimethyloctaethylporphyrinatozirconium(IV),[6] (octaethylporphyrinato)trimethylsilylmethylzirconium(IV)[7] and bis(trimethylsilylmethyl)octaethylporphyrinzirconium.[8] All the complexes mentioned feature the zirconium atom displaced out of the average plane of four nitrogen atoms, a convex macrocycle and the *cis*-configuration of extraligands, except the (octaethylporphyrinato)trimethylsilylmethyl-zirconium, where only one axial substituent is present.

The present study aims at extending the knowledge of Zr complexes with macrohetrocyclic ligands as well as at comparison with similar well-studied TiO coordination compounds.

Computational

The molecules of oxozirconium complexes have been studied by density functional theory (DFT) computations utilizing the B3LYP hybrid method (Becke + Slater + HF exchange and LYP + VWN5 correlation). All geometry optimization and force field calculations were performed using PC GAMESS 7.0 QC package,[9] which is partially based on the GAMESS (US) software package,[10] running under Linux operating system.

The core electron shells (1s2s2p3s3p3d) of the zirconium atom were described by a relativistic effective core potential (ECP).[11] For description of the zirconium valence shells a (8s7p6d2f1g/6s5p3d2f1g) basis set[11,12] has been used. All other atoms (C, N, O, H) were described by triple-ζ valence basis sets (10s6p/5s3p) in case of C, N, O and (5s/3s) in case of H[13] (designated TZV in GAMESS) with addition of polarization functions (ζ_d = 1.28 (O), ζ_d = 0.98 (N), ζ_d = 0.72[14] and ζ_p = 1.0 (H)[15]). Such level of theory has been found to yield accurate structural parameters in earlier combined (experimental and theoretical) studies of oxotitanium phthalocyanine[2] and other large macroheterocyclic molecules.[16-20]

Singlet and triplet excited states and the electronic spectra were studied using time-dependent density functional theory (TDDFT) implemented in PC GAMESS 7.0.[9] In all four molecules the molecular orbitals formed mostly by 1*s* orbitals of C, N, and O atoms, namely 25 first (lowest energy) orbitals in oxozirconium porphyrin and porphyrazine, 33 in octamethylporphyrin and 41 in phthalocyanine, were excluded (“frozen”) from the TDDFT calculations.

Visualization of the results has been done using the MacMolPlt software.[21] Supplementary material is available at http://dx.doi.org/10.6060/mhc2012.120257z

Results and Discussion

According to the results of our calculations all four molecules have the equilibrium structures of C_{4v} symmetry, shown in Figures 1-4. The structural parameters (bond distances, valence angles and dihedral angles significantly differ from either 0 or 180 degrees) of the molecules in question are presented in Table 1; data from study[3] of oxotitanium complexes are given for comparison.

The structural parameters of the macroheterocyclic ligands remained almost unchanged compared to the oxotitanium complexes, with two noticeable exceptions. In porphyrin and octamethylporphyrin oxozirconium complexes the distances between C_{p1} atoms in the pyrrole rings and C_m (*meso*-atoms) are longer than the corresponding distances in similar oxotitanium complexes by 0.008 A. Porphyrazine and phthalocyanine complexes feature similar elongations of $r(C_{p1}\text{-}N_m)$ distances, but to a lesser extent (0.004-0.005 Å). The other differences are in the values of $\alpha(N\text{-}C_{p1}\text{-}C_{p2})$ valence angles; they are smaller by 0.7 degrees in ZrOP and ZrO(OMP) compared to TiOP and TiO(OMP) and by 0.3-0.5 degrees in ZrOPz and ZrOPc compared to TiOPz and TiOPc. The changes of $r(C_{p1}\text{-}C_m)/r(C_{p1}\text{-}N_m)$ distances and $\alpha(N\text{-}C_{p1}\text{-}C_{p2})$ valence angles are clearly interdependent. The described changes result in a significant increase of the size of the coordination cavity. Thus, the N···N distance (*i.e.* the side of the square formed by four central nitrogen atoms) increased by 0.063 Å in porphyrins, from 2.892-2.893 Å in TiOP and TiO(OMP) to 2.955-2.956 Å in ZrOP and ZrO(OMP). The change in phthalocyanine and porphyrazine complexes is slightly smaller, 0.057 Å (from 2.805 to 2.862 Å in phthalocyanine and from 2.766 to 2.823 Å in porphyrazine).

This widening of the coordination cavity is certainly caused by a larger size of the Zr^{4+} ion with ionic radius of 0.72 Å, compared to 0.60 Å of Ti^{4+}. The increase of the ionic radius also results in significant heightening of the ZrO_4 pyramid in comparison to TiO_4, to 0.831 Å in oxozirconium porphyrin, 0.836 Å in octamethylporphyrin, 0.976 Å in porphyrazine and 0.933 Å in phthalocyanine complexes (the heights in oxotitanium complexes are 0.577 to 0.690 Å,[3]).

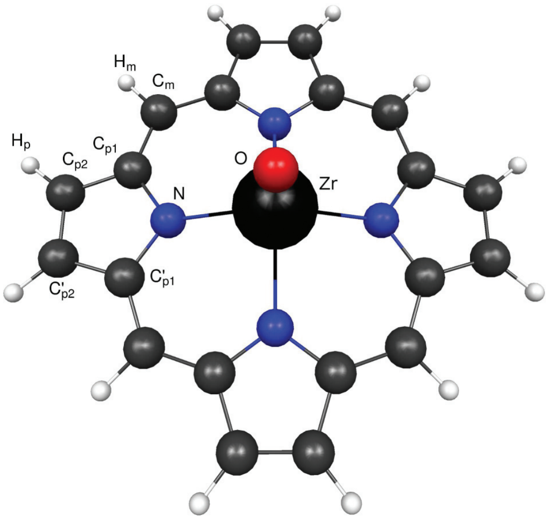

Figure 1. Molecular structure of oxozirconium porphyrin.

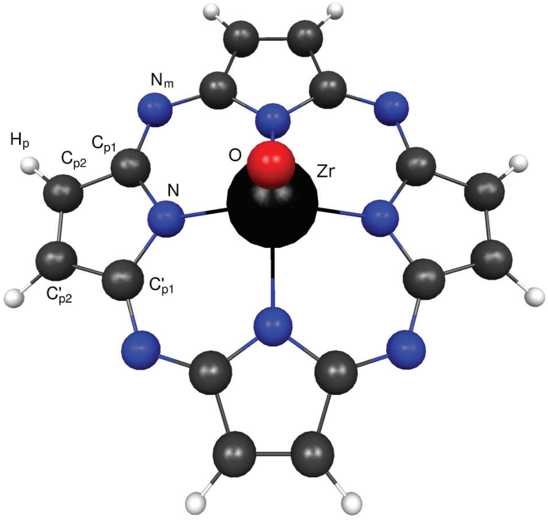

Figure 3. Molecular structure of oxozirconium porphyrazine.

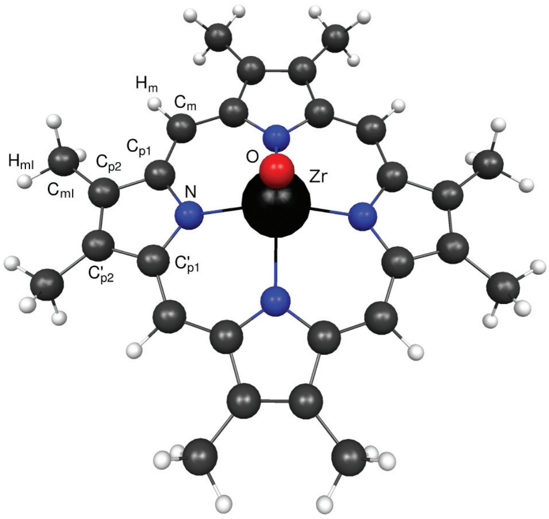

Figure 2. Molecular structure of oxozirconium octamethylporphyrin.

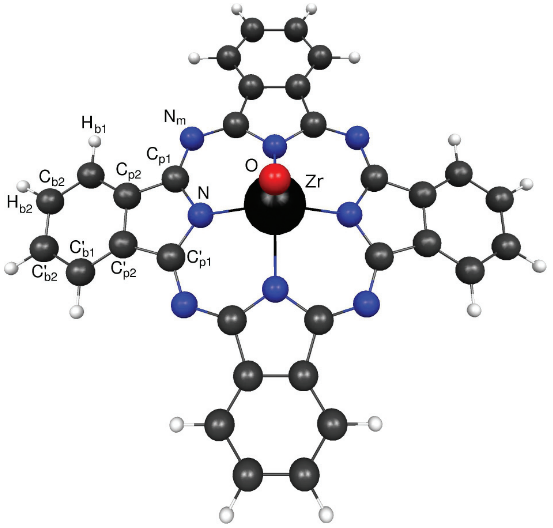

Figure 4. Molecular structure of oxozirconium phthalocyanine.

Table 1. Structural parameters of oxozirconium and oxotitanium (data from study [3]) complexes (P – porphyrin, OMP – octamethylporphyrin, Pz – porphyrazine, Pc – phthalocyanine)[a]

	Oxozirconium complexes				Oxotitanium complexes[3]			
	P	OMP	Pz	Pc	P	OMP	Pz	Pc
Bond distances, Å								
$r(Zr\text{-}O)$	1.768	1.774	1.771	1.769	1.614	1.617	1.620	1.617
$r(Zr\text{-}N)$	2.249	2.251	2.222	2.229	2.125	2.125	2.074	2.087
$r(N\text{-}C_{p1})$	1.372	1.370	1.372	1.375	1.373	1.372	1.373	1.376
$r(Cm\text{-}C_{p1})/r(N_m\text{-}C_{p1})^b$	1.400	1.400	1.331	1.327	1.392	1.392	1.327	1.323
$r(C_{p1}\text{-}C_{p2})$	1.443	1.453	1.455	1.458	1.441	1.450	1.453	1.456
$r(C_{p2}\text{-}C0_{p2})$	1.363	1.372	1.358	1.409	1.361	1.370	1.357	1.406
$r(C_{p2}\text{-}C_{ml})$		1.497				1.498		
$r(C_{p2}\text{-}C_{b1})$				1.393				1.393
$r(C_{b1}\text{-}C_{b2})$				1.391				1.391
$r(C_{b2}\text{-}C'_{b2})$				1.405				1.406
$r(C_m\text{-}H_m)$	1.083	1.083			1.083	1.082		
$r(C_{p2}\text{-}H_p)$	1.079		1.078		1.079		1.078	
$r(C_{ml}\text{-}H_{ml})$		1.090				1.090		
$r(C_{ml}\text{-}H'_{ml})$, $r(C_{ml}\text{-}H''_{ml})$		1.094				1.094		
$r(C_{b1}\text{-}H_{b1})$				1.082				1.082
$r(C_{b2}\text{-}H_{b2})$				1.083				1.083
Valence angles, degrees								
$\alpha(O\text{-}Zr\text{-}N)$	111.7	111.8	116.1	114.7	105.8	105.8	109.4	108.1
$\alpha(Zr\text{-}N\text{-}C_{p1})$	125.0	125.0	125.3	124.3	125.6	125.7	125.4	124.6
$\alpha(N\text{-}C_{p1}\text{-}C_m)^b$	125.2	124.9	127.4	127.5	125.2	124.9	127.3	127.5
$\alpha(N\text{-}C_{p1}\text{-}C_{p2})$	108.8	109.3	108.8	108.3	109.5	110.0	109.1	108.8
$\alpha(C_{p1}\text{-}C_{p2}\text{-}C0_{p2})$	107.2	106.8	107.2	106.7	107.1	106.7	107.1	106.7
$\alpha(C_{p1}\text{-}C_{p2}\text{-}C_{ml})$		124.6				124.6		
$\alpha(C_{p1}\text{-}C_{p2}\text{-}C_{b1})$				132.2				132.2
$\alpha(C_{p1}\text{-}C_{p2}\text{-}H_p)$	125.0		123.8		124.9		123.7	
$\alpha(C_{p2}\text{-}C_{ml}\text{-}H_{ml})$		111.5				111.4		
$\alpha(C_{p2}\text{-}C_{ml}\text{-}H'_{ml})$		111.4				111.5		
$\alpha(C_{p2}\text{-}C_{ml}\text{-}H''_{ml})$		111.6				111.6		
$\alpha(C_{p2}\text{-}C_{b1}\text{-}C_{b2})$				117.8				117.7
$\alpha(C_{b1}\text{-}C_{b2}\text{-}C'_{b2})$				121.2				121.2
$\alpha(C_{p2}\text{-}C_{b1}\text{-}H_{b1})$				120.7				120.7
$\alpha(C_{b1}\text{-}C_{b2}\text{-}H_{b2})$				119.6				119.6
Dihedral angles, degrees								
$\gamma(O\text{-}Zr\text{-}N\text{-}C_{p1})$	-80.7	-80.4	-82.1	-81.8	81.3	81.0	81.8	81.9
$\gamma(Zr\text{-}N\text{-}C_{p1}\text{-}C_m)^b$	-20.6	-20.9	-22.1	-21.7	16.7	16.9	18.6	17.7
$\gamma(Zr\text{-}N\text{-}C_{p1}\text{-}C_{p2})$	162.7	162.1	163.1	162.2	-165.0	-164.5	-164.5	-164.5
$\gamma(C_{p2}\text{-}C'_{p2}\text{-}C_{ml}\text{-}H_{ml})$		3.4				-2.0		
$\gamma(C_{p2}\text{-}C'_{p2}\text{-}C_{ml}\text{-}H'_{ml})$		123.5				-122.0		
$\gamma(C_{p2}\text{-}C'_{p2}\text{-}C_{ml}\text{-}H''_{ml})$		116.6				118.0		

[a] The labeling of atoms used throughout the text and tables is the following (see also Figures 1-4): N – N atoms in the pyrrole rings; C_m and N_m – *meso* (methine bridge) C atoms (ZrOP, ZrO(OMP)) and *meso* N atoms (ZrOPz, ZrOPc), respectively; C_{p1} – C atoms in the pyrrole rings bonded to N; C_{p2} – C atoms in the pyrrole rings bonded to C_{p1}; C_{ml} – C atoms in the methyl groups (ZrO(OMP)); C_{b1} – C atoms in the benzene rings bonded to C_{p2} (ZrOPc); C_{b2} – C atoms in the benzene rings bonded to C_{b1} (ZrOPc). H atoms have the same indices as the C atoms that they are bonded.

[b] C_m in ZrOP and ZrO(OMP), N_m in ZrOPz and ZrOPc.

Table 2. Excited states of oxozirconium porphyrin and octamethylporphyrin (with excitation energies less than 4 eV for the singlet states). Data for similar oxotitanium complexes [3] are given for comparison.

	E, eV	λ, nm	*f* [a]		*E*, eV	λ, nm		*E*, eV	λ, nm	*f* [a]		*E*, eV	λ, nm
		Oxozirconium porphyrin							Oxotitanium porphyrin[3]				
^1E	2.337	530	$5\cdot10^{-5}$	^3E	1.680	738	^1E	2.386	520	0.003	^3E	1.745	711
^1E	3.224	385	0.798	^3E	2.018	614	$^1B_2$	2.960	419	0	^3E	2.040	608
$^1A_2$	3.323	373	0	$^3B_2$	3.066	404	$^1B_1$	3.109	399	0	$^3B_2$	2.942	421
$^1B_2$	3.335	372	0	$^3A_2$	3.109	399	^1E	3.402	364	1.610	$^3B_1$	3.095	401
$^1B_1$	3.361	369	0	^3E	3.152	393	$^1A_2$	3.620	342	0	$^3B_2$	3.132	421
$^1A_1$	3.414	363	0.003	$^3A_1$	3.179	390							
^1E	3.723	333	1.217	$^3B_1$	3.231	384							
^1E	3.729	333	0.024	$^3B_2$	3.335	372							
$^1B_2$	3.801	326	0	^3E	3.420	362							
$^1A_2$	3.891	319	0	$^3B_2$	3.561	348							
$^1B_2$	3.910	317	0	$^3A_2$	3.573	347							
		Oxozirconium octamethylporphyrin							Oxotitanium octamethylporphyrin [3]				
^1E	2.293	541	0.018	^3E	1.690	734	^1E	2.327	533	0.033	^3E	1.715	723
^1E	3.135	395	0.855	^3E	1.961	632	$^1B_1$	2.902	427	0	^3E	2.019	614
$^1A_2$	3.269	379	0	$^3B_2$	2.875	431	$^1B_2$	2.997	414	0	$^3B_1$	2.888	429
$^1B_2$	3.278	378	0	$^3A_2$	2.899	428	^1E	3.289	377	1.499	$^3B_2$	2.909	426
$^1B_1$	3.344	371	0	^3E	2.913	426	$^1A_2$	3.381	366	0	$^3A_2$	2.938	422
$^1A_1$	3.403	364	0.004	$^3A_1$	3.063	405	$^1B_2$	3.392	366	0	$^3B_2$	2.977	416
^1E	3.424	362	0.017	$^3B_1$	3.113	398	^1E	3.481	356	0.144	^3E	2.992	414
^1E	3.617	343	1.459	^3E	3.233	383	$^1B_1$	3.501	354	0	$^3A_1$	3.098	400
$^1B_2$	3.711	334	0	$^3B_2$	3.421	362	$^1A_1$	3.582	346	0.002	$^3B_1$	3.166	392
$^1A_2$	3.713	334	0	$^3B_1$	3.476	357							
$^1B_1$	3.767	329	0	$^3B_2$	3.564	349							
$^1A_1$	3.800	326	$3\cdot10^{-5}$	$^3A_2$	3.569	347							
$^1B_2$	3.807	326	0	$^3A_1$	3.591	345							
$^1B_1$	3.837	323	0	$^3B_1$	3.619	343							

[a] Oscillator strength, multiplied by 2 for doubly-degenerate ^1E states.

As in the Ti species, there is clear correlation between the size of the coordination cavity and the pyramid height, the larger the cavity, the lower the pyramid. The changes of all other parameters are within 0.003 Å for distances and 0.1 degrees for angles, being probably too small for discussing them.

Vibrational modes of the studied oxozirconium complexes can be classified among the symmetry species as follows:

$$\Gamma = 16A_1 + 11A_2 + 13B_1 + 14B_2 + 27E \text{ (ZrOP)};$$
$$\Gamma = 14A_1 + 10A_2 + 12B_1 + 12B_2 + 24E \text{ (ZrOPz)};$$
$$\Gamma = 5\,A_1 + 20\,A_2 + 22B_1 + 23B_2 + 45E \text{ (ZrO(OMP))};$$
$$\Gamma = 23A_1 + 19\,A_2 + 21B_1 + 21B_2 + 42E \text{ (ZrOPc)}.$$

This labeling corresponds to the orientation of the molecules in such a way that the Zr-N bonds are located in *xz* and *yz* planes. Modes of A_1 and E symmetries are active in the infrared spectra. The calculated infrared spectra of four oxotitanium complexes are presented in Figure 5 (Tables of numerical values of frequencies and intensities are available as Supplementary information.) In order to simulate the shape of a typical experimental spectrum the individual bands were described by Lorentz curves with a half-width of 10 cm^{-1}.

Excited states of the four studied macroheterocyclic complexes (with the excitation energies less than 4 eV) are listed in Tables 2 and 3; data for oxotitanium complexes from study [3] are given for comparison. It is interesting to note that the lowest excited states in all molecules are very similar to ones in the corresponding oxotitanium complexes (see ref. [3]). All of them are ^1E states and the corresponding wavelengths differ by no more than 10 nm from those in the TiO complexes. Oxozirconium phthalocyanine is especially demonstrative: the calculated wavelength of its *Q* band is only 1 nm larger than in oxotitanium phthalocyanine[3] (618 *vs.* 617 nm). Hence, it may be suggested that the nature of the central ion has very little influence on the first excited electronic states of these molecules in their isolated states.

The Soret band in ZrO porphyrin and octamethylporphyrin complexes is bathochromically shifted by *ca*. 20 nm in comparison to oxotitanium species (from 364 to 385 nm in porphyrin and from 377 to 395 nm in octamethylporphyrin). The visible part of the phthalocyanine spectrum remains

Table 3. Excited states of oxozirconium porphyrazine and phthalocyanine (with excitation energies less than 4 eV for the singlet states). Data for similar oxotitanium complexes [3] are given for comparison.

	E, eV	λ, nm	f [a]		E, eV	λ, nm							
		Oxozirconium porphyrazine							Oxotitanium porphyrazine[3]				
$^{1}\mathrm{E}$	2.394	517	0.229	$^{3}\mathrm{E}$	1.440	861	$^{1}\mathrm{E}$	2.429	510	0.291	$^{3}\mathrm{E}$	1.450	855
$^{1}\mathrm{E}$	2.842	436	0.145	$^{3}\mathrm{E}$	2.440	508	$^{1}\mathrm{A}_{2}$	3.228	384	0	$^{3}\mathrm{E}$	2.621	473
$^{1}\mathrm{A}_{2}$	2.856	434	0	$^{3}\mathrm{B}_{2}$	2.684	462	$^{1}\mathrm{B}_{1}$	3.231	384	0	$^{3}\mathrm{B}_{2}$	2.752	451
$^{1}\mathrm{B}_{2}$	2.865	433	0	$^{3}\mathrm{A}_{2}$	2.698	459	$^{1}\mathrm{B}_{2}$	3.250	381	0	$^{3}\mathrm{A}_{2}$	2.768	448
$^{1}\mathrm{B}_{1}$	2.889	429	0	$^{3}\mathrm{E}$	2.713	457	$^{1}\mathrm{E}$	3.312	374	$2\cdot10^{-5}$	$^{3}\mathrm{E}$	2.860	434
$^{1}\mathrm{A}_{1}$	2.934	423	0.003	$^{3}\mathrm{A}_{1}$	2.801	443	$^{1}\mathrm{E}$	3.329	372	0.045	$^{3}\mathrm{A}_{1}$	3.037	408
$^{1}\mathrm{E}$	3.221	384	$8\cdot10^{-4}$	$^{3}\mathrm{B}_{1}$	2.824	439	$^{1}\mathrm{B}_{1}$	3.358	369	0	$^{3}\mathrm{E}$	3.066	404
$^{1}\mathrm{E}$	3.284	378	0.008	$^{3}\mathrm{E}$	2.974	417	$^{1}\mathrm{A}_{1}$	3.452	359	0.003	$^{3}\mathrm{B}_{1}$	3.095	401
$^{1}\mathrm{A}_{2}$	3.475	356	0	$^{3}\mathrm{A}_{2}$	3.054	406	$^{1}\mathrm{E}$	3.555	349	0.207	$^{3}\mathrm{B}_{1}$	3.210	386
$^{1}\mathrm{B}_{2}$	3.479	356	0	$^{3}\mathrm{E}$	3.133	396							
$^{1}\mathrm{A}_{1}$	3.576	347	0.004	$^{3}\mathrm{A}_{1}$	3.172	391							
$^{1}\mathrm{B}_{1}$	3.586	345	0	$^{3}\mathrm{B}_{2}$	3.270	379							
$^{1}\mathrm{B}_{2}$	3.634	341	0	$^{3}\mathrm{A}_{1}$	3.323	373							
$^{1}\mathrm{A}_{2}$	3.677	337	0	$^{3}\mathrm{B}_{1}$	3.337	372							
$^{1}\mathrm{B}_{1}$	3.703	335	0	$^{3}\mathrm{B}_{1}$	3.345	371							
$^{1}\mathrm{A}_{1}$	3.705	335	$2\cdot10^{-4}$	$^{3}\mathrm{A}_{2}$	3.612	343							
$^{1}\mathrm{E}$	3.940	314	1.054	$^{3}\mathrm{B}_{1}$	3.622	342							
$^{1}\mathrm{B}_{1}$	3.958	313	0	$^{3}\mathrm{E}$	3.650	340							
		Oxozirconium phthalocyanine							Oxotitanium phthalocyanine[3]				
$^{1}\mathrm{E}$	2.007	618	0.774	$^{3}\mathrm{E}$	1.063	1167	$^{1}\mathrm{E}$	2.009	617	0.779	$^{3}\mathrm{E}$	1.069	1160
$^{1}\mathrm{E}$	3.100	400	0.081	$^{3}\mathrm{E}$	2.761	449	$^{1}\mathrm{B}_{1}$	2.433	510	0	$^{3}\mathrm{B}_{1}$	2.419	513
$^{1}\mathrm{A}_{2}$	3.139	394	0	$^{3}\mathrm{B}_{2}$	2.841	436	$^{1}\mathrm{B}_{2}$	3.264	380	0	$^{3}\mathrm{B}_{2}$	2.848	435
$^{1}\mathrm{B}_{2}$	3.144	394	0	$^{3}\mathrm{E}$	2.887	429	$^{1}\mathrm{A}_{2}$	3.265	380	0	$^{3}\mathrm{E}$	2.862	433
$^{1}\mathrm{B}_{1}$	3.228	384	0	$^{3}\mathrm{A}_{2}$	2.894	428	$^{1}\mathrm{E}$	3.311	375	0.013	$^{3}\mathrm{A}_{2}$	2.923	424
$^{1}\mathrm{B}_{1}$	3.203	387	0	$^{3}\mathrm{B}_{1}$	2.972	417	$^{1}\mathrm{B}_{1}$	3.377	367	0	$^{3}\mathrm{B}_{1}$	2.999	413
$^{1}\mathrm{A}_{1}$	3.270	379	0.004	$^{3}\mathrm{A}_{1}$	3.010	412	$^{1}\mathrm{B}_{2}$	3.418	363	0	$^{3}\mathrm{A}_{1}$	3.064	405
$^{1}\mathrm{E}$	3.289	377	$4\cdot10^{-6}$	$^{3}\mathrm{B}_{2}$	3.066	404	$^{1}\mathrm{B}_{1}$	3.465	358	0	$^{3}\mathrm{B}_{2}$	3.066	404
$^{1}\mathrm{E}$	3.398	365	0.006	$^{3}\mathrm{B}_{1}$	3.073	403	$^{1}\mathrm{A}_{1}$	3.475	357	0.002	$^{3}\mathrm{E}$	3.071	404
$^{1}\mathrm{B}_{2}$	3.441	360	0	$^{3}\mathrm{E}$	3.193	388	$^{1}\mathrm{E}$	3.499	354	0.005	$^{3}\mathrm{B}_{1}$	3.145	394
$^{1}\mathrm{A}_{2}$	3.462	358	0	$^{3}\mathrm{E}$	3.209	386	$^{1}\mathrm{A}_{2}$	3.554	349	0	$^{3}\mathrm{A}_{2}$	3.249	382
$^{1}\mathrm{B}_{2}$	3.497	355	0	$^{3}\mathrm{A}_{2}$	3.229	384	$^{1}\mathrm{E}$	3.576	347	0.238	$^{3}\mathrm{E}$	3.283	378
$^{1}\mathrm{A}_{1}$	3.525	352	$2\cdot10^{-5}$	$^{3}\mathrm{B}_{1}$	3.234	383							
$^{1}\mathrm{A}_{2}$	3.533	351	0	$^{3}\mathrm{A}_{1}$	3.240	383							
$^{1}\mathrm{B}_{1}$	3.551	349	0	$^{3}\mathrm{B}_{2}$	3.295	376							
$^{1}\mathrm{E}$	3.588	346	0.855	$^{3}\mathrm{E}$	3.339	371							
$^{1}\mathrm{B}_{2}$	3.639	341	0	$^{3}\mathrm{B}_{1}$	3.346	371							
$^{1}\mathrm{E}$	3.638	341	0.463	$^{3}\mathrm{A}_{2}$	3.376	367							
$^{1}\mathrm{A}_{1}$	3.708	334	0.004	$^{3}\mathrm{A}_{1}$	3.388	366							
$^{1}\mathrm{B}_{1}$	3.715	334	0	$^{3}\mathrm{B}_{2}$	3.409	364							
$^{1}\mathrm{A}_{2}$	3.753	330	0	$^{3}\mathrm{B}_{1}$	3.411	363							
$^{1}\mathrm{A}_{2}$	3.858	321	0	$^{3}\mathrm{E}$	3.508	353							
$^{1}\mathrm{B}_{1}$	3.869	320	0	$^{3}\mathrm{A}_{2}$	3.542	350							
$^{1}\mathrm{E}$	3.876	320	0.118	$^{3}\mathrm{A}_{1}$	3.566	348							
$^{1}\mathrm{A}_{1}$	3.888	319	0.002	$^{3}\mathrm{B}_{2}$	3.603	344							
$^{1}\mathrm{B}_{2}$	3.892	319	0	$^{3}\mathrm{A}_{2}$	3.790	327							

[a] Oscillator strength, multiplied by 2 for doubly-degenerate $^{1}\mathrm{E}$ states.

almost unchanged. On the other hand, in the visible spectrum of oxozirconium porphyrazine an absorption band at 436 nm is present, that has no analogue in the oxotitanium complex. The corresponding ^{1}E excited state in ZrOPz has a significant contribution of the HOMO-1→LUMO+1 excitation (with the weight of 0.73). In turn, the HOMO-1 orbital is composed partially of *d*-type AOs of zirconium. Therefore, the oxozirconium porphyrazine represent the case of a very significant influence of the central ion on the visible electronic spectrum.

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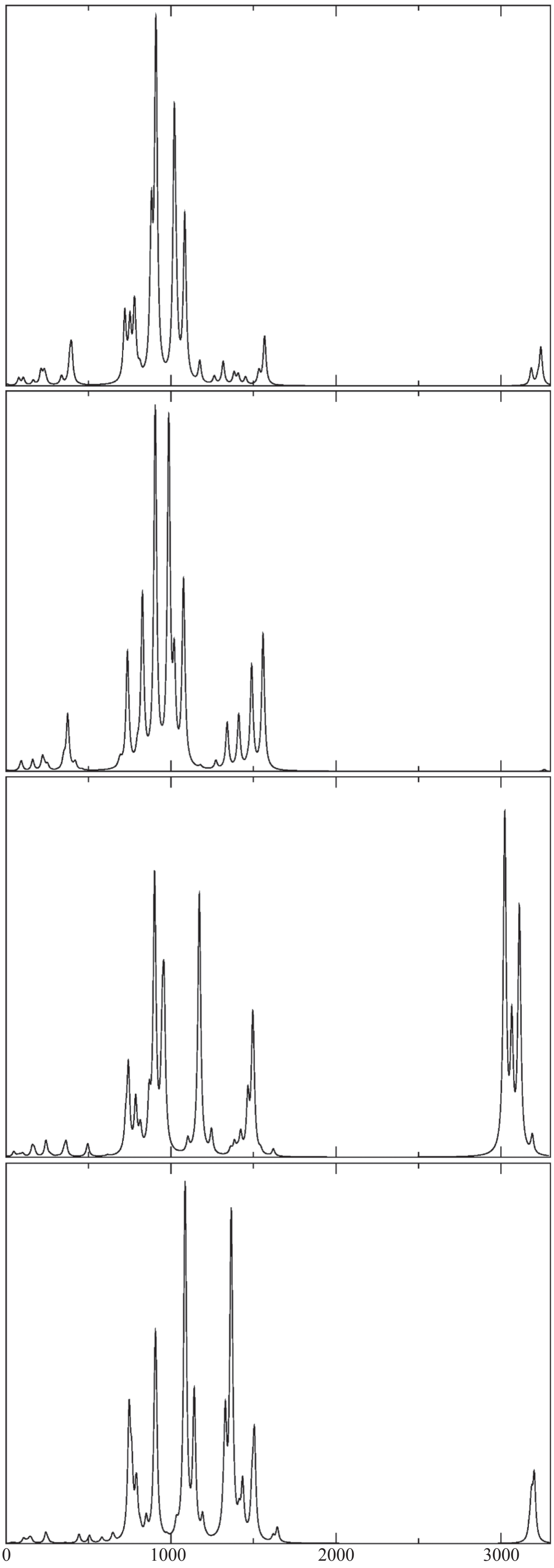

Figure 5. Calculated infrared spectra of ZrOP, ZrOPz, ZrO(OMP), and ZrOPc (top to bottom, frequencies in cm^{-1}, intensities in arbitrary units).

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