Synthesis, Spectral Characterisation and Crystal Structure of (1,24-Bicyclophthalocyaninato)bismuth(III)

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A new orange bicyclophthalocyanine complex of bismuth(III), [Bi($C_{48}H_{24}N_{13}$)], has been synthesised by means of the template reaction of bismuth(III) acetate with phthalodinitrile. The ligand consists of the phthalocyanine skeleton, which is bridged by two additional isoindole units. The conjugation of the phthalocyanine ring is interrupted by the two bridgehead sp^3-hybridised carbon atoms. The main difference between this new bicyclophthalocyanine and those previously reported in the literature lies in the position of the bridgehead carbon atoms. In order to differentiate between these bicyclophthalocyaninato complexes, we propose a nomenclature: [Bi($C_{48}H_{24}N_{13}$)] is named Bi(1,24-Pcc), and the other bicyclic ligands already reported in the literature are named (1,16-Pcc) and (1,17-Pcc). The molecular structure of Bi(1,24-Pcc) shows the coordination polyhedron around the bismuth atom, made up of the six isoindole nitrogen atoms of the macrocycle, as a strongly distorted trigonal prism. The two Bi–N_{iso} bonds of the bridge and two of the four Bi–N_{iso} bonds of the (Pc) ring have bond lengths between 2.40 and 2.47 Å. One of the remaining bonds is longer (2.55 Å), and the sixth has a very short length of 2.20 Å. This new complex was fully characterised by UV/Vis and IR spectroscopy, also reported here.

Introduction

We recently reported the synthesis and characterisation of a new phase of the triple-decker compound, $Bi_2(Pc)_3$.[1] During the preparation of $Bi_2(Pc)_3$, if reaction mixture was heated to approximately 240 °C and allowed to cool to room temperature, we obtained many bright, orange−red crystals. This compound, **1**, was characterised by X-ray diffraction as a complex containing six units of phthalonitrile organised in three cycles per bismuth atom. The ligand consists of a phthalocyanine skeleton bridged by two additional isoindole moieties (Figure 1). The conjugation of the phthalocyanine ring is interrupted by the two bridgehead pyrrole C_α atoms, which are sp^3 hybridised. Similar phthalocyanine complex precursors were reported by Baumann et al.,[2] and by Perkins and Whelen[3] with cobalt and copper as the central metal atoms, and by Barnhart and Skiles with copper and nickel as the central metal atoms.[4] Although the molecular structure had not yet been elucidated, these authors proposed a structure similar to the one that we obtained. The complete resolution of the molecular structure of a neighbouring yellow−green complex, the bicyclophthalocyaninatochloroniobium(IV), [Nb($C_{48}H_{24}N_{13}$)Cl] (**2**) was reported for the first time by Gingl and Strähle.[5] Janczac and Kubiak obtained other green bicyclophthalocyanine complexes, $M^{III}(C_{48}H_{24}N_{13})$ **3**, with indium(III), gadolinium(III), thallium(III), and cerium(III),[6] and reported the molecular structure of the Gd,[7] In,[6] and Tl[8] complexes. All these complexes contain a ligand with the same overall formula ($C_{48}H_{24}N_{13}$), but these ligands have different structures and point symmetries. The main difference between these macrocyclic ligands lies in the bridgehead carbon atoms.

In **3**, the bridgehead atoms are the pyrrole C_α atoms (C1 and C17 in our numbering scheme, proposed in Figure 1) which belong to the two opposite isoindole rings of the phthalocyanine skeleton, and are on both sides of the metal(III). In **2**, the bridgehead atoms are the pyrrole C_α atoms (C1 and C16) that belong to the two neighbouring isoindole rings of the phthalocyanine skeleton. In **1**, the bridgehead atoms are the pyrrole C_α atoms (C1 and C24) belonging to the two opposite isoindole rings as is the case in **3**, but they are on the same side of the bismuth atom. Thus this bicyclophthalocyanine ligand has an original structure.

Results and Discussion

Proposal for Nomenclature

In the literature, the names of these bicyclophthalocyanines are confusing. The empirical formula of the ligand ($C_{48}H_{24}N_{13}$) does not indicate either the nature of the ligand related to phthalocyanine or the different positions of the bridgehead carbons. The substitutive nomenclature of IUPAC is not easy to use. For example, compound **3** in which the trivalent metal is substituted by three hydrogen atoms, is named 29*H*,31*H*,35*H*-19,5-(nitrilo[1,3]isoindolediylidenenitrilo[1]isoindolyl[3]ylidenenitrilo)phthalocyan-

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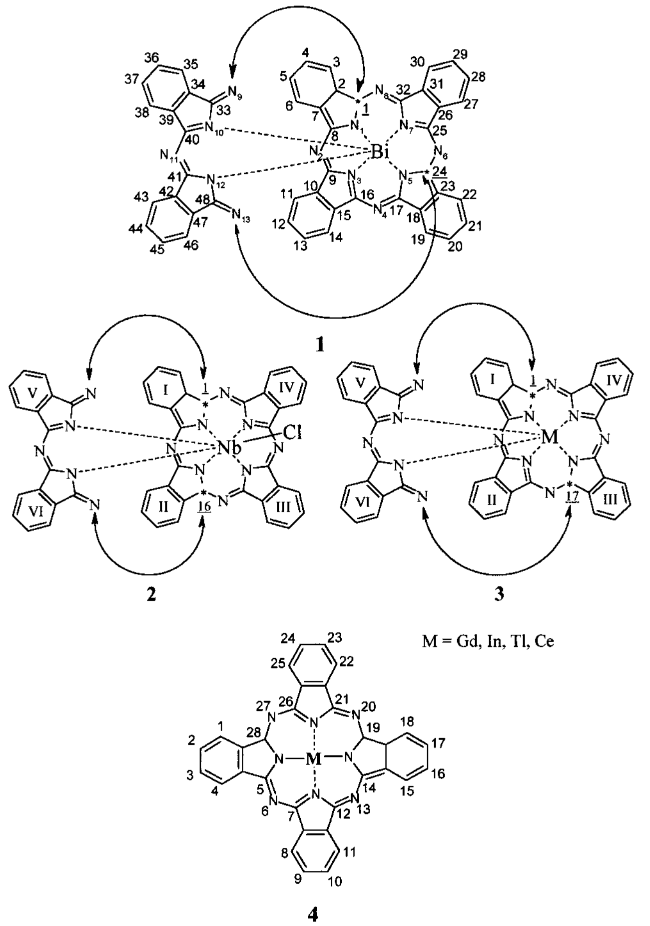


Figure 1. Structure of **1**, Bi(1,24-Pcc), compared to bicyclophthalocyanine complexes **2**, NbCl (1,16-Pcc), and **3**, M(1,17-Pcc) (M = Gd, In, Tl); reported in the literature. Our numbering scheme is used for all structures rather than that adopted for substituted phthalocyanine macrocycles **4**

ine.[9] For simplification, in reference[7] and subsequent papers, Janczak et al. named the bicyclic macrocycle in compound **3** as Pcc, and this name is now an accepted abbreviation of this hexapyrrole ligand.[9] Since three different hexapyrrole ligands of this kind have now been synthesised, we propose to indicate the numbering of the bridgehead carbons as prefixes in the letter code. For phthalocyanine compounds, the numbering scheme generally used in the literature[9,10] is shown in Figures 1−4. It was selected by the authors to indicate the position of the substituted groups at the periphery of the phthalocyanine macrocycle. The IUPAC name mentioned above follows this numbering scheme, but in the clockwise sequence, the numbering prefixes being as small as possible. We think that this numbering scheme is not suitable for that kind of complex. Bicyclophthalocyanines are not substituted phthalocyanines: the colour is different, the visible spectrum does not show the intense Q-band characteristic of phthalocyanine systems, and finally, bicyclophthalocyanines are chemically more reactive than the usual phthalocyanines. All these differences are explained by the interruption of the π-conjugation of the phthalocyanine ring. Furthermore, the differences in the colours of the three different bicyclophthalocyanine ligands reported in the literature are probably due to the different number of benzopyrrole moieties involved in the π-electron delocalisation between the two bridgehead carbon atoms. So it seems to us that the positional indices of the bridgehead atoms have priority over the indices of possible substituents at the periphery of the benzene rings. In the same way as R. Kubiak and J. Janczak,[8,11−13] and some other authors[14−16] did for crystallographic purposes, we started the numbering of the carbons from one pyrrole carbon C_α so that the carbon atoms of the first isoindole ring (I) are numbered from 1 to 8, those of the second (II) from 9 to 16, those of the third (III) from 17 to 24 and those of the fourth (IV) from 25 to 32, nitrogen atoms being numbered separately. In order to have the substitution prefixes as small as possible, we started the numbering of the carbon atoms from a bridgehead carbon. With this numbering scheme, compounds **2** and **3** are named NbCl(1,16-Pcc) and M(1,17-Pcc) (M = Gd, In, Tl), respectively, and **1** is named Bi(1,24-Pcc). There are some advantages in this numbering scheme: a) The indices are independent of the clockwise or anticlockwise sequence and of the bridgehead carbon atom chosen as number one; b) The second index directly indicates the number of benzopyrrole moieties between the two bridgehead carbon atoms, each benzopyrrole moiety being made up of eight carbon atoms.

Synthesis and Properties

It is not surprising that the structure of the bicyclophthalocyanine with niobium(IV), in which the metal is bonded to a chlorine atom, is different to that of bicyclophthalocyanines with trivalent metals, but it is unexpected that **1** has a structure different from those of all the metal(III) bicyclophthalocyanines prepared by Janczak et al. These authors had stated that the chemical composition of the metallophthalocyanines with trivalent metals was strongly dependent on their preparation method.[17] Effectively, **1** and **3** were prepared differently, with a change in the metallation agents, the weight proportions, the pressure and the nature of the atmosphere, the temperature and the reaction time. But we think that the formation of Bi(1,24-Pcc) can also be explained by the properties of the bismuth atom, which are different from those of indium(III), gadolinium(III), and thallium(III) ones. Compound **1** was first obtained using the method employed in the preparation of $Bi_2(Pc)_3$,[1] and the heating was interrupted at approximately 230−240 °C. However, the evolution of the reaction mixture to the triple-decker compound was very fast, and hence, the formation of a larger amount of orange crystals was easier when the ratio of phthalodinitrile/bismuth acetate was reduced to 7.

Compound **1** has been synthesised from the template reaction of phthalodinitrile around the bismuth(III) acetate following the reaction:

$$6\,[C_6H_4(CN)_2] + {}^1/_2\,N_2 + 3\,e^- + Bi^{3+} \rightarrow [C_{48}H_{24}N_{13}]Bi$$

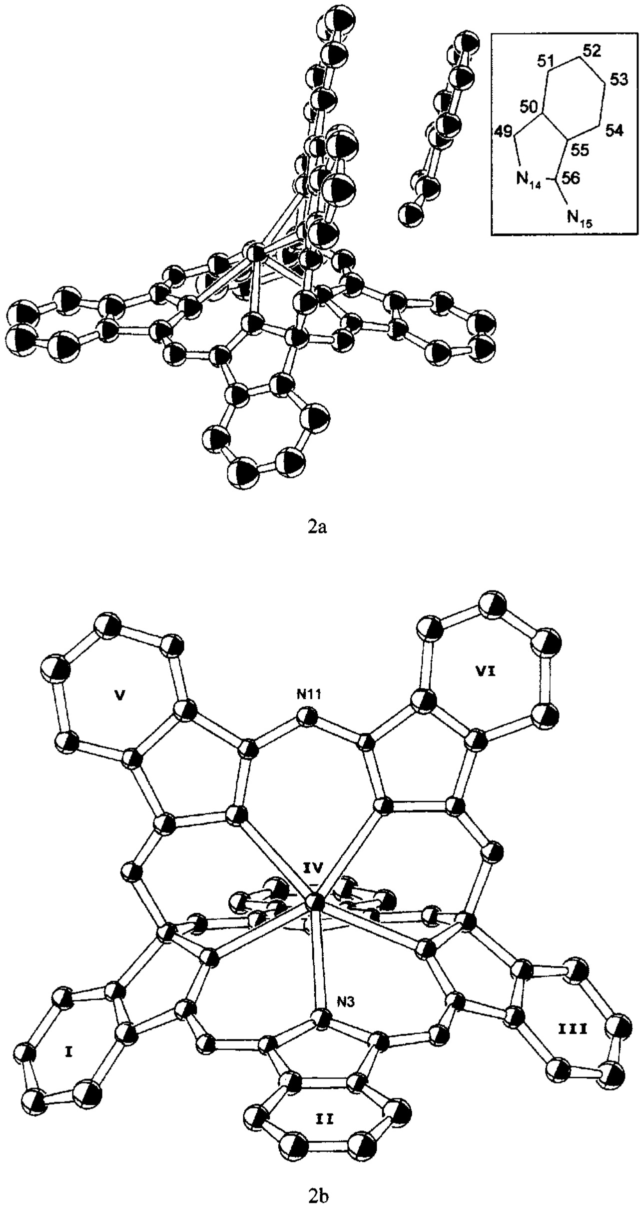
That reaction was performed in air. The phthalodinitrile was involved in an hexamerisation reaction, but was also partly sublimed, and partly involved in secondary polymerisation reactions and in decomposition reactions.[10,18] We believe that the additional nitrogen atom, as well as the three electrons that allow for the formation of the trianionic ligand $[C_{48}H_{24}N_{13}]^{3-}$, arise from these secondary reactions.

Like Tl^{III}(1,17-Pcc), **1** was not soluble in conventional organic solvents: acetone, DMF, DMSO, benzene, toluene, chloronaphthalene. Washing with these solvents allowed us to separate **1** from other by-products of the reaction. A mixture of orange crystals and a light grey powder was retained by the filter. Crystals of **1** are very hydrophobic and, in spite of a very high density (1.48), floated at the interface of a water/acetone/pentane (1/1/1) mixture, while the light grey powder fell to the bottom of the vessel. The crystals were large and very crumbly, and their quality was not good enough for a diffraction study. When dissolved in concentrated acids, the triple-decker compound $Bi_2(Pc)_3$, and **1** decomposed, giving bismuth salts, but the former was converted into free phthalocyanine $H_2(Pc)$ while the latter was converted into phthalimide, the hydrolysis product of phthalonitrile. This experimental result showed that the $(Pcc)^{3-}$ ligand is effectively less stable than the $(Pc)^{2-}$ ligand, as assumed by Gingl and Strähle,[5] because of the interruption of the π-conjugation along the inner 16-membered ring.

Kasuga and Tsutsui reported that the bicyclophthalocyanine complexes have bright colors.[19] Superphthalocyanines are dark blue,[20] metallophthalocyanines with a rigorously planar phthalocyanine ligand, such as Cu(Pc) or Co(Pc), are dark blue−violet and metallophthalocyanines, such as Pb(Pc), in which the ligand is saucer-shaped, are dark green. Janczak and Kubiak assumed that this interruption of the π-conjugation undoubtedly accounts for the specific green colour of metallobicyclophthalocyanines. They suggested that the blue−violet colour was characteristic of all phthalocyanines in which there is full delocalisation of π-electrons along the inner 16-membered ring, and that green was the characteristic colour of bicyclophthalocyanines in which the π-electron delocalisation is interrupted.[7,8] Effectively, all reported bicyclophthalocyanines complexes with the (1,17-Pcc) ligand are green. As proved by X-ray analysis, **1** and **2** are also bicyclophthalocyanines in which the π-electron delocalisation is interrupted: **2** is yellow−green, **1** is not green, but bright orange, closer to red than to yellow. We believe that the color of the complex depends on the length of the π-electron delocalisation and particularly on the number of benzopyrrole moieties involved in the delocalisation. In **2** and **3**, the interruption of the π-conjugation divides the macrocycle (Pc) into two parts, each containing two benzopyrrole moieties, while in **1** there are three benzopyrrole moieties in one part and only one in the other part. Note that boron subphthalocyanines (SubPc)B, which contain only three benzopyrrole moieties, are characterised by their bright color.[21] (SubPc)BPh, which has a phenyl group on the boron atom, is a golden brown solid,[21] and finally, a boron subphthalocyanine substituted with *tert*-butyl groups at the periphery of the macrocycle is magenta-coloured.[22] The bright orange colour of the crystals of Bi(1,24-Pcc) is probably due to the extension of the π-delocalisation along three benzopyrrole moieties.

Crystal Structure of Bi(1,24-Pcc)

Figure 2 shows two ORTEP views of **1**. Part (a) shows a co-crystallised molecule of VII behind the bridging cycle. The molecular structure of **1** was determined unambiguously by the X-ray diffraction study, and a last series of Fourier difference cycles revealed some electronic densities, all lying in the same plane. Among these electronic densities, the most identifiable scheme was a five-membered cycle. They were attributed to a strongly disordered co-crystallised molecule.



2a

2b

Figure 2. ORTEP drawings of **1** with the co-crystallised molecule (with the atoms numbered in the inset) (2a), and facially viewed with the numbering of all benzopyrrole moieties (2b)

Compound **1** was formed in molten phthalonitrile, and during several attempts to purify it by sublimation, the orange crystals broke up and gave a yellow−orange powder and some sublimed light yellow powder, the IR spectrum of which suggested the presence of a large amount of phthalonitrile. Furthermore, the formation of $Bi_2(Pc)_3$ by heating only washed orange crystals is impossible, but the heating of orange crystals in molten phthalonitrile up to 310 °C always produced the triple-decker compound. On the basis of these experimental observations, we attributed these residual densities to a cyclised phthalonitrile, probably an intermediate in the synthesis of $Bi_2(Pc)_3$, stabilised by the interaction with Bi(1,24-Pcc) in the crystal. This additional benzopyrrole moiety was fixed as $C_8H_4N_2H_2$, numbered as indicated in Figure 2(a) and named VII.

Gingl and Strähle have described their bicyclic complex as two phthalocyaninato anions having a common half. Effectively, in **2**, the macrocycle formed by the benzopyrrole rings I, II, III, and IV on the one hand and that formed by the benzopyrrole rings I, II,VI, and V on the other, make up a ring similar to a phthalocyanine with eight pyrrole α carbons and four N_{aza} bridges, but it is not really a phthalocyanine system owing to the interruption of the π-conjugation. In **3** there is only one phthalocyanine-like ring formed by benzopyrrole rings I, II, III, and IV. The macrocycle formed by I, II,VI, and V rings on the one hand and that formed by the III, IV,VI, and V rings on the other, both have eight pyrrole α carbons but five N_{aza} bridges, and not four. Compound **1** is a molecule that contains a ring similar to a superphthalocyanine formed by the five benzopyrrole moieties I, II, III, V, and VI, and a phthalocyanine-like ring formed by the four benzopyrrole moieties I, II, III, and IV. These two macrocycles have three common isoindole rings (I, II, and III).

While **2** has a twofold axis passing through the Cl and Nb atoms, and through the (N2) N_{aza} atom of the common half (Pc) ring, **1** and **3** have no crystallographic symmetry element. In Figure 2(b) it seems that there is a molecular pseudo symmetry plane passing through N3, N7, and N11, and through the bismuth atom, but the angle values and the bond lengths around the two sp^3 carbons, reported in Table 1, show that some pseudo-symmetrical distances are not equal in the estimated standard deviation limits (e.g., compare C1−N8 and C24−N6 bond lengths). This disymmetry is probably due to the co-crystallised molecule. The observed values are typical for normal sp^3 carbon atoms that are σ-bonded to an sp^2 nitrogen atom or to another sp^2 carbon atom. Furthermore, all bond lengths of the macrocyclic skeleton of **1** are comparable to the corresponding lengths reported for **2**[5] and **3**.[6−8] Because of the interruption of the π-conjugation, the (Pc)-like ring is not planar and it is difficult to find reference planes, as is the case in **3**, in which there are three similar planes, each containing two benzopyrrole units. We choose two reference planes for **1**. The first, P1 is the mean-plane formed by the isoindole nitrogens N1, N3, N5, and N7 and is the reference for the phthalocyanine ring atoms. N1 and N5 are above P1, while N3 and N7 are under P1. The second reference plane P2, formed by C1, N10, N12, and C24, is taken as a reference for the atoms belonging to the bridging cycle. The deviation from P2 of these four atoms is very small (below $2 \cdot 10^{-3}$ Å). P3 is the mean plane of the co-crystallised molecule. As shown in Figure 3, the dihedral angle between P1 and P2 is 101.70° (±2.96°) and the bismuth atom lies at a distance of 1.259 Å from P1 and 1.212 Å from P2.

Table 1. Characteristic values (bond lengths and angles) around the two sp^3-hybridised carbon atoms

C1 Atom		C24 Atom	
Bond lengths [Å]			
C1−N1	1.513(1)	C24−N5	1.468(1)
C1−N8	1.424(2)	C24−N6	1.476(1)
C1−N9	1.484(2)	C24−N13	1.446(2)
C1−C2	1.492(2)	C24−C23	1.516(2)
Angles [deg.]			
N1−C1−N9	108.1(1)	N5−C24−N13	110.9(1)
N1−C1−C2	104.1(1)	N5−C24−C23	101.7(1)
N1−C1−N8	114.8(1)	N5−C24−N6	117.9(1)
N8−C1−N9	109.2(1)	N6−C24−N13	109.2(1)
N8−C1−C2	110.8(2)	N6−C24−C23	107.6(1)
N9−C1−C2	109.6(1)	N13−C24−C23	109.0(1)

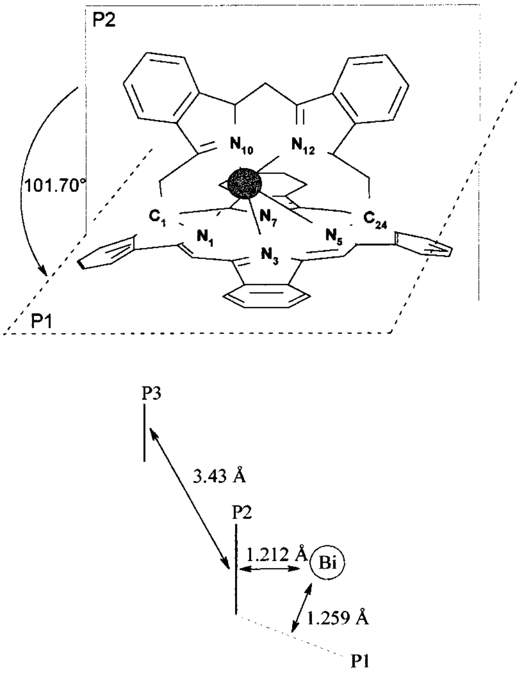


Figure 3. (Above) Dihedral angles [deg.] between mean planes P1 and P2. (Below) Distances [Å] between: 1) the bismuth(III) atom and these planes; 2) mean planes P2 and P3

All benzopyrrole units are planar, and the dihedral angles between the pyrrole and the benzene rings are smaller than the estimated standard deviation. Figure 2 clearly shows that the benzopyrrole II is nearly in P1, but that the other three benzopyrrole groups deviate strongly from P1. The dihedral angles of the benzopyrrole mean planes I, II, III, and IV with P1 are 38.1, 2.9, 38.6, and 22.0° respectively, and the estimated standard deviation is equal to 3.6°. In the bridging moiety, the dihedral angles between mean planes VI and V, and P2 are 7.4° and 170.7°, respectively. P3 was

Table 2. Selected bond lengths [Å] characterising the coordination polyhedron of **1** compared with those of other bicyclophthalocyanine compounds reported in the literature

Compound	(1,16-Pcc)Nb^{IV}Cl[5]	(1,17-Pcc)Gd^{III} [7]	(1,17-Pcc)In^{III} [6]	(1,17-Pcc)Tl^{III} [8]	(1,24-Pcc)Bi^{III} (this work)
M−N Bond					
M−N1	2.148(2)	2.235(7)	2.203(4)	2.238(14)	2.4125(9)
M−N3	2.148(2)	2.263(7)	2.221(4)	2.245(17)	2.5538(9)
M−N5	2.257(1)	2.231(6)	2.208(4)	2.266(18)	2.4041(9)
M−N7	2.215(2)	2.241(7)	2.221(5)	2.278(15)	2.2004(8)
M−N10	2.257(1)	2.274(6)	2.262(4)	2.282(13)	2.477(1)
M−N12	2.215(2)	2.282(6)	2.267(4)	2.310(13)	2.460(1)
Ionic radii [pm][26]	82	107.8	94	102.5	117

calculated in order to determine its position relative to the bridging ring, and particularly to unit VI. The dihedral angle between mean plane VI and P3 is 7.9°, with an estimated standard deviation of 4.7° so that the co-crystallised molecule may be considered as nearly parallel to the benzopyrrole VI. The two mean planes are separated by 3.43 Å, but the N15 atom lies only 2.97 Å from mean plane VI: there is some interaction between the co-crystallised molecule and the benzopyrrole VI, and we believe that this interaction allows for the immediate stabilisation of the crystal and a cyclised form of the benzonitrile, an intermediate in the synthesis of the triple-decker compound.

The coordination polyhedron, made up of the six isoindole nitrogen atoms is a strongly distorted trigonal prism. Related distances are reported in Table 2 and compared with other bond lengths for bicyclophthalocyanine compounds reported in the literature. In both phases of $Bi_2(Pc)_3$,[24,1] the bismuth is bonded to the internal (Pc) ring by long $Bi-N_{iso}$ distances (mean value: 2.734 Å) and to the external (Pc) rings by short $Bi-N_{iso}$ distances (mean value: 2.334 Å). In **1** we note that four $Bi-N_{iso}$ bonds (N1, N5, N10, and N12) have bond lengths between 2.40 and 2.47 Å, but that the Bi−N3 bond is longer [2.554(1) Å] and the Bi−N7 bond has a very short length of 2.200(1) Å. The first result is comparable with that found in $Bi(Pc)_2(CH_2Cl_2)$ (2.47 Å) described by Homborg,[23] and slightly larger than that found for $Bi-N_{iso}$ bonds of the external macrocycles in the triple-decker compounds. The second value is intermediate between the two different values obtained in the triple-decker compounds. The Bi−N7 bond length is shorter than the $Bi-N_{iso}$ distances reported by Janczak and Kubiak for $[Bi(Pc)]_4(Bi_4I_{16})$ as the smallest known among the bismuth phthalocyanine complexes[25] [between 2.260(11) and 2.283(10) Å]. The $Bi(Pc)^+$ moiety in $[Bi(Pc)]_4(Bi_4I_{16})$ is the only bismuth monophthalocyanine with an elucidated structure. In the other known phthalocyanine complexes, the metal is sandwiched between two phthalocyanine rings and it is reasonable that the $Bi-N_{iso}$ distances are longer.

We now compare the coordination polyhedron with those of the other bicyclophthalocyanines (Table 2). Except for Bi−N7, all the $Bi-N_{iso}$ bond lengths are longer than those of the $M-N_{iso}$ bonds reported in the literature for bicyclophthalocyanine compounds with M = Gd, Nb, Tl, and In. This is consistent with the fact that the Bi^{3+} cation has the largest ionic radius in the series, as reported by Shannon[26] for a coordination number of six. In **2** and **3**, the shortest $M-N_{iso}$ bond lengths are those in which the pyrrole nitrogen atoms are directly bonded to the sp^3 carbon atoms. Furthermore, in compounds **3** and except for M−N5 in (1,17-Pcc)Tl, the longest $M-N_{iso}$ bonds are those related to the pyrrole nitrogen atom of the bridging cycle. In **1**, the bridge divides the macrocycle (Pc) so that there are three benzopyrrole moieties in the one section and only one in the other section. This disymmetry displaces the bismuth atom on the same side as the lone benzopyrrole so that Bi−N7 is the smallest known $Bi-N_{iso}$ bond among bismuth phthalocyanine complexes and, on the opposite side, Bi−N3 is then the longest $Bi-N_{iso}$ bond in **1**. Among the four remaining $Bi-N_{iso}$ bonds, as observed in the compounds **2** and **3**, the shortest $Bi-N_{iso}$ bond lengths are those in which the nitrogen atoms of the pyrrole moiety are directly bonded to the sp^3 carbon atom and the longest $Bi-N_{iso}$ bonds are those related to the pyrrole nitrogen atoms of the bridge. Compound **1** has six $M^{III}-N_{iso}$ σ-bonds, like compound **3**, but the cation Bi^{3+} has two valence electrons more than thallium or indium. That electron pair is not necessary for the formation of the six bonds and may be located as a non-bonding electron pair on the bis-

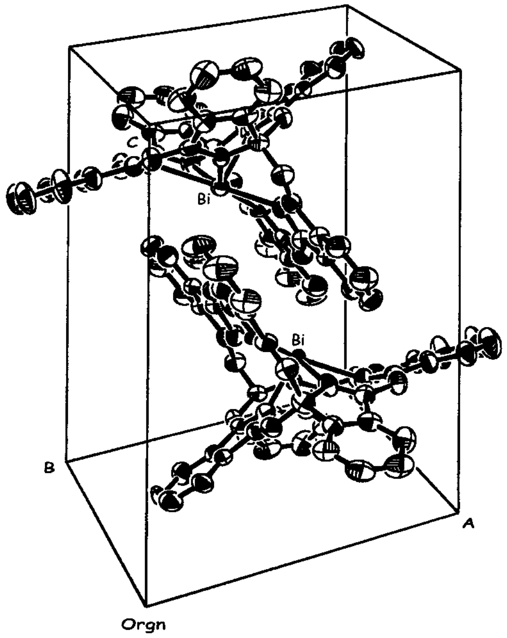


Figure 4. Relative position of two molecules of **1** in the crystal cell

muth atom, inducing the distortion of the coordination polyhedron.

Figure 4 shows the relative position of two molecules of **1** in the crystal cell. Compound **1** is first formed during the synthesis of $Bi_2(Pc)_3$ and its stoichiometry is exactly half that of $Bi_2(Pc)_3$. One can easily deduce that the relative position of these two molecules of **1** in the crystal cell determines the first stage of the dimerisation of **1** to give the triple-decker bismuth phthalocyanine.

The shortest interatomic distances between two successive bicyclophthalocyanine molecules are N3···C29 (3.42 Å) and C28···C8 (3.47 Å). These distances indicate a very weak interaction between the π-electron delocalisation systems of the related benzopyrrole rings. Nevertheless, interactions concerning carbon atoms at the periphery of the phenyl rings cannot participate in the formation of $Bi_2(Pc)_3$. More interesting are the distances between the aza-nitrogen of the first molecule and the α-carbons of the pyrrole ring of the second molecule. These distances can be considered as too long to allow for a dimerisation through these atoms (N9···C48 = 5.66 Å and N13···C33 = 5.64 Å). It is remarkable that two successive bicyclic molecules are closer in **3** than in **1**. These distances are 3.25, 3.36, and 3.36 Å for the indium, gadolinium, and thallium complexes, respectively.

UV/Vis Spectroscopy

Figure 5 shows the UV/Vis spectrum of **1**. We distinguish a very small Q band at $\lambda = 630$ nm and a very large and intense B band at 302 nm with two shoulders at 392 nm and at approximately 455 nm. The spectrum of **1** is very different from that of the monophthalocyanine Bi(Pc)Cl reported by Isago and Kagaya.[27] All the bands of **1** are blue-shifted, and the most striking difference is the almost complete disappearance of the Q band.

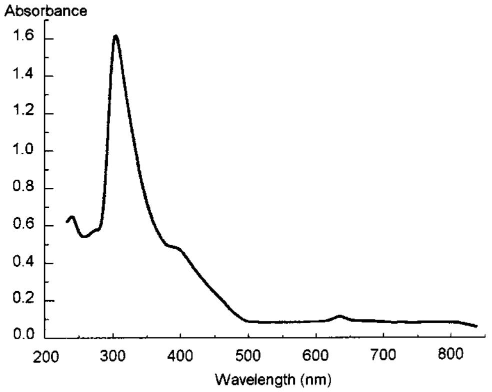


Figure 5. UV/Vis spectrum of **1** recorded using a KBr pellet medium (0.5%)

The appearance of an intense Q band generally characterises the phthalocyanine group and is assigned in the literature to a $\pi \rightarrow \pi^*$ transition delocalised over the (Pc) ring.[28] It is then understandable that the interruption of the π-conjugation in the (Pc) ring in **1** involves the important decrease in the Q band. The shoulder between 380 and 480 nm contains at least two bands. Such a shoulder in the visible/near-UV region was reported by Gouterman et al.[28] in the spectrum of Pb(Pc), and was attributed to the presence of an allowed $6p_z$ (metal)→π^* (Pc) charge-transfer transition (MLCT: Metal-to-Ligand Charge Transfer), by analogy with the (porphyrinato)lead(II) complex. Following this conclusion, Isago et al.[27] have assigned the extra 415 nm band in the visible spectrum of Bi(Pc)Cl to an hyper MLCT band, an excitation from an $a_{2u}(6p_z)$ orbital of bismuth(III) to an $eg(\pi^*)$ (Pc) orbital. In the same way, Lever et al.[29] and Stillman et al.[30] assigned the transitions at approximately 450 nm to metal-to-ligand (MLCT) or ligand-to-metal (LMCT) charge-transfer transitions, depending on the oxidation state of the transition metal. Other authors have assigned this broad band as evidence for the existence of a free radical (Pc) ring, which is not inconsistent with the proposal of a charge-transfer transition. In the lithium phthalocyanine radical, Li(Pc), a doublet at 427 and 473 nm has been attributed to the free radical monophthalocyanine[31−33] while a similar broad band centred at approximately 450−470 nm has also been attributed to a free-radical phthalocyanine ring in $Ln(Pc)_2$[34−36] and in $In(Pc)_2$.[37] It is difficult to use the interpretation of monophthalocyanine or diphthalocyanine spectra for the interpretation of the spectrum of the compound **1** because Bi(Pc)Cl and other phthalocyanine compounds have a C_{4v} or D_{4h} symmetry, while **1** has no symmetry element, the allowed transitions are different and the molecular orbitals should have different energies and a different electron-density distribution. Nevertheless the shape and the energy of the transition at approximately 390−480 nm is very similar to those reported for Pb(Pc),[28] Bi(Pc)Cl,[27] or $In(Pc)_2$,[37] so we propose to assign that transition to a charge transfer from bismuth to the bicyclophthalocyaninato ligand. The B band, which is mostly an $a_{2u} \rightarrow e_g$ transition, has the same shape as the B band of Bi(Pc)Cl and is very intense, with an ε value of $0.6 \cdot 10^5$ $M^{-1}cm^{-1}$, close to that measured in porphyrin compounds. In the phthalocyanine compounds, the B band has an ε value much smaller than 10^5 $M^{-1}cm^{-1}$.[28] In addition to the B band, some authors[38−40] described two other bands at lower wavelengths: the N band resulting mainly from a $b_{2u}(\pi) \rightarrow e_g(\pi^*)$ transition, and the L band resulting from a combination of $a_{2u}(\pi) \rightarrow e_g(\pi^*)$ and $b_{2u}(\pi) \rightarrow e_g(\pi^*)$ transitions.[38] The bands appearing in the spectrum of **1** at 275 nm, as a shoulder of the B band, and at 238 nm may be assigned to the N and L transitions, respectively.

Infra-Red Spectroscopy

Figure 6 shows the FTIR spectrum of **1** between 500 and 2000 cm^{-1} (Figure 6a) and between 50 and 650 cm^{-1} (Figure 6b). Our assignments were made based on literature reports[37,41−51] and by comparison with those made for Pb(Pc).[1,27] Some very intense and fairly intense bands characteristic of Pb(Pc) are evident in the spectrum of Bi(1,24-Pcc), with only a slight modification. These are for Pb(Pc)/Bi(1,24-Pcc), respectively: bands at 725/720 cm^{-1} [out-of-plane C−H deformations γ(C−H)[27]], 772/774 cm^{-1} [C−N stretching vibration in pyrrole skeleton, ν(C−N)], 950/953 cm^{-1} and that at 1003/997 cm^{-1}, the band at 1080/1065 cm^{-1} and that at 1161/1162 cm^{-1} both assigned to C−N stretching vibration, and the bands at 1282/1299 and 1479/1482 cm^{-1}, all in the range of the C−C stretching vibration frequencies in the isoindole skeleton, ν(C−C).

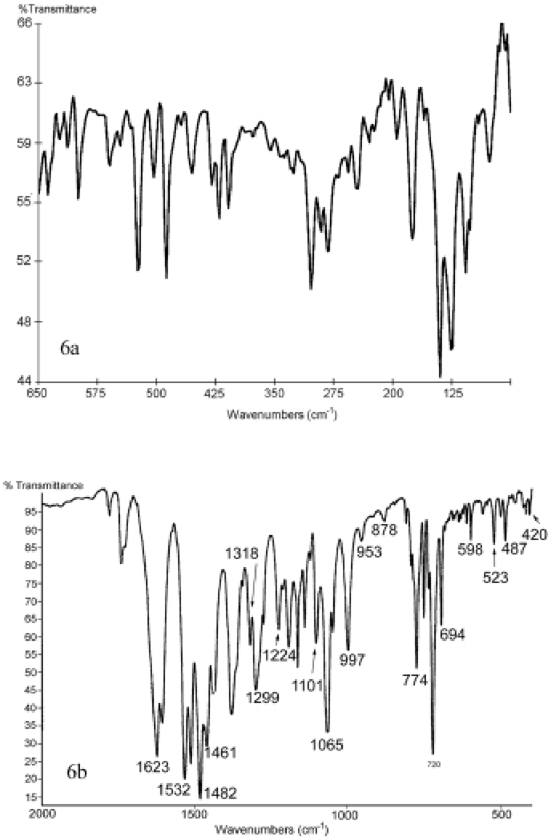


Figure 6. Far (6a) and middle (6b) infra-red spectra of **1**, recorded using 10% polyethylene and 0.5−1% KBr pellets, respectively

Other very intense or fairly intense bands in the spectrum of Pb(Pc) became smaller in the spectrum of Bi(1,24-Pcc): the band at 742/750 cm^{-1}, [out-of-plane C−H deformations γ(C−H)[27]], the bands at 1059/1047 cm^{-1} and 1113/1101 cm^{-1} [both in-plane C−H deformations, β(C−H)], and the band at 1313/1318 cm^{-1} in the range of the C−C stretching vibrations frequencies in the isoindole skeleton, ν(C−C). The band at 882 cm^{-1}, described as a metal-dependent vibration of the macrocycle,[46] is very sharp and intense in Pb(Pc) and becomes very small and broad at 878 cm^{-1} in **1**. That modification is probably due to important differences in the coordination polyhedra of the two complexes. In the range of the ν(C−C) or ν(C−N) stretching vibration frequencies, the bands at 1329 and 1404 cm^{-1} disappear and many new bands appear at 1139, 1192, 1224, 1461, 1512, 1532, and 1623 cm^{-1}. A medium band at 1606 cm^{-1} in the Pb(Pc) spectrum becomes very intense. The complexity of the Bi(1,24-Pcc) spectrum and the large number of new bands in the range of aromatic ν(C−C) or ν(C−N) stretching vibration frequencies is due to the lack of symmetry elements and to the large range of bond lengths observed in the different isoindole rings constituting the Bi(1,24-Pcc) molecule, particularly for the bonds around the sp^3 carbon atoms which are longer than normal $C_\alpha-N_{iso}$ or $C_\alpha-C_\beta$ bonds.

Owing to the presence of a sharp band at 1745 cm^{-1}, we first assumed that the co-crystallised molecule should be a phthalimide, which has an intense C=O vibration at 1746 cm^{-1} and a medium band for the N−H vibration at 3203 cm^{-1}. However, the position and the intensities of the residual electronic densities detected around the identified five-membered cycle in the X-ray diffraction study are not consistent with oxygen atoms. In the IR spectrum, we did not find any band between 2000 and 4000 cm^{-1} which would allow for the unambiguous characterisation of the co-crystallised molecule. This is probably due to the non-stoichiometric ratio of this cyclised phthalonitrile, compared to the six benzopyrrole units in the Bi(1,24-Pcc). Between 3000 and 3200 cm^{-1}, we observed a broad group of small bands that is evident in all phthalocyanine spectra, including that of $Bi_2(Pc)_3$, characteristic of the aromatic C−H vibrations. At approximately 2240 cm^{-1}, a very small band was observed, which we assigned to −CN groups of residual phthalonitrile in the crystal, or to a co-crystallised molecule, intermediate in the synthesis of $Bi_2(Pc)_3$. Janczac and Kubiak studied the formation of the phthalocyaninato (2-) ring from o-dicyanobenzene molecules and observed that, depending on the reaction conditions, only one of the cyano groups of *o*-dicyanobenzene undergoes a transformation, with a change from sp to sp^2 hybridisation.[18]

Below 700 cm^{-1} the spectrum of **1** is not a typical spectrum of phthalocyanine compounds. There is a very sharp and fairly intense band at 694 cm^{-1}, which is not present in usual phthalocyanine spectra. In Pb(Pc) and other common metallophthalocyanines, only four or five bands, characteristic of phthalocyanine ring deformations, are evident between 700 and 360cm^{-1}. For Pb(Pc),[1] they lie at 627, 560, 497, and 436 cm^{-1}. In the spectrum 6b, we observe 13 bands between 360 and 650 cm^{-1}. The ligand of **1** is not a phthalocyanine but, as shown in the structural part, a macrocycle made up of a superphthalocyanine-like ring and a phthalocyanine-like ring having three common isoindole moieties. This fact and the absence of symmetry elements explain the large number of allowed vibrations. The band at 353 cm^{-1} appears with the same shape and intensity in the spectra of Pb(Pc) and $Bi_2(Pc)_3$,[1] at 351 cm^{-1}. It has been described as metal dependant and due to the isoindole ring out-of-plane deformations.[34,44] Between 200 and 350 cm^{-1} in the spectrum of Pb(Pc), only two bands were observed at 231 and 271 cm^{-1}, assigned in the literature to the metal−nitrogen vibrations.[1,37,49] In the same wavenumber range, spectrum 6b shows many bands that we assign to the $Bi-N_{iso}$ stretching vibrations of the different $Bi-N_{iso}$ bonds. Below 200 cm^{-1}, we observe two new bands at 194 and 174 cm^{-1}. The two intense bands at 146 and 125 cm^{-1} in the spectrum of Pb(Pc) are at 140 and 126 cm^{-1} in the spectrum of **1**, in which we note two supplementary new bands at 107 and 101 cm^{-1}. The spectrum of lattice vibrations between 50 and 100 cm^{-1} shows few differences between Pb(Pc) and **1**.

Conclusion

We have prepared a new orange bismuth(III) bicyclophthalocyanine complex. It is a new member of the family of the hexapyrrole ligand complexes in which a $N(C_8H_4N)N(C_8H_4N)N$ bridge is extended between two Cα pyrrole carbon atoms of a phthalocyanine ring, interrupting the π-conjugation of the macrocycle. These hexapyrrole complexes can be now classified into three groups of ligands, differing by the position of the bridgehead carbon atoms. In this paper, we have proposed a numbering scheme in order to differentiate each group of this class of compounds by their names. The positional indices of the bridgehead carbons are indicated as a prefix in front of the letter code (Pcc) of the hexapyrrole ligand. With this numbering scheme indicating the number of benzopyrrole units over which the π-delocalisation is extended, NbCl(1,16-Pcc)[5] is the only reported member of the first group, M(1,17-Pcc) (with M = Gd, In, Tl, and Ce)[6−8] describes the second group, and Bi(1,24-Pcc) is the first member of a new group. This new complex was fully characterised by UV/Vis and IR spectroscopy. The most striking feature of the UV/Vis spectrum is the almost complete disappearance of the Q band, explained by the interruption of the π-conjugation through the (Pc) ring. The IR spectrum from 50 cm^{-1} to 2000 cm^{-1} was reported and compared to usual IR phthalocyanine spectra. The large number of new bands can be explained by the lack of symmetry elements and by the large range of bond lengths observed in the different isoindole rings making up the Bi(1,24-Pcc) molecule, particularly for the bonds around the sp^3 carbon atoms and in the coordination polyhedron. The molecular structure of **1** was established and shows the smallest known $Bi-N_{iso}$ bond among bismuth phthalocyanine complexes. The relative position of the molecules of Bi(1,24-Pcc) in the crystal cell, and the distances between the atoms of two neighbouring molecules indicate a very weak interaction between the two π-electron systems. The distances between the aza-nitrogen atom of the first molecule, and the α-carbons of the pyrrole ring of the second molecule are too long to explain the formation of $Bi_2(Pc)_3$ by a direct dimerisation of two molecules of Bi(1,24-Pcc). This is confirmed by the fact that the isolation of $Bi_2(Pc)_3$ by heating only washed orange crystals is impossible while the heating of orange crystals in molten phthalonitrile up to 310 °C always produced the triple-decker compound. We observed a co-crystallised molecule VII, nearly parallel to one of the two benzopyrrole units of the bridge, and 3.43 Å apart. This strongly disordered molecule was not fully characterised. The IR spectroscopy and X-ray diffraction results suggest that it is a cyclised phthalonitrile molecule. Some experiments are currently underway to identify it, and to understand its importance in the reaction mechanism of the synthesis of $Bi_2(Pc)_3$.

Experimental Section

General Remarks: FT-IR: Nicolet 20 SXB spectrometer with 2 cm^{-1} resolution. Perkin−Elmer Spectrum 1000 with 1 cm^{-1} resolution. KBr pellets (1%) and polyethylene pellets (10%) were used within the range of 4000−400 cm^{-1} and 400−50 cm^{-1}, respectively. Pellets were prepared with some clean crystals, picked out under a microscope. − UV/Vis: Unicam UV 4 spectrometer.

Synthesis and Purification: The synthesis of **1** was performed using the method for the synthesis of $Bi_2(Pc)_3$, in the same vessel and apparatus.[1] Bismuth acetate (1.6 g, 4 mmol), and phthalonitrile (3.64 g, 28 mmol, puriss. 99% Fluka) were ground and placed in an open-reaction vessel which was put in the oven, pre-heated to 180 °C. The temperature probe was placed between the wall of the oven and that of the reaction vessel. The temperature was raised slowly (2°/min) to 230−240° C. The mixture was then slowly cooled to room temperature. The crude product was a mixture of orange crystals with some remaining reactants and by-products. Using a Soxhlet apparatus, the crystals were washed with acetone, DMF, toluene, and then ethanol. The isolated dry powder was a mixture of orange crystals and a light-grey powder, and was shaken in a mixture of acetone/water/pentane (1:1:1). Crystals of **1** were floating at the interface of the phases, (water + acetone/pentane) while the light-grey powder was deposited at the bottom of the vessel. The interface of the solvents was sucked up with a Pasteur pipette connected to a water aspirator pump, and orange crystals were isolated (440 mg, 0.392 mmol, 9.8%). It was impossible to get reliable elemental analytical data: the yield is low (<10%) and the calculations are not precise because of the disordered co-crystallised molecule, in a non-stoichiometric ratio. In spite of these unreliable analyses, the molecular structure of Bi(1,24-Pcc) was determined unambiguously by the X-ray diffraction study.

X-Ray Crystallographic Study: A suitable orange crystal of small size (0.1 × 0.1 × 0.05 mm) was mounted on an Enraf−Nonius Kappa CCD[52] diffractometer. Despite its well-defined shape, the crystal gave a diffraction pattern of medium quality, showing some light rings of diffusion, probably due to the precipitate that could be observed on the surface of the sample. A 180° (through 2°-steps of 240 seconds each) φ scan measurement was performed at room temperature using the Mo-K_α wavelength. The cell parameters were refined (Denzo[53]) with the use of 7053 reflections and are reported in Table 3 with the crystallographic parameters. The data were first corrected for absorption effects with Sortav.[54] The bismuth atom and some cycles of the organic ligand could then easily be located with SIR92.[55] As some remaining undefined fragments could not be assigned in the first steps of the calculations, we performed a series of anisotropic refinements (MaXus[56]), only on the well-defined bicyclophthalocyanine moiety, adding the hydrogen atoms at idealised positions, until the *R* factor reached a reasonable value. A last Fourier difference gave some peaks of density (all rigorously lying in the same plane) that could be attributed to a cyclised phthalonitrile solvate. The most identifiable scheme among these electron densities was a five-membered cycle. These atoms were finally introduced (with isotropic displacement parameters) in the calculations as $C_8H_4N_2H_2$ and refined as a rigid block fragment to the final *R* indices: R_1 $[F^2 > 3\sigma(F^2)] = 0.059$, wR_1 $[w = 1/\sigma^2 (F^2) + 0.03F^2] = 0.093$. The residual positive Fourier peak is equal to 1.58 $e\AA^3$ and is located near the bismuth atom. This density cannot be unambiguously attributed to a free electron pair on the bismuth atom as it can also be due to an absorption problem. This point could not be clarified either by the empirical correction used, or by a numerical one that we also tested. Crystallographic data (ex-

Table 3. Crystallographic data for **1**

Crystal data	
Formula	$C_{56}H_{30}BiN_{15}$
M_w	1121.95
Crystal system	triclinic
Space group	P-1
a [Å]	12.544(2)
b [Å]	13.654(1)
c [Å]	14.868(1)
α [°]	73.83(1)
β [°]	78.75(1)
γ [°]	68.20(1)
V [Å^3]	2258.8(2)
D_{calc} [g cm^{-3}]	1.25
Z	2
μ(Mo-K_α) [cm-1]	78.32
Data collection	
T [K]	298
Scan mode	Φ scan
Scan width	2
$2\theta_{max}$ [°]	48.06
Measured reflections	7113
Unique reflections	7053
R_{int}	0.064
Refinement parameters	
Absorption correction	empirical (Sortav: Blessing, 1997)
Reflections used for refinement	5015
Refined parameters	566
Refinement cut-off	$F^2 > 3\sigma(F^2)$
H atoms	included, not refined
R_1	0.059
wR_1	0.093
Weighting scheme	$w = 1/(\sigma^2(Fo^2) + 0.03000 \times Fo^2)$
(Shift/e.s.d.)$_{max}$	0.454
Goodness of fit	2.61
$\Delta\rho_{fin}$.(max./min.) [eÅ^3]	1.58; −2.43

cluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133562. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(0)1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] K. Benihya, M. Mossoyan-Déneux, F. Hahn, N. Boucharat, G. Terzian, *Eur. J. Inorg. Chem.* **2000**, 1771−1779

[2] F. Baumann, B. Bienert, G. Rösch, H. Vollmann, W. Wolf, *Angew. Chem.* **1956**, *68*, 133−150

[3] M. A. Perkins, M. S. Whelen, **1957** *U. S. Pat* 2,782,207

[4] G. Barnhart, B. F. Skiles, *1956 U. S. Pat* 2,772,284, *British Pat.* 745359

[5] F. Gingl, J. Strähle, *Acta Cryst.* **1990**, *C46*, 1841−1843

[6] J. Janczak, R. Kubiak, *J. Chem. Soc., Dalton Trans.* **1994**, 2539−2543.

[7] J. Janczak, R. Kubiak, *Acta Cryst.* **1995**, *C51*, 2039−2042

[8] J. Janczak, R. Kubiak, *Acta Chem. Scand.* **1995**, *49*, 871−877.

[9] *The porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), vol 3, p. 249, Academic Press, Burlington, MA, USA, **2000**.

[10] C. C. Leznoff, *Phthalocyanines (Properties and Applications)* (Eds.: C. C. Leznoff, A. B. P. Lever), vol 1, VCH Publishers, Weinheim, **1989**.

[11] R. Kubiak, J. Janczak, *J. Alloys Comp.* **1992**, *189*, 107−111.

[12] R. Kubiak, J. Janczak, *J. Alloys Comp.* **1992**, *190*, 117−120.

[13] J. Janczak, R. Kubiak, *J. Alloys Comp.* **1992**, *190*, 121−124.

[14] M. S. Haghighi, C. L. Teske. H. Homborg, *Z. Anorg. Allg. Chem.* **1992**, *608*, 73−80.

[15] C. J. Brown, *J. Chem. Soc. A* **1968**, 2494−2498.

[16] K. J. Wynne, *Inorg. Chem.* **1985**, *24*, 1339−1343.

[17] J. Janczak, R. Kubiak, *J. Chem. Soc., Dalton Trans.* **1993**, 3809−3812.

[18] J. Janczak, R. Kubiak, *J. Mol. Struct.* **2000**, *553*, 157−166.

[19] K. Kasuga, M. Tsutsui, *Coord. Chem. Rev.* **1980**, *32*, 67−95.

[20] T. J. Marks, D. R. Stojakovic, *J. Am. Chem. Soc.* **1978**, *100*, 1695−1705.

[21] J. Rauschnabel, M. Hanack, *Tetrahedron Lett.* **1995**, *36*, 1629−1632.

[22] N. Kobayashi, *J. Chem. Soc., Chem. Commun.* **1991**, 1203−1205.

[23] G. Ostendorp, H. Homborg, *Z. Anorg. Allg. Chem.* **1996**, *662*, 873−880.

[24] J. Janczak, R. Kubiak, *Polyhedron.* **1999**, *18*, 2775−2780.

[25] R. Kubiak, K. Ejsmont, *J. Mol. Struct.* **1999**, *474*, 275−281.

[26] R. D. Shannon, *Acta Cryst.* **1976**, *A32*, 751−767.

[27] H. Isago, Y. Kagaya, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 383−389.

[28] P. Sayer, M. Gouterman, C. R. Connell, *Acc. Chem. Res.* **1982**, *15*, 73−79.

[29] A. B. P. Lever, S. R. Pickens, P. C. Minor, S. Licoccia, B. S. Ramaswamy, K. Magnell, *J. Am. Chem. Soc.* **1981**, *103*, 6800−6806.

[30] M. J. Stillman, A. J. Thomson, *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 790−804.

[31] H. Homborg, W. Kalz, *Z. Naturforsch.* **1978**, *33b*, 1067−1071.

[32] H. Sugimoto, T. Higashi, M. Mori, *J. Chem. Soc.,Chem. Commun.* **1983**, 622−623.

[33] P. Turek, J. J. André, J. Giraudeau, J. Simon, *Chem. Phys. Lett.* **1987**, *134*, 471−476.

[34] C. Clarisse, M. T. Riou, *Inorg. Chim. Acta.* **1987**, *130*, 139−144.

[35] D. Markovitsi, T. H. Tran-Thi, R. Even, J. Simon, *Chem. Phys. Lett.* **1987**, *137*, 107−112.

[36] E. Orti, J. L. Bredas, C. Clarisse, *J. Chem Phys.* **1990**, *92*, 1228−1235.

[37] J. Janczak, *Pol. J. Chem.* **1998**, *72*, 1871−1878.

[38] L. K. Lee, N. H. Sabelli, P. R. Lebreton, *J. Phys. Chem.* **1982**, *86*, 3926−3931.

[39] A. Henrikson, B. Roos, M. Sundbom, *Theoret. Chim. Acta* **1972**, *27*, 303−313.

[40] H. Shirai, H. Tsuiki, E. Masuda, T. Koyama, K. Hanabusa, N. Kobayashi, *J. Phys. Chem.* **1991**, *95*, 417−423.

[41] A. N. Sidorov, I. P. Kotlyar, *Opt. Spectr.* **1961**, *11*, 92−96.

[42] H. F. Shurvell, L. Pinzuti, *Can. J. Chem.* **1966**, *44*, 125−136.

[43] T. Kobayashi, F. Kurokawa, N. Uyeda, E. Suito, *Spectrochim. Acta, Ser. A* **1970**, *26*, 1305−1311.

[44] T. Kobayashi, *Spectrochim. Acta, Ser. A* **1970**, *26*, 1313−1322.

[45] F. Cariati, F. Morazzoni, M. Zocchi, *J. Chem. Soc., Dalton Trans.* **1978**, 1018−1024.

[46] F. Morazzoni, F. Cariati, G. Micera, *Spectrochim. Acta* **1980**, *36A*, 867−870.

[47] W. Kalz, H. Homborg, *Z. Naturforsch.* **1983**, *38b*, 470−484.

[48] H. Homborg, W. Kalz, *Z. Naturforsch.* **1984**, *39b*, 1490−1499.

[49] G. Terzian, B. Moubaraki, M. Mossoyan-Déneux, D. Benlian, *Spectrochim. Acta* **1989**, *45*, 675−677.

[50] W. J. Kroenke, M. E. Kenney, *Inorg. Chem.* **1964**, *3*, 696−698.
[51] M .S. Haghighi, H. Homborg, *Z. Anorg. Allg. Chem.* **1994**, *620*, 1278−1284.
[52] Nonius (**1998**). *Kappa CCD Reference Manual.* Nonius B. V., P. O. Box 811, 2600 Av, Delft, The Netherlands.
[53] Z. Otwinowski, W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode*, Methods in Enzymology, *Volume 276*: Macromolecular Crystallography, part A, pp. 307−326, **1997** (Eds.: C. W. Carter, Jr., R. M. Sweet), Academic Press.
[54] R. H. Blessing, *J. Appl. Cryst.* **1997**, *30*, 421−426.
[55] A. Altamore, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst.* **1994**, *27*, 435−436.
[56] S. Mackay, C. J. Gilmore, C. Edwards, M. Tremayne, N. Stewart, K. Shankland, *maXus: a computer program for the solution and refinement of crystal structures from diffraction data* University of Glasgow, Scotland, UK, Nonius BV, Delft, The Netherlands and MacScience Co. Ltd., Yokohama, Japan, **1998**.

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