Article

DFT/TD-DFT Framework of Mixed-Metal Complexes with Symmetrical and Unsymmetrical Bridging Ligands—Step-By-Step Investigations: Mononuclear, Dinuclear Homometallic, and Heterometallic for Optoelectronic Applications

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Abstract: Recently, mono- and dinuclear complexes have been in the interest of scientists due to their potential application in optoelectronics. Herein, progressive theoretical investigations starting from mononuclear followed by homo- and heterometallic dinuclear osmium and/or ruthenium complexes with NCN-cyclometalating bridging ligands substituted by one or two kinds of heteroaryl groups (pyrazol-1-yl and 4-(2,2-dimethylpropyloxy)pyrid-2-yl) providing the short/long axial symmetry or asymmetry are presented. Step-by-step information about the particular part that built the mixed-metal complexes is crucial to understanding their behavior and checking the necessity of their eventual studies. Evaluation by using density functional theory (DFT) calculations allowed gaining information about the frontier orbitals, energy gaps, and physical parameters of complexes and their oxidized forms. Through time-dependent density functional theory (TD-DFT), calculations showed the optical properties, with a particular emphasis on the nature of low-energy bands. The presented results are a clear indication for other scientists in the field of chemistry and materials science.

Keywords: pyrene bridging ligands; complexes; osmium; ruthenium; DFT; TD-DFT

1. Introduction

In recent years, mono- and dinuclear complexes containing bridging ligands have been in scientists’ interest [1–5]. The reason for such a comprehensive investigation is the wide possibility of applying those kinds of molecules; they can be used in the area of energy-conversion materials and molecular electronics, but the area of application strongly depends on the applied metal centers [6–9]. The subgroup of dinuclear complexes of this type is the mixed-metal complexes, which are thus far described only by a few scientific teams. In the reported examples of dinuclear heterometallic complexes, such as the bridging ligands, 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tpy) was used most often. In 1993, Karen J. Brewer et al. initiated investigations in this area by reporting the Ir(III)/Ru(II) mixed-metal complex [(tpy)Ru(tpp)IrCl$_3$]$^{2+}$ and the monometallic fragments [Ir(tpp)Cl$_3$] and [Ru(tpy)(tpp)]$^{2+}$ [10]. The photochemical, electrochemical, and spectroelectrochemical studies proved the excellent communication between the metals in the case of a dinuclear, heterometallic complex. Later, the same authors presented bimetallic complexes [(tpy)Os(tpp)RuCl$_3$]$^{2+}$ and [(tpy)Os(tpp)Ru(tpp)]$^{1+}$ and their analogues containing only ruthenium [11], Ru(II)/Rh(III) [12], Ru(II)/Pt(II) [13], and multimetallic complexes [14]. The significant differences in the localization of frontier orbitals were evidence of the influence of the terminal ligands on the properties of the complexes. M. Haga and co-workers reported dinuclear ruthenium and osmium complexes with 1,3,4,6-tetrakis(2-pyridyl)benzene (tpb) as a bridging ligand [15]. Those kinds of complexes exhibited successive one-electron redox processes that correspond to M(II/III) and also a M(III/IV) couple (M = Ru, Os).
Dinuclear homometallic complexes bridging by NCN-cyclometalating pyrene ligands substituted by one kind of a heteroaryl group have been already discussed in terms of the differences between mono- and dinuclear complexes [1,16], symmetrical and unsymmetrical complexes [16], the influence of the various metal centers [3], and terminal ligands on the properties of complexes [17].

Moreover, it was recently presented that in the case of mononuclear osmium complexes with various NCN-cyclometalating pyrene ligands containing 4-(2,2-dimethylpropyloxy)pyrid-2-yl, pyrazol-1-yl, 1-decy1-1H-1,2,3-triazol-4-yl, and 2-butyl-2H-1,2,3,4-tetrazol-5-yl substituents, significant differences between the properties and behavior of complexes during oxidation were observed [18]. This was caused by the contribution of individual parts of molecules in the creation of frontier orbitals in reference to substituted heteroaryl groups at pyrene.

Furthermore, it was reported that in the case of disubstituted pyrenes at the non-K region, the substitution pattern does not play a role in the properties of the molecules [19]. Whereas studies in the area of tetrasubstituted pyrenes containing two kinds of substituents providing short axial symmetry, long axial symmetry or asymmetry showed significant differences among the examined group compared to analogues with the same four substituents [20,21].

Moreover, the possibility of synthesis of tetrasubstituted pyrenes substituted by two groups providing the short axial symmetry or asymmetry to the structure, i.e., pyrazol-1-yl, 4-(2,2-dimethylpropyloxy)pyrid-2-yl and 1-decy1-1,2,3-triazol-4-yl substituent, has been already presented [20,22]. The photophysical properties of obtained compounds, such as good solubility and thermal stability, allow them to be used as the NCN-cyclometalating ligands in the synthesis of target complexes.

Taking into account the fact that metal–metal interactions strongly depend, besides on the metal ion, on the nature of the bridging and terminal ligands [23], herein based on the previous research and already developed parameters of the theoretical calculations (DFT method), which correlate well with experimental data, the theoretical investigations of mono- and dinuclear homo- and heterometallic complexes containing osmium and/or ruthenium metals bridging by symmetrical or asymmetrical double NCN-cyclometalating pyrene ligands substituted by pyrazol-1-yl and 4-(2,2-dimethylpropyloxy)pyrid-2-yl group are presented.

2. Computational Methods

The DFT and TD-DFT calculations were performed with the B3LYP [24] exchange-correlation functional implemented in the Gaussian 09 program [25]. The Def2-TZVP basis set was used for osmium and ruthenium, and 6-31G(d,p) was employed for other atoms. The calculations were performed with acetonitrile as the solvent in the polarizable continuum model (PCM) [26]. The frequency calculations confirmed the energy minimum of the stationary state of all optimized geometries. All orbitals were computed at an isovalue of 0.02 e/bohr^3 (spin-density—the isosurface contour value 0.002 e/bohr^3). The contribution of each moiety in the creation of the selected orbitals was calculated by using Chemissian software (Version 4.60, Skripnikov Leonid 2005–2018). (https://www.chemissian.com/). The theoretical spectra and the extinction coefficients were based on Gaussian convolution by the GaussSum software (Version 3.0, Dublin, Ireland) [27]. The full-width half-maximum (FWHM) value used for the simulated spectra was 2000 cm^{-1}. Cartesian coordinates of DFT-optimized structure of all complexes with values of charge and multiplicity are presented in Supplementary Materials.

3. Results and Discussion

As the NCN-cyclometalating ligands, six pyrene derivatives substituted at positions 1, 3, 6, and 8 by one or two kinds of substituents (pyrazol-1-yl and 4-(2,2-dimethylpropyloxy)pyrid-2-yl) providing symmetry or asymmetry to the whole structure were used. The
synthesis way of these ligands and their nature has already been demonstrated. In the case of terminal ligand, 2,2′:6′,2″-terpyridine was applied (Figure 1).

**Figure 1.** The structures of bridging ligands and terminal ligand.

### 3.1. Mononuclear Osmium and Ruthenium Complexes

To check the influence of the NCN-cyclometalating pyrene ligands and coordinated metal on the properties of the target dinuclear complexes, first, the mononuclear complexes with osmium Os(I) 1a-6a and ruthenium Ru(I) 1b-6b were designed, as presented in Figure 2.

**Figure 2.** The structures of the mononuclear osmium 1a-6a and ruthenium 1b-6b complexes.

The optimized structures of molecules 1a-6a and 1b-6b are presented in Table 1. The contribution of individual parts of molecules in the creation of frontier orbitals is presented in Figure 3.
Table 1. The optimized structures with HOMOs and LUMOs contours for molecules 1a-6a and 1b-6b.

|   | HOMO | LUMO | HOMO | LUMO |
|---|------|------|------|------|
| 1a| ![Image](image1.png) | ![Image](image2.png) | 1b   | ![Image](image3.png) | ![Image](image4.png) |
| 2a| ![Image](image5.png) | ![Image](image6.png) | 2b   | ![Image](image7.png) | ![Image](image8.png) |
| 3a| ![Image](image9.png) | ![Image](image10.png) | 3b   | ![Image](image11.png) | ![Image](image12.png) |
| 4a| ![Image](image13.png) | ![Image](image14.png) | 4b   | ![Image](image15.png) | ![Image](image16.png) |
| 5a| ![Image](image17.png) | ![Image](image18.png) | 5b   | ![Image](image19.png) | ![Image](image20.png) |
| 6a| ![Image](image21.png) | ![Image](image22.png) | 6b   | ![Image](image23.png) | ![Image](image24.png) |
The contribution of ruthenium (46–48%) in creating the highest-occupied molecular orbitals of molecules 1b-6b is slightly higher than the contribution of osmium (44–46%) in the analogue molecules 1a-6a. The sum of contribution in the creation of HOMOs by coordinating heteroaryl groups equals ≈11% for 1a-6a and ≈10% for 1b-6b. When two kinds of heteroaryl groups participate in the coordination of metal (5a and 6a), the contribution of pyrazolyl groups is around two times higher than pyridyl substituents. The localization of the lowest unoccupied molecular orbitals for molecules 1a/b, 2a/b, 5a/b, and 6a/b does not show any significant differences; the contribution of pyrene is the highest, whereas LUMOs in 3a/b and 4a/b, where the coordination proceeds by pyrazolyl groups, are majorly localized on terpyridine. Moreover, for molecules 4a/b with pyrene substituted by two kinds of groups providing long axial symmetry, the contribution of terminal ligand (TPY) is very high, i.e., 85% for 4a and 87% for 4b. The values of energy of HOMOs, LUMOs, energy gaps, and bond lengths M(II)-C for molecules 1a-6a and 1b-6b are listed in Table 2.

Table 2. Energies of HOMOs and LUMOs, values of energy gaps, and bond lengths M(II)-C for complexes 1a-6a and 1b-6b.

|      | 1a  | 2a  | 3a  | 4a  | 5a  | 6a  | 1b  | 2b  | 3b  | 4b  | 5b  | 6b  |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| HOMO (eV) | -4.94 | -5.00 | -5.05 | -4.98 | -4.99 | -4.99 | -5.08 | -5.14 | -5.23 | -5.15 | -5.14 | -5.14 |
| LUMO (eV) | -2.43 | -2.47 | -2.31 | -2.23 | -2.37 | -2.38 | -2.41 | -2.47 | -2.30 | -2.24 | -2.36 | -2.36 |
| ΔE (eV)  | 2.51 | 2.53 | 2.74 | 2.75 | 2.62 | 2.61 | 2.67 | 2.67 | 2.93 | 2.91 | 2.78 | 2.78 |
| M(II)-C (Å) | 1.994 | 1.992 | 1.998 | 2.000 | 1.995 | 1.995 | 1.974 | 1.972 | 1.980 | 1.981 | 1.976 | 1.976 |

The energy gaps for mononuclear osmium complexes 1a-6a are lower than the values for corresponding ruthenium molecules 1b-6b (Figure 4). The order of the increasing values of the energy gaps does not follow the same trend. In the case of osmium complexes, the lowest ΔE was achieved by complex 1a followed by 2a < 6a < 5a < 3a < 4a, whereas the change of energy gaps’ values for ruthenium complexes followed the trend 1b = 2b < 5b = 6b < 4b < 3b.
Table 3. Calculated TD-DFT low-energy wavelengths in absorption spectra with oscillator strengths and dominant transitions (>10%) of molecules 1a-6a and 1b-6b.

Figure 4. The energies of frontier orbitals with the values of energy gaps for molecules 1a-6a and 1b-6b.

The lengths of the bond metal–carbon for osmium complexes 1a-6a are higher than for ruthenium complexes 1b-6b. Among the groups, the lengths differ from each other; the longest was achieved for complexes 4a (2.000 Å) and 4b (1.981 Å), respectively, where the coordination proceeds by pyrazolyl groups, whereas the shortest was for 2a (1.992 Å) and 2b (1.972 Å) with coordination by pyridyl groups. It is worth emphasizing that NCN-cyclometalating pyrene ligands in the case of 2a, 2b, 4a, and 4b are substituted by two kinds of groups providing long axial symmetry.

Absorption spectra of 1a-6a and 1b-6b were calculated by time-dependent density functional calculations (TD-DFT) presented in Figure 5.

Figure 5. Theoretical absorption spectra of complexes 1a-6a and 1b-6b.

The shape of the absorption spectra of complexes 1a-6a and 1b-6b is similar but with a noticeable difference in the area of low-energy bands 525–800 nm for 1a-6a and 500–700 nm for 1b-6b. It is caused by the character of the transition, which creates the lowest-energy bands dominated by transition H-1→LUMO (Table 3).
Table 3. Calculated TD-DFT low-energy wavelengths in absorption spectra with oscillator strengths and dominant transitions (>10%) of molecules 1a-6a and 1b-6b.

|    | Calculated Wavelengths [nm] | Oscillator Strengths | Dominant Transitions (Contribution) |
|----|-----------------------------|----------------------|-------------------------------------|
| 1a | 595.16                      | 0.2499               | H-1→LUMO (93%)                       |
| 2a | 601.37                      | 0.2030               | H-1→LUMO (95%)                       |
| 3a | 529.94                      | 0.1365               | H-1→LUMO (57%), H-1→L + 1 (31%), H-1→L + 2 (19%) |
| 4a | 524.38                      | 0.1993               | H-1→L + 1 (72%), H-1→L + 2 (16%)    |
| 5a | 567.98                      | 0.1843               | H-1→LUMO (80%), H-1→L + 2 (10%)     |
| 6a | 568.11                      | 0.1790               | H-1→LUMO (79%), H-1→L + 2 (10%)     |
| 1b | 550.77                      | 0.3083               | H-1→LUMO (84%), H-3→LUMO (10%)      |
| 2b | 556.08                      | 0.2317               | H-1→LUMO (88%)                       |
| 3b | 488.65                      | 0.2036               | H-1→L + 1 (44%), H-1→LUMO (36%)     |
| 4b | 485.74                      | 0.3345               | H-1→L + 1 (66%), H-2→L + 1 (21%)    |
| 5b | 524.27                      | 0.2768               | H-1→LUMO (78%), H-3→LUMO (11%)      |
| 6b | 524.56                      | 0.2686               | H-1→LUMO (77%), H-3→LUMO (11%)      |

To better understand the nature of the lowest energy bands for complexes 1a-6a and 1b-6b, NTO analysis for complexes containing osmium is presented in Table 4. Analysis of complexes 1a-6a showed that the lowest energy transitions were observed for complexes 1a and 2a, where the coordination proceeds by pyridyl substituents and can be described as the excited state S₄. In the case of molecules 3a and 4a, where pyrazolyl groups coordinate the metal, the excited state S₆ corresponds to the transition with the highest energy among the lowest-energy transitions. Excited-state S₅ corresponds to the low-energy bands for compounds 5a-6a. In contrast to molecules 1a-4a, the significant contribution of terminal ligand (TPY) in the creation of LUTO for 5a and 6a was observed. Moreover, the behavior of the complexes 5a and 6a is similar; there are no meaningful differences in relation to pyrene ligand substituted in a long-axis symmetrical way or asymmetrical when the coordination proceeds by two various heteroaryl groups. The natural transition orbitals with pairs of holes–electrons, and the contribution of the particular part in their creation for ruthenium complexes 1b-6b are listed in Table 5. The character of the lowest-energy transitions in the case of molecules 1b-6b is similar to 1a-6a, with a slightly higher contribution of the ruthenium than osmium. All the lowest-energy transitions can be assigned as metal-to-ligand-charge-transfer (MLCT).
Table 4. Natural transition orbitals (NTOs) with pairs occupied (holes) and unoccupied (electrons) of 1a-6a with the contribution of particular parts of molecules: Os/pyrene/pyridine C/pyrazole C/pyridine NC/pyrazole NC/TPY (C = coordinating, NC = not coordinating). The respective number of the state, transition energy, and oscillator strength is listed for each state.

|   | Hole (HOTO) | Electron (LUTO) |
|---|-------------|-----------------|
| 1a | ![Hole](image1) | ![Electron](image2) |
|   | 2.083 eV    | 0.2030 H-1 →LUMO (95%) |
|   | (0.250)     | 0.09/0.18/-/0.00/-/0.16 |
|   | 97%         | 0.02/0.64/-/0.08/-/0.03 |
| 2a | ![Hole](image3) | ![Electron](image4) |
|   | 2.062 eV    | 0.1365 H-1→LUMO (94%) |
|   | (0.203)     | 0.57/0.07/0.18/-/0.00/0.17 |
|   | 98%         | 0.01/0.67/-/0.05/0.03 |
| 3a | ![Hole](image5) | ![Electron](image6) |
|   | 2.340 eV    | 0.1990 H-1→LUMO (79%) |
|   | (0.137)     | 0.57/0.08/-/0.19/-/0.00/0.16 |
|   | 87%         | 0.02/0.77/-/0.15/-0.05/0.01 |
| 4a | ![Hole](image7) | ![Electron](image8) |
|   | 2.364 eV    | 0.1990 H-1→LUMO (78%) |
|   | (0.199)     | 0.54/0.14/-/0.17/0.00/-/0.15 |
|   | 88%         | 0.01/0.72/-/0.15/0.12/-/0.00 |
| 5a | ![Hole](image9) | ![Electron](image10) |
|   | 2.183 eV    | 0.1840 H-1→LUMO (36%) |
|   | (0.184)     | 0.57/0.13/0.10/0.06/0.00/0.14 |
|   | 95%         | 0.00/0.51/0.12/0.05/0.04/0.02/0.26 |
| 6a | ![Hole](image11) | ![Electron](image12) |
|   | 2.182 eV    | 0.1790 H-1→LUMO (10%) |
|   | (0.179)     | 0.56/0.13/0.10/0.06/0.00/0.15 |
|   | 95%         | 0.00/0.52/0.12/0.05/0.04/0.02/0.25 |
Table 5. Natural transition orbitals (NTOs) with pairs occupied (holes) and unoccupied (electrons) of 1b-6b with the contribution of particular parts of molecules: Ru/pyrene/pyridine C/pyrazole C/pyridine NC/pyrazole NC/TPY (C = coordinating, NC = not coordinating). The respective number of the state, transition energy, and oscillator strength is listed for each state.

|        | Hole (HOTO) | Electron (LUTO) |
|--------|-------------|-----------------|
| **1b** | ![Image](image1.png) | ![Image](image2.png) |
| $S_5$  | 2.251 eV    | 0.58/0.13/0.16 |-0.00/-0.12 |
|        | (0.308)     | 0.00/0.66/0.23 |-0.09/-0.02 |
|        | 94%         |                 |
| **2b** | ![Image](image3.png) | ![Image](image4.png) |
| $S_5$  | 2.230 eV    | 0.61/0.09/0.17 |-0.00/0.12 |
|        | (0.232)     | 0.01/0.69/0.24 |-0.05/0.02 |
|        | 96%         |                 |
| **3b** | ![Image](image5.png) | ![Image](image6.png) |
| $S_5$  | 2.537 eV    | 0.62/0.06/-0.18/-0.00/0.13 |
|        | (0.204)     | 0.00/0.72/-0.14/-0.05/0.08 |
|        | 91%         |                 |
| **4b** | ![Image](image7.png) | ![Image](image8.png) |
| $S_5$  | 2.553 eV    | 0.58/0.13/-0.17/-0.01/-0.11 |
|        | (0.335)     | 0.00/0.65/-0.14/-0.10/-0.10 |
|        | 88%         |                 |
| **5b** | ![Image](image9.png) | ![Image](image10.png) |
| $S_5$  | 2.365 eV    | 0.58/0.14/0.09/0.07/0.00/0.00/0.11 |
|        | (0.277)     | 0.00/0.64/0.14/0.05/0.05/0.02/0.08 |
|        | 96%         |                 |
| **6b** | ![Image](image11.png) | ![Image](image12.png) |
| $S_5$  | 2.364 eV    | 0.58/0.14/0.09/0.07/0.00/0.00/0.11 |
|        | (0.269)     | 0.00/0.65/0.14/0.06/0.05/0.02/0.08 |
|        | 96%         |                 |
The affinity of metallic centers, hence the whole molecule, for change can be identified by calculation of the spin-density distribution of the lowest energy triplet state (multiplicity = 3) with the values of spin distribution on metals (Mulliken population). Data obtained for molecules 1a-6a and 1b-6b are listed in Table 6. The tendency of changes does not follow the same trend for the osmium complexes 1a-6a as for the ruthenium complexes 1b-6b. In the case of the first group of molecules, the spin-density distribution on metal is the highest for 5a, whereas for the second group, 6b. The significant differences between 4a vs. 4b and 5a vs. 5b were noticed; the difference between the analogues molecules, which differ from each other only by coordinated metal, was even 20 times. In all cases besides compound 5b, the spin density on metal is higher for ruthenium than for the corresponding osmium complex.

Table 6. Spin-density distribution of the lowest energy triplet state for molecules 1a-6a and 1b-6b.

|     | 1a | 2a | 3a | 4a | 5a | 6a |
|-----|----|----|----|----|----|----|
| 1a  |    |    |    |    |    |    |
| 2a  |    |    |    |    |    |    |
| 3a  |    |    |    |    |    |    |
| 4a  |    |    |    |    |    |    |
| 5a  |    |    |    |    |    |    |
| 6a  |    |    |    |    |    |    |

The higher spin distribution on the metal of complexes may cause the most significant differences before and after oxidation. The structures of oxidized Os(II) 1aox-6aox and Ru(II) 1box-6box complexes were optimized; the contours of selected α and β-spin orbitals (HOSO and LUSO) are presented in Table S1 in Supplementary Materials. Energies of α and β-spin orbitals (HOSO and LUSO) and bond lengths of oxidized complexes are listed in Table 7. The bond M(III)-C lengths for oxidized complexes are lower than 1a-6a and 1b-6b. The most significant differences were observed for 4a/4aox and 4b/4box with the change 0.030 Å and 0.035 Å, respectively. The slightest change was observed for the shortest bonds 2a/2aox and 2b/2box.

Table 7. Energies of HOSOs and LUSOs and bond lengths M-C for complexes 1aox-6aox and 1box-6box.

|     | 1aox | 2aox | 3aox | 4aox | 5aox | 6aox | 1box | 2box | 3box | 4box | 5box | 6box |
|-----|------|------|------|------|------|------|------|------|------|------|------|------|
| HOSO [eV] | α    | -5.75 | -5.81 | -5.86 | -5.77 | -5.77 | -5.78 | -5.78 | -5.84 | -5.87 | -5.78 | -5.80 | -5.80 |
| LUSO [eV] | β    | -5.64 | -5.71 | -5.79 | -5.68 | -5.69 | -5.69 | -5.75 | -5.81 | -5.70 | -5.73 | -5.73 | -5.73 |
| ΔE [eV] | α    | -2.82 | -2.88 | -2.90 | -2.86 | -2.86 | -2.86 | -2.89 | -2.88 | -2.84 | -2.85 | -2.85 | -2.85 |
|        | β    | -4.12 | -4.15 | -4.28 | -4.23 | -4.16 | -4.17 | -4.27 | -4.46 | -4.40 | -4.31 | -4.31 | -4.31 |
| M-C [Å] |      | 1.975 | 1.981 | 1.980 | 1.970 | 1.982 | 1.982 | 1.951 | 1.957 | 1.953 | 1.946 | 1.958 | 1.957 |
The calculated absorption spectra of oxidized complexes 1aox-6aox and 1box-6box are presented in Figure 6, and the calculated lowest energy transitions are listed in Table 8.

![Figure 6. Theoretical absorption spectra of complexes 1aox-6aox and 1box-6box.](image)

**Table 8.** Calculated TD-DFT low-energy wavelengths in absorption spectra with oscillator strengths and dominant transitions (>10%) of molecules 1aox-6aox and 1box-6box.

|   | Calculated Wavelengths (nm) | Oscillator Strengths | Dominant Transitions (Contribution) |
|---|-----------------------------|----------------------|--------------------------------------|
| 1aox | 626.88 | 0.0811 | H-3(β)→LUSO(β) (64%), H-7(β)→LUSO(β) (11%) |
| 2aox | 601.78 | 0.0488 | H-3(β)→LUSO(β) (55%), H-8(β)→LUSO(β) (12%), H-7(β)→LUSO(β) (12%) |
| 3aox | 601.75 | 0.0785 | H-3(β)→LUSO(β) (47%), H-7(β)→LUSO(β) (27%) |
| 4aox | 628.12 | 0.1183 | H-5(β)→LUSO(β) (16%), H-3(β)→LUSO(β) (53%) |
| 5aox | 607.38 | 0.0594 | H-3(β)→LUSO(β) (58%), H-7(β)→LUSO(β) (15%) |
| 6aox | 607.08 | 0.0600 | H-3(β)→LUSO(β) (44%), H-4(β)→LUSO(β) (13%), H-6(β)→LUSO(β) (10%), H-7(β)→LUSO(β) (10%) |
| 1box | 662.66 | 0.0862 | H-3(β)→LUSO(β) (57%), HOSO(α)→LUSO(α) (11%) |
| 2box | 636.34 | 0.0592 | H-3(β)→LUSO(β) (49%), H-8(β)→LUSO(β) (13%), H-7(β)→LUSO(β) (10%) |
| 3box | 645.95 | 0.0616 | H-3(β)→LUSO(β) (32%), HOSO(α)→L + 1(α) (23%), H-7(β)→LUSO(β) (17%), HOSO(β)→L + 3(β) (11%) |
| 4box | 667.77 | 0.0540 | HOSO(α)→L + 1(α) (36%), HOSO(β)→L + 3(β) (24%), H-2(β)→LUSO(β) (24%) |
| 5box | 650.87 | 0.0683 | H-3(β)→LUSO(β) (48%), H-7(β)→LUSO(β) (12%) |
| 6box | 650.09 | 0.0687 | H-3(β)→LUSO(β) (33%), H-6(β)→LUSO(β) (14%), H-4(β)→LUSO(β) (13%) |
The intensity of the low-energy bands of oxidized complexes $1_{\text{aox}}$-$6_{\text{aox}}$ and $1_{\text{box}}$-$6_{\text{box}}$ decreased compared to non-oxidized complexes $1_a$-$6_a$ and $1_b$-$6_b$, but significant differences in the behavior of respective complexes were observed. The greatest change of oscillator strength from 0.3345 to 0.0540 (0.2805) was observed for $1_{\text{box}}$; the differences among osmium complexes $1_a$-$6_a$ vs. $1_{\text{aox}}$-$6_{\text{aox}}$ are lower in comparison to ruthenium analogues $1_b$-$6_b$ vs. $1_{\text{box}}$-$6_{\text{box}}$. The most intense band for oxidized complexes was observed for $4_{\text{aox}}$ and $1_{\text{box}}$, whereas it was the least intense for $2_{\text{aox}}$ and $4_{\text{box}}$; this can be caused by the character of oxidation, which can be described as metal-dominated oxidation [18].

It can be noticed that $\beta$-spin orbitals take part in the creation of the low-energy bands, but $1_{\text{box}}$ also occupied $\alpha$-spin orbital. All calculated low-energy bands of $1_{\text{aox}}$-$6_{\text{aox}}$ and $1_{\text{box}}$-$6_{\text{box}}$ are red-shifted up to 182 nm for $4_b$/4box; among osmium complexes, the most significant shift was observed for $4_a$/4aox.

### 3.2. Dinuclear Osmium and Ruthenium Complexes

Optimized structures of mononuclear Os(II) $1_a$-$6_a$ and Ru(II) $1_b$-$6_b$ complexes were used in the next part of the investigations dedicated to dinuclear homometallic complexes containing osmium or ruthenium metals bridging by the same double NCN-cyclometalating pyrene ligands; the structures are presented in Figure 7.

*Figure 7. The structures of the dinuclear osmium 7a-11a and ruthenium 7b-11b complexes.*
The optimized structures of molecules 7a-11a and 7b-11b are presented in Table 9. The contribution of individual parts of molecules in the creation of frontier orbitals is presented in Figure 8.

**Table 9.** The optimized structures with HOMOs and LUMOs contours for molecules 7a-11a and 7b-11b.

|   | HOMO | LUMO | HOMO | LUMO |
|---|------|------|------|------|
| 7a | ![HOMO](image) | ![LUMO](image) | ![HOMO](image) | ![LUMO](image) |
| 8a | ![HOMO](image) | ![LUMO](image) | ![HOMO](image) | ![LUMO](image) |
| 9a | ![HOMO](image) | ![LUMO](image) | ![HOMO](image) | ![LUMO](image) |
| 10a | ![HOMO](image) | ![LUMO](image) | ![HOMO](image) | ![LUMO](image) |
| 11a | ![HOMO](image) | ![LUMO](image) | ![HOMO](image) | ![LUMO](image) |

**Figure 8.** The contribution of the individual part of molecules in the creation of frontier orbitals for molecules 7a-11a and 7b-11b.

The sum of the percentage contribution of ruthenium and osmium in the creation of HOMOs of 7a-11a and 7b-11b is the same (42–44%). Only in the case of complexes 9a and 9b, the contribution of the particular metal M1 and M2 differs from each other, with the dominance of metal where the coordination proceeds from one side by a pyridyl...
group and from the second side by a pyrazolyl substituent. Moreover, the sum of the substituents’ contribution in HOMOs is in the range of 10–12%. In the case of the lowest unoccupied molecular orbitals, they are delocalized on the same part of complexes with the exception of 8a and 8b, where the contribution of the terpyridine ligand is significantly higher (11% for 8a and 6% for 8b) than for the rest of the osmium (3–4%) and ruthenium (2%) complexes. The energy values of HOMOs, LUMOs, energy gaps, and bond lengths M(II)-C for molecules 7a-11a and 7b-11b are listed in Table 10.

Table 10. Energies of HOMOs and LUMOs, values of energy gaps, and bond lengths M-C for complexes 7a-11a and 7b-11b.

|       | 7a  | 8a  | 9a  | 10a | 11a | 7b  | 8b  | 9b  | 10b | 11b |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| HOMO [eV] | -4.73 | -4.77 | -4.75 | -4.74 | -4.74 | -4.87 | -4.96 | -4.91 | -4.90 | -4.91 |
| LUMO [eV] | -2.67 | -2.31 | -2.51 | -2.53 | -2.51 | -2.64 | -2.28 | -2.48 | -2.50 | -2.49 |
| ΔE [eV] | 2.06  | 2.46  | 2.24  | 2.21  | 2.23  | 2.23  | 2.68  | 2.43  | 2.40  | 2.42  |
| M1-C/M2-C [Å] | 1.995/ | 2.001/ | 1.997/ | 1.997/ | 1.975/ | 1.975/ | 1.982/ | 1.974/ | 1.978/ | 1.978/ |

The energy gaps for osmium complexes 7a-11a are lower than the values for corresponding ruthenium molecules 7b-11b (Figure 9). The order of the increasing values of the energy gaps follows the same trend; among two groups, the lowest ΔE was achieved by complex 7a and 7b, followed by 10a/10b < 11a/11b < 9a/9b < 8a/8b.

Figure 9. The energies of frontier orbitals with the values of energy gaps for molecules 7a-11a and 7b-11b.

The lengths of the bond of metal–carbon for osmium complexes 7a-11a are higher than for ruthenium complexes 7b-11b. The shortest was achieved for complexes 7a (1.995 Å) and 7b (1.975 Å), where the coordination proceeds by pyridyl groups, whereas the longest for 9a (2.002 Å) and 9b (1.983 Å) from the side where metal is coordinated by pyrazolyl groups, also compared to dinuclear homometallic complex with ligands containing only pyrazolyl groups 8a/b, is a higher value. The same tendency was also observed for mononuclear complexes 1a-6a and 1b-6b.

TD-DFT calculated absorption spectra of 7a-11a and 7b-11b are presented in Figure 10.
The energy gaps for osmium complexes 7a-11a are lower than the values for corresponding ruthenium molecules 7b-11b. The absorbance range for ruthenium analogues 7b-11b is narrower, up to $\lambda = 800-850$ nm. The bands with the lowest energy can be mainly assigned to HOMO→LUMO transitions; thereby, metal-to-ligand charge-transfer (MLCT) transitions from the metal centers to the bridging pyrene ligands (Table 11).

**Table 11.** Calculated TD-DFT low-energy wavelengths in absorption spectra with oscillator strengths and dominant transitions (>10%) of molecules 7a-11a and 7b-11b.

|   | Calculated Wavelengths (nm) | Oscillator Strengths | Dominant Transitions (Contribution) |
|---|-----------------------------|---------------------|-------------------------------------|
| 7a | 771.43                      | 0.1088              | HOMO→LUMO (99%)                     |
| 8a | 620.45                      | 0.0652              | HOMO→LUMO (89%)                     |
| 9a | 696.97                      | 0.0975              | HOMO→LUMO (97%)                     |
| 10a | 705.26                     | 0.0882              | HOMO→LUMO (89%)                     |
| 11a | 699.02                     | 0.0736              | HOMO→LUMO (77%), HOMO→L + 1 (11%)  |
| 7b | 702.22                      | 0.1203              | HOMO→LUMO (98%)                     |
| 8b | 562.93                      | 0.0695              | HOMO→LUMO (85%)                     |
| 9b | 653.75                      | 0.0574              | HOMO→LUMO (96%)                     |
| 10b | 641.54                     | 0.0903              | HOMO→LUMO (78%), HOMO→L + 1 (14%)  |
| 11b | 634.74                     | 0.0849              | HOMO→LUMO (76%), HOMO→L + 2 (16%)  |

The most intense MCLT transitions were observed for 7a ($\lambda = 771.43$ nm, $f = 0.1088$) and 7b ($\lambda = 702.22$ nm, $f = 0.1203$), which are red-shifted in comparison to the rest molecules; the lowest transitions were calculated for 8a ($\lambda = 620.45$ nm, $f = 0.0652$) and 9b ($\lambda = 653.75$ nm, $f = 0.0574$). The similar broad MLCT transition of ruthenium and osmium complexes as those for discussed molecules 7a-11a and 7b-11b with other bridging and terminal ligands.
have been already presented [3,28]. Hence, there is no impact of the various methods of substitution of pyrene by two kinds of heteroaryl groups on the optical properties of non-oxidized complexes.

The spin-density distribution of the lowest-energy triplet state with the values of spin distribution on metals (Mulliken population) for molecules 7a-11a and 7b-11b are presented in Table 12.

Table 12. Spin-density distribution of the lowest-energy triplet state for molecules 7a-11a and 7b-11b.

|   | 7a       | 8a     | 9a    | 10a   | 11a      |
|---|----------|--------|-------|-------|----------|
|   | 0.345/0.345 | 0.331/0.331 | 0.540/0.155 | 0.320/0.320 | 0.306/0.376 |
| 7b   | 0.333/0.333 | 0.316/0.316 | 0.610/0.090 | 0.167/0.167 | 0.320/0.331 |

Complexes containing NCN-cyclometalating substituted by heteroaryl groups, providing a center of symmetry 7a, 8a, 10a, 7b, 8b, 10b have the same spin-density distribution of two metal centers. In contrast, substitution pattern with two kinds of heteroaryl substituents influences the various spin-density distribution; the most significant difference is observed for the derivatives 9a and 9b with a long axial, symmetric bridging ligand. Higher values are achieved from the side where the coordination proceeds by pyridyl groups.

The structures of oxidized Os(II)-Os(III) 7aox-11aox and Ru(II)-Ru(III) 7box-11box complexes were optimized; the contours of selected α and β-spin orbitals (β-HOSO and β-LUSO) are presented in Table 13, whereas energies of α-spin and β-spin orbitals (α-HOSO, β-HOSO, α-LUSO, β-LUSO) and bonds lengths of oxidized complexes are listed in Table 14.
Table 13. The $\beta$-HOSO and $\beta$-LUSO contours for the complexes $7\text{aox}$-$11\text{aox}$ and $7\text{box}$-$11\text{box}$.

|       | $\beta$-HOSO | $\beta$-LUSO | $\beta$-HOSO | $\beta$-LUSO |
|-------|-------------|-------------|-------------|-------------|
| $7\text{aox}$ | ![Image](image1) | ![Image](image2) | ![Image](image3) | ![Image](image4) |
| $8\text{aox}$ | ![Image](image5) | ![Image](image6) | ![Image](image7) | ![Image](image8) |
| $9\text{aox}$ | ![Image](image9) | ![Image](image10) | ![Image](image11) | ![Image](image12) |
| $10\text{aox}$ | ![Image](image13) | ![Image](image14) | ![Image](image15) | ![Image](image16) |
| $11\text{aox}$ | ![Image](image17) | ![Image](image18) | ![Image](image19) | ![Image](image20) |

Table 14. Energies of HOSOs and LUSOs and bond lengths M-C for complexes $7\text{aox}$-$11\text{aox}$ and $7\text{box}$-$11\text{box}$.

|          | $\alpha$ [eV] | $\beta$ [eV] | $\alpha$ [eV] | $\beta$ [eV] | $\Delta E$ [eV] | M-C [Å] |
|----------|---------------|--------------|---------------|--------------|----------------|---------|
| HOSO     | $7\text{aox}$ | $8\text{aox}$ | $9\text{aox}$ | $10\text{aox}$ | $11\text{aox}$ | $7\text{box}$ | $8\text{box}$ | $9\text{box}$ | $10\text{box}$ | $11\text{box}$ |
| $\alpha$ | $\beta$       | $\alpha$     | $\beta$       | $\alpha$     | $\beta$       | $\alpha$     | $\beta$       | $\alpha$     | $\beta$       | $\alpha$     | $\beta$       | $\alpha$     | $\beta$       | $\alpha$     | $\beta$       | $\alpha$     | $\beta$       | $\alpha$     | $\beta$       | $\alpha$     | $\beta$       |
|          | $5.35$        | $5.13$       | $5.70$        | $5.61$       | $5.38$        | $5.47$        | $5.39$        | $5.33$       | $5.32$        | $5.39$        | $5.39$        | $5.35$        | $5.35$        | $5.38$        | $5.38$        | $5.39$       | $5.38$        | $5.39$       | $5.39$        | $5.37$       | $5.38$        |
|          | $5.45$        | $5.22$       | $5.46$        | $5.61$       | $5.19$        | $5.28$        | $5.39$        | $5.46$       | $5.34$        | $5.39$        | $5.39$        | $5.47$        | $5.47$        | $5.38$        | $5.38$        | $5.39$       | $5.39$        | $5.39$        | $5.39$        | $5.37$        | $5.38$        |
|          | $5.31$        | $5.19$       | $5.39$        | $5.39$       | $5.20$        | $5.28$        | $5.39$        | $5.46$       | $5.34$        | $5.39$        | $5.39$        | $5.28$        | $5.28$        | $5.38$        | $5.38$        | $5.39$       | $5.39$        | $5.39$        | $5.39$        | $5.37$        | $5.38$        |
|          | $5.39$        | $5.19$       | $5.39$        | $5.39$       | $5.20$        | $5.28$        | $5.39$        | $5.46$       | $5.34$        | $5.39$        | $5.39$        | $5.28$        | $5.28$        | $5.38$        | $5.38$        | $5.39$       | $5.39$        | $5.39$        | $5.39$        | $5.37$        | $5.38$        |
|          | $5.38$        | $5.19$       | $5.39$        | $5.39$       | $5.20$        | $5.28$        | $5.39$        | $5.46$       | $5.34$        | $5.39$        | $5.39$        | $5.28$        | $5.28$        | $5.38$        | $5.38$        | $5.39$       | $5.39$        | $5.39$        | $5.39$        | $5.37$        | $5.38$        |
|          | $5.39$        | $5.19$       | $5.39$        | $5.39$       | $5.20$        | $5.28$        | $5.39$        | $5.46$       | $5.34$        | $5.39$        | $5.39$        | $5.28$        | $5.28$        | $5.38$        | $5.38$        | $5.39$       | $5.39$        | $5.39$        | $5.39$        | $5.37$        | $5.38$        |
|          | $5.47$        | $5.28$       | $5.39$        | $5.39$       | $5.20$        | $5.28$        | $5.39$        | $5.46$       | $5.34$        | $5.39$        | $5.39$        | $5.28$        | $5.28$        | $5.38$        | $5.38$        | $5.39$       | $5.39$        | $5.39$        | $5.39$        | $5.37$        | $5.38$        |
|          | $5.38$        | $5.20$       | $5.39$        | $5.39$       | $5.20$        | $5.28$        | $5.39$        | $5.46$       | $5.34$        | $5.39$        | $5.39$        | $5.28$        | $5.28$        | $5.38$        | $5.38$        | $5.39$       | $5.39$        | $5.39$        | $5.39$        | $5.37$        | $5.38$        |
|          | $5.39$        | $5.20$       | $5.39$        | $5.39$       | $5.20$        | $5.28$        | $5.39$        | $5.46$       | $5.34$        | $5.39$        | $5.39$        | $5.28$        | $5.28$        | $5.38$        | $5.38$        | $5.39$       | $5.39$        | $5.39$        | $5.39$        | $5.37$        | $5.38$        |
|          | $5.38$        | $5.20$       | $5.39$        | $5.39$       | $5.20$        | $5.28$        | $5.39$        | $5.46$       | $5.34$        | $5.39$        | $5.39$        | $5.28$        | $5.28$        | $5.38$        | $5.38$        | $5.39$       | $5.39$        | $5.39$        | $5.39$        | $5.37$        | $5.38$        |

Taking into account the contours of $\beta$-HOSO and $\beta$-LUSO for $9\text{aox}$ and $9\text{box}$, the already observed blue-shifted low-energy band can also be caused by the significant differences of the contribution of particular coordinated metals; $\beta$-HOSO is mainly created by Os/Ru coordinated by pyrazolyl groups, whereas $\beta$-LUSO by Os/Ru is coordinated by pyridyl substituents. In the case of other molecules, the distribution of the frontier $\beta$-spin orbitals is symmetric. The M-C bond lengths for oxidized complexes are lower than for $\text{7a-11a}$ and $\text{7b-11b}$, with differences up to 0.038 Å.
The calculated absorption spectra of oxidized complexes 7aox-11aox and 7box-11box are presented in Figure 11, and the calculated lowest-energy transitions are listed in Table 15.

![Figure 11. Theoretical absorption spectra of complexes 7aox-11aox and 7box-11box.](image)

Table 15. Calculated TD-DFT low-energy wavelengths in absorption spectra with oscillator strengths and dominant transitions (>10%) of molecules 7aox-11aox and 7box-11box.

|       | Calculated Wavelengths (nm) | Oscillator Strengths | Dominant Transitions (Contribution)       |
|-------|----------------------------|---------------------|------------------------------------------|
| 7aox  | 2479.19                    | 0.4520              | HOSO(β)→LUSO(β) (93%)                    |
| 8aox  | 2172.11                    | 0.5407              | HOSO(β)→LUSO(β) (96%)                    |
| 9aox  | 1988.84                    | 0.4308              | HOSO(β)→LUSO(β) (94%)                    |
| 10aox | 2444.48                    | 0.2490              | HOSO(β)→LUSO(β) (61%), H-2(β)→LUSO(β) (36%) |
| 11aox | 2289.64                    | 0.4195              | HOSO(β)→LUSO(β) (83%), H-2(β)→LUSO(β) (13%) |
| 7box  | 2265.79                    | 0.1105              | H-5(β)→LUSO(β) (70%), HOSO(β)→LUSO(β) (27%) |
| 8box  | 2260.42                    | 0.5043              | HOSO(β)→LUSO(β) (96%)                    |
| 9box  | 1765.15                    | 0.3460              | HOSO(β)→LUSO(β) (95%)                    |
| 10box | 2431.54                    | 0.3392              | HOSO(β)→LUSO(β) (78%), H-2(β)→LUSO(β) (19%) |
| 11box | 2295.15                    | 0.4071              | HOSO(β)→LUSO(β) (92%)                    |

The intensity of the low-energy bands of oxidized complexes 7aox-11aox and 7box-11box significantly increased compared to non-oxidized complexes 7a-11a and 7b-11b. The appeared bands are strongly red-shifted in the NIR region. The intensity of the band for osmium 7aox-11aox is slightly higher than ruthenium complexes 7box-11box. The most intense band was observed for 7aox (λ = 2479.19 nm, f = 0.4520) and its analogue with ruthenium 7box. Furthermore, the low-energy band for molecules 9aox (λ = 1988.84 nm,
f = 0.4308) and 9box (λ = 1765.15 nm, f = 0.3460) is shifted to the shorter wavelength; it can be caused by the character of oxidation and significant differences between spin-density distributions on particular metals in reference to coordinating heteroaryls (Table 12). Intense bands for complexes 10aox (λ = 2444.48 nm, f = 0.2490; λ = 2082.02 nm, f = 0.2460), 7box (λ = 2265.79 nm, f = 0.1105; λ = 2189.37 nm, f = 0.2830), and 10box (λ = 2431.54 nm, f = 0.3392; λ = 2069.85 nm, f = 0.1275) are built by two bands. Moreover, it can be noticed that in the creation of the low-energy band, only β-spin orbitals are involved; major transitions can be described as HOSO(β)→LUSO(β).

### 3.3. Dinuclear Mixed-Metal Osmium/Ruthenium Complexes

Based on the optimized structures, a comprehensive evaluation of the mononuclear and dinuclear homometallic osmium and ruthenium complexes bridged by double NCN-cyclometalating pyrene ligands allowed us to conduct the calculations of dinuclear heterometallic complexes Os(II)-Ru(II) 12-17, which is presented in Figure 12.

The optimized structures of molecules 12-17 are presented in Table 16. The contribution of individual parts of molecules in the creation of frontier orbitals is presented in Figure 13.

![Figure 12](image-url)
Table 16. The optimized structures with HOMO-1, HOMO, LUMO, and LUMO+1 contours for molecules 12-17.

|   | HOMO-1 | HOMO   | LUMO   | LUMO+1  |
|---|--------|--------|--------|---------|
| 12| ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) | ![Image](image4.png) |
| 13| ![Image](image5.png) | ![Image](image6.png) | ![Image](image7.png) | ![Image](image8.png) |
| 14| ![Image](image9.png) | ![Image](image10.png) | ![Image](image11.png) | ![Image](image12.png) |
| 15| ![Image](image13.png) | ![Image](image14.png) | ![Image](image15.png) | ![Image](image16.png) |
| 16| ![Image](image17.png) | ![Image](image18.png) | ![Image](image19.png) | ![Image](image20.png) |
| 17| ![Image](image21.png) | ![Image](image22.png) | ![Image](image23.png) | ![Image](image24.png) |

Figure 13. The contribution of the individual part of molecules in the creation of frontier orbitals for molecules 12-17.
The sum of the percentage contribution of ruthenium and osmium in the creation of HOMOs of 12-17 is in the range of 42–44%, with significant dominance of osmium, up to 30% for molecules 13 and 14. In contrast, ruthenium takes part in the creation of HOMOs up to 16% for complex 15. Generally, the contribution of osmium is one time higher than that of ruthenium. There are no differences in the impact of bridging and terminal ligands in creating the highest occupied molecular orbitals. Furthermore, the lowest unoccupied molecular orbitals are created by 2% coordinated metals (1% Os and 1% Ru); major delocalization of LUMO is on pyrene up to 62% for 13. The localization of the frontier orbitals on only bridging ligands is already published [20,22]. The energy values of HOMOs, LUMOs, energy gaps, and bond lengths M(II)-C for molecules 12-17 are listed in Table 17.

Table 17. Energies of HOMOs and LUMOs, values of energy gaps, and bond lengths M-C for complexes 12-17.

|     | 12   | 13   | 14   | 15   | 16   | 17   |
|-----|------|------|------|------|------|------|
| HOMO [eV] | -4.79 | -4.85 | -4.82 | -4.81 | -4.82 | -4.81 |
| LUMO [eV]  | -2.66 | -2.30 | -2.50 | -2.49 | -2.50 | -2.52 |
| ΔE [eV]    | 2.13  | 2.55  | 2.32  | 2.32  | 2.32  | 2.29  |
| Os(II)-C [Å] | 1.995 | 2.001 | 1.994 | 2.002 | 1.997 | 1.997 |
| Ru(II)-C [Å] | 1.975 | 1.982 | 1.983 | 1.974 | 1.978 | 1.978 |

The values of energy gaps for complexes 12-17 are lower than the values for corresponding ruthenium molecules 7b-11b but higher than for osmium complexes 7a-11a (Figure 14). Among the dinuclear heterometallic complexes, the lowest ΔE was achieved by complex 12, followed by 17; the same values of energy gaps are present for molecules 14, 15, and 16, and the highest one was for 13. Interestingly, substituted pyrene ligands containing a symmetric center decrease the value of the energy band; the same phenomenon was observed for dinuclear homometallic complexes 10b and 10a, containing the same NCN-cyclometalating ligand. The lengths and the tendency of change of the bond of metal–carbon for 12-17 are the same as for dinuclear homometallic complexes 7a-11a and 7b-11b. The longest bonds were achieved when the coordination proceeds by pyrazolyl groups, when the NCN-cyclometalating ligands contain two kinds of heteroaryl groups 14 (Ru(II)-C 1.983 Å) and 15 (Os(II)-C 2.002 Å); in the case of compound 13, which contains only pyrazolyl groups, the bonds’ lengths are slightly shorter (Ru(II)-C 1.982 Å and Os(II)-C 2.001 Å).

Figure 14. The energies of frontier orbitals with the values of energy gaps for molecules 12-17.
T. Nagashima et al. reported that there are two electronic coupling mechanisms: electron transfer and hole transfer superexchange [15]. The mixing between metal dπ(M1 and M2) and bridging ligand π* is ascendant for the Os 5dπ level in comparison to the Ru 4dπ level; on the other hand, the mixing between metal dπ(M1 and M2) and bridging ligand π is dominant for the Ru 4dπ level. The HOMO and HOMO-1 of 12-17 are mainly localized on osmium dπ orbitals and bridging ligand π orbitals. In the case of HOMO, the contribution of the ruthenium dπ orbitals is more significant, especially for 15, but still definitely lower than osmium. It can suggest that the metal—metal interaction takes place through a hole-transfer mechanism. The LUMOs of 12-17 are composed of the bridging ligand π* orbitals. In the case of 13, the LUMO is localized significantly on terminal ligands π* orbitals—terpyridine. The LUMO+1 of 12-14 and 16-17 are composed of the ruthenium dπ orbitals with terminal ligand π* orbitals. Dinuclear complex 15 differ significantly; the LUMO+1 is composed of the osmium dπ orbitals with terpyridine π* orbitals. The ruthenium 4dπ orbitals interacted strongly with the terpyridine π* orbitals (except for 15), whereas the osmium 5dπ orbitals strongly mixed with bridging ligand orbitals, determining the degree of strength of the metal—metal interaction. This suggests that the substitution pattern of the bridging ligand and the coordinated metals have a significant impact on the properties of the dinuclear heterometallic complexes.

TD-DFT calculated absorption spectra of 12-17 are presented in Figure 15.

![Figure 15. Theoretical absorption spectra of complexes 12-17.](image)

Calculated absorptions spectra for 12-17 have the same shape as the spectra calculated for dinuclear homometallic complexes 7a-11a and 7b-11b. The bands in the UV region can also be associated with IL and LLCT transitions. The intensities and the absorption range (up to λ = 1000 nm for 12 and up to λ = 800 nm for 13-17) of the dinuclear heterometallic complexes 12-17 follow the behavior of osmium complexes 7a-11a, which is in accordance with the higher contribution of osmium in the creation of frontier orbitals in comparison to ruthenium.

The bands with the lowest energy can be assigned mainly as HOMO→LUMO transitions—MLTC, the same as for 7a-11a and 7b-11b (Table 18). The most intense one was calculated for complex 12 (λ = 739.63 nm, f = 0.1111); the lowest was for 13 (λ = 588.50 nm, f = 0.0647).
Table 18. Calculated TD-DFT low-energy wavelengths in absorption spectra with oscillator strengths and dominant transitions (>10%) of molecules 12-17.

|     | Calculated Wavelengths (nm) | Oscillator Strengths | Dominant Transitions (Contribution)     |
|-----|-----------------------------|----------------------|------------------------------------------|
| 12  | 739.63                      | 0.1111               | HOMO→LUMO (98%)                          |
| 13  | 588.50                      | 0.0647               | HOMO→LUMO (53%), HOMO→L + 4 (41%)        |
| 14  | 673.24                      | 0.0982               | HOMO→LUMO (97%)                          |
| 15  | 664.69                      | 0.1011               | HOMO→LUMO (98%)                          |
| 16  | 670.55                      | 0.0950               | HOMO→LUMO (97%)                          |
| 17  | 674.93                      | 0.1012               | HOMO→LUMO (91%)                          |

The spin-density distribution of the lowest energy triplet state with the values of spin distribution on metals (Mulliken population) for molecules 12-17 are presented in Table 19.

Table 19. Spin-density distribution of the lowest energy triplet state (Os/Ru) for molecules 12-17 (left side Os, right side Ru).

|     | 12       | 13       | 14       | 15       | 16       | 17       |
|-----|----------|----------|----------|----------|----------|----------|
|     | 0.593/0.106 | 0.579/0.089 | 0.643/0.064 | 0.500/0.164 | 0.594/0.096 | 0.539/0.110 |

Higher spin-density distribution of the lowest-energy triplet state takes place on osmium metals—up to 10 times higher in the case of molecule 14. Complexes containing a bridging ligand derivative with the same four heteroaryl groups 12 and 13 cause the distribution difference between Os and Ru up to 6 times. The same differences were observed for the analogue complexes with the same ligands 9a and 9b.

The structures of oxidized complexes 12ox-17ox were optimized; the contours of the highest occupied α and β-spin orbitals (α-HOSO and β-HOSO) and lowest unoccupied α and β-spin orbitals (α-LUSO and β-LUSO) are presented in Table 20. Energies of α-spin and β-spin orbitals and bonds lengths of oxidized complexes are listed in Table 21.

Table 20. The α-HOSO, β-HOSO, α-LUSO, and β-LUSO contours for the complexes 12ox-17ox (left side, Os; right side, Ru).
Table 20. Cont.

|       | 12ox | 13ox |       | 14ox | 15ox |       | 16ox | 17ox |
|-------|------|------|-------|------|------|-------|------|------|
| α-LUSO | ![Image](image1) | ![Image](image2) | β-LUSO | ![Image](image3) | ![Image](image4) |
| β-LUSO | ![Image](image5) | ![Image](image6) | α-LUSO | ![Image](image7) | ![Image](image8) |
| α-HOSO | ![Image](image9) | ![Image](image10) | β-HOSO | ![Image](image11) | ![Image](image12) |
| β-HOSO | ![Image](image13) | ![Image](image14) | α-HOSO | ![Image](image15) | ![Image](image16) |
| α-LUSO | ![Image](image17) | ![Image](image18) | β-LUSO | ![Image](image19) | ![Image](image20) |
| α-LUSO | ![Image](image21) | ![Image](image22) | β-LUSO | ![Image](image23) | ![Image](image24) |
| α-HOSO | ![Image](image25) | ![Image](image26) | β-HOSO | ![Image](image27) | ![Image](image28) |
| β-HOSO | ![Image](image29) | ![Image](image30) | α-HOSO | ![Image](image31) | ![Image](image32) |
| α-LUSO | ![Image](image33) | ![Image](image34) | β-LUSO | ![Image](image35) | ![Image](image36) |
| α-LUSO | ![Image](image37) | ![Image](image38) | β-LUSO | ![Image](image39) | ![Image](image40) |
Table 21. Energies of HOSOs and LUSOs and bond lengths M-C for complexes 12ox-17ox.

|      | 12ox | 13ox | 14ox | 15ox | 16ox | 17ox |
|------|------|------|------|------|------|------|
| HOSO [eV] | α  | −5.32 | −5.45 | −5.38 | −5.40 | −5.37 | −5.38 |
|        | β  | −5.31 | −5.41 | −5.39 | −5.31 | −5.34 | −5.36 |
| LUSO [eV] | α  | −3.01 | −2.80 | −2.88 | −2.87 | −2.88 | −2.90 |
|        | β  | −4.11 | −4.22 | −4.12 | −4.20 | −4.16 | −4.16 |
| ΔE [eV] | α  | 2.31  | 2.65  | 2.50  | 2.53  | 2.49  | 2.48  |
|        | β  | 1.20  | 1.19  | 1.27  | 1.11  | 1.18  | 1.20  |
| Os-C [Å] | 1.965 | 1.965 | 1.967 | 1.965 | 1.966 | 1.964 |
| Ru-C [Å] | 1.957 | 1.961 | 1.966 | 1.951 | 1.960 | 1.958 |

Among the oxidized complexes 12ox-17ox, the energy gap value in the case of β-spin orbitals for 15ox is the lowest (1.11 eV). The bond M-C lengths for oxidized complexes 12ox-17ox are shorter than for 12-17, with the highest difference for 15ox vs. 15, for osmium 0.037 Å and for ruthenium 0.023 Å.

The calculated absorption spectra of oxidized complexes 12ox-17ox are presented in Figure 16, and the calculated lowest-energy transitions are listed in Table 22.

Figure 16. Normalized theoretical absorption spectra of complexes 12ox-17ox.

Table 22. Calculated TD-DFT low-energy wavelengths (nm) in absorption spectra with oscillator strengths and dominant transitions (>10%) of molecules 12ox-17ox.

|      | Calculated Wavelengths (nm) | Oscillator Strengths | Dominant Transitions (Contribution) |
|------|-----------------------------|----------------------|-------------------------------------|
| 12ox | 1654.67                     | 0.3155               | HOSO(β)→LUSO(β) (95%)               |
| 13ox | 1618.17                     | 0.3813               | HOSO(β)→LUSO(β) (97%)               |
| 14ox | 1476.53                     | 0.3011               | HOSO(β)→LUSO(β) (93%)               |
| 15ox | 1876.27                     | 0.1030               | H-1(β)→LUSO(β) (63%), HOSO(β)→LUSO(β) (26%) |
|      | 1873.72                     | 0.2977               | HOSO(β)→LUSO(β) (70%), H-1(β)→LUSO(β) (23%) |
| 16ox | 1668.25                     | 0.2636               | HOSO(β)→LUSO(β) (75%), H-1(β)→LUSO(β) (19%) |
| 17ox | 1630.30                     | 0.3009               | HOSO(β)→LUSO(β) (84%), H-1(β)→LUSO(β) (11%) |
Similar to 7a-11a and 7b-11b, the intensity of the low-energy bands strongly red-shifted in the NIR region of oxidized complexes 12ox-17ox significantly increased compared to non-oxidized complexes 12-17. In the case of 12ox-17ox, their intensities are lower than for analogues 7aox-11aox and 7box-11box. The most intense and red-shifted band was observed for 15ox built by two components (λ = 1876.27 nm, f = 0.1030; λ = 1873.72 nm, f = 0.2977), where the coordination proceeds by pyrazolyl for Os and pyridyl for Ru, which is in accordance with the tendency observed among studied compounds 12-17 presented in Table 16. It is opposite to dinuclear homometallic complexes 9aox (λ = 1988.84 nm, f = 0.4308) and 9box (λ = 1765.15 nm, f = 0.3460) with the same bridging ligand, where the low-energy bands were the least intense and shifted to the shorter wavelength among all oxidized complexes 7aox-11aox and 7box-11box. Furthermore, only β-spin orbitals, the same as for 7aox-11aox and 7box-11box, are involved in the creation of the low-energy bands with major transitions HOSO(β)→LUSO(β).

4. Conclusions

Step-by-step investigations starting from mononuclear followed by homo- and heterometallic dinuclear osmium and/or ruthenium complexes with NCN-cyclometalating bridging ligands substituted by one or two kinds of heteroaryl groups (pyrazol-1-yl and 4-(2,2-dimethylpropyloxy)pyrid-2-yl) in a method providing the short/long axial symmetry or asymmetry has shown significant differences between and within the studied groups. The thorough knowledge of mononuclear and homometallic dinuclear osmium and/or ruthenium complexes was crucial to understanding the properties of heterometallic dinuclear Os/Ru coordination compounds. In the case of mononuclear complexes, when two kinds of heteroaryl groups participate in the coordination of metal, the contribution of pyrazolyl groups is around two times higher than pyridyl substituents. When these groups are substituted in a method providing long axial symmetry, the contribution of terminal ligand in the creation of LUMO is very high. The shape of the absorption spectra of mononuclear complexes is similar in the UV region, with a noticeable difference in the area of low-energy bands caused by the character of the transition, which creates the lowest-energy bands that can be assigned as metal-to-ligand-charge-transfer (MLCT). In the case of homometallic dinuclear osmium or ruthenium complexes, the contribution of the particular metal differs from each other, with the dominance of metal where the coordination proceeds from the one side by a pyridyl group and from the second side by a pyrazolyl substituent. Electronic absorptions in the UV region are associated with intraligand (IL) and ligand-to-ligand-charge-transfer (LLCT) transitions from the bridging and terminal ligands. Osmium complexes absorb light in a wider range in comparison to ruthenium analogues. The bands with the lowest energy can be assigned mainly as HOMO→LUMO, thereby MLCT transitions. There is no impact of the various method of substitution of pyrene by two kinds of heteroaryl groups on the optical properties of non-oxidized complexes. In contrast, in the case of oxidized complexes, the intensity of the low-energy bands significantly increased; bands were strongly red-shifted in the NIR region. For heterometallic dinuclear osmium and ruthenium complexes, the significant dominance of osmium in contrast to ruthenium in the creation of HOMOs was observed. The values of energy gaps for heterometallic dinuclear complexes are lower than the values for corresponding ruthenium molecules and higher than for osmium analogues. Complexes containing NCN-cyclometalating pyrene ligands substituted providing the symmetric center decrease the value of energy band. The calculated absorptions spectra have the same shape as the spectra calculated for dinuclear homometallic complexes and follow the behavior of osmium complexes, which is in accordance with the higher contribution of osmium in the creation of frontier orbitals in comparison to ruthenium. Definitely higher (up to 10 times) spin-density distribution of the lowest-energy triplet state takes place on osmium metals. The low-energy bands of oxidized complexes are strongly red-shifted in the NIR region, with higher intensities than non-oxidized but lower than homometallic analogues. The most intense and red-shifted band was observed where the
coordination proceeds by pyrazolyl for Os and pyridyl for Ru. This is opposite to dinuclear homometallic complexes with the same bridging ligand, where the low-energy bands were the least intense and shifted to the shorter wavelength among all oxidized complexes. The presented results showed that the properties of studied compounds depend on the nature of the metals and the nature of bridging ligands. They demonstrate the necessity of synthesis and experimental studies, especially dinuclear heterometallic complexes with NCN-cyclometalating ligands, which are substituted by two kinds of the heteroaryl groups symmetrically with respect to the center of symmetry.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/ma14247783/s1, Table S1: The α-HOSO and β-HOSO, α-LUSO, β-LUSO contours for the complexes 1a-6a and 1box-6box. Cartesian coordinates of DFT-optimized structure of complexes 1a-6a, 1b-6b, 1box-6box, 7a-11a, 7b-11b, 7aox-11aox, 7box-11box, 12-17, 12ox-17ox with values of charge and multiplicity.

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