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Synthesis, crystal structure and charge transport properties of one-electron oxidized zirconium diphthalocyanine, $[ZrPc_2]IBr_2$

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Abstract

Crystals of the new one-electron oxidized zirconium diphthalocyanine, $[ZrPc_2]IBr_2$ ($Pc = C_{32}H_{16}N_8$) were grown directly from phthalonitrile and pure zirconium powder under the oxidation conditions of IBr at 220 °C. $[ZrPc_2]IBr_2$ crystallises in the space group $P2_1/m$ of the monoclinic system, with lattice parameters of: $a = 6.697(1)$, $b = 25.483(5)$, $c = 16.918(3)$ Å, $\beta = 100.03(3)°$ and $Z = 2$. The crystals of $[ZrPc_2]IBr_2$ are built up from one-electron oxidized $[ZrPc_2]^+$ units that form stacks parallel to a axis of the crystal and mixed electron-rich trihalide ions of IBr_2^-. The iodine atom of the IBr_2 ions is located at the inversion center, so the IBr_2^- ions are linear and symmetrical. The mutual arrangement of $[ZrPc_2]^+$ and IBr_2^- ions is different to that found in the one-electron oxidized $[ZrPc_2]I_3 \cdot I_2$ complex as well as to that found in the tetragonal crystals of partially oxidized $[ZrPc_2](I_3)_{2/3}$. EPR experiment shows that the oxidation of the diamagnetic $ZrPc_2$ complex by IBr is ligand centered. The UV–Vis spectrum of $[ZrPc_2]IBr_2$ shows, besides the bands observed in the spectrum of $ZrPc_2$, one additional band at ~496 nm, which indicates the existence of the one-electron oxidized phthalocyaninato(1−)π-radical ligand and it is assigned to the electronic transition from a deeper level to the half-occupied HOMO level. The single-crystal electrical conductivity data shows anisotropy and non-metallic character in conductivity ($d\sigma/dT > 0$). The charge transport mainly proceeds along the stacks of one-electron oxidized $[ZrPc_2]^+$ units. The relatively high conductivity along the $[ZrPc_2]^+$ stack results from the staggered configuration of the Pc-rings (rotation angle 45.0(3)°) that makes short inter-ring C_α(pyrrole)–C_α(pyrrole) contacts (2.858(2)–3.017(3) Å) and greatest overlap of the HOMO orbitals that form the conduction band of the molecular materials.

Keywords: Zirconium diphthalocyanine; Partially oxidized diphthalocyanine; Crystal structure; Magnetic properties; Electrical conductivity

1. Introduction

Partial oxidation by iodine of phthalocyaninato-like metallomacrocyclic complexes has yielded a series of one-dimensional highly conducting molecular materials [1–14]. Generally, the electrical properties of these materials are strictly connected with the structural and electronic features of the macrocyclic ring, which is the site of the extensive π-electron delocalisation, as well as on the nature and the electronic structure of the central metal ion [4]. The majority of the partially oxidized metallophthalocyaninato complexes crystallise in the tetragonal system and retain a single structural motif that consists of metal-over-metal pseudo-mono-dimensional columnar stacks of partially oxidized $MPc^{\delta+}$ units surrounded by linear chains of symmetrical triiodide anions [6]. The arrangement of the macrocycles in the stacks can be described by an ABAB pattern along the *c* axis, with a rotation angle φ between the adjacent A and B macrocycles. The interplanar spacing between the macrocycles within the stacks is not too different from the average value of ~3.25 Å, i.e. half of the *c* parameter of the crystals, which indicates a strong π–π interaction between the macrocycles within the stacks [15,16]. The π–π interaction between the partially oxidized macrocyclic rings is responsible for the observed high conductivity of these materials [17,18].

An understanding of the charge transport in these partially oxidized macrocyclic molecular materials requires

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the knowledge of the 'ionicity', i.e. degree of the partial oxidation. Resonance Raman and ^{129}I Mössbauer spectroscopies as well as diffuse X-ray scattering techniques are simple means of characterising the anionic polyiodine species and determine the 'ionicity' [19–23]. On the other hand, EPR spectroscopy is useful for characterising the materials, if both parts of the complex, i.e. the central metal (for example Mn, Fe, Co) and the π-electron macrocyclic ligand, are redox active since both oxidized forms $M^{2+}(Pc^{(1-)})I$ and $M^{3+}(Pc^{(2-)})I$ exhibit different EPR spectra. Additionally, EPR spectroscopy provides clear evidence for exchange coupling between the localised unpaired electron on the central metal ion and the π-carriers of the macrocycle within the stacks, as observed for CoPcI [24] and CuPcI [25], both linear-chain metal-spine conductors.

Although a few partially oxidized metallodiphthalocyaninato complexes are known [26], the correlation between the structure, π-orbital overlap and conductivity has not been systematically examined for such a system. In the course of our studies on metallodiphthalocyaninato complexes, the partially oxidized sandwich-type metallodiphthalocyanines are divided into two categories: (1) undoped metal(III) diphthalocyanines [27–32] and (2) iodine-doped partially oxidized metal(III) and metal(IV) diphthalocyanines [33–39]. In the first category M(III)Pc_2, exhibiting semiconducting properties, the central metal M(III) is sandwiched between the Pc^{2-} and one-electron oxidized $Pc^{-\cdot}$ radical ligand, however, the X-ray single crystal analysis shows that both halves of these sandwich complexes are equivalent structurally, thus a non-integral oxidation state should be assigned to both of them ($\rho = -1.5$). In the second category, iodine-doped metal(III) and metal(IV) diphthalocyanines, the conductivity depends strongly on the amount of iodine-doped atoms, which is closely correlated with the formal oxidation state of Pc macrocyclic ring.

Similar to iodine-doped metallomonophthalocyanines, the iodine-doped metallodiphthalocyaninato complexes also crystallise in the tetragonal system, in which the central metal ion is disordered over two symmetrically equivalent positions [33–39]. Quite recently we have stated that iodine-doped zirconium diphthalocyanine, depending on the crystallisation process and the amount of the iodine, can crystallise also in the monoclinic system [39]. Using a slightly modified method [40] we have obtained a new partially oxidized zirconium diphthalocyanine $[ZrPc_2]IBr_2$. Although, this complex contains the trihalide ions IBr_2^-, similar to the tetragonal iodine doped zirconium diphthalocyanine $[ZrPc_2](I_3)_{2/3}$ that contains the I_3^- ion [38], the complexes are not isostructural. Therefore for understanding the charge transport properties of $[ZrPc_2]IBr_2$ complex a knowledge of its crystal structure is needed. Additionally, the correlation between the crystal structures and charge transport properties of the two iodine-doped different zirconium diphthalocyaninato complexes $[ZrPc_2](I_3)_{2/3}$, $[ZrPc_2]I_3 \cdot I_2$, described earlier [38,39], with the third complex $[ZrPc_2]IBr_2$, described here, are reported. The crystal structures and properties of the partially oxidized zirconium diphthalocyanine complexes are discussed and compared with the undoped $ZrPc_2$ complex [41].

2. Experimental

2.1. Synthesis

All reagents were of the highest grade commercially available and were used as received. The crystals of $[ZrPc_2]IBr_2$ were obtained directly by the reaction of pure powdered zirconium and phthalonitrile under a stream of IBr. The powdered zirconium (0.182 g), phthalonitrile (2.050 g) and IBr (0.450 g) in a molar proportion of 1:8:2, with about 5% excess of IBr, were mixed together and pressed into pellets. The pellets were inserted into an evacuated glass ampoule (ca. 25 cm long) and sealed. The part of ampoule with the pellets was heated at about 220 °C for one day. At this temperature the liquid phthalonitrile undergoes catalytic tetramerization forming the phthalocyaninato rings, which accepts the electron from the zirconium and forms sandwich $ZrPc_2$ molecules. Simultaneously IBr partially oxidized the $ZrPc_2$ molecules and transforms into IBr_2^- ions and neutral diiodine molecules, yielding good quality single crystals with the composition $[ZrPc_2]IBr_2$. The major part of the iodine formed during formation of the $[ZrPc_2]IBr_2$ crystals resublimed at the cooler part of the ampoule. After opening the ampoule, the iodine that formed from IBr during the preparation procedure as an impurity is easily lost after expose to air at room temperature (3–4 days) or by slowly heating to about 40–45 °C. The elemental analysis has been performed on an energy dispersive spectrometer. Calc. for $C_{64}H_{32}N_{16}ZrIBr_2$: Zr, 6.50; I, 9.04; Br, 11.38; C, 54.78; N, 15.96; H, 2.34. Found: Zr, 6.45; I, 9.15; Br, 11.33; C, 54.84; N, 15.98; H, 2.29%.

2.2. X-ray diffraction study of $[ZrPc_2]IBr_2$

The X-ray single crystal data were collected on a KUMA KM-4 diffractometer equipped with a two-dimensional area CCD detector from a single crystal (black-violet) with dimensions of $0.22 \times 0.18 \times 0.14$ mm. The graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) and ω-scan technique with $\Delta\omega = 0.75°$ for one image were used. 960 images for six different runs covering over 95% of the Ewald sphere were performed. The exposure times were 20 s/image. Accurate cell parameters were refined by least-squares methods on the basis of 2577 of the strongest reflections. One image was monitored as a standard after every 40 images for a control of the stability of the crystal. Integration of the intensities, corrections for Lorentz and polarisation effects were carried out using KUMA KM-4 CCD software [42]. Face-indexed analytical absorption was calculated using the SHELXTL program [43]. The minimum and maximum transmission factors are 0.641 and 0.744, respectively. A total of 25 532 (6899 independent, $R_{int} = 0.0306$) reflections were integrated and used for the crystal