Available online at www.sciencedirect.com
ScienceDirect
Polyhedron 26 (2007) 4179–4186
POLYHEDRON
www.elsevier.com/locate/poly

Comparative study of beryllium, magnesium and zinc phthalocyanine complexes with 4-picoline

R. Kubiak, J. Janczak *, M. Śledź, E. Bukowska

Institute for Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2 str., P.O. Box 1410, 50-450 Wrocław, Poland

Received 11 April 2007; accepted 9 May 2007
Available online 24 May 2007

Abstract

Three new Be(II), Mg(II) and Zn(II) phthalocyaninato(2-) complexes with 4-picoline (4-Mepy) in the crystalline form have been obtained by recrystallization of the respective M(II)Pc in 4-picoline under water-free conditions. BePc and ZnPc in 4-picoline solution form 4 + 1 coordinated complexes, while the 4-Mepy molecules biaxially ligate MgPc. The planar phthalocyaninato(2-) macroring of BePc and ZnPc upon mono-axial ligation by the 4-Mepy molecule adopts the saucer-shape form. The interaction of the central M(II) with the ligated 4-Mepy molecule leads to a deviation of the metal from the centre cavity by ~0.31 Å and ~0.35 Å in the Be and Zn phthalocyaninato complexes, respectively. In MgPc, the Pc ring upon biaxial ligation retains a planar configuration. The axial M(II)–N(4-Mepy) bond is longer than the four equatorial M(II)–N_{iso} bonds in Mg and Zn phthalocyaninato complexes, while in the Be complex the opposite relation between the axial and equatorial Be–N bonds is observed. Thermogravimetric analysis for all these compounds exhibits only one slope down, due to the loss of 4-Mepy molecules from the complexes, which transform finally into the respective M(II)Pc complexes in the β-form.

Keywords: Phthalocyanine; Beryllium; Magnesium; Zinc; 4-Picoline; Crystal structure

1. Introduction

Beryllium, magnesium and zinc phthalocyaninato(2-) complexes belong to the monometallophthalocyanines family pigments, crystallizing in the β-MPc form, known since the early papers of Linstead and Robertson [1,2]. However, the details of their crystal structures, especially the BePc and MgPc, were reported relatively recently [3,4] in relation to ZnPc and other M(II) phthalocyanines [5]. The common feature of these three metals (M) is the +2 oxidation state and the changing of it in any chemical reaction is improbable, since they are not redox active. This corresponds to the respective closed-shell electronic configuration ([He], [Ne] and [Ar] $3d^{10}$) of the Be^{2+}, Mg^{2+} and Zn^{2+} ions. On the other hand, these M(II) ions show relatively big differences in their ionic radii [6,7]. In this sense beryllium, magnesium and zinc differ distinctly from manganese, iron, cobalt, nickel and copper, whose M(II)Pc's form another homologue of the β-family. Besides, among the metallophthalocyanines, which are usually thermally and chemically very stable, the BePc and MgPc are exclusive and possess high affinity to water and they are air unstable due to formation of aqua phthalocyaninato complexes [8,9] or complexes with O_2 or/and N_2 [10].

In contrast to BePc and MgPc, ZnPc is stable and may be stored even for years in ambient laboratory air without marked optically observed or XRD registered changes. However, it was shown just for a ZnPc sample stored in the ambient atmosphere that the photo current measured was over 40-thy times lower than in the sample degassed in a high vacuum [11]. In our laboratory, we are especially interested on the crystalline phases formed as a result of the recrystallization of M(II)Pc in N or O donor solvents [12–15]. The N-organic bases are well known as readily ligating ligands suitable as solvents for MPc's [16,17].

---

* Corresponding author. Tel.: +48 71 343 5021; fax: +48 71 344 1029. *E-mail address:* J.Janczak@int.pan.wroc.pl (J. Janczak).

0277-5387/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2007.05.018

In particular, it was shown that 4-picoline (4-Mepy) formed isostructural complexes with iron and cobalt phthalocyanines, in which the central M is biaxially ligated by 4-Mepy, and the compounds crystallized with the composition $[MPc(4\text{-}Mepy)_2] \cdot 2(4\text{-}Mepy)$ [18]. For these reasons, we expected that the beryllium, magnesium and zinc phthalocyanines, when recrystallized in 4-Mepy, will show significant individuality in features of the eventually formed crystalline complexes, in particular for the coordination geometry of the central metal. Additionally, all of the new metallophthalocyanine complexes are potentially interesting colorants and materials for modern industry [19].

2. Experimental

2.1. Synthesis

Firstly, it should be stressed here that an attempt was made to perform the reactions of BePc as well as MgPc and ZnPc with 4-Mepy in water-free conditions.

The BePc sample used in the synthesis was obtained as described elsewhere [3]. The magnesium phthalocyanine (90% dye content) and zinc phthalocyanine (97% dye content) as well as 4-picoline (bp 145 °C) were purchased from Sigma–Aldrich Co. Before use, the magnesium and zinc phthalocyanines were zone refined. The transformative recrystallization processes of the BePc, MgPc and ZnPc samples with 4-picoline were performed as follows. A sample of one of the selected M(II)Pc's was pressed into a pellet, about 0.5 g in mass. The pellet was inserted in a glass ampoule and covered with c.a. 8 mL 4-picoline. The sample was then degassed and sealed off. Next, the suspension was thermally processed over the several days to ensure the completeness of the transformative process as well as effective crystallization. Next the crystalline product was immediately filtered after opening the ampoule. The best single crystals of the respective compounds, [BePc(4-Mepy)]-(4-Mepy) – (**I**), $MgPc(4\text{-}Mepy)_2$ – (**II**) and ZnPc(4-Mepy) – (**III**), were obtained by prolonged heating of the suspension of the beryllium phthalocyanine at 80 °C, the magnesium phthalocyanine at 120 °C and the zinc phthalocyanine at 160 °C. Routinely the crystalline products (**I**, **II** and **III**) were checked by X-ray powder diffraction and energy dispersive spectroscopy for their uniformity and composition. Elemental *Anal.* Calc. for $C_{44}H_{30}N_{10}Be$ (**I**): Be, 1.27; C, 74.67; N, 19.79, H, 4.27. Found: Be, 1.25; C, 74.72; N, 19.73; H, 4.30%. Elemental *Anal.* Calc. for $C_{44}H_{30}N_{10}Mg$ (**II**): Mg, 3.36; C, 73.09; N, 19.37; H, 4.18. Found: Mg, 3.30; C, 73.27; N, 19.29; H, 4.09%. Elemental *Anal.* Calc. for $C_{38}H_{23}N_9Zn$ (**III**): Zn, 9.74; C, 68.02; N, 18.79; H, 3.46. Found: Zn, 9.60; C, 68.12; N, 18.87; H, 3.40%.

2.2. X-ray single crystal diffraction

Single crystals of **I**, **II** and **III** were used for data collection on a four-circle KUMA KM4 diffractometer equipped with a two dimensional CCD area detector. Graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) and the ω-scan technique ($\Delta\omega = 1°$) were used for data collection. Data collection and reduction along with absorption correction were performed using the CRYSALIS software package [20].

The structures were solved by direct methods using SHELXS-97, revealing positions of almost all the non-hydrogen atoms. The remaining atoms were located from subsequent difference Fourier syntheses. The structures were refined using SHELXL-97 [21] with anisotropic thermal displacement parameters. Hydrogen atoms were located from the difference Fourier maps, but in the final refinement the positions of all hydrogen atoms were constrained. Details of the data collection parameters, crystallographic data and final agreement parameters are collected in Table 1. Selected geometrical parameters are listed in Table 2.

2.3. Thermal measurements

The thermogravimetric measurements (TG) and differential thermal analyses (DTA) were carried out on a Linseis L-81 thermobalance with Pt crucibles. The initial sample masses were about 15 mg. Powder Al_2O_3 was used as a reference. The measurements of the sample were performed under static air and recorded at the heating rate of 5 °C min^{-1}. Upper temperature limits were introduced to prevent eventual contamination of the apparatus, as indicated by our previous experiences. The observed weight loss is ~26.5%, 25.5% and 13.9% for compounds **I**, **II** and **III**, respectively. The respective values calculated for these compounds are 26.30%, 25.74% and 13.87%.

2.4. X-ray powder diffraction measurement

The rest of the sample left after thermogravimetric analyses was measured on a STOE powder diffractometer equipped with a linear PSD detector [22] using Cu Kα1 radiation ($\lambda = 1.54060$ Å) at room temperature.

3. Results and discussion

3.1. Synthesis: equilibrium in solution

The procedure described in Section 2.1 gave for each complex (**I**, **II** and **III**) well developed crystals suitable for X-ray analysis, showing the typical red-violet colour for the phthalocyanines. However, we want here to add some observation registered during the thermal processing of the ampoule with the beryllium phthalocyanine in 4-picoline suspension. Namely, it occurs that by heating the ampoule resting in the oven, the liquid seen over the sedimented solid species is practically non-transparent, as could be expected, but it was so only till up ca. 100 °C. With further temperature increase, being however still

Table 1
Crystallographic data for **I**, **II** and **III**

Formula	$C_{44}H_{30}N_{10}Be$	$C_{44}H_{30}N_{10}Mg$	$C_{38}H_{23}N_9Zn$
Molecular weight	707.79	723.09	671.02
Temperature (K)	295(2)	295(2)	295(2)
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a (Å)	12.387(2)	11.736(2)	9.626(2)
b (Å)	14.205(3)	18.249(3)	13.167(2)
c (Å)	23.347(4)	8.693(2)	13.966(3)
α (°)	106.64(2)		105.67(1)
β (°)	96.79(2)	105.04(2)	105.87(1)
γ (°)	102.94(2)		109.64(1)
V (Å^3)	3762.2(13)	1798.0(6)	1470.0(5)
Z	4	2	2
D_{obs} (Mg m^{-3})	1.25	1.33	1.51
D_{calc} (Mg m^{-3})	1.250	1.336	1.516
μ (mm^{-1})	0.077	0.099	0.883
Crystal size (mm^3)	$0.24 \times 0.22 \times 0.18$	$0.22 \times 0.15 \times 0.11$	$0.28 \times 0.22 \times 0.21$
Total/unique/observed reflections [R_{int}]	32671/14758/7432 [0.0872]	9223/4096/2788 [0.0385]	15939/6979/5817 [0.0190]
$R[F^2 > 2\sigma(F^2)]$[a]	0.0785	0.0657	0.0311
$wR[F^2$ all reflections][b]	0.1294	0.1459	0.0804
S	1.001	1.012	1.001
Residual electron density, $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	+0.282, −0.200	+0.214, −0.372	+0.302, −0.467

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

[b] $wR = \{\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2$ where $P = (F_o^2 + 2F_c^2)/3$. The a parameter is 0.015 for **I**, 0.064 for **II**, 0.0488 for **III**.

Table 2
Selected bond lengths (Å) and angles (°)

BePc(4-Mepy) · 4-Mepy (**I**)	
Be1–N1a	1.878(5)
Be1–N3a	1.899(5)
Be1–N5a	1.935(5)
Be1–N7a	1.943(5)
Be1–N9a	1.839(4)
N1a–Be1–N3a	89.8(2)
N3a–Be1–N5a	89.4(2)
N5a–Be1–N7a	89.1(2)
N7a–Be1–N1a	89.0(2)
N1a–Be1–N9a	99.8(2)
N3a–Be1–N9a	100.1(2)
N5a–Be1–N9a	98.5(2)
N7a–Be1–N9a	97.9(2)
Be2–N1b	1.839(4)
Be2–N3b	1.891(5)
Be2–N5b	1.915(5)
Be2–N7b	1.925(5)
Be2–N9b	1.830(4)
N1b–Be1–N3b	89.4(2)
N3b–Be1–N5b	88.1(2)
N5b–Be1–N7b	87.9(2)
N7b–Be1–N1b	88.2(2)
N1b–Be1–N9b	98.5(2)
N3b–Be1–N9b	100.2(2)
N5b–Be1–N9b	100.7(2)
N7b–Be1–N9b	99.1(2)
MgPc(4-Mepy)$_2$ (**II**)	
Mg–N1	2.009(2)
Mg–N3	2.005(2)
Mg–N5	2.412(2)
N1–Mg–N3	89.57(8)
N1–Mg–N5	90.07(8)
N1–Mg–N3^i	90.43(8)
Symmetry code: (i) $1 - x, -y, 1 - z$	
ZnPc(4-Mepy) (**III**)	
Zn–N1	2.020(2)
Zn–N3	2.021(2)
Zn–N5	2.006(2)
Zn–N7	2.034(2)
Zn–N9	2.166(2)
N1–Zn–N3	89.32(6)
N1–Zn–N7	87.13(5)
N3–Zn–N5	87.32(5)
N5–Zn–N7	89.28(5)
N1–Zn–N9	100.02(5)
N3–Zn–N9	106.84(6)
N5–Zn–N9	99.84(5)
N7–Zn–N9	93.259(6)

below the boiling point of the 4-picoline, it becomes markedly brilliant and eye transparent. This phenomenon is fully reversible if subsequently the temperature is lowered, and is undoubtedly connected with the releasing and, respectively, binding of the 4-picoline molecules by beryllium ions of the BePc molecules. The observed strong light absorption changes are evidently correlated with the appropriate TG plot as shown in Fig. 1. The crystals of all compounds have been obtained in water-free conditions, since, especially for Be and Mg complexes, the crystals in the 4-Mepy solution under conditions of moist atmosphere transform into a polycrystalline form after several days. During this process the crystals of BePc-(4-Mepy) · 4-Mepy (**I**), as well as the crystals of MgPc-(4-Mepy)$_2$ (**II**), interact with water molecules and convert into aqua(phthalocyaninato) complexes according to the equation illustrated in Scheme 1. The speed of the conversion takes place several times quicker in a solution of non-purified 4-Mepy.

Studies of the aqua complexes formed during the transformations of complexes **I** and **II** in the 4-Mepy/H_2O solution are still under investigation.

3.2. Thermal measurements and analysis

The thermogravimetric analyses (TG) together with the differential thermal analyses (DTA) of the solid state samples of compounds **I**, **II** and **III** are shown in Fig. 1a, b and c, respectively. For a better comparison, the most characteristic data resulting from the TG and DTA plots and XRD powder measurements of the residues left are collected in Table 3.

As can be seen from Fig. 1a, compound **I** losses the solvated as well as coordinated 4-Mepy molecules at the same

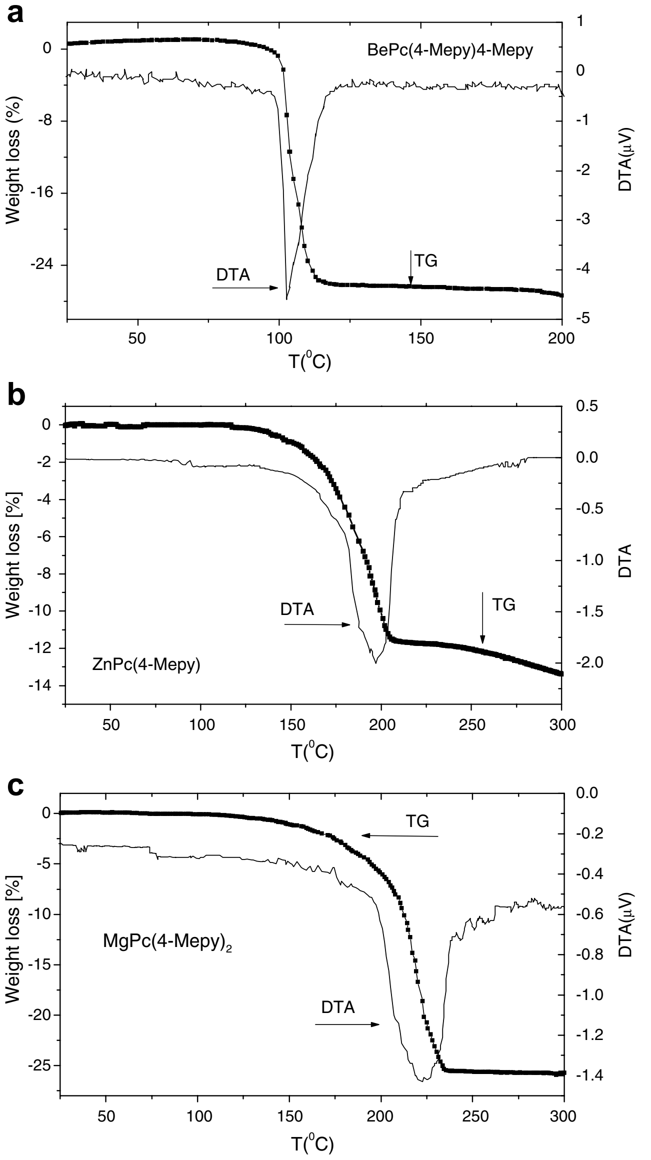


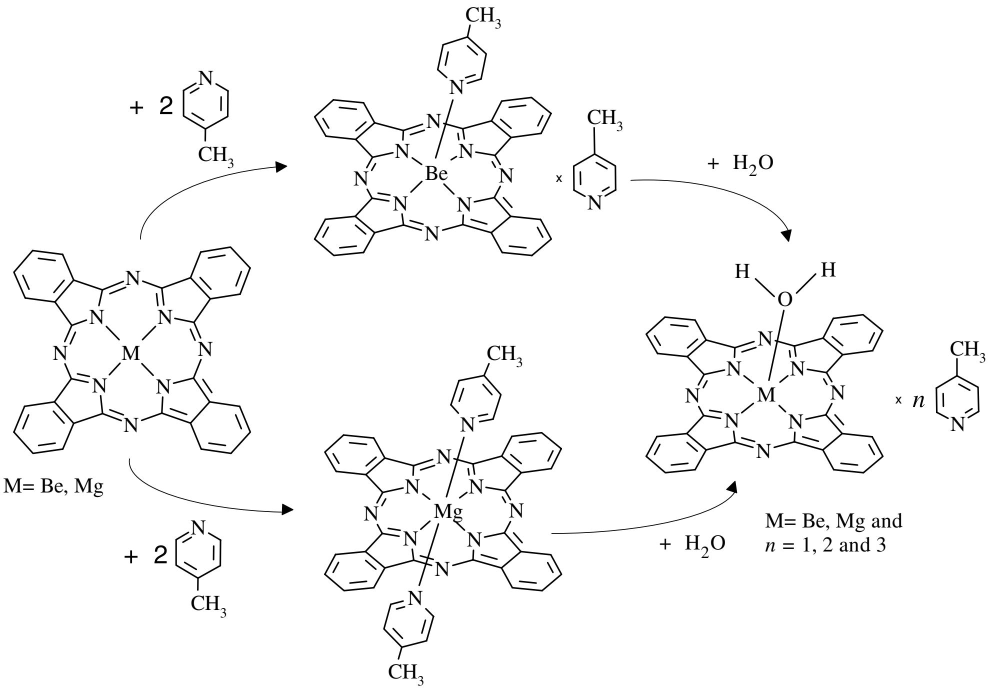
Fig. 1. Thermograms for the solid state samples of **I** (a), **II** (b) and **III** (c).

temperature (~100 °C), although in the crystal of **I** there are two crystallographically independent units (BePc-(4-Mepy) · 4-Mepy) and different 4-Mepy molecules. One of them is the 4-Mepy molecule coordinated to Be(II) of the BePc molecule and the other one is solvated. As seen in the TG analysis of **I** (the weight loss of ~26.5%), both solvated and coordinated 4-Mepy molecules are released simultaneously. This can be understood, if we take into account the arrangement of the (BePc(4-Mepy) · 4-Mepy) units and solvated 4-Mepy molecules in the crystalline network. The ligated and solvated 4-Mepy molecules are located in channels formed by the BePc molecules that are aligned almost parallel to the [100] direction in the crystal. The high thermal vibration of solvated 4-Mepy molecules at $T \sim 100$ °C accounts for the breaking of the Be–N bond of the coordinated 4-Mepy molecule in the solid sample of **I**, and as a result we have in the TG only one slope down (Fig. 1a). We suppose that in the case of compound **I**, besides the molecular arrangement, the exclusively narrow temperature range for the loss of the ligand molecules results from the extremely small radius of the beryllium ion [6,7], which in relation to the Mg and Zn ions in **II** and **III**, respectively, is over two times smaller. Therefore, as the temperature only reaches the value of the Be(N_{iso})$_4$–N(4-Mepy) bonding energy, the 4-Mepy molecule is released and the beryllium ion comes back to its equilibrium position in the BePc center, where the beryllium ion is no longer able to attract the ligand molecules. This is because it sits between the four N_{iso} atoms as in a square well, as described in [3]. In consequence, only the repulsion forces between the basal N_{iso} atoms and apical N(4-Mepy) atom become effective and at these conditions the ligand can readily be liberated.

The compounds **II** and **III** liberate the coordinated 4-Mepy molecules at significantly higher temperatures and also with wider temperature ranges. The slightly different decomposition temperature of **II** and **III**, corresponding to the release of the 4-Mepy molecules (see Fig. 1b and c), is connected not only with the strength of the axial M(II)–N bonds joining the 4-Mepy molecules, but also with the molecular arrangement. In **II**, both axial Mg–N bonds break simultaneously, releasing the 4-Mepy molecules. In all samples, the thermal process leading to the loss of 4-Mepy molecules and conversion of the remaining samples into the respective M(II)Pc's in the β-form was verified by powder X-ray diffraction. For these three compounds, the process of releasing of 4-Mepy molecules is endothermic.

3.3. Stereochemistry and crystal structures

All three structures are built up of independent moieties of **I**, **II** and **III** arranged in a different fashion. The crystalline network of the beryllium compound (**I**) consists of BePc and 4-Mepy molecular units in the proportion 1:2. One of the two 4-Mepy molecules is axially coordinated to Be of the BePc unit and the another one is a solvated molecule. Thus the Be(II) ion has a 4 + 1 coordination. In the crystal, there are two independent BePc-(4-Mepy) · 4-Mepy units (Fig. 2a). However, in the two independent units we have not observed any geometrical differences greater than 3 e.s.d's, but they show a different orientation of the ligated 4-Mepy in relation to BePc. Additionally, the geometries of the ligated and solvated 4-Mepy molecules are also very similar. The BePc(4-Mepy) molecule is not planar. The planar BePc molecule adopts a saucer-shape form due to the axial ligation by 4-Mepy. Interaction between the N atom of 4-Mepy, with a lone-pair of electrons, and the positively charged Be(II) ion of the BePc molecule leads to the deviation of Be by 0.302(3) and 0.320(3) Å from the plane defined by the four *N*-isoindole atoms of Pc in both crystallographically independent BePc(4-Mepy) units. The orientation of the 4-Mepy molecule in one of the two crystallographically independent BePc(4-Mepy) molecules is stabilized by a



Scheme 1.

Table 3
Comparison of the TG, DTA and XRD data for the complexes **I**, **II** and **III**

Compound	TG, 4-Mepy loss	DTA, 4-Mepy releasing guide	XRD identified residue
I	at 100 °C, sharp steep	endothermal	β-form
II	at 180–220 °C range, gradual diffused	endothermal	β-form
III	at 190 °C, diffused	endothermal	β-form

C–H···N(azamethine) interaction between the H atom in the ortho- position of 4-Mepy and the azamethine N atoms of the Pc ring (the N1a–Be1–N9a–C37a torsion angle is equal to −46.8°). In the second independent BePc(4-Mepy) molecule, the interaction in the crystalline network with the neighbouring molecule makes the respective torsion angle (N1b–Be2–N9b–C37b) equal to −29.3°. Two pairs of symmetrically equivalent BePc(4-Mepy) molecules related by an inversion center are π–π stacked in a back-to-back fashion as dimers with an interplanar distance of $\sim$3.4 Å (see Fig. 3), indicating the interaction between the π-clouds of the phthalocyaninato(2-) macrorings, since the distance is comparable to the typical distance between aromatic rings in systems with such an interaction [23]. This mutual arrangement of BePc(4-Mepy) molecules forms channels in which the solvated 4-Mepy molecules are located. The solvated 4-Mepy molecules possess relatively higher thermal ellipsoids in comparison with the BePc(4-Mepy) molecules, since they are taking more than the necessary space in the structure at room temperature. The voids in the solvent region have been found by the SQUEEZE procedure of the PLATON software package [24,25], but no significant residual electron density was observed. So, the thermal displacement of solvated 4-Mepy is considered as the effect of the high temperature crystallization process of compound **I** (at $\sim$80 °C), in which these molecules possess quite high kinetic energy. Therefore, they require more space in the crystal structure, in comparison with the room temperature at which the X-ray measurement was performed.

The crystalline network of the magnesium compound (**II**) consists of MgPc and 4-Mepy molecular units, similar to **I**, in the proportion 1:2. However, in the magnesium compound two 4-Mepy units are biaxially coordinated to the central Mg(II) atom of the MgPc molecule (Fig. 2b). The central Mg(II) cation, lying on the inversion center and in the plane defined by the four isoindole nitrogen atoms of the Pc macroring, coordinates all four nitrogen atoms of the Pc macroring and two nitrogen atoms of the 4-Mepy molecules in a distorted tetragonal bi-pyramid (4 + 2 coordination). The axial Mg–N bonds are longer by $\sim$0.4 Å than the four equatorial Mg–N$_{\mathrm{iso}}$ bonds (see Table 2). The axial M–N(4-Mepy) bonds are slightly weaker (2.412(2) Å) than the corresponding axial Mg–N(py) bonds (2.376(2) Å) in the biaxially ligated complex of MgPc(py)$_2$ [26]. The phthalocyaninato macroring in the MgPc-(4-Mepy)$_2$ molecule is almost planar. The 4-Mepy molecules, ligated on both sides of the MgPc molecular plane, are not perpendicular to it. The dihedral angle between the N$_4$–isoindole plane and the 4-Mepy molecular plane is equal to 83.2(2)° and the torsion N1–Mg–N5–C21 describing the orientation of the coordinated 4-Mepy molecule in relation to the Pc ring is equal to −19.1(2)°. This inclination is similar to that in CoPc(4-Mepy)$_2$ and is slightly greater than that in FePc(4-Mepy)$_2$ [18]. This incli-

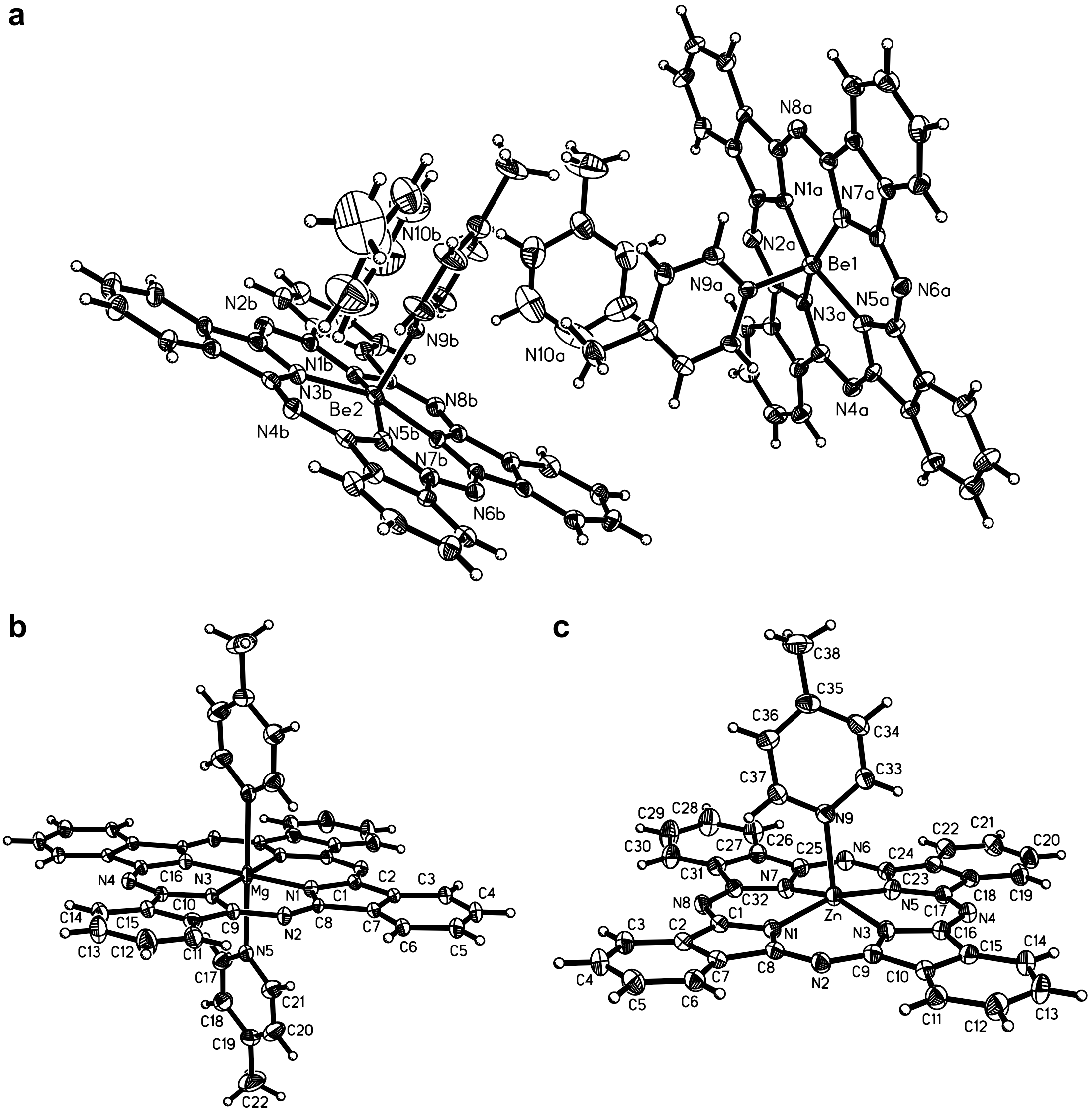


Fig. 2. Molecular structure of independent parts of **I** (a), **II** (b) and **III** (c).

nation correlates well with the molecular arrangement in the crystal, where one MgPc(4-Mepy)$_2$ molecule is oriented by the coordinated 4-Mepy molecules close to the phenyl ring of the Pc ring of a neighbouring MgPc(4-Mepy)$_2$ molecule, forcing the non-perpendicular coordination. Additionally, this interaction causes the rotation of the ligated 4-Mepy molecules in relation to the Pc ring from 45°, for the most stable conformation, to 19.1(2)° (N1–Mg–N5–C21). In the biaxially coordinated MgPc(py)$_2$ analogue [26] and in the other CoPc(py)$_2$, FePc(py)$_2$ and MnPc(py)$_2$ complexes, the corresponding angles are close to 90° [27,28]. The arrangement of MgPc(4-Mepy)$_2$ molecules in the crystal is shown in Fig. 4. The MgPc(4-Mepy)$_2$ molecules are arranged in a herring-bone fashion and form alternating sheets parallel to the *ac*-plane. The MgPc planes are parallel within one sheet (and separated by ~3.26 Å), whereas they make an angle of ~72° in relation to the neighbouring sheets.

The crystal structure of **III** consists of mono-axially coordinated ZnPc(4-Mepy) molecules (Fig. 2c). The planar ZnPc molecule, upon ligation by the 4-Mepy molecule, adopts the saucer-shape form, due to the interaction of the positively charged Zn(II) central atom of ZnPc with the ring N atom of the 4-Mepy molecule. This interaction leads to a deviation of Zn(II) from the centre cavity of the Pc macroring toward the coordinated 4-Mepy molecule, making the four equatorial Zn–N$_{iso}$ bonds longer by 0.04 Å in relation to ZnPc [5]. The deviation of the Zn atom from the plane defined by the four isoindole nitrogen atoms is equal to 0.352(2) Å toward the coordinated 4-Mepy molecule, thus the Zn atom has a 4 + 1 coordination environment. The displacement of Zn(II) from the N$_4$–isoindole plane in **III** is smaller than that in ZnPc(*n*-hexylamine), ~0.48 Å [29] and ZnPcCl, ~0.59 Å [30] and is comparable to ZnPc(H$_2$O) · 2DMF, ~0.38 Å [31]. The molecular plane of the ligated 4-Mepy is not perpendicular

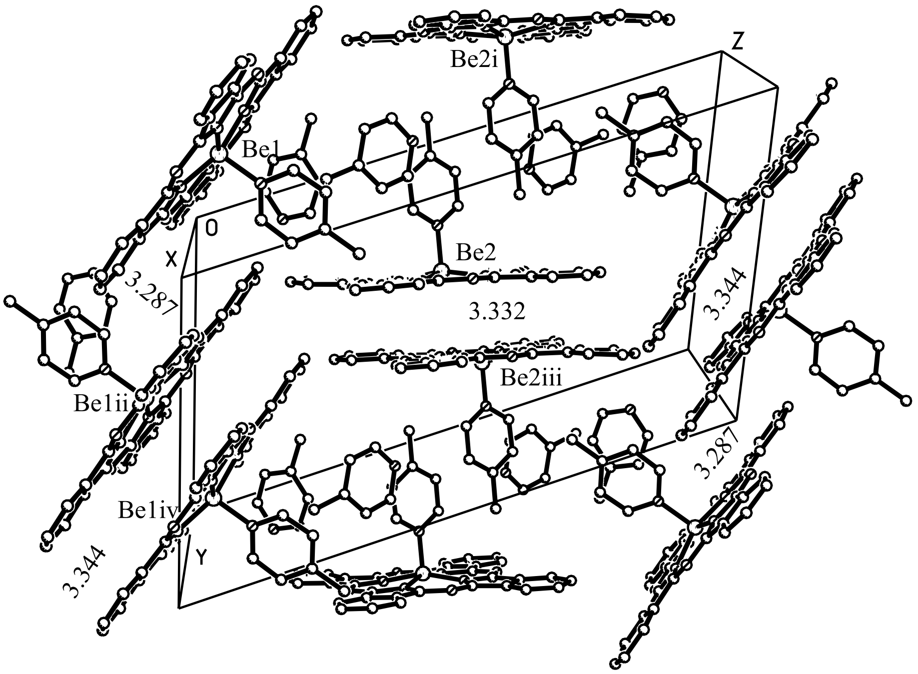


Fig. 3. View of the molecular arrangement of **I** showing the channels of the 4-Mepy solvent along the [001] direction and the π–π interacting stacked back-to-back dimers. H atoms are omitted for clarity. Symmetry code: (i) $1 - x, -y, -z$; (ii) $2 - x, -y, -z$; (iii) $1 - x, 1 - y, 1 - z$ and (iv) $x, 1 - y, z$.

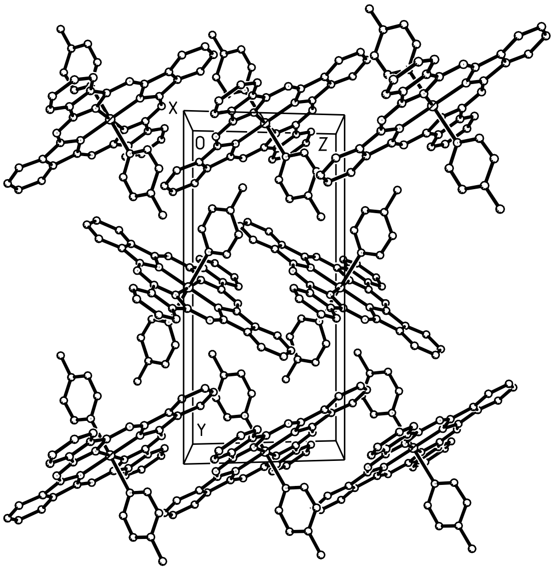


Fig. 4. Arrangement of the $MgPc(4\text{-}Mepy)_2$ molecules in the unit cell. H atoms are omitted for clarity.

to the N_4–isoindole plane of the Pc ring, but is inclined. The dihedral angle between the N_4-plane and the plane of the coordinated 4-Mepy molecule is equal to 77.8(1)°. The inclination of the 4-Mepy to ZnPc plane results from the mutual interaction of the ligated 4-Mepy with the Pc ring of a neighbouring ZnPc(4-Mepy) in the crystal. The ZnPc(4-Mepy) molecules related by an inversion center are stacked in a back-to-back fashion as dimers with an interplanar distance of ∼3.4 Å between the N_4–isoindole planes (see Fig. 5).

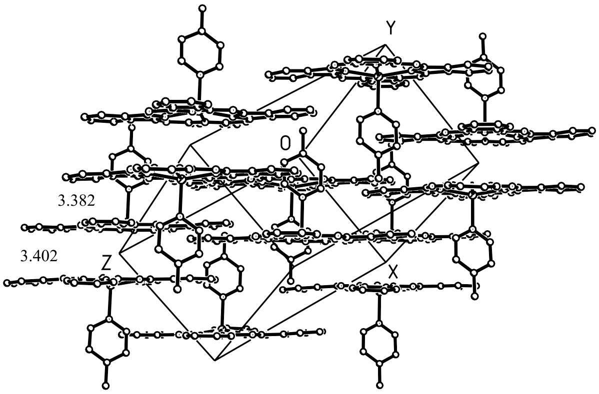


Fig. 5. Arrangement of the ZnPc(4-Mepy) molecules in the unit cell showing the π–π interacting stacked back-to-back molecules. H atoms are omitted for clarity.

In these three compounds, the chemically equivalent C–N and C–C bonds of the Pc(2-) macroring and 4-Mepy molecules are similar and very typical, and corresponding well with $MPc(4\text{-}Mepy)_2$ (M = Fe, Co) [18]. The main stereo chemical data for the metal atoms in the complexes **I**, **II** and **III** are collected in Table 4. For completeness, the data of the Fe and Co analogue compounds [18] are also included. As can be seen from the table, only in the case of the beryllium compound is the axial M–N(4-Mepy) distance smaller than the four equatorial M–N distances. It is noteworthy that also in the case of the BePc complex with an O-donor ligand such an exclusive correlation between the axial and equatorial bonds is observed [3]. It may be, however, easier understood if we recognize that for the

Table 4
Comparison of the coordination of the central M(II) atom in mono- and biaxially coordinated by 4-Mepy complexes

Compound	Average equatorial M–N distance (Å)	Axial M–N distance (Å)	Deviation of M from the N_4 plane	Coordination geometry of M
BePc(4-Mepy) · 4-Mepy	1.914(6) (Be1)	1.839(4)	0.320(3)	square pyramid
	1.892(6) (Be2)	1.830(4)	0.302(3)	
$MgPc(4\text{-}Mepy)_2$	2.007(2)	2.412(2)	0	elongated octahedral
ZnPc(4-Mepy)	2.020(2)	2.166(2)	0.352(2)	square pyramid
$FePc(4\text{-}Mepy)_2 \cdot 2(4\text{-}Mepy)$	1.935(3)	2.040(3)	0	elongated octahedral
$CoPc(4\text{-}Mepy)_2 \cdot 2(4\text{-}Mepy)$	1.930(4)	2.322(5)	0	

beryllium ion the central hole of the essentially planar and rigid Pc moiety is far too big. For comparison in the case of a compound in which the beryllium ion is, as is normal for it, tetrahedrally coordinated, the relative two Be–N(py) bonds are only 1.753 (Å) long and another two Be–N(thiocyanate) bonds completing the tetrahedra are yet shorter by 0.1 Å [32].

4. Conclusions

In the compounds studied here, the central M(II) ion of BePc and ZnPc is mono-axially ligated by the ring nitrogen atom of the 4-Mepy molecule, while in MgPc biaxial ligation has been observed. These complexes differ significantly in the axial M(II)–N(4-Mepy) bond strength and the ligand releasing temperature increases in the order Be < Zn < Mg. The BePc(4-Mepy) and $MgPc(4\text{-}Mepy)_2$ complexes transform into the aqua complexes $M(II)PcH_2O \cdot n(4\text{-}Mepy)$ in a solution of 4-Mepy/H_2O(M(II) = Be, Mg and $n = 1$, 2 and 3).

Appendix A. Supplementary material

CCDC 639016, 639017 and 639018 contain the supplementary crystallographic data for **I**, **II** and **III**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (+44) 1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.05.018.

References

[1] R.P. Linstead, J.M. Robertson, J. Chem. Soc. (1936) 1736.
[2] J.M. Robertson, J. Chem. Soc. (1936) 1135.
[3] R. Kubiak, A. Waśkowska, M. Śledź, A. Jezierski, Inorg. Chim. Acta 359 (2006) 1344.
[4] J. Janczak, R. Kubiak, Polyhedron 20 (2001) 2901.
[5] W.R. Scheidt, W. Dow, J. Am. Chem. Soc. 99 (1977) 1101.
[6] I.D. Brown, Acta Crystallogr. B 44 (1988) 545.
[7] R.D. Shannon, Acta Crystallogr. A 32 (1994) 751.
[8] J. Janczak, Y.M. Idemori, Polyhedron 22 (2003) 1167.
[9] J. Mizuguchi, Z. Kristallogr, NCS 217 (2002) 251.
[10] R. Kubiak, J. Janczak, K. Ejsmont, Chem. Phys. Lett. 245 (1995) 249.
[11] P. Day, R.J.P. Williams, J. Chem. Phys. 37 (1962) 567.
[12] R. Kubiak, A. Waśkowska, J. Mol. Struct. 649 (2003) 55.
[13] V. Kinzhybalo, J. Janczak, Acta Crystallogr. C 63 (2007) m105.
[14] J. Janczak, R. Kubiak, Polyhedron, (2007) 2997.
[15] V. Kinzhybalo, J. Janczak, J. Mol. Struct., in press, doi:10.1016/j.molstruc.2006.10.064.
[16] K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphiryn Handbook, Phthalocyanines: Properties and Materials, vol. 17, Academic Press, Elsevier, 2003.
[17] F. Cariati, F. Morazzoni, M. Zocchi, J. Chem. Soc., Dalton Trans. (1975) 556.
[18] F. Cariati, F. Morazzoni, M. Zocchi, J. Chem. Soc., Dalton Trans. (1978) 1018.
[19] K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphryn Handbook, Application of Phthalocyanines, vol. 19, Academic Press, Elsevier, 2003.
[20] CRYSALIS CCD and CRYSALIS RED Program Package. Oxford Diffraction Poland, Wrocław, Poland, 2005.
[21] G.M. Sheldrick, SHELXS-97, SHELXL-97. Programs for Crystal Structure Solution and Refinement, University of Göttingen, Göttingen, Germany, 1997.
[22] WinXPow Software Manual, STOE & CIE GmbH, Darmstadt, Germany, 2003.
[23] L. Pauling, The Nature of the Chemical Bond, third ed., Cornell University Press, Ithaca, New York, 1960.
[24] P. Sluis, A.L. Spek, Acta Crystallogr. A 46 (1990) 194.
[25] A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7.
[26] J. Janczak, R. Kubiak, Polyhedron 21 (2002) 265.
[27] J. Janczak, R. Kubiak, Inorg. Chim. Acta 342 (2003) 64.
[28] J. Janczak, R. Kubiak, M. Śledź, H. Borman, Yu. Grin, Polyhedron 22 (2003) 2685.
[29] T. Kobayashi, T. Ashida, N. Uyeda, E. Suito, M. Kakudo, Bull. Chem. Soc. Jpn. 44 (1971) 2095.
[30] M.M. Deneux, D. Benlian, M. Pierrot, A. Fournel, J.P. Sorbiel, Inorg. Chem. 24 (1985) 1878.
[31] L.Y. Cui, J. Yang, Q. Fu, B.Z. Zhao, L. Tian, H.L. Yu, J. Mol. Struct. 827 (2007) 149.
[32] H. Rohland, W. Hang, M. Noltenmeyer, A. Meller, H.G. Schmidt, Fersenius J. Anal. Chem. 361 (1998) 725.