Synthesis, Crystal Structure and Spectral Characterization, of a New Phase of Tris(phthalocyaninato)dibismuth(III), $Bi_2(Pc)_3$

Karim Benihya,[a] Mireille Mossoyan-Déneux,*[a] Friedemann Hahn,[b] Nancy Boucharat,[a] and George Terzian[a]

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Direct-template synthesis and purification of a new phase of the triple-decker bismuth(III) phthalocyanine $Bi_2(Pc)_3$, prepared from bismuth acetate and phthalonitrile, are described. X-ray analysis shows a triple-decker molecular structure involving three phthalocyanine rings and two bismuth atoms that are 3.838(9) Å apart. The coordination polyhedron is a distorted square anti-prism. The average distances between the bismuth(III) and the isoindolic nitrogens are 2.336 Å and 2.726 Å, respectively, for the external saucer-shape ring and the more planar inner ring. The intramolecular distance between two neighbouring $4N_{iso}$ mean-planes is 3.17 Å, the inner Pc ring being rotated by 38.3° with respect to the peripheral ones. The shortest intermolecular distance between two carbon atoms in the crystal packing is 3.284 Å. This black phase is a regular stack of phthalocyanine rings that have their π system all overlapping. UV/Visible and FT-IR spectra are discussed in relation to the molecular structure and fully characterize this triple-decker compound.

Introduction

Heavy metal phthalocyanines have interesting electronic properties in the solid state. Rare-earth phthalocyanines and lead phthalocyanine Pb(Pc) have been studied intensively,[1−5] but only recently have some reports been published on phthalocyanine complexes with vicinal element: bismuth.[6,7] H. Isago and Y. Kagaya reported the synthesis, spectral characterization, and redox potential of bromo and chloro(phthalocyaninato) bismuth (III) complexes.[8,9] R. Kubiak et al. described the crystal structure of a bismuth phthalocyanine-bismuth iodide complex with formula $(Bi(Pc))_4(Bi_4I_{16})$,[10] and the synthesis and structure of an iodine-doped bismuth(III) diphthalocyanine $Bi(Pc)_2I_{1.5}$.[11] G. Ostendorp and H. Homborg described the synthesis, structure, and electrochemical and spectral properties of a bisphthalocyanine $Bi(Pc)_2,CH_2Cl_2$.[12] Bismuth(III) is very close to lanthanoids (III) in its ionic radius[13] and its ability to coordinate a large number of atoms.[14] Rare earth phthalocyanines have been investigated as monophthalocyanines,[15] bisphthalocyanines $Ln(Pc)_2$ [15−18] (double-decker compounds), or trisphthalocyanines $Ln_2(Pc)_3$ [19−21] (triple-decker compounds), because all these compounds can have many applications in electronic and display devices. Among all these complexes, the more recently studied are the triple-decker compounds, particularly the mixed ligand phthalocyanine-porphyrin lanthanide molecules.[22−25] Some homoleptic triple-decker sandwich molecules built with three phthalocyanine macrocycles have been reported: (Pc)M(Pc)M(Pc) synthetized by K. Kasuga et al.[26] with M = Y, Nd, Gd, Er, and Lu; (Pc)Lu(CRPc)Lu(Pc) with CRPc = crown-ether-substituted phthalocyanine,[27] synthesized by N. Ishikawa and Y. Kaizu who introduced the crown-ether at the periphery of the macrocycle to give these compounds greater solubility, and the $M_2(obPc)_3$ (obPc = 2,3,9,10,16,17,23,24-octabutoxyphthalocyanine, M = ytterbium, dysprosium,[28] lanthanum and lutetium[29]) synthesized by K. Takahashi et al. The only reported triple-decker phthalocyanine complexes built around a metal without any f orbitals are the indium complex[30] and, very recently, a red-violet phase of bismuth triple-decker phthalocyanine,[31] both obtained by J. Janczak et al. In this report, we present the preparation of a black phase of the same molecule $Bi_2(Pc)_3$, and discuss its crystal and molecular structures, as well as its characterization by FT-IR and UV/Visible spectroscopies.

Results and Discussion

Synthesis and Characterization

All the preparations of triple-decker rare earth phthalocyanine complexes reported in the literature are long, or include many steps.[26,27] Their purification is performed through precipitation and/or extraction with various solvents, and repeated chromatographic procedures on alumina. Janczak and Kubiak have proposed a new method[32] that allowed them to synthesize indium(III) triple-decker phthalocyanine. However, they could not obtain the $Bi_2(Pc)_3$ complex by this method since the oxidation potential of the reaction $Bi \rightarrow Bi^{3+}$ is too high. For the synthesis

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[a] Université de Provence, Laboratoire de chimie de coordination, case D22,
Av. de l'escadrille Normandie-Niemen, 13397 Marseille Cedex 20, France
Fax: (internat.) +33-4/91028959
E-mail: Mireille.Mossoyan-Deneux@LCC.u-3mrs.fr
[b] STOE & CIE GmbH,
Hilpertstraße 10, D-64295 Darmstadt, Germany

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of $Bi_2(Pc)_3$ they used a mixture of Bi_2Se_3 and phthalonitrile, pressed into pellets, heated at 220 °C for 24 h[31]. Our preparation method of the tris (phthalocyaninato) dibismuth(III), presented here, is very fast and simple. A mixture of bismuth acetate with a large excess of phthalonitrile was heated to 310 °C during 30 min. The obtained black powder was washed with organic solvents, and placed under reflux in an aqueous solution of NaOH for 30 min. $Bi_2(Pc)_3$ is not soluble in any of the usual solvents (water, acetone, alcohol), and is very slightly soluble in DMF or DMSO, as well as aromatic solvents like chloronaphthalene or quinoline, but not enough to recrystallize. Attempts to obtain sublimed crystals or powder by vacuum sublimation with a very slight stream of nitrogen were unsuccessful. Instead, while using the tubular oven, a very thin metallic mirror (probably metallic bismuth) was deposited on the cold wall of the quartz tube. Further away a dark blue layer, characterized as $H_2(Pc)$ by its IR spectrum, and still further needles of phthalonitrile were also found. This shows the instability of our compound, which is moreover photosensitive: slow decomposition at room temperature was observed when solutions were left in daylight whereas solid samples or dissolved samples kept in the dark at 4−10 °C, remained unchanged over several years. Contact with dilute acids led to demetallation, yielding $H_2(Pc)$. Thus $Bi_2(Pc)_3$, like Pb(Pc), appears to be a labile metallophthalocyanine.

Crystal Structure

Figure 1 shows the triple-decker structure of the molecule. We named the internal macrocycle A, and the two external macrocycles B and B′. The centre of the square formed by the four pyrrolic nitrogens of cycle A (Ct_A) form a crystallographically-imposed inversion centre of the molecule, so that the two macrocycles B and B′ are equivalent. The coordinates of each atom of the B′ ring are deduced from those of the corresponding atom of the B ring by inversion operation: $C(x, y, z) \rightarrow C'(-x, -y + 1, -z)$.

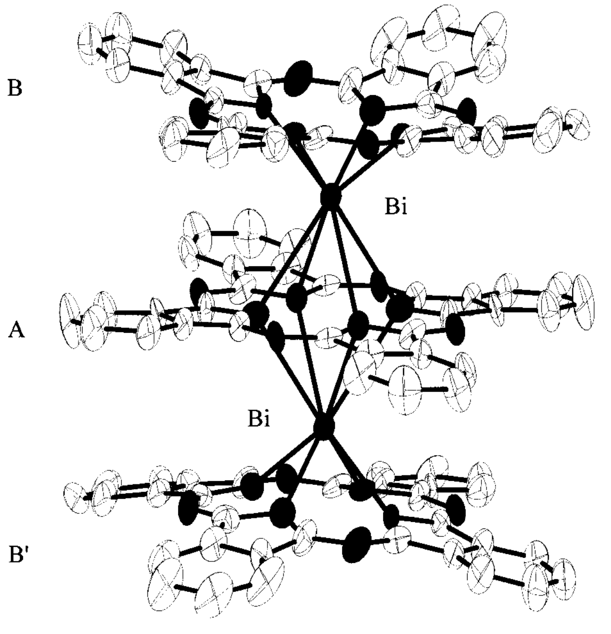

Figure 1. ORTEP drawing of $Bi_2(Pc)_3$ viewed along the *b* axis, with thermal ellipsoids shown at the 50% probability level. H atoms are omitted for clarity. The internal macrocycle is named A and the two external macrocycles B and B′

Figure 2,a is a view of the molecule along the Bi−Bi′ axis, and Figure 2,b shows this split molecule with the three macrocycles projected along the Bi−Bi′ axis, with the numbering scheme, and the staggering angles between the macrocycles. The distances between each bismuth and the centres (Ct) of the squares formed by the four pyrrolic nitrogens of the cycles A (Ct_A), B (Ct_B), and B′ (Ct_B') are indicated at the right of the scheme. As in all the other triple-decker compounds,[30,31,33] the metallic ions are not equidistant from Ct_A and Ct_B: the distance from the metallic ion is 1.918(0) Å for Ct_A and 1.247(1) Å for Ct_B or $Ct_{B'}$. The larger distance to ring A reflects the fact that the benzopyrrolic nitrogens (N_{iso}) of this macrocycle are bridging the two bismuth(III) atoms Bi and Bi′. Interestingly, these bridging nitrogens are not equivalent; selected bond lengths and angles characterizing the coordination polyhedron are given in Table 1: N11 and N9′ are closer to Bi than to Bi′, and N9 and N11′ are closer to Bi′: N11−Bi = 2.695(8) Å, N11−Bi′ = 2.774(10) Å, N9−Bi′ = 2.693(11) Å, N9−Bi = 2,740(10) Å, while the four $Bi-N_{iso}$ bonds lengths of the cycles B or B′ are equivalent (mean length = 2.34 Å). The mean rotational angles between the macrocycles A and B, and between B and B′, measured on the more external benzene carbon atoms, are 38.3° and 0.5°, respectively. The distance between the two bismuth atoms in the molecule is 3.839(0) Å, and the distance between the two centres (Ct_A) and (Ct_B) of the macrocycles is 3.17 Å. We found many distances for pyrrolic carbon atoms between neighbouring A and B planes shorter than 3.3 Å. For example: C25′−C48 = 3.275 Å, C1−C40 = 3.262 Å, C41−C8 = 3.220 Å, C48−C9 = 3.289 Å. These distances are shorter than the van der Waals distance (3.4 Å) for aromatic carbon atoms, so that adjacent phthalocyanine planes are interacting by their π orbitals. The two mean-planes $4N_{iso\ B}$ and $4N_{iso\ B'}$ are strictly parallel on account of symmetry. The angle between these two mean-planes and the $4N_{iso\ A}$ plane is approximately 3.10° (±1.94). Thus, the coordination polyhedron is a distorted square anti-prism. We note that the hole at the centre of the macrocycle B (and B′) is slightly larger than the hole at the centre of the macrocycle A (the distances between N3 and N7 and between N1 and N5 are both 3.95 Å, while the distance between N11 and N11′ is 3.90 Å and between N9 and N9′ is 3.85 Å).

The deviations from the $4N_{iso\ A}$ plane and the $4N_{iso\ B}$ mean-plane for each atom of the asymmetric unit of the molecule are shown on Figure 2,b. Benzopyrrole cycles are numbered I, II, III, IV, V, and VI. We named the 5-membered and the 6-membered ring of benzopyrrole I as I5 and I6, respectively, and the 5-membered and the 6-membered ring of benzopyrrole II as II5 and II6, and so on. The macrocycles B and B′ are slightly convex, the four mean-planes of the pyrrole rings making dihedral angles of 6.26 (I), 6.67 (II), 10.46 (III), and 8.12° (IV) with the $4N_{iso\ B}$ mean-plane

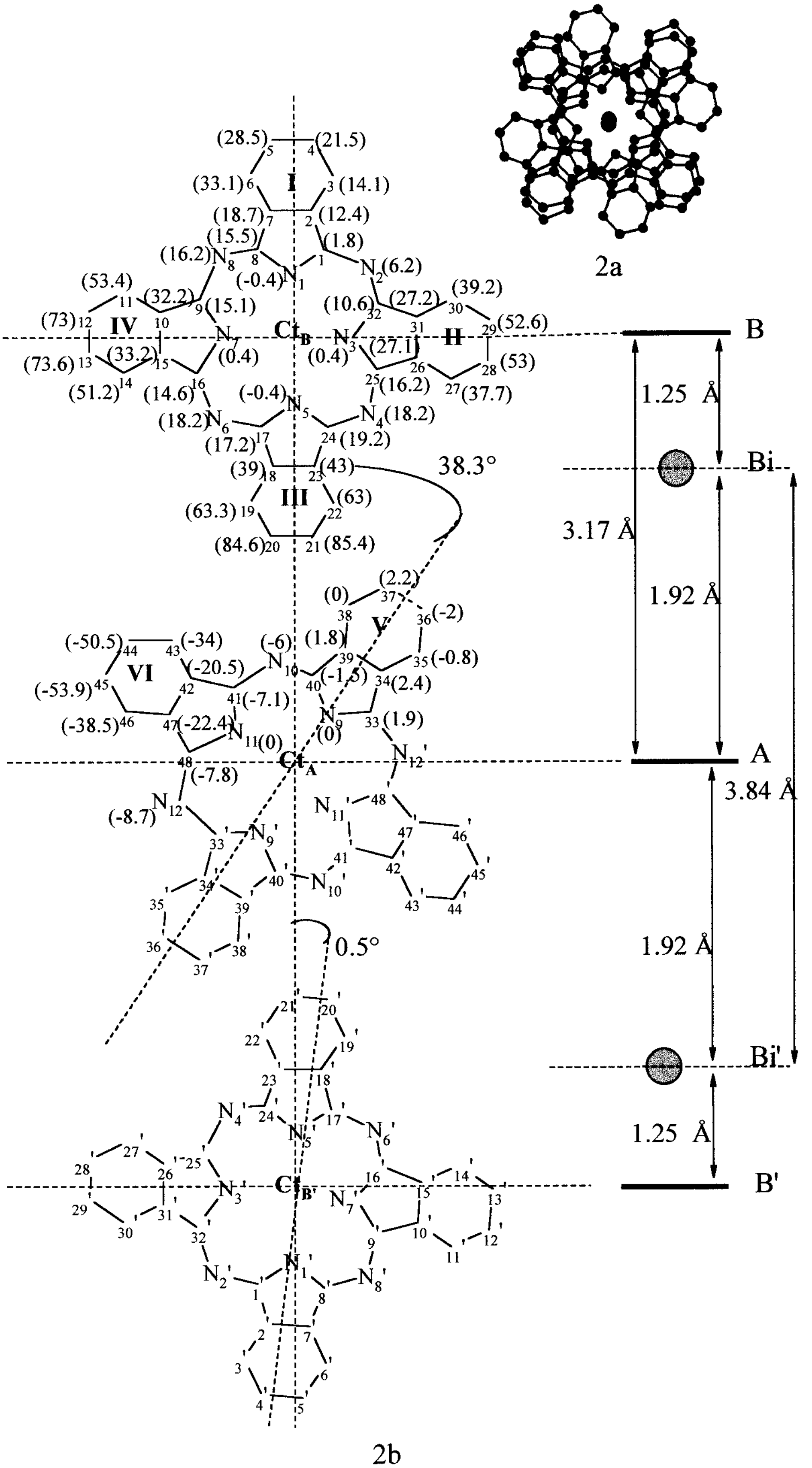

Figure 2. 2a) ORTEP drawing of $Bi_2(Pc)_3$ viewed along the Bi−Bi′ axis. − 2b) Split molecule of $Bi_2(Pc)_3$ with the three phthalocyanine rings projected along the Bi−Bi′ axis showing the numbering scheme and the staggering angles between the macrocycles. The deviation of each atom from the $4N_{iso\ A}$ and $4N_{iso\ B}$ mean-planes, respectively, are indicated in parentheses for the asymmetric unit

Table 1. Selected bond lengths (Å) and angles (deg) for $Bi_2(Pc)_3$

Bond lengths (Å)		Angles (deg)			
Bi−N1	2.339(10)	N1−Bi−N3	72.8(4)	N3−Bi−N11	149.4(3)
Bi−N3	2.348(9)	N1−Bi−N5	115.7(3)	N5−Bi−N7	74.5(4)
Bi−N5	2.330(9)	N1−Bi−N7	73.6(4)	N5−Bi−N9	147.7(3)
Bi−N7	2.326(11)	N1−Bi−N9	85.0(3)	N5−Bi−N11	137.7(3)
Bi−N9	2.740(10)	N1−Bi−N11	90.1(3)	N7−Bi−N9	137.4(3)
Bi−N11	2.695(8)	N3−Bi−N5	72.8(4)	N7−Bi−N11	82.3(3)
Bi−N9′	2.693(11)	N3−Bi−N7	115.3(4)	N9−Bi−N11	60.8(3)
Bi−N11′	2.774(10)	Bi−N9−Bi′	89.9(3)	Bi−N11−Bi′	89.1(4)
Bi−Bi′	3.838(9)	N3−Bi−N9	91.9(3)		
Bi−Bi	8.036(9)				

Table 2. Dihedral angles (deg) between $4N_{iso}$ mean-planes and pyrrolic cycles, and between pyrrole and benzene rings labelled 5 and 6, respectively

Mean-planes			Angles (deg)	
A	B	C	A−B	B−C
$4N_{isoB}$	I_5	I_6	6.26	1.75
$4N_{isoB}$	II_5	II_6	6.67	1.24
$4N_{isoB}$	III_5	III_6	10.46	0.53
$4N_{isoB}$	IV_5	IV_6	8.12	1.77
$4N_{isoA}$	V_5	V_6	0.92	1.52
$4N_{isoA}$	VI_5	VI_6	5.54	2.08

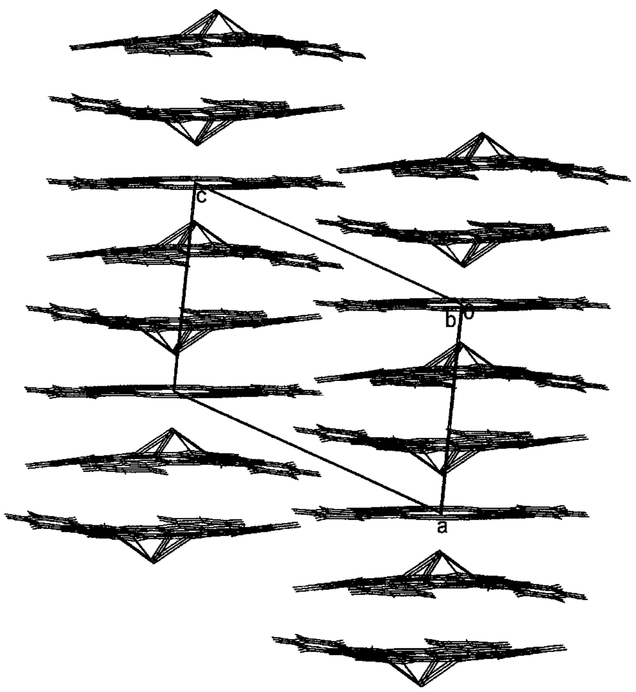

Figure 3. Projection along the *b* axis showing the columnar structure of the stacking of $Bi_2(Pc)_3$ molecules

(Table 2). Nevertheless, each benzopyrrole is nearly planar: all the angles between the pyrrole and benzene mean-planes are smaller than 1.8°. The most planar benzopyrrole (III) shows the greatest deviation from the mean-plane $4N_{iso\ B}$, and has the furthest external carbon atoms (C30 and C31) from the $4N_{iso\ B}$ mean-plane. Cycle A is nearly perfectly planar, but the benzopyrroles V and V′ are more coplanar than cycles VI and VI′, which spread slightly up and down from the $4N_{iso\ A}$ plane. The two mean-planes of the pyrrole rings make dihedral angles of 0.92 and 5.54° (±3.02) (V and VI). Dihedral angles between the pyrrole and benzene mean-planes are 1.52 (V) and 2.08° (VI).

Figure 3 shows the relative position of successive molecules in the stacking, viewed along the b axis. The stacking axis is the a axis. The closest atoms of two successive molecules in the stack lie at the distance of 3.284 Å (C4−C16). That distance is also lower than the van der Waals distance for aromatic carbon atoms. Adjacent external macrocycles of two neighbouring molecules in the stacking are also interacting by their π orbitals, so that all the phthalocyanine macrocycles are in interaction. The closest atoms in two neighbouring stacks, in the direction of the c axis, are C44 and C21, and lie at the distance of 3.497 Å apart. We have a columnar structure, in which $Bi_2(Pc)_3$ molecules are stacked segregatively, with the π orbitals of all the macrocycles interacting with each other along the column. Such a structure favours a good electrical conductivity, but since $Bi_2(Pc)_3$ is a closed-shell molecule, we think that this compound cannot be an electrical conductor without partial oxidation. Electrical properties of this triple-decker complex are currently being studied.

Similar to the comparisons made for lanthanoid phthalocyanines in the literature,[15,34,35] Table 3 compares our structure with those of double-decker compounds $Bi(Pc)_2,CH_2Cl_2$,[12] and $Bi(Pc)_2I_{1.5}$,[11] and with that of the bismuth monophthalocyanine-bismuth iodide complex.[10] The later contains a $BiPc^+$ moiety, and has the shortest distances for Bi−Ct (1.14 Å) and $Bi-N_{iso}$ (2.27 Å). In $Bi(Pc)_2,CH_2Cl_2$ the bismuth atom is nearly equidistant (1.48 and 1.50 Å) from the centres of the two $4N_{iso}$ mean-planes with a $Bi-N_{iso}$ length mean value of 2.47 Å, while in $Bi(Pc)_2I_{1.5}$, the Bi^{III} atom is not equidistant from the two Pc macrocycles (1.337 Å and 1.938 Å), and the structure shows alternating short and long $Bi-N_{iso}$ bond lengths (2.34 Å and 2.76 Å, respectively). The distance between the $4N_{iso}$ mean-planes that we observe for our triple-decker compound (3.17 Å) is intermediate between those of the two double-decker complexes $Bi(Pc)_2,CH_2Cl_2$ and $Bi(Pc)_2I_{1.5}$ (2.98 Å and 3.275 Å, respectively), in which the phthalocyanine macrocycles are oxidized. The benzopyrrole cycles of our complex have the same dimensions as those of the bisphthalocyanine, except the $N_{iso}-C_{\alpha}$ lengths that are longer in the triple-decker complex and the $C_{\delta}-C_{\delta}$ and $C_{\beta}-C_{\beta}$ bond lengths that are shorter.

It is very interesting to compare the structure of this black phase with the red-violet phase obtained by J. Janczak et al.[31] It is well-known that metallophthalocyanines crystallize in different phases depending of the crystallization method.[36] Generally, the molecular structure is only slightly affected but the stacking is different. In our case too, the molecular data of the two phases look very similar (Table 4), but there are some differences, principally in the stacking. The two molecules are alike with nearly the same coordination polyhedron, but the distances $Bi-N_{iso\ A}$ are slightly longer in the red-violet phase (2.747 Å) than in the black phase (2.726 Å). The staggering angle is equal to

Table 3. Comparison of the geometrical parameters for the black phase of $Bi_2(Pc)_3$ with those of other bismuth phthalocyanine complexes: the red-violet triple-decker phase,[31] the double-decker,[11–12] and monophthalocyanine[10] structures, reported in the literature

Compound Reference	$Bi_2(Pc)_3$ This work	$Bi_2(Pc)_3$ [31]	$Bi(Pc)_2$,CH_2Cl_2 [12]	$Bi(Pc)_2I_{1.5}$ [11]	$Bi(Pc)^+$ [10]
$M-Ct_A$ (Å)	1.92	1.92	1.48	1.94	
$M-Ct_B$ (Å)	1.25	1.25	1.5	1.34	1.14
$M-N_{iso\ A}$(Å)	2.72*[a]	2.75*[a]		2.76*[a]	
$M-N_{iso\ B}$(Å)	2.34*[a]	2.33*[a]	2.47*[a]	2.38*[a]	2.27*[a]
Rotation angle (deg)					
A–B	38.3	36.4	45	39.4	
B–B′	0.5	0	–	–	
Distance between planes (Å)	3.17	3.10	2.98	3.27	
Distance N–C (Å)					
$N_{iso\ A}-C_{\alpha A}$[b]	1.40*[a]				
$N_{iso\ B}-C_{\alpha B}$	1.40*[a]	1.39*[a]	1.36*[a]		1.38*[a]
$N_{aza\ A}-C_{\alpha A}$	1.34*[a]				
$N_{aza\ B}-C_{\alpha B}$	1.33*[a]	1.32	1.33*[a]		1.32*[a]
Distance C–C (Å)					
$C_\alpha-C_\beta$[c]	1.46*[a]		1.46*[a]		
$C_\beta-C_\gamma$[d]	1.38*[a]		1.38*[a]		
$C_\gamma-C_\delta$[e]	1.38*[a]	1.38*[a]	1.38*[a]		1.39*[a]
$C_\delta-C_\delta$	1.37*[a]		1.39*[a]		
$C_\beta-C_\beta$	1.37*[a]		1.38*[a]		

[a] Distances with asterisk (*) are mean distances. – [b] C_α = C1, C8, C9, C16, C17, C24, C25, C32, C33, C40, C41 and C48. – [c] C_β = C2, C7, C10, C15, C18, C23, C26, C31, C34, C39, C42 and C47. – [d] C_γ = C3, C6, C11, C14, C19, C22, C27, C30, C35, C38, C43 and C46. – [e] C_δ = C4, C5, C12, C13, C20, C21, C28, C29, C36, C37, C44 and C45.

Table 4. Crystallographic data for $Bi_2(Pc)_3$. Black and red-violet phases are compared

	Black phase (this work)	Red-violet phase[31]
Formula	$Bi_2C_{96}H_{48}N_{24}$	$(C_{32}H_{16}N_8)Bi_2$
Cryst. size, mm	0.03 × 0.04 × 0.08	0.14 × 0.12 × 0.07
Colour	black	red-violet
Cryst. syst.	triclinic	triclinic
Mol. wt	1955.6	1955.54
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	11.2179(5)	11.217(2)
b, Å	13.6180(6)	13.616(3)
c, Å	14.8834(8)	14.931(3)
α, deg	107.756(5)	107.7(3)
β, deg	99.725(5)	100.14(3)
γ, deg	112.932(4)	112.82(3)
V, Å^3	1883.8	1887.4(7)
Z	1	1
d_{calcd}	1.724	1.721
Diffractometer	STOE IPDS	
Radiation	(graphite monochromator) Mo-K_α, 0.71073 Å	
μ mm^{-1}	4.53	4.726
Scan mode	φ scan	
Scan step, deg	0.5	
Scan time, min/deg	12	
Scan total, deg	180	
2θ limits, deg	$2.9 \leq 2\theta \leq 48.4$	$2 \leq 2\theta \leq 52.2$
No. of data measured	6255	11996
No. of refined parameters	550	
Unique reflections	3572	6499
R_{int}(SHELXL-93):	0.0747	
Unique data with[$F_0 > 4\sigma$ (F_0)]	2026	
R_1	0.0398	0.0611
wR_2	0.0617	0.0720
Goodness-of-fit	0.619	1.005

36.4° in the red-violet phase and 38.3° in the other. The major difference between the two phases is found, as we have said, in the stacking. The red-violet phase is constituted of molecules stacked back to back along the stacking axis without interaction between the π orbitals of adjacent molecules, with the shortest intermolecular distances between the overlapping phthalocyaninato ring planes being 3.56 Å. Such an alternating of short and long distances between the phthalocyanines rings along the stack does not favour good electrical conductivity. In the black phase, the shortest interatomic distances between two adjacent molecules is 3.284 Å, while there are many interatomic distances between two adjacent (Pc) rings in the same molecule shorter than 3.3 Å. So the black phase appears as a regular stack of phthalocyanines rings which have their π systems in interaction with each other, and that structure favours good conductivity.

Infrared Spectroscopy

Literature on the vibrational spectroscopy of triple-decker Pc complexes is poor. The site of one-electron oxidation in several lanthanide porphyrin-phthalocyanine triple-decker complexes was studied by resonance Raman spectroscopy[22] and some mixed phthalocyaninato-porphyrinato europium(III) triple-decker complexes were characterized by IR and Raman spectroscopies.[25] Previous studies[37−44] on monophthalocyanines have separated and assigned the frequencies of the vibrations (strongly coupled in the macrocyclic ligand). Janczak recently reported IR and far IR spectra of $In_2(Pc)_3$ compared with those of $In(Pc)_2$. [37] Figures 4 and 5 show the far and middle infrared spectra, respectively, of our complex (a), compared with the well-known spectra (b)[1,40] of lead monophthalocyanine Pb(Pc). Isago et al.[8] reported that spectra of Bi(Pc)X (X = Cl, Br) in the middle IR region, resemble those of Pb(Pc). In both spectra of $Bi_2(Pc)_3$, (middle and far infrared) we observe the same absorptions at nearly the same frequencies as in the Pb(Pc) spectra. We attribute these absorptions to the vibrations of the two parts of $Bi_2(Pc)_3$ constituted by one bismuth ion and one macrocycle B or B′, which have the same structure as Pb(Pc). We note some supplementary absorptions in each group of vibrations that we attribute to the vibrations of the moiety formed by the two bismuth atoms and the macrocycle A.

Analysis of the Far Infrared Spectra

Far and middle IR spectra of $In_2(Pc)_3$ were reported recently.[37] The far IR spectrum is slightly more complicated than that of $Bi_2(Pc)_3$, while the middle IR spectra are very similar. Due to the fact that Bi atom is heavier than In, many bands are shifted to lower frequencies for the $Bi_2(Pc)_3$ spectrum. Five bands or groups of bands are characteristic of phthalocyanine ring deformations. They lie around 625, 560−600, 490, 430−440, and 350 cm^{-1}, nearly at the same frequencies for Pb(Pc) and $Bi_2(Pc)_3$. A more thorough examination of the spectra shows that the bands for $Bi_2(Pc)_3$ are larger and less resolved than the corresponding ones in Pb(Pc). Expansions of some of these bands followed by a deconvolution are shown on Figure 5,(I) and Figure 5,(II). The group centred at 625 cm^{-1} contains only one band at 626 cm^{-1} with a shoulder at 617 cm^{-1} in the spectrum of Pb(Pc), and three bands at 626, 617, and 622 cm^{-1} in the spectrum of $Bi_2(Pc)_3$ [Figure 5,(II)]. We assigned the two first bands to the deformation of the phthalocyanine rings B and B′, and the absorption at 622 cm^{-1} to the deformation of ring A. In Figure 4, the two bands at 279 and 154 cm^{-1} for $Bi_2(Pc)_3$ have the same intensity ratio and the same wavenumber difference as the two bands at 271 and 147 cm^{-1} for Pb(Pc). We assign these two bands, respectively, to the symmetric and asymmetric stretching modes of $N_{iso}-Bi-N_{iso}$ for B and B′ rings, and to the symmetric and asymmetric stretching modes of $N_{iso}-Pb-N_{iso}$, by reference to previous work.[44,47] We equally note two supplementary bands at 223 and 94 cm^{-1} in the spectrum of

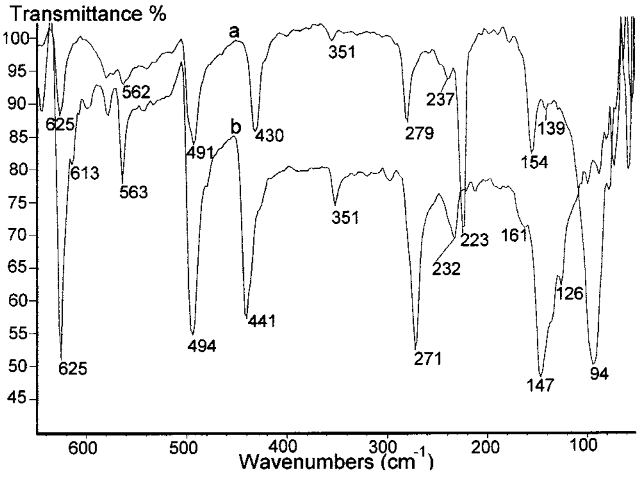

Figure 4. Far infrared spectrum of $Bi_2(Pc)_3$ (a) compared to that of Pb(Pc) (b)

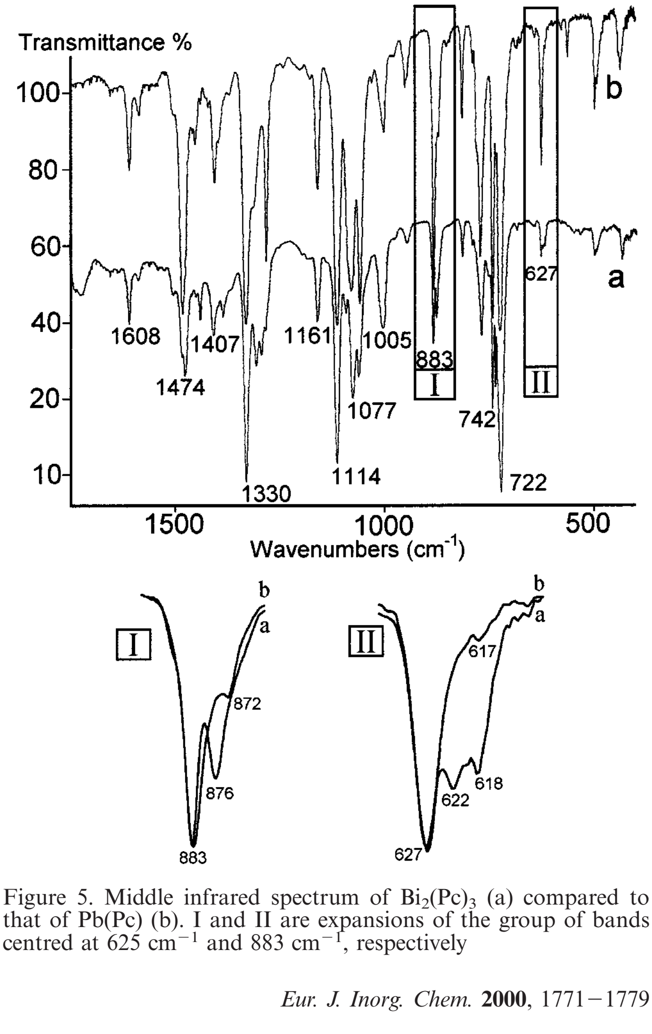

Figure 5. Middle infrared spectrum of $Bi_2(Pc)_3$ (a) compared to that of Pb(Pc) (b). I and II are expansions of the group of bands centred at 625 cm^{-1} and 883 cm^{-1}, respectively

$Bi_2(Pc)_3$. We assign these two new bands to the symmetric and asymmetric stretching modes of $N_{iso}-Bi-N_{iso}$ of macrocycle A. Their frequencies are lower than those of the same modes in the B macrocycle. This is in accordance with the bond lengths difference: 2.34 Å for the $Bi-N_{iso}$ distance of macrocycle B and B′, and 2.72 Å for the $Bi-N_{iso}$ distance of macrocycle A.

Analysis of Spectra in the Middle Infrared

The band, which lies at 883 cm^{-1} in both the spectra of Pb(Pc) and $Bi_2(Pc)_3$, is described in the literature as a metal-dependant vibration of the macrocycle.[39] This band, extended in Figure 5,(I), presents a new band at 876 cm^{-1} in the $Bi_2(Pc)_3$ spectrum, at the low wavenumbers side beyond a shoulder at 872 cm^{-1} which is evident in both spectra. We still consider this new band as a metal-dependant vibration of macrocycle A. Other supplementary bands assigned to macrocycle A are visible at 1294, 1306, and 1474 cm^{-1} in the area of the C−C stretching modes. A small band at 1385 cm^{-1} becomes very intense when the sample is allowed to age in dark at 4−10 °C for several months. The initial IR spectrum is restored when the aged sample is placed under reflux in an aqueous solution of 0.2 M NaOH.

In conclusion of this paragraph, we consider that the new bands assigned to macrocycle A, and particularly the bands related to the $Bi-N_{iso}$ vibrations, are a typical fingerprint of homoleptic triple-decker phthalocyanine complexes.

UV/Visible Spectroscopy

UV/Visible spectroscopy was largely used for the study and the characterization of rare earth triple-decker phthalocyanines. The spectra of $M_2(Pc)_3$ (M = Ln, In) are characterized by the presence of a large absorption band around 640 nm, with a shoulder or a little band more or less separated at larger wavelengths.[19,21,2,37] These two bands (Q_2 and Q_1, respectively) are due to an intramolecular π-π* interaction among the ligands, and are dependant on the distance between cycles in the triple-decker complex.[26,29] Theoretical studies[20,27] on $Lu_2(Pc)_3$ were compared with the experimental spectrum of (Pc)Lu(CRPc)Lu(Pc), which shows two major bands at 633 (Q_2) and 716 (Q_1) nm. The most intense band (633 nm) was assigned to an exciton coupling state, in which all the transitions moments in the Pc planes are in the same direction, the second (716 nm) was attributable mainly to a charge resonance state between two outer Pc′s. Two shoulder bands were observed at 580 and 550 nm. The former was assigned to a vibronic band associated with the 633 nm intense band, and the later attributed to another electronic excitation. In the B band region a broad band was observed at 330 nm.

We recorded the UV/Visible spectrum of $Bi_2(Pc)_3$ in pyridine (Figure 6, a), DMF (b), and DMSO (c). At the same concentration, spectra in pyridine and DMSO are similar. In DMF the spectrum is identical with that recorded in pyridine, but there is an hypsochromic shift of 43 nm ±3 for all the bands observable in the studied wavelength field. DMSO and pyridine are both molecules which are known to coordinate strongly in apical position the metal of the monophthalocyanines. DMF has the same behaviour, but is a weaker ligand. In all our spectra, the Q band exhibits splitting in Q_1 and Q_2 bands. In pyridine Q_1 lies at 718 nm and Q_2 at 644 nm. In disagreement with the observations reported about the spectra of $Ln_2(Pc)_3$ and that of $In_2(Pc)_3$,[37] the most intense band is Q_1 at 718 nm, while Q_2 at 644 nm is smaller. Another remark refers to the value of the Q band splitting, which is reported to decrease as the interplanar distance increases.[20,28] For (Pc)Lu(CRPc)Lu(Pc) this splitting value is 83 nm with a interplanar distance fixed at 2.9 Å. As our interplanar distance is measured by the crystallographic study (3.17 Å), we expected a splitting value significantly smaller than 83 nm. The difference in the position of Q_1 and Q_2 bands is 74 nm. Nevertheless, K. Takahashi et al.[29] reported that as the interplanar distance lengthens, the intensity of Q_1 decreases, and that of Q_2 increases. One important difference with these results is the inversion of the intensities of the Q_1 and Q_2 bands. The B band region is more complicated and varies with the solvent. Some authors[48,49] have described, in addition to the B band, two other bands at lower wavelengths, the N band resulting mainly from a transition $b_{2u}(\pi) \rightarrow e_g(\pi^*)$, 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. In pyridine, the B and N bands are visible at 342 nm and 288 nm, respectively. In DMSO, the B band also lies at 342 nm, while the N band shifts to 272 nm, and the L band appears at 235 nm.

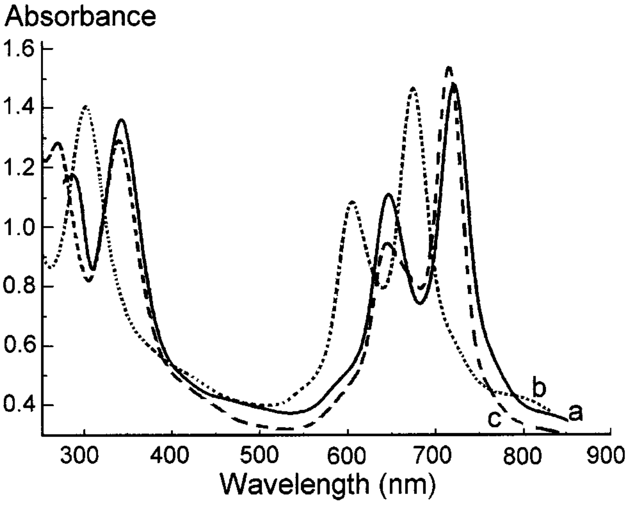

Figure 6. UV/Visible spectra of $Bi_2(Pc)_3$ in pyridine (a), DMF (b), and DMSO (c)

Conclusion

We have prepared a black phase of the tris(phthalocyaninato)dibismuth(III), $Bi_2(Pc)_3$, by a direct and fast template synthesis from bismuth acetate and phthalodinitrile. X-ray crystal analysis shows a triple-decker structure with two bismuth cations sandwiched between three phthalocyaninato ligands, the central macrocycle being rigorously planar, and the two external macrocycles convex. These latter are al-most superimposable, while the central ligand is rotated by about 38.3° in relation to the peripheral Pc rings. The four Bi−N bond lengths involving isoindole nitrogens of the external phthalocyanines (mean: 2.34 Å) are shorter than those involving isoindole nitrogens of the central plane (mean: 2.72 Å). The distance between $4N_{iso}$ mean-planes in the molecule is 3.17 Å, and the shortest distance between two atoms belonging to two neighbouring molecules is 3.28 Å. This structure is closely related to that described by J. Janczak and R. Kubiak for a red-violet phase of $Bi_2(Pc)_3$, but the stacking is more compact and more regular in the black phase. The infrared spectra of $Bi_2(Pc)_3$ compared with that of Pb(Pc) allowed us to distinguish some deformations typical of the internal macrocycle from those of the peripheral ones. Particularly, the symmetric and asymmetric stretching modes of the $N_{iso}-Bi-N_{iso}$ groups related to the isoindole nitrogens of the central ring are identified, and differentiated from the similar groups belonging to the external rings. That differentiation is proposed as a typical fingerprint of homoleptic triple-decker phthalocyanine complexes having a similar structure. The UV/Visible spectrum of $Bi_2(Pc)_3$ is similar to all those published for $Ln_2(Pc)_3$ compounds, with the Q band split into two bands, Q_1 and Q_2. Nevertheless, we observe an inversion of the intensities of these bands, Q_1 being significantly more intense than Q_2. The presentation of these results which associates a complete crystallographic structure and the UV/Visible spectrum may be the first step for a theoretical study of the excited electronic states of $Bi_2(Pc)_3$.

Experimental Section

General Remarks: The FT-IR spectra were recorded on either a Nicolet 20 SXB spectrometer with 2 cm^{-1} resolution, or a Perkin−Elmer spectrum 1000 with 1 cm^{-1} resolution, using KBr pellets (1%) on 4000−400 cm^{-1} range and polyethylene pellets (10%) on 400−80 cm^{-1} range. UV/Visible Spectra were recorded on an Unicam UV 4 spectrometer using 10^{-4} M solution concentrations.

Synthesis and Purification: Bismuth acetate was prepared in the laboratory from bismuth nitrate·$5H_2O$ (R.P. Prolabo) using the classic method of preparation of metallic acetates,[50] by dissolving metals or metallic salts in a minimum quantity of hot concentrated nitric acid and subsequent addition of acetic anhydride (puriss. p.a. Fluka AG). Bismuth acetate (1.9 g, 5 mmol) and phthalonitrile (6.5 g, 50 mmol, puriss 99% Fluka chemica) were ground, and placed in a long glass tube, one end of which was sealed and welded with a glass rod. This reaction vessel was placed in a tubular oven at 240 °C and the extremity of the glass rod, which is out of the oven, is fixed in a chuck of a stirring shaft. The reaction mixture was rapidly heated to 310 °C during 30 min. When the reaction tube was taken out of the oven immediately after the end of the reaction and then kept at room temperature, the crude product contained many crystals. The obtained powder was washed with organic solvents in the following sequence: acetone, ethanol, benzene, acetone, dimethylformamide, chloronaphthalene, then quinoline, benzene and finally washed with ethanol and dried. The product was poured in an aqueous solution of NaOH 0.2 M and placed under reflux for 30 min. The solution was filtered and rinsed with hot distilled water until complete neutralisation of the filtrate. After washing with ethanol the product was dried at 60 °C (yield ca. 63%). This washing procedure produced a shiny black crystalline powder. Very little crystals were selected and manipulated under binocular lens at the magnifying power ×64.

Chemical Analysis: The demetallation of $Bi_2(Pc)_3$, by contact with acidic solutions was used for a chemical analysis giving the number of phthalocyanine macrocycles for one bismuth. $Bi_2(Pc)_3$ (833 mg, 0.426 mmol) was heated under reflux in 20 mL of a 35% HCl solution for two hours. The hydrolysis produced insoluble $H_2(Pc)$ and a soluble salt of bismuth (chloride or oxychlorides). Filtration, repeated washing procedures, and drying led to 665 mg (1.29 mmol) of $H_2(Pc)$ characterized by IR spectroscopy. An identical hydrolysis procedure was performed from 755.8 mg (0.38 mmol) of $Bi_2(Pc)_3$. The filtrate and the washing solutions together were made up to 500 mL with the addition of distilled water. The content of bismuth of the resulting solution, determined by AAS led to 0.76 mmol of elemental bismuth. Then we obtained 3 mol of $H_2(Pc)$ and 2 mol of bismuth for each mol of starting $Bi_2(Pc)_3$. That confirmed the high purity of our product.

X-ray Crystallographic Study:[51] One of the largest crystals (0.03×0.04×0.08 mm) obtained from the crude product after washing was picked out and stuck on a glass needle. Data collection and analysis were performed using STOE IPDS V2.78 Software on a STOE IPDS diffractometer. The crystal is a weak scatterer because of its size. By inspecting the reciprocal space with RECIPE program, reflections from three crystal domains could be detected. Reflections of all domains were integrated simultaneously with TWIN, which showed that the volume ratio of the domains was 16:11:1. All crystal systems shared a nearly common c^* axis in the reciprocal space. For the structure solution, the intensity data set of the biggest domain was employed. The structure was refined with isotropic-, then anisotropic temperature factors by full-matrix least-squares techniques using the SHELXL 97 program. The hydrogen atoms of the phenyl groups were located with geometrical correlation, and their thermal parameters were fixed. The final unweighted and weighted agreement factors converged to $R_1 = 0.0398$ and $wR_2 = 0.0617$; a goodness-of-fit calculation resulted in a value of 0.619. The drawing preparations were made by using the graphic program of the SHELXTL package. Crystal data details are given in Table 4.

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[1] A. Ahmad, R. A. Collins, *J. Phys. D: Appl. Phys.* **1991**, *24*, 1894−1897.

[2] K. Kumazawa, M. Yamanaka, *Jpn. J. Appl. Phys.* **1991**, *30*, 530−531.

[3] H. Tada, K. Saiki, A. Koma, *Surf. Sc.* **1992**, *268*, 387−396.

[4] L. Ottaviano, L. Lozzi, S. Santucci, S. Di Nardo, M. Passacantando, *Surf. Sc.* **1997**, *392*, 52−61.

[5] N. Papageorgiou, J. C. Mossoyan, M. Mossoyan-Déneux, G. Terzian, E. Janin, M. Göthelid, L. Giovanelli, J. M. Layet, G. Le Lay, *Applied Surf. Science* to be published.

[6] A. W. Snow, N. L. Jarvis, *J. Am. Chem. Soc.* **1984**, *106*, 4706−4711.

[7] R. B. Freas, J. E. Campana, *Inorg. Chem.* **1984**, *23*, 4654−4658.

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

[9] H. Isago, Y. Kagaya, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 3212−3215.

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

[11] J. Janczak, R. Kubiak, F. Hahn, *Inorg. Chim. Acta.* **1998**, *281*, 195−200.

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

[13] R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751−767.

[14] R. D. Rogers, A. H. Bond, S. Aguinaga, *J. Am. Chem. Soc.* **1992**, *114*, 2960–2967.

[15] A. De Cian, M. Moussavi, J. Fischer, R. Weiss, *Inorg. Chem.* **1985**, *24*, 3162–3167.

[16] P. N. Moskalev, I. S. Kirin, *Russ. J. Phys. Chem.* **1972**, *46*, 1019–1022.

[17] G. C. S. Collins, D. J. Schiffrin; *J. Electroanal. Chem.* **1982**, *139*, 335–369.

[18] M. Mossoyan-Déneux, D. Benlian, A. Baldy, M. Pierrot, *Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt.* **1988**, *156*, 247–256.

[19] M. M′Sadak, J. Roncali, F. Garnier, *J. Chim. Phys.* **1986**, *83*, 211–216.

[20] N. Ishikawa, Y. Kaizu, *J. Phys. Chem.* **1996**, *100*, 8722–8730.

[21] M. M′Sadak, J. Roncali, F. Garnier, *J. Electroanal. Chem.* **1985**, *189*, 99–111.

[22] T-H. Tran-Thi, T. A. Mattioli, D. Chabach, A. De Cian, R. Weiss, *J. Phys. Chem.* **1994**, *98*, 8279–8288.

[23] D. Chabach, A. De Cian, J. Fischer, R. Weiss, M. El Malouli Bibout, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 898–899.

[24] J. Jiang, R. L. C. Lau, T. W. D. Chan, T. C. W. Mak, D. K. P. Ng, *Inorg. Chim. Acta.* **1997**, *255*, 59–64.

[25] D. P. Arnold, J. Jiang, *Chem. Lett.* **1999**, *6*, 483–484.

[26] K. Kasuga, M Ando, H. Morimoto, M. Isa, *Chem. Lett.* **1986**, 1095–1098.

[27] N. Ishikawa, Y. Kaizu, *Chem. Phys. Lett.* **1994**, *228*, 625–632.

[28] K. Takahashi, Y. Tomita, Y. Hada, K. Tsubota, M. Handa, K. Kasuga, K. Sogabe, T. Tokii, *Chem. Lett.* **1992**, 759–762.

[29] K. Takahashi, J. Shimoda, M. Itoh, Y. Fuchita, H. Okawa, *Chem. Lett.* **1998**, 173–174.

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

[31] J. Janczak, R. Kubiak, *Polyhedron* **1999**, *18*, 2775–2780.

[32] R. Kubiak, J. Janczak, *J. Alloys Compd.* **1993**, *200*, L7–L8

[33] D. Chabach, M. Lachkar, A. De Cian, J. Fischer, R. Weiss, *New J. Chem.* **1992**, *16*, 431–433.

[34] J. W. Buchler, A. De Cian, J. Fischer, M. Kihn-Botulinski, H. Paulus, R. Weiss, *J. Am. Chem. Soc.* **1986**, *108*, 3652–3659.

[35] M. Moussavi, A. De Cian, J. Fisher, R. Weiss, *Inorg. Chem.* **1986**, *25*, 2107–2108.

[36] F. Iwatsu, T. Kobayashi, N. Uyeda, *J. Phys. Chem.* **1980**, *84*, 3223–3230.

[37] J. Janczak, *Pol. J. Chem.* **1998**, *72(8)*, 1871–1878

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

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

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

[41] T. Kobayashi, F. Kurokawa, N. Uyeda, E. Suito, *Spectrochim. Acta* **1970**, *26A*, 1313–1322.

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

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

[44] W. Kalz, H. Homborg; *Z. Naturforsch* **1983**, *38b*, 470–484.

[45] H. Homborg, W. Kalz; *Z. Naturforsch* **1984**, *39b*, 1490–1499.

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

[47] W.J. Kroenke, M. E. Kenney, *Inorg. Chem.* **1964**, *3*, 696–698.

[48] M .S. Haghighi, H. Homborg, *Z. Anorg. Allg. Chem.* **1994**, *620*, 1278–1284.

[49] A. Henrikson, B. Roos, M. Sundbom, *Theoret. Chim. Acta (Berl.)* **1972**, *27*, 303–313.

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

[51] T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, G. Wilkinson, *J. Chem. Soc.* **1965**, *6*, 3632–3640.

[52] Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-117152. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk]

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