Synthesis, Crystal Structure, and Magnetic Properties of Indium(III) Diphthalocyanine

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New form indium(III) phthalocyanine was obtained by the direct reaction of InMg alloy with 1,2-dicyanobenzene at 210 °C. The $InPc_2$ is isostructural with $SnPc_2$; it crystallizes in the orthorhombic system, space group $P2_12_12_1$, with unit cell parameters $a = 10.569(3)$ Å, $b = 50.868(11)$ Å, $c = 8.899(2)$ Å, $V = 4784.1$ Å^3, and $Z = 4$. The crystal structure was refined to $R = 0.0322$, $R_w = 0.0457$, and $S = 1.11$ for 731 refined parameters and 3898 independent reflections having with $F > 4\sigma(F)$. The crystals of $InPc_2$ contain sandwich-type molecules in which the indium atom is 8-fold coordinated by the isoindole nitrogens of two phthalocyanine rings. The average value of the In–N bond distance is 2.333 Å (2.327(4)–2.346(4) Å). The distance between phthalocyanine planes in this sandwich macromolecule is equal to 2.741(7) Å. The two phthalocyaninato moieties are rotated about 41.2(4)° with respect to one another. The magnetic susceptibility measurement shows a typical Curie–Weiss behavior. The effective magnetic moment is 1.67 μ_B. The EPR spectrum of $InPc_2$ exhibits a single strong signal at $g = 2.0025$.

Introduction

Metallodiphthalocyanines of the general formula MPc_2 (where M = metal and Pc = tetradendate phthalocyaninato ligand) form sandwich-type complexes. The central atoms in these compounds have a coordination number of eight. Among the large number of publications reporting metallodiphthalocyanines, until now few have dealt with the crystal structures of MPc_2, until now.[1–8] Similar to the metal-free phthalocyanine, which forms three crystalline forms: α, β and γ - form,[9–11] the metallodiphthalocyanines also exist in different crystalline modifications. For instance, α-tetragonal and β-monoclinic forms of $NdPc_2$ and β-monoclinic and γ-orthorhombic forms of $SnPc_2$ are known in the literature.[2,4,5] Moreover, Dorovskikh et al.[5] suggested that $NdPc_2$ also crystallizes in orthorhombic γ-form, for which the lattice parameters obtained from the powder diffraction diagram correspond to the known orthorhombic form of $SnPc_2$.[2]

Several authors have reported the preparation of two forms (blue and green) of rare-earth-metal phthalocyanine compounds[12–18]. MacKay et al.[15] reported that both the blue and green forms are rare-earth-metal diphthalocyanines. The blue lanthanide complexes were identified by Kirin et al.[13] as diphthalocyanines by elemental analysis, and the authors suggested that the green form was a monophthalocyanine, despite the lack of an elemental analysis. Similar suggestions have been reported by Yamana[19] for the dysprosium phthalocyanines Moussavi et al.[20] and De Cian et al.[21] stated that lutetium diphthalocyanine also exist in green and blue forms. Their study showed that the blue form is EPR inactive and diamagnetic and the green form is paramagnetic.

In our previous papers[22,23] we reported the synthesis and crystal structures of two forms of indium(III) phthalocyanines (blue-violet and green). The blue-violet form was identified as diindium triphthalocyanine. We stated that the green form is a bicyclic phthalocyanine.[23] Moreover we proved that the elemental analysis of $GdPc_2$ given by MacKay et al.[15] agrees much better with the formula appropriate for bicyclic phthalocyanine.[24] Therefore we suppose that the green phthalocyanines with the three valent metals are bicyclic phthalocyanines[23,24] not diphthalocyanines. Recently we obtained in the crystalline form the third complex (also blue-violet) of indium phthalocyanine. Its elemental analysis corresponds to the diphthalocyanine. Here we report the crystal structure and magnetic properties of $InPc_2$.

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Table 1. Crystallographic Data for $InPc_2$

chem formula	$C_{64}H_{32}N_{16}In$
fw	1139.9
space group	$P2_1 2_1 2_1$ (No. 19)
a/Å	10.569(3)
b/Å	50.868(11)
c/Å	8.899(2)
vol/Å^3	4784.3(17)
Z	4
T/°C	25
ϱ_{obsd}/g cm^{-3}	1.577 (by flotation)
ϱ_{calcd}/g cm^{-3}	1.582
λ/Å	1.5418
μ/cm^{-1}	45.32
$R = \sum\|\|F_o\| - \|F_c\|/\sum\|F_o\|\|$	0.0322
$R_w = (\sum w(\|F_o\| - \|F_c\|)^2/\sum w F_o^2)^{1/2}$	0.0457
$w = 1/[\sigma^2(F) + 0.0011F^2]$	

Experimental Section

Synthesis. The indium diphthalocyanine was prepared from InMg alloy and 1,2-dicyanobenzene, in 1:2 weight proportion, mixed together and pressed into pellets. The pellets were inserted into an evacuated glass ampule and sealed. The ampule was heated at 210 °C for 1 day, which yielded blue-violet good quality rectangular crystals with the edge up to 1 mm and also a blue polycrystalline material. Anal. Found on an energy-dispersive spectrometer for rectangular crystals: In, 10.10; C, 67.28; N, 19.81. Calcd for $C_{64}H_{32}N_{16}In$: In, 10.07; C, 67.44; N, 19.66 and H, 2.83. The polycrystalline material was identified (by X-ray powder diffraction and elemental analysis) as MgPc.

Crystallography. A blue-violet parallelepipedal single crystal of $InC_{64}H_{32}N_{16}$, having a mean edge of 0.25 mm, was used for data collection on a four-circle KUMA KM-4 diffractometer equipped with a graphite monochromator and Cu Kα radiation ($\lambda = 1.5418$ Å). Initial examination of the crystal by rotation and Weissenberg photographs indicated an orthorhombic system. The lattice parameters were refined by least-squares fit of 25 reflections measured in the 2θ range 30–50°. A total of 8020 reflections were measured in the range $4 \le 2\theta \le 160°$ [$((\sin\theta)/\lambda)_{max} = 0.639$] using the $\omega-2\theta$ scan technique. Three standard reflections were monitored every 100. They showed no significant intensity variations. Intensities and their standard deviations were corrected for Lorentz and polarization effects. A spherical absorption correction was applied ($\mu R = 0.566$). An empirical secondary extinction correction was applied according to the formula $F_{cor} = F(1 + 0.002\kappa F^2/\sin^2\theta)^{-1/4}$ where κ converged to 0.0012(1). 4670 independent reflections [3898 with $F > 4\sigma(F)$] were used in the structure solution and refinement.

Structure Solution and Refinement. The structure was solved by the Patterson heavy-atom method, which revealed the position of the indium atom. The remaining atoms were located in a difference Fourier synthesis. The structure was refined with anisotropic thermal parameters by the block-diagonal least-squares method, using the SHELXTL program system.[25] Hydrogen atoms of the phenyl rings were introduced in the structure factor calculations by their computed coordinates (C–H = 0.98 Å) and isotropic temperature factors. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weighting scheme $w = 1/[\sigma^2(F) + 0.0011F^2]$. The final unweighted and weighted agreement factors converged to $R = 0.0322$ and $R_w = 0.0457$; a goodness of fit calculation resulted in a value of 1.11 at final convergence. The final difference map calculation showed no peaks of chemical significance; the largest was 0.60 e/Å^3 and was associated with the indium atom. Scattering factors for neutral atoms and corrections for anomalous dispersion were as given in the SHELXTL program system, which was used for all calculations and drawings. The absolute structure was determined, the two enantiomers differ by 0.0361 and 0.0484 on R and R_w, respectively. Final agreement factors and crystallographic data are given in Table 1 and in the supporting information. Final positional parameters are given in Table 2. Anisotropic thermal parameters and hydrogen atom parameters are deposited as supporting information.

Magnetic Susceptibility Measurement. The ac susceptibility measurements in the range 4.2–304 K were performed on a Lake Shore Series 7000 ac susceptometer. The external dc magnetic field was set at $H = 0$, the amplitude of the magnetizing field was equal to 10 Oe with a frequency of 333.3 Hz. Instrument calibration was routinely checked with $KCr(SO_4)_2$. The temperature dependent studies were carried out on a 50 mg sample. The reciprocal of the molar magnetic susceptibility *vs* temperature is presented in Figure 1.

Electron Paramagnetic Resonance Measurements. EPR measurements were made on SE-Radiopan and ESP 300E-Bruker X-band spectrometers at room temperature. The studies were carried out on solid samples of 2–5 mg. A single-line EPR spectrum at $g = 2.0025$ was observed for $InPc_2$. DPPH, TEMPO, and TEMPOL free radicals were used as standards for calculation of the spin concentration. The calculation of the spin concentration is 5.05×10^{20} spins/g (≅0.96 electron per macrocycle).

Results and Discussion

Description of the Structure. The crystal of the indium(III) diphthalocyanine complex consists of discrete $InPc_2$ molecules. A view of the molecule is shown in Figure 2, which also gives the numbering scheme. Selected bond distances and angles are collected in Table 3.

The macromolecule consists of indium atom and two phthalocyaninato ligands. The indium atom is located between two saucer-shaped isoindole phthalocyaninato units and is coordinated by eight nitrogen isoindole atoms, which form an irregular square antiprism. The ring systems are rotated by 41.2(4)° with respect to one another. For comparison, in other diphthalocyanines the ring systems are rotated: 42° in the orthorhombic γ-form of $SnPc_2$,[2] 37.9° in the monoclinic β-form of $SnPc_2$,[4] and 41° in $LuHPc_2$ and $LuPc_2$.[20,21] The two opposite squares of isoindole nitrogen atoms are 2.741(7) Å apart in $InPc_2$. The distances between the phthalocyaninato rings in other orthorhombic diphthalocyanines are 2.700 Å in $SnPc_2$[2] and 2.701 Å in $LuHPc_2$.[20] A shorter distance between the two opposite *N*-isoindole planes is seen only for $TiPc_2C_{10}H_7Cl$ (2.32 Å), because in this structure the two C–C σ bonds are present, which “staple” together both phthalocyaninato moieties at the opposite sites of the titanium ion.[26,27]

It appears that a rotation of exactly 45° in the diphthalocyanine structures would be hindered by the mutual overlap of the α-isoindole carbon atoms between the rings. The phthalocyaninato ligands are much closer than van der Waals distance of 3.4 Å for aromatic carbon atoms[28] which indicates that the carbon atoms between the phthalocyaninato planes are interacting.

The two phthalocyaninato tetradentate ligands are neither perfectly planar nor parallel to one another, but the each phthalocyaninato moieties bend away one from the other. The isoindole rings bend outward at angles of 5.9 to 10.5° relative to the planes defined by the four isoindole nitrogen atoms bond to the indium ion. The phenyl rings make angles of 0.8 to 11.0° with respect to the same (isoindole) planes.

The mean value of the 48 C–C distances and C–C–C angles in the phenyl rings are 1.390 Å and 120°, respectively. Despite the normal C–C and C–C–C values, the phenyl rings are not perfectly hexagonal. The largest deviation of the angle from 120° exists in the C(2)–C(7) ring; the angle at C(3) is equal to

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Table 2. Atomic Coordinates (×10^5) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $InPc_2$

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
In	92 636(4)	87 591(1)	79 807(4)	28(1)	C(25)	123 144(43)	87 733(12)	70 343(49)	37(1)
N(1)	96 993(40)	84 569(10)	98 912(43)	35(1)	C(26)	132 933(46)	85 956(13)	65 713(49)	41(1)
N(2)	81 118(42)	85 781(10)	117 642(43)	38(1)	C(27)	144 044(48)	86 322(15)	57 545(51)	55(1)
N(3)	87 793(39)	89 543(9)	102 756(42)	30(1)	C(28)	151 657(51)	84 110(17)	54 826(54)	67(1)
N(4)	90 526(39)	94 190(10)	96 436(42)	33(1)	C(29)	148 277(49)	81 656(14)	60 454(52)	53(1)
N(5)	104 762(39)	91 400(10)	81 990(43)	35(1)	C(30)	137 472(47)	81 279(13)	68 900(51)	46(1)
N(6)	123 597(40)	90 323(10)	67 550(45)	38(1)	C(31)	129 953(43)	83 507(12)	71 177(49)	37(1)
N(7)	114 075(37)	86 415(9)	78 654(45)	30(1)	C(32)	118 202(41)	83 842(11)	79 607(49)	33(1)
N(8)	113 305(40)	81 892(10)	87 586(45)	36(1)	C(33)	71 247(46)	82 981(13)	86 114(48)	38(1)
N(9)	72 948(39)	85 651(10)	83 553(42)	33(1)	C(34)	60 236(46)	82 542(14)	95 685(50)	43(1)
N(10)	59 693(40)	89 434(11)	89 187(44)	40(1)	C(35)	55 254(49)	80 278(13)	101 947(51)	51(1)
N(11)	77 137(39)	90 622(10)	72 640(42)	32(1)	C(36)	44 532(49)	80 564(15)	110 596(53)	62(1)
N(12)	88 521(42)	93 242(11)	54 423(44)	39(1)	C(37)	39 185(50)	82 996(19)	113 183(55)	72(1)
N(13)	96 049(40)	88 720(10)	54 782(43)	34(1)	C(38)	44 386(49)	85 279(15)	106 969(53)	60(1)
N(14)	106 295(42)	84 789(10)	45 198(43)	38(1)	C(39)	54 864(45)	85 013(14)	98 334(49)	41(1)
N(15)	91 844(41)	83 763(10)	65 410(41)	33(1)	C(40)	62 540(44)	86 900(13)	90 216(47)	35(1)
N(16)	77 966(40)	81 020(10)	80 449(46)	39(1)	C(41)	66 295(44)	91 107(12)	80 898(49)	37(1)
C(1)	103 736(45)	82 279(12)	96 703(48)	36(1)	C(42)	62 331(47)	93 830(14)	79 059(51)	45(1)
C(2)	98 723(47)	80 201(13)	106 332(48)	39(1)	C(43)	52 642(49)	95 308(15)	85 366(52)	53(1)
C(3)	101 352(50)	77 488(14)	106 773(50)	51(1)	C(44)	51 877(49)	97 942(16)	81 345(55)	62(1)
C(4)	94 028(52)	76 021(14)	116 561(51)	61(1)	C(45)	60 328(48)	99 042(14)	71 094(53)	57(1)
C(5)	84 287(51)	77 129(15)	125 055(51)	58(1)	C(46)	69 883(50)	97 561(15)	64 569(51)	54(1)
C(6)	82 118(49)	79 807(14)	124 967(49)	48(1)	C(47)	70 859(44)	94 955(12)	69 018(48)	35(1)
C(7)	89 394(45)	81 314(13)	115 123(48)	38(1)	C(48)	79 656(46)	92 904(12)	64 746(47)	36(1)
C(8)	88 722(43)	84 087(12)	110 785(47)	33(1)	C(49)	95 825(44)	91 308(13)	49 832(46)	35(1)
C(9)	81 237(43)	88 312(12)	113 674(47)	35(1)	C(50)	104 367(46)	91 607(13)	37 217(48)	40(1)
C(10)	73 448(47)	90 189(13)	122 114(47)	40(1)	C(51)	108 060(48)	93 782(13)	28 818(50)	48(1)
C(11)	64 501(49)	89 892(14)	133 415(50)	51(1)	C(52)	116 728(48)	93 452(15)	17 406(49)	50(1)
C(12)	58 140(50)	92 129(15)	137 976(52)	59(1)	C(53)	121 396(50)	90 883(17)	14 194(51)	60(1)
C(13)	60 470(48)	94 576(15)	131 439(52)	56(1)	C(54)	117 870(48)	88 747(16)	22 470(51)	55(1)
C(14)	69 157(46)	94 931(13)	120 467(51)	45(1)	C(55)	109 123(47)	89 126(14)	33 980(46)	43(1)
C(15)	75 725(47)	92 661(12)	115 659(46)	38(1)	C(56)	103 919(44)	87 339(14)	45 227(46)	38(1)
C(16)	84 961(45)	92 224(12)	103 937(48)	33(1)	C(57)	100 509(46)	83 186(13)	54 609(47)	37(1)
C(17)	99 839(45)	93 788(12)	86 831(48)	36(1)	C(58)	102 541(46)	80 332(12)	53 962(48)	37(1)
C(18)	106 564(46)	95 926(11)	79 851(49)	39(1)	C(59)	111 010(48)	78 734(14)	45 865(50)	48(1)
C(19)	104 726(47)	98 649(12)	80 120(52)	49(1)	C(60)	110 668(50)	76 085(14)	48 550(52)	57(1)
C(20)	112 926(50)	100 154(13)	71 313(54)	62(1)	C(61)	102 209(51)	74 970(14)	58 765(52)	57(1)
C(21)	122 571(51)	99 013(14)	63 083(54)	65(1)	C(62)	93 631(50)	76 505(14)	66 746(49)	50(1)
C(22)	124 339(48)	96 320(14)	62 622(52)	50(1)	C(63)	93 984(47)	79 217(12)	64 118(49)	40(1)
C(23)	116 141(45)	94 766(12)	71 365(51)	40(1)	C(64)	87 252(44)	81 375(11)	70 853(49)	35(1)
C(24)	115 135(45)	91 966(13)	73 311(47)	36(1)					

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

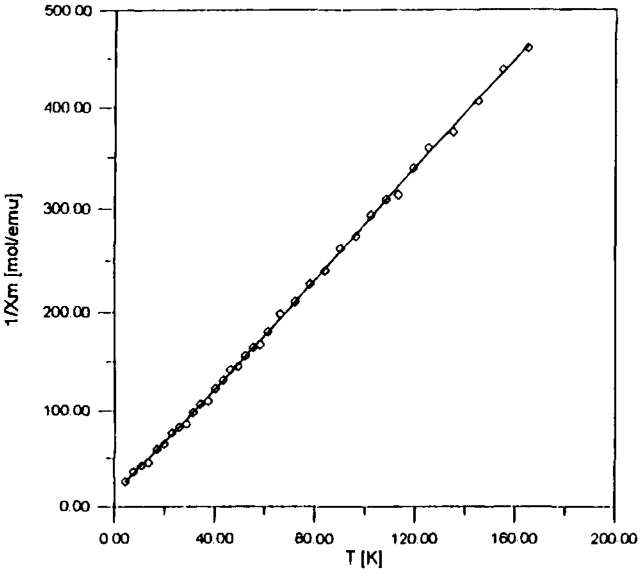

Figure 1. Plot of inverse molar susceptibility versus temperature for indium(III) diphthalocyanine.

115.8(5)°. Similar distortion has been noted in the other metallophthalocyanines,[29-34] but not explained.

The carbon–nitrogen distances in the isoindole rings range from 1.338(7) to 1.402(7) Å (mean 1.383 Å). The involving azamethine N–C distances range from 1.311(6) to 1.342(8) Å [mean 1.325 Å]. These distances are similar to those observed in other phthalocyanine structures.[35-39]

The indium–nitrogen distances range from 2.327(4) to 2.346(4) Å [mean 2.334 Å]. For comparison, in In_2Pc_3 the values are in the range from 2.184(3) to 2.352(3) Å[22] and run from 2.203(4) to 2.267(4) Å in the indium bicyclic phthalocyanine.[23] Shorter In–N distances are known to exist in an indium(III) porphyrin derivative [2.146(4)–2.160(4) Å].[40]

The four N–In–N base angles (nitrogen with the same phthalocyaninato plane) have a mean value of 71.6°, the two

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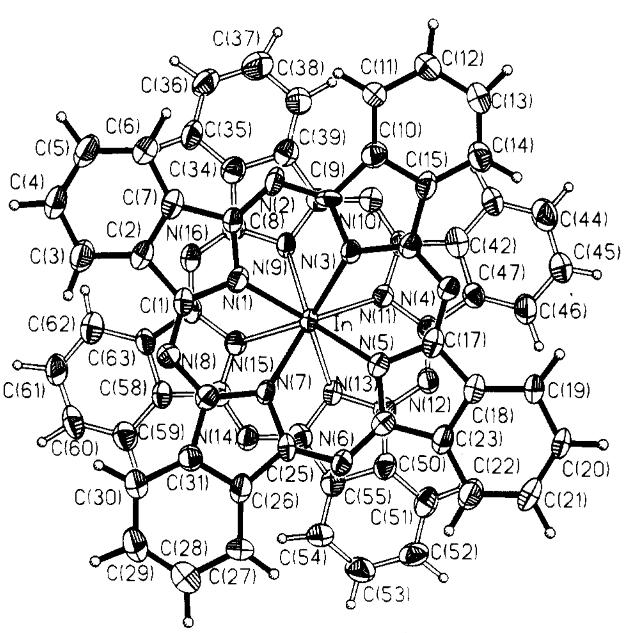

Figure 2. View of the $InPc_2$ and labeling scheme. Displacement ellipsoids are shown at the 50 % probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $InPc_2$

In–N(1)	2.338(4)	In–N(3)	2.328(4)
In–N(5)	2.331(5)	In–N(7)	2.346(4)
In–N(9)	2.327(4)	In–N(11)	2.338(5)
In–N(13)	2.328(4)	In–N(15)	2.332(5)
N(1)–In–N(3)	71.7(2)	N(1)–In–N(5)	112.2(2)
N(3)–In–N(5)	72.1(1)	N(1)–In–N(7)	71.0(1)
N(3)–In–N(7)	111.1(1)	N(5)–In–N(7)	71.6(2)
N(1)–In–N(9)	78.1(1)	N(3)–In–N(9)	81.9(1)
N(5)–In–N(9)	146.3(2)	N(7)–In–N(9)	139.6(2)
N(1)–In–N(11)	140.3(1)	N(3)–In–N(11)	78.7(1)
N(5)–In–N(11)	81.9(2)	N(7)–In–N(11)	146.4(2)
N(9)–In–N(11)	72.1(2)	N(1)–In–N(13)	145.8(2)
N(3)–In–N(13)	140.2(2)	N(5)–In–N(13)	77.9(2)
N(7)–In–N(13)	82.6(1)	N(9)–In–N(13)	112.3(1)
N(11)–In–N(13)	71.6(1)	N(1)–In–N(15)	81.8(2)
N(3)–In–N(15)	146.1(2)	N(5)–In–N(15)	139.4(1)
N(7)–In–N(15)	78.3(2)	N(9)–In–N(15)	72.1(2)
N(11)–In–N(15)	112.1(1)	N(13)–In–N(15)	71.7(2)

obtuse N–In–N angles being 111.1(2) and 112(2)°. The value of N–In–N angles have the same correlation in the second phthalocyaninato plane. The indium ion is located in the center of the molecule. The displacement of the phthalocyaninato planes from the In atom are equal to 1.312 and 1.303 Å, respectively for N(1), N(3), N(5), and N(7) and N(9), N(11), N(13), and N(15) planes.

The mutual arrangement of the $InPc_2$ molecules in the unit cell is illustrated in Figure 3. The structure is composed of two approximately perpendicular sheets. The intermolecular distance between indium atoms in the sheet is equal to 8.899 Å, and that between the two sheets is equal to 13.895 Å.

Magnetic Properties. Figure 1 shows the plot of inverse molar susceptibility versus temperature for indium(III) diphthalocyanine. A typical Curie–Weiss behavior is observed with no observable magnetic ordering down to 4.2 K ($\Theta \cong -7$). The effective magnetic moment, temperature-independent, is 1.67 μ_B and shows one unpaired electron per $InPc_2$ molecule. This unpaired electron is also exhibited by EPR spectroscopy as a strong signal at $g = 2{,}0025$ with a band width $\Gamma = 0.8$ G. For comparison, the values are $g = 2.002$ and $\Gamma = 2$ G for $LuPc_2$[41,42] and are comparable to those observed for a radical species of a π-conjugated ring systems.[43]

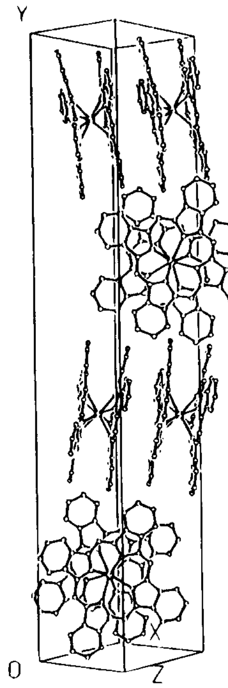

Figure 3. Molecular arrangement of the $InPc_2$ molecules in the unit cell.

The magnetic and EPR measurements are compatible with the $InPc_2$ formula. The diamagnetic closed-shell d^{10} indium (3+) cation is sandwiched between a phthalocyanine (Pc^{2-}) and a one electron oxidized phthalocyanine ($Pc^{\bullet-}$), which is responsible for the observed paramagnetism.

With the X-ray analysis no significant differences in In–N distances for both phthalocyaninato moieties were observed. Therefore, it is not clear whether the unpaired electron present in this complex is localized on one phthalocyanine ring or, more probably, delocalized over both phthalocyanine rings.

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Supporting Information Available: Tables of X-ray crystallographic details, full bond lengths, bond angles, anisotropic thermal parameters, H-atom coordinates, and isotropic thermal parameters (9 pages). Ordering information is given on any current masthead page.

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