

# Synthesis and Crystal Structure of Thallium(III) Bicyclic Phthalocyanine

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Janczak, J. and Kubiak, R., 1995. Synthesis and Crystal Structure of Thallium(III) Bicyclic Phthalocyanine. – Acta Chem. Scand. 49: 871–877 © Acta Chemica Scandinavica 1995.

A new synthesis of thallium bicyclic phthalocyanine {14,28-[3-(3-isoindolylimino)-1,1' isoindolediylidenodiaminothallium(III),  $C_{48}H_{24}N_{13}Tl = TIPcc$ ] has been performed from thallium and 1,2-dicyanobenzene under a low nitrogen pressure at 210 °C. The green complex compound of TIPcc crystallizes in the triclinic system, space group  $P\bar{1}$ , with  $z = 2$  in a unit cell of dimensions:  $a = 11.677(2)$ ,  $b = 12.391(3)$ ,  $c = 16.047(3)$  Å,  $\alpha = 75.65(3)$ ,  $\beta = 86.44(3)$ ,  $\gamma = 65.33(3)^\circ$ ,  $V = 2041.8(9)$  Å<sup>3</sup>. The structure was solved and refined on  $F$  to  $R = 0.0628$ ,  $wR = 0.0820$  and  $S = 0.77$  for 3524 independent reflection with  $4 \leq 2\theta \leq 50^\circ$  (Mo K $\alpha$  radiation) and 656 refined parameters. The crystal contains separate molecules of TIPcc. The bicyclic phthalocyaninato macrocyclic hexadentate ligand is composed of six isoindole units forming a distorted trigonal prism with its six N-donor atoms. The central place of the macrocyclic ligand is occupied by the thallium cation. The Tl–N distances range from 2.238(14) to 2.310(13) Å. The conjugation in the inner 16-membered ring is interrupted by the two  $sp^3$ -hybridized C atoms. The details of the crystal structure are compared and discussed in relation to the structure of other phthalocyanines known in the literature.

Metallophthalocyanines have been intensively investigated for their application as molecular conductors or semiconductors and in the pigment industry.<sup>1–8</sup> Metallophthalocyanines of metals of the third main group of the periodic system have been less investigated. Until now only a few crystal structures with the metals of the third group have been described. For example, Wynne reported the crystal and molecular structures of chloro- and fluorophthalocyaninatogallium and aluminium and of  $[Al(Pc)]_2O$  and their iodine-doped derivatives.<sup>9–13</sup>

For the first time the thallium and indium phthalocyanine complexes have been obtained in the crystalline form by us.<sup>14</sup> Dithallium phthalocyanine possess a very high electrical conductivity, comparable even to metals.<sup>15</sup> This high conductivity may be assigned with the existence of the two-dimensional skeleton of –N–Tl–Tl–N–Tl–Tl–N–Tl–Tl–... bonds in the structure.<sup>16</sup>

The indium phthalocyanine complexes have been obtained in three different forms and can be expressed as  $In_2Pc_3$ ,  $InPc_2$  and  $InPcc$ . The first two indium phthalocyanines are blue–violet,<sup>17,18</sup> and the third is a green bicyclic phthalocyanine.<sup>19</sup> Several authors have also reported blue–violet and green compounds as products formed during the preparation of various lanthanide phthalocyanine complexes.<sup>20–25</sup> Kirin *et al.* identified, by elemental analysis, the blue–violet form as the lanthanide diphthalocyanine complex  $LnPc_2H$  and suggested a sandwich-type structure.<sup>26,27</sup> Later this suggestion was con-

firmed by X-ray single-crystal analysis,<sup>28–31</sup> but the acidic hydrogen could not be located.

For a long time analyses of the green compounds were inconsistent. Kirin *et al.*<sup>32</sup> suggested for the green form the formula  $Ln(Pc)Cl$ , because its optical spectrum was similar to that of monophthalocyanines. Misumi and Kasuga<sup>33</sup> prepared some rare-earth phthalocyanine complexes, which were characterized by elemental analysis and visible spectra. They also found the green complex, which they presumed to be a monophthalocyanine, and concluded that the blue–violet compound was a diphthalocyanine. However, MacKay *et al.*<sup>34</sup> concluded that under different conditions gadolinium diphthalocyanine could be green or blue–violet and that colour changes could be due to changes in the  $\pi$ -electron distribution. The elemental analysis given in Ref. 34 for the green form of Gd phthalocyanine does not conform to theoretical calculations for diphthalocyanine. In the previous papers we reported the preparation and structure of the green gadolinium(III) bicyclic phthalocyanine.<sup>35</sup>

Since both metals, indium and thallium, belong to the same main group in the periodic table, we attempted to synthesise the thallium analogues. However, until now only the formation of the dithallium phthalocyanine has been experimentally evidenced. The synthesis and crystal structure determination of the green thallium bicyclic phthalocyanine (TIPcc) are presented in this paper.

## Experimental

**Synthesis.** Thallium bicyclic phthalocyanine was obtained by the reaction of thallium (pure 99.999%) with 1,2-dicyanobenzene under a low nitrogen pressure (about  $10^{-1}$  atm). Filings of thallium were mixed with 1,2-dicyanobenzene in a weight proportion of 1:4. Next the mixture was pressed into pellets. The pellets were inserted into a glass ampoule under nitrogen pressure and sealed off. The ampoule was heated at 210°C. The heating process, continued for two days, led to the growing of single, green, good-quality crystals of the title compound. An analysis carried out on an energy-dispersive spectrometer (EDAX) gave: Tl, 21.02; C, 58.27; N, 18.52%. Calculated for  $C_{48}H_{24}N_{13}Tl$ : Tl, 20.70; C, 58.40, N, 18.45 and H, 2.45%.

**X-ray data collection.** The green parallelepipedal single crystal of  $C_{48}H_{24}N_{13}Tl$  (TlPcc) had a mean edge of 0.3 mm. Preliminary examination of the crystal by rotation and Weissenberg photographs indicated the triclinic system. Next the crystal was transferred to a four-circle Kuma Diffraction KM-4 diffractometer equipped with a graphite monochromator (Mo  $K\alpha$  radiation). The orientation matrices and unit-cell dimensions were refined by

the least-squares fit of 20 accurately centered reflections measured in the range  $15 \leq 2\theta \leq 20^\circ$ . A total of 5978 reflections were measured in the range  $4 \leq 2\theta \leq 50^\circ$  using the  $\omega/2\theta$  scan technique. Two standard reflections were monitored every 50 reflections. They showed no significant intensity variations. Intensities and standard deviations on intensities were corrected for Lorentz and polarization effects. A spherical absorption correction was made ( $\mu R = 0.61$ ). 5756 independent reflections ( $R_{int} = 0.0408$ , 3524 with  $F > 4\sigma$ ) were used for the crystal structure solution and refinement.

**Structure determination and refinement.** The structure was solved by the Patterson method, which revealed the position of the thallium atom. The remaining atoms were located in successive difference Fourier syntheses. Initially the structure was refined with isotropic, then anisotropic temperature factors by block-diagonal least-squares techniques, using the SHELXTL program system.<sup>36</sup> The hydrogen atoms of the phenyl rings were located by geometrical correlation and their positions and isotropic displacement parameters were refined. The function minimized was  $\sum w(F_o - F_c)^2$  with the weighting scheme  $w = 1/(\sigma^2 + 0.01 F^2)$ . An empirical secondary extinction correction was applied according to the for-

Table 1. Crystallographic data for TlPcc.

Formula	$C_{48}H_{24}N_{13}Tl$
Color	Green
Mol. wt.	987.2
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 11.677(2) \text{ \AA}$ $b = 12.391(3) \text{ \AA}$ $c = 16.047(3) \text{ \AA}$ $\alpha = 75.65(3)^\circ$ $\beta = 86.44(3)^\circ$ $\gamma = 65.33(3)^\circ$
Volume	$V = 2041.8(9) \text{ \AA}^3$
Z	2
$F(000)$	968
$D_{cal.}$	1.606
$D_{obs.}$ (flotation)/ $\text{g cm}^{-3}$	1.60
Radiation	Mo $K\alpha$
Diffractometer	Kuma Diffraction KM-4
Temperature	298 K
Scan speed/ $^\circ \text{ s}^{-1}$	Variable, 0.02–0.1
Scan width/ $^\circ$	1.3
$2\theta$ range/ $^\circ$	4–50
Index range	$-12 \leq h \leq 12, -13 \leq k \leq 13, 0 \leq l \leq 16$
Reflections collected	5978
Independent reflections	5756 ( $R_{int} = 0.0408$ )
Observed reflections	3524 ( $F > 4\sigma$ )
Standard reflections	2 measured every 50
LS parameters	565
Data/LS parameters	5.40
Abs. coeff., $\mu/\text{mm}^{-1}$	
Corrections	Lorentz polarizations, spherical absorption ( $\mu R = 0.61$ ), extinction
$R$ and $wR$ for observed reflections	0.0628, 0.0820
Goodness of fit	0.77
Mean $\Delta/\sigma$	0.013
Residual electron density/ $e \text{ \AA}^{-3}$	+2.40, -1.82

mula  $F_{\text{cor}} = F(1 + 0.002 \kappa F^2 / \sin 2\Theta)^{-1/4}$  where  $\kappa$  converged to 0.00075(13). The final unweighted and weighted residual error indices converged to  $R = 0.0628$  and  $wR = 0.0820$  for 3524 unique reflections. Residual electron density in the final Fourier difference synthesis was within  $+2.40$  and  $-1.82 \text{ e \AA}^{-3}$ . Scattering factors for neutral atoms and corrections for anomalous dispersion were as in SHELXTL, which was used for all the crystal structure calculations and drawing preparation (on an IBM PC AT computer). Details of the data collection parameters, crystal data and final agreement factors are collected in the Table 1.

## Results and discussion

*Synthesis and reactivity of TIPcc.* In a previous report<sup>14</sup> the reaction of metal fillings with molten 1,2-dicyanobenzene (in vacuum) was reported leading to the growth of phthalocyanine crystals. Here we slightly modified this method. In the present case the reaction was carried out under a low nitrogen pressure (ca.  $10^{-1}$  atm) in a sealed ampoule. Under these conditions green single crystals of TIPcc are formed beside  $\beta$ -Pc<sup>37</sup> and  $\text{Tl}_2\text{Pc}$ .<sup>15</sup>

The catalytic tetramerisation of 1,2-dicyanobenzene and formation of  $\beta$ -Pc is a competitive process to the formation of thallium bicyclic phthalocyanine. Although the reaction product was not homogenous, the separation of these compounds by the floating method was possible because the TIPcc crystals did not show observable solubility in the organic solvents used (benzene, cyclohexane, acetone,  $\alpha$ -bromonaphthalene, hexane etc.). The crystal showed no evidence of decomposition after 1 month of exposure to X-rays and the atmosphere. TIPcc, like another metallophthalocyanines, has a high thermal and chemical stability. These observations are in agreement with the suggestions derived from the crystal structure analysis. The most characteristic feature of TIPcc is its green colour, which is characteristic of bicyclic phthalocyanines, in which the  $\pi$ -electron delocalization in the inner 16-membered ring is interrupted by two  $\text{sp}^3$ -hybridized C atoms.

*Crystal structure of TIPcc.* The final positional coordinates and isotropic thermal parameters of the non-H atoms are given in Table 2. A view of the molecule together with the labelling scheme is shown in Fig. 1. Bond lengths and angles are collected in Tables 3 and 4, respectively.

The crystal structure of the thallium(III) bicyclic phthalocyanine consists of discrete molecules of six-coordinate  $\text{Tl(III)}$  surrounded by the six isoindole nitrogen atoms of the bicyclic phthalocyaninato chelate ligand.

The bicyclic phthalocyaninato ligand consists of a phthalocyaninato skeleton of four isoindole units bridged by two additional isoindole moieties (I and II). The six N-donor atoms of the whole bicyclic phthalocyaninato ligand coordinated to the central Tl atom form a distorted trigonal prism. The macrocyclic hexadentate chelate

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^3$ ).

Atom	x	y	z	$U(\text{eq})^a$
Tl(1)	806(1)	4552(1)	2630(1)	30(1)
N(1)	2675(13)	4669(13)	2452(10)	38(5)
N(2)	4151(13)	2593(14)	2430(10)	41(5)
N(3)	1929(13)	2913(14)	2083(10)	42(5)
N(4)	501(13)	3002(12)	1042(9)	32(4)
N(5)	-367(12)	4956(12)	1417(9)	33(4)
N(6)	-1777(12)	7121(12)	1230(9)	33(4)
N(7)	154(12)	6581(12)	2154(10)	35(4)
N(8)	2047(12)	6882(12)	2230(10)	38(4)
N(9)	3276(13)	1460(13)	3356(10)	34(4)
N(10)	1369(14)	2957(13)	3852(9)	38(5)
N(11)	-295(14)	3689(14)	4798(9)	43(5)
N(12)	-802(12)	5319(12)	3498(9)	33(4)
N(13)	-2053(13)	7415(13)	2597(10)	39(5)
C(1)	2857(16)	5733(17)	2369(11)	38(5)
C(2)	4211(18)	5412(17)	2374(14)	41(5)
C(3)	4889(16)	6148(5)	2361(12)	43(5)
C(4)	6201(18)	5562(19)	2351(13)	56(5)
C(5)	6848(10)	4298(19)	2375(12)	58(5)
C(6)	6136(16)	3555(4)	2407(12)	48(5)
C(7)	4866(17)	4174(18)	2419(11)	44(5)
C(8)	3859(16)	3722(16)	2426(11)	39(5)
C(9)	3233(14)	2063(15)	2473(11)	32(5)
C(10)	3646(16)	1119(14)	1933(12)	37(5)
C(11)	4766(13)	108(16)	2008(8)	39(5)
C(12)	4881(9)	-665(12)	1429(15)	51(5)
C(13)	3890(17)	-408(14)	862(12)	49(5)
C(14)	2707(14)	671(16)	812(9)	44(5)
C(15)	2665(15)	1371(14)	1402(12)	32(5)
C(16)	1596(16)	2515(14)	1525(11)	33(5)
C(17)	-357(15)	4114(15)	996(12)	36(5)
C(18)	-1523(16)	4639(14)	467(10)	30(5)
C(19)	-1988(11)	4060(10)	14(12)	45(5)
C(20)	-3248(16)	4777(17)	-373(12)	46(5)
C(21)	-3914(12)	6009(16)	-333(10)	45(5)
C(22)	-3361(14)	6570(7)	135(12)	42(5)
C(23)	-2181(14)	5815(14)	516(10)	28(5)
C(24)	-1444(14)	6065(14)	1105(11)	30(5)
C(25)	-1207(15)	7359(15)	1898(11)	34(5)
C(26)	-1196(16)	8646(15)	1581(11)	36(5)
C(27)	-2197(8)	9786(18)	1240(12)	48(5)
C(28)	-1905(12)	10788(9)	990(14)	52(5)
C(29)	-709(24)	10738(14)	1194(17)	76(6)
C(30)	346(5)	9532(15)	1545(12)	45(5)
C(31)	10(17)	8566(16)	1711(13)	42(5)
C(32)	794(16)	7238(15)	2076(11)	38(5)
C(33)	2514(16)	1841(15)	3912(11)	35(5)
C(34)	2589(17)	1135(18)	4818(14)	49(5)
C(35)	3531(14)	-37(14)	5255(9)	46(5)
C(36)	3323(20)	-499(5)	6095(15)	65(6)
C(37)	2219(19)	165(19)	6531(10)	61(6)
C(38)	1264(9)	1345(16)	6062(12)	48(5)
C(39)	1536(16)	1786(16)	5221(10)	34(5)
C(40)	803(15)	2917(15)	4578(11)	33(5)
C(41)	-1018(16)	4760(15)	4268(12)	40(5)
C(42)	-2306(17)	5495(16)	4564(13)	43(5)
C(43)	-2974(20)	5125(7)	5272(12)	60(5)
C(44)	-4169(19)	5989(19)	5335(13)	77(6)
C(45)	-4704(8)	7125(19)	4711(16)	70(6)
C(46)	-4045(16)	7434(13)	3975(8)	58(5)
C(47)	-2774(16)	6549(16)	3944(11)	37(5)
C(48)	-1880(16)	6509(16)	3251(12)	35(5)

<sup>a</sup> Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

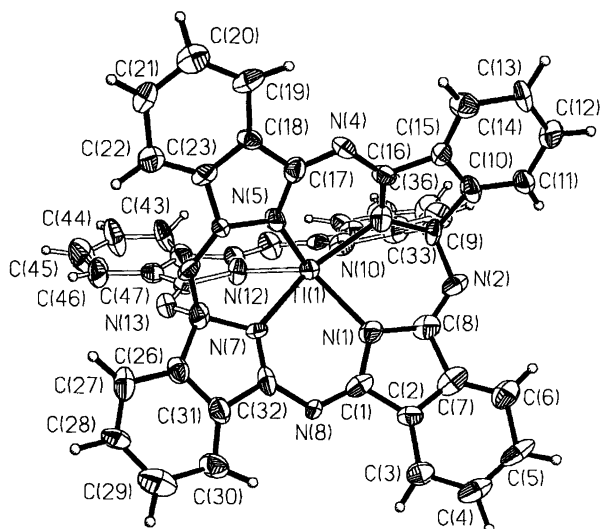


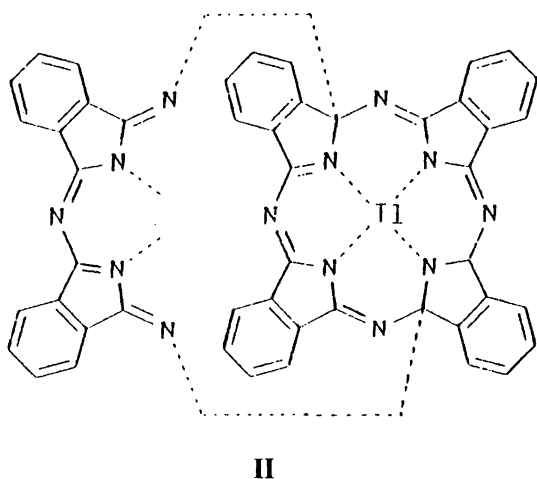
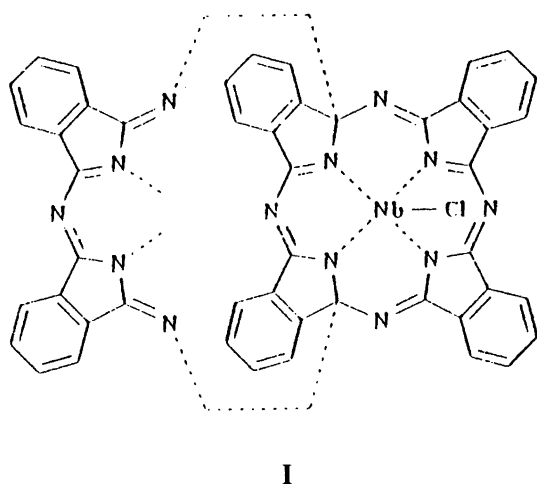
Fig. 1. View of the molecular structure of the  $C_{48}H_{24}N_{13}Ti$  complex with the atom numbering.

Table 3. Bond lengths (in Å).

Ti(1)–N(1)	2.245(17)	Ti(1)–N(3)	2.266(16)
Ti(1)–N(5)	2.278(15)	Ti(1)–N(7)	2.238(14)
Ti(1)–N(10)	2.310(13)	Ti(1)–N(12)	2.282(13)
N(1)–C(1)	1.394(30)	N(1)–C(8)	1.397(20)
N(2)–C(8)	1.292(27)	N(2)–C(9)	1.464(28)
N(3)–C(9)	1.507(19)	N(3)–C(16)	1.271(29)
N(4)–C(16)	1.359(22)	N(4)–C(17)	1.309(19)
N(5)–C(17)	1.373(27)	N(5)–C(24)	1.420(16)
N(6)–C(24)	1.265(24)	N(6)–C(25)	1.445(27)
N(7)–C(25)	1.494(19)	N(7)–C(32)	1.297(28)
N(8)–C(1)	1.310(21)	N(8)–C(32)	1.359(23)
N(9)–C(9)	1.422(22)	N(9)–C(33)	1.253(23)
N(10)–C(33)	1.454(19)	N(10)–C(40)	1.303(22)
N(11)–C(40)	1.331(20)	N(11)–C(41)	1.338(19)
N(12)–C(41)	1.324(23)	N(12)–C(48)	1.463(18)
N(13)–C(25)	1.443(23)	N(13)–C(48)	1.286(22)
C(1)–C(2)	1.461(28)	C(2)–C(3)	1.432(31)
C(2)–C(7)	1.384(28)	C(3)–C(4)	1.396(25)
C(4)–C(5)	1.417(30)	C(5)–C(6)	1.467(28)
C(6)–C(7)	1.357(23)	C(7)–C(8)	1.498(34)
C(9)–C(10)	1.527(28)	C(10)–C(11)	1.368(19)
C(10)–C(15)	1.351(27)	C(11)–C(12)	1.455(29)
C(12)–C(13)	1.396(27)	C(13)–C(14)	1.456(20)
C(14)–C(15)	1.419(28)	C(15)–C(16)	1.496(20)
C(17)–C(18)	1.459(24)	C(18)–C(19)	1.404(28)
C(18)–C(23)	1.355(22)	C(19)–C(20)	1.446(20)
C(20)–C(21)	1.411(26)	C(21)–C(22)	1.469(28)
C(22)–C(23)	1.377(20)	C(23)–C(24)	1.482(28)
C(25)–C(26)	1.554(28)	C(26)–C(27)	1.406(19)
C(26)–C(31)	1.396(29)	C(27)–C(28)	1.381(25)
C(28)–C(29)	1.426(33)	C(29)–C(30)	1.483(20)
C(30)–C(31)	1.370(28)	C(31)–C(32)	1.490(21)
C(33)–C(34)	1.487(26)	C(34)–C(35)	1.438(20)
C(34)–C(39)	1.382(25)	C(35)–C(36)	1.378(26)
C(36)–C(37)	1.455(27)	C(37)–C(38)	1.465(21)
C(38)–C(39)	1.396(24)	C(39)–C(40)	1.467(20)
C(41)–C(42)	1.516(24)	C(42)–C(43)	1.428(28)
C(42)–C(47)	1.350(22)	C(43)–C(44)	1.376(24)
C(44)–C(45)	1.421(26)	C(45)–C(46)	1.429(26)
C(46)–C(47)	1.438(21)	C(47)–C(48)	1.473(25)

Table 4. Bond angles (in Å)

N(1)–Ti(1)–N(3)	78.5(6)	N(1)–Ti(1)–N(5)	117.2(5)
N(3)–Ti(1)–N(5)	77.5(5)	N(1)–Ti(1)–N(7)	80.0(5)
N(3)–Ti(1)–N(7)	135.1(5)	N(5)–Ti(1)–N(7)	78.2(6)
N(1)–Ti(1)–N(10)	97.8(5)	N(3)–Ti(1)–N(10)	78.1(5)
N(5)–Ti(1)–N(10)	131.5(6)	N(7)–Ti(1)–N(10)	143.9(6)
N(1)–Ti(1)–N(12)	131.6(6)	N(3)–Ti(1)–N(12)	144.3(6)
N(5)–Ti(1)–N(12)	98.6(5)	N(7)–Ti(1)–N(12)	76.5(5)
N(10)–Ti(1)–N(12)	78.7(4)	Ti(1)–N(1)–C(1)	124.8(10)
Ti(1)–N(1)–C(8)	127.8(14)	C(1)–N(1)–C(8)	107.3(16)
C(8)–N(2)–C(9)	124.1(14)	Ti(1)–N(3)–C(9)	117.9(13)
Ti(1)–N(3)–C(16)	129.8(10)	C(9)–N(3)–C(16)	112.0(14)
C(16)–N(4)–C(17)	122.7(18)	C(9)–N(3)–C(17)	126.3(9)
Ti(1)–N(5)–C(24)	123.9(12)	C(17)–N(5)–C(24)	108.0(14)
C(24)–N(6)–C(25)	123.3(13)	Ti(1)–N(7)–C(25)	119.1(13)
Ti(1)–N(7)–C(32)	129.3(10)	C(25)–N(7)–C(32)	111.5(13)
C(1)–N(8)–C(32)	122.1(19)	C(9)–N(9)–C(33)	127.2(12)
Ti(1)–N(10)–C(33)	121.7(11)	Ti(1)–N(10)–C(40)	127.9(10)
C(33)–N(10)–C(40)	110.3(12)	C(40)–N(11)–C(41)	122.9(15)
Ti(1)–N(12)–C(41)	128.1(10)	Ti(1)–N(12)–C(48)	124.9(10)
C(41)–N(12)–C(48)	106.7(13)	C(25)–N(13)–C(48)	123.5(13)
N(1)–C(1)–N(8)	130.9(18)	N(1)–C(1)–C(2)	108.5(15)
N(8)–C(1)–C(2)	120.3(21)	C(1)–C(2)–C(3)	130.7(17)
C(1)–C(2)–C(7)	109.6(21)	C(3)–C(2)–C(7)	119.7(17)
C(2)–C(3)–C(4)	116.5(14)	C(3)–C(4)–C(5)	122.6(21)
C(4)–C(5)–C(6)	120.0(13)	C(5)–C(6)–C(7)	114.7(13)
C(2)–C(7)–C(6)	126.4(22)	C(2)–C(7)–C(8)	104.4(16)
C(6)–C(7)–C(8)	129.1(18)	N(1)–C(8)–N(2)	129.7(20)
N(1)–C(8)–C(7)	109.8(17)	N(2)–C(8)–C(7)	120.6(15)
N(2)–C(9)–N(3)	116.9(14)	N(2)–C(9)–N(9)	104.4(15)
N(3)–C(9)–N(9)	115.0(13)	N(2)–C(9)–C(10)	109.9(14)
N(3)–C(9)–C(10)	101.2(15)	N(9)–C(9)–C(10)	109.3(14)
C(9)–C(10)–C(11)	127.3(17)	C(9)–C(10)–C(15)	108.6(13)
C(11)–C(10)–C(15)	123.8(19)	C(10)–C(11)–C(12)	115.4(15)
C(11)–C(12)–C(13)	121.7(11)	C(12)–C(13)–C(14)	120.9(17)
C(13)–C(14)–C(15)	114.0(15)	C(10)–C(15)–C(14)	124.0(13)
C(10)–C(15)–C(16)	108.2(17)	C(14)–C(15)–C(16)	127.7(15)
N(3)–C(16)–N(4)	129.9(15)	N(3)–C(16)–C(15)	109.6(15)
N(4)–C(16)–C(15)	120.4(18)	N(4)–C(17)–N(5)	128.8(17)
N(4)–C(17)–C(18)	122.5(19)	N(5)–C(17)–C(18)	108.7(13)
C(17)–C(18)–C(19)	128.5(14)	C(17)–C(18)–C(23)	108.6(18)
C(19)–C(18)–C(23)	122.9(14)	C(18)–C(19)–C(20)	116.0(13)
C(19)–C(20)–C(21)	120.6(19)	C(20)–C(21)–C(22)	120.6(13)
C(21)–C(22)–C(23)	115.4(12)	C(18)–C(23)–C(22)	124.4(18)
C(18)–C(23)–C(24)	107.3(13)	C(22)–C(23)–C(24)	128.1(15)
N(5)–C(24)–N(6)	131.1(18)	N(5)–C(24)–C(23)	107.0(15)
N(6)–C(24)–C(23)	121.9(13)	N(6)–C(25)–N(7)	118.7(14)
N(6)–C(25)–N(13)	105.2(16)	N(7)–C(25)–N(13)	114.9(13)
N(6)–C(25)–C(26)	109.3(13)	N(7)–C(25)–C(26)	100.9(15)
N(13)–C(25)–C(26)	107.2(14)	C(25)–C(26)–C(27)	129.4(18)
C(25)–C(26)–C(31)	110.0(13)	C(27)–C(26)–C(31)	120.5(18)
C(26)–C(27)–C(28)	116.9(14)	C(27)–C(28)–C(29)	122.6(11)
C(28)–C(29)–C(30)	119.4(17)	C(29)–C(30)–C(31)	114.0(14)
C(26)–C(31)–C(30)	125.7(13)	C(23)–C(31)–C(32)	104.9(18)
C(30)–C(31)–C(32)	129.4(17)	N(7)–C(32)–N(8)	129.7(14)
N(7)–C(32)–C(31)	112.6(15)	N(8)–C(32)–C(31)	117.6(18)
N(9)–C(33)–N(10)	131.5(14)	N(9)–C(33)–C(34)	124.3(14)
N(10)–C(33)–C(34)	104.2(14)	C(33)–C(34)–C(35)	129.4(16)
C(33)–C(34)–C(39)	108.4(13)	C(35)–C(34)–C(39)	122.2(17)
C(34)–C(35)–C(36)	116.7(14)	C(35)–C(36)–C(37)	122.2(11)
C(36)–C(37)–C(38)	119.8(14)	C(37)–C(38)–C(39)	115.7(13)
C(34)–C(39)–C(38)	123.4(14)	C(34)–C(39)–C(40)	106.4(15)
C(38)–C(39)–C(40)	130.1(14)	N(10)–C(40)–N(11)	131.1(14)
N(10)–C(40)–C(39)	110.7(13)	N(11)–C(40)–C(39)	118.2(15)
N(11)–C(41)–N(12)	130.5(15)	N(11)–C(41)–C(42)	117.6(16)
N(12)–C(41)–C(42)	111.9(13)	C(41)–C(42)–C(43)	128.9(14)
C(41)–C(42)–C(47)	104.7(16)	C(43)–C(42)–C(47)	126.0(15)
C(42)–C(43)–C(44)	114.6(13)	C(43)–C(44)–C(45)	121.8(18)
C(44)–C(45)–C(46)	122.3(13)	C(45)–C(46)–C(47)	115.0(12)
C(42)–C(47)–C(46)	120.0(16)	C(42)–C(47)–C(48)	109.9(14)
C(46)–C(47)–C(48)	129.5(13)	N(12)–C(48)–N(13)	129.8(15)
N(12)–C(48)–C(47)	106.6(13)	N(13)–C(48)–C(47)	123.4(14)



ligand can also be described as two phthalocyaninato anions having one common half. It can be assumed that the macrocyclic ligand is less stable than the phthalocyaninato anion as the  $\pi$ -conjugation along the inner 16-membered ring is interrupted at the two  $sp^3$ -hybridized atoms C(9) and C(25) joining the ring to the bicyclic system. The interruption of the  $\pi$ -conjugation in the 16-membered ring is undoubtedly the reason for the specific green colour of metallobicyclic phthalocyanines. This is also the main reason for the two connected phthalocyaninato moieties not being planar. The whole macrocyclic chelate ligand is an anion with three negative charges. The same cyclic hexadentate ligand can be found in the indium and gadolinium complexes, which were also described by us.<sup>19,35</sup> A similar hexadentate ligand can be seen in  $[\text{Nb}(\text{Cl})(\text{C}_{48}\text{H}_{24}\text{N}_{13})]$ .<sup>38</sup> Although both thallium and niobium chelate compounds contain the ligand of the same chemical composition ( $\text{C}_{48}\text{H}_{24}\text{N}_{13}$ ), the ligands in them have a different structure. The main difference between these macrocyclic ligands is in the bridged atom heads. In TlPcc the bridged C atom heads belong to two opposite

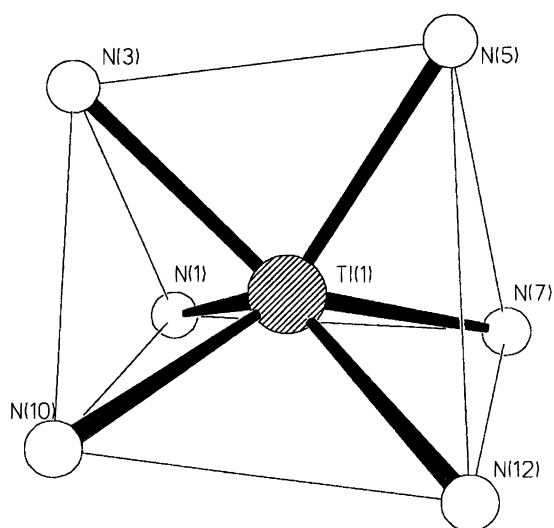


Fig. 2. Coordination of the central ion by isoindole N atoms in the bicyclic phthalocyanine.

isoindole rings of the phthalocyaninato units, whereas in the  $\text{Nb}(\text{Cl})\text{C}_{48}\text{H}_{24}\text{N}_{13}$  the bridged C atoms belong to two neighbouring isoindole units (I and II).

The C–N bond lengths in bicyclic phthalocyaninato ligand reflect the effect of conjugation. The C–N bonds at the head atoms C(9) and C(25) have average length of 1.464 and 1.460 Å, respectively, and are comparable to the corresponding bond lengths in InPcc,<sup>19</sup> GdPcc<sup>35</sup> and  $\text{Nb}(\text{Cl})\text{C}_{48}\text{H}_{24}\text{N}_{13}$ .<sup>38</sup> The bonds C(9)–C(10) and C(25)–C(26) are 1.527(28) and 1.554(28) Å, respectively, indi-

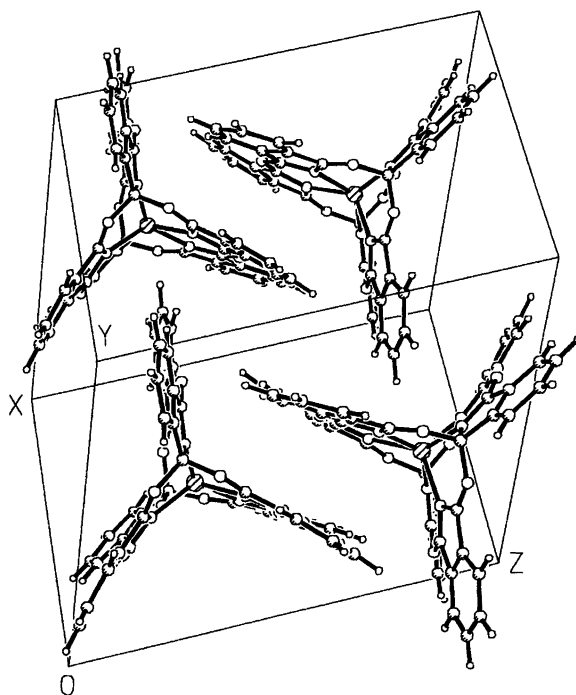


Fig. 3. Mutual arrangement of  $\text{C}_{48}\text{H}_{24}\text{N}_{13}\text{Tl}$  in the unit cell.

cating bond orders of 1. Five C–N bonds in the ring, with an average length of 1.278 Å, are double bonds, and the remaining fifteen C–N bonds in the macrocycle are intermediate between single and double bonds. This is typical for a conjugated  $\pi$ -electron system and comparable with the C–N bonds in other phthalocyanine structures.<sup>40–50</sup>

The dihedral angles between the two neighbouring mean least-squares planes of phthalocyaninato moieties are 104.2(3), 125.4(3) and 130.0(4)°. Each of the six isoindole rings are not exactly planar, the values of the dihedral angles between the pyrrole and the fused benzene rings ranging from 0.3(3) to 7.0(3)°. Comparison of some details from the crystal structures of other bicyclic phthalocyanines are collected in Table 5.

The central place of the bicyclic phthalocyaninato ligand is occupied the by thallium atom, the six Tl–N bonds lengths ranging from 2.238(14) to 2.310(13) Å. The geometry around the  $Tl^{3+}$  ion is shown in Fig. 2, the N–Tl–N angles are given in Table 4.

The mutual arrangement of the TIPcc molecules in the unit cell is shown in Fig. 3. The characteristic feature of the TIPcc crystal structure is the propeller like shape of the TIPcc molecules which are arranged so that the wings from adjacent molecules interpenetrate, similar to cogwheels in mechanical machinery. The shortest intermolecular distance between two neighbouring phthalocyaninato moieties planes is 3.359 Å. This value is comparable to the van der Waals distance of 3.4 Å for an aromatic carbon atom,<sup>51</sup> and indicates a weak interaction between

Table 5. Comparison between green metallobicyclic phthalocyanines ( $MC_{48}H_{24}N_{13}$ ).

	Tl	Gd	In
M–N distance/Å			
Min.	2.238(14)	2.231(6)	2.203(4)
Max.	2.310(13)	2.282(6)	2.267(4)
N–N distances in trigonal prism/Å			
N(1)–N(3)	2.853(18)	2.857(10)	2.853(13)
N(1)–N(7)	2.881(19)	2.873(9)	2.846(12)
N(1)–N(10)	3.434(21)	3.373(12)	3.320(16)
N(3)–N(5)	2.844(17)	2.832(11)	2.819(12)
N(3)–N(10)	2.883(20)	2.807(9)	2.793(12)
N(5)–N(7)	2.849(18)	2.856(10)	2.823(11)
N(5)–N(12)	3.458(22)	3.431(12)	3.343(15)
N(7)–N(12)	2.798(21)	2.776(10)	2.757(11)
N(11)–N(12)	2.911(19)	2.919(12)	2.881(12)
Dihedral angle between phthalocyaninato moieties (°)			
P1 and P2 <sup>a</sup>	130.0(4)	133.8(4)	134.1(4)
P1 and P3	125(3)	120.6(3)	120.0(3)
P2 and P3	104.2(3)	105.4(3)	105.9(3)
Dihedral angles between isoindole and fused phenyl ring planes	0.3(3)–7.0(4)°	0.9(3)–7.4(4)°	1.2(3)–7.6(4)°
Distance of Tl from plane defined by atoms: (in Å)			
N(1)N(3)N(10)	1.404(3)	1.402(3)	1.396(3)
N(5)N(7)N(12)	1.404(3)	1.404(3)	1.396(3)
N(3)N(5)N(10)N(12)	0.789(2)	0.786(2)	0.791(2)
N(1)N(3)N(5)N(7)	1.024(2)	0.989(2)	0.947(2)
Ionic radius (Å) for $M^{3+}$ and coordination number = 6	0.89	0.94	0.80
Ref.	This work	35	19

<sup>a</sup> Plane P1 defined by N(1),N(2),N(7),N(8),C(1)–C(8) and C(25)–C(32); P2 by N(3),N(4),N(5) and C(9)–C(24); P3 by N(11),N(12),N(13) and C(33)–C(48).

the atoms from these planes. This interaction is also observed in the sandwich type metallobisphthalocyanines.<sup>52-55</sup>

On the basis of our studies<sup>14,15-19,35,37,40,41,55,56</sup> we suggest in conclusion that the blue-violet colour is characteristic for all phthalocyanines in which full  $\pi$ -electron delocalization along the inner 16-membered ring exists, and green is the characteristic colour for bicyclic phthalocyanines where the  $\pi$ -electron delocalization is interrupted.

*Supplementary material.* Lists of observed and calculated structural factors and anisotropic thermal parameters, as well as other details, are available from the authors on request.

*Acknowledgement.* We would like to thank Professor Z. Gałdecki, Technical University of Łódź, Poland, for the opportunity to make the calculation using the SHELXTL program system in his laboratory. This work was supported by grant (No. 2 P303 117 06) from the Polish State Committee for Scientific Research.

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Received March 23, 1995.