



Synthesis, characterisation and structural investigations of iodine-doped indium(III) and zirconium(IV) diphthalocyanines: $[\text{InPc}_2]\text{I}_2$ and $[\text{ZrPc}_2]\text{I}_2$

Jan Janczak^{a,b,*}, Ynara Marina Idemori^a

^a Instituto de Ciências Exatas, Departamento de Química, Universidade Federal de Minas Gerais, CEP 31270-901 Belo Horizonte—MG, Brazil

^b Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław, Poland

Received 27 April 2001; accepted 14 August 2001

Abstract

Crystals of iodine-doped indium(III) and zirconium(IV) diphthalocyanines, $[\text{InPc}_2]\text{I}_2$ and $[\text{ZrPc}_2]\text{I}_2$, were grown directly in the reaction of In–Tl alloy or zirconium powder with 1,2-dicyanobenzene under a stream of iodine at about 200 °C. Both partially oxidised diphthalocyaninato complexes crystallise in the $P4/mcc$ space group of the tetragonal system with one molecule per unit cell. The space group of $P4/mcc$ requires that the central metal ions are disordered in these structures. The crystal structures shown columnar pseudo-one-dimensional stacks of $[\text{InPc}_2]$ or $[\text{ZrPc}_2]$ units with a non-integral charge and linear chains of symmetrical triiodide I_3^- ions, which were detected by a Raman spectroscopy. The pseudo-one-dimensional aggregates of $[\text{InPc}_2]^{2/3+}$ or $[\text{ZrPc}_2]^{2/3+}$ as well as the chains of I_3^- ions are aligned along the [001] direction. The formal oxidation state of the Pc macrorings equals to $\cong -1.167$ and $\cong -1.667$ in indium(III) and zirconium(IV) diphthalocyaninato complexes. The EPR measurement shows a single sharp EPR line at $g = 2.0028$ and 2.0026 for the indium and zirconium complexes, respectively. The conductivity measurement on polycrystalline samples at room temperature equals $2.7\text{--}3.1 \times 10^{-2}$ and $5.2\text{--}5.5 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ for $[\text{InPc}_2]\text{I}_2$ and $[\text{ZrPc}_2]\text{I}_2$, respectively. The charge transport proceeds mainly along the pseudo-one-dimensional $[\text{MPc}_2]^{2/3+}$ aggregates. Both iodine-doped metallodiphthalocyaninato complexes exhibit non-metallic character in conductivity ($d\sigma/dT > 0$). © 2001 Published by Elsevier Science B.V.

Keywords: Indium(III) and zirconium(IV) diphthalocyanine; Sandwich-type metallodiphthalocyanine; EPR spectroscopy; Raman spectroscopy; Electronic spectra; Conductivity

1. Introduction

Partially oxidised metallodiphthalocyaninato complexes are divided into two subgroups: (1) undoped metal(III) diphthalocyanines (Scheme 1(a)) [1–5] and (2) doped (by I, Br or another monovalent ions such as ClO_4^- or BF_4^-) metal(III) and metal(IV) diphthalocyanines (Scheme 1(b)) [6–12]. In the first category M(III)Pc_2 , exhibiting semiconducting properties, the trivalent central metal ion is surrounded by two different ligands: Pc^{2-} and one-oxidised $\text{Pc}^{\cdot-}$ radical ion. For example, the magnetic susceptibility measurement of the InPc_2 complex with one free unpaired electron

clearly shows its paramagnetic character and a free unpaired electron has also been detected by EPR spectroscopy [5]. However, the crystal structure analysis of the $\alpha_1\text{-ErPc}_2$ [4] and InPc_2 [5] shows that both halves of these sandwich-type complexes are equivalent structurally, thus no integral formal oxidation state should be assigned to either of them ($\rho = -1.5$). In the second category doped metal(III) and metal(IV) diphthalocyaninato complexes the conductivity depends strongly on the amount of the doped atoms, which is closely correlated with the formal oxidation state of the phthalocyaninato macrocyclic rings. For example, in $\alpha\text{-[PrPc}_2]\text{Br}_{1.5}$ [6], $\alpha\text{-[SmPc}_2]\text{Br}_{1.45}$ [8b] and in $[\text{BiPc}_2]\text{I}_{1.5}$ [9] the formal oxidation state of the Pc moieties equal to $\cong -1.25$, while in the $[\text{YbPc}_2]\text{I}_2$ the formal oxidation state of Pc macrorings equals to $\cong -1.167$ [11].

* Corresponding author.

E-mail address: jjanek@dedaluss.lcc.ufmg.br (J. Janczak).

The formal oxidation state of Pc macrocycles in the iodine-doped metal(IV) diphthalocyanine complexes such as $[\text{TiPc}_2]\text{I}_2$ [7] and $[\text{UPc}_2]\text{I}_2$ [12] equals to -1.667 , whereas in the $[\text{UPc}_2]\text{I}_{5/3}$ the formal oxidation state of Pc macrocyclic rings equals to -1.722 [10]. The further oxidation of above mentioned semiconducting metalodiphthalocyaninato complexes leads to the Mott–Hubbard isolator (Scheme 1(c)) in which, similar to the lithium phthalocyanine (LiPc) the formal oxidation state of the Pc ring equals to -1 (Scheme 1(d)) [13].

Understanding of the charge transport in these partially oxidised materials requires the knowledge of their ‘ionicity’ or degree of partial oxidation. The resonance Raman and ^{129}I Mössbauer spectroscopy as well as diffuse X-ray scattering technique offer a simple means of characterising the polyiodine species [14]. Extensive theoretical and experimental investigations suggest two pathways for the charge transport. The high conductivity of these iodine-doped metalodiphthalocyaninato complexes can be explained by: (1) the strong interaction of the neighbouring π -ligand orbitals, as in organic molecular metals [15] with the charge propagation through p – π orbitals of the macrocyclic rings; and (2) linear-chain metal spine conductors that propagate charge through the metal character a_{1g} (d_z^2) orbitals [16].

Recently, we have reported the synthesis, structure and some properties of a new iodine-doped complexes

with the composition of $[\text{YbPc}_2]\text{I}_2$ and $[(\text{AsPc})(\text{Pc})]\text{I}_2$ [11]. Although the As complex can be described as $[\text{AsPc}_2]\text{I}_2$ (with the same general formula as other metalodiphthalocyaninato complexes— $[\text{MPc}_2]\text{I}_2$) the X-ray and EPR investigations clearly shows that the crystals of iodine-doped As–phthalocyaninato complex are built up from two different partially oxidised components: the arsenic phthalocyanine units (AsPc) and phthalocyaninato rings, and linear chains of symmetrical triiodide ions [11].

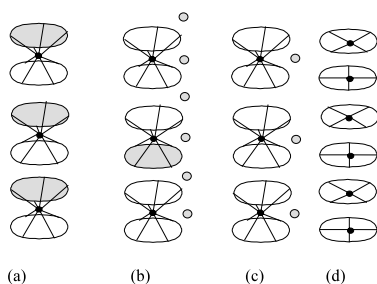
The majority of the known iodine-doped metalodiphthalocyaninato complexes crystallise in the space group $P4/mcc$ of the tetragonal system. The $[\text{UPc}_2]\text{I}_2$ is a unique example of iodine-doped metalodiphthalocyaninato complexes, since it crystallises not in $P4/mcc$ but in the $P4/nmc$ space group [12]. Thus the iodine-doped uranium(IV) diphthalocyanine complex— $[\text{UPc}_2]\text{I}_x$ depends on the crystallisation conditions and/or on the amount of iodine that could be formed from two different crystallographic modifications ($[\text{UPc}_2]\text{I}_{5/3}$ — $P4/mcc$ and $[\text{UPc}_2]\text{I}_2$ — $P4/nmc$). The main difference between these modifications could be found in the disorder of the central metal (uranium) atom [10,12].

The aim of our work is to obtain in the crystalline form a new iodine-doped metal(III) and metal(IV) diphthalocyanine complexes with the same index of iodine atom, and find the correlation between the crystal structures and their properties. The elemental analysis of the obtained iodine-doped indium(III) and zirconium(IV) diphthalocyaninato complexes shows that in both complexes the relation M/I is equal to 1:2, thus both complexes can be described as $[\text{InPc}_2]\text{I}_2$ and $[\text{ZrPc}_2]\text{I}_2$.

2. Experimental

2.1. Preparation

All reagents were of the highest grade commercially available and were used as received. The crystals of $[\text{ZrPc}_2]\text{I}_2$ were obtained directly by the reaction of the pure powdered zirconium and 1,2-dicyanobenzene under a stream of iodine. The powdered zirconium, 1,2-dicyanobenzene and iodine in a molar proportion of 1:8:2, with about 5% excess of iodine, were mixed together and pressed into pellets. The pellets were inserted into an evacuated glass ampoule and sealed. The ampoule was heated at $200\text{ }^\circ\text{C}$ for about 6 h. At this temperature ($200\text{ }^\circ\text{C}$), the liquid 1,2-dicyanobenzene undergoes catalytic tetramerisation forming the phthalocyaninato skeleton which accepts the electrons from zirconium forming the ZrPc_2 complex. Simultaneously the iodine atoms (as an oxidant) partially oxidised the ZrPc_2 molecules yielding good quality

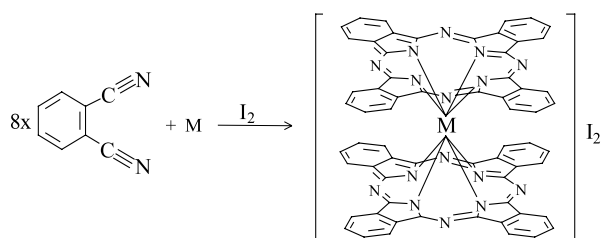


(a) α - $[\text{ErPc}_2]$; ($\rho = -1.5$), (b) α - $[\text{PrPc}_2]\text{Br}_{1.5}$; ($\rho \cong -1.2$), (semiconductor)
(c) α - $[\text{LnPc}_2]\text{Br}$ and (d) LiPc ($\rho = -1.0$), (Mott–Hubbard isolator)

Where:



Scheme 1.



Scheme 2.

black–violet single crystals of $[\text{ZrPc}_2]\text{I}_2$ (Scheme 2). The crystals of $[\text{InPc}_2]\text{I}_2$ were obtained under the same conditions, but indium–thallium alloy was used in the reaction. The elemental analysis of both compounds has been carried out in an energy dispersive spectrometer. Found for zirconium complex: C, 56.20; H, 2.36; I, 18.57; N, 16.32; Zr, 6.58%, and for indium complex: C, 55.11; H, 2.24; I, 18.25; In, 8.28; N, 16.12%. Calc. for $\text{C}_{64}\text{H}_{32}\text{N}_{16}\text{I}_2\text{Zr}$: C, 56.11; H, 2.35; I, 18.52; N, 16.36; Zr, 6.66% and calc. for $\text{C}_{64}\text{H}_{32}\text{N}_{16}\text{I}_2\text{In}$: C, 55.16; H, 2.31; I, 18.21; In, 8.24; N, 16.08%.

2.2. X-ray data collection

The single crystals of $[\text{ZrPc}_2]\text{I}_2$ and $[\text{InPc}_2]\text{I}_2$ with dimensions of $0.15 \times 0.10 \times 0.10$ mm and $0.28 \times 0.10 \times 0.10$ mm, respectively, were used for data collection on a four-circle KUMA KM-4 diffractometer equipped with a two-dimensional area CCD detector. The graphite monochromatised Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å) and ω -scan technique with the $\Delta\omega = 0.75^\circ$ for one image were used for data collection. The 960 images for six different runs covering over 96% of the Ewald sphere were performed. Initially the lattice parameters were refined on 155 (for the Zr complex) and 144 (for the In complex) reflections obtained from 40 images for eight runs with different orientations in the reciprocal space. Finally the lattice parameters were refined by least-squares method on the basis of all collected reflections with $F^2 > 2\sigma(F^2)$. One image was monitored as a standard after every 40 images. Integration of the intensities, correction for Lorentz and polarisation effects were performed using a KUMA KM-4 CCD software [17]. Systematic absences were observed for the reflections hhl and $0kl$ with l odd, consistent with the space group of $P4/mcc$ or $P4cc$. Successive refinement of these structures confirmed the choice of D_{4h}^2 — $P4/mcc$ as a correct space group. The face-indexed analytical absorption was calculated using the SHELXTL program [18]. A total of 10 823 (942 independent, $R_{\text{int}} = 0.0343$) and 9177 (825 independent, $R_{\text{int}} = 0.0321$) reflections were integrated for the crystals of the Zr and In complexes, respectively.

2.3. Structures' determination and refinement

Both structures were solved by the Patterson heavy-atom method. The Patterson maps revealed the positions of the Zr and I (or In and I) atoms at the positions of $(1/2, 1/2, 1/4)$ and $(0, 0, 1/4)$ for the metal (Zr or In) and iodine atoms, respectively. The space group of $P4/mcc$ requires that the metal ion is statistically distributed over two equivalent positions. The remaining atoms were located from difference Fourier synthesis. The hydrogen atoms of the phenyl rings were introduced in their computed coordinates (HFIX 43).

The subsequent refinement of the crystal structures using the SHELXL-97 program [19] with anisotropic temperature parameters for all non-hydrogen atoms (for H atoms the $U_{\text{iso}} = 1.2U_{\text{iso}}$, i.e. 20% higher than the carbon atom directly bonded the H atom) showed that iodine atom have high anisotropic thermal parameters. Especially, the anisotropic thermal parameter along the $[001]$ direction (U_{33}) is about three times larger than its perpendicular. The final difference Fourier maps showed no peaks of chemical significance. The final agreement factor and details of the data collection are listed in Table 1. Selected bond lengths and angles are summarised in Table 2.

2.4. UV–Vis spectroscopy

Measurements of the electronic spectra of both complexes were carried out at room temperature using a Cary-Varian 2300 spectrometer. The UV–Vis spectra were recorded from solution in DMSO in 0.5 cm quartz cell.

2.5. Raman spectroscopy

The Raman spectra were recorded at room temperature in a Jobin-Yvon Ramanor U-1000 spectrometer equipped with a photomultiplier-type detector and phonon-counting hardware. The 90° geometry was used. An argon-ion laser line at 514.5 nm, of power 100 mW, was used as the exciting radiation. Resolution was set up to 3 cm^{-1} .

2.6. Electron paramagnetic resonance measurements

Quantitative EPR studies were carried out on solid state samples of $[\text{ZrPc}_2]\text{I}_2$ and $[\text{InPc}_2]\text{I}_2$. For both complexes the EPR spectra were recorded at room temperature using X-band microwave frequencies: SE-Radiopan and ESR 300 E—Bruker spectrometers. The g factor and the line width of the signals were determined. A nuclear magnetometer, frequency counter and the EPR standards were used to calculate the g parameter and magnetic field calibration. Quantitative techniques were used (2–10 mg samples, quartz tubes of constant volume, constant modulation amplitude 0.1 G, microwave power of 0.2 mW, etc.). The concentration 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 free radicals and Rickitt's ultramarine were used as standards for the calculation of the spin concentration. A single EPR line at $g = 2.0026$ ($\Gamma \approx 6.6$ G) and at $g = 2.0028$ ($\Gamma \approx 7.1$) was observed for the Zr and In complexes, respectively. The calculation of the spin concentration results 4.27×10^{19}

Table 1
Crystal data and structure refinement parameters for $[\text{InPc}_2](\text{I}_3)_{2/3}$ and $[\text{ZrPc}_2](\text{I}_3)_{2/3}$

Empirical formula	$\text{C}_{64}\text{H}_{32}\text{N}_{16}\text{I}_2\text{In}$	$\text{C}_{64}\text{H}_{32}\text{N}_{16}\text{I}_2\text{Zr}$
Molecular weight	1393.68	1370.08
Crystal system	tetragonal	tetragonal
Space group	$P4/mcc$	$P4/mcc$
Unit cell dimensions		
a (Å)	13.984(2)	13.941(2)
b (Å)	6.393(1)	6.487(1)
V (Å ³)	1250.2(3)	1260.8(3)
Z	1	1
D_{calc} (g cm ⁻³)	1.851	1.805
D_{obs} (measured, floatation) (g cm ⁻³)	1.85	1.80
Radiation, Mo K α (Å)	0.71073	0.71073
Index ranges	$-18 \leq h \leq 18, -17 \leq k \leq 17, -5 \leq l \leq 8$	$-14 \leq h \leq 19, -19 \leq k \leq 19, -8 \leq l \leq 8$
Reflections collected	9177	10 283
Independent reflections	825 [$R_{\text{int}} = 0.0321$]	942 [$R_{\text{int}} = 0.0343$]
Observed reflections	623	742
Absorption coefficient, μ (mm ⁻¹)	1.773	1.507
Correction	Lorentz, polarisation, face-indexed analytical absorption, $T_{\text{min}} = 0.6367, T_{\text{max}} = 0.8427$	Lorentz, polarisation, face-indexed analytical absorption, $T_{\text{min}} = 0.8063, T_{\text{max}} = 0.8647$
Refinement on F^2		
R ($F^2 > \sigma$)	0.0428	0.0640
wR (F^2 all reflections)	0.0805	0.0655
Goodness-of-fit, S	1.175	1.276
Largest Δ/σ	0.002	0.002
Residual electron density (e Å ⁻³)	+0.242, -0.461	+0.570, -0.766

$R = \sum ||F_o| - |F_c|| / \sum F_o$. $wR(F^2) = \{\sum(w(F_o^2 - F_c^2)^2) / \sum wF_o^4\}^{1/2}$. $w^{-1} = [\sigma^2(F_o^2) + (0.0398P)^2]$ for the In complex and $w^{-1} = [\sigma^2(F_o^2) + 1.8268P]$ for the Zr complex where $P = (F_o^2 + 2F_c^2)/3$.

spins/g (≈ 0.099 spins per molecule) and 8.12×10^{19} spins/g (≈ 0.185 spins per molecule) for $[\text{InPc}_2]\text{I}_2$ and $[\text{ZrPc}_2]\text{I}_2$ complexes, respectively.

2.7. Conductivity measurements

Conductivity measurements were carried out on the several polycrystalline compacted samples pressed into pellets ($\sim 10^5$ kPa) by using a standard four-point probe technique [20] with a sampling current of 20 μA at room temperature and with decreasing temperature. Variation of the temperature was achieved by placing the samples in a cool-gas stream of N_2 .

3. Results and discussion

Our preparation method of iodine-doped indium(III) and zirconium(IV) diphthalocyanines is fast and simple. Additionally, this method directly leads to obtain a good quality single crystals. Both the complexes obtained are not soluble in any of the usual solvents

(water, acetone, and alcohol) and are slightly soluble in DMF or DMSO as well as in aromatic solvents like chloronaphthalene or quinoline. However, after several days from the solution in DMSO black powder materials were obtained. The elemental analysis of these powder materials is consistent with the non-iodinated sandwich complexes— InPc_2 and ZrPc_2 . Thus it was found that the decomposition process of $[\text{MPc}_2]\text{I}_2$ ($M = \text{In, Zr}$) to MPc_2 and I_2 takes place in the solution. This process strongly depends on the temperature, and takes place several times quicker in hot solvents. Contact with dilute acids led to the demetallation yielding the α -form of metal-free phthalocyanine (H_2Pc) [21] and appropriate salts. Using pure indium instead of the In–Tl alloy in the preparation procedure could only yield iodine monophthalocyanine indium complex— InPcI , in which the iodine atom is directly joined to the central indium metal [22]. Similar observations have been noticed during the preparation of non-iodinated sandwich and homoleptic triple-decker indium(III) phthalocyaninato complexes— InPc_2 and In_2Pc_3 . Both complexes could be obtained if the indium alloy was used in the reaction [5,23].

Refinement of the crystal structures of both the In and Zr iodine-doped diphthalocyaninato complexes established that the central metal ion similarly as in the crystal structure of titanium analogue [7] is statistically distributed over two symmetrically equivalent positions (1/2, 1/2, 1/4) and (1/2, 1/2, 3/4). Additionally, we stated that the iodine-doped atoms occupy besides the

Table 2
Selected bond lengths (Å) and bond angles (°)

[InPc ₂](I ₃) _{2/3}		[ZrPc ₂](I ₃) _{2/3}	
<i>Bond lengths</i>			
In–N2	2.522(2)	Zr–N2	2.527(3)
N1–C1	1.323(3)	N1–C1	1.324(3)
N2–C1	1.363(4)	N2–C1	1.367(5)
N2–C8	1.357(4)	N2–C8	1.368(5)
C1–C2	1.475(4)	C1–C2	1.454(5)
C2–C3	1.374(4)	C2–C3	1.379(5)
C3–C4	1.383(5)	C3–C4	1.381(6)
C4–C5	1.388(5)	C4–C5	1.396(7)
C5–C6	1.394(4)	C5–C6	1.377(6)
C6–C7	1.376(4)	C6–C7	1.400(6)
C7–C8	1.441(4)	C7–C8	1.446(6)
C8–N1 ⁱ	1.339(4)	C8–N1 ⁱ	1.329(6)
<i>Bond angles</i>			
N2–In–N2 ⁱ	149.3(1)	N2–Zr–N2 ⁱ	149.1(2)
N2–In–N2 ⁱⁱ	66.3(1)	N2–Zr–N2 ⁱⁱ	65.7(1)
N2–In–N2 ⁱⁱⁱ	86.7(1)	N2–Zr–N2 ⁱⁱⁱ	88.0(1)
N2–In–N2 ^{iv}	91.0(1)	N2–Zr–N2 ^{iv}	91.6(1)
N2–In–N2 ^v	141.9(1)	N2–Zr–N2 ^v	142.6(2)
N2–In–N2 ^{vi}	101.4(1)	N2–Zr–N2 ^{vi}	100.2(1)
N2–In–N2 ^{vii}	50.7(1)	N2–Zr–N2 ^{vii}	50.1(1)
N2–In–N2 ^{viii}	129.3(1)	N2–Zr–N2 ^{viii}	129.9(1)

Symmetry code: (i) 1–y, 1–x, 1/2+z; (ii) 1–y, x, z; (iii) y, x, 1/2–z; (iv) x, 1–y, 1/2+z; (v) 1–x, y, 1/2–z; (vi) 1–x, 1–y, –z; (vii) y, 1–x, –z; (viii) 1–x, 1–y, 1–z.

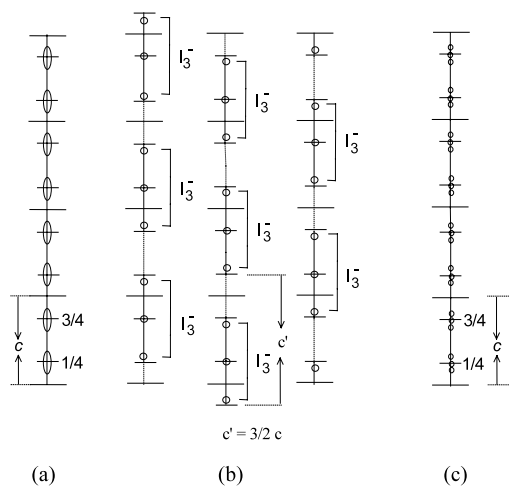


Fig. 1. Model of the disorder of the symmetrically triiodide chains in [MPc₂](I₃)_{2/3} (M = In, Zr). Average positions, $z = 1/4$ and equivalent positions, (a) great anisotropic temperature factor (U_{33}). The three distinct orderings of the symmetric I_3^- ions (that are disordered (translated)) with $c' = 3/2c$ are shown in (b), and the statistical disorder of the polyiodide chains is shown in (c).

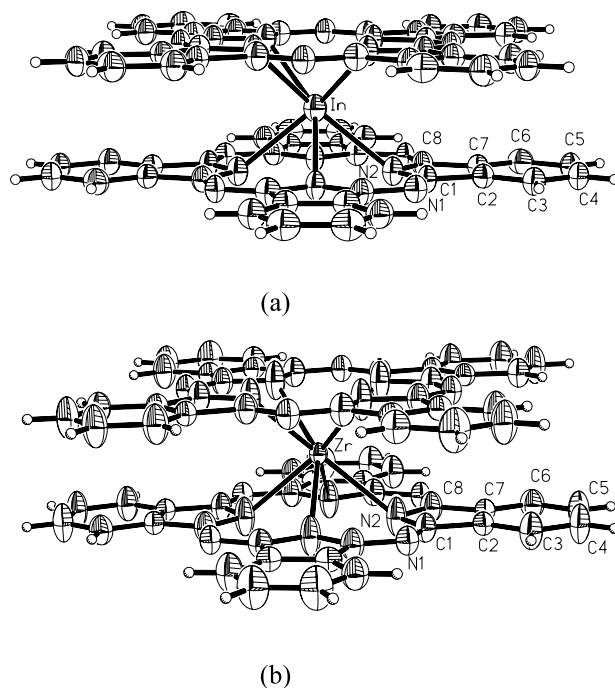


Fig. 2. View of the partially oxidised of: (a) [InPc₂]^{2/3+} and (b) [ZrPc₂]^{2/3+} units and labelling scheme. Displacement ellipsoids are shown at the 50% probability level.

special position (0, 0, 1/4) also the (0, 0, z) position, since the refinement of both structures with the iodine atom only at the special position of (0, 0, 1/4) gave a high anisotropic temperature factor (U_{33} for iodine atom) and therefore the structure refinement using the model as schematically presented in Fig. 1(c) was also checked. The parameter z of the iodine-doped atom equals 0.238(3) and 0.234(3) in iodine-doped In and Zr diphthalocyanine structures, respectively. Thus iodine atoms as dopands in these structures are disordered. Additionally, in contrast to the crystal structure of [TiPc₂]₂ in which all atoms of the Pc rings are statistically distributed over two symmetrically equivalent positions [7] in these crystals of iodine-doped In and Zr diphthalocyanines all atoms of the Pc rings are ordered.

The molecular structure of partially oxidised indium and zirconium diphthalocyaninato units is shown in Fig. 2(a) and (b). Both Pc macrocyclic rings of the MPc₂ units (M = In, Zr) similarly as in the crystal structure of [BiPc₂]₂I_{1.5} [9], [UPc₂]₂I_{5/3} [10] and [YbPc₂]₂ [11] are closely planar, since they lie on the site symmetry of $8m$. In other partially oxidised metallodiphthalocyanines the Pc macrorings are not closely planar. For example, the vertical displacement of the outermost atoms from the plane defined by four isoindole nitrogen atoms equals to 0.356 Å in [CePc₂](BF₄)_{0.33} [8a] and to 0.63 Å in [SmPc₂](ClO₄)_{0.64} [8b] and correlate well with the diameter of the anionic part of the complexes. The In³⁺ (and Zr⁴⁺) ion is sandwiched between two partially oxidised macrocyclic Pc rings. The rings are stag-

gered by $40.0(1)^\circ$ (in the In complex) and $40.6(1)^\circ$ (in the Zr complex) with respect to each other, forming a distorted square antiprism. In both iodine-doped complexes the M–N_{isoinidole} (M = In, Zr) bond lengths are longer by ~ 0.2 Å (see Table 3) than those observed in the non-iodinated indium and zirconium diphthalocyanine complexes [5,24]. This is likely due to the weaker interaction (attraction forces) between the central metal ion (In³⁺, Zr⁴⁺) with the less negatively (partially oxidised by iodine) conjugated π -electron macrocyclic ligands. The C–C and C–N bond distances and angles of phthalocyaninato ring for chemically equivalent bonds do not differ significantly and correlate well with bond lengths and angles in other metallophthalocyanine structures.

The structure of [InPc₂]I₂ and [ZrPc₂]I₂ consists of pseudo-mono-dimensional columnar stacks of partially oxidised [MPc₂]^{2/3+} units with their molecular Pc planes normal to the *c*-axis and separated by *c*/2. Thus the interplanar Pc–Pc distance of about 3.2 Å is shorter than the van der Waals distance of 3.4 Å for aromatic carbon atoms [25] which indicates that the carbon atoms between the phthalocyaninato planes are interacting. The iodine-doped atoms are located in the channels between the partially oxidised [MPc₂]^{2/3+} units

form oppositely charged one-dimensional chains which are parallel to the *c*-axis. Both crystal structures shown in Fig. 3 are statistically built up from two real units, which are presented as (a) and (b) also in Fig. 3.

The resonance Raman spectra of polycrystalline samples of both complexes measured at room temperature are similar, exhibit a sharp fundamental band at ~ 109 cm⁻¹, with an overtone progression of bands at ~ 220 and ~ 330 cm⁻¹ (Fig. 4). This pattern is characteristic for compounds containing the linear chains of symmetrical triiodide ions [26–28]. The absence of any peaks with observable intensities at ~ 160 or ~ 180 cm⁻¹ eliminates I₅⁻ ion or I₂ molecule coordinated to a Lewis base I₃⁻ (I₂–I₃⁻), as a predominant iodine form. The absence of a band at ~ 200 cm⁻¹ eliminates the free I₂ molecule as an impurity. Also, there is no evidence in the spectrum of [InPc₂]I₂ and [ZrPc₂]I₂ for the presence of alternative iodine aggregates such as I₄²⁻ [29], I₅⁻ [30], I₇⁻ [31] or I₈²⁻ [32]. The assignment of the iodine species as I₃⁻ in both (In, Zr) diphthalocyaninato complexes implies a +2/3 formal oxidation state for [InPc₂] and [ZrPc₂] units; so these complexes can be better formulated as [InPc₂](I₃)_{2/3} and [ZrPc₂](I₃)_{2/3}, where one electron per 3/2 MPc₂ molecules has been transferred to the I₃⁻ counter ion.

Table 3
Comparison of the coordination of the central ion in the iodine-doped and undoped indium(III) and zirconium(IV) diphthalocyaninato complexes

Compound	[InPc ₂](I ₃) _{2/3}	InPc ₂	[ZrPc ₂](I ₃) _{2/3}	ZrPc ₂
Formal oxidation state of Pc macroring	-1.167	-1.5	-1.667	-2
M–N (Å)	2.523(2)	2.333(9)	2.527(3)	2.30
Distance between <i>N</i> -isoinidole plane (Å)	3.196(1)	2.741(9)	3.244(1)	2.52
Rotation of the Pc rings (°)	40.0(1)	42.2(4)	40.6(1)	42.0
Reference	this work	[5]	this work	[24]

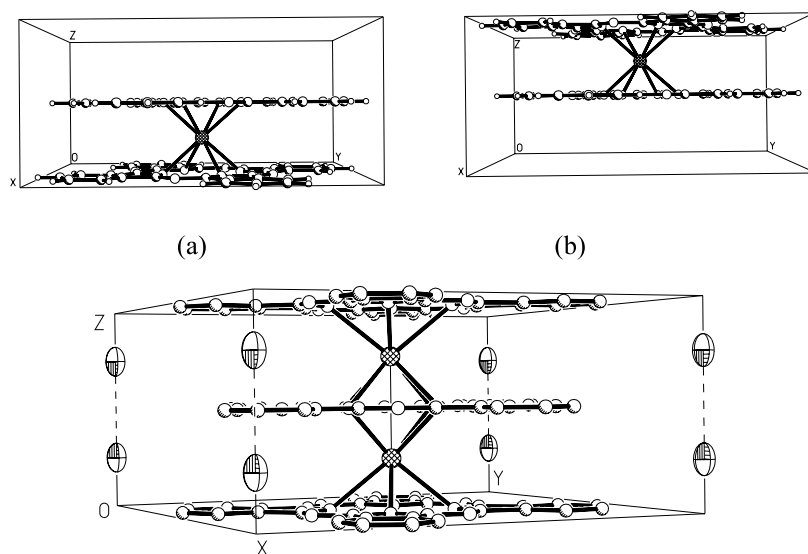


Fig. 3. Crystal structure of [MPc₂]I₂ (M = In, Zr) viewed perpendicular to the macrocycle stacking direction. (a) and (b) are shown at the 50% probability level.

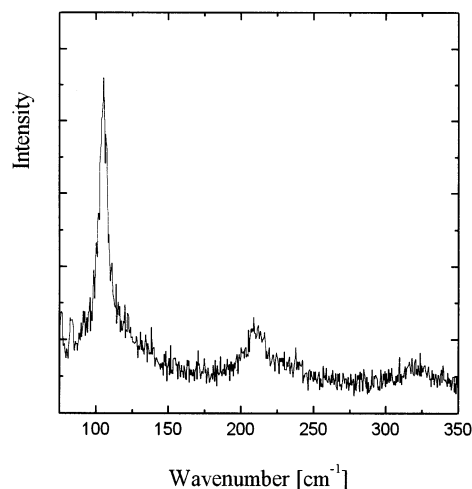


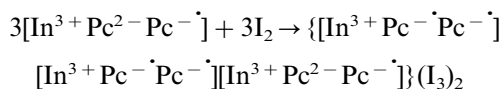
Fig. 4. Resonance Raman spectra of polycrystalline sample of $[\text{MPc}_2]\text{I}_2$ ($M = \text{In}, \text{Zr}$) at room temperature.

Consequently the one Pc macrocyclic ring would have the formal oxidation state of -1.167 ($-7/6$) and -1.667 ($-5/3$) in the indium and zirconium diphthalocyaninato complexes, respectively, since the crystal structure analysis shown that both Pc macrorings of the MPc_2 unit in these structures are identical in bond lengths and angles. Recently, for understanding the nature of the bonding in the I_3^- ion, i.e. electron-rich three-centre bonding in more details, the theoretical calculations using the qualitative molecular orbitals theory have been performed [33]. The I– I_2 bonding energy in the symmetrical triiodide I_3^- ion was calculated to be $37.5 \text{ kcal mol}^{-1}$. The calculated charge on the two terminal iodine atoms equals to -0.418 while the central iodine has only charge of -0.163 . The I–I bond lengths in the I_3^- ion calculated on the basis of the optimised geometry of the I_3^- ion ($D_{\infty h}$) equal to $\sim 3.14 \text{ \AA}$ and are approximately 0.3 \AA longer than the I–I bond length in optimised neutral diiodine (I_2) molecule (2.86 \AA) [33]. The I–I bond lengths in the symmetrical I_3^- ion in both crystal structures are similar and equal to $3.046(6)$ and $3.042(6) \text{ \AA}$ in the In and Zr diphthalocyaninato complexes, respectively. These values correlate with the optimised ones if we take into account the I–I bond length of $2.715(6) \text{ \AA}$ in pure iodine in solid state (at $-163 \text{ }^\circ\text{C}$) [34] that is shorter by about 0.1 \AA than those in the optimised gas-phase I_2 molecule.

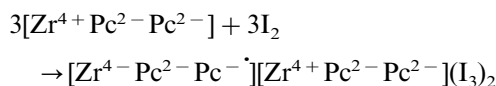
From both X-ray and Raman investigations we concluded that iodine-doped atoms in both (In and Zr) crystals form ordered chains of symmetrical triiodide I_3^- ions, that are disordered (translated) with respect to their neighbour as schematically illustrated in Fig. 1. This conclusion is consistent with the diffuse X-ray scattering lines observed in the planes perpendicular to the stacking direction. In both iodine-doped indium

and zirconium diphthalocyanine crystals the diffuse X-ray scattering lines were not able to be indexed on the basis of a superlattice spacing of about 9.6 \AA ($3/2c$), which is typical of a triiodide superlattice containing the iodine-doped metallomonophthalocyanine as $\text{NiPc}(\text{I}_3)_{1/3}$ [35] or $\text{Ni}(\text{tbp})(\text{I}_3)_{1/3}$ [36], since the diffuse lines are slightly modulated. This fact indicates that there is a small degree of the three-dimensional order, and therefore both crystal structures have been determined on the basis lattice. Earlier we reported that besides the iodine-doped complexes containing symmetrical triiodide ions (I_3^-), the iodine-doped atoms can form unsymmetrical I_3^- ions in the metallophthalocyanines structures as in MoOPcI_3 [37] or in SbPcI_3 [38] as well as can form a neutral molecule of I_2 , which is a bridge for a dimerisation or for developing a polymeric form of mono- and diiodometallophthalocyanine complexes [39,40].

The EPR spectrum on the solid samples of $[\text{InPc}_2](\text{I}_3)_{2/3}$ and $[\text{ZrPc}_2](\text{I}_3)_{2/3}$ at room temperature exhibits a single signal at $g = 2.0028$ and 2.0026 , respectively. For a comparison, the EPR spectrum of the undoped InPc_2 complex also shows single signal with a slightly lowered g parameter (2.0025) [5]. Since both central cations in these complexes are closed-shell diamagnetic (In^{3+} (d^{10}) and Zr^{4+} (d^0)) ions, we suggest that both complexes are ligand-centred π radicals. Integration of the EPR signals results only ~ 0.099 and ~ 0.185 spins per $[\text{InPc}_2](\text{I}_3)_{2/3}$ and $[\text{ZrPc}_2](\text{I}_3)_{2/3}$ molecule, respectively. These values are significantly lower than the values postulated by Raman spectroscopy. For better understanding of the lowered EPR signal, the partial oxidation process may be described as postulated from Raman experiment:



and similarly for Zr complex:



For the In complex it should be stated that in the first two units $[\text{In}^{3+} + \text{Pc}^{\cdot-} - \text{Pc}^{\cdot-}]$ the electrons could interact with each other, which gives $S = 0$. The third unit $[\text{In}^{3+} + \text{Pc}^{2-} - \text{Pc}^{\cdot-}]$ with one unpaired electron is EPR active, thus one free unpaired electron per three $[\text{InPc}_2]$ units should be given about 0.33 spins per $[\text{InPc}_2](\text{I}_3)_{2/3}$ molecule. For the zirconium complex the first two $[\text{Zr}^{4+} + \text{Pc}^{2-} - \text{Pc}^{\cdot-}]$ units contain unpaired electron that give about 0.66 spins per $[\text{ZrPc}_2](\text{I}_3)_{2/3}$ molecule. The distinctly lowered spins concentration observed in the EPR experiments can be explained by a strong interaction between the $\text{Pc}^{\cdot-}$ radical, since the interplanar spacing between the Pc planes is relatively short, $\sim 3.2 \text{ \AA}$ for both complexes.

The electronic absorption spectra of both complexes recorded in DMSO are similar in the spectral region of B-Soret band (Fig. 5(a) and (b)), but they differ in the region of Q band. The B-Soret band is centred at about 355 nm for both complexes, and corresponds well with the transition observed in other metallodiphtalocyaninato complexes [41]. In the spectral region 550–800 nm we observe four bands. The most prominent band

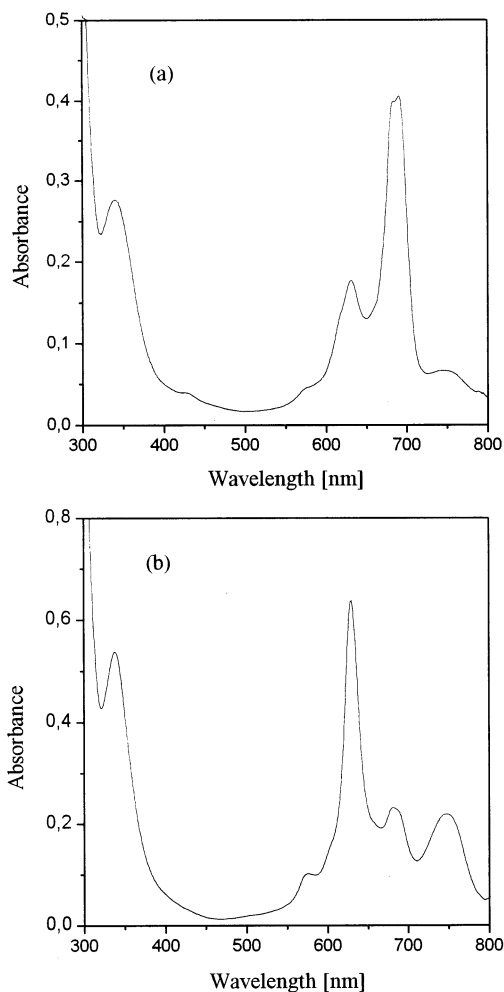
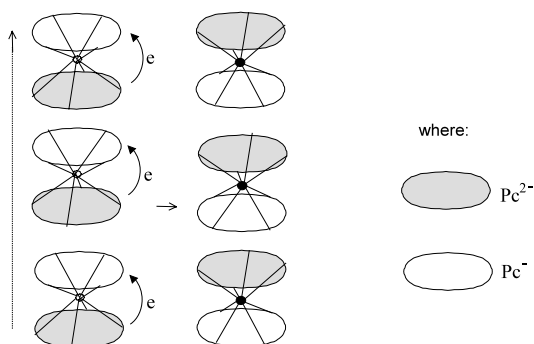


Fig. 5. Electronic spectra of $[\text{InPc}_2]\text{I}_2$ (a) and $[\text{ZrPc}_2]\text{I}_2$ (b) in DMSO.



Scheme 3.

in the spectrum of $[\text{InPc}_2]\text{I}_2$ complex in DMSO lies at ~ 688 nm (the other bands lie at about 575, 630 and 750 nm) while in the spectrum of $[\text{ZrPc}_2]\text{I}_2$ complex it lies at 632 nm (the other bands lie at about 573, 686 and 750 nm). The Q band is assigned to the excitation between the HOMO A_{1g} ground state ($(a_{1u}^2)(\pi)$) and the degenerate LUMO ($(e_g)(\pi^*)$)—the first excited state. Several authors reported [42] that the splitting value of Q band (~ 60 nm) decreases as the interplanar Pc–Pc distance increases. Additionally, Takahashi et al. [43] reported that as interplanar distance lengthens, the intensity of the Q_1 band decreases and that of Q_2 increases. As can be seen from the X-ray structure analysis the interplanar Pc–Pc distance in the complex of $[\text{InPc}_2]\text{I}_2$ is shorter by about 0.05 \AA than that found in the zirconium analogue. Thus in the spectrum of indium diphtalocyaninato complex we attributed the bands at ~ 688 and ~ 630 nm to Q_1 and Q_2 bands, respectively. The equivalent Q_1 and Q_2 bands in the spectrum of the zirconium complex lie at ~ 686 and ~ 633 nm. The inversion of the intensities of the Q_1 and Q_2 bands and the splitting value of ~ 58 nm (in the spectrum of $[\text{InPc}_2]\text{I}_2$) and ~ 53 nm (in the spectrum of $[\text{ZrPc}_2]\text{I}_2$) correlate well with the X-ray experiment.

The electrical conductivities of $[\text{InPc}_2](\text{I}_3)_{2/3}$ and $[\text{ZrPc}_2](\text{I}_3)_{2/3}$ at room temperature measured on several samples are equal to $2.7\text{--}3.1 \times 10^{-2}$ and $5.2\text{--}5.5 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$, respectively. With decreasing of the temperature the conductivity also decreases, thus both iodine-doped complexes exhibit non-metallic character in conductivity ($d\sigma/dT > 0$). The conductivity at liquid nitrogen ($\sim 78 \text{ K}$) is smaller by about two order. These data have been obtained on compressed polycrystalline samples and suffer from interparticle contact resistance effects and from being averaged over all crystallographic orientations. The charge propagation mainly proceeds along the pseudo-mono-dimensional $[\text{MPc}_2]^{2/3+}$ aggregates. During charge transport there is no need to change the population distribution among the sites, since both crystals of iodine-doped diphtalocyaninato complexes with closed-shell (d^{10} or d^0) metal(III) or metal(IV) cation contain partially oxidised phthalocyaninato macrorings (as was evidenced by EPR spectroscopy). Thus the jumping of the electron from one side to another with the pre-formed hole takes place between isoenergetic configuration (Scheme 3). 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 $10^2\text{--}10^3$ [35].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Data Centre, CCDC Nos. 161029 and 161030 for InPc_2I_2 and ZrPc_2I_2 respectively. Copies of this information may be obtained free of charge from The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

The authors thank the CNPq foundation for the financial support.

References

- [1] (a) A.N. Darovskikh, A.K. Tsytsenko, O.F. Frank-Kamenskaya, V.S. Fundamenskii, P.N. Moskalev, *Sov. Phys. Crystallogr.* 29 (1984) 273;
(b) A.N. Darovskikh, O.F. Frank-Kamenskaya, V.S. Fundamenskii, A.M. Golubev, *Sov. Phys. Crystallogr.* 31 (1986) 165;
(c) A.N. Darovskikh, O.F. Frank-Kamenskaya, V.S. Fundamenskii, *Sov. Phys. Crystallogr.* 31 (1986) 534.
- [2] (a) A. Darovsky, L.Y. Wu, P. Lee, H.S. Shen, *Acta Crystallogr., Sect. C* 47 (1991) 1836;
(b) A. Darovsky, V. Keserashvili, R. Harlow, I. Mutikainen, *Acta Crystallogr., Sect. B* 50 (1994) 582.
- [3] (a) A. DeCian, M. Moussavi, J. Fischer, R. Weiss, *Inorg. Chem.* 24 (1984) 273;
(b) D. Chabach, M. Lachbar, A. DeCian, J. Fischer, R. Weiss, *New J. Chem.* 16 (1992) 431.
- [4] G. Ostedorp, J.P. Werner, H. Homborg, *Acta Crystallogr., Sect. C* 51 (1995) 1125.
- [5] J. Janczak, R. Kubiak, A. Jezierski, *Inorg. Chem.* 34 (1995) 3505.
- [6] M. Safarpour-Haghihi, H. Rath, H.W. Rotter, H. Homborg, *Z. Anorg. Allg. Chem.* 619 (1993) 1897.
- [7] A. Capobianchi, C. Ercolani, A.M. Paoletti, G. Pennesi, G. Rossi, A. Chiesi-Villa, C. Rizzoli, *Inorg. Chem.* 32 (1993) 4605.
- [8] (a) G. Ostedorp, H.W. Rotter, H. Homborg, *Z. Naturforsch., Teil B* 51 (1996) 567;
(b) G. Ostedorp, H.W. Rotter, H. Homborg, *Z. Anorg. Allg. Chem.* 622 (1996) 235.
- [9] J. Janczak, R. Kubiak, F. Hahn, *Inorg. Chim. Acta* 281 (1998) 195.
- [10] J. Janczak, R. Kubiak, *Polyhedron* 18 (1999) 1621.
- [11] J. Janczak, R. Kubiak, A. Jezierski, *Inorg. Chem.* 38 (1999) 2043.
- [12] J. Janczak, R. Kubiak, I. Svoboda, A. Jezierski, H. Fuess, *Inorg. Chim. Acta* 304 (2000) 150.
- [13] H. Homborg, Ch.L. Teske, *Z. Anorg. Allg. Chem.* 527 (1985) 45.
- [14] (a) T.J. Marks, *Ann. N.Y. Acad. Sci.* (1978) 594;
(b) M. Cowie, A. Gleizes, G.W. Gryniewicz, D.W. Kalina, M.S. McClure, R.P. Scaringe, R.C. Teitelbaum, S.L. Ruby, J.A. Ibers, C.R. Kannewurf, T.J. Marks, *J. Am. Chem. Soc.* 110 (1979) 2921;
(c) T.J. Marks, K.F. Schock Jr., B.B. Kundalkar, *Synth. Met.* 1 (1980) 337;
(d) R.P. Scaringe, J.A. Ibers, *Acta Crystallogr., Sect. A* 35 (1979) 803;
(e) H. Enders, H.J. Keller, M. Mégnamisi-Belombé, *Acta Crystallogr., Sect. A* 32 (1976) 945;
(f) S. Mogtert, J.P. Pougetand, R. Comés, *Ann. N.Y. Acad. Sci.* (1978) 234.
- [15] (a) C.J. Schramm, D.R. Stojakovic, B.M. Hoffman, T.J. Marks, *Science* 200 (1978) 47;
(b) J. Martinsen, S.M. Palmer, J. Tanaka, R.L. Greene, B.M. Hoffman, J.A. Ibers, *Phys. Rev., B (Condens. Matter)* 30 (1984) 6269;
(c) T.J. Marks, *Science* 227 (1985) 881;
(d) M.Y. Ogawa, J. Martinsen, S.M. Palmer, J.L. Stanton, J. Tanaka, R.L. Greene, B.M. Hoffman, J.A. Ibers, *J. Am. Chem. Soc.* 109 (1987) 1115.
- [16] (a) J.M. Williams, A.J. Schultz, A.E. Underhill, K. Carnerio, in: J.S. Miller (Ed.), *Extended Linear Chain Compounds*, vol. 1, Plenum Press, New York, 1982, pp. 73–118;
(b) M.C. Bohm, in: *One Dimensional Organometallic Material*, Lecture Notes in Chemistry, vol. 45, Springer, Berlin, 1987.
- [17] KUMA KM-4 CCD User's Guide, Wroclaw, Poland, 1999.
- [18] G.M. Sheldrick, SHELXTL Program, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1990.
- [19] G.M. Sheldrick, SHELXL-97, Program for the Solution and Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.
- [20] T.E. Phillips, J.R. Anderson, C.J. Schramm, B.M. Hoffman, *Rev. Sci. Instrum.* 50 (1979) 263.
- [21] J. Janczak, *Pol. J. Chem.* 74 (2000) 157.
- [22] J. Janczak, R. Kubiak, *Inorg. Chim. Acta* 288 (1999) 174.
- [23] J. Janczak, R. Kubiak, *J. Chem. Soc., Dalton Trans.* (1993) 3809.
- [24] J. Silver, P. Lukes, S.D. Howe, B. Howlin, *J. Mater. Chem.* 1 (1991) 29.
- [25] L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, 1960, p. 262.
- [26] R.C. Teitelbaum, S.L. Ruby, T.J. Marks, *J. Am. Chem. Soc.* 100 (1978) 3215.
- [27] R.C. Teitelbaum, S.L. Ruby, T.J. Marks, *J. Am. Chem. Soc.* 102 (1980) 3222.
- [28] M. Mizuno, J. Tanaka, I. Harada, *J. Phys. Chem.* 85 (1981) 1788.
- [29] M.F. Belicchi, G.G. Fava, C. Pelizzi, *Acta Crystallogr., Sect. B* 37 (1981) 924.
- [30] D.C. Miller, J.C. Bollinger, B.M. Hoffman, J.A. Ibers, *Inorg. Chem.* 33 (1994) 3354.
- [31] O. Hessel, H. Hope, *Acta Chem. Scand.* 15 (1961) 407.
- [32] A.J. Jiricitano, M.C. Colton, K.B. Mertes, *Inorg. Chem.* 20 (1981) 890.
- [33] G.A. Landrum, N. Goldberg, R. Hoffmann, *J. Chem. Soc., Dalton Trans.* (1997) 3605.
- [34] F. Van Bolhuis, B.P. Koster, T. Migchelsen, *Acta Crystallogr.* 23 (1967) 90.
- [35] C.J. Schramm, R.P. Scaringe, D.R. Stojakovic, B.M. Hoffman, J.A. Ibers, T.J. Marks, *J. Am. Chem. Soc.* 102 (1980) 6702.
- [36] J. Martinsen, L.J. Pace, T.E. Phillips, B.M. Hoffman, J.A. Ibers, *J. Am. Chem. Soc.* 104 (1982) 83.
- [37] J. Janczak, R. Kubiak, *Inorg. Chem.* 38 (1999) 2429.
- [38] R. Kubiak, J. Janczak, M. Razik, *Inorg. Chim. Acta* 293 (1999) 155.
- [39] J. Janczak, R. Kubiak, F. Hahn, *Inorg. Chim. Acta* 287 (1999) 101.
- [40] J. Janczak, M. Razik, R. Kubiak, *Acta Crystallogr., Sect. C* 55 (1999) 359.
- [41] (a) R. Aroca, R.E. Clavijo, C.A. Jennings, G.J. Kovac, J.M. Duff, R.O. Loutfy, *Spectrochim. Acta, Sect. A* 45 (1989) 957;
(b) C. Clarisse, T.I. Riou, *Inorg. Chim. Acta* 130 (1987) 139;
(c) D. Markovitsi, T.H. Tran-Thi, R. Even, J. Simon, *Chem. Phys. Lett.* 137 (1987) 107.
- [42] (a) N. Ishikawa, Y. Kaizu, *J. Phys. Chem.* 100 (1996) 8722;
(b) K. Takahashi, Y. Tomita, Y. Harada, K. Tsubota, M. Honda, K. Kasuga, K. Sogabe, T. Tokii, *Chem. Lett.* (1992) 759.
- [43] K. Takahashi, J. Shimoda, M. Itoh, Y. Fuchita, H. Okawa, *Chem. Lett.* (1998) 173.