**SUPPLEMENTARY MATERIALS – ДОПОЛНИТЕЛЬНЫЕ МАТЕРИАЛЫ**

**μ-Nitrido and μ-carbido-dimeric macroheterocyclic complexes of iron and ruthenium as a molecular platform for modeling oxidative enzymes (review)**

**μ-Нитридо- и μ-карбидодимерные макрогетероциклические комплексы железа и рутения как молекулярная платформа для моделирования окислительных ферментов (обзор)**

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**Table S1.** Characteristic bands in the EAS and IR spectra of μ-nitride and μ-carbide dimeric complexes of iron and ruthenium with macrocyclic ligands.

**Таблица S1.** Характеристичные полосы в ЭСП и ИК-спектрах μ-нитридо- и μ-карбидодимерных комплексов железа и рутения с макроциклическими лигандами.

|  |  |  |
| --- | --- | --- |
| Complex | EAS (λmax, nm) | νas (М-X-М), cm-1 |
| μ-О(FeIIIPc(SO3H)4)2 | 632, 326 [86] |  |
| µ-О(FeIIIOPrTAP)2 | 613, 350 [78] |  |
| μ-N(FeIII,IVPc(SO3H)4)2 | 640, 336 [86] | 929 [86] |
| µ-N(FeIII,IVOPrTAP)2 | 584, 316 [78] |  |
| µ-N(FeIVPc(*t*Bu)4)2 | 644, 343 [54, 90] | 938[54] |
| µ-N(FeIII,IVPc(*t*Bu)4)2 | 637, 340 [106] | 938 [106] |
| μ-N(FeIII,IVTPP)2 | 529, 410 [104] |  |
| μ-C(FeIVTPP)2 | 530, 400, [93]522, 400 [53] | 940 [93]960[53], 954[51] |
| μ-C(FeIVOEP)2 | 581, 376 [69]585, 298 [78] | 976[69] |
| μ-C(FeIVPc)2 | 620, 309[100, 94] | 997[94] |
| μ-С(FeIVPc(*t*Bu)4)2 | 633, 302 [52]635 [100] | 984 [52] |
| μ-С(FeIVPcFeIVPc(*t*Bu)4) | 632 [100] |  |
| μ-С(FeIVPc(SO3H)8)2 | 625 [97] | 991/987[97] |
| µ-С(FeIVOPrTAP)2 | 585, 298 [78]582-584, 313 [50, 51] | 971[51], 967[50] |
| μ-С(RuIVPc(*t*Bu)4)2 | 616, 312[101]619, 310 [99] | 1003 [101]1016 [99] |
| μ-С(RuIVPc(OBu)8)2 | 607, 303 [61, 99] | 1013 [61] |

**Table S2.** Structural parameters of μ-oxo, μ-nitrido and μ-carbide dimeric iron complexes with octapropylporphyrazine [78].

**Таблица S2.** Структурные параметры μ-оксо-, μ-нитридо- и μ-карбидодимерных комплексов железа с октапропилпорфиразином [78].

|  |  |  |  |
| --- | --- | --- | --- |
| Parameter / complex | μ-О | μ-N | μ-С |
| Bond Fe-Npyr, Å | Fe(1)1.934-1.936Fe(2)1.936-1.946 | Fe(1)1.914-1.929Fe(2)1.915-1.932 | Fe(1)1.910-1.916Fe(2)1.911-1.915 |
| Bond Fe-μ-Х, Å | 1.760-1.750 | 1.656-1.662 | 1.669-1.671 |
| Displacement of Fe atoms from the plane of the macrocycle, Å | 0.3360.367 | 0.2830.291 | 0.2140.219 |
| Angle Fe-X-Fe, ° | 158.52 | 168.5 | 175.10 |
| Conformational angle, ° | 24.2 | 26.2 | 24.2 |
| Dihedral angle between two planes, ° | 19.3 | 11.5 | 8.2 |

**Table S3.** Structural parameters of μ-oxo-, μ-nitrido- and μ-carbide dimeric porphyrinates, porphyrazinates, and phthalocyaninates of iron [76, 78, 101, 104, 105].

**Таблица S3.** Структурные параметры μ-оксо-, μ-нитридо- и μ-карбидодимерных порфиринатов, порфиразинатов и фталоцианинатов железа [76, 78, 101, 104, 105]**.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Ligand | μ-О | μ-N | μ-C |
| Bond Fe-μX, Å | TPP | 1.763 | 1.68/1.66 | 1.68/1.66 |
| OPrTAP | 1.75, 1.76 | 1.656, 1.662 | 1.669, 1.671 |
| Pc | 1.76 | 1.64 | 1.66 |
| Out-of-plane distance Fe, Å | TPP | 0.500 | 0.492 | 0.260 |
| OPrTAP | 0.336. 0.367 | 0.283. 0.291 | 0.214. 0.219 |
| Pc | - | - | - |
| Angle Fe-X-Fe, ° | TPP | 174 | 177 | 180 |
| PzPr8 | 158.52 | 168.50 | 175.10 |
| Pc | - | - | - |

**Table. S4.** X-ray structural data of µ-nitridodimeric iron complexes with phthalocyanine and porphyrin.

**Таблица. S4.** Рентгеноструктурные данные µ-нитридодимерных комплексов железа с фталоцианином и порфирином.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Complex | N(FeIII,IVTPP)2 [104] | N(FeIII,IVОЕP)2 [60] | N(FeIIIРсFeIVТРP) [68] | N(FeIVPc)2Br2/N(FeIII,IVPc*t*Bu)2/N(FeIVPc*t*Bu)2Br2 [91] |
| М-N-М, ° | 177.0 | 175.2 | 179.0 | 180/178/179 |
| M-µ-N*bridge*,° | 1.679 | 1.657 | 1.6251.655 | 1.639/1.65/1.69 |
| Distance М-М,Å | 3.36 | 3.31 | 3.28 | 3.28/3.33/3.39 |
| Interplanar distance,Å | 3.93 | 3.83 | 3.51 | 3.28 |
| M-N*pyrrole*,Å | 2.003 | 2.005 | 2.00 | 1.945/1.94/1.93 |
| Conformational angle, ° | 28.7 | 23.1 | - | 39 |
| Fe-Hal, Å |  |  |  | 2.49/2.54 |

**Table S5.** EAS of μ-carbide dimeric iron (IV) complexes with peroxides in benzene [50, 52, 53, 89-91, 97, 101].

**Таблица S5.** ЭСП μ-карбидодимерных комплексов железа(IV) с пероксидами в бензоле [50, 52, 53, 89-91, 97, 101].

|  |  |
| --- | --- |
| Complex | max, nm |
| μ-N(FeIVPc(*t*Bu)4)2+DCP | 680, 626, 538 |
| μ-N(FeIVPc(*t*Bu)4)2+TBP | 689, 622, 530 |
| μ-N(FeIVPc(*t*Bu)4)2+TBHP | 682, 626, 532 |
| μ-С(FeIVTPP)2+TBHP | 627, 572, 413 |
| μ-C(FeOPrTAP)2+DCP | 673, 566, 309 |
| μ-C(FeOPrTAP)2+TBP | 675, 613, 563, 306 |
| μ-C(FeOPrTAP)2+TBHP | 675, 557, 304 |
| μ-C(FeIVPc(*t*Bu)4)2+TBP | 671, 596, 300 |
| μ-C(FeIVPc(*t*Bu)4)2+TBHP | 676, 595, 298 |
| μ-С(FeIVPc(HSO3)8)2+TBHP | 674 |
| μ-C(RuIVPc(*t*Bu)4)2+TBHP | 666 |

DCP - Dicumyl peroxide

TBP - Di-*tert*-butyl peroxide

TBHP - *tert-*Butyl hydroperoxide



**Fig. S1.** Mass spectrum MALDI TOF spectrum μ-С(RuIVPc(*t*Bu)4)2 in acetonitrile.

**Рис. S1.** Масс-спектр MALDI TOF спектр μ-С(RuIVPc(*t*Bu)4)2 в ацетонитриле.



**Fig. S2.** IR spectra of μ–carbido dimeric iron (IV) complexes of iron(IV) in the presence of nitrogen-containing bases. μ-С(FeIVOPrTAP)2in KBr; μ-C(FeIVPc(*t*Bu)4)2 and μ-С(FeIVTPP)2- benzene.

**Рис. S2.** ИК-спектры μ–карбидодимерных комплексов железа(IV) в присутствии азотсодержащих оснований. μ-С(FeIVOPrTAP)2 в KBr; μ-C(FeIVPc(*t*Bu)4)2 и μ-С(FeIVTPP)2 – бензол.



**Fig. S3.** Mass spectra of μ-С(FeIVOPrTAP)2 and μ-С(FeIVТРP)2 (*c* = 3.5·10–5 mol/l) in the presence of bases (*c*Im = 5.35·10–3 mol/l, *c*2-MeIm = 6.74·10–3 mol/l, *c*Et2NH = 1.52·10–2 mol/l).

**Рис. S3.** Масс-спектры μ-С(FeIVOPrTAP)2 и μ-С(FeIVТРP)2 (*с* = 3.5·10–5 моль/л) в присутствии оснований (*с*Im = 5.35·10–3 моль/л, *c*2-MeIm = 6.74·10–3 моль/л, *c*Et2NH = 1.52·10–2 моль/л).



**Fig. S4.** MALDI-TOF spectrum of the μ-С(RuIVPc(*t*Bu)4)2-TBHP system in acetonitrile: μ-С(RuIVPc(*t*Bu)4)2 (m/z = 1688.89), (О)RuIVPc•+(*t*Bu)4С(*t*Bu)4PcRuIV (m / z = 1703.95).

**Рис. S4.** MALDI-TOF-спектр системы μ-С(RuIVPc(*t*Bu)4)2-TBHP в ацетонитриле: μ-С(RuIVPc(*t*Bu)4)2 (m/z = 1688.89), (О)RuIVPc•+(*t*Bu)4С(*t*Bu)4PcRuIV (m/z = 1703.95).



**Fig. S5.** IR spectra (benzene): μ-N(FeIVPc(*t*Bu)4)2Cl (a); μ-N(FeIVPc(*t*Bu)4)2Cl with TBHP immediately after mixing (b); μ-N(FeIVPc(*t*Bu)4)2Cl with TBHP at the end of reaction (*c* = 1.4·10–5 mol/l, *c*TBHP = 2.3·10–2 mol/l) (c); μ-C(RuIVPc(*t*Bu)4)2 (d); μ-C(RuIVPc(*t*Bu)4)2 with TBHP at the end of the reaction (*c* = 5.2∙10–6 mol/l; *c*TBHP = 2.74·10–3 mol/l) (e).

**Рис. S5.** ИК-спектры (бензол): μ-N(FeIVPc(*t*Bu)4)2Cl (a); μ-N(FeIVPc(*t*Bu)4)2Cl с TBHP сразу после смешивания (b); μ-N(FeIVPc(*t*Bu)4)2Cl с TBHP в конце реакции (*с* = 1.4·10–5 моль/л, *с*TBHP = 2.3·10–2 моль/л) (c); μ-C(RuIVPc(*t*Bu)4)2 (d); μ-C(RuIVPc(*t*Bu)4)2 с TBHP в конце реакции (*с* = 5.2∙10–6 моль/л; *с*TBHP = 2.74·10–3 моль/л) (e).



**Fig. S6.** Mass spectra of μ-C(FeIVOPrTAP)2 (*c* = 8.2∙10–6 mol/l) after reaction with TBP (*c*TBP = 1.15∙10–2 mol/l): without imidazole (a); in the presence of imidazole (*с*Im = 5.35∙10-3 mol/l) (b)

**Рис. S6.** Масс-спектры μ-C(FeIVOPrTAP)2 (*с* = 8.2∙10–6 моль/л) после реакции с TBP (*с*TBP = 1.15∙10–2 моль/л): без имидазола (a); в присутствии имидазола (*с*Im = 5.35∙10–3 моль/л) (b)