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Electrochemical Study of the Lanthanide Complexes of Tetra(1,2,5-thiadiazolo)porphyrazine, [TSDPzLn(acac)] (Ln = Sm^{III}, Eu^{III}, Dy^{III}, Er^{III}, Lu^{III})

Mahmoud Hamdoush, Sergey Sigunov, Ivan A. Skvortsov, Ekaterina N. Tarakanova, and Pavel A. Stuzhin@

Research Institute of Macroheterocycles, Ivanovo State University of Chemistry and Technology, 153000 Ivanovo, Russia
@Corresponding author E-mail: stuzhin@isuct.ru

Complexes of tetra(1,2,5-thiadiazolo)porphyrazine with lanthanides (Ln = Sm^{III}, Eu^{III}, Dy^{III}, Er^{III}, Lu^{III}) were prepared by complexation of the metal free macrocycle [$TSDPzH_2$] with the corresponding trisacetylacetonates $Ln(acac)_3$ in o-dichlorobenzene in the presence of DBU. The analytical and spectral data evidence that complexes were isolated as dihydrates [TSDPzLn(acac)]·$2H_2O$. In their IR spectra coupled C⎓O and C⎓C stretching vibration bands of acetylacetonate at 1515–1530 and 1580–1590 cm^{-1}, as well as deformation vibrations of coordinated water molecule at 1620–1650 cm^{-1} are observed. Electronic absorption spectra contain an intense and narrow Q band at ca. 650 nm due to almost pure $3a_2 \rightarrow 1e^*$ transition and two bands in the UV region having maxima at 292–296 and 364–366 nm which are much broader due to complex configuration interaction with predominant contribution of $5a_1 \rightarrow 1e^*$ and $4a_1 \rightarrow 1e^*$ transitions. Cyclovoltammetric study in DMF solution reveals two reversible reductions at -0.63±0.03 and –1.18±0.03 V, and non-reversible oxidation at +1.22±0.06 V (vs. Ag/AgCl). Negative shift of the reduction potentials in comparison with complexes with p- and d-metals is indicative of stronger ionic character of the coordination bonds between central metal and pyrrolic nitrogen atoms in the lanthanide complexes.

Keywords: Porphyrazines, 1,2,5-thiadiazole, lanthanides, cyclovoltammetry, electronic absorption spectra.

Электрохимическое исследование комплексов лантанидов с тетра(1,2,5-тиадиазоло)порфиразином, [TSDPzLn(acac)] (Ln = Sm^{III}, Eu^{III}, Dy^{III}, Er^{III}, Lu^{III})

М. Хамдуш, С. Сигунов, И. А. Скворцов, Е. Н. Тараканова, П. А. Стужин@

НИИ Макрогетероциклических соединений, Ивановский государственный химико-технологический университет, 153000 Иваново, Россия
@E-mail: stuzhin@isuct.ru

Комплексы тетра(1,2,5-тиадиазоло)порфиразина с лантанидами (Ln = Sm^{III}, Eu^{III}, Dy^{III}, Er^{III}, Lu^{III}) получены комплексообразованием безметального макроцикла [$TSDPzH_2$] с соответствующими трис-ацетилацетонатами $Ln(acac)_3$ в о-дихлорбензоле в присутствии DBU. Согласно аналитическим и спектральным данным комплексы выделены в виде дигидратов [TSDPzLn(acac)]·$2H_2O$. В их ИК спектрах валентные колебания C⎓O и C⎓C связей ацетилацетоната наблюдаются при 1515–1530 и 1580–1590 $см^{-1}$, а деформационные колебания координированной воды – при 1620–1650 $см^{-1}$. Электронные спектры поглощения содержат интенсивную узкую Q полосу при ~650 нм ($3a_2 \rightarrow 1e^*$ переход) и две более широкие полосы в УФ области с максимумами при 292–296 и 364–366 нм (конфигурационное взаимодействие $5a_1 \rightarrow 1e^*$ и $4a_1 \rightarrow 1e^*$ переходов). Цикловольтамперометрические исследования в ДМФА показали наличие двух обратимых процессов восстановления макроцикла при -0.63±0.03 и -1.18±0.03 В и необратимое окисление при +1.22±0.06 В (отн. Ag/AgCl). Катодный сдвиг потенциалов восстановления по сравнению с комплексами p- и d-металлов указывает на более ионный характер связи металла с пиррольными атомами азота в комплексах лантанидов.

Ключевые слова: Порфиразины, 1,2,5-тиадиазол, лантаниды, цикловольтамперометрия, электронные спектры поглощения.

Introduction

Phthalocyanine analogues bearing four annulated electron deficient 1,2,5-thiadiazole rings instead of benzene fragments, [TSDPzM], attract much attention[1] due to their remarkably enhanced electron affinity as compared to common phthalocyanines [PcM] (Chart 1). Strong electron affinity of the macrocycle combined with their ability to form two-dimensional layered structures in the solid state[2] allow to consider TSDPz complexes as perspective *n*-type conducting functional materials for organic electronic applications, *e.g.* as *n*-type organic semiconductors in prototypes of the field-effect transistors and photovoltaic cells.[3–7] Preparation and physicochemical characterization of the metal free macrocycle, [TSDPzH$_2$], and its complexes with Mg^{II},[8] Li^{I},[9] trivalent *p*-metals [TSDPzM(X)] (M = Al^{III}, Ga^{III}, In^{III})[10] and first row transition metals [TSDPzM] (M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, V^{IV}=O)[11–13] have been reported.

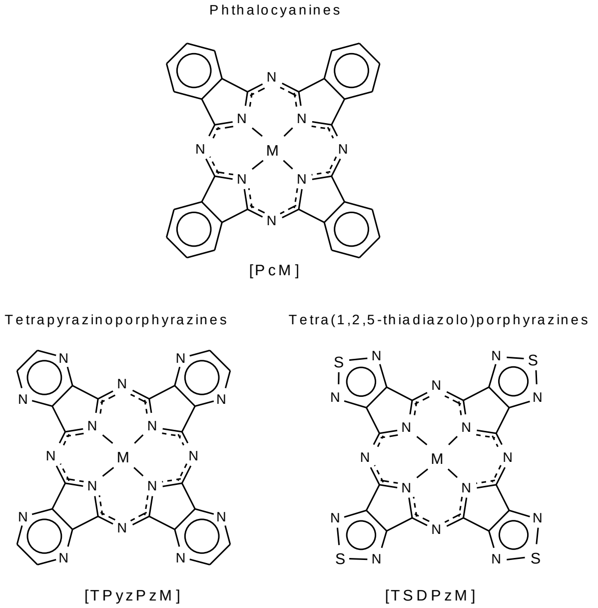
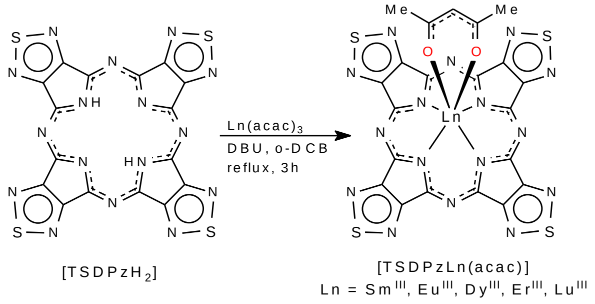


Chart 1. Structures of phthalocyanine and its heterocyclic analogues.

Rare earth elements (REE) can form with tetrapyrrolic macrocycles (porphyrins, porphyrazines and phthalocyanines) monomeric (1:1) and sandwich-type (1:2, 2:3) complexes.[14,15] Due to their magnetic properties and rich redox chemistry sandwich-type lanthanide complexes with phthalocyanines are very interesting for the development of functional magnetic, electronic and optical materials,[16–19] *e.g.* single molecule magnets (SMMs),[20] molecular switches,[21] sensors,[22] organic field effect transistors,[16,23] and nonlinear optical materials.[24] Compared to the sandwich-type 1:2 complexes lanthanide monoporphyrazinates and monophthalocyaninates (1:1 complexes) remain much less studied, although their potential application as semiconductors,[25,26] photo- or electroluminescent materials,[27,28] and SMMs[29] was demonstrated. Lanthanide monoporphyrazinates/monophthalocyaninates with unsaturated coordination sphere (n= 5 or 6) are often unstable but can be stabilized by its saturation due to binding of additional *cis*-ligands.[30] They are convenient precursors for the synthesis of heteroleptic sandwich-type species with different types of macrocycles (not limited to tetrapyrrolic).[15,31]



Scheme 1. Synthesis of lanthanide complexes [TSDPzLn(acac)].

The ability of lanthanides to form neutral or charged homo- and heteroleptic sandwich complexes with tetrapyrrolic macrocycles and their stability is determined by coordination and redox-properties of the macrocycle. Annulation of electron-deficient heterocycles instead of benzene rings in phthalocyanines can strongly influence the coordination ability of porphyrazine macrocycle and its electron affinity. Complexes of lanthanides have so far only been reported for heterocyclic phthalocyanine analogues containing fused pyrazine[32–35] or 2,3-thiophene fragments.[36] Recently we have obtained complexes with Y^{III} and Lu^{III} as first representatives of the rare earth porphyrazines with annulated 1,2,5-thiadiazole rings, [TSDPzY(acac)] and [TSDPzLu(acac)],[37] and conducted DFT study of their molecular and electronic structure.[38] In this work we present synthesis, spectral and electrochemical study of new complexes from the lanthanide series – tetra(1,2,5-thiadiazolo)porphyrazines containing samarium(III), europium(III), dysprosium(III), erbium(III) and lutetium(III) as central metal and coordinated acetylacetonate as extraligand, [TSDPzLn(acac)], Ln = Sm^{III}, Eu^{III}, Dy^{III}, Er^{III}, Lu^{III} (Scheme 1).

Experimental

General

Electronic absorption spectra were recorded using a Cary 60 spectrophotometer. The IR spectra were obtained on a Cary 630 FT-IR spectrometer. Elemental analyses were performed on a Flash EA 1112 CHN analyzer and mass-spectrometric measurements were carried out on a MALDI TOF Shimadzu Biotech Axima Confidence mass-spectrometer at the Center of the Collective Usage at Ivanovo State University of Chemistry and Technology. Commercially available solvents were dried and distilled prior to use. Tetra(1,2,5-thiadiazolo)porphyrazine [TSDPzH$_2$][8,9] and its Lu^{III} complex [TSDPzLu(acac)][37] were prepared as described earlier. Lanthanide acetylacetonates Ln(acac)$_3$·2H$_2$O were commercial products or prepared from the corresponding acetates and acetylacetone.

Synthesis of [TSDPzLn(acac)] (Ln = Sm, Eu, Dy, Er)

In a common procedure the mixture of [TSDPzH$_2$] (0.1–0.2 mmol) and lanthanide acetylacetonate dihydrate, Ln(acac)$_3$·2H$_2$O, taken in 1:2 or 1:3 molar ratio was refluxed in *o*-dichlorobenzene (5 mL) in the presence of DBU (0.1–0.15 mL) with intense stirring under Ar for 2h. After cooling the reaction mixture was poured into hexane, the precipitate was filtered and washed with 2 % water solution of acetic acid, then with hot aqueous 75 % methanol and dried overnight at 50 ^{o}C.

[TSDPzSm(acac)]. From 0.11 mmol [$TSDPzH_2$] and 0.23 mmol $Sm(acac)_3$. Yield: 72 %. Anal. Found C, 30.23; H, 1.28; N, 27.16; S, 15.20%. Calcd. for $C_{21}H_7N_{16}O_2S_4Sm\cdot 2H_2O$: C, 30.39; H, 1.34; N, 27.00; S, 15.45%. UV-Vis (DMF) λ_{max} nm (lgε): 365 (4.58), 593 (4.10), 623 (4.32), 649 (4.93). FTIR (KBr) ν cm^{-1}: **510m**, **675s**, 760w, **1094s**, **1256vs**, 1392w, 1516m, 1580m, 1647m, 2853w, 2927m.

[TSDPzEu(acac)]. From 0.22 mmol [$TSDPzH_2$] and 0.66 mmol $Eu(acac)_3$. Yield: 70 %. Anal. Found C, 30.51; H, 1.22; N, 26.91; S, 15.24%. Calcd. for $C_{21}H_7N_{16}O_2S_4Eu\cdot 2H_2O$: C, 30.33; H, 1.33; N, 26.95; S, 15.42%. UV-Vis (DMF) λ_{max} nm (lgε): 366 (4.53), 592 (4.09), 623 (4.31), 655 (4.99). FTIR (KBr) ν cm^{-1}: 408w, **510m**, 675s, 734w, 760w, 818w, **1094s**, **1254vs**, 1397w, 1526m, 1586m, 1644m, 2857w, 2928m.

[TSDPzDy(acac)]. From 0.18 mmol [$TSDPzH_2$] and 0.55 mmol $Dy(acac)_3$. Yield: 75 %. Anal. Found C, 29.83; H, 1.40; N, 26.47; S, 14.97%. Calcd. for $C_{21}H_7N_{16}O_2S_4Dy\cdot 2H_2O$: C, 29.95; H, 1.32; N, 26.61; S, 15.23%. UV-Vis (DMF) λ_{max} nm (lgε): 364 (4.50), 592 (4.02), 623 (4.22), 651 (4.88). FTIR (KBr) ν cm^{-1}: 409w, **511m**, **676s**, 734w, 761w, **1098s**, **1256vs**, 1323, 1397w, 1528m, 1588m, 1610w, 1643m, 2853w, 2928m.

[TSDPzEr(acac)]. From 0.11 mmol [$TSDPzH_2$] and 0.33 mmol $Er(acac)_3$. Yield: 73 %. Anal. Found C, 29.74; H, 1.39; N, 26.32; S, 14.88%. Calcd. for $C_{21}H_7N_{16}O_2S_4Er\cdot 2H_2O$: C, 29.78; H, 1.31; N, 26.46; S, 15.14%. UV-Vis (DMF) λ_{max} nm (lgε): 364 (4.53), 592 (4.01), 624 (4.22), 651 (4.86). FTIR (KBr) ν cm^{-1}: 411w, **510m**, **676s**, 760w, **1088s**, **1260vs**, 1373w, 1532m, 1550m, 1620m, 2853w, 2924m.

Cyclovoltammetric Measurements

Cyclovoltammetric measurements were performed in dimethylformamide (DMF) using a three-electrode electrochemical cell with a glassy carbon working electrode, a Pt wire counter electrode and an Ag/AgCl reference electrode on a potentiostat Elins P-4. The solutions containing 0.001 M [TSDPzLn(acac)] and 0.1 M tetrabutylammonium perchlorate as supporting electrolyte were deoxygenated with argon. The reference Fc/Fc^+ couple in DMF was observed at +0.567 V *vs*. Ag/AgCl. The obtained potential values are shifted versus Standard Calomel Electrode (SCE) by −0.045 V.[39]

Results and Discussion

Synthesis and Spectral Characterization

Complexes of TSDPz macrocycle with Sm^{III}, Eu^{III}, Dy^{III} and Er^{III} were prepared similarly to the previously reported complexes with Y^{III} and Lu^{III}[37] by complexation of the metal free macrocycle [$TSDPzH_2$] with corresponding lanthanide acetylacetonate (1:2 – 1:3 molar ratio) in *o*-dichlorobenzene in the presence of DBU under reflux. The target complexes were isolated from the reaction mixture by precipitation into hexane and excess of unreacted acetylacetonate and by-products was removed by washing with slightly acidified water and aqueous methanol. According to analysis results the products were obtained as hydrated materials [TSDPzLn(acac)]·$2H_2O$. Two water molecules complete the coordination sphere of the lanthanide ions which are able to bind up to eight donor atoms as was shown by X-ray study for the Lu^{III} phthalocyanine with bidentate coordinated acetate [$PcLu(OAc)(H_2O)_2$].[40] In the following discussion water will be omitted in the abbreviations.

IR Spectra

IR spectra of the lanthanide complexes [TSDPzLn(acac)] contain intense bands at 1260, 1090-1100, 675 and 510 cm^{-1} (Figure 1). These bands are also typical for the spectra of TSDPz complexes with *p*- and *d*-metals[8,10,11] and were assigned to skeletal vibrations 1,2,5-thiadiazolo-pyrrole fragments constituting the macrocycle.[38,41–43] It should be noted that above 1400 cm^{-1} for tetracoordinated complexes with transition metals [TSDPzM] (M = Zn, Cu, Ni, Fe, Mn) only one band of medium intensity is observed at 1535–1555 cm^{-1}[11] (Table 1).

Table 1. Assignment of the IR vibrations (in cm^{-1}) of the TSDPz macrocycle.

Vibrational mode^{a}	[TSDPzLn(acac)]					[TSDPzM]		
	Sm	Eu	Dy	Er	Lu[38]	Li[9]	Zn[48]	Ni[43]
TSDPz macrocycle								
fold($N_t\cdots N_t$)	**510m**	**510m**	**511m**	**510m**	**513m**	**503s**	**512m**	**511m**
$\varphi(N_pC_\alpha C_\beta)$, $\varphi(N_mC_\alpha C_\beta)$	**675s**	**675s**	**676s**	**676s**	**678s**	**684s**	**684s**	**689s**
r(S-N_t), $\varphi(C_\alpha N_m C_\alpha)$	736w	734w	734w		738w	727w	730w	741w
r(S-N_t), $\varphi(C_\alpha N_m C_\alpha)$, $\varphi(C_\alpha C_\beta N_t)$	762w	760w	761w	760w	764w	760w	766w	763w
In-plane bending (pyrrole+thiaziazole)	821m	820w	820w	820w	822w	818m	825w	827w
Breathing (pyrrole+thiadiazole)	867w	865w	866	866w	868w	870w	872w	895w
r(N_p-C_α), $\varphi(N_pC_\alpha C_\beta)$	**1094s**	**1094s**	**1098s**	**1088s**	**1090s**	**1092s**	**1087s**	**1108s**
r(C_α-C_β), r(C_α-N_m), $\varphi(N_pC_\alpha C_\beta)$, r($C_\beta$-$N_t$)								1118s
$\varphi(N_mC_\alpha C_\beta)$, $\varphi(C_\alpha N_m C_\alpha)$	**1256vs**	**1254vs**	**1256vs**	**1260vs**	**1262vs**	**1260vs**	1269vs	1269vs
r(C_α-N_m), $\varphi(N_pC_\alpha C_\beta)$; r($C_\beta$-$N_t$), r($C_\alpha$-$C_\beta$)	*	*	*	*	*	1523m	1530m	1552m
Axial ligands								
$\nu(C\overset{\cdots}{=}O)$	1516m	1526m	**1528m**	**1532m**	1522vs			
$\nu(C\overset{\cdots}{=}C)$	1580m	1586m	**1588m**	**1550m**				
$\delta(H_2O)$	1647m	1644m	**1643m**	**1620m**				
$\nu(CH_3)$	2853w	2857w	2853w	2853w				
	2927m	2928m	2928m	2924m				

^{a}Assignment is based on the theoretical calculation for the Li^{I} [9] and Lu^{III} [38] complexes.

* Masked by stronger vibrations of acac ligand.

This band is predominantly contributed by $C_{\alpha}N_{meso}$ stretching vibrations.[41–43] In the case of the lanthanide complexes [TSDPzLn(acac)] this vibration is masked by three strong-to-medium intensity bands appearing in the 1500–1650 cm^{-1} region. The bands at 1515–1530 and 1580–1590 cm^{-1} can be assigned to characteristic coupled C$\overset{...}{-}$O and C$\overset{...}{-}$C stretching vibrations of the acetylacetonate ligand.[44,45] Similar bands of the coordinated acac ligand appear also in the IR spectra of the corresponding lanthanide complexes of phthalocyanine [PcLn(acac)][46] and *meso*-tetraphenylporphyrin [TPPLn(acac)].[47] Deformation vibrations of coordinated water appear at 1620–1650 cm^{-1}.

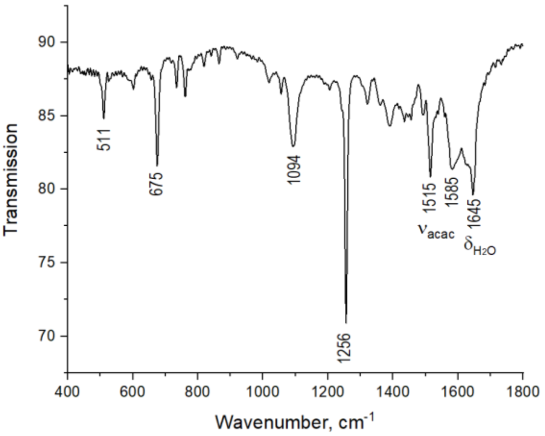


Figure 1. IR spectrum of [TSDPzSm(acac)] in KBr.

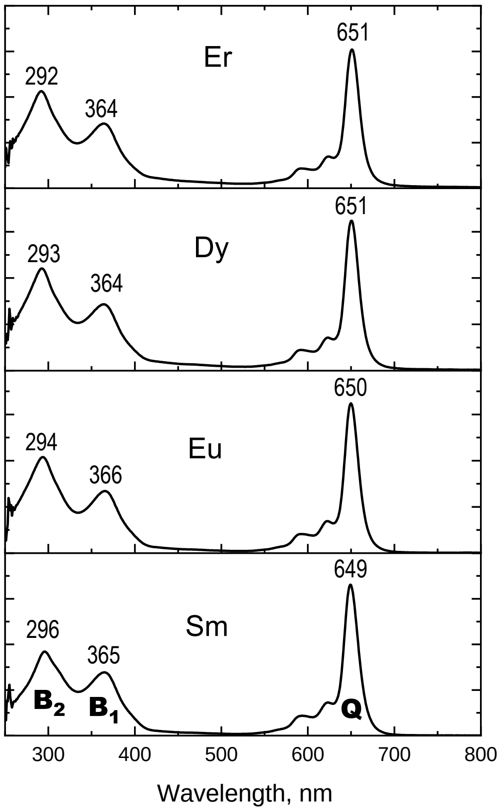


Figure 2. Electronic absorption spectra of [TSDPzLn(acac)] (Ln = Sm^{III}, Eu^{III}, Dy^{III}, Er^{III}) in DMF.

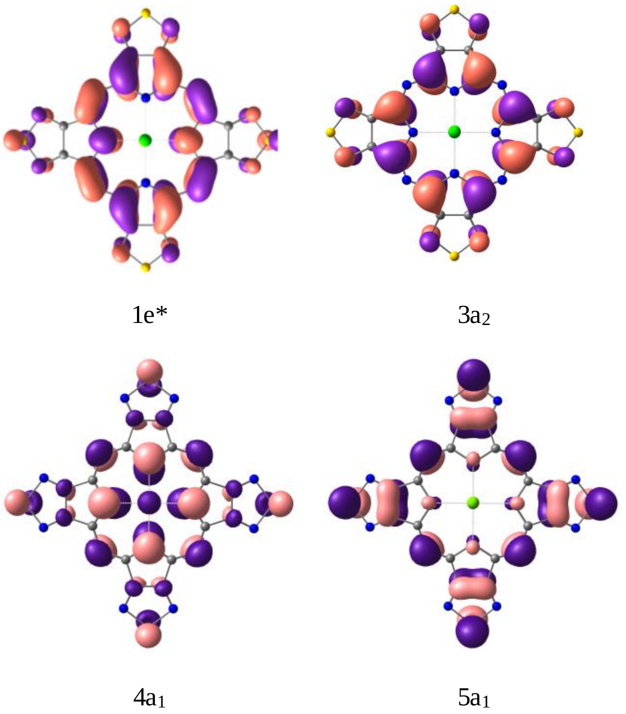


Figure 3. π-Molecular orbitals involved in the electronic transitions. Molecular model for [TSDPzLu(Cl)].[38]

Electronic Absorption Spectra

Electronic absorption spectra of all lanthanide complexes [TSDPzM(acac)] (M = Sm^{III}, Eu^{III}, Dy^{III}, Er^{III}) are very similar to one another (Figure 2) and to previously reported complexes with Y^{III}, Lu^{III}.[37] In the visible region they contain an intense Q band at ~650 nm with vibronic satellites at 624 and 593 nm. In the UV-region two broad bands at ~365 and 290–300 nm are observed. According to TD-DFT calculations performed for the rare earth complexes [TSDPzM(Cl)] (M = Y, La, Lu)[38] the Q band in the visible region arise from an almost pure Gouterman type HOMO-LUMO ππ*- transition $3a_2 \rightarrow 1e^*$, while two intense excited states observed in the UV-region denoted as B_1 and B_2 are mainly contributed by strong configuration interaction of $5a_1 \rightarrow 1e^*$ and $4a_1 \rightarrow 1e^*$ transitions. The coordinating pyrrolic nitrogen atoms have no contribution to the $3a_2$ orbital, minor to the $5a_1$ orbital and strong to the $4a_1$ orbital (Figure 3). Therefore, the metal center should have practically no influence on the position of the Q band, and its effect on the B_1 and B_2 bands reflects contribution of the $4a_1 \rightarrow 1e^*$ transition. Similar situation is expected for TSDPz complexes with alkali earth metals - Mg^{II},[41] Ca^{II}[42] forming substantially ionic M-N_{pyr} bonds. Complexes with d-metals have more covalent M-N_{pyr} bonds due to interaction of macrocyclic π-MOs with d_{π} orbitals and in the case of Zn^{II}[42] and Ni^{II}[43] the energy of the Q band depends on the central metal and the configuration composition of transition in the UV-region is different.[8,11]

In the case of monophthalocyaninates [PcLn(acac)] (Ln = Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III}, Er^{III}, Tm^{III}, Lu^{III}) the maximum of the Q band is also independent of the lanthanide ion and observed at ~675 nm.[46] The hypsochromic shift by *ca.* 25 nm observed for [TSDPzLn(acac)] complexes as compared to the corresponding [PcLn(acac)] complexes is typical for heteroatom substitution of C_4H_4 fragments in benzene rings of phthalocyanines by NSN moiety in 1,2.5-thiadiazole rings leading to widening of the HOMO-LUMO gap due to stronger stabilization of HOMO.[1] In the case of pyrazine fused analogues [TPyzPzLn(acac)] (Ln = = Er^{III}, Lu^{III}) and their alkyl substituted derivatives [R$_8$TPyzPzLn(acac)] (Ln = Er^{III}, Tm^{III}, Yb^{III}, Lu^{III}; R = Et, or H, *tert*-Bu) the maximum of the Q band is observed at ca 640 nm[33] indicating larger HOMO-LUMO gap. However, octaphenyl substituted tetrapyrazinoporphyrazine [Ph$_8$TPyzPzLn(OAc)] (Ln = Y^{III}, Eu^{III}, Gd^{III}, Dy^{III}, Er^{III}, Yb^{III}, Lu^{III}, Tm^{III})[33,35,49] has the Q-band maximum at 663-665 nm due to destabilization of HOMO.

Table 2. UV-Vis spectra of [TSDPzM(acac)] (M = Y, Sm, Eu, Dy, Er, Lu) and related porphyrazine complexes.

Porphyrazine complex	Solvent	Absorption maximum, nm					Ref.
		Soret region		Q band			
		B$_2$	B$_1$				
[TSDPzZn]	DMF	320	372, 400sh	588	617	644	[11,48]
[TSDPzAl(Cl)]	Py	340	364sh, 393sh	590	622	647	[10]
[TSDPzGa(Cl)]	Py	337	367sh, 400sh	585	617	645	[10]
[TSDPzIn(OAc)]	Py	321	365sh, 390sh	602		658	[10]
[TSDPzCa]	Py					647	[42]
[TSDPzLi]$^-$	DMF	298	372	585	611	639	[9]
[TSDPzY(acac)]	CH_2Cl_2		360 (4.20)	590 (3.70)	624 (4.00)	651 (4.60)	[37]
[TSDPzSm(acac)]	DMF	296	365 (4.58)	593 (4.10)	623 (4.32)	649 (4.93)	tw
[TSDPzEu(acac)]	DMF	294	366 (4.53)	592 (4.09)	623 (4.31)	650 (4.99)	tw
[TSDPzDy(acac)]	DMF	293	364 (4.50)	592 (4.02)	623 (4.22)	651 (4.88)	tw
[TSDPzEr(acac)]	DMF	292	364 (4.53)	592 (4.01)	624 (4.22)	651 (4.86)	tw
[TSDPzLu(acac)]	CH_2Cl_2		360	592	623	650	[37]
[PcLu(Cl)]	*o*-DCB		344	606		672	[50]
[TPyzPzLu(acac)]	DMF		365	581		638	[33]
[tBu$_4$TPyzPzLu(acac)]	DMF		341	584		640	[33]
[Ph$_8$TPyzPzLu(acac)]	DMF		367	598		657	[33]

Table 3. Half-wave potentials (*vs*. Ag/AgCl) of lanthanide complexes of tetra(1,2,5-thiadiazolo)porphyrazine and related complexes of porphyrazines, phthalocyanine and *meso*-tetraphenylporphyrin.

Compound	Reduction		Oxidation		Ref.
	$E^1_{1/2}$	$E^2_{1/2}$	E_{pc}	Solvent	
[TSDPzZn]	-0.44	-0.87		DMF	[50]
[TSDPzAl(Cl)]	-0.10	-0.54		DMF	[10]
[TSDPzLi]$^-$	-0.94	-1.24		DMSO	[9]
[TSDPzSm(acac)]	-0.59	-1.15	1.16	DMF	tw
[TSDPzEu(acac)]	-0.59	-1.16	1.18	DMF	tw
[TSDPzDy(acac)]	-0.65	-1.21	1.26	DMF	tw
[TSDPzEr(acac)]	-0.61	-1.17	1.28	DMF	tw
[TSDPzLu(acac)]	-0.62	-1.20 (quasi)	1.26	DMF	tw
[Ph$_8$TPyzPzEr(OAc)]	-0.74	-0.98	0.86	Py	[35]
[tBu$_4$TPyzPzLu(Cl)]	-0.96	-1.68	1.02	DCM	[32]
[PcEu(acac)]	-1.08	-1.44	0.56	DMSO, SCE	[46]
[acacDyPc]	-1.09	-1.39	0.55	DMSO, SCE	[46]
[PcEr(acac)]	-1.09	-1.39	0.55	DMSO, SCE	[46]
[PcLu(acac)]	-1.07	-1.33	0.55	DMSO, SCE	[46]
[TPPSm(acac)]	-1.51		0.41	DMSO, SCE	[47]
[TPPEu(acac)]	-1.37	-1.67	0.60	DMSO, SCE	[47]
[TPPDy(acac)]	-1.33	-1.68	0.63	DMSO, SCE	[47]
[TPPEr(acac)]	-1.32	-1.69	0.69	DMSO, SCE	[47]
[TPPLu(acac)]	-1.33	-1.69	0.76	DMSO, SCE	[47]

Electrochemical Properties

Cyclic voltammetry measurements were performed for 1 mM solutions of the lanthanide complexes [TSDPzLn(acac)] in DMF in the potential range from -1.5 to 1.5 V *vs.* Ag/AgCl. In the cathodic region for all compounds two reversible reduction processes are observed at $E^1_{1/2}$= -0.63±0.03 V and $E^2_{1/2}$= -1.18±0.03 V, while non-reversible oxidation is observed in the anodic region with E_{pc} = +1.22±0.06 V. The central lanthanide ion has only minor effect on the redox potentials (Figure 4). However, the reduction potentials of the lanthanide complexes are by 0.2-0.3 V more negative than those of the complexes with bivalent *p*- and *d*-metals [TSDPzM] (M = Mg^{II}, Zn^{II}, Cu^{II}),[51] and by 0.5 V than those of complexes with tervalent *p*-metals [TSDPzM(Cl)] (M = Al^{III}, Ga^{III}).[10] This can be explained by more ionic character of the coordination bond of the lanthanide ions with TSDPz macrocycle as compared to the M-N$_{Pyr}$ bond in the complexes of *p*- and *d*-metals. As a result the negative charge of the coordinating dianion TSDPz^2 is not effectively compensated by the lanthanide ions and macrocycle in [TSDPzLn(acac)] is more difficultly reduced than in more covalent complexes such as [TSDPzZn] or [TSDPzAl(Cl)] (see Table 3). It is noteworthy, that anionic lithate complex [TSDPzLi]$^-$ having full negative charge on the macrocycle is reduced at potential of -0.94 V,[9] *i.e.* by 0.4 V more difficult than the lanthanide complexes.

At the same time, as can be seen from Table 3, the redox potentials for [TSDPzLn(acac)] are considerably shifted as compared to the corresponding lanthanide complexes of phthalocyanines [PcLn(acac)] ($E^{Red1}_{1/2}$ ~ -1.10 and $E^{Ox1}_{1/2}$ ~ +0.56 V *vs.* SCE[46]) and porphyrins [TPPLn(acac)] ($E^{Red1}_{1/2}$~ -1.35±0.03 and $E^{Ox1}_{1/2}$ ~ +0.68±0.08 V *vs.* SCE[47]). 1,2,5-Thiadiazole fused porphyrazine macrocycle in the lanthanide complexes can be easier reduced as compared with the corresponding phthalocyanine and porphyrin complexes (by 0.5 and 0.6 V, respectively), while its oxidation is by 0.65 and 0.55 V more difficult. It is especially important and indicates that formation of the neutral sandwich-type lanthanide complexes [(TSDPz)$_2$Ln^{III}], in which one macrocyclic unit is oxidized, should be much less favorable than in the case of sandwich bisphthalocyaninates [(Pc)$_2$Ln^{III}] and bisporphyrinates [(TPP)$_2$Ln^{III}]. Indeed, we have not so far observed the formation of homoleptic bisporphyrazinates [(TSDPz)$_2$Ln^{III}] neither as by-products in the complexation reaction between [TSDPzH$_2$] and excess of Ln(acac)$_3$ nor in the reaction of the monoporphyrazinates [TSDPzLn(acac)] with the lithate complex [TSDPzLi]$^-$. Probably heteroleptic sandwich complexes, such as [(TSDPz)Ln(Pc)] or [TSDPz)Ln(TPP)] combining TSDPz^{2-} deck and oxidized Pc$^{-\cdot}$ or TPP$^{-\cdot}$ deck, can be more easily prepared. Available electrochemical data on lanthanide complexes of pyrazine fused porphyrazines [tBu$_4$TPyzPzLu(Cl)][32] and [Ph$_8$TPyzPzEr(OAc)][35] show that TPyzPz macrocycle is by 0.15–0.35 more difficult to reduce and by 0.15–0.40 V more easy to oxidize. And, indeed, sandwich complex [(tBu$_4$TPyzPz)$_2$Lu] was reported.[32]

The difference between first reduction and oxidation potential $\Delta E_{Red/Ox}$ is 1.88 V is in a good correspondence with the optical HOMO-LUMO gap ΔE_{opt} = 1.91 eV calculated from the energy of the long wave ππ*-transition (Q band 650 nm, 15385 cm^{-1} for [TSDPzLu(acac)]. These experimental values are smaller than the theoretical HOMO-LUMO gap 2.248 eV obtained from DFT calculations.[38] This is not surprising since DFT calculations overestimate the value of the HOMO-LUMO gap and failed to predict the correct level of the frontier orbitals. Thus, the LUMO level can be estimated using its correlation with the $E^{Red1}_{1/2}$ potential:[52]

$$E_{LUMO}(CVA) = 1.19\ (E_{½}(Fc/Fc^+) - E^{Red1}_{1/2}) - 4.78$$

The E_{LUMO} value obtained from this correlation for [TSDPzLu(acac)] is –3.37. eV, which is much higher than -4.15 eV obtained by DFT modelling of [TSDPzLu(Cl)].[38]

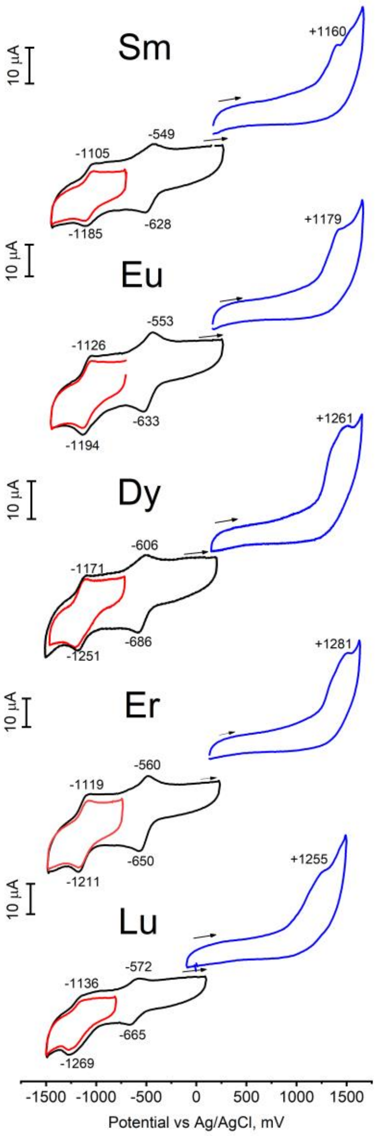


Figure 4. Cyclic voltammograms for the lanthanide complexes [TSDPzLn(acac)] (Ln = Sm^{III}, Eu^{III}, Dy^{III}, Er^{III}, Lu^{III}) in DMF with 0.1 M tbaClO$_4$ as supporting electrolyte. Scan rate - 50 mV/s.

Conclusions

Lanthanide complexes of tetra(1,2,5-thiadiazolo)-porphyrazine [TSDPzLn(acac)]·2H$_2$O (Ln = Sm^{III}, Eu^{III}, Dy^{III}, Er^{III}) can be prepared by complexation of the metal-free macrocycle [TSDPzH_2] with corresponding acetylacetonate Ln(acac)$_3$ in the presence of DBU as a base in dichlorobenzene. An intense and narrow Q band at *ca*. 650 nm in the electronic absorption spectra is due to almost pure Gouterman type $3a_2 \rightarrow 1e^*$ transition, while two broader bands in the UV-region with maxima at 292–296 (B_2) and 364–366 (B_1) nm have a complex configuration interaction structure with predominant contribution of $5a_1 \rightarrow 1e^*$ and $4a_1 \rightarrow 1e^*$ transitions. Cyclovoltammertric study in DMF solution reveals two reversible reductions at -0.63±0.03 and -1.18±0.03 V, and non-reversible oxidation at +1.22±0.06 V. Negative shift of the reduction potentials in comparison to complexes with *p*- and *d*-metals is indicative about stronger ionic character of the coordination bonds between central metal and pyrrolic nitrogen atoms in the lanthanide complexes.

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