

Mixed-Valence, Disordered Structures and Characterization of Iodine-Doped Phthalocyanines: [YbPc₂]I₂ and [(AsPc)(Pc)]I₂

Jan Janczak,*[†] Ryszard Kubiak,[†] and Adam Jezierski[‡]

W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 2 Okólna Str., P.O. Box 1410, 50-950 Wrocław, Poland, and Institute of Chemistry, University of Wrocław, 14 F. Joliot-Curie Str., 50-383 Wrocław, Poland

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Crystals of C₆₄H₃₂N₁₆YbI₂ and C₆₄H₃₂N₁₆AsI₂ were grown directly in the reaction of ytterbium or arsenic powder with 1,2-dicyanobenzene under a stream of iodine at 200 °C. Both partially oxidized phthalocyanine complexes crystallize in the *P4/mcc* space group of the tetragonal system with one molecule per unit cell, with the cell dimensions $a = 13.927(2)$ Å, $c = 6.409(1)$ Å, and $a = 13.926(2)$ Å, $c = 6.433(1)$ Å for the Yb and As complexes, respectively. The space group of *P4/mcc* requires that both heavy (iodine and metal) atoms are disordered in these structures. The structures show columnar pseudo-monodimensional stacks of [YbPc₂] or [(AsPc)(Pc)] units with an average nonintegral charge of $+2/3$ and linear chains of triiodide I₃⁻ ions, which were detected by Raman spectroscopy. The monodimensional chains of I₃⁻ ions and pseudo-monodimensional aggregates of [YbPc₂]^{2/3+} or [(AsPc)(Pc)]^{2/3+} are aligned along the *c*-axis of the crystals. The Yb³⁺ ion lies in the center, whereas in the [(AsPc)(Pc)] unit the As³⁺ ion does not lie in the center between the Pc rings. In the crystal of [(AsPc)(Pc)]I₂ both components in the [(AsPc)(Pc)]^{2/3+} unit (e.g., AsPc and Pc) with opposite charge are electrostatically interacting. The magnetic susceptibility measurement of the [YbPc₂]I₂ shows typical Curie–Weiss behavior, and the effective magnetic moment is about 4.60 μ_B. The EPR measurement shows no signal for the Yb complex, while for [(AsPc)(Pc)]I₂ two signals are observed: a sharp narrow line at $g = 2.0028$ of width ≈2 G and a broad line at $g = 2.0036$ of width ≈9 G. The two EPR signals are associated with two different radical components: a phthalocyaninato (Pc^{-•}) ring and [AsPc^{-•}], respectively. Both free radicals are in resonance: [(As³⁺Pc²⁻)(Pc^{-•})] ↔ [(As³⁺Pc^{-•})(Pc²⁻)]. Oxygen effects on the EPR signal of the [(AsPc)(Pc)]I₂ crystal have been detected. The conductivity measured on polycrystalline samples at room temperature equals 2.5–4 × 10⁻² and 2.2–3.5 × 10⁻⁴ Ω⁻¹ cm⁻¹ for [YbPc₂]I₂ and [AsPc(Pc)]I₂, respectively. Both complexes exhibit nonmetallic character in conductivity ($d\sigma/dT > 0$).

Introduction

Partially oxidized metallophthalocyanines such as NiPcI with the formal oxidation state of -1.67 of the Pc macrocycle and related compounds are a class of molecular materials exhibiting metallic behavior.¹ These materials are built up from quasi-one-dimensional stacks of strongly interacting mainly planar macrocycles with interactions between adjacent stacks, this leading to the unusual charge transport properties.² A single

structural motive, retained throughout this series of molecular conductors or semiconductors, consists of metal-over-metal stacks of partially oxidized macrocycles which are surrounded by iodide chains of doped iodine atoms.³ The macrocyclic rings in the pseudo-one-dimensional aggregates are staggered by about 40° and separated by a distance of $c/2$; the average value is not too different from 3.25 Å. The highest conductivity of these materials occurs when the rotation angle equals 45°; this angle provides the greatest overlap of the a_{1u} HOMO π-orbitals of the macrocycles.^{4,5}

Extensive theoretical and experimental investigations of these materials suggest two pathways for the charge transport. The high conductivity of these materials can be explained by (1) a concept of organic molecular metals^{6,7} with charge transport

* Corresponding author. E-mail: janczak@highscreen.int.pan.wroc.pl.

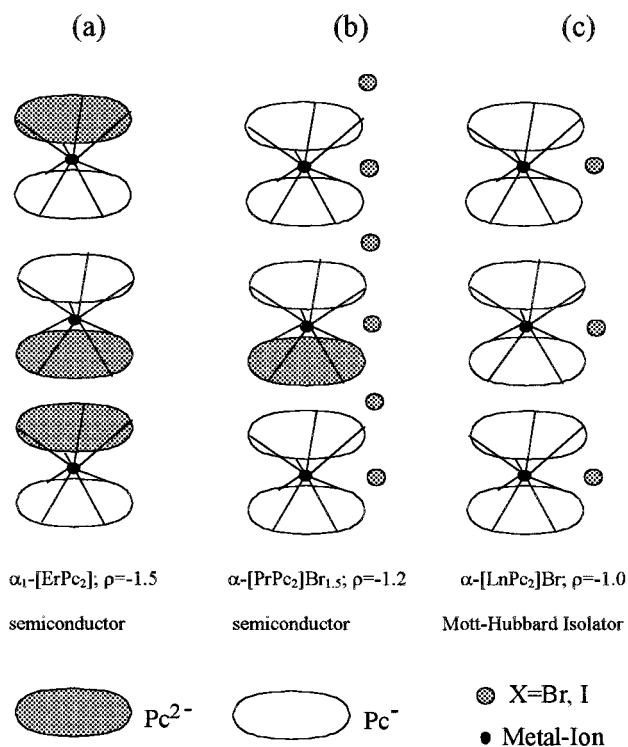
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[‡] University of Wrocław.

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Chart 1



through p - π orbitals of the macrocyclic rings and (2) linear-chain-metal spin conductors⁸⁻¹¹ with the charge propagation through the metal-based a_{1g} (d_{z^2}) orbitals.

The majority of the known iodine-doped phthalocyanines contain I_3^- ions, which were identified using resonance Raman methods,¹²⁹ Mössbauer spectroscopy,¹²⁻¹⁵ and diffuse X-ray scattering techniques.¹⁶⁻¹⁸

On the other hand, not all partially oxidized metallophthalocyanines are conductors or semiconductors. For example, LiPc with the formal oxidation state of the Pc macrocyclic ligand $\rho = -1$ represents a Mott-Hubbard isolator.¹⁹

The partially oxidized sandwich-type metalodiphthalocyanines are less studied. This family of partially oxidized complexes is divided into two categories (see Chart 1): (1) undoped metal(III) diphthalocyanines²⁰⁻²⁸ and (2) doped (I or

Br or another monovalent ions such as ClO_4^- or BF_4^-) metalodiphthalocyanines.²⁹⁻³¹ In the first category, exhibiting semiconducting properties, the trivalent metal ion is surrounded by two different ligands: Pc^{2-} and half-oxidized Pc^- ions. However, from the crystal structure analysis of the InPc_2 ²⁸ and α - ErPc_2 ³⁰ both halves of the sandwich molecule are structurally equivalent; thus no integral formal oxidation number can be assigned to either of them ($\rho = -1.5$). In the second category, doped metalodiphthalocyanines, the electrical properties depend on the amount of doped atoms (see Chart 1b,c). The amount of doped atoms closely correlates with the formal oxidation state of the Pc macrocycle; for example, in α -[PrPc₂]Br_{1.5}²⁹ and in α -[SmPc₂]Br_{1.45},³¹ the formal oxidation state of Pc $\cong -1.2$. The further oxidization of the above semiconducting materials leads to the Mott-Hubbard isolator (Chart 1c) in which, similarly to the LiPc , the formal oxidation state of the Pc rings equals -1 .

The $[\text{TiPc}_2](\text{I}_3)_{0.66}$ is the first iodine-doped sandwich type diphthalocyanine well characterized in a single-crystal investigation.³² The characteristic feature of this semiconducting material is statistical disorder of both heavy (Ti and I) atoms. Additionally, all atoms in both Pc partially oxidized rings are also statistically distributed.³²

Recently, using a slightly modified preparation method,³³ a new mixed valence of the Pc rings of iodine-doped metallophthalocyanines $[\text{BiPc}_2]\text{I}_{3/2}$ ³⁴ and $[\text{UPc}_2]\text{I}_{5/3}$ ³⁵ has been obtained. In this method the metallophthalocyanines are directly formed by cyclotetramerization of 1,2-dicyanobenzene in the presence of pure powdered metal or intermetallic alloy.³⁶ The present paper describes the structure and some properties of new iodine-doped phthalocyanines $[\text{YbPc}_2]\text{I}_2$ and $[(\text{AsPc})(\text{Pc})\text{I}_2]$.

Experimental Section

Preparation. The crystals of $[\text{YbPc}_2]\text{I}_2$ and $[(\text{AsPc})(\text{Pc})\text{I}_2]$ ($\text{Pc} = \text{C}_{32}\text{H}_{16}\text{N}_8$) were obtained directly by the reaction of pure powdered metal (Yb or As) and 1,2-dicyanobenzene under a stream of iodine.

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The powdered ytterbium (or arsenic), 1,2-dicyanobenzene, and iodine (in a molar proportion of 1:8:2, with about 10% excess 1,2-dicyanobenzene and iodine in relation to the metal) were mixed together and pressed into pellets. The pellets were inserted into an evacuated glass ampule and sealed. The ampule was heated at 200 °C for several hours. At this temperature (200 °C) the liquid 1,2-dicyanobenzene undergoes catalytic tetramerization forming the phthalocyanine units. Simultaneously the iodine atoms present in the reaction as an oxidant, partially oxidized the ytterbium (or arsenic) phthalocyanine complex, yielding black-violet crystals of good quality. The elemental analysis has been made on an energy dispersive spectrometer. Found for iodine-doped ytterbium diphthalocyanine: Yb, 11.88; C, 52.96; N, 15.40; I, 17.53. Found for mixed arsenic and metal-free phthalocyanine: As, 5.55; C, 56.73; N, 16.58; I, 18.81. Calcd for $\text{YbC}_{64}\text{H}_{32}\text{N}_{16}\text{I}_2$: Yb, 11.92; C, 52.94; N, 15.43; I, 17.48; H, 2.23. Calcd for $\text{AsC}_{64}\text{H}_{32}\text{N}_{16}\text{I}_2$: As, 5.53; C, 56.78; N, 16.55; I, 18.76; H, 2.38.

X-ray Data Collection. Black-violet single crystals of $[\text{YbPc}_2]\text{I}_2$ and $[(\text{AsPc})(\text{Pc})]\text{I}_2$ of approximate dimensions $0.1 \times 0.1 \times 0.4 \text{ mm}^3$ and $0.1 \times 0.12 \times 0.26 \text{ mm}^3$ for $[\text{YbPc}_2]\text{I}_2$ and $[(\text{AsPc})(\text{Pc})]\text{I}_2$, respectively, were used for data collection on a four-circle KM4 KUMA diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Both crystals were preliminarily checked by the rotation and Weissenberg X-ray photographs and were assigned to Laue group $4/mmm$ of the tetragonal system. The only systematic absences observed were for $0kl$ and hhl with l odd, consistent with the space groups $P4/mcc$ or $P4cc$. Successful refinement of these structures supports the choice of the centrosymmetric space group D_{4h}^2-P4/mcc . In addition to Bragg scattering, oscillation and Weissenberg photographs showed weak diffuse scattering localized in planes perpendicular to the c^* -axis. This type of diffuse scattering pattern is commonly observed in other crystals that contain one-dimensionally disordered polyiodide chains.^{1a,d,e,3a-d,4} The unit cell parameters for both crystals were determined by a least-squares refinement of 25 reflections measured in the 2θ range of $15-26^\circ$. A total of 1309 and 821 reflections were measured using $\omega-2\theta$ scan techniques for iodine-doped Yb and As phthalocyanine complexes, respectively. Two standard reflections were monitored every 50. The intensity variations of the control reflection were less than 2%. Intensities and their standard deviations were corrected for Lorentz and polarization effects. A face-indexed analytical absorption correction was calculated using the SHELXTL program system.³⁷

Structure Solution and Refinement. The structures were solved by Patterson heavy-atom methods. The Patterson map revealed the positions of Yb (or As) and I atoms at $(1/2, 1/2, 1/4)$ and $(0, 0, 1/4)$, respectively. This requires, the Yb (As) atom to be statistically distributed over two equivalent positions. The remaining atoms were located from difference Fourier synthesis. The subsequent ΔF maps showed that the I atoms have high anisotropic temperature factors. Especially the anisotropic thermal parameter of the iodine atoms is about three times larger along the chain direction than it is perpendicular to the chain. Refinement of the crystal structure of the As complex showed that the As atom is also not located at the special position, but takes the position $(1/2, 1/2, z)$ with $z \neq 1/4$. Hydrogen atoms of the phenyl rings were introduced in their computed coordinates and isotropic thermal parameters fixed. Scattering factors for neutral atoms and correction for anomalous dispersion were as given in the SHELXTL program system,³⁷ which was also used for drawing preparation. Final agreement factors, crystallographic data, and experimental conditions are listed in Table 1. Both crystal structures were refined using the SHELXL97 program.³⁸

Raman Spectroscopy. The Raman spectra were recorded at room temperature on a Jobin-Yvon Ramanor U-1000 spectrometer equipped with photomultiplier-type detector and phonon-counting hardware. The 90° geometry was used. An argon ion laser line at 514.5 nm, of power 200 mW, was used as exciting radiation. Resolution was set up to 3 cm^{-1} .

Table 1. Crystal Data, Data Collection Conditions, and Refinement Details

	$\text{C}_{64}\text{H}_{32}\text{N}_{16}\text{YbI}_2$	$\text{C}_{64}\text{H}_{32}\text{N}_{16}\text{AsI}_2$
formula	$\text{C}_{64}\text{H}_{32}\text{N}_{16}\text{YbI}_2$	$\text{C}_{64}\text{H}_{32}\text{N}_{16}\text{AsI}_2$
mol wt	1451.90	1353.78
cryst syst	tetragonal	tetragonal
space group	$P4/mcc$	$P4/mcc$
unit cell dimens		
a (Å)	13.927(2)	13.926(2)
c (Å)	6.409(1)	6.433(1)
vol, V (Å ³)	1243.1(3)	1247.6(3)
temp (K)	295(2)	295(2)
Z	1	1
D_{calc} (g cm ⁻³)	1.939	1.802
D_{obs} (g cm ⁻³)	1.93	1.78
radiation, Mo K α (Å)	0.71073	0.71073
abs coeff, μ (mm ⁻¹)	3.188	1.984
face-indexed anal. abs correction, $T_{\text{min}}, T_{\text{max}}$	0.685 62, 0.749 63	0.785 63, 0.883 65
$R[F^2 > 2\sigma(F^2)]^a$	0.0390	0.0638
$R_w(F^2)^a$	0.1124	0.2008

^a $R = \sum ||F_o| - |F_c|| / \sum F_o$. $R_w(F^2) = \{ \sum (w(F_o^2 - F_c^2)^2) / \sum wF_o^4 \}^{1/2}$. $w^{-1} = \sigma^2(F_o^2) + (0.0520P)^2 + 1.4115P$ where $P = (F_o^2 + 2F_c^2)/3$ for $[\text{YbPc}_2]\text{I}_2$ and $w^{-1} = \sigma^2(F_o^2) + (0.1103P)^2 + 1.4875P$ where $P = (F_o^2 + 2F_c^2)/3$ for $[(\text{AsPc})(\text{Pc})]\text{I}_2$.

Magnetic Susceptibility Measurements. The temperature dependence of the magnetic susceptibility of $[\text{YbPc}_2]\text{I}_2$ was taken from 300 to 1.8 K with a Quantum Design SQUID magnetometer (San Diego, CA). Data were recorded at a magnetic field of 0.5 T on a sample of 50 mg.

Electron Paramagnetic Resonance Measurements. Quantitative EPR studies were carried out on solid state samples. The EPR spectra were recorded at room temperature using X-band microwave frequencies: SE-Radiopan and ESP 300 E-Bruker spectrometers. The g -factors and the line widths of the signals were determined. A nuclear magnetometer, a frequency counter, and the EPR standards were used to calculate g -factors and magnetic field calibration. Quantitative techniques were used (2–5 mg samples, quartz tubes of constant volume, constant modulation amplitude 0.1 G, microwave power 0.2 mW, etc.). The concentrations of the free radicals in the samples were calculated using standard integration of the derivative signal and by comparing the area of the free radical EPR signal with the area determined with the free radical standard (DPPH, TEMPO, TEMPOL, and Rickitt's ultramarine).²⁸

Two EPR lines, one very strong signal at $g = 2.0028$, with a bandwidth of $\Gamma = 2 \text{ G}$, the second signal at $g = 2.0036$ several times broader ($\Gamma \cong 9 \text{ G}$), were observed for $[(\text{AsPc})(\text{Pc})]\text{I}_2$, while for the YbPc_2I_2 no EPR signal was observed. The calculation of the sum of spin concentrations gave 1.2×10^{20} spins/g, i.e., $\cong 0.27$ unpaired electron per $[(\text{AsPc})(\text{Pc})]\text{I}_2$. After about 5 months the EPR measurement on the same sample of $[(\text{AsPc})(\text{Pc})]\text{I}_2$ was made again. The EPR spectrum exhibits only one broad signal at $g = 2.0035$ ($\Gamma \cong 10.5 \text{ G}$); the strong signal (which was observed at the beginning) has completely vanished. The calculation of the spin concentration (with the second EPR measurement) was less than 5%.

Conductivity Measurement. Conductivity measurements were carried out on the several polycrystalline compacted samples (pressed into pellets, $\sim 10^5 \text{ kPa}$) by using a standard four-point probe technique with a sampling current of $20 \mu\text{A}$ at room temperature and with decreasing (to liquid nitrogen) temperature.

Results and Discussion

Refinement of the crystal structures of both iodine-doped phthalocyanines established that in contrast to the known structure of $[\text{TiPc}_2]\text{I}_2$,³² in which the iodine atoms lie at 422 sites at $(0, 0, 1/4)$, in the present structures, the iodine atoms occupy besides the $(0, 0, 1/4)$ also the $(0, 0, z)$ position, since the refinement of both structures with an iodine atom at the special position $(0, 0, 1/4)$ gave a high anisotropic temperature factor (U_{33} for I), and therefore structure refinement using the model as

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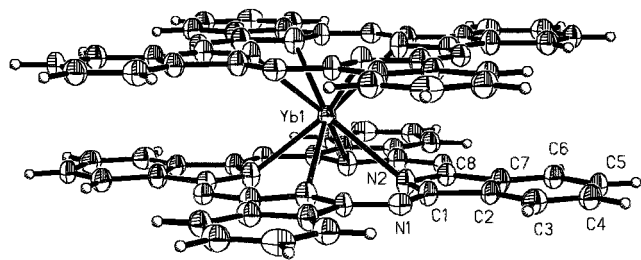


Figure 1. View of the partially oxidized $[\text{YbPc}_2]$ unit and labeling scheme.

presented in Figure 6c was also checked. The parameter z of the iodine atom equals 0.2265(5) and 0.2264(10) in iodine-doped Yb and As phthalocyanine structures, respectively. Thus iodine atoms as a dopants in these structures are disordered.

In $[\text{YbPc}_2]\text{I}_2$ the central metal atom lies in a special position 422 at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{4})$. Since the space group is $P4/mcc$, this requires that the Yb atom be statistically distributed over two positions, whereas in $[(\text{AsPc})(\text{Pc})]\text{I}_2$ the As atom does not lie in the 422 site, it is located at the $(\frac{1}{2}, \frac{1}{2}, z)$ position, with $z = 0.152(2)$; therefore in this structure the As atom is tetradisordered (As statistically occupies four equivalent positions).

The molecular structure of the YbPc_2 unit is shown in Figure 1. Both Pc macrocyclic rings in the YbPc_2 unit, similarly as in $[\text{BiPc}_2]\text{I}_{1.5}$ ³⁴ and in $[\text{UPc}_2]\text{I}_{1.667}$,³⁵ are closely planar, since they lie on the site symmetry of $8m$. In other partially oxidized diphthalocyanines the Pc rings are not closely planar. For example, the vertical displacement of the outermost atoms from the mean Pc plane is about 0.15 Å in α - $[\text{PrPc}_2]\text{Br}_{1.5}$,²⁹ 0.365 Å in $[\text{CePc}_2][\text{BF}_4]_{0.33}$,³¹ and even 0.63 Å in α - $[\text{SmPc}_2](\text{ClO}_4)_{0.63}$.³⁰ The Yb^{3+} ion is sandwiched between two partially oxidized macrocyclic Pc rings that are staggered by $39.9(5)^\circ$. The Yb^{3+} is located in the center of the YbPc_2 unit and is surrounded by eight isoindole nitrogen atoms of the two N_4 systems, forming a distorted square antiprism.

The structure of $[\text{YbPc}_2]\text{I}_2$ consists of pseudo-monodimensional columnar stacks of the partially oxidized $[\text{YbPc}_2]^{2/3+}$ units with their molecular Pc planes normal to the c axis and separated by $c/2$. The disordered iodine doped atoms are located in the channels between the $[\text{YbPc}_2]$ units forming a one-dimensional chains, which are parallel to the c axis. The structure shown in Figure 2 is statistically built up with two real units, which are presented as I and II also in Figure 2. Both units (I and II) are present in 50% in the unit cell.

In contrast to the crystal structure of $[\text{YbPc}_2]\text{I}_2$, which is an iodine-doped sandwich diphthalocyanine, from the crystal structure analysis of $[(\text{AsPc})(\text{Pc})]\text{I}_2$ (and also from EPR spectroscopy) we stated that, although both are iodine-doped phthalocyanines, having the same general formula of $[\text{MPc}_2]\text{I}_2$ ($M = \text{Yb}$ or As), the iodine-doped arsenic phthalocyanine is not a diphthalocyanine, but this crystal is built up of a unique mixture of iodine-doped arsenic monophthalocyanine (AsPc) and phthalocyaninato (Pc) rings. Both units with opposite charge (positive on AsPc and negative on the phthalocyaninato (Pc) ring) are electrostatically interacting in the crystal. The molecular structure of the AsPc unit is shown in Figure 3. The AsPc unit is not planar. The displacement of the As ion from the Pc plane equals 0.975(8) Å. Similar nonplanar phthalocyanine molecules were found in SnPc and PbPc. For comparison, the displacement of the central ion from the Pc plane equals 1.12 Å for SnPc³⁹

and 1.28 and 0.91 Å for PbPc triclinic⁴⁰ and monoclinic⁴¹ forms, respectively.

The structure of $[(\text{AsPc})(\text{Pc})]\text{I}_2$ consists of pseudo-monodimensional columnar stacks of the two different components: the arsenic phthalocyanine unit (AsPc) and the phthalocyaninato (Pc) ring. Both components in the columnar stacks are present in 50%. The Pc planes of both components are normal to the c axis and separated by $c/2$. The Pc-macrocyclic ring of AsPc and the partially oxidized phthalocyaninato Pc ring are staggered by $38.9(7)^\circ$ with respect to each other.

The disordered iodine-doped atoms are located similarly as in $[\text{YbPc}_2]\text{I}_2$ in the channels between the pseudo-monodimensional aggregates forming one-dimensional polyiodide chains, which are parallel to the four-fold axis. The structure shown in Figure 4 is statistically built up of four real units, which are presented as I, II, III, and IV also in Figure 4. Each of the four units consists of two components: AsPc and the phthalocyaninato (Pc) ring are present in 25% in the unit cell. The difference between units I and II (or III and IV) is only in the translation by $c/2$ along the c axis. The unit III (or IV) may be obtained from the unit I (or IV) by a rotation around the a or b axis by 180° .

The I–I distances in the disordered polyiodide chains in $[\text{YbPc}_2]\text{I}_2$ equal 2.967(13) and 3.681(15) Å, while the equivalent distances in the $[(\text{AsPc})(\text{Pc})]\text{I}_2$ equal 2.969(15) and 3.711(15) Å, respectively (see Table 2). The shorter I–I distance in both structures is longer than the I–I distance in pure I_2 (2.662 Å in gaseous I_2 ⁴² and 2.715(6) Å in the solid state at -163°C)⁴³. The I–I distances of 2.967(13) and 2.969(15) Å in the structure of $[(\text{AsPc})(\text{Pc})]\text{I}_2$ and in $[\text{YbPc}_2]\text{I}_2$, respectively, is typical for the symmetrical I_3^- ions, which are usually present in this family of iodine-doped complexes. The longer I–I distances (3.681(15) and 3.711(15) Å for Yb and As complex, respectively) are longer than the van der Waals contact in pure iodine⁴³ and correspond to the I–I nonbonded contacts observed in other iodine-doped phthalocyaninato-like complexes.^{1a–d,3a,c,d,4} The C–C and C–N bond lengths and angles for chemically equivalent bonds do not differ significantly, and they compare well with the bond lengths and angles of the other phthalocyanine structures.

The resonance Raman spectra of both $[\text{YbPc}_2]\text{I}_2$ (Figure 5a) and $[(\text{AsPc})(\text{Pc})]\text{I}_2$ (Figure 5b) exhibit the intense stretching fundamental at $\sim 109\text{ cm}^{-1}$, with the characteristic overtone progression of peaks at ~ 220 and $\sim 332\text{ cm}^{-1}$. This band system is unequivocally indicative of the presence of I_3^- ions in both crystal structures.^{44–46} This pattern is characteristic for the linear chains of the symmetric triiodide ions detected in other iodine-doped phthalocyanine complexes.^{1e,i,3a–3e,g,32,47} Although the crystal structure analysis shows that the shortest I–I distance is comparable to the distance in pure I_2 , there is no evidence in the spectrum of the presence of an iodine molecule ($\text{I}_2 \sim 200\text{ cm}^{-1}$) or an I_2 molecule coordinated to a Lewis base I_3^- ($\sim 180\text{ cm}^{-1}$). The absence of a band at $\sim 200\text{ cm}^{-1}$ eliminates the free

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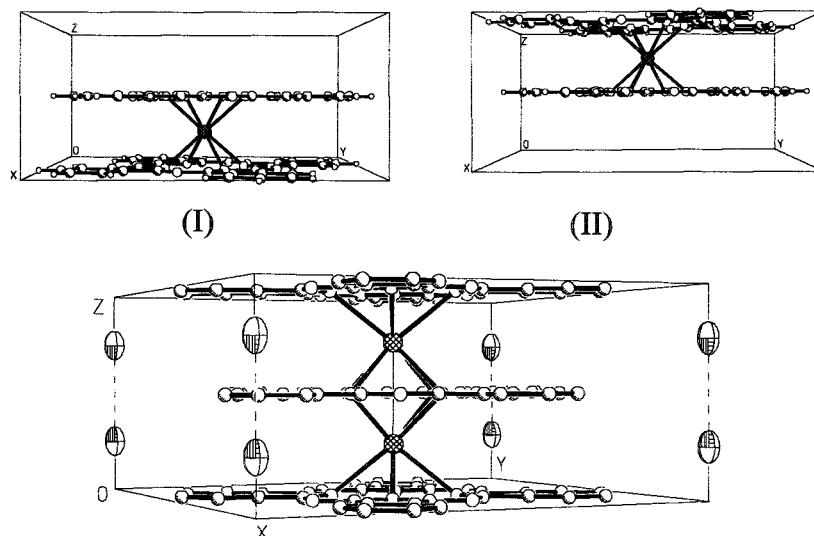


Figure 2. Crystal structure of $[\text{YbPc}_2]\text{I}_2$ viewed perpendicular to the macrocycle stacking direction. Forms I and II are present in 50%. For I atoms 50% probability displacement ellipsoids are illustrated. H atoms have been omitted for clarity.

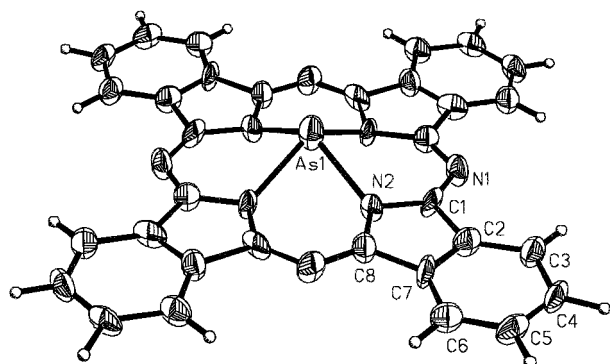


Figure 3. View of the AsPc unit and labeling scheme.

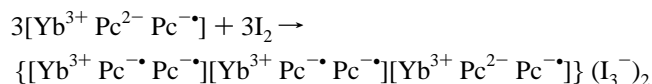
I_2 as an impurity, and simultaneously the absence of a band at $\sim 160\text{ cm}^{-1}$ eliminates the I_5^- ions.

From both X-ray and Raman investigations we concluded that iodine-doped atoms in the crystals form ordered chains of I_3^- ions that are disordered with respect to their neighbor as shown in Figure 6. The disorder model of iodine atoms in the iodine-doped normal metal(II) phthalocyaninato complexes has been widely discussed in detail.^{1a,d,e,3a-c,4}

The assignment of the iodine species as I_3^- in both phthalocyanine complexes implies a $+2/3$ oxidation state of the $[\text{YbPc}_2]$ and $[(\text{AsPc})(\text{Pc})]$ units, and these complexes are best formulated as $[\text{YbPc}_2](\text{I}_3)_{2/3}$ and $[(\text{AsPc})(\text{Pc})](\text{I}_3)_{2/3}$, where one electron per $^{3/2}[\text{YbPc}_2]$ and $[(\text{AsPc})(\text{Pc})]$ molecule has been transferred to the one I_3^- ion. From the crystal structure analysis we stated that both Pc macrocyclic ligands in $[\text{YbPc}_2]\text{I}_2$ are identical in bond lengths and angles; therefore it may be assumed that the oxidation states of both Pc ligands are also identical and equal to -1.166 ($=-7/6$). It is likely that, in contrast to $[\text{YbPc}_2]\text{I}_2$, in the crystal of $[(\text{AsPc})(\text{Pc})](\text{I}_3)_{2/3}$ both Pc ligands of both components, i.e., AsPc and the phthalocyaninato Pc ring, have different oxidation states. This hypothesis seems also to be supported by EPR measurements (see below).

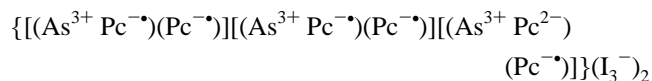
Figure 7 shows the plot of the inverse molar susceptibility versus temperature for $[\text{YbPc}_2]\text{I}_2$. Typical Curie–Weiss behavior is observed with no observable magnetic ordering to 1.8 K ($\Theta \cong -9.5$). The effective magnetic moment (μ_{eff} , temperature-independent, is $4.60\ \mu_{\text{B}}$. This value is comparable to the effective moment of the free Yb^{3+} ion ($4.53\ \mu_{\text{B}}$).

Although the Yb^{3+} ion is paramagnetic with one unpaired electron (f^{13}), the EPR measurement of the iodine-doped ytterbium diphthalocyanine did not show any EPR signal. The I_3^- ions present in this structure, detected by Raman spectroscopy, are formed by the transfer of one electron per $^{3/2}[\text{YbPc}_2]$ molecule (or two electrons from three $[\text{YbPc}_2]$ to the two I_3^- ions); thus, for better understanding of the absence of the EPR signal, this phthalocyanine complex may be described as

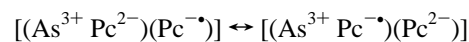


The sum of the unpaired electrons in this complex described as above equals 8 (the 5 electrons of the Pc^{2-} rings and 3 electrons of the three Yb^{3+} ions). The absence of the EPR signal in this complex can be explained by a strong interaction between these spin and/or a very short time of relaxation; this phenomenon is typical for the 4f lanthanide ions.

The EPR spectrum of a disordered crystal of $[(\text{AsPc})(\text{Pc})]\text{I}_2$ that is partially oxidized by iodine exhibits two signals. The first line is narrow and sharp, and the second one is much broader. This indicates the existence of two different radicals and the absence of the exchange interactions between these two spin systems. It is likely that the narrow sharp signal at $g = 2.0028$ with a line width of $\Gamma \approx 2\text{ G}$ is attributed to the partially oxidized phthalocyaninato ring, whereas the broad signal at $g = 2.0036$ with a bandwidth of $\Gamma \approx 9\text{ G}$ is associated with the arsenic phthalocyanine. Integration of these signals yields ≈ 0.013 spin and ≈ 0.26 spin for the sharp and the broad signal, respectively. If the complex is described as



then the two radicals in the first two units $[(\text{As}^{3+} \text{Pc}^{-})(\text{Pc}^{-})]$ could interact with each other, which gives $S = 0$. The third unit with an unpaired electron on a phthalocyaninato Pc ring is in resonance with the other structure with the unpaired electron on the AsPc unit; this is in agreement with the EPR spectrum:



Thus statistically one unpaired electron per three $[(\text{AsPc})(\text{Pc})]$ -

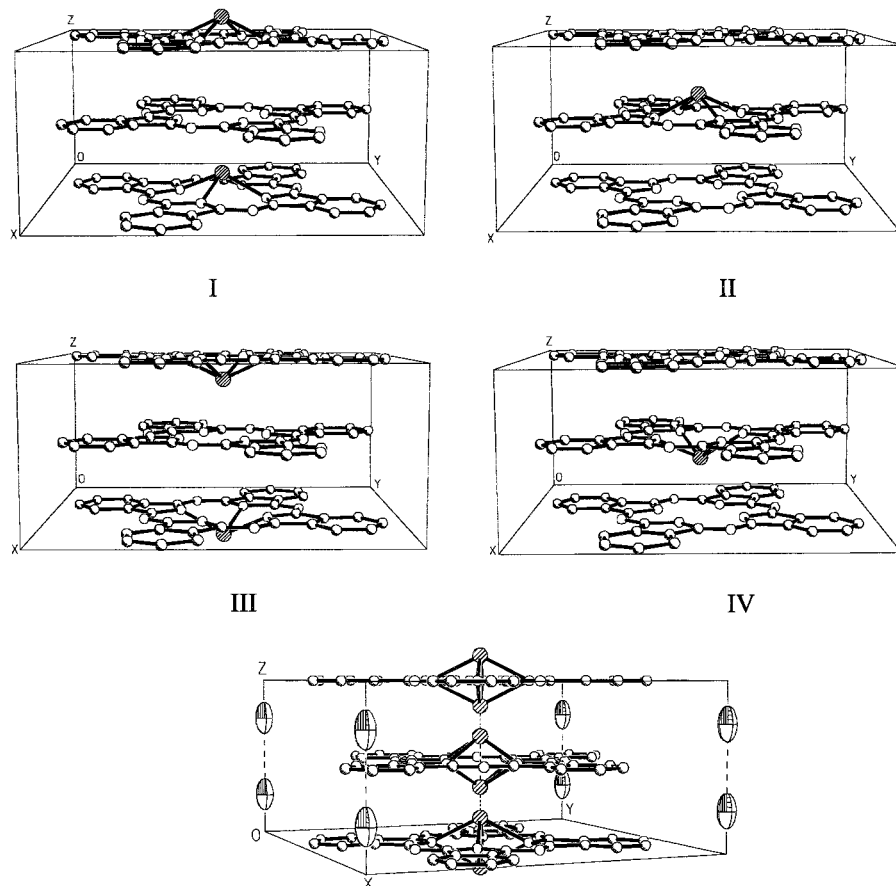


Figure 4. Crystal structure of $[(AsPc)(Pc)]I_2$ viewed perpendicular to the macrocycle stacking direction. Forms I, II, III, and IV are present in 25%. For I atoms 50% probability displacement ellipsoids are illustrated. H atoms have been omitted for clarity.

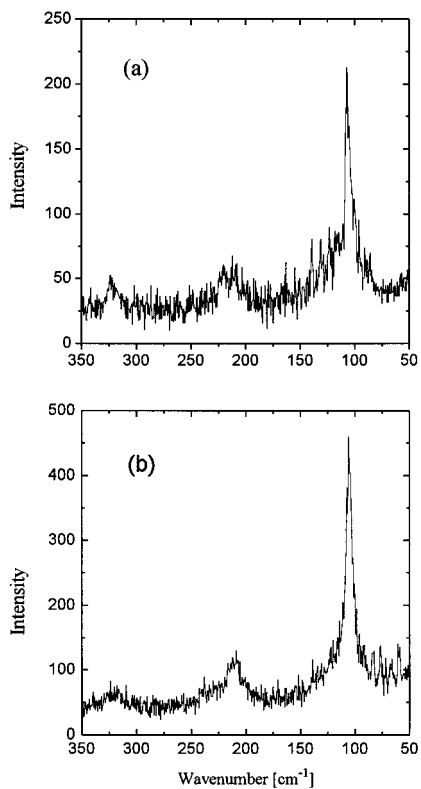


Figure 5. Resonance Raman spectra of polycrystalline samples of (a) $[YbPc_2]I_2$ and (b) $[(AsPc)(Pc)]I_2$ at room temperature.

I_2 molecules is present. The sum of the spin concentrations calculated from the EPR measurement gives a smaller number

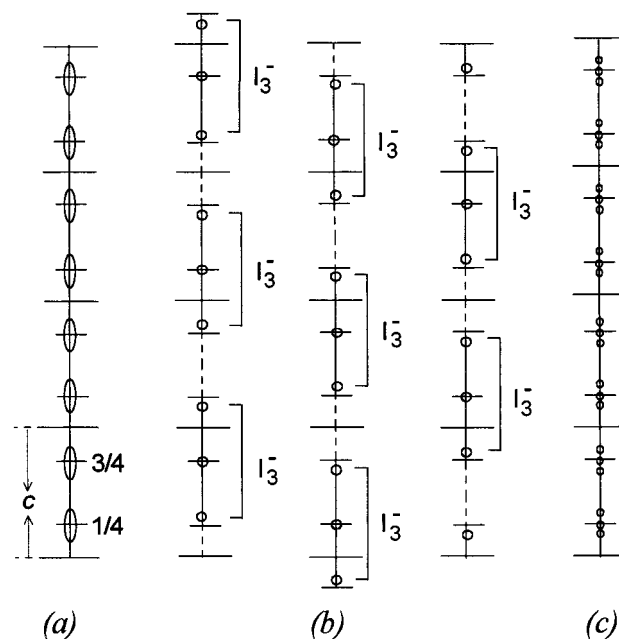


Figure 6. Model of the disorder of the iodine chains in $[YbPc_2]I_2$ and $[(AsPc)(Pc)]I_2$. Average positions ($z = 1/4$ and equivalent positions) are shown on the left (a); the three distinct orderings of the I_3^- ions are shown in the middle (b); and the statistical disorder of the polyiodine chains is shown on the right (c).

of unpaired electrons per molecule (0.273). The unpaired electron is mainly localized on the (AsPc) unit ($\approx 95\%$).

After about 5 months the narrow, sharp EPR line, which was attributed to the phthalocyaninato Pc ring of the crystal of

Table 2. Selected Bond Distances (Å) and Angles (deg)

[YbPc ₂]I ₂			
I1–I2 ⁱ	2.967(13)	I2–I2 ⁱⁱ	3.681(15)
Yb1–N2	2.526(6)		
N1–C1	1.331(12)	N2–C8	1.349(11)
N2–C1	1.368(11)	C1–C2	1.455(11)
C2–C3	1.359(13)	C2–C7	1.372(13)
C3–C4	1.395(17)	C4–C5	1.372(16)
C5–C6	1.372(15)	C6–C7	1.387(15)
C7–C8	1.489(12)	C8–N1 ⁱⁱⁱ	1.308(11)
N2–Yb1–N2 ⁱⁱⁱ	66.3(1)	N2–Yb1–N ^{iv}	91.1(3)
N2–Yb1–N ^v	101.2(2)	N2–Yb1–N2 ^{vi}	141.8(3)
N2–Yb1–N2 ^{vii}	149.4(3)	N2–Yb1–N2 ^{viii}	86.8(3)

symmetry code:

(i) $x, y, -z$; (ii) $x, y, 1 - z$; (iii) $y, 1 - x, -z$; (iv) $1 - x, y, 0.5 - z$;
 (v) $1 - x, 1 - y, -z$; (vi) $x, 1 - y, 0.5 + z$; (vii) $1 - y, 1 - x, 0.5 + z$;
 (viii) $y, x, 0.5 - z$

[(AsPc)(Pc)]I ₂			
I1–I2 ⁱ	2.969(15)	I2–I2 ⁱⁱ	3.711(15)
As1–N2	2.178(13)		
N1–C1	1.31(3)	N2–C8	1.36(2)
N2–C1	1.36(2)	C1–C2	1.47(2)
C2–C3	1.42(2)	C2–C7	1.36(2)
C3–C4	1.42(2)	C4–C5	1.40(2)
C5–C6	1.35(2)	C6–C7	1.40(2)
C7–C8	1.46(2)	C8–N1 ⁱⁱⁱ	1.31(2)
N2–As1–N2 ^{iv}	77.8(2)	N2–As1–N2 ^v	125.4(7)

symmetry code:

(i) $x, y, -z$; (ii) $x, y, 1 - z$; (iii) $y, 1 - x, -z$; (iv) $1 - y, x, z$;
 (v) $1 - x, 1 - y, -z$

[(AsPc)(Pc)]I₂, has completely disappeared, whereas the broad signal (attributed to the AsPc component) is almost unchanged. The absence of the EPR signal, associated with the partially oxidized phthalocyaninato Pc ring and slightly broadening signal of the AsPc component, may be attributed to the effect of a dioxygen paramagnetic molecule. Oxygen can diffuse inside to the crystal through the not fully filled channels formed by disordered triiodide I₃[−] ions. The interactions between the spins of (Pc^{•−}) and the $S = 1$ spins of oxygen molecules lead to the vanishing of the sharp EPR line, while the interactions with the spins of the AsPc component give in result a broadening of this EPR signal and less decreasing of the spin concentration (by $\approx 5\%$). The role of the dioxygen molecule in the EPR signal has been also detected in other tetragonal, partially oxidized structures of metallophthalocyanines, especially in the tetragonal crystal of LiPc.⁴⁸

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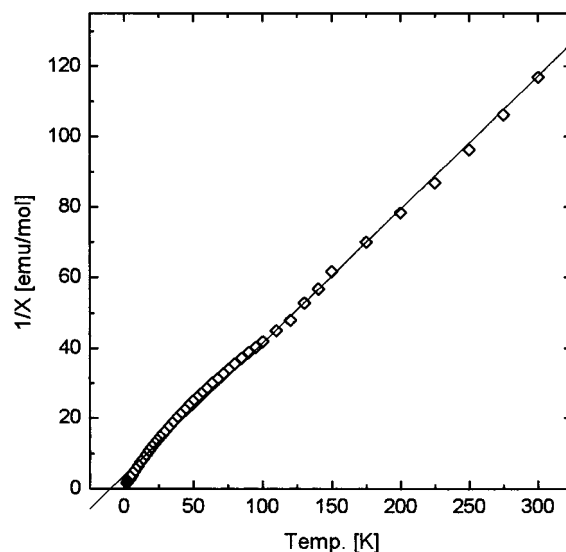


Figure 7. Plot of inverse molar susceptibility versus temperature for [YbPc₂]I₂.

The electrical conductivities of [YbPc₂]I₂ and [(AsPc)(Pc)]I₂ at room temperature equal $2.5\text{--}4 \times 10^{-2}$ and $2.2\text{--}3.5 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$, respectively. With decreasing temperature the conductivity also decreases, and at liquid nitrogen temperature (~ 78 K) the conductivity is smaller by 2 orders. Thus both Yb and As complexes exhibit nonmetallic character in conductivity ($d\sigma/dT > 0$). These data are for compressed polycrystalline samples and suffer from interparticle contact resistance effects and from being averaged over all crystallographic orientations. Nevertheless, the powder and single-crystal data for other “molecular metals” indicate that single-crystal conductivities along the molecular stacking direction is greater by a factor of $10^2\text{--}10^3$.^{1e}

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Supporting Information Available: Crystallographic data for both structures ([YbPc₂]I₂ and [(AsPc)(Pc)]I₂), crystal details, structure determination, fractional atomic coordinates, anisotropic temperature factors, bond lengths, and bond angles in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.