

Available online at www.sciencedirect.com



Inorganica Chimica Acta 342 (2003) 64-76

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Stereochemistry and properties of the M(II)–N(py) coordination bond in the low-spin dipyridinated iron(II) and cobalt(II) phthalocyanines

Jan Janczak*, Ryszard Kubiak

W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, PL-50-950 Wroclaw, Poland

Received 23 January 2002

Abstract

A comparison between the coordination bond M(II)-N(py) and vibrational properties and stereochemistry of the dipyridinated iron(II) and cobalt(II) phthalocyaninato complexes, $FePc(py)_2$ and $CoPc(py)_2$ ($Pc = C_{32}H_{16}N_8$, $py = C_5H_5N$), is carried out using the single crystal X-ray diffraction and the vibrational spectroscopy. Both dipyridinated complexes have been synthesized in crystalline form by heating of the β -FePc or β -CoPc in pyridine at 160 °C. The crystals are formed during the slowly cooling process. The crystal of FePc(py)₂ and CoPc(py)₂ are isostructural. They crystallize in the space group $P2_1/c$ of the monoclinic system with two molecules per unit cell. The structural results and coordination bond properties are strictly related in these complexes. The Fe^{2+} and Co^{2+} cations are coordinated by four N-isoindole atoms of the phthalocyaninato(2-) macrocycle and axially by two nitrogen atoms of pyridine molecules to form a tetragonal bypyramid. The vibrational M-Nisoindole parameters are much more affected than the corresponding structural parameters by the difference in the electronic structure of the Co and Fe. The axial M(II)-N(py) bond length depends strongly on the electron configuration of the central metal. The value of the M(II)-N(py)bond length of 2.039(2) Å in FePc(py)₂ and 2.340(2) Å in CoPc(py)₂ clearly evidences on the localization of the unpaired electron on the d_z^2 orbital of the Co in the cobalt complex. The electron paramagnetic resonance (EPR) spectroscopy and magnetic susceptibility measurements have also detected the unpaired electron in the molecule of CoPc(py)₂. EPR and magnetic susceptibility measurements performed on a solid sample of FePc(py)₂ shown on its diamagnetic character. The importance of the $d(\pi) \rightarrow$ $\pi^*(Pc)$ back donation is manifested in the difference between the values of the C-N_{isoindole} and C-N_{azamethine} bond lengths of the Pc macrocycle.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Metallophthalocyanines; Iron(II) and cobalt(II) complexes; Crystal structures; Low-spin complexes; Spectroscopy; EPR

1. Introduction

The stereochemistry and electronic properties of the metal(II) phthalocyaninato(2-) complexes (M(II)Pc) have been widely studied [1]. Metallophthalocyanines have many unique properties that make them important and useable in different fields. Especially, they are used as colorants in the chemical industry [2], organic semiconductors for gas-sensor [3], visual pigments in display devices [4], photochemical redox agents in solar

energy conversion [5] and even as photosensitizers for photodynamic cancer therapy [6]. Many of these applications closely depend on the nature of the metal ion incorporated at the center of the 18π -electron aromatic phthalocyaninato(2-) macroring. The mobile π -electrons of the phthalocyaninato(2-) macrocycle and the possibility of the macrocycle to oxidation or reduction can serve as current carriers and provide the basis for semiconducting and conducting properties [7].

The solid state properties of the metal(II) phthalocyanines depend on their crystalline modification. Most of the metal(II) phthalocyanines crystallize in two, α and β , crystalline modifications. However, up to now both forms are structurally characterized by X-ray on single crystal only for metal-free phthalocyanine [8,9]. In the

^{*} Corresponding author. Tel.: +48-71-343 5021; fax: +48-71-441 029

E-mail address: janczak@int.pan.wroc.pl (J. Janczak).

^{0020-1693/02/\$ -} see front matter O 2002 Elsevier Science B.V. All rights reserved. PII: S 0 0 2 0 - 1 6 9 3 (0 2) 0 1 0 6 0 - 5

course of our investigations of metallophthalocyanines we have stated on the basis of X-ray single crystal examination that magnesium phthalocyanine molecules in the crystal form dimers of (MgPc)₂ [10]. This is in contrast to the metal(II) phthalocyaninato(2-) complexes of the d-block metals (Mn, Fe, Co, Ni, Cu and Zn), which β form crystal structures are stabilized by the 4+2 coordination of the central metal ion. The dimers of $(MgPc)_2$ are stabilized in the crystal by 4+1coordination of the magnesium ion as a result of the intermolecular Mg. .. Nazamethine interaction. This interaction leads to the significantly great deviation of the magnesium atom from the phthalocyaninato(2-) plane and is undoubtedly the reason for the unusual solidstate properties of magnesium phthalocyanine as well as for the unstability of the crystals under ambient atmosphere and/or under pure O2 or N2. The magnesium phthalocyanine in this condition undergoes transformation to form some complexes with the compositions of $(MgPc)_2O_2$ and $(MgPc)_2N_2$ [11].

The ability of the metal(II) phthalocyanines to coordinate additional ligands or solvent molecules containing N or O n-donor atoms is well known. Lever [12] has mentioned the existence of pyridine complexes in solution for FePc, MgPc and for MnPc. However, later it has been stated that the MnPc is able to form a stable pyridine complex only in an oxidative form; and μ -oxo-bis(phthalocyaninato(2-)) manganese(III) the complex, (MnPc(py))₂O, has been isolated and structurally characterized [13,14]. An existence of the sixcoordinated complex between 4-methylpyridine and FePc has also been reported [15]. Later this bis(4methylpyridine) phthalocyaninato(2-) iron(II) complex and the corresponding cobalt phthalocyanine complex have been structurally characterized [16]. Subsequently for CoPc the five- and six-coordinated pyridine complexes, CoPc(py) and CoPc(py)₂, have been reported [17,18], however, well-characterized solid compounds on single crystal have never been described.

In the course of our investigations, quite recently, studying the magnesium phthalocyanine in pyridine solution, we have obtained the dipyridinated magnesium phthalocyanine MgPc(py)₂ complex in crystalline form [19]. Additionally we have stated that the crystals of $MgPc(py)_2$ are stable under dry atmosphere, and under moist this complex interacts with the water molecules and converts into the MgPcH₂O·2py according to the scheme: $MgPc(py)_2 + H_2O \rightarrow MgPcH_2O \cdot 2py$. The complex of MgPcH₂O·2py has been previously structurally characterized [20]. For the complex of MgPc axially ligated by two pyridine molecules, we have not observed any evidence for the existence of the 1:1 complex as was mentioned for the complex of CoPc with pyridine [18]. In addition it has been shown that zinc phthalocyanine forms some complexes with various amines [21,22], and one of them, the zinc phthalocyanine complex with nhexylamine has been characterized by single crystal X-ray diffraction [22].

The goal of this study was to obtain the iron(II) and cobalt(II) dipyridineted phthalocyaninato complexes in the crystalline form and the information concerning their stability. Subsequently, to extend the information about the stereochemistry and the coordination bond properties we compared the crystal structures of FePc(py)₂ and CoPc(py)₂ with the previously described structure of MgPc(py)₂ complex [19]. In order to rationalize, the dependence of the M–N bonds strength on their electronic configuration has been discussed.

2. Experimental

2.1. Syntheses of the complexes

The FePc and CoPc were obtained from Aldrich. Although, the bottles were labeled as iron and cobalt phthalocyanines the analysis implies on the small amount of impurity. Both metallophthalocyanines were purified by heating under vacuum at about 210 °C. After 1 day the purity of both metallophthalocyanines have been checked on an energy dispersive spectrometer (the purity over 99.0%). The X-ray powder diffraction patterns clearly shown that both M(II)Pc after heating procedure exist in β -crystalline modification. The single crystals of $FePc(py)_2$ and $CoPc(py)_2$ suitable for X-ray analysis have been obtained by following procedure. A suspension of 0.2 g FePc or CoPc (both in β -form) in 50 ml of twice distilled and dry pyridine was heated in an evacuated glass ampoule at 160 °C for 5 h. Next the ampoule was slowly cooled to the room temperature (r.t.) (3 °C h⁻¹). During the cooling procedure the parallelepiped violet crystal of $FePc(py)_2$ or $CoPc(py)_2$ in various size were formed. Elemental analysis was carried out on an energy dispersive spectrometer. Found for FePc(py)₂: C, 69.49; H, 3.70; Fe, 7.47 and N, 19.34%, for CoPc(py)₂: C, 69.22; H, 3.51; Co, 8.12; and N, 19.15%. Calc. for C₃₂H₁₆N₈Fe(C₅H₅N)₂: C, 69.43; H, 3.61; Fe, 7.69 and N, 19.27% and for C₃₂H₁₆N₈Co(C₅H₅N)₂: C, 69.14; H, 3.58; Co, 8.08 and N, 19.20%.

2.2. Thermal measurements

Thermal analyses were carried out on a Lineis L81 thermobalance aparaturs with Pt crucibles. The powdered Al_2O_3 has been used as a standard reference. The measurements on the several samples have been performed under static air atmosphere on heating from r.t. to about 300 °C with the heating rate of 2 °C min⁻¹.

Table 1

Crystal data, data collection and refinement details for FePc(py)2 and CoPc(py)2

Formula	C ₃₂ H ₁₆ N ₈ Fe(C ₅ H ₅ N) ₂	C32H16N8Co(C5H5N)2
Molecular weight	726.58	729.66
Crystal system	monoclinic	monoclinic
Space group	$P 2_1/c$	$P2_1/c$
Unit cell dimensions		
a (Å)	9.576(2)	9.865(2)
b (Å)	19.929(4)	19.904(4)
b (Å)	9.179(2)	9.142(2)
β (°)	111.68(3)	112.10(3)
Volume, V (Å)	1627.8(6)	1663.8(6)
Ζ	2	2
$D_{\text{calc.}} (\text{g cm}^{-3})$	1.482	1.457
$D_{\rm obs.}$ (measured, floatation) (g cm ⁻³)	1.48	1.45
Radiation, Mo Ka (Å)	0.71073	0.71073
Index ranges		
h	$-13 \rightarrow 12$	$-13 \rightarrow 13$
k	$-26 \rightarrow 27$	$-25 \rightarrow 27$
1	$-10 \rightarrow 12$	$-11 \rightarrow 12$
Reflections collected	15 338	13 345
Independent reflections	4236 ($R_{\rm int} = 0.0629$)	$3934 \ (R_{\rm int} = 0.0427)$
Observed reflections	1901 $[I > 2\sigma(I)]$	2295 $[I > 2\sigma(I)]$
Absorption coefficient μ (mm ⁻¹)	0.514	0.566
Correction: Lorentz polarization, face-indexed analytical absorption	$T_{\min} = 0.8527, \ T_{\max} = 0.9456$	$T_{\min} = 0.8053, \ T_{\max} = 0.9352$
Refinement on F^2		
$R(F^2 > \sigma)$	0.0548	0.0417
$wR(F^2 \text{ all reflections})$	0.0665	0.0809
Goodness-of-fit, S	0.996	1.015
Largest Δ/σ	0.000	0.000
Residual electron density e $Å^{-3}$	+0.380, -0.577	+0.312, -0.283

 $R = \Sigma ||F_{o}| - |F_{c}|| \Sigma F_{o} w R(F^{2}) = \{\Sigma(w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma w F_{o}^{4}\}^{1/2}; w^{-1} = [\sigma^{2}(F_{o}^{2}) + (0.0143P)^{2}] \text{ for Fe complex and } w^{-1} = [\sigma^{2}(F_{o}^{2}) + 0.0312P] \text{ for Co complex where } P = (F_{o}^{2} + 2F_{c}^{2}) / 3.$

2.3. X-ray single crystal measurements

Data collection for both single crystals were carried out on a four-circle KUMA KM-4 diffractometer equipped with a two-dimensional area CCD detector. The graphite monochromatized Mo K α radiation ($\lambda =$ 0.71073 Å) and ω -scan technique with $\Delta \omega = 0.75^{\circ}$ for one image were used for data collection. The 960 images for six-different runs covering over 90% of the Ewald sphere were performed. One image as a standard was used for monitoring the intensities after every 40 images. Integration of the intensities, correction for Lorenz and polarization effects were performed using a KUMA KM-4 CCD software [23]. The face-indexed analytical absorption was calculated using the SHELXTL program [24]. Almost 4236 for FePc(py)₂ and 3934 for CoPc(py)₂ independent reflections (total 15338 and 13345, $R_{int} =$ 0.0640 and 0.0427, for Fe and Co crystal, respectively) were used for crystal structure solution and refinement. Both structures were solved by the Patterson method. The hydrogen atoms of the phenyl rings were located from $\Delta \rho$ maps, but in the final refinement their positions were constrained using HFIX 43 with the isotropic thermal parameters of $1.2U_{eq}$ of the carbon atoms linked directly to the H atoms. Both structures were refined with anisotropic thermal parameters for all non-hydrogen atoms by full-matrix least-squares methods using SHELXL-97 program [25]. More details on data collection and refinement parameters are collected in Table 1.

2.4. Electron paramagnetic resonance measurements

Electron paramagnetic resonance (EPR) measurements were carried out on SE-Radiopan and ESP 300 E-Bruker X-band spectrometers at r.t. The studies were performed on solid samples of 2-10 mg. The *g*-factors and the line widths of the signals were determined. The concentration of the free radicals in the CoPc(py)₂ samples were calculated using standard integration of the derivative signal and by comparing the area of the free EPR signal with the area determined with the free radical standard. DPPH, TEMPO, TEMPOL and Rickitt's ultramarine were used as standards [26].

2.5. Magnetic susceptibility measurements

The temperature dependence of the magnetic susceptibility were taken from 300 to 1.8 K with a Quantum Design SQUID magnetometer (San Diego, CA). Data were recorded at the magnetic field of 0.5 T on samples of 30-100 mg.

2.6. Spectroscopic measurements

Middle-IR spectra of the solid material (KBr pellets) and Far-IR spectra (Nujol mulls, polyethylene disc) were recorded at r.t. on a Bruker IFS 113 V FTIR spectrometer. Measurements of the electronic spectra were carried out at r.t. using a CARRY VARIAN/ 5EUV-VIS-NIR spectrometer. The UV–Vis spectra were recorded from solution in dichloromethane, pyridine and DMSO in 0.5 cm quartz cell.

3. Results and discussion

3.1. Synthesis and characterization

Our preparation method of the single crystals of the dipyridinated iron and cobalt phthalocyaninato(2-) complexes, $FePc(py)_2$ and $CoPc(py)_2$, is very fast and simple. A suspension of β -FePc and β -CoPc in purified pyridine was heated in an evacuated glass ampoule at 160 °C by 5 h. During the heating process the molecule of FePc or CoPc interacts by its positively charged central metal atom with the lone electron pair of nitrogen atom of pyridine molecule. As a result of the interaction the dipyridinated complexes are formed. During a slowly cooling process $(10^{\circ} h^{-1})$ the violet crystals are appeared. The first crystals have been observed at about 100 °C; from this temperature point the cooling process was twice slower. The obtained crystals of $FePc(py)_2$ and $CoPc(py)_2$ are well soluble in pyridine, DMF, DMSO and other N- and O-donor solvents as well as in an aromatic solvents like guinoline or chloronaphthalene. The solubility in water is not significant.

In contrast to the crystals of $MgPc(py)_2$ which are unstable under laboratory atmosphere, both dipyridineated iron and cobalt phthalocyaninato(2-) complexes are stable. The crystals of MgPc(py)₂ under moist atmosphere interact with water molecules and transform into a hydrated complex with the composition of $(MgPcH_2O) \cdot 2py$. In the crystal of $(MgPcH_2O) \cdot 2py$ the water molecule is coordinated to the magnesium cation, while the pyridine molecules as acceptors are joined to the MgPcH₂O by $O-H \cdots N(py)$ hydrogen bonds with water molecule [15]. Thus, the coordination Mg-O bond is stronger than coordination Mg-N(py) in magnesium phthalocyaninato complexes, while in both Fe and Co complexes the coordination bonds with axial pyridine molecules are stronger than the bonds with ligands containing oxygen atom. This is probably due to the $d\pi(\text{metal}) \rightarrow \pi^*(\text{Pc})$ back donation which make the central metal ion (Fe, Co) much more positive in



Fig. 1. Thermograms of the solid state samples of the $FePc(py)_2$ (a) and $CoPc(py)_2$ (b) complexes.

relation to the magnesium ion and, therefore, the coordination M-N(py) bonds (M = Fe, Co) are much stronger than in the magnesium analogue [15]. Contact of the FePc(py)₂ and CoPc(py)₂ with dilute acid lead to the demetallation, yielding metal-free phthalocyanine in the α form, which was identified by X-ray powder diffraction method [9].

As can be seen from the thermograms (Fig. 1(a) and (b)), the FePc(py)₂ complex is more stable than the cobalt analogue. Thus, it should be stated that the axial coordination Fe–N(py) bonds in FePc(py)₂ are stronger than the Co–N(py) bonds in the CoPc(py)₂ complex. The CoPc(py)₂ complex is stable up to about 140 °C, while the FePc(py)₂ complex is stable up to about 225 °C. Above these temperature points two axial equivalent bonds in FePc(py)₂ and in CoPc(py)₂ break simultaneously giving FePc and CoPc in powdered form. Their X-ray powder diffraction patterns indicate on the β modification. There was no evidence on the formation of the 1:1 adducts (M(II)Pc:py) by the thermal dissociation.

3.2. Description of the structures

The crystals of the two complexes are isostructural. The molecular structure of the dipyridinated iron and cobalt phthalocyaninato(2-) complexes is illustrated in Fig. 2. The metal cations (Fe, Co) lie at the inversion center, thus, the M(II)Pc(py)₂ molecules are centrosymmetric. The coordination polyhedron around Fe(II) and Co(II) approximates to a tetragonal bypiramid. In both complexes the central metal ion (Fe²⁺, Co²⁺) and the four coordinated isoindole nitrogen atoms of the phthalocyaninato(2-) macrocycle lie on a plane. The



Fig. 2. Molecular structure of the $FePc(py)_2$ (a) and $CoPc(py)_2$ (b) with the labeling of the atoms. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of an arbitrary radius.

two axial pyridine molecules are coordinated by their lone-electron pair at the nitrogen atom to the central metal cation. The dihedral angle between the N₄isoindole plane of phthalocyaninato macrocycle and that containing the axially coordinated pyridine molecules is only slightly different from 90° (89.37(8) and $89.04(8)^{\circ}$ in FePc(py)₂ and in CoPc(py)₂, respectively). The orientation of the axial pyridine ligands relative to the phthalocyaninato(2-) ring is well described by the torsion angle of N3–M–N5–C17 (M = Fe, Co). The rotation of pyridine ligand around the M-N5 axis would reduce the steric effect, i.e. the non-bonding distances between the hydrogen atoms of the axial pyridine ligand in orto positions and the atoms of the phthalocyaninato(2-) macrocycle. In particular, if the rotation angle is equal 0, the pyridine plane is parallel to the M-N3 bond, or at equivalent position rotated by 90° , the pyridine molecule is parallel to the M–N1 bond, making the non-bonding $C \cdots H$ distances greater than 2.5 Å. The second orientation, with the rotation angle of

Table 2											
Selected	bond	lengths	(Å) a	nd	angles	(°)	for	FePc(py) ₂	and	CoPc()	py) ₂

	FePc(py) ₂	CoPc(py) ₂
Bond lengths		
M-N1	1.938(2)	1.930(2)
M-N3	1.939(2)	1.931(2)
M-N5	2.039(2)	2.340(2)
N1-C1	1.366(3)	1.376(2)
N1-C8	1.382(3)	1.376(2)
N2-C8	1.333(3)	1.333(2)
N2-C9	1.330(3)	1.329(2)
N3-C9	1.381(3)	1.376(2)
N3-C16	1.378(3)	1.377(2)
$N4-C1^{i}$	1.335(3)	1.327(2)
N4-C16	1.325(3)	1.327(2)
Bond angles		
N1-M-N3	90.19(8)	90.01(7)
$N1-M-N3^{i}$	89.81(8)	89.99(7)
N1-M-N5	90.47(8)	91.28(6)
$N1-M-N5^{i}$	89.53(8)	88.72(6)
N3-M-N5	90.00(8)	89.33(6)
$N3-M-N5^{i}$	90.00(8)	90.67(6)

45°, makes the axial pyridine ligand plane parallel to the M-N_(azamethine) axis and reduces the non-bonding distances between hydrogen atoms of pyridine (H in orto positions) and the azamethine nitrogen atoms of phthalocyaninato(2-) macrocycle. This conformation of $MPc(py)_2$ complexes is the most stable, and is preferable in the solution, since the greatest interaction (attractive forces) between the hydrogen atoms of pyridine molecules in orto positions and the N-azamethine atoms. The intermolecular interactions as well as the crystal packing forces present in the crystal make the rotation angle of the axial pyridine plane to the value of $28.6(2)^{\circ}$ in $CoPc(py)_2$ and $36.1(2)^\circ$ in $FePc(py)_2$. These angles are significantly different to that observed in the axially ligated by 4-methylpyridine cobalt and iron phthalocyaninato(2-) complexes (see Table 3); this is likely due to the additional interaction with the additional 4-methylpyridine molecule, since they crystallizes with 4-methylpyridine molecules as solvent [16]. In the isostructural crystals of MgPc(py)₂ the rotation angle of axial pyridine molecule is much more similar to the cobalt than to the iron complex, $26.6(2)^{\circ}$ [19].

The main differences between FePc(py)₂ and CoPc(py)₂ structures are found in the axial M–N(py) bond distances (Table 2), which are longer in the CoPc(py)₂ [2.340(2) Å] than in the FePc(py)₂ [2.039(2) Å], and as mentioned above in the rotation angle of axially coordinated pyridine ligands. The long Co–N(py) axial bond in CoPc(py)₂ is likely due to the unpaired electron which is essentially localized on the d_z^2 orbital of the Co²⁺. The unpaired electron has also been detected by EPR measurement on a solid state sample. The values of the M–N(py) coordination bond length in

Table 3			
Comparison of the coordination of the central metal	ion in dipyridinated	phthalocyaninato(2-)	complexes

Compound	FePc(py) ₂	FePc(4-Mepy) ₂	FePc	CoPc(py) ₂	CoPc(4-Mepy) ₂	CoPc	MgPc(py) ₂	MgPc
M-N _{iso} (Å)	1.938(2)	1.935(3)	1.926(2)	1.930(2)	1.930(4)	1.908(2)	2.006(2)	2.011(3)
M-Naxial (Å)	2.039(2)	2.040(3)		2.340(2)	2.322(5)		2.376(2)	
Rotation angle (°)	36.1(2)	42.6(4)		28.6(2)	35.7(5)		26.6(2)	
C-N _{iso} (Å)	1.377(3)	1.373(7)	1.378(3)	1.376(2)	1.373(7)	1.368(4)	1.367(2)	1.376(2)
C-N _{aza} (Å)	1.331(3)	1.328(4)	1.322(3)	1.329(2)	1.334(7)	1.318(4)	1.343(2)	1.334(2)
Reference	This work	[16]	[35]	This work	[16]	[33]	[19]	[10]

both complexes indicate on their strength and well correlate with the stability of these complexes. The axial pyridine molecules are stronger coordinated in Fecomplex, and the FePc(py)₂ complex is more stable than the CoPc(py)₂ complex, as shown the termogravimetric experiments. A similar correlation between the short, in Pc-plane, and long, perpendicular to the Pc, M-N bond distances are observed in cobalt phthalocyaninato(2-) complex with two axially coordinated 4methylpyridine molecules [16] and in the isostructural crystal of MgPc(py)₂ (Table 3) [19]. The long M-N coordinated bonds have also been observed in several axially coordinated porphyrinato magnesium complexes [27–30], and in axially coordinated porphyrinato cobalt(II) complexes [31,32].

The coordination bond distance calculated by Little and Ibers Co(III)–N(sp²) is equal to 2.05 Å (in the absence of electron localization on the d_z^2 orbital) [32]. Therefore, the lengthening of the axial Co(II)–N(py) bond by about 0.3 Å in octaethyl-prophyrinato(2-)cobalt(II) complex ligated axially by two molecule of 3methylpyridine is attributed to the occupancy of d_z^2 orbital by a single unpaired electron. The value of 2.05 Å for the Co(III)–N(sp²) bond in absence of electron on d_z^2 orbital correlate well with the value of 2.039(2) Å observed in the low-spin FePc(py)₂ complex for axially coordinated pyridine molecules. This is in agreement with the absence of the EPR signal for the solid state sample of FePc(py)₂ (the low-spin complexes of Fe(II) are EPR inactive).

The C–C and C–N bond distances of the phthalocyaninato(2-) macrocycle in both $M(II)Pc(py)_2$ complexes are normal, the values of the chemically equivalent bond lengths are not different from the corresponding values found in other metallophthalocyaninato complexes [33–36]. However, it should be noted that the good accuracy of the present structure determinations and relatively low standard deviations indicate on the small differences between the average values of C–N_{iso} and C–N_{aza} bond lengths (Table 3). These differences indicate an accumulation of the charge density on the outer carbon atoms of pyrrole rings as well as on the bridging azamethine nitrogen atoms of the phthalocyaninato(2-) macrocycle and can, therefore, be explained by an important electron back donation from



Fig. 3. Arrangement of the $M(II)Pc(py)_2$ molecules (M = Fe,Co) in the unit cell.

the metal $d(\pi)$ orbitals to the ligand $\pi^*(e_g)$ antibonding orbital, since the calculated maximum charge density is mainly located on those atoms [37–39]. The accumulation of the charge density on the outer carbon atoms of pyrrole rings and on the bridging azamethine nitrogen atoms of the phthalocyaninato(2-) macrocycle has been also evidenced in the experimental density maps derived from the low temperature high resolution X-ray experiments [40].

The arrangement of the FePc(py)₂ and CoPc(py)₂ molecules in the unit cell is illustrated in Fig. 3. Both crystals are built up from isolated M(II)Pc(py)₂ molecules, which form alternating sheets, which molecules related by a screw axis and glide plane. In one sheet the planes of phthalocyaninato(2-) macrocycle are parallel to each other, while between the sheets the phthalocyaninato(2-) planes are perpendicular. Within each sheet the neighboring molecules are overlapped by their two phenyl rings which are separated by about 3.3 Å in FePc(py)₂ and about 3.4 Å in CoPc(py)₂. These values



Fig. 4. Fra-IR spectrum of FePc(py)₂ (a) and CoPc(py)₂ (b).

are comparable with the van der Waals distance (~ 3.4 Å) [41] for an aromatic carbon atoms and indicate on the $\pi-\pi$ clouds interaction between the ring system.

3.3. Vibrational properties

The vibrational properties, especially that in the lowfrequency spectroscopic region, can be easily related to the stereochemical features, since they can serve to provide information about the reflect changes in the metal oxidation state and the symmetry surrounding the central metal as well as giving direct information on the

M-N coordination bond strength. Therefore, this method have also been used for characterization of the dipyridineated iron and cobalt phthalocyaninato complexes. The IR spectra of $FePc(py)_2$ and $CoPc(py)_2$ complexes in the low-frequency region $(500-100 \text{ cm}^{-1})$ are shown in Fig. 4(a) and (b). A comparison of the frequencies of the dipyridinated iron and cobalt phthalocyaninato complexes with their non-ligated FePc and CoPc are collected in Table 4. As can be seen from Table 4 all the bands related the vibration of the phthalocyaninato(2-) macrocyclic ligand are shifted to the higher frequency compared with the metal-free phthalocyanine [42–44]. However, the M–N stretching assignments for several metallophthalocvaninato complexes by Kobavashi [43], which are widely cited, were done only on the basis of the appearance of the bands in the spectra of metallophthalocyanines, which did not appear in the spectrum of metal-free phthalocyanine. Therefore, the assignment of the M-N stretching vibration band for several metallophthalocyanines in the spectral region from 185 to 98 cm⁻¹ presents some difficulties, since the bands in this region could be attributed to the bending N–M–N motion.

The assignments of the M–N stretching vibration and the N-M-N angular deformation presented here are empirical but supported by analogy to that carried out for several isotope-substituted metallophthalocyanines [44] and metalloporphirines [45-50]. The normal coordinate analyses for metallophthalocyanines [51] as well as the semi-empirical calculated spectra predict one IR-active M–N stretching mode [52,53], however, since the conjugated ring system in this mode may be mixed with the macrocyclic motions and distributed into more than one absorption [45]. The comparison between FePc and CoPc and their dipyridinated complexes are comprised in Table 4. In the non-ligated FePc and CoPc complexes, the one M–N stretching vibration band (E_u) has been observed in agreement with the D_{4h} symmetry of chromofore. The ligation of FePc and CoPc by two pyridine molecules leads to the lowering of the complexes to the D_{2h} symmetry, and two IR-active bands $(B_{2u}+B_{3u})$ should be expected. However, in both

Table 4

Comparison of the far-infrared spectral data of the FePc(py)₂ and CoPc(py)₂ and their non-ligated phthalocyanines: β-FePc and β-CoPc

Compound $v(M-N(py)) = \delta(N-M-N)$ Ring deformation bands		Ring deformation bands	Reference	
β-FePc	308s	160vs, 154sh	515m, 435vs, 343w, 292m, 232w, 124s	[42,43,45,63]
$FePc(py)_2$	331s	165m	519m, 443vs, 366w, 301m, 240w, 195w, 128m	This work
FePc(4-Mepy) ₂	330s	160s	520m, 444vs, 389w, 300s, 246m, 118m	[16]
β-CoPc	314s	172vs	519m, 435vs, 372w, 302s, 240w, 122s	[42,43,63]
$CoPc(py)_2$	312s	173s	516s, 435vs, 429w, 300m, 228w, 122w-	this work
CoPc(4-Mepy) ₂	312s	172vs, 166sh	518s, 435vs, 298m, 228w, 124m	[16,54]
β -H ₂ Pc		· · · · ·	498m, 435m, 342m, 282s, 238w, 140w, 127w	[42,43,63]

v, very; s, strong; m, medium; w, weak; sh, shoulder.

dipyridinated complexes only one stretching vibration band is observed (Fig. 4(a) and (b)). This is probably due to the long axial bond, especially observed in the Co-complex, resulting in a reduction of the splitting of the E_u stretching band; undoubtedly the difference between the M-N(py) bond length in Fe and Co complexes of 0.28 Å is not effective in this context as suggested Cariati et al. [16]. The splitting of the N(pc)-M-N(pc) angular deformation observed in the spectrum of cobalt phthalocyanine ligated axially by two molecule of 4-methylpyridine is in agreement with the observed difference between the N1(pc)-Co-N3(pc) and N1(pc)- $Co-N3^{1}(pc)$ angles [16,54]. A similar splitting of the N(pc)-Fe-N(pc) is observed in the spectrum of β -FePc. The angular anisotropy of the β -FePc is in agreement with the X-ray structural results [35], they have shown the difference between the N1-Fe-N3 and N1-Fe-N3¹ angles and confirm that the bending vibrational frequencies are more sensitive to the structural changes than the stretching vibration. In these dipyridinated iron and cobalt phthalocyaninato complexes, the X-ray structural results have clearly shown that the N1-M-N3 and N1–M–N3¹ angles (M = Fe, Co) are almost identical and almost equal to 90°, therefore, a single unsplitt N(pc)-M-N(pc) angular deformation band has been observed in both far-infrared spectra. Comparing the far-infrared spectra of $FePc(py)_2$ and $CoPc(py)_2$ (presented here) with the spectra of their non-ligated FePc and CoPc complexes [43,45] (Table 4), we were not able to assign any band to the Fe-N(py) and Co-N(py)vibration, which would be expected near 300 cm^{-1} . This is probably due to their weak intensity or/and coupled.

The frequency of the v(Fe-N(pc)) stretching vibration is strongly affected by the axial coordinated pyridine molecules in FePc(py)₂ (the shift ~ 23 cm⁻¹ in relation to β -FePc), while the frequencies of the v(Co-N(pc)) stretching vibration in β -CoPc as well as in $CoPc(py)_2$ are almost the same (see Table 4). This can be explained by the change of the ground-state configurations of the ligated iron phthalocyanine $(FePc(py)_2)$ in relation to non-ligated iron phthalocyaninie (β -FePc) and unchanged ground state configuration in ligated and non-ligated cobalt phtalocyaninato complexes. In accordance to the magnetic properties [55-58] and EPR measurements [59] performed on the β -CoPc the ground-state configuration can be expressed: $e_g^4 b_{2g}^2 a_{1g}$. The EPR and magnetic measurements performed on the ligated dipyridinated cobalt phthalocyanine (presented here) clearly show the unchanged ground-state configuration of the central cobalt ion. The ground-state configuration of intermediate-spin complex of iron(II) phthalocyanine (β -FePc) with the spin S = 1 [35] according to the EPR, magnetic and Mössbauer measurements can be expressed as: $e_{g}^{3}b_{2g}^{2}a_{1g}^{1}$ or $e_{g}^{2}b_{2g}^{2}a_{1g}^{2}$ [60–62]. The ligation of FePc by two pyridine molecules leads to the change of the ground state configuration to $e_g^4 b_{2g}^2$, which

is in agreement with the EPR measurement (no EPR signal for the $FePc(py)_2$ complex was observed). The occupation of the eg orbitals, to which back donation is done, increases from β -FePc to FePc(py)₂. This is in agreement with the large shift of the v(Fe-N(pc))stretching vibration in $FePc(py)_2$ to a higher frequency. This cannot be the case for the cobalt complexes, which have the same ground-state configuration. The difference in the electronic configurations also explains the differences in the M-N(pc) energy between the $FePc(py)_2$ and $CoPc(py)_2$ complexes. The contribution of the double excited configuration $e_g^3 b_2^2 a_{1g}^2$ to the ground state of the cobalt complex is certainly more important than the triplet excited configuration $e_g^3 b_2^2 a_{1g}$ to the ground-state of FePc(py)₂ complex, what explains the observed lower value of v(Co-N(pc)) vibrational frequency in the spectrum of the $CoPc(py)_2$ complex. The vibrational data clearly evidence that the electronic ground-state configuration is mainly responsible for the change of the v(Co-N(pc)) vibrational frequencies observed in the spectra of Fepc(py)₂ and CoPc(py)₂ complexes. The difference of the mass between the iron and cobalt complexes play minor role, otherwise the difference in the stretching vibration v(M-N(pc)) between these dipyridinated complexes would be compar-



Fig. 5. Middle IR spectrum of FePc(py)₂ (a) and CoPc(py)₂ (b).

Table 5 Middle-IR spectral data for $FePc(py)_2$ and $CoPc(py)_2$ (in cm⁻¹)

FePc(py) ₂ ^a	FePc [63]	CoPc(py) ₂	CoPc [63]	Assignment
571 (m)	574 (w)	572 (m)	574 (m)	ϕ (C–C) macrocycle ring deformation
641 (w)	642 (w)	641 (w)	642 (m)	ϕ (C–C) macrocycle ring deformation
698 (m)		695 (m)		γ (C-H) in pyridine
727 (vs)	732 (vs)	727 (vs)	730 (vs)	γ (C–H) out of plane deformation
736 (m)		737 (m)		γ (C-H) in pyridine
752 (m)	755 (s)	754 (m)	755 (s)	γ (C–H) out of plane deformation
779 (w)	781 (m)	775 (m)	780 (s)	v(C-N) stretching
869 (w)	875 (w)	868 (w)	865 (w)	γ (C–H) out of plane deformation
915 (w)	909 (m)	913 (m)	911 (s)	γ (C–H) out of plane deformation
931 (w)		935 (w)		v(C-N) in pyridine
1040 (w)		1034 (w)		β (C–H) in pyridine
1069 (m)	1069 (m)	1072 (m)	1072 (s)	β (C–H) in plane deformation
1089 (m)	1084 (s)	1091 (s)	1086 (s)	v(C-N) stretching in pyrrole
1096 (m)		1097 (m)		v(C-N) in pyridine
1117 (s)	1120 (vs)	1120 (s)	1120 (vs)	β (C–H) bending in plane
1160 (m)		1158 (m)		β (C–H) bending in pyridine
1165 (m)	1163 (s)	1165 (m)	1162 (s)	v(C-N) in plane
1216 (w)		1216 (w)		v(C-N) in pyridine
1286 (m)	1288 (m)	1286 (m)	1288 (s)	v(C-N) in isoindole
1327 (m)	1332 (s)	1328 (m)	1333 (vs)	v(C-C) in isoindole
1367 (m)		1368 (m)		v(C-C) in pyridine
1377 (vs)		1378 (vs)		v(C-C) in pyridine
1421 (m)	1420 (s)	1421 (m)	1426 (s)	v(C-C) in isoindole
1445 (m)		1446 (m)		v(C-C) in pyridine
1465 (vs)		1463 (vs)		v(C-C) in pyridine
1482 (s)		1480 (m)		v(C-C) in pyridine
1509 (w)	1510 (s)	1519 (m)	1520 (s)	v(C-C) in pyrrole

^a v, very; s, strong; m, medium; w, weak.

able with that between the β -FePc and β -CoPc. It can be concluded that the vibrational data can be correlated with the structural results only if the electronic configuration does not change.

The middle IR spectra of $FePc(py)_2$ and $CoPc(py)_2$ are shown in Fig. 5(a) and (b), respectively. Comparison with their non-ligated β -FePc and β -CoPc complexes is listed in Table 5. The spectroscopic characterization of



Fig. 6. Plot of the inverse molar susceptibility vs. temperature for the $CoPc(py)_2$ complex.

the FePc and CoPc assignment of the bands for β -FePc and β -CoPc are widely described in the literature [42,43,45,63]. As can be seen from Table 5 the most of the IR bands present in the spectrum of β -FePc and β -CoPc are also observed in the spectrum of dipyridinated iron and cobalt phthalocyaninato complexes but with slightly modified frequencies. The assignment of the bands related to the axially coordinated pyridine molecules is supported by correlation with the spectrum of free pyridine and several metallodipyridinated complexes $M(py)_2X_2$ [64]. The discussion of the spectroscopic properties in more details and assignments of the vibrational bands in the middle IR spectrum have been made in previous paper [19] which reported the spectroscopic properties and structure of dipyridinated magnesium phthalocyanine, MgPc(py)₂.

3.4. Magnetic properties

A plot of the reciprocal molar susceptibility versus temperature for the CoPc(py)₂ complex is shown in Fig. 6. To the molar susceptibility the correction for diamagnetic susceptibility of the phthalocyanine molecule has been included [58]. The experimental data are well approximated by a Curie–Weiss law with the value of $\theta \simeq -8.5$ K for the Curie constant. The effective

Table 6 Effective magnetic moment for M(II)Pc and M(II)Pc(py)₂ complexes

Compound	Coordination number of the central metal	Number of unpaired electrons	$\mu_{\mathrm{eff}}\left(\mu_{\mathrm{B}}\right)$	Theoretical spin-only (μ_B)	Theoretical L-S (μ_B)	Reference
α-CoPc	4	1	2.14-2.38	1.73	3.00	[55,59,61]
β-CoPc	4	1	2.66 - 2.73	1.73	3.00	[55,57,59]
$CoPc(py)_2$	6	1	1.82	1.73	3.00	this work
β-FePc	4	2	3.71-3.85	2.83	4.47	[55,57,61,65]
FePc(py) ₂	6	0	0	0	0	this work
CrPc	4	4	3.49	4.89	5.48	[55]
CrPc(py) ₂	6	2	3.16	2.83	4.47	[55]

magnetic moment calculated for the CoPc(py)₂ at room temperature (298 K) is $\mu_{eff} = 1.82 \mu_B$, and indicates on the one unpaired electron per CoPc(py)₂ molecule. For a comparison, the effective magnetic moment measured on the non-ligated cobalt(II) phthalocyanine depends on the crystal modification of the CoPc complex. The effective magnetic moment at room temperature reported by several authors [55,57,59,61,65] for the α -CoPc is about 15% lower than that observe for β -CoPc. The comparison of magnetic properties for $CoPc(py)_2$ and α -CoPc and β -CoPc is collected in Table 6, which also comprise the properties of other ligated and nonligated phthalocyaninato complexes, M(II)Pc and $M(II)Pc(py)_2$. The effective magnetic moment of the $CoPc(py)_2$ is slightly greater than the spin-only value of 1.73 $\mu_{\rm B}$, but significantly smaller than those found in both α -CoPc and β -CoPc. The greater values of the magnetic moment in the α -CoPc and β -CoPc complexes in relation to the dipyridinated complex can be explained by a greater contribution of the orbital moment to the ground state. The value of the magnetic moment of 1.82 μ_B indicates on the low-spin CoPc(py)₂ complex.

The EPR measurement on a solid crystalline sample of CoPc(py)₂ shows axial magnetic symmetry with two principal g values: $g_{\perp} = 2.2157$ and $g_{\parallel} = 1.9987$. The calculation of the spin concentration yields 8.29×10^{20} spins per g, i.e. $\cong 1$ unpaired electron per CoPc(py)₂ molecule. The EPR measurements of α -CoPc and β -CoPc modifications have been performed on a solid

Table 7

The EPR g parameters of cobalt(II) phthalocyaninato(2-) complexes at room temperature (298 K)

Compound	g_\perp	$g_{ }$	Reference
α -CoPc (solid state) ^a	2.422	2.007	[65]
β -CoPc (solid state) ^a	2.89	1.91	[65]
CoPc (in solution)	2.268	2.016	[17]
CoPc(py) (solid state)	2.28	2.13	[18]
$CoPc(py)_2$ (solid state)	2.2157	1.9987	This work
CoPc(4-Mepy) (solid state)	2.27	2.11	[18]
CoPc(4-Mepy) ₂ (solid state)	2.21	2.02	[18]

^a Diluted in isomorphic crystals of α-ZnPc and β-ZnPc, respectively.

samples magnetically diluted by isomorphic crystal of diamagnetic metal-free phthalocyanine, NiPc or ZnPc [59]. The EPR spectra of both α - and β -CoPc complexes exhibit, similarly to the CoPc(py)₂ complex, an axial symmetry (see Table 7). The resolving of the hyperfine coupling is hindered in the polycrystalline solid sample, but the shift of the g_{\perp} value towards higher fields is observed, correlating to the greater strength of the axial ligands.

The magnetic susceptibility of the iron phthalocyanine, FePc, has been performed several times [55,57,61,65] and the effective magnetic moment (Table 6) is intermediate between theoretical spin-only values S = 1 and S = 2 state. The Mössbauer studies on the FePc [60,66,67] indicate that the central ion in the FePc molecule is in S = 1 state with a large zero-field splitting such that the level $M_s=O$ lies about 70 cm⁻¹ below the doublet $M_S = \pm 1[60]$. The electronic configuration was assumed to be $(d_{xz}d_{yz})^3(d_{xy})^2(d_z^2)^1$ giving na orbitally non-degenerate ground term ³B_{2g} with two unpaired electrons. The EPR measurement performed on a solid polycrystalline sample of FePc(py)₂ showed no resonance signal. The magnetic susceptibility experiment on polycrystalline sample of FePc(py)2 shows its diamagnetic character. Both EPR and magnetic susceptibility



Scheme 1. A σ bonding diagram for Fe(II) in a strong-field tetragonal environment.



Fig. 7. UV-Vis spectrum of FePc(py)₂ (a) and CoPc(py)₂ (b).

experiments clearly shown that ligation of the iron phthalocyanine by pyridine molecules leads to the change of the ground-state from S = 1 (for FePc, $e_g^3 b_{2g}^2 a_{1g}^1$) to S = 0 (FePc(py)₂, $e_g^4 b_{2g}^2$). The FePc(py)₂ is a low-spin complex, according to the molecular orbital diagram (Scheme 1) of Fe(II) in a strong-field tetragonal environment [68].

3.5. UV–Vis spectroscopy

The electronic absorption spectra of $\text{FePc}(\text{py})_2$ and $\text{CoPc}(\text{py})_2$ in dichloromethane are shown in Fig. 7(a) and (b), respectively. The observed bands are listed in the Table 8, which also comprise the electronic absorption bands for the non-ligated phthalocyaninato iron

Table 8			
UV-Vis	spectral	bands	[nm]

and cobalt complexes of the vapor phase. Several theoretical calculations for the D_{4h} symmetry of the metallophthalocyanine molecules predict five distinct bands (Q, B, N, L and C) in the spectral region between 200 and 800 nm [69,70]. The Q band corresponds to the excitation between HOMO (a_{1u}) to LUMO (e_e) , while B band is mostly an $a_{2u} \rightarrow e_g$ transition. Both (Q and B) bands are characteristic for the phthalocyaninato ligand. As can be seen from Fig. 7 the Q band in both $FePc(py)_2$ and CoPc(py)₂ spectrum splits into two bands. The splitting value of Q band is equal to ≈ 60 nm and is likely due to the vibronic coupling in the excited state [71]. The N, L and C bands resulting from a contributions of $a_{2u} \rightarrow e_g$, $b_{2u} \rightarrow e_g$ and $a_{1u} \rightarrow e_g$ transitions [72]. As can be seen from Table 8 the spectra of CoPc and $CoPc(py)_2$ are similar, since they have the same ground state configuration of the cobalt(II). However, one additional band at ~ 415 nm is observed in the spectrum of $FePc(py)_2$ in relation to the spectrum of FePc. Several authors have assigned this band to the electronic transition from a deeper level to the halfoccupied HOMO level. Thus, the band is an evidence for the existence of the one-oxidized free radical phthalocyaninato(1-) ring as observed in the spectrum of oneoxidized metallophthalocyaninato complexes, such as LiPc, LnPc₂ or InPc₂ [73]. However, the EPR measurement on the solid sample of $FePc(py)_2$ showed no signal, therefore, the bands at 415 nm cannot be attributed to the transition in the radical form, since the low-spin (S = 0) dipyridinated iron(II) phthalocyanine $(e_g^4 b_{2g}^2)$ do not posses a hole in their eg level. Further, as suggested by Lever et al. [74] this band cannot be attributed to the LMCT transition. Kobayashi and Yanagawa [75] studied the dipyridinated iron(II) tetraphenyl porphrine assigned the band at 21 000 cm⁻¹ (~415 nm) to the charge transfer from iron to axially coordinated pyridine molecules, $b_{2g}(d_{\pi}) \rightarrow b_{3u}(2p_x^*)$. This assignment seems entirely reasonable.

4. Conclusions

Our investigations showed that both axially dipyridinated iron(II) and cobalt(II) phthalocyaninato(2-) complexes are stable under normal conditions, in contrast to the dipyridinated magnesium phthalocyanine

Compound	Q		В		Ν	L	С	Reference	
FePc	676	610		340	300	242	212	[70]	
$FePc(py)_2$ in CH_2Cl_2	650	594	415	322	282	240	210	This work	
CoPc	657	600		315	280	240	210	[70]	
CoPc(py) ₂ in CH ₂ Cl ₂	670	605		344	282	238	212	This work	

(MgPc(py)₂), which is unstable and interacts with water molecule converts into 4+1 coordinated complex of (MgPcH₂O)·2py [19]. The stability of the FePc(py)₂ and CoPc(py)₂ complexes correlate well with the strength of the axial M(II)–N(py) bonds. The Co–N(py) bond is longer than the Fe–N(py) bond due to the unpaired electron localized on d_z^2 orbital of Co. Ligation of the inermediate-spin iron(II) phthalocyanine by pyridine molecules leads to the change of the ground state configuration of the central ion from S = 1 (FePc, e_g^3 $b_{2g}^2 a_{1g}^1$) to S = 0 (FePc(py)₂, $e_g^4 b_{2g}^2$), while in the cobalt phthalocyanine the ligation not change the ground state configuration of the central Co ion ($e_g^4 b_{2g}^2 a_{1g}^1$, S = 1/2). This is fully consistent with the EPR and magnetic susceptibility measurements.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 176533 and 176534 for CoPc(py)₂ and FePc(py)₂, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This research was supported by a grant (No 3 T09A 180 19) from the Polish State Committee for Scientific Research.

References

- (a) C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, vol. 1, VCH Publishers, New York, 1988;
 (b) C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, vol. 2, VCH Publishers, New York, 1993;
 (c) C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, vol. 3, VCH Publishers, New York, 1993;
 (d) C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, vol. 4, VCH Publishers, New York, 1996.
- [2] (a) H. Jahnke, M. Schoborn, G. Zimmerman, Top. Curr. Chem. 61 (1976) 133;
- (b) P. Gregory, J. Porphyr. Phthalocyanines 4 (2000) 432.
- [3] (a) G.G. Roberts, Sens. Actuat. 4 (1983) 131;
- (b) M.K. Debe, K.K. Kam, Thin Solid Films 186 (1990) 289.
- [4] R.O. Loufty, A.M. Hor, G. DiPaola-Baranyj, C.K. Hasio, J. Imag. Sci. 29 (1985) 116.
- [5] (a) V. Balzani, L. Moggi, M.F. Maniri, F. Bolletta, M. Gleria, Science 189 (1975) 852;
 - (b) J.R. Balton, Solar Energy 20 (1978) 181.
- [6] (a) M.M. Qualls, D.H. Thompson, Int. J. Cancer 93 (2001) 384;
 (b) L.Y. Xue, S.M. Chiu, N.L. Oleinick, Oncogene 123 (2001) 3420;

(c) T.C. Oldham, D. Phillips, J. Photochem. Photobiol. B55 (2000) 16;

- (d) W.S. Chan, J.F. Marshall, G.Y.F. Lam, I.R. Hart, Cancer Res. 48 (1988) 3040;
- (e) Q. Peng, J. Moan, J.M. Nesland, C. Remington, Int. J. Cancer 61 (1990) 719;
- (f) R.W. Boyle, B. Paquette, J.S. van Lier, Br. J. Cancer 65 (1992) 813;
- (g) C.S. Loh, J. Bedwell, A.J. MacRobert, H. Krasner, D. Phillips, S.G. Brown, Br. J. Cancer 66 (1993) 452.
- [7] (a) J. Janczak, R. Kubiak, A. Jezierski, Inorg. Chem. 38 (1999) 2043;
 - (b) J. Janczak, R. Kubiak, F. Hahn, Inorg. Chim. Acta 281 (1998) 195;
 - (c) J. Janczak, R. Kubiak, Polyhedron 18 (1999) 1621;
 - (d) J. Janczak, R. Kubiak, I. Svoboda, A. Jezierski, H. Fuess, Inorg. Chim. Acta 304 (2000) 150;
 - (e) J. Janczak, Y.M. Idemori, Inorg. Chim. Acta 325 (2001) 85; (f) T.J. Marks, Science 227 (1985) 881.
- [8] (a) J.M. Robertson, J. Chem. Soc. (1936) 1195;
- (b) S. Matsumoto, K. Matsuhama, J. Mizuguchi, Acta Crystallogr., C 55 (1999) 131.
- [9] J. Janczak, Pol. J .Chem. 74 (2000) 157.
- [10] J. Janczak, R. Kubiak, Polyhedron 20 (2001) 2901.
- [11] R. Kubiak, J. Janczak, K. Ejsmont, Chem. Phys. Lett. 245 (1995) 249.
- [12] A.B.P. Lever, Adv. Inorg. Chem. Radiochem. 7 (1965) 27.
- [13] L.H. Vogt, A. Zalkin, D.H. Tempelton, Science 151 (1966) 569.
- [14] L.H. Vogt, A. Zalkin, D.H. Tempelton, Inorg. Chem. 6 (1967) 1725.
- [15] T. Kobayashi, F. Kurokoawa, T. Ashida, N. Uyeda, E. Suito, J. Chem. Soc., Chem. Commun. (1971) 1631.
- [16] F. Cariati, F. Morazzoni, M. Zocchi, J. Chem. Soc., Dalton Trans. (1978) 1018.
- [17] J.M. Assour, J. Am. Chem. Soc. 87 (1965) 4701.
- [18] F. Cariati, D. Galizzoli, F. Morazzoni, J. Chem. Soc., Dalton (1975) 556.
- [19] J. Janczak, R. Kubiak, Polyhedron, 21 (2002) 265.
- [20] M.S. Fischer, D.H. Templeton, A. Zalkin, M. Calvin, J. Am. Chem. Soc. 93 (1971) 2622.
- [21] T. Kobayshi, N. Uyeda, E. Suito, J. Phys. Chem. 72 (1968) 2446.
- [22] T. Kobaysahi, T. Ashida, N. Uyeda, E. Suito, M. Kakudo, Bull. Chem. Soc. Jpn. 44 (1971) 2095.
- [23] KUMA Diffraction, KM-4 CCD program package, Ver. 163, Wroclaw, Poland, 1999.
- [24] G.M. Sheldrick, SHELXTL Program, Siemens Analytical X-ray Instruments Inc, Madison, WI, 1990.
- [25] G.M. Sheldrick, SHELXL-97. Program for the Solution and Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.
- [26] J. Janczak, R. Kubiak, A. Jezierski, Inorg. Chem. 34 (1995) 3505.
- [27] J. Bonnett, M.B. Hursthouse, K.M.A. Malik, B. Mateen, J. Chem. Soc., Perkin Trans. 2 (1977) 2072.
- [28] V. McKee, C.C. Ong, G.A. Rodley, Inorg. Chem. 23 (1984) 4242.
- [29] V. McKee, G.A. Rodle y, Inorg. Chim. Acta 151 (1988) 233.
- [30] M.P. Byrn, C.J. Curtis, Y. Hsiou, S.I. Kahn, S.H. Tendick, A. Terzis, C.E. Stouse, J. Am. Chem. Soc. 115 (1993) 9480.
- [31] W.R. Scheidt, J. Am. Chem. Soc. 96 (1974) 84.
- [32] R.G. Little, J.A. Ibers, J. Am. Chem. Soc. 96 (1974) 4440.
- [33] R. Mason, G.A. Williams, P.E. Fielding, J. Chem. Soc., Dalton Trans. (1979) 676.
- [34] B.N. Figgis, E.S. Kucharski, P.A. Reynolds, J. Am. Chem. Soc. 111 (1989) 1683.
- [35] J.F. Kirner, W. Dow, W.R. Scheidt, Inorg. Chem. 15 (1976) 1685.
- [36] C.J. Brown, J. Chem. Soc. A (1968) 2488.
- [37] D.C. Grenoble, H.G. Drickamer, J. Chem. Phys. 55 (1971) 1624.

- [38] P.S. Braterman, R.C. Davies, R.J.P. Williams, Adv. Chem. Phys. 7 (1964) 359.
- [39] M.H. Whangbo, K.R. Stewart, Isr. J. Chem. 23 (1983) 133.
- [40] (a) P. Coppens, L. Liand, N.J. Zhu, J. Am. Chem. Soc. 105 (1983) 6173;

(b) A. Holladay, P. Leung, P. Coppens, Acta Crystallogr., A 39 (1983) 377;

(c) C. Lecomte, R.H. Blessing, P. Coppens, J. Am. Chem. Soc. 108 (1986) 6942;

- (d) P. Coppens, L. Li, J. Chem. Phys. 81 (1984) 1983;
- (e) K. Tanaka, E. Elkaim, L. Li, N.J. Zhu, J. Chem. Phys. 84 (1986) 6969;

(f) N. Li, Z. Su, P. Coppens, J. Landrum, J. Am. Chem. Soc. 112 (1990) 7294.

- [41] L. Pauling, The Nature of the Chemical Bonds, Cornell University Press, Ithaca, NY, 1960.
- [42] H.F. Shurvell, L. Pinzuti, Can. J. Chem. 44 (1966) 125.
- [43] T. Kobayashi, Spectrochim. Acta, Part A 26 (1970) 1313.
- [44] C. Clarise, M.T. Riou, Inorg. Chim. Acta 130 (1987) 139.
- [45] B. Hutchinson, B. Specncer, R. Thompson, P. Neill, Spectrochim. Acta, Part A 43 (1987) 631.
- [46] H. Ogoshi, E. Watanabe, Z. Yosida, J. Kincald, K. Nakamoto, J. Am. Chem. Soc. 95 (1973) 2845.
- [47] H. Ogoshi, Y. Saito, K. Nakamoto, J. Chem. Phys. 57 (1972) 4194.
- [48] H. Burger, R. Burczyd, J.A. Fuhrhop, Tetrahedron 27 (1971) 3257.
- [49] J. Kincaid, K. Nakamoto, J. Inorg. Nucl. Chem. 37 (1975) 85.
- [50] T. Yoshimura, T. Ozaki, Y. Shintani, H. Watanabe, J. Inorg. Nucl. Chem. 38 (1976) 1879.
- [51] C.A. Melenders, V.A. Maroni, J. Raman Spectrosc. 15 (1984) 323.
- [52] B.J. Palys, D.M. Ham, W. Briels, D. Feil, J. Raman Spectrosc. 26 (1995) 63.
- [53] H. Ding, S. Wang, S. Xi, J. Mol. Struct. 475 (1999) 175.
- [54] F. Morazzoni, F. Cariati, G. Micera, Spectrochim. Acta, Part A 36 (1980) 867.
- [55] A.B.P. Lever, J. Chem. Soc. (London) (1965) 1821.
- [56] R.L. Martin, S. Mitra, Chem. Phys. Lett. 3 (1969) 183.
- [57] B.N. Figgis, R.S. Nyholm, J. Chem. Soc. (1959) 338.
- [58] R. Havemann, W. Haberditzl, K.H. Mader, Z. Phys. Chem. 218 (1961) 71.
- [59] J.M. Assour, W.K. Kahn, J. Am. Chem. Soc. 87 (1965) 207.
- [60] B.W. Dale, R.J.P. Williams, R.P. Edwards, C.E. Johnson, J. Chem. Phys. 49 (1965) 3445.
- [61] B.W. Dale, R.J.P. Williams, T.L. Throp, J. Chem. Phys. 49 (1965) 3441.
- [62] B.W. Dale, Mol. Phys. 28 (1974) 503.

- [63] T. Kobayashi, F. Kurokawa, N. Uyeda, E. Suito, Spectrochim. Acta, Part A 26 (1970) 1305.
- [64] N.S. Gill, R.H. Nuttall, D.E. Scaife, D.W.A. Sharp, J. Inorg. Nucl. Chem. 18 (1961) 79.
- [65] C.G. Barraclough, R.L. Martin, S. Mitra, R.C. Sherwood, J. Chem. Phys. 53 (1970) 1643.
- [66] A. Hudson, H.J. Whitefield, Inorg. Chem. 6 (1967) 1120.
- [67] T.H. Moss, A.B. Robinson, Inorg. Chem. 7 (1968) 1692.
- [68] B.W. Dale, R.J.P. Williams, R.P. Edwards, C.E. Johnson, Trans. Faraday Soc. 64 (1968) 620.
- [69] (a) M. Gouterman, G.H. Wagiere, L.C. Snycer, J. Mol. Spectrosc. 11 (1963) 108;
 - (b) S.C. Mathur, J. Chem. Phys. 45 (1968) 3470;
 - (c) M. Zerner, M. Gouterman, Theor. Chim. Acta 4 (1966) 44;
 (d) A.M. Schaffer, M. Gouterman, Theor. Chim. Acta 25 (1973) 62;
 - (e) A.M. Schaffer, M. Gouterman, E.R. Davidson, Theor. Chim. Acta 30 (1973) 9;
 - (f) M. Zerner, M. Gouterman, H. Kobayashi, Theor. Chim. Acta 6 (1966) 44.
- [70] L. Edwards, M. Gouterman, J. Mol. Spectrosc. 33 (1970) 292.
- [71] (a) T. Nozawa, N. Kobayashi, H. Hatamo, M. Ueda, M. Sogami, Biochim. Biophys. Acta 626 (1980) 282;
 (b) T. Nykong, Z. Gasyna, M.J. Stillman, Inorg. Chem. 26 (1987) 1087;
 (c) T.C. VanCott, J.L. Rose, G.M. Meisener, B.E. Willamson, A.E. Schrimp, M.E. Boyle, P.N. Schatz, J. Phys. Chem. 93 (1989) 2999.
- [72] (a) L.K. Lee, N.H. Sabelli, P.R. Lebreton, J. Phys. Chem. 86 (1982) 3926;
 (b) A. Haprilson, B. Bass, P. Sunden, Theor. Chim. Acta 27

(b) A. Henrikson, B. Roos, R. Sundon, Theor. Chim. Acta 27 (1972) 303;

(c) H. Shiari, H. Tsuiki, E. Masuda, T. Koyama, K. Hanabusa, N. Kobayashi, J. Phys. Chem. 95 (1991) 417.

- [73] (a) J. Janczak, Pol. J. Chem. 72 (1998) 1871;
 - (b) P. Turek, J.J. Andre, J. Giraudeau, J. Simon, Chem. Phys. Lett. 134 (1987) 471;
 (c) H. Homborg, W. Kaltz, Z. Naturforsch., Teil. B 33 (1978) 1067:
 - (d) E. Ort, J.E. Bredas, C. Clarisse, J. Chem. Phys. 92 (1990) 1228;
 (e) H. Sugimoto, T. Higashi, M. Mori, J. Chem. Soc., Chem. Commun. (1983) 622;

(f) H. Sugimoto, T. Higashi, M. Mori, Chem. Lett. (1983) 1167.

- [74] A.B.P. Lever, S.R. Pickens, P.C. Minor, S. Licoccia, B.S. Ramaswamy, K. Mangell, J. Am. Chem. Soc. 103 (1981) 6800.
- [75] T. Kobayashi, Y. Yanagawa, Bull. Chem. Soc. Jpn. 45 (1972) 450.