Crystal and Molecular Structure of Diindium Triphthalocyaninate at 300 K*

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The new complex diindium triphthalocyaninate has been synthesised in crystalline form from the reaction of In–Sn alloy with 1,2-dicyanobenzene at 210 °C. It crystallizes in the triclinic system, space group $P\bar{1}$ with $Z = 1$ in a unit cell of dimensions $a = 14.492(3)$, $b = 13.179(3)$, $c = 11.493(2)$ Å, $\alpha = 113.96(2)$, $\beta = 97.15(2)$ and $\gamma = 66.13(2)°$. The structure was solved by Patterson and Fourier difference methods and refined by block-diagonal least-squares techniques to $R = 0.0282$, $R' = 0.0372$ and $S = 1.22$ for 7019 independent reflections having $F_o > 4\sigma(F)$. The centrosymmetric molecule consists of three phthalocyaninate ligands and two indium anions. The planes of the two peripheral ligands are parallel to each other, while the third central ligand is rotated about 37.5° in relation to the peripheral rings. The mean intramolecular distance between phthalocyanine planes is 2.954(5) Å. The angle of inclination of the central to the peripheral planes is 5.2°. The indium anions are located between the phthalocyaninate ligands and have six-co-ordinate geometry. The four In–N bonds involving isoindole nitrogens from peripheral phthalocyaninates [mean 2.223(3) Å] are shorter than the two involving isoindole nitrogens from the central phthalocyaninate [mean 2.350(3) Å]. The intramolecular distance between indium atoms is 4.036(5) Å. The shortest intermolecular distance between neighbouring successive phthalocyanine planes is 3.477(5) Å.

The composition and structure of the known metallophthalocyanines with elements of the main third group of the Periodic Table can be expressed by the general formula M(pc)X (X = monovalent anion) or $[M(pc)]_2Y$ (Y = divalent anion). Until now only a few crystal structures with trivalent metals have been described. Wynne reported the crystal and molecular structures of chlorophthalocyaninato-gallium(III) and -aluminium(III)[1] and of $[Al(pc)]_2O$.[2] High conductivity, thermal stability and other interesting physical properties are exhibited by fluoroaluminium and fluorogallium phthalocyaninates[3,4] and their partially iodine-doped derivatives.[5–7] The characteristic feature of the crystal structures of these fluoride phthalocyaninates is the existence of bridged-stacked polymers.[8] The chemical composition of the metallophthalocyanines with trivalent metals is strongly dependent on their method of preparation.[9–12] Contrary to the known and usually employed methods, we proposed a new method which allowed metallophthalocyanines to be obtained in crystalline form without additional anions.[13] By this method we obtained dithallium phthalocyaninate (its crystal structure was recently published by us[14]) and other phthalocyanines.[15–18] In this paper we present the crystal structure investigation of diindium triphthalocyaninate.

Experimental

Synthesis.—The compound $In_2(pc)_3$ was prepared from $InSn_4$ filings ($InSn_4$ alloy was obtained by melting indium and tin, in stoichiometric proportion, both 99.999% pure, under vacuum in a glass ampula) and 1,2-dicyanobenzene, in 1:2 weight proportion, mixed together and pressed into pellets. The pellets were inserted into an evacuated glass ampoule and sealed. The ampoule was heated at 480 K for 2 d which yielded two kinds of good-quality crystals. One kind was identified as Sn(pc);[17] the second as $In_2(pc)_3$.

Crystallography.—A violet parallelepipedal single crystal of $In_2(pc)_3$ having a mean edge of 0.30 mm was used for data collection on a four-circle Kuma KM-4 diffractometer equipped with a graphite monochromator and Cu-Kα radiation ($\lambda = 1.540\,56$ Å). Preliminary examination of the crystal by rotation and Weissenberg photographs indicated the triclinic system. The unit-cell parameters were refined by least-squares method fit of 20 reflections measured in the 2θ range 20–30°. A total 14 276 reflections were measured in the range $4 \leqslant 2\theta \leqslant 164°$ $[(\sin\theta/\lambda)_{max} = 0.643]$ using the ω–2θ scan technique. Two standard reflections $[(\bar{5}3\bar{1})$ and $(1\bar{2}\bar{3})]$ were monitored every 50. They showed no significant intensity variations. Intensities and their standard deviations were corrected for Lorentz and polarization effects. A spherical absorption correction was applied ($\mu R = 0.855$), but no extinction correction. 7288 Independent reflections [7019 with $F > 4\sigma(F)$, $R_{int} = 0.0345$] were used in the structure solution and refinement.

Structure determination and refinement. The structure was solved by using the Patterson heavy-atom method, which revealed the position of the In atoms. The remaining atoms were located in successive Fourier difference syntheses. Initially the structure was refined with isotropic, then anisotropic thermal parameters for all atoms (except H atoms) by the block-diagonal least-squares method, using the SHELXTL program system.[19] Hydrogen atoms were located, and their positions and isotropic thermal parameters were refined. The function minimized was $\Sigma w(|F_o|) - (|F_c|)^2$ with the weighting scheme $w = 1/\sigma^2$. The final unweighted and weighted agreement factors converged to $R = 0.0282$ and $R' = 0.0372$ for 7019 unique reflections (0.0306 and 0.0457 for all measured reflections). The residual electron density in the final Fourier difference syntheses was within -0.71 to 0.81 e Å^{-3}. Scattering factors for neutral atoms and corrections for anomalous dispersion were as in SHELXTL program system, which was used for all the crystal structure calculations and drawings (on an IBM PC AT computer). Final agreement factors and crystallographic data are given in Table 1, final positional parameters in Table 2.

Additional material available from the Cambridge Crystal-

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

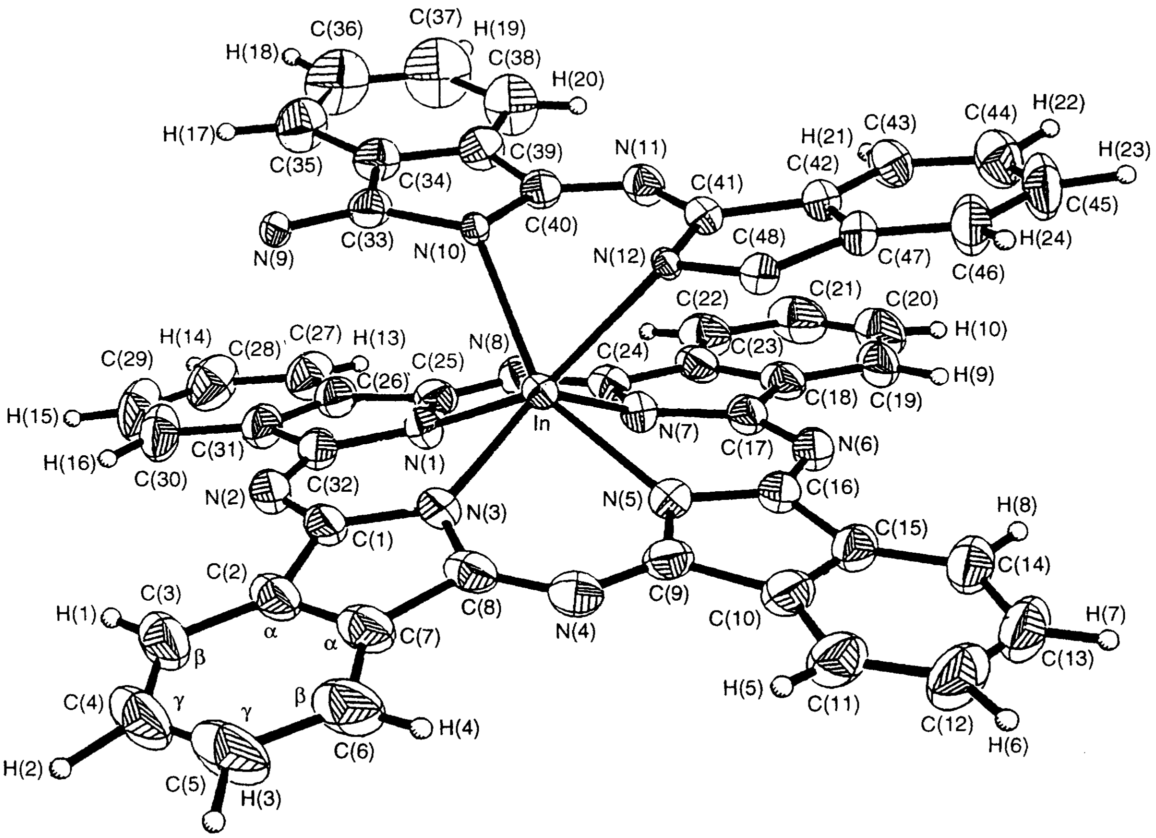

Fig. 1 View of molecular structure of the independent unit of $In_2(pc)_3$ and atom numbering

Table 1 Crystallographic data for $In_2(pc)_3$

Formula	$C_{96}H_{48}In_2N_{24}$
M	589.1
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	14.492(3)
b/Å	13.179(3)
c/Å	11.493(2)
α/°	113.96(2)
β/°	97.15(2)
γ/°	66.13(2)
U/Å^3	1832.2(6)
Z	1
F(000)	890
D_m/g cm^{-3}	1.58 (by flotation)
D_c/g cm^{-3}	1.602
Scan speed/° s^{-1}	Variable, 0.02–0.1
Scan width/°	1.3
h,k,l ranges	−16 to 16, −15 to 15, −13 to 13
Total reflections	14 276
Unique data	7288
Observed data	7019 [$F > 4\sigma(F)$]
Parameters	541 (+96 for H atoms)
Data/parameters	12.97 (11.02 with refinement H atoms)
μ/cm^{-1}	56.97
R	0.0282 (0.0306 for all reflections)
R'	0.0372 (0.0457 for all reflections)
Goodness of fit	1.22
Largest and mean Δ/σ	0.019, 0.002

lographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The crystal consists of discrete diindium triphthalocyaninate molecules. The independent part of the centrosymmetrically molecule is shown in Fig. 1, which also gives the numbering scheme. Important bond distances and angles for $In_2(pc)_3$ are in Table 3.

The macromolecule consists of two indium atoms and three phthalocyanine ligands. The indium atoms are located between phthalocyanine planes. The peripheral saucer-shaped phthalocyaninate unit is co-ordinated through four nitrogen isoindole atoms and the central phthalocyaninate moieties by two nitrogen isoindole atoms. All of the atoms in the peripheral unit lie below the isoindole nitrogen atom plane (plane 1). The closest non-hydrogen atom to the plane is C(17) at 0.010 Å, and the furthest are C(4) and C(5) at about −1.25(1) Å. The dihedral angle between this four-nitrogen plane (plane 1) and the all-atom (in this pc unit) least-squares plane is 3.9°. The distances of the atoms from the nitrogen isoindole plane increase from the centre to the periphery of the macrocyclic ligand. The phenyl ring C(18)–C(23) is closest to the plane at an average distance of −0.126 Å. Average distances from plane 1 are −0.505 Å for ring C(26)–C(31), −0.634 Å for ring C(10)–C(15) and −0.923 Å for ring C(2)–C(7). The dihedral angles of the phenyl rings with plane 1 show a similar pattern being 15.9, 10.2, 4.1 and 8.5° for rings C(2)–C(7), C(10)–C(15), C(18)–C(23) and C(26)–C(31), respectively. The phenyl ring C(2)–C(7) has the largest average displacement from the plane and bends toward a hole, away from the isoindole of an adjoining molecule. The isoindole rings are planar and show the same trend as that of the phenyl groups. The dihedral angles between plane 1 and the four isoindole planes are 16.1, 10.7, 3.8 and 7.6°, respectively. The central phthalocyaninate ligand plane (plane 10) makes an angle 5.2° with plane 1. The displacement of the phenyl ring C(34)–C(39) (average 0.734 Å) is smaller than that of the C(42)–(47) ring (0.854 Å) from the central pc plane. The isoindole [N(10)–C(33)–C(34)–C(39)–C(40)] and [N(12)–C(41)–C(42)–C(47)–C(48)] rings exhibit the same trend, the average atom distances from plane 10 being 0.265 and 0.326 Å. The dihedral angles of the above phenyl and isoindole

Table 2 Atomic coordinates (× 10^5) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
In(1)	50 851(1)	54 318(2)	85 324(2)
N(1)	65 208(17)	45 157(23)	73 384(24)
N(2)	76 013(19)	53 311(25)	88 744(26)
N(3)	58 419(18)	66 674(23)	95 105(24)
N(4)	44 076(20)	85 826(23)	104 109(26)
N(5)	38 715(18)	71 739(22)	86 479(25)
N(6)	28 178(18)	64 480(24)	69 835(25)
N(7)	45 492(17)	49 796(22)	65 583(23)
N(8)	60 280(19)	32 713(23)	53 512(25)
N(9)	73 806(17)	30 083(22)	93 178(24)
N(10)	56 685(16)	35 079(20)	85 810(23)
N(11)	42 534(18)	31 512(22)	73 668(24)
N(12)	37 386(16)	51 248(21)	90 852(23)
C(1)	68 739(23)	63 410(30)	95 834(30)
C(2)	70 669(26)	73 612(33)	105 525(32)
C(3)	79 583(29)	75 194(40)	110 120(37)
C(4)	78 693(38)	86 284(48)	119 421(42)
C(5)	69 322(41)	95 597(45)	123 957(43)
C(6)	60 462(33)	94 171(37)	119 317(39)
C(7)	61 342(27)	83 011(32)	110 037(32)
C(8)	53 693(24)	78 604(29)	103 096(30)
C(9)	37 287(23)	82 631(27)	96 313(30)
C(10)	26 921(24)	91 017(29)	96 569(33)
C(11)	21 712(28)	102 963(32)	104 723(38)
C(12)	11 699(30)	108 372(35)	102 362(44)
C(13)	7 065(28)	102 286(37)	92 299(44)
C(14)	12 176(25)	90 356(35)	84 139(37)
C(15)	22 268(23)	84 816(29)	86 579(32)
C(16)	29 896(22)	72 685(28)	80 210(30)
C(17)	35 407(22)	54 036(28)	63 051(29)
C(18)	33 725(24)	45 507(30)	50 979(30)
C(19)	24 998(26)	45 066(35)	44 567(35)
C(20)	26 167(33)	35 334(42)	33 127(39)
C(21)	35 626(35)	26 452(40)	28 005(37)
C(22)	44 338(29)	26 905(33)	34 328(34)
C(23)	43 138(24)	36 464(29)	46 074(30)
C(24)	50 465(22)	39 369(27)	55 333(28)
C(25)	66 981(22)	35 594(27)	61 777(30)
C(26)	77 817(23)	28 758(30)	59 309(32)
C(27)	83 457(27)	18 575(34)	49 001(37)
C(28)	93 869(29)	14 371(38)	49 665(41)
C(29)	98 466(27)	20 069(44)	60 113(45)
C(30)	92 910(25)	30 245(38)	70 417(38)
C(31)	82 436(22)	34 554(31)	69 748(33)
C(32)	74 357(21)	45 030(29)	78 349(30)
C(33)	66 763(20)	27 555(25)	85 517(28)
C(34)	68 765(23)	15 842(27)	75 137(29)
C(35)	77 471(26)	5 309(31)	70 955(36)
C(36)	76 578(34)	−4 526(35)	60 885(44)
C(37)	67 496(38)	−3 933(38)	55 176(45)
C(38)	58 830(31)	6 502(34)	59 311(39)
C(39)	59 668(23)	16 353(28)	69 495(30)
C(40)	52 175(21)	28 308(25)	76 283(28)
C(41)	35 593(20)	42 131(26)	80 776(28)
C(42)	24 812(21)	45 386(28)	79 214(30)
C(43)	19 235(25)	39 681(33)	70 184(35)
C(44)	8 827(28)	45 449(39)	71 627(42)
C(45)	4 107(26)	56 252(41)	81 938(45)
C(46)	9 597(24)	61 972(35)	90 928(38)
C(47)	20 103(21)	56 420(28)	89 152(30)
C(48)	28 056(20)	59 909(26)	96 395(28)

Table 3 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses

In(1)–N(1)	2.236(3)	In(1)–N(3)	2.184(3)
In(1)–N(5)	2.219(2)	In(1)–N(7)	2.223(2)
In(1)–N(10)	2.348(3)	In(1)–N(12)	2.352(3)
N(1)–In–N(3)	78.6(1)	N(1)–In–N(5)	124.5(1)
N(3)–In–N(5)	79.2(1)	N(1)–In–N(7)	77.2(1)
N(3)–In–N(7)	127.5(1)	N(5)–In–N(7)	77.6(1)
N(1)–In–N(10)	79.7(1)	N(3)–In–N(10)	121.9(1)
N(5)–In–N(10)	152.6(1)	N(7)–In–N(10)	98.3(1)
N(1)–In–N(12)	143.8(1)	N(3)–In–N(12)	134.5(1)
N(5)–In–N(12)	82.7(1)	N(7)–In–N(12)	87.8(1)
N(10)–In–N(12)	70.0(1)		

rings with the central pc plane 10 are 14.0, 13.6, 13.0 and 15.0°, respectively.

The six phenyl rings are planar, the largest deviation being 0.022 Å for C(47). The mean values of the 36 C–C distances and C–C–C angles are 1.388(5) Å and 120.0(4)°. The C–C–C angles range from 116.5 to 122.0°. The mean value of the 24 C–H distances is 0.98 Å. Despite the normal C–C and C–C–C values, the phenyl rings are not perfectly hexagonal. They show a distortion, the C^{α}–C^{β}–C^{γ} angles being less than 120°. Similar distortions have been noted in other phthalocyanines[14,20–22] but not explained.

The carbon–nitrogen distances in the macrocycle fall into two groups. Those of the isoindole rings range from 1.372(4) to 1.391(4) Å [mean 1.378(4) Å]. Those involving the azomethine N range from 1.319(4) to 1.332(4) Å [mean 1.323(4) Å]. These distances are similar to those observed in other phthalocyanine structures.[17,20–22]

The intramolecular distance between two pc ligand planes is 2.954 Å. The two peripheral phthalocyanine planes in $In_2(pc)_3$ are parallel and 5.818 Å apart, the third pc ring being is rotated by 37.5° with respect to them. For comparison, the rings are rotated by 37° and the planes are separated by 2.81 Å in $U(pc)_2$,[23] 38° and 2.94 Å in $Nd(pc)_2$,[24] 37.9° and 2.572(3) Å in β-$Sn(pc)_2$[18] and −42.0° and 2.70(4) Å in γ-$Sn(pc)_2$,[25] respectively.

The phthalocyanine rings in $In_2(pc)_3$ are much closer than the van der Waals distance of 3.4 Å for aromatic carbon atoms.[26] The average distance for an α-pyrrole carbon atom between neighbouring pc planes is 3.045 Å, and indicates that these carbon atoms interact weakly. The isoindole nitrogens belonging to the same ring form a square with a side 2.78 Å in length. Comparable values are observed for $U(pc)_2$ (2.80 Å),[23] Pt(pc) (2.80 Å),[22] α-pc (2.78 Å),[16] β-pc (2.83 Å)[15] and Sn(pc) (2.78 Å).[17]

The indium–nitrogen distances fall into two groups. The four involving isoindole atoms from the peripheral pc are shorter than the two involving isoindole atoms from the central pc. The averages are 2.223(3) and 2.350(3) Å, respectively. The remaining two isoindole nitrogen atoms from the central pc ring are at about 3.2 Å. The In atoms are located nearer to the peripheral pc plane than to the central pc plane, the distances being 1.005 and 1.838 Å, respectively. It appears that the indium atoms are more strongly connected to the peripheral pc rings than to the central pc ring. The displacements of In from the pc planes are much longer than in a indium(III) porphyrin derivative.[27]

The four N–In–N base angles (nitrogen with the same peripheral pc plane) have a mean value of 78.3(2)°, the two obtuse N–In–N angles being 124.5(2) and 127.6(2)°. The angle N–In–N (nitrogen with the central pc plane) is 70.0(2)°. The four N–In–N angles (nitrogen with neighbouring phthalocyanine plane) range from 79.7(2) to 98.3(2)°. The intramolecular In • • • In distance is 4.036 Å.

The packing of the $In_2(pc)_3$ molecules is illustrated in Fig. 2. The structure is composed of sheets of approximately parallel and overlapping molecules. These sheets are inclined at about 80, 50 and 41° to the *a*, *b* and *c* axes. The maximum overlap occurs between molecules stacked back to back along the

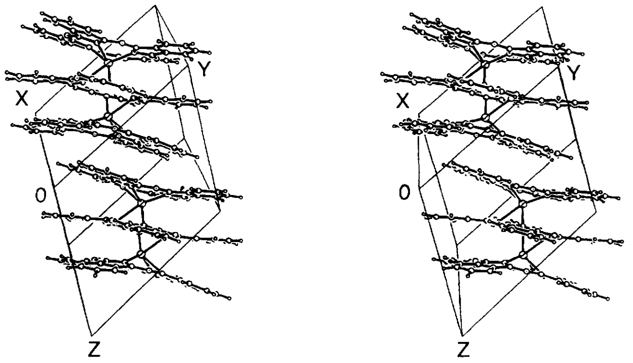

Fig. 2 Stereopacking diagram of the unit cell of $In_2(pc)_3$

stacking axis perpendicular to the pc planes. The shortest intramolecular distance between two successive molecules is 3.475(5) Å and less than the van der Waals distance (3.4 Å) for aromatic carbon atoms. The intermolecular hydrogen–nitrogen contacts are greater than 2.9 Å, the closest distance being 2.981(5) Å between N(9) and H(24^{I}) (I $1 - x$, $1 - y$, $2 - z$). This shows that dimers are absent.

From the results it can be seen that the $In_2(pc)_3$ molecule is a double-sandwich type complex. This structure represents a new type for trivalent metals. However, it is to some extent similar to that of a cerium(IV) porphyrin complex.[28]

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