

Electrochemistry and Spectroelectrochemistry of Zirconium(IV) and Hafnium(IV) Phthalocyanines with β -Diketone Axial Ligands in Nonaqueous Media

Zhongping Ou,^{a,b} Riqiang Zhan,^a Larisa A. Tomachynski,^c Victor Ya. Chernii,^c and Karl M. Kadish^{a@}

Dedicated to Professor Claudio Ercolani on the occasion of his 75th birthday

^aDepartment of Chemistry, University of Houston, Houston, Texas 77204-5003, USA

^bSchool of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, P. R. China

^cInstitute of General and Inorganic Chemistry, Kiev, Ukraine

@Corresponding author E-mail: kkadish@uh.edu

Fourteen Zr^{IV} and Hf^{IV} phthalocyanines containing different β -diketone axial ligands were characterized in CH₂Cl₂ containing 0.1 M TBAP as to their electrochemical and spectroelectrochemical properties. No significant difference in electrochemical behavior was seen between the Zr^{IV} and Hf^{IV} complexes. These compounds exhibit up to three oxidations and four reductions under the given solution conditions and the HOMO-LUMO gap ranges from 1.56 to 1.67 V. The changes in redox potentials and the spectra of the compounds as a function of substituents attached on the β -ketone axial ligands were evaluated using linear free energy relationships. The thin-layer UV-visible spectroelectrochemistry indicates that phthalocyanine π -cation radicals and π -anion radicals were formed upon the first oxidation and first reduction, respectively.

Keywords: Zr^{IV} and Hf^{IV} phthalocyanines, electrochemistry, spectroelectrochemistry, substituent effect.

Introduction

Phthalocyanines have received considerable attention because they have a great deal of applications,^[1-10] particularly in the fields of molecular photovoltaics,^[1] photobiology^[4] and advanced materials.^[5,9] Each of these applications requires a detailed understanding of the redox processes which occur in the utilized macrocyclic complexes. Phthalocyanines are aromatic systems containing 18 π electrons and may be electrooxidized in two steps or electroreduced in four steps, each of which involves one electron.^[11-13] Although a large number of transition metal phthalocyanines have been prepared and characterized over the last four decades, only a few studies involving the redox properties of phthalocyanines containing group IVB elements have been reported.^[14] Our own groups have been particularly interested in the chemistry of zirconium and hafnium phthalocyanines because of their coordination chemistry and electrochemical properties.^[15-27]

Metallophthalocyanines in which the central atom has a valence of three or more are known to possess one or two out of plane axial ligands.^[28-31] We recently reported the synthesis of zirconium and hafnium phthalocyanine complexes with various β -diketones and polyphenols which were made by replacing the two Cl⁻ ions of the dichloro(phthalocyanine) complexes with organic ligands^[17,23,24,27] and this was followed by a preliminary electrochemical study on some of these compounds.^[32] The present work is a continuation of these studies and involves the electrochemical and spectroelectrochemical characterization of fourteen related Zr^{IV} and Hf^{IV} derivatives whose structures are shown in Chart 1. Some of the compounds were previously

synthesized and characterized as to their redox properties^[24,32] while others are reported for the first time in the present paper. None of the compounds' UV-visible spectra has been reported after oxidation or reduction and one purpose of this study was therefore to systematically examine spectra of

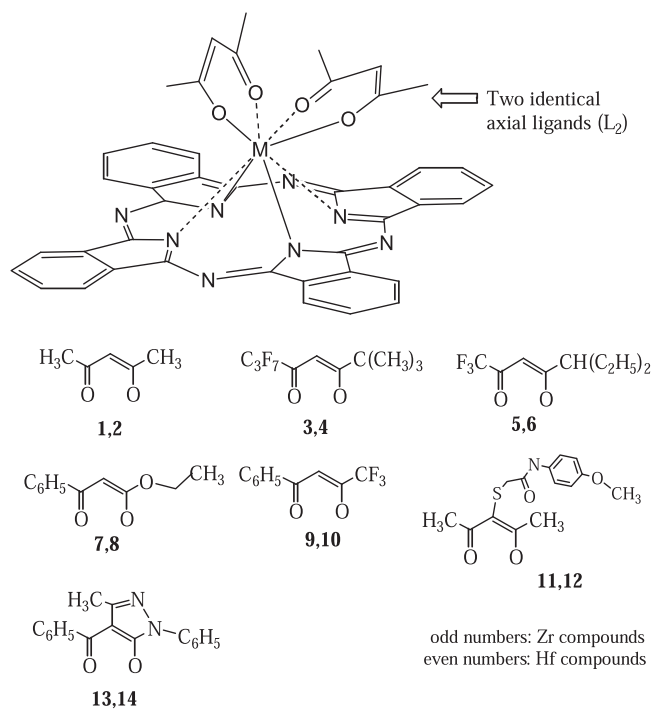


Chart 1. Structures of investigated phthalocyanines

the newly synthesized compounds using thin-layer UV-vis spectroelectrochemistry.

Experimental

Instrumentation

Cyclic voltammetry was carried out using an EG&G Princeton Applied Research (PAR) 173 Potentiostat/Galvanostat or an IBM model EC 225 voltammetric analyzer. A home-made three-electrode cell was used for cyclic voltammetric measurements and consisted of a platinum button or glassy carbon working electrode, a platinum counter electrode and a homemade saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted glass bridge of low porosity that contained the solvent/supporting electrolyte mixture. UV-visible spectroelectrochemical experiments were performed with a home-built thin-layer cell that had a light transparent platinum gauze working electrode. Potentials were applied and monitored with an EG&G PAR Model 173 Potentiostat. Time-resolved UV-visible spectra were recorded with a Hewlett-Packard Model 8453 diode array spectrophotometer. A dry ice/acetone mixture was used to obtain low temperatures that varied from 22 to -60°C . For low temperature measurements, the cell was centered in a slush bath containing dry ice and acetone and the exact temperature was monitored using a mercury thermometer.

Chemicals

Zr^{IV} and Hf^{IV} phthalocyanines were synthesized as previously described.^[17,24] Absolute dichloromethane (CH_2Cl_2) was used as received without further purification. High purity N_2 from Trigas was used to deoxygenate the solution before each electrochemical experiment. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Sigma Chemical or Fluka Chemika Co., recrystallized from ethyl alcohol and dried under vacuum at 40°C for at least one week prior to use.

Results and Discussion

Electrochemistry. Electrochemical properties of the fourteen investigated complexes **1–14** (see Chart 1) were measured in CH_2Cl_2 containing 0.1 M TBAP. Ordinarily, phthalocyanines may be electrooxidized in two one-electron transfer steps while electroreduction may involve up to four

one-electron additions depending upon the compound and solution conditions.^[11,13] However, in the case of the Zr^{IV} and Hf^{IV} complexes, only two reductions have been reported in the literature.^[13] In contrast to phthalocyanines that contain redox active metal centers, the electrochemical properties of the zirconium and hafnium phthalocyanines are determined by the nature of the phthalocyanine macrocycle and the out of plane axial ligands.^[28] The half-wave potentials for oxidation and reduction of the investigated compounds are summarized in Table 1 and examples of cyclic voltammograms for compounds **1**, **2**, **11** and **12** in CH_2Cl_2 containing 0.1 M TBAP are shown in Figure 1. Most of the redox processes

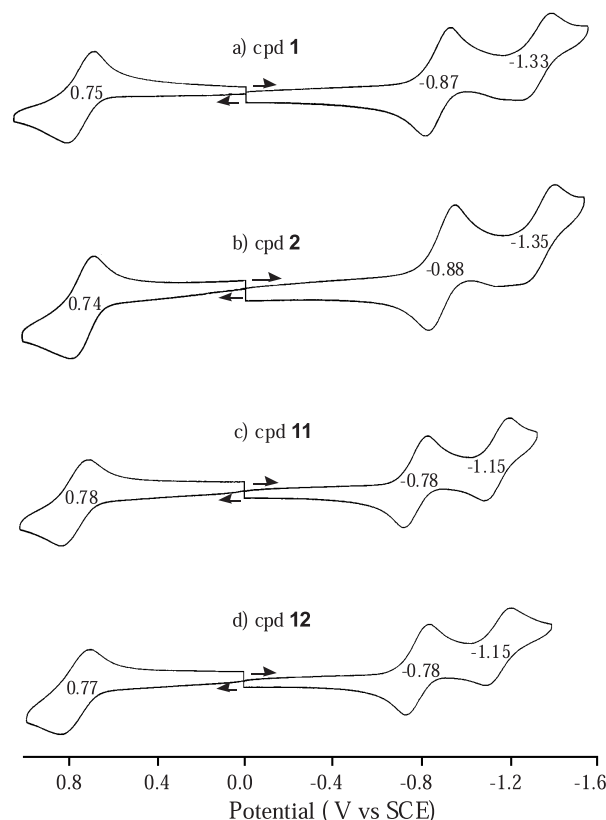


Figure 1. Cyclic voltammograms of (a) **1**, (b) **2**, (c) **11** and (d) **12** in CH_2Cl_2 containing 0.1 M TBAP. Scan rate = 0.1 V/s.

Table 1. Half-wave potentials (V vs. SCE) of investigated zirconium and hafnium phthalocyanines in CH_2Cl_2 containing 0.1 M TBAP.

compound	oxidation			reduction			
	3rd	2nd	1st	1st	2nd	3rd	4th
1		1.49 ^a	0.75	-0.87	-1.33		
2		1.49 ^a	0.74	-0.88	-1.35		
3		1.60 ^a	0.84	-0.83	-1.34	-1.88 ^{b,c}	
4		1.63 ^a	0.86	-0.81	-1.32	-1.90 ^{b,c}	
5		1.58 ^a	0.84	-0.83	-1.27	-1.96 ^{b,c}	
6		1.60 ^a	0.84	-0.83	-1.28	-1.98 ^{b,c}	
7		1.47 ^a	0.75	-0.85	-1.23	-2.10 ^d	
8		1.48 ^a	0.77	-0.87	-1.32	-2.10 ^d	
9	1.55 ^a	0.88	0.79	-0.79	-1.06	-1.19	-1.80 ^{b,c}
10	1.60 ^a	0.93	0.83	-0.76	-1.08	-1.17	-1.78 ^b
11		1.56 ^a	0.78	-0.78	-1.15	-2.02 ^{b,d}	
12		1.56 ^a	0.77	-0.78	-1.15	-2.02 ^{b,d}	
13	1.53 ^a	0.81	0.73	-0.84	-1.28	-1.92 ^b	
14	1.54 ^a	0.81	0.71	-0.85	-1.29	-1.92 ^{b,c}	

^aPeak potential E_{pc} at scan rate = 0.1 mV/s. ^bPeak potential E_{pa} at scan rate = 0.1 mV/s. ^cA small peak can also be observed at $E_{\text{pc}} = -1.54$ V. ^dAt -60°C .

are well-defined under given experimental conditions and the resulting data are discussed below.

Electrooxidation. Compounds **1**, **8**, **11** and **12** undergo two oxidations, the first of which is reversible and located at $E_{1/2} = 0.74$ to 0.86 V vs. SCE, a potential close to previously published values for the same derivatives.^[32,33] The second oxidation is irreversible and located between $E_{pc} = 1.48$ to 1.58 V (see Table 1). As observed for other Zr^{IV} and Hf^{IV} phthalocyanines,^[33] compounds **9**, **10**, **13** and **14** exhibit two reversible oxidations which are located at $E_{1/2} = 0.71$ to 0.81 V and 0.81 to 0.95 V, respectively. There is also an irreversible oxidation located at $E_{pc} = 1.53$ to 1.60 V (Table 1). The peak current for the first two oxidations of cpds **9**, **10**, **13** and **14** is about 50% of the peak current for the first reduction of the same compounds and the two oxidations are much better defined at a temperature of -60°C . As examples, the cyclic voltammograms of compounds **13** and **14** at different temperatures are shown in Figure 2.

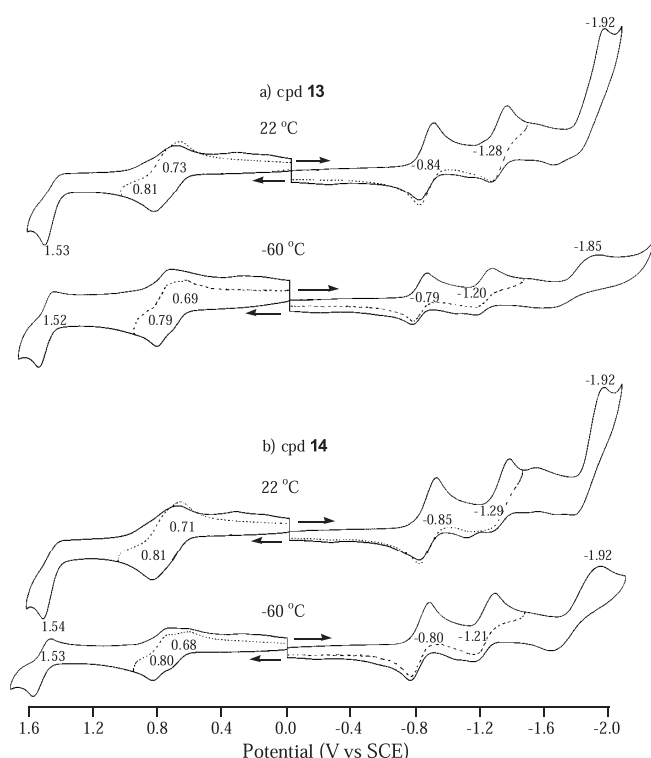


Figure 2. Cyclic voltammograms of (a) **13** and (b) **14** in CH_2Cl_2 containing 0.1 M TBAP. Scan rate = 0.1 V/s.

Electroreduction. Compounds **1** and **2** undergo two reversible reductions while **9** and **10** show four reductions, the first three of which are reversible. The others compounds show two reversible and one irreversible reduction under the same experiment conditions (see Table 1). The reversible reductions are located at $E_{1/2} = -0.76$ to -0.88 and -1.06 to -1.35 V vs. SCE, respectively, values which match the reduction potentials of previously investigated Zr^{IV} and Hf^{IV} phthalocyanines.^[32] The third reduction of **9** and **10** is located at -1.19 and -1.17 V, respectively. The irreversible reduction potentials of all the compounds ranges from -1.78 to -2.02 V while a small peak is seen at $E_p = -1.54$ V for some of the compounds (Table 1).

The potential difference between the first reduction and first oxidation of the complexes, the HOMO–LUMO gap,

ranges from 1.48 to 1.67 V. These values are close to the average the HOMO–LUMO gap of 1.56 V seen for other phthalocyanines when the oxidation and reduction both occur at the conjugated π -ring system.^[11,13] The redox properties fit the general behavior observed for metallophthalocyanines containing non-electroactive metal ions. The potential difference between the first two reductions ranges from 0.27 to 0.51 V.

Electrochemical behavior of **3**, **4**, **5** and **6** is different from that of **1** and **2**, which can be explained by the presence the CF_3 or C_6F_7 group for complexes **3**–**6**. The carbon atom in both CH_3 and CF_3 groups of the out-plane ligands have sp^3 -hybridization and effect of hyper conjugation of these electron orbitals with π -orbitals of quasi aromatic rings takes place. The negative inductive and methomeric effects of the fluoroalkyl groups leads to better delocalization of the negative charge in the π -anion-radical and a reduction in the energy of the molecular orbitals (both occupied and vacant). This effect leads to the appearance of additional reductions and easier reductions as well as more difficult oxidations for compounds **3**, **4**, **5** and **6** as compared to compounds **1** and **2**. The influence of negative inductive and weak positive methomeric effects of the thioalkyl groups in **11**, **12** and the phenyl group conjugated with a quasiaromatic system in **7** and **8** leads to an analogous effect.

The appearance of new oxidation processes for complexes **9** and **10** is a result of concerted action of the CF_3 and phenyl groups. The influence of CF_3 on the phenyl group through conjugated bonds leads to an increased delocalization of positive charge that can be a cause of this effect. The presence of only a phenyl group without a CF_3 on the macrocycle is not enough to affect the oxidation processes (compounds **7** and **8**). In the case of reduction, the influences of CF_3 and the phenyl groups are additive.

Conjugation of the pyrazole ring with the phenyl group in complexes **13** and **14** leads to the appearance of additional oxidations like seen is for compounds **9** and **10**. The behavior of **13** and **14** on reduction process like compounds **7** and **8** are results from the influence of the phenyl group.

Calculations of the influence of such groups as CH_3 , CF_3 and C_6H_5 in positions 1 and 3 of β -diketonates on characteristics of chemical bonds in molecules were earlier performed.^[34] It was found that the influence of the nature of the substituent on bond order is weak but at the same time this is important for atomic charge distribution.^[34–37] The additivity of contributions of substituents in the change of charge state of the central atom leads to the following order of substituent effects: $\text{CF}_3 > \text{C}_6\text{H}_5 > \text{CH}_3 \cong \text{C}(\text{CH}_3)_3 \cong \text{OC}_2\text{H}_5 \cong \text{C}_2\text{H}_5$.

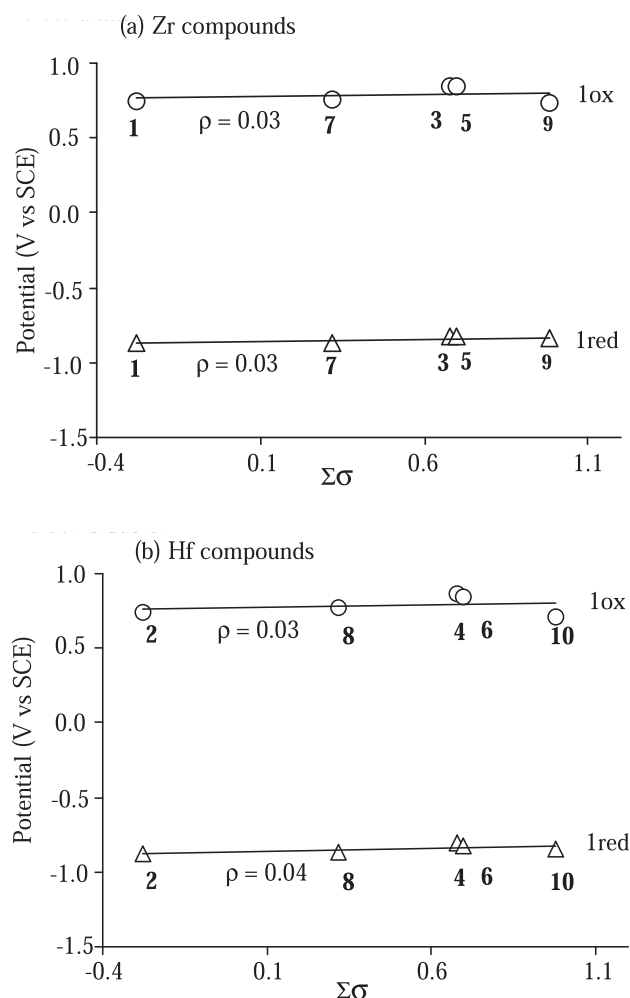
Substituent effect. The difference between the seven Zr^{IV} and Hf^{IV} phthalocyanines is the substituents on the axial ligands but not all the Hammet values of the substituents are available and the available values are summarized in Table 2. Though the total Hammet values ($\Sigma\sigma$)^[38] are so different, the first oxidation and first reduction potentials shift very slightly. For example, from the most electron-donation groups (2CH_3 , 2CH_3) in compound **1** or **2** to the most electron-withdrawing groups ($2\text{C}_6\text{H}_5$, 2CF_3) in compound **9** or **10**, the Hammet values is from -0.28 to 0.98 but the absolute values of the first oxidation and first reduction potentials only shift 0.02 and 0.03 V, respectively, and the HOMO–LUMO gap only changes

Table 2. The first oxidation and first reduction potentials (V vs. SCE) of Zr^{IV} compounds **1**, **3**, **5**, **7** and **9**, Hf^{IV} compounds **2**, **4**, **6**, **8** and **10** and the Hammett values^[37] of their substituents on the axial ligands.

M	cpd	substituents		$\Sigma\sigma$	E_{lox}	E_{red}	$\Delta E(\text{V})^a$
Zr	1	2CH ₃	2CH ₃	-0.28	0.75	-0.87	1.62
	7	2C ₆ H ₅	2OCH ₂ CH ₃	0.32	0.76	-0.87	1.63
	3	2C(CH ₃) ₃	2C ₃ F ₇	0.68	0.84	-0.83	1.67
	5	2CH(C ₂ H ₅) ₂	2CF ₃	0.70	0.84	-0.83	1.67
	9	2C ₆ H ₅	2CF ₃	0.98	0.73	-0.84	1.57
Hf	2	2CH ₃	2CH ₃	-0.28	0.74	-0.88	1.62
	8	2C ₆ H ₅	2OCH ₂ CH ₃	0.32	0.77	-0.87	1.64
	4	2C(CH ₃) ₃	2C ₃ F ₇	0.68	0.86	-0.81	1.67
	6	2CH(C ₂ H ₅) ₂	2CF ₃	0.70	0.84	-0.83	1.67
	10	2C ₆ H ₅	2CF ₃	0.98	0.71	-0.85	1.56

^aPotential difference between the first oxidation (E_{lox}) and first reduction (E_{red}) (HOMO-LUMO gap).

0.05–0.06 V (see Table 2). The same results also observed for the seven Hf^{IV} phthalocyanines. So the substituent effect on $E_{1/2}$ is insensitive both in oxidation and reduction and the slopes of $E_{1/2}$ vs. Hammett values are around 0.0 for both Zr^{IV} and Hf^{IV} phthalocyanines (see Figure 3). A reasonable explanation for such results is because the substituents are far away from the phthalocyanine macrocycle and it is hard to affect to the ring oxidation and reduction potentials through the β -ketones and central metals.

**Figure 3.** Substituent effect on half-wave potentials of Zr^{IV} and Hf^{IV} compounds containing different axial ligands (see Table 2 for substituents in detail) in CH₂Cl₂ containing 0.1 M TBAP.

UV-visible spectra and spectroelectrochemistry.

The spectra of the neutral, singly reduced and singly oxidized species were measured in CH₂Cl₂ and the data are summarized in Table 3–5. UV-visible spectra of the neutral complexes show typical patterns of metallophthalocyanines with characteristic *B*- and *Q*-bands located at 333–350 and 685–695 nm, respectively (Table 3).^[39] A slight bathochromic shift of the *Q*-band occurs from the starting (Pc)MCl₂ in the spectra of all complexes, except for **7** and **8**. An insignificant hypsochromic shift of 2–3 nm is also seen for compounds **7** and **8**. The splitting of the *Q*-band in the UV-vis spectra of each phthalocyanine except for complexes **13** and **14** is observed, thus providing evidence for decreased molecule symmetry and a *cis*-coordination at the metal center.

Table 3. UV-visible spectral data for neutral zirconium and hafnium phthalocyanines in CH₂Cl₂ containing 0.1 M TBAP.

compound	λ , nm ($\epsilon \times 10^{-4}$)			
	Soret band	visible bands		
1	347 (4.6)	615 (2.4)	681 (12.0)	688 (12.5)
2	346 (4.3)	615 (2.1)	680 (11.1)	688 (11.7)
3	341 (4.4)	615 (2.4)	681 (12.4)	687 (12.6)
4	341 (3.7)	614 (1.2)	679 (10.4)	686 (10.5)
5	338 (4.4)	615 (2.2)	680 (11.6)	688 (11.7)
6	338 (4.0)	614 (2.0)	678 (10.1)	688 (10.2)
7	327 (4.4)	617 (2.2)	653 (1.8)	685 (12.0)
8	330 (5.9)	616 (3.0)	657 (2.5)	683 (16.9)
9	330 (6.8)	618 (1.8)	683 (9.6)	691 (9.9)
10	328 (7.4)	617 (2.1)	682 (11.6)	691 (12.1)
11	341 (5.4)	616 (2.3)	680 (12.3)	691 (13.4)
12	341 (5.0)	617 (2.2)	680 (11.4)	692 (12.7)
13	333 (4.8)	622 (2.2)	691 (11.6)	
14	333 (6.6)	622 (3.0)	689 (15.9)	

UV-visible spectra of compounds **1–4**, **9** and **10** were also measured in CDCl₃.^[24] The Soret bands of **1** and **2** are red-shifted by 3 and 6 nm in CH₂Cl₂, respectively and the visible bands are blue shifted by 0–4 nm; at the same time, λ_{max} for the Soret bands of **3** and **4** are identical in CDCl₃ while the visible bands differ from each other by 1–3 nm. The Soret bands of **9** and **10** are blue shifted, by 13 nm for cpd **9** and 16 nm for **10**, in CH₂Cl₂; at the same time the visible bands shift slightly (about 0–3 nm) which is similar to

Table 4. UV-visible spectral data for singly oxidized zirconium and hafnium phthalocyanines in CH₂Cl₂ containing 0.1 M TBAP.

compound	λ , nm ($\epsilon \times 10^{-4}$)				
	Soret region			visible region	
[1] ⁺	329 (3.8)	384 (2.2)	518 (2.6)	734 (1.1)	847 (2.7)
[2] ⁺	331 (3.4)	384 (1.7)	517 (2.1)	733 (0.5)	848 (2.2)
[3] ⁺	331 (3.9)	387 (2.0)	531 (2.3)	737 (0.6)	851 (2.6)
[4] ⁺	331 (3.1)	388 (1.7)	530 (1.8)	736 (0.3)	851 (2.0)
[5] ⁺	331 (3.5)	390 (1.6)	532 (2.0)	735 (0.5)	848 (2.1)
[6] ⁺	329 (3.2)	387 (1.5)	531 (1.7)	735 (0.4)	848 (1.8)
[7] ⁺	317 (4.5)	395 (1.6)	523 (1.7)	736 (0.4)	851 (1.9)
[8] ⁺	308 (6.4)	394 (2.1)	523 (2.4)	736 (0.6)	849 (2.8)
[9] ⁺	327 (6.1)	392 (1.0)	533 (2.5)	738 (0.7)	848 (3.4)
[10] ⁺	326 (7.4)	393 (2.5)	531 (2.9)	734 (1.5)	851 (3.1)
[11] ⁺	330 (4.8)	383 (2.3)	520 (2.7)	736 (0.8)	851 (2.8)
[12] ⁺	328 (4.2)	390 (2.4)	520 (3.3)	738 (1.5)	850 (3.4)
[13] ⁺	318 (4.9)	390 (1.6)	533 (2.1)	747 (0.8)	858 (2.5)
[14] ⁺	314 (6.7)	387 (2.0)	528 (2.6)	747 (0.8)	859 (3.3)

Table 5. UV-visible spectral data for singly reduced zirconium and hafnium phthalocyanines in CH₂Cl₂ containing 0.1 M TBAP.

compound	λ , nm ($\epsilon \times 10^{-4}$)			
	Soret region		visible region	
[1] ⁻	317 (3.1)	590 (4.8)	631 (3.5)	974 (2.0)
[2] ⁻	350 (2.4)	587 (3.9)	630 (2.7)	975 (1.3)
[3] ⁻	305 (2.9)	589 (4.3)	628 (3.0)	979 (1.3)
[4] ⁻	303 (2.3)	586 (3.8)	627 (2.7)	977 (1.0)
[5] ⁻	310 (3.0)	588 (4.1)	625 (3.0)	982 (1.4)
[6] ⁻	302 (3.8)	584 (3.4)	627 (2.5)	981 (0.9)
[7] ⁻	319 (3.5)	592 (3.7)	633 (2.6)	980 (1.0)
[8] ⁻	313 (5.1)	590 (4.8)	633 (3.6)	979 (1.1)
[9] ⁻	330 (4.0)	591 (3.6)	624 (3.1)	972 (2.3)
[10] ⁻	328 (4.4)	587 (3.3)	625 (2.5)	976 (1.3)
[11] ⁻	342 (3.1)	587 (4.6)	622 (3.3)	985 (1.9)
[12] ⁻	341 (2.8)	583 (4.3)	625 (2.9)	985 (1.6)
[13] ⁻	333 (3.2)	597 (4.4)	631 (3.2)	986 (1.8)
[14] ⁻	309 (4.9)	592 (5.7)	632 (4.3)	985 (2.2)

Table 6. The HOMO-LUMO gap, ΔE (V) and absorption maximum (nm and eV) of visible bands for fourteen investigated phthalocyanines.

M	cpd	ΔE (V)	visible band		
			$\lambda_{\max}$ (nm)	E ($\times 10^{-19}$ J)	E (eV)
Zr	1	1.62	688	2.89	1.80
	3	1.67	687	2.89	1.80
	5	1.67	688	2.89	1.80
	7	1.60	685	2.98	1.81
	9	1.58	691	2.88	1.80
	11	1.56	691	2.88	1.80
	13	1.57	691	2.88	1.80
	14	1.56	689	2.88	1.80
Hf	2	1.62	688	2.89	1.80
	4	1.67	686	2.90	1.81
	6	1.67	688	2.89	1.80
	8	1.64	683	2.91	1.82
	10	1.59	691	2.88	1.80
	12	1.55	692	2.81	1.80
	13	1.57	691	2.88	1.80
	14	1.56	689	2.88	1.80

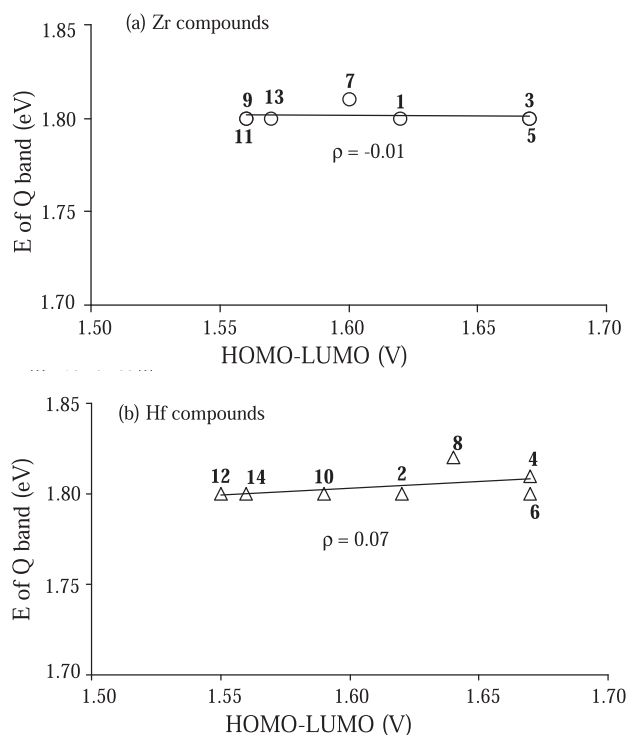


Figure 4. The relationship between the HOMO-LUMO gap and the energy of the strong Q bands of Zr^{IV} and Hf^{IV} in CH_2Cl_2 containing 0.1 M TBAP.

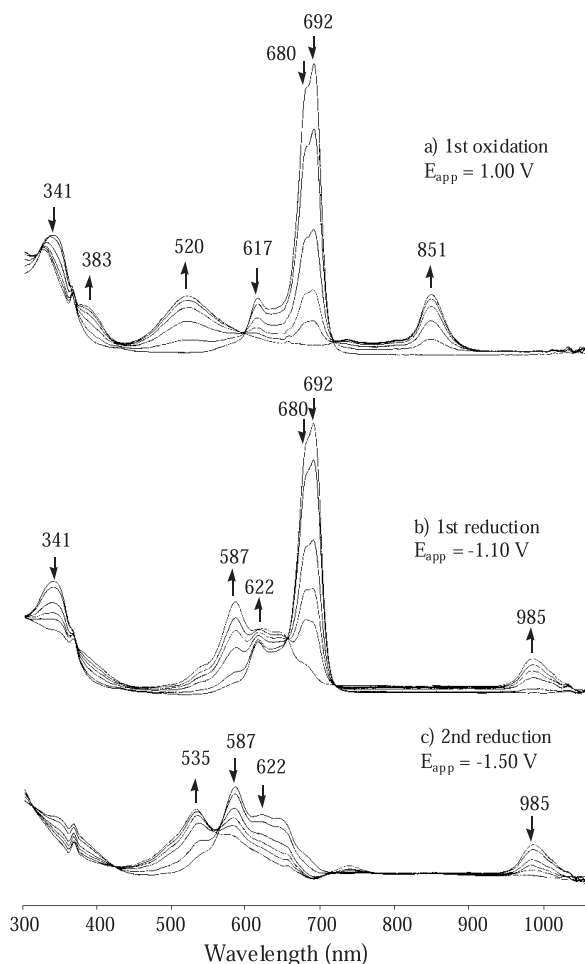


Figure 5. UV-visible spectra obtained during (a) the first oxidation, (b) the first reduction and (c) the second reduction of the complex **12** in CH_2Cl_2 containing 0.1 M TBAP.

what is seen for **14**.^[24] The molar absorptivity (ϵ) in CH_2Cl_2 is slightly smaller than in $CDCl_3$.^[24] Figure 4 shows how the HOMO-LUMO gap (ΔE) affects the spectra of the strong Q bands of all the investigated compounds and the related data are summarized in Table 6. From the Figure 4, we can see the HOMO-LUMO gap affects the energy of the Q bands very slightly and the slopes (ρ) of E vs. HOMO-LUMO gap are around 0.00 in both cases of Zr^{IV} and Hf^{IV} phthalocyanines.

The UV-visible spectral changes for each investigated complex are nearly identical in CH_2Cl_2 containing 0.1 M TBAP. Upon the first oxidation and the first reduction, well-defined bands are observed at 847–859 and 972–986 nm, respectively. Examples of the spectral changes seen for compound **12** are shown in Figure 5. Upon the first oxidation at a controlled potential of 1.00 V, the intensity of the Soret band at 341 nm decreases while the visible bands at 680 and 692 nm disappear as a new visible band grows in at 851 nm; this is consistent with formation of a π -cation radical.^[40,41] Upon the first reduction at a potential of -1.10 V, the Soret band at 341 nm disappears along with the two strong visible bands at 680 and 692 nm while a new visible band at 985 nm appears. The band at 985 nm can be considered as a marker band for formation of the Pc π -anion radical^[25,42] and this band is red-shifted by about 20 nm. The second reduction is also ring-centered and leads to formation of dianions (Figure 5).

Conclusions

The electrochemistry and spectroelectrochemistry of fourteen Zr^{IV} and Hf^{IV} phthalocyanines containing different β -diketone axial ligands were carried out in CH_2Cl_2 , 0.1 M TBAP. Introducing electron-withdrawing substituents on the axial ligands can lead to the appearance of additional reductions and easier reductions as well as more difficult oxidations of the compounds, but the effect of substituents on the ring redox potentials is weak because they are far away from the phthalocyanine macrocycle and minimally affect the ring through the β -ketone axial ligands and central metals. The effect of HOMO-LUMO gap on the energy of the Q bands is also weak and the slope of the energy (E , eV) vs. the HOMO-LUMO gap is close to zero for both the Zr^{IV} and Hf^{IV} phthalocyanine set of compounds. The spectroelectrochemical data obtained upon the first oxidation and first reduction of the phthalocyanines indicates formation of π -cation radicals and π -anion radicals, respectively.

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References

1. Bottari G., de la Torre G., Guldi D. M., Torres T. *Chem. Rev.* **2010**, *110*, 6768–6816.
2. Claessens C.G., Hahn U., Torres T. *Chem. Rec.* **2008**, *8*, 75–97.
3. In: *The Porphyrin Handbook* (Kadish K.M., Smith K.M., Guillard R., Eds). New York: Academic Press, **2003**, Vol. 19, Ch. 117–120.
4. Ben-Hur E., Chan W.S. In: *The Porphyrin Handbook* (Kadish K.M., Smith K.M., Guillard R., Eds). New York: Academic Press, **2003**, Vol. 19, Ch. 117.

5. Wark M. In: *The Porphyrin Handbook* (Kadish K.M., Smith K.M., Guillard R., Eds). New York: Academic Press, **2003**, Vol.17, pp. 247-283.
6. Kobayashi N., Nakai K. *Chem. Commun.* **2007**, 4077-4092.
7. Gonzalez-Rodriguez D., Bottari G. *J. Porphyrins Phthalocyanines* **2009**, *13*, 624-636.
8. Martinez-Diaz M.V., Bottari G. *J. Porphyrins Phthalocyanines* **2009**, *13*, 471-480.
9. Bottari G., Diaz D.D., Torres T. *J. Porphyrins Phthalocyanines* **2006**, *10*, 1083-1100.
10. Jiang J., Ng D.K.P. *Acc. Chem. Res.* **2009**, *42*, 79-88.
11. Lever A.B.P., Milaeva E.R., Spier G. In: *Phthalocyanines: Properties and Applications* (Leznoff C.C., Lever A.B.P., Eds.). New York: VCH, **1993**, Vol. 3, Ch. 1.
12. In: *The Porphyrin Handbook* (Kadish K.M., Smith K.M., Guillard R., Eds). New York: Academic Press, **2002**, Vol. 15.
13. L'Her M., Pondaven A. In: *The Porphyrin Handbook* (Kadish K.M., Smith K.M., Guillard R., Eds). New York: Academic Press, **2002**, Vol.16, Ch. 104, 117-169.
14. In: *The Porphyrin Handbook* (Kadish K.M., Smith K.M., Guillard R., Eds). New York: Academic Press, **2002**, Vol. 16.
15. Gerasymchuk Y. S., Chernii V.Y., Tomachynski L.A., Kowalska M., Legendziewicz J., Radzki S. *Optical Materials* **2010**, *32*, 1193-1201.
16. Krasnov Y.S., Kolbasov G.Y., Tretyakova I.N., Tomachynski L.A., Chernii V.Y., Volkov S.V. *Solid State Ionics* **2009**, *180*, 928-933.
17. Tomachynski L.A., Tretyakova I.N., Chernii V.Y., Volkov S.V., Kowalska M., Legendziewicz J., Gerasymchuk Y.S., Radzki S. *Inorg. Chim. Acta* **2008**, *361*, 2569-2581.
18. Tretyakova I.N., Chernii V.Y., Tomachynski L.A., Volkov S.V. *Dyes Pigm.* **2007**, *75*, 67-72.
19. Tomachynski L.A., Chernii V.Y., Kolotilova Y.Y., Chernega A.N., Howard J.A.K., Volkov S.V. *Inorg. Chim. Acta* **2007**, *360*, 1493-1501.
20. Gerasymchuk Y.S., Chernii V.Y., Tomachynski L.A., Legendziewicz J., Radzki S. *Optical Materials* **2005**, *27*, 1484-1494.
21. Gerasymchuk Y.S., Volkov S.V., Chernii V.Y., Tomachynski L.A., Radzki S. *J. Alloys Compd.* **2004**, *380*, 186-190.
22. Tomachynski L.A., Chernii V.Y., Gorbenko H.N., Filonenko V.V., Volkov S.V. *Chem. Biodiversity* **2004**, *1*, 862-867.
23. Tomachynski L.A., Chernii V.Y., Volkov S.V. *J. Porphyrins Phthalocyanines* **2001**, *5*, 731-734.
24. Tomachynski L.A., Chernii V.Y., Volkov S.V. *J. Porphyrins Phthalocyanines* **2002**, *6*, 114-121.
25. Guillard R., Barbe J.M., Ibnlfassi A., Zrineh A., Adamian V.A., Kadish K.M. *Inorg. Chem.* **1995**, *34*, 1472-1481.
26. Tomachynski L.A., Chernii V.Y., Gorbenko H.N., Filonenko V.V., Volkov S.V. *Chem. Biodiversity* **2004**, *1*, 862-867.
27. Voloshin Y.Z., Varzatskii O.A., Korobko S.V., Chernii V.Y., Volkov S.V., Tomachynski L.A., Pehn'o V.I., Antipin M.Y., Starikova Z.A. *Inorg. Chem.* **2005**, *44*, 822-824.
28. Guillard R., Dormond A., Belkalem M., Anderson J.E., Liu Y.H., Kadish K.M. *Inorg. Chem.* **1987**, *26*, 1410-1414.
29. Sugimoto H., Higashi T., Maeda A., Hirai Y., Teraoka J., Mori M. *J. Less-Common Metals* **1985**, *112*, 387-392.
30. Iwase A., Tanaka K. *Electrochimica Acta* **1990**, *35*, 1707-1712.
31. Qi M.H., Liu G.F. *J. Porphyrins Phthalocyanines* **2004**, *8*, 1187-1195.
32. Tomachinskaya L.A., Kolotilova Y.Y., Chernii V.Y., Volkov S.V. *Theor. Experim. Chem.* **2003**, *39*, 104-108.
33. Tomilova L.G., Ovchinnikova N.A., Luk'yanets E.A. *Zh. Obshch. Khim.* **1987**, *57*, 2100-2104 (in Russ.).
34. Noskova M.P., Kazanova N.N. *Zh. Strukt. Khim.* **1969**, *10*, 718-721 (in Russ.).
35. Alexandrova I.P., Shigorin D.N., Skoldinov A.P. *Zh. Fiz. Khim.* **1964**, *28*, 1203-1209 (in Russ.).
36. Larsson R., Folkesson B. *Chem. Scripta* **1973**, *4*, 189-192.
37. Khudorozhko G.F., Mazalov L.N., Igumenov I.K., Chumachenko Y.V. *Koord. Khim.* **1980**, *6*, 358-360 (in Russ.).
38. Hansch C., Leo A., Taft R.W. *Chem. Rev.* **1991**, *91*, 165-195.
39. Kobayashi N., Konami H. In: *Phthalocyanines: Properties and Applications* (Leznoff C.C., Lever A.B.P., Eds.). New York: VCH, **1996**, Vol. 4, Ch. 9.
40. Nyokong T., Gasyna Z., Stillman M.J. *Inorg. Chem.* **1987**, *26*, 548-553.
41. Ough E.O., Gasyna Z., Stillman M. J. *Inorg. Chem.* **1991**, *30*, 2301-2310.
42. Mack J., Stillman M. J. *J. Am. Chem. Soc.* **1994**, *116*, 1292-1304.

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