



Mixed-valence, disordered structures and characterization of iodine-doped phthalocyanines: $[\text{YbPc}_2]\text{I}_2$ and $[(\text{AsPc})(\text{Pc})]\text{I}_2$.

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Artykuł

Crystals of $C_{64}H_{32}N_{16}YbI_2$ and $C_{64}H_{32}N_{16}AsI_2$ 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 $[YbPc_2]$ or $[(AsPc)(Pc)]$ units with an average nonintegral charge of $+^{2/3}$ and linear chains of triiodide I_3^- ions, which were detected by Raman spectroscopy. The monodimensional chains of I_3^- ions and pseudo-monodimensional aggregates of $[YbPc_2]^{2/3+}$ or $[(AsPc)(Pc)]^{2/3+}$ are aligned along the c -axis of the crystals. The Yb^{3+} ion lies in the center, whereas in the $[(AsPc)(Pc)]$ unit the As^{3+} ion does not lie in the center between the Pc rings. In the crystal of $[(AsPc)(Pc)]I_2$ 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 $[YbPc_2]I_2$ shows typical Curie–Weiss behavior, and the effective magnetic moment is about $4.60 \mu_B$. The EPR measurement shows no signal for the Yb complex, while for $[(AsPc)(Pc)]I_2$ 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 ($Pc^{\bullet-}$) ring and $[AsPc^{\bullet-}]$, respectively. Both free radicals are in resonance: $[(As^{3+}Pc^{2-})(Pc^{\bullet-})] \leftrightarrow [(As^{3+}Pc^{\bullet-})(Pc^{2-})]$. Oxygen effects on the EPR signal of the $[(AsPc)(Pc)]I_2$ crystal have been detected. The conductivity measured on polycrystalline samples at room temperature equals $2.5\text{--}4 \times 10^{-2}$ and $2.2\text{--}3.5 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ for $[YbPc_2]I_2$ and $[AsPc(Pc)]I_2$, respectively. Both complexes exhibit nonmetallic character in conductivity ($d\sigma/dT > 0$).

Słowa kluczowe

Crystal structure, Electron paramagnetic resonance spectroscopy, Iodine, Ions, Phthalocyanine

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