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Complexes of zinc phthalocyanine with monoaxially coordinated imidazole-derivative ligands

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ABSTRACT

Three complexes of zinc phthalocyanine (ZnPc) monoaxially ligated by imidazole, *N*-methylimidazole and *N*-(2-pyrimidinyl)imidazole were obtained in crystalline forms. Complexes containing imidazole and *N*-methylimidazole crystallise in the centrosymmetric space group of the triclinic system, while with the *N*-(2-pyrimidinyl)imidazole complex crystallises in P2₁/n space group of monoclinic system. Interaction of the electropositive polarised Zn centre of a planar ZnPc with nucleophilic ring nitrogen atom of imidazole derivatives leads to deviation of Zn form the N₄-plane of phthalocyaninato(2-) macrocycle by ~0.45 Å. Steric hindrance of the axial ligands of ZnPc-L complexes modify the $\pi \cdots \pi$ interactions between the Pc(2-) macrocycles when compared to that of the parent ZnPc pigment. The calculated three-dimensional MESP maps are helpful for understanding of the interaction between the ZnPc and imidazole derivatives forming the monoaxially ligated complexes. Theoretical calculations of axial bonds energies and UV–Vis spectroscopic measurements in solutions also were performed.

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1. Introduction

Phthalocyanine and its metal complexes, originally developed as industrial dyes and pigments, in spite of the fact that they have known since several dozen years, still arouses interest because of the many important features exhibited which offer varied application. Phthalocyanines are intensively studied as multiply functional compounds useful for modern technology as well as in medicine [1–6]. Structurally, phthalocyanine consists of four iso-indole units connected by azamethine bridges to form an 18- π aromatic macrocycle. Thus, the shape of phthalocyaninato(2-) anion determines the square-planar coordination environment of the central metal cation.

Among the M(II)Pc's, the zinc phthalocyanine is one of the still intensively studied compounds, since it is thermally and chemically stable and exhibits a range of promising and usable properties [7-10]. A wide application of MPcs for technological purposes is limited by their relatively low solubility in most organic solvents. The well-known way to tune the properties of ZnPc, as well as other M(II)Pcs, is to modify the Pc(2-) macrocycle by placement of alkyl or aryl groups as peripheral or non-peripheral substituents [11-13] or

* Corresponding author. E-mail address: j.janczak@int.pan.wroc.pl (J. Janczak). by additive metal center complexation [14–17]. The peripheral and non-peripheral substituents as well as the metal center complexation can increase the solubility of the MPc-complexes by lowering their aggregation in solution due to decrease of the $\pi \cdots \pi$ interactions between the Pc(2–) macrocycles. At the same time this process can change the physical or chemical properties of M(II)Pc complexes.

According to the literature and our experience, zinc phthalocyanine exhibits a special affinity to nitrogen-containing ligands, over oxygen, sulphur or phosphorus ligands. The aim of this work is the synthesis and characterization of a new crystalline class of ZnPc 4 + 1 complexes with imidazole-derivative ligands and comparison with another ZnPc 4 + 1 complexes containing alkylamines and pyridine derivatives as an axial ligands [18,19].

2. Experimental

2.1. Materials and methods

Zinc phthalocyanine, 1*H*-imidazole, 1-methylimidazole are commercially available and were used as received. *N*-(2pyrimidinyl)imidazole was synthesised according to procedure described in part 2.2. The composition of the obtained crystals was checked with a Perkin–Elmer 2400 elemental analyser and with energy dispersive spectroscopy (EDS). EDS spectra were acquired





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and analysed using an EDAX Pegasus XM4 spectrometer with SDD Apollo 4D detector mounted on a FEI Nova NanoSEM 230 microscope. The electronic absorption spectra of complexes **1**, **2** and **3** were carried out at room temperature using Cary Varian SE UV–Vis–NIR spectrometer. The spectra were recorded in solutions over a range of concentration 10^{-6} mol/dm³ not later than 1 h after preparation. Thermogravimetric analyses were achieved on ~ 6–7 mg samples with TG-DTA *Setaram* SETSYS 16/18 analyser with heating rate 5 °C/min. The Fourier transform infrared spectra of **1-3** complexes were recorded in KBr pellet between 4000 and 400 cm⁻¹ on a Bruker IFS 113 V FTIR spectrometer. Resolution was set up to 2 cm⁻¹.

2.2. Preparation

2.2.1. N-(2-Pyrimidinyl)imidazole

Imidazole (4.46 g, 65.5 mmol), potassium carbonate (4.54 g, 32.8 mmol), and catalytic amount of copper sulphate pentahydrate (0.100 g, 0.400 mmol) were ground in a mortar and then transferred to 100 mL round-bottom flask. 2-Chloropyrimidine (3.00 g, 26.2 mmol) was ground separately and also transferred to the flask. The content was thoroughly shaken to mix reagents; self-initiation of the reaction occurred. Flask was then inserted to the oil bath (140 °C) and heated at that temperature for 3 h. Next, brown mixture was cooled down and aqueous ammonia solution (5%, 20 mL) was added and the crude product was pulverized (ammonia solution is used to remove copper impurities from product). The residue was filtered off and crystallized twice from aqueous ammonia solution providing light beige solid. Yield: 2.10 g (55%), mp. 126–128 °C.

¹H NMR (500 MHz, CD₃OD, 300 K) δ:7.16 (s, 1H), 7.42 (t, 1H, ${}^{3}J = 4.9$ Hz), 8.03 (s,1H), 8.69 (s, 1H), 8.82 (d, 2H, ${}^{3}J = 4.9$ Hz) ppm.

2.2.2. 1H-imidazole(phthalocyaninato)zinc (1)

Zinc phthalocyanine (pastille, 100 mg, 0.173 mmol) and 1Himidazole (3.000 g) were placed in a glass, elongated ampoule, which was degassed and then sealed. The ampoule was heated in 250 °C to total dissolvation of ZnPc pastille (a few hours) and then temperature was being slowly decreased to 100 °C and this temperature was maintained 3 h. Then, the ampoule was left at ambient temperature to cool. After opening the ampoule, solidified imidazole was washed out with acetone, giving crystals of 1 (56 mg, 50%). Analysis: C, 65.32; N, 21.88, Zn, 9.80 and H, 3.00%. Calculated for $C_{35}H_{20}N_{10}Zn$: C, 65.08; N, 21.68; Zn, 10.12 and H, 3.12%. IR (cm⁻¹): 3144(vw), 3122(vw), 3080(w), 3049(vw), 2947(w), 2910(w), 2831(w), 2615(vw), 2533(vw), 1609(w), 1585(w), 1539(w), 1486(s), 1456(w), 1411(w), 1358(w), 1330(s), 1283(m), 1259(w), 1245(w), 1180(w), 1166(m), 1157(m), 1143(w), 1120(s), 1114(s), 1098(m), 1085(s), 1060(s), 1004(w), 939(m), 868(w), 827(w) 819(w), 772(m), 763(w), 750(s), 720(s), 715(s), 689(w), 658(m), 642(w), 633(m), 622(w), 568(m), 499(w), 492(w), 433(w).

2.2.3. N-Methylimidazole(phthalocyaninato)zinc (2)

Zinc phthalocyanine (pastille, 100 mg, 0.173 mmol), *N*-methylimidazole (3 mL, 37.76 mmol) and 2-aminoethanol (0.3 mL, 4.97 mmol) were placed in glass ampoule, which was degassed and then sealed. It was heated at 150 °C over 24 h. The crystals of **2** were obtained on the edge of the solution in the ampule during the heating, after cooling the ampule was opened, the crystals were isolated by filtration and washed with acetone, yield 61 mg (53%). Analysis: C, 65.40; N, 21.29, Zn, 9.97 and H, 3.24%. Calculated for $C_{36}H_{22}N_{10}Zn: C, 65.51; N, 21.22; Zn, 9.91 and H, 3.35%. IR (cm⁻¹):$ 3139(vw), 3118(vw), 3077(vw), 3046(vw), 2728(vw), 2623(vw),2542(vw), 1607(w), 1583(w), 1531(m), 1518(w), 1484(s), 1454(m),1407(w), 1383(w), 1369(w), 1220(s), 1283(s), 1233(m), 1189(w), 1162(s), 1114(vs), 1090(vs), 1059(s), 1026(w), 1004(w), 977(w), 942(w), 885(m), 824(m), 774(m), 750(s), 728(vs), 685(w), 657(m), 633(m), 618(m), 569(m), 500(m), 434(m).

2.2.4. N-(2-Pyrimidinyl)imidazole(phthalocyaninato)zinc (3)

Zinc phthalocyanine (25 mg pastille), *N*-(2-pirymidynyl)imidazole (800 mg) were placed in glass ampoule, which was degassed and then sealed. The ampoule was heated at 150 °C over 24 h. Welldeveloped single crystals of **3** were obtained on the edge of the solution during the heating. The crystals were isolated by washing out solidified *N*-(2-pirymidynyl)imidazole with acetone, yield 13 mg (41%). Analysis: C, 65.05; N, 23.02, Zn, 8.93 and H, 3.00%. Calculated for $C_{39}H_{22}N_{12}Zn$: C, 64.70; N, 23.21; Zn, 9.03 and H, 3.06%. IR (cm⁻¹): 3142(vw), 3127(vw), 3072(vw), 3049(vw), 2622(vw), 2534(vw), 1609(w), 1583(w), 1484(s), 1466(s), 1414(w), 1332(s), 1284(m), 1283(w), 1260(w), 1244(w), 1177(w), 1164(w), 1159(w), 1144(w), 1120(w), 1115(m), 1100(w), 1086(m), 1062(s), 938(m), 886(m), 827(w) 820(w), 772(w), 763(w), 750(s), 728(m), 721(w), 715(m), 688(w), 658(m), 641(w), 634(m), 622(w), 568(w), 501(w), 491(w), 434(w).

2.3. X-ray single crystal measurements and crystal structure analysis

Single crystal X-ray diffraction measurements of 1, 2 and 3 were carried out at 295 (2) K on a four-circle KUMA KM4 diffractometer equipped with a two-dimensional CCD area detector. Graphite monochromatised Mo-K α radiation ($\alpha = 0.71073$ Å) and ω -scan technique with step $\Delta \omega = 1^{\circ}$ were used for data collection. Data collection and reduction with absorption correction were performed using the *CrysAlis* software package [20]. The structures were solved by direct methods using SHELXS-97 program [21] which revealed the positions of almost all non-hydrogen atoms. The remaining atoms were located from subsequent difference Fourier synthesis. The structures were refined using SHELXL-97 program [21] with anisotropic thermal displacement parameters. The hydrogen atoms were refined using the riding model with isotropic thermal displacement parameters 20% greater than aromatic carbon atoms, and 50% greater than aliphatic ones. Visualisation of the structures was made with Diamond 3.0 program [22]. Details of the data collection parameters, crystallographic data and final refinement parameters are collected in Table 1. Selected geometrical parameters for 1, 2 and 3 are listed in Table 2.

2.4. Theoretical calculation

Theoretical calculations with geometry optimization of complexes **1**, **2** and **3** as well as ligands (imidazole, *N*-methylimidazole and *N*-(2-pyrimidinyl)imidazole) and zinc phthalocyanine were performed with Gaussian09 program package [23]. All calculations were carried out with the DFT method using the Becke3-Lee-Yang-Parr correlation functional (B3LYP) [24–26] with the 6-31 + G* basis set assuming the geometry from the X-ray diffraction study as the starting structure. As convergence criterions the threshold limits of 0.00045 and 0.0018 a.u. were applied for the maximum force and the displacement, respectively. GaussView 5.0 program was used for visualization of the three-dimensional molecular electrostatic potential [27]. Energies of axial Zn–N_L bonds were calculated for optimized geometries of complexes with elimination of basis set superposition error by counterpoise method [28].

Table 1

Crystallographic data and final refinement parameters for 1-3 crystals.

	1	2	3
Empirical formula	$C_{35}H_{20}N_{10}Zn$	C ₃₆ H ₂₂ N ₁₀ Zn	C39H22N12Zn
Formula weight	645.98	660.01	724.06
Crystal system,	triclinic,	triclinic	triclinic
space group	P-1	P-1	$P2_1/n$
a [Å]	10.870 (1)	14.434 (1)	12.313 (1)
b [Å]	11.248 (1)	14.820 (1)	15.404 (1)
c [Å]	12.299 (1)	15.540 (1)	17.991 (1)
α [°]	103.853 (5)	98.279 (4)	
β [°]	104.401 (6)	111.162 (5)	108.656 (6)
γ [°]	100.221 (5)	102.482 (4)	
V [Å ³]	1368.4 (2)	2935.2 (2)	3233.2 (3)
$D_{calc}/D_{obs} (g \cdot cm^{-3})$	1.568/1.56	1.494/1.49	1.487/1.48
$\mu (mm^{-1})$	0.946	0.884	0.811
F(000)	660	1352	1480
Crystal size (mm ³)	$0.25 \times 0.22 \times 0.20$	$0.38\times0.31\times0.22$	$0.27\times0.18\times0.12$
Radiation type,	Μο Κα,	Μο Κα,	Μο Κα,
wavelength, λ (Å)	0.71073	0.71073	0.71073
Temperature (K)	295 (2)	295 (2)	295 (2)
θ range(°)	2.94-27.20	2.87-28.00	2.75-28.5
Absorption correction	Numerical	Numerical	Numerical
T _{min} /T _{max}	0.8122/0.8473	0.7323/0.8317	0.8223/0.9124
Reflections collected/unique/observed	13151/6016/3099	37853/14112/6544	44865/8144/4870
R _{int}	0.0581	0.0726	0.0601
Refinement on	F ²	F ²	F ²
$R[F_2 > 2\sigma(F_2)]^a$	0.0519	0.0790	0.0620
wR (F ² all reflections) ^b	0.0777	0.1125	0.1089
Goodness-of-fit, S	1.005	1.041	1.041
Δho_{max} , Δho_{min} (e Å ⁻³)	0.411, -0.359	0.771, -0.393	0.480, -0.387

^a $R = \sum ||F_o| - |F_c|| / \sum F_o.$

^b wR = $\left[\sum |w(F_0^2 - F_c^2)^2]/\sum wF_0^4\right]^{1/2}$; $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$, where $P = (F_0^2 + 2F_c^2)/3$ and a = 0.0240, b = 0.0000 for structure **1**; a = 0.0119, b = 3.2982 for structure **2**; a = 0.0246, b = 0.7166 for structure **3**.

Table 2	
Selected geometrical parameters $(Å^{0})$ for 1-3 complexes together with the DFT optimized values.	

	1		2			3	
	X-ray	DFT	X-ray		DFT	X-ray	DFT
	_	_	Mol A	Mol B	_	_	_
Zn–N1	2.020 (2)	2.050	2.019 (3)	2.021 (3)	2.053	2.026 (3)	2.056
Zn–N3	2.018 (2)	2.045	2.021 (3)	2.011 (3)	2.046	2.028 (3)	2.051
Zn–N5	2.032 (2)	2.050	2.026 (3)	2.027 (3)	2.052	2.021 (3)	2.056
Zn–N7	2.033 (2)	2.050	2.009 (3)	2.021 (4)	2.054	2.017 (3)	2.055
Zn–N9	2.071 (2)	2.164	2.083 (3)	2.083 (3)	2.151	2.053 (3)	2.156
N1–Zn–N3	86.48 (10)	87.50	87.10 (14)	86.87 (14)	87.30	87.05 (13)	87.86
N3–Zn–N5	88.45 (9)	87.50	87.73 (13)	87.33 (14)	87.30	86.96 (13)	87.85
N5–Zn–N7	85.68 (10)	87.35	87.50 (13)	87.91 (16)	87.18	87.92 (13)	87.75
N7–Zn–N1	87.83 (10)	87.35	87.50 (13)	87.52 (15)	87.18	86.54 (13)	87.75
N1–Zn–N9	103.87 (9)	102.60	102.22 (13)	103.86 (14)	102.96	100.12 (13)	101.62
N3–Zn–N9	102.98 (10)	103.05	100.79 (14)	98.71 (14)	103.67	99.25 (12)	101.50
N5–Zn–N9	102.95 (9)	102.59	102.59 (13)	101.28 (14)	102.97	106.25 (12)	101.61
N7–Zn–N9	102.12 (10)	100.72	103.05 (14)	105.19 (15)	100.88	106.09 (12)	100.45
Zn-N ₄	0.455 (3)	0.434	0.426 (3)	0.432 (3)	0.460	0.453 (4)	0.393
N7-Zn-N9-C33	25.7 (3)	-89.6	4.0 (5)	23.9 (5)	-0.01	45.6 (4)	109.40

3. Results and discussion

3.1. Synthesis and characterisation

Reported complexes were synthesised and crystallised in onestep procedure in degassed sealed glass ampoules. During the heating process the electrophilic Zn center of a planar ZnPc interacts with a nucleophilic ring nitrogen atom of imidazole, Nmethylimidazole or N-(2-pyrimidyl)imidazole leading to respective 4 + 1 coordinated ZnPc-derivatives with the axial Zn–N coordinated bond. During the prolonged heating process, the interactions between the new 4 + 1 coordinated ZnPc-derivative molecules leads to nucleation and crystallization. Crystallization resulting in well-developed violet elongated crystals suitable for the X-ray analysis. Compounds **1**, **2** and **3** are more soluble in organic solvents than the parent zinc phthalocyanine. Obviously, increase of solubility of the obtained ZnPc-derivatives in relation to ZnPc can be ascribed to formation of highly soluble pentacoordinated ZnPcL derivatives. As show in the X-ray single crystal analyses arrangement of the pentacoordinated ZnPcL complexes is less stabilised comparing with the parent ZnPc dye due to the steric hindrance of the axially coordinated ligands. Therefore the $\pi \cdots \pi$ stabilisation energy in these complexes is lower than that in the stacking structure of a planar ZnPc [29].

3.2. Thermal stability

Thermogravimetric analyses performed on the samples (~10 mg) show one-step decomposition, which start at temperatures 235, 230 and ~200 °C for samples **1**, **2** and **3**, respectively. The mass loss is connected with dissociation of Zn–N_L bond and release of respective molecule. Fig. 1 shows thermograms of the samples. The values of weight loss during the heating are 10.66, 12.30 and 19.79% related with the loss of imidazole, N-methylimidazole or N-(2-pyrimidyl)imidazole molecules from the complexes **1**, **2** and **3** are in good agreement with calculated values of 10.68, 12.58 and 20.31%, respectively. Calculated bond energy is almost the same for each complex and is ~11 kJ/mol higher than in the case of complexes with alkylamines [18] and pyridine derivatives [19], which is manifest significantly higher decomposition temperature. More detailed discussion taking into account the thermal stability is included in part 3.3.

3.3. Description of the structures and molecular arrangement

Complex **1** crystallises in centrosymmetric triclinic space group. An asymmetric part of the unit cell contains a whole molecule of the imidazole – ZnPc complex (Fig. 2a). Two molecules of the complex, related with the centre of symmetry, in the unit cell are linked by two hydrogen bonds N10–H10···N6, formed between imidazole moieties and azamethine nitrogen atoms, giving dimeric units (Table 3, Fig. 2b).

The arrangement of structure is mainly determined by two types of $\pi \cdots \pi$ interaction between phthalocyaninato moieties. First, typical for 4 + 1 type complexes, is back-to-back type with distance between Pcs^{2–} 3.559(3) Å and it is an interaction between the outer surfaces of the dimers (marked red in Fig. 2c). The chain formed by this model of interacting dimers is propagated along the *b* axis. The second takes place between internal Pc^{2–} surfaces of the adjacent dimers (as a consequence of insertion of an adjacent chain), and only benzene rings, marked orange in Fig. 2c, are involved and the distance between them is 3.471(4) Å. The sum of these interactions causes very poor solubility of crystals of **1** (this fact is also mentioned in part 3.5).

Complex **2** also crystallises in centrosymmetric triclinic space group, but the asymmetric part of the unit cell contains two



Fig. 1. Thermograms for samples of complexes **1** (red line), **2** (blue line) and **3** (green line) recorded for heat rate 5 $^{\circ}$ C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. Asymmetric unit of crystal of complex **1** with numeration of atoms with thermal displacement ellipsoids drawn with 50% probability level (a), dimeric unit of **1** with marked N10–H10···N6 hydrogen bonds (b) and the unit cell packing diagram viewed along [101] direction with dimeric unit marked red and inserted benzene rings (marked orange) giving additional $\pi \cdots \pi$ interaction (c). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

molecules of the N-methylimidazole – ZnPc complex with inclination angle $70.69(9)^{\circ}$ between N₄-planes. Both of them involved into a centrosymmetric back-to-back fashion, with distances

Table 3 Hydrogen-bonding geometry in 1 (Å,°).

Bond	D–H	Н…А	D…A	D–H…A
N10-H10N6	0.86	2.123 (3)	2.934 (5)	157



Fig. 3. Molecule of complex **2** with numeration of atoms with thermal displacement ellipsoids drawn with 50% probability level (a) and the unit cell packing diagram viewed along [100] direction with back-to-back and head-to-head chains along [010] (marked green) and [001] (marked orange) as well as indicated asymmetric part of the unit cell (blue) (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.619(3) and 3.402(3) Å, due to $\pi \cdots \pi$ interaction of Pcs^{2–}. Each of them is involved in back-to-back and head-to-head propagated chains along the [010] and [001] directions (marked green and orange, respectively, in the Fig. 3b). This type of packing results formation of channel-like structure along [100] direction with ligand moieties on its interior. The closure of *N*-methylimidazole moieties causes the highest temperature of decomposition of the complex **2** among the reported compounds. Both molecules exhibits the same values of Zn–N_L bond length and displacement of



Fig. 4. Asymmetric unit of crystal of complex **3** with numeration of atoms with thermal displacement ellipsoids drawn with 50% probability level (a) and the unit cell packing of **3** (b). All atoms are represented by spheres with arbitrarily adopted radii. Hydrogen atoms have been omitted for clarity.

Zn ion but the ligand moieties have a different orientation that is expressed by dihedral angle N7–Zn–N9–C33 (Table 2).

Complex **3** crystallises in a monoclinic system in space group $P2_1/n$. The asymmetric part of the unit cell contains a whole molecule of the *N*-(2-pyrimidinyl)imidazole – ZnPc complex (Fig. 4a). The molecules exhibit a back-to-back fashion with distance 6.784(3) Å and they are separated by the ligand moieties of the other two perpendicularly oriented complex molecules (Fig. 4b). The crystalline complex **3** exhibits the same way of packing as the complex of ZnPc with 3,4-dimethylpyridine, reported earlier [19]. Nevertheless, higher surface of the aromatic ligand and the lack of substituents cause decrease of the distance between Pcs^{2–} by 0.35 Å.

The zinc cation exhibits monoaxial ligation and a little distorted square pyramidal coordination environment what causes its displacement out of the plane determined by four isoindole nitrogen atoms (N₄-plane) by 0.455(3), 0.429(3) and 0.453(4) Å for

complexes **1**, **2** and **3**, respectively. The distortion of the coordination polyhedron is expressed by an angle between the normal to N₄-plane and line determined by Zn–N9 bond, which is equal $0.55(8)^{\circ}$ in crystal **1**, 3.62(15) and $1.10(13)^{\circ}$ in crystal **2** (two different values for two independent molecules in an asymmetric part of the unit cell) and $4.56(8)^{\circ}$ in crystal **3**.

The axial Zn–N9 bonds are slightly longer in comparison to some complexes found in the literature. The zinc chloridebis(imidazole) complex [30] exhibits average Zn-N bond length equal 2.008(9) Å and it is 0.05-0.07 Å shorter than Zn-N9 bonds in reported complexes. Nevertheless, it is not due to the different coordination number of the zinc cation, because other pentacoordinated ZnN₅ complexes with clearly distinguishable equatorial and axial Zn–N bonds (an axial is involved in Zn – imidazole connection) also exhibited slightly shorter axial bonds than in the case of our compounds. We talk about two complexes, i.e. imidazolate-bridged copper-zinc heterobinuclear complex (Z.-W. Mao et al. [31]) and amino-imidazolate complex reported by L.-Y. Kong et al. [32]. They have axial bonds with length equal 2.007 (7) Å and 2.003 (8) Å, respectively. Therefore, elongation of the Zn-N bond in the reported complexes is caused by repulsive interaction of the axially coordinated species the with aromatic system of the Pc^{2–}

3.4. Computational studies

Selected geometrical parameters of complexes, optimised by B3LYP method with $6-31 + G^*$ basis set are listed in Table 2 and are compared with crystal structures. A full list of optimised geometrical parameters is included in the Table S1-S3 in the supplementary information. It should be noted that the experimental results were obtained for the solid phase and theoretical calculations for the gas phase. Thus, most of the calculated bond lengths are slightly higher than observed in crystals. The length of axial Zn-N9 bond is ~0.1 Å higher in the gas phase than in the solid state in each reported complex. The most essential difference between the experiment and the calculations concerns the dihedral angle N7-Zn–N9–C33 (Table 2) that is connected with a rotation of the ligand around Zn-N9 axial bond. The energetic minimum for a complex molecule require the value $\sim 0^{\circ}$ and only one molecule (Mol A, Table 2) of the crystal **2** exhibit very close value (-4°) . Compounds **1** and 3 exhibit energetically higher conformation than molecule (Mol A) of 2, it means the value of the angle is equal 25.7(3), 23.9(4) and $45.6(5)^{\circ}$ in the case of **1**, second (Mol B) molecule of **2** and **3**, respectively (see Table 2). It let to claim that energy profit of interactions in the solid state compensate slight conformational increasing of the energy. The calculated energy of the Zn-N9 is equal 84.37, 85.72 and 85.01 kJ/mol in the case of 1, 2 and 3, and these values are the highest among the reported 4 + 1 ZnPc complexes. Considering the bond lengths, the biggest variation between the experimental and calculated values can be found as expected for the C-H bonds. It is well-known that the X-rayderived values of C-H bond lengths are systematically shorter than the values derived from other methods, because the electron density peak observed in the X-ray experiment corresponding to the hydrogen atom is shifted toward the carbon atom upon C-H bond formation.

3.5. Molecular electrostatic potential

The molecular electrostatic potential V(r) that is created in the space around a molecule by its nuclei and electrons is established as a guide to molecular reactive behaviour. It is defined as V(r) = Σ_A ($Z_A/(R_A - r)$) – $\int (\rho(r')/|r'-r|)dr$, where Z_A is the charge on nucleus A having a position vector R_A and the $\rho(r')$ is the electronic density

function of the molecule, and r' is the dummy integration variable [33,34]. The molecular electrostatic potential (MESP) is related to the electronic density in molecule and is a very useful tool in determining sites for electrophilic and nucleophilic reactions as well as for intermolecular interactions and organisation in solid-state [35–38].

The three-dimensional MESP maps are obtained on the basis of the DFT (B3LYP/6-31 + G(d)) optimised geometries of ZnPc(*Ima*), ZnPc(*N-MeIma*) and ZnPc(*2-N-phenylimiazole*) molecules as well as for reactant molecules ZnPc, imidazole, *N*-methylimidazole and *N*-(2-pyrimidinyl)imidazole. The calculated 3D MESP mapped onto the total electron density isosurface (0.008 eÅ⁻³) for each molecule is shown in Fig. 5. The colour code of MESP is in the range of -0.05 (red) to 0.05 eÅ⁻¹ (blue). Regions of negative MESP are usually associated with the lone pair of electronegative atoms or related to electrophilic reactivity, whereas the regions of positive MESP are associated with the electropositive atoms or related to nucleophilic reactivity of molecule.

For the ZnPc molecule the calculated 3D MESP map displays the electrophilic region near the Zn center on both side of the planar ZnPc molecule and the nucleophilic regions near the four bridged azamethine nitrogen atoms (Fig. 5a). In addition, less positive value of MESP than that near the Zn center and less negative value of MESP comparing to that of azamethine N atoms are observed on both sides of the planar ZnPc across the extended 18 π -electron of the conjugation in the Pc macrocycle and on the phenyl rings, respectively. The calculated 3D MESP map for the three imidazole derivatives displays in each molecule the nucleophilic region near the ring N atom(s) containing the lone electron pair (Fig. 5b). The calculated 3D MESP maps are helpful for understanding the interactions between the reacted molecules yielding the final ZnPccomplexes axially ligated by the three imidazole derivatives. During reaction the electropositive polarised Zn center of ZnPc molecule interacts with the electronegative polarised N ring atom of imidazole derivative resulting in formation of the Zn-N coordination bond. The calculated 3D MESP maps for the three ZnPc-L complexes are illustrated in Fig. 5c. These maps are helpful for understanding the interactions between the ZnPc-L molecules in the solid-state. As can be seen from the Fig. 5 upon coordination of the respective imidazole derivatives to the ZnPc, the region near the H atoms of coordinated imidazole derivatives displays more positive value of MESP comparing to that of isolated imidazole derivative molecules (Fig. 5b). In addition, the 3D MESP maps for the ZnPc-L complexes are helpful for the better understanding of the back-to-back organization of the molecules in the solid-state.

3.6. UV-vis spectroscopy

Electronic absorption spectra of solutions of complexes **1**. **2** and 3 in chloroform and DMF are shown in the Fig. 6. The spectra show two bands (Q and B) characteristic of the phthalocyaninate(2-) macrocycle [39]. The characteristic Q band, derived from the HOMO-LUMO transition, is observed at 674 nm in solutions of chloroform. In the case of solutions in DMF a minimal blue-shift to 670 nm is observed. Complexes 2 and 3 exhibits similar solubility in chloroform and DMF, whereas the solubility of 1 is drastically lower in less polar chloroform contrary to DMF. The poor solubility of crystalline complex 1 is due to additional interactions that were described in part 3.3. The fact that spectra of the complexes do not exhibit deviation in comparison with the spectrum of parent ZnPc pigment [40] testify that the electronic structure of the Pc(2-) macroring is not perturbed by axial ligation. The frontier HOMO and LUMO orbitals evaluated for the parent ZnPc pigment are comparable with that of **1-3** derivatives (Fig. 7). Thus ligation of the Zn center of ZnPc pigment by the N ring atom of imidazole and



Fig. 5. Three-dimensional molecular electrostatic potential maps (-0.05 eÅ^{-1} , red and $+0.05 \text{ eÅ}^{-1}$, blue) mapped on the surface of total electron density (0.008 eÅ^{-3}) for reacted molecules: ZnPc (a), imidazole derivatives (imidazole, *N*-methylimidazole and *N*-(2-pyrimidinyl)imidazole) (b) and the final **1-3** products (c). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 6. UV–Vis spectra for complexes **1** (red), **2** (blue) and **3** (green) recorded in DMF (solid lines) and chloroform (dotted lines). The spectra are spaced by 0.1 unit on the absorbance scale for the clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

derivatives e.g *N*-methylimidazole and *N*-(2-pyrimidinyl)imidazole, does not perturb the HOMO and LUMO frontier orbitals. The HOMO and LUMO orbitals are located on the free-base phthalocyaninate(2-) macrocycle.

4. Conclusion

Reaction of ZnPc pigment with imidazole and derivatives, *N*-methylimidazole and *N*-(2-pyrimidinyl)imidazole, leads to the formations of pentacoordinated **1-3** ZnPc-derivatives. As shown the molecular electrostatic potential maps, the interactions between the ZnPc and imidazole derivatives take place between the oppositely polarised electrophilic (Zn center of ZnPc) and nucleophilic N-ring atom of imidazole derivatives. Ligation of ZnPc by the imidazole derivatives does not change the colouring properties compared with the parent ZnPc pigment, since the energy gap of HOMO-LUMO level is not disturbed by the axial ligands. Decreasing of the $\pi \cdot \cdot \cdot \pi$ interactions between the Pc(2-) macrocycles in the studied pentacoordinated **1-3** ZnPc derivatives makes them more



ZnPc





ZnPc(Imidazole)



ZnPc(N-methylimidazole)



ZnPc(*N*-(2-pyrimidinyl)imidazole)

Fig. 7. Frontier of HOMO and LUMO orbitals for ZnPc and its 1-3 derivatives.

soluble compared with the ZnPc pigment with the $\pi \cdots \pi$ strongly interacted stacking structure.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2016.03.010.

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