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Oxidation and oxygenation of carbonyl ruthenium(II) azuliporphyrin.

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Streszczenie

Chemical oxidation and oxygenation of carbonyl ruthenium(II) azuliporphyrin [Ru(TPAP)(CO)] were explored. [Ru(TPAP)(CO)] reacts with dioxygen giving carbonyl ruthenium(II) 21-oxyazuliporphyrin [Ru(TPAP-O)(CO)] revealing the activation the Ru–C bond inside azuliporphyrin coordination cavity. Solution and X-ray structural studies confirmed the tendency of [Ru(TPAP-O)(CO)] to form dimeric $[Ru(TPAP-O)(CO)]_2$. The dimer adopts a head-to-tail structure with the azulenolate groups forming bridges from one macrocycle to the ruthenium(II) in the adjacent unit. One-electron oxidation of [Ru(TPAP)(CO)] gives the first π-cation radical of metallocarbaporphyrinoid—$[Ru(TPAP)(CO)]^{+\bullet}$—with extraordinary participation of the azulene unit in the spin delocalization. The most characteristic ^{1}H NMR features of the radical are large, sign-alternating isotropic shifts of resonances assigned to *meso*-aryl, azulene, and pyrrolic hydrogen atoms. The spin distribution determined by density functional theory confirmed the π-cation radical electronic structure reproducing the diagnostic spectroscopic features including π-delocalization a t *meso*-aryl resonances and very characteristic sign alternation of contact shifts for an azulene moiety.

Adres publiczny

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