Data Article

Computational DFT data related to the redox behaviour of tris(β-diketonato)ruthenium(III) compounds

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A R T I C L E   I N F O

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The data presented in this paper are related to the research article titled “Redox Behaviour of [Ru(β-diketonato)3] Compounds” [1]. This paper presents structural and energy data obtained from the density functional theory (DFT) computations. The energy data is related to experimentally obtained redox potential values. Various relationships are presented for the RuIII/II and RuIII/IV redox couples, involving both their experimental redox data as well as DFT calculated data, such as frontier orbital energies ($E_{\text{HOMO}}$ and $E_{\text{LUMO}}$) and calculated Mulliken electronegativity values.

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Specifications Table

| Subject | Chemistry |
|---------|-----------|
| Specific subject area | Computational chemistry |
| Type of data | Table |
| How data were acquired | Electronic structure calculations, using the Amsterdam Density Functional (ADF) 2018 and Gaussian 16 programmes. |
| Data format | Raw |
| Parameters for data collection | Input coordinates were constructed manually, using ChemCraft |
| Description of data collection | Computational DFT data was obtained with the ADF 2018 and Gaussian 16 programmes on the High Performance Computing facility of the University of the Free State |
| Data source location | Department of Chemistry, University of the Free State, Nelson Mandela Street, Bloemfontein, South Africa |
| Data accessibility | Data is included with article and in the supplementary file |
| Related research article | J. Conradie, Redox Behaviour of [Ru(β-diketonato)] Compounds. Electrochim. Acta. 337 (2020) 135801. https://doi:10.1016/j.electacta.2020.135801. |

Value of the Data

- Density functional theory (DFT) calculated optimized xyz-data (coordinates) for a series of 14 tris(β-diketonato)ruthenium(III) compounds are provided.
- DFT optimized geometrical data (coordinates) can be used to visualize the DFT calculated structures of a series of 14 tris(β-diketonato)ruthenium(III) compounds.
- This data provides highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies ($E_{\text{HOMO}}$ and $E_{\text{LUMO}}$) of different tris(β-diketonato)ruthenium(III) compounds.
- Relationships between experimental redox data and DFT calculated frontier orbital energies and calculated Mulliken electronegativity ($\chi$) for tris(β-diketonato)ruthenium(III) compounds containing different electron donating and electron withdrawing substituents, obtained by different DFT methods, all produced similar $R^2$ values.
- $E_{\text{HOMO}}$, $E_{\text{LUMO}}$ and $\chi_{\text{calc}}$ data obtained by the different DFT methods show the same trend, namely [Ru(β-diketonato)$_3$] compounds containing electron withdrawing substituents on the β-diketonato ligand have lower $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$, and higher $\chi_{\text{calc}}$ values than [Ru(β-diketonato)$_3$] compounds containing electron donating substituents on the β-diketonato ligand.
- Electronic energy data of different spin states of neutral, oxidized and reduced tris(acetylacetonato)ruthenium(III) provide the lowest energy spin state of the neutral, oxidized and reduced tris(acetylacetonato)ruthenium(III).
- Linear relationships obtained from this data enable further prediction of the properties of novel complexes prior to synthesis, to be confirmed by laboratory tests.

1. Data Description

This data article provides data related to Ru(III) compounds 1 – 14 (Fig. 1). A summary of the Hammett meta-substituent sigma constants, $\sigma_R$ [2], of both the R and R’ substituents on the β-diketonato ligand of the [Ru(β-diketonato)$_3$] compounds 1 – 14, is provided in Table 1. The $\sigma_R$ values provide an indication of the electron donating (smaller value) and electron withdrawing (larger value) property of the individual substituents R and R’ on the β-diketonato ligand of the [Ru(β-diketonato)$_3$] compounds 1 – 14. On the other hand, the data of the sum ($\sigma_R + \sigma_{R’}$) provides an indication of the electron donating (smaller value) and electron withdrawing (larger value) property of the β-diketonato ligand with its two substituents.
Ru(III) compounds 1 – 14 (Fig. 1) were optimized by different density functional theory (DFT) methods in the solvent phase (CH$_3$CN). Table 2 and Table 3 lists the DFT solvent phase (CH$_3$CN) computed data, namely the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies ($E_{\text{HOMO}}$ and $E_{\text{LUMO}}$) and Mulliken electronegativity ($\chi_{\text{calc}}$), a measure of the tendency of an atom or molecule to attract electrons [3]) of the series of tris($\beta$-diketonato)ruthenium(III) compounds 1 – 14 (Fig. 1). Experimental electrochemical data (potential $E$ vs Fe/Fe$^+$) of compounds 1 – 14, obtained from literature [4,5], are also given in Table 2. Different $E_{\text{HOMO}}$, $E_{\text{LUMO}}$ and $\chi_{\text{calc}}$ values are obtained by the different DFT methods, though all methods show the same trend, namely [Ru($\beta$-diketonato)$_3$] compounds containing electron withdrawing substituents on the $\beta$-diketonato ligand (e.g. complexes 1 – 6 containing a CF$_3$ group) have lower $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$, and higher $\chi_{\text{calc}}$ values than [Ru($\beta$-diketonato)$_3$] compounds containing electron donating substituents on the $\beta$-diketonato ligand (e.g. complexes 9 – 14), see Table 2 and Table 3.

The relationships between the experimental values of the reduction (Ru$^{III/II}$) and oxidation (Ru$^{III/IV}$) couples [4,5] and the solvent (CH$_3$CN) phase calculated $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ energies and their $\chi_{\text{calc}}$ and $\omega_{\text{calc}}$ values, obtained via different DFT methods using generalized gradient approximations (gga) functionals, PW91/TZ2P and OLYP/TZ2P, are shown in Fig. 2 and obtained via different DFT methods using hybrid functionals, B3LYP/6-311G(d,p)/LANL2dz, B3LYP/TZ2P and OPBE0/TZ2P, are shown in Fig. 3. The relationships obtained by these different solvent phase DFT methods, taking the experimental solvent (CH$_3$CN) used for electrochemical experiments [4,5] into account in the calculations, all produced similar $R^2$ values, comparable with the gas phase B3LYP/6-311G(d,p)/LANL2dz calculated relationships obtained from reference [1]. The slopes of

Fig. 1. Structure of the fourteen [Ru($\beta$-diketonato)$_3$] compounds 1 – 14.

| Compound no | R | R' | $\sigma_R$ | $\sigma_{R'}$ | ($\sigma_R + \sigma_{R'}$) |
|-------------|---|----|------------|--------------|-------------------|
| 1           | CF$_3$ | CF$_3$ | 0.43       | 0.43         | 0.86              |
| 2           | CF$_3$ | C$_4$H$_9$O | 0.43       | 0.06         | 0.49              |
| 3           | CF$_3$ | C$_4$H$_9$S | 0.43       | 0.09         | 0.52              |
| 4           | CF$_3$ | Ph    | 0.43       | 0.06         | 0.49              |
| 5           | CF$_3$ | CH$_3$ | 0.43       | -0.069       | 0.36              |
| 6           | CF$_3$ | C(CH$_3$)$_3$ | 0.43       | -0.1         | 0.33              |
| 7           | Ph     | Ph    | 0.06       | 0.06         | 0.12              |
| 8           | CH$_3$ | Ph    | -0.069     | 0.06         | -0.01             |
| 9           | CH$_3$ | CH$_3$ | -0.069     | -0.069       | -0.14             |
| 10          | C(CH$_3$)$_3$ | C(CH$_3$)$_3$ | -0.10     | -0.10        | -0.20             |
| 11          | Et     | Et    | -0.07      | -0.07        | -0.14             |
| 12          | Pr     | Pr    | -0.06      | -0.06        | -0.12             |
| 13          | Bu     | Bu    | -0.08      | -0.08        | -0.16             |
| 14          | iPr    | iPr   | -0.04      | -0.04        | -0.08             |
Table 2
DFT calculated data from this data article, as well as experimental electrochemical data ($E$ vs Fc/Fc$^+$) obtained from literature [4,5], of the [Ru($\beta$-diketonato)$_3$] compounds 1 – 14. Where $\beta$-diketonato ligand = (RCOCHCOR′)$^+$ with the R and R' substituents as shown in Fig. 1. DFT data was computed using two different gga functionals PW91 and OLYP.

|   | $E$ (Ru$^{III}$)$^a$ | $E$ (Ru$^{IV}$)$^a$ | PW91/STO-TZ2P | OLYP/STO-TZ2P |
|---|--------------------|--------------------|----------------|---------------|
|   | E$_{HOMO}$ (eV) | E$_{LUMO}$ (eV) | $\chi$ calc (eV)$^c$ | E$_{HOMO}$ (eV) | E$_{LUMO}$ (eV) | $\chi$ calc (eV)$^c$ |
| 1 | CF$_3$ | CF$_3$ | 0.34 | -5.856 | -5.585 | 5.720 | -5.573 | -5.337 | 5.455 |
| 2 | CF$_3$ | C$_4$H$_7$O | -0.34 | 1.20 | -5.067 | -4.744 | 4.906 | -4.793 | -4.522 | 4.657 |
| 3 | CF$_3$ | C$_4$H$_7$S | -0.35 | 1.19 | -5.014 | -4.753 | 4.883 | -4.766 | -4.486 | 4.626 |
| 4 | CF$_3$ | Ph | -0.35 | 1.26 | -5.134 | -4.838 | 4.986 | -4.865 | -4.606 | 4.736 |
| 5 | CF$_3$ | CH$_3$ | -0.47 | 1.29 | -5.132 | -4.812 | 4.972 | -4.869 | -4.596 | 4.733 |
| 6 | CF$_3$ | C(CH$_3$)$_3$ | -0.55 | 1.30 | -5.065 | -4.777 | 4.921 | -4.782 | -4.513 | 4.648 |
| 7 | Ph | Ph | -0.90 | 0.66 | -4.622 | -4.294 | 4.458 | -4.339 | -4.070 | 4.205 |
| 8 | CH$_3$ | Ph | -1.04 | 0.64 | -4.529 | -4.193 | 4.361 | -4.260 | -3.969 | 4.114 |
| 9 | CH$_3$ | CH$_3$ | -1.16 | 0.61 | -4.437 | -4.137 | 4.287 | -4.176 | -3.911 | 4.044 |
| 10 | C(CH$_3$)$_3$ | C(CH$_3$)$_3$ | -1.46 | 0.44 | -4.125 | -3.843 | 3.984 | -3.823 | -3.581 | 3.702 |
| 11 | Et | Et | -1.308 | 0.549 | -4.335 | -4.004 | 4.170 | -4.056 | -3.785 | 3.921 |
| 12 | Pr | Pr | -1.324 | 0.547 | -4.316 | -4.001 | 4.187 | -4.039 | -3.768 | 3.903 |
| 13 | Bu | Bu | -1.330 | 0.535 | -4.307 | -3.979 | 4.143 | -4.024 | -3.766 | 3.895 |
| 14 | iPr | iPr | -1.392 | 0.509 | -4.196 | -3.930 | 4.063 | -3.900 | -3.682 | 3.791 |

$^a$ Experimental values for $E$ vs Fc/Fc$^+$ from references [4,5]. In order to convert to potential vs Fc/Fc$^+$ for comparative reasons, the following have been used: $E^{*}$ (Fc/Fc$^+$) = 0.66(5) V vs NHE in solvent [($\text{Bu}_4\text{N}$)][PF$_6$]/CH$_3$CN [9]; Saturated calomel (SCE) = 0.2444 V vs NHE; Ag/Ag$^+$ = 0.400 V vs SCE [10].

$^b$ $\chi$ = Electronegativity
Table 3
DFT calculated data from this data article, as well as experimental electrochemical data (E vs Fc/Fc+) obtained from literature [4,5], of the [Ru(β-diketonato)] compounds 1 – 14. Where β-diketonato ligand=\((\text{RCOCHCOR})^+\) with the R and R’ substituents as shown in Fig. 1. DFT data was computed using two different hybrid functionals OPBE0 and B3LYP.

| R   | R’  | E (RuIII) \(\Delta\)  | E (RuIII/IV) \(\Delta\) | OPBE0/STO-TZ2P | B3LYP/STO-TZ2P | B3LYP/STO-6-311G(d,p)/Lanl2dz |
|-----|-----|------------------------|--------------------------|----------------|----------------|-----------------------------|
|     |     |                        |                          | \(E_{\text{HOMO}}\) (eV) | \(E_{\text{LUMO}}\) (eV) | \(X_{\text{calc}}\) (eV)  |
| 1   | CF₃ | CF₃                    | 0.34                     | -7.183         | -4.200         | 5.692                       |
| 2   | CF₃ | C₄H₉O                 | -0.34                    | 1.20           | -6.404         | 4.906                       |
| 3   | CF₃ | C₆H₁₂S                | -0.35                    | 1.19           | -6.393         | 4.901                       |
| 4   | CF₃ | Ph                     | -0.35                    | 1.26           | -6.528         | 5.005                       |
| 5   | CF₃ | CH₂                   | -0.47                    | 1.29           | -6.519         | 4.966                       |
| 6   | CF₃ | C(CH₃)₃               | -0.55                    | 1.30           | -6.420         | 4.881                       |
| 7   | Ph  | Ph                     | -0.90                    | 0.66           | -5.987         | 4.483                       |
| 8   | CH₂ | Ph                     | -1.04                    | 0.64           | -5.922         | 4.393                       |
| 9   | CH₂ | CH₂                   | -1.16                    | 0.61           | -5.863         | 4.291                       |
| 10  | C(CH₃)₃| C(CH₃)₃             | -1.46                    | 0.44           | -5.467         | 3.935                       |
| 11  | Et  | Et                     | -1.308                   | 0.549          | -5.722         | 4.155                       |
| 12  | Pr  | Pr                     | -1.324                   | 0.547          | -5.703         | 4.140                       |
| 13  | Bu  | Bu                     | -1.330                   | 0.535          | -5.681         | 4.123                       |
| 14  | iPr | iPr                    | -1.392                   | 0.509          | -5.523         | 3.996                       |

\(\Delta\) = Experimental values for E vs Fc/Fc\(^+\) from references [4,5]. In order to convert to potential vs Fc/Fc\(^+\) for comparative reasons, the following values have been used: \(E^{\text{Fc/Fc}^+} = 0.66(5)\) V vs NHE in solvent [\(n\)(Bu₄N)][PF₆] with CH₂CN [9]; Saturated calomel (SCE) = 0.2444 V vs NHE; Ag/Ag\(^+\) = 0.400 V vs SCE [10]. \(\chi = \text{Electronegativity}\)
Fig. 2. Relationships obtained between the experimental redox potential $E^\circ$ (vs Fc/Fc$^+$) of both the reduction (Ru$^{III/II}$) and the oxidation (Ru$^{III/IV}$) redox couples of the fourteen [Ru($\beta$-diketonato)$_3$] compounds 1 – 14 of this data article, with the DFT calculated data, namely (a) the LUMO (Ru$^{III/II}$) and HOMO (Ru$^{III/IV}$) energies $E_{HOMO/LUMO}$, (b) calculated Mulliken electronegativity $\chi$. All calculations were conducted in CH$_3$CN as solvent, using the indicated gga functionals.

### Redox potentials and frontier orbital energies

#### Oxidation redox couple Ru$^{III/IV}$:

- **$E^\circ$ (Ru$^{III/IV}$) = -0.80 $E_{HOMO}$(Ru$^{III}$) - 4.00**  
  $R^2 = 0.98$  
  (gas phase B3LYP/6-311G(d,p)/Lanl2dz) [1]

- **$E^\circ$ (Ru$^{III/IV}$) = -1.19 $E_{HOMO}$(Ru$^{III}$) - 6.72**  
  $R^2 = 0.99$  
  (CH$_3$CN phase B3LYP/6-311G(d,p)/Lanl2dz)

- **$E^\circ$ (Ru$^{III/IV}$) = -0.94 $E_{HOMO}$(Ru$^{III}$) - 4.52**  
  $R^2 = 0.98$  
  (CH$_3$CN phase B3LYP/TZ2P)

- **$E^\circ$ (Ru$^{III/IV}$) = -0.88 $E_{HOMO}$(Ru$^{III}$) - 4.47**  
  $R^2 = 0.95$  
  (CH$_3$CN phase OPBE0/TZ2P)

- **$E^\circ$ (Ru$^{III/IV}$) = -0.90 $E_{HOMO}$(Ru$^{III}$) - 3.33**  
  $R^2 = 0.96$  
  (CH$_3$CN phase PW91/TZ2P)

- **$E^\circ$ (Ru$^{III/IV}$) = -0.87 $E_{HOMO}$(Ru$^{III}$) - 2.98**  
  $R^2 = 0.96$  
  (CH$_3$CN phase OLYP/TZ2P)

#### Reduction redox couple Ru$^{III/II}$:

- **$E^\circ$ (Ru$^{III/II}$) = -0.72 $E_{LUMO}$(Ru$^{III}$) - 2.21**  
  $R^2 = 0.98$  
  (gas phase B3LYP/6-311G(d,p)/Lanl2dz) [1]

- **$E^\circ$ (Ru$^{III/II}$) = -0.91 $E_{LUMO}$(Ru$^{III}$) - 2.81**  
  $R^2 = 0.94$  
  (CH$_3$CN phase B3LYP/6-311G(d,p)/Lanl2dz)

- **$E^\circ$ (Ru$^{III/II}$) = -1.06 $E_{LUMO}$(Ru$^{III}$) - 4.38**  
  $R^2 = 0.98$  
  (CH$_3$CN phase B3LYP/TZ2P)

- **$E^\circ$ (Ru$^{III/II}$) = -1.04 $E_{LUMO}$(Ru$^{III}$) - 3.99**  
  $R^2 = 0.99$  
  (CH$_3$CN phase OPBE0/TZ2P)

- **$E^\circ$ (Ru$^{III/II}$) = -1.08 $E_{LUMO}$(Ru$^{III}$) - 5.59**  
  $R^2 = 0.98$  
  (CH$_3$CN phase PW91/TZ2P)

- **$E^\circ$ (Ru$^{III/II}$) = -1.10 $E_{LUMO}$(Ru$^{III}$) - 5.36**  
  $R^2 = 0.98$  
  (CH$_3$CN phase OLYP/TZ2P)
HOMO (LUMO) energies are directly related to the absolute oxidation potential since the product of the HOMO (LUMO) energies (in eV) and the electron charge (-1) gives absolute oxidation potential in eV [6]. The nearer the slope of the graph of oxidation (reduction) potential versus HOMO (LUMO) energies is to -1, the more accurate the DFT method used to calculate the HOMO (LUMO) energies. The intercept of the graph should be equal to the absolute potential of reference used, namely the Fc\(^+\)/Fc couple in acetonitrile for which benchmark values varies between +4.97 V (SMDB3LYP-D2/def2-QZVPDP//B3LYP/LanL2TZd/6-31G(d)) [7] and 4.988 V (G3(MP2)-RAD-Full-TZ) using gas-phase energies and COSMO-RS solvation energies [8]. In this study slopes of 0.7 – 1.2 and intercepts of 2.21 – 6.71 are obtained.

Redox potentials and global Mulliken electronegativity:

Oxidation redox couple Ru\(^{III/IV}\):

\[ E^{o}(\text{Ru}^{III/IV}) = 0.67 \times \chi_{\text{calc}} - 1.80 \]
\[ R^2 = 0.96 \]

(gas phase B3LYP/6-311G(d,p)/LanL2dz) [1]

\[ E^{o}(\text{Ru}^{III/IV}) = 0.86 \times \chi_{\text{calc}} - 2.81 \]
\[ R^2 = 0.90 \]

(CH\(_2\)CN phase B3LYP/6-311G(d,p)/LanL2dz) [1]

\[ E^{o}(\text{Ru}^{III/IV}) = 0.91 \times \chi_{\text{calc}} - 3.26 \]
\[ R^2 = 0.98 \]

(CH\(_2\)CN phase B3LYP/TZ2P)

\[ E^{o}(\text{Ru}^{III/IV}) = 0.86 \times \chi_{\text{calc}} - 3.00 \]
\[ R^2 = 0.95 \]

(CH\(_2\)CN phase OPBE0/TZ2P)

\[ E^{o}(\text{Ru}^{III/IV}) = 0.90 \times \chi_{\text{calc}} - 3.19 \]
\[ R^2 = 0.97 \]

(CH\(_2\)CN phase PW91/TZ2P)

\[ E^{o}(\text{Ru}^{III/IV}) = 0.89 \times \chi_{\text{calc}} - 2.91 \]
\[ R^2 = 0.96 \]

(CH\(_2\)CN phase OLYP/TZ2P)

Reduction redox couple Ru\(^{III/II}\):

\[ E^{o}(\text{Ru}^{III/II}) = 0.81 \times \chi_{\text{calc}} - 4.09 \]
\[ R^2 = 0.98 \]

(gas phase B3LYP/6-311G(d,p)/LanL2dz) [1]

\[ E^{o}(\text{Ru}^{III/II}) = 1.12 \times \chi_{\text{calc}} - 5.64 \]
\[ R^2 = 0.99 \]

(CH\(_2\)CN phase B3LYP/6-311G(d,p)/LanL2dz)

\[ E^{o}(\text{Ru}^{III/II}) = 1.08 \times \chi_{\text{calc}} - 5.78 \]
\[ R^2 = 0.97 \]

(CH\(_2\)CN phase B3LYP/TZ2P)

\[ E^{o}(\text{Ru}^{III/II}) = 1.07 \times \chi_{\text{calc}} - 5.93 \]
\[ R^2 = 0.99 \]

(CH\(_2\)CN phase OPBE0/TZ2P)

\[ E^{o}(\text{Ru}^{III/II}) = 1.09 \times \chi_{\text{calc}} - 5.79 \]
\[ R^2 = 0.98 \]

(CH\(_2\)CN phase PW91/TZ2P)

\[ E^{o}(\text{Ru}^{III/II}) = 1.08 \times \chi_{\text{calc}} - 5.51 \]
\[ R^2 = 0.98 \]

(CH\(_2\)CN phase OLYP/TZ2P)

The energies relative to the ground state energy for the different possible spin states of the neutral, oxidized and reduced [Ru(acetylacetonato)\(_3\)] compound 9 are provided in Table 4. The lowest energy value for each spin state showed that the neutral compound is low spin, S = \(\frac{1}{2}\) (doublet, one unpaired electron), in agreement with experiment [11]. The anion is diamagnetic with S = 0 (singlet), and the cation is paramagnetic with S = 1 (triplet, two unpaired electrons).
2. Experimental Design, Materials, and Methods

DFT calculations on all fourteen \([\text{Ru}(\beta\text{-diketonato})_3]\) compounds were performed in the CH\(_3\)CN solvent phase, using the following DFT methods:

(i) B3LYP/GTO-6-311G(d,p)/Lanl2dz: The hybrid functional B3LYP, which is composed of the Becke 88 exchange functional was applied in combination with the LYP correlation functional, as implemented in the Gaussian 16 package [12], applying the GTO (Gaussian type orbital) triple-\(\zeta\) basis set 6-311G(d,p) for the lighter atoms (C, H, N, O, F) and the Lanl2dz (Los Alamos National Laboratory 2-double-\(\zeta\)) basis set for the heavier Ru metal. The optimization is performed using Berny algorithm using GEDIIS [13] as implemented in the Gaussian 16 suite of programs [12]. The convergence is reached when the root mean square force, the maximum force, the root mean square displacement and the maximum displacement are within the threshold of 0.00030, 0.00045, 0.0012 and 0.0018 atomic units, respectively. The requested convergence on energy is 1.0D-6 atomic unit. The solvation model density (SMD) of the polarizable continuum model (PCM) was used, which also solved the non-homogeneous Poisson equation, by applying the integral equation formalism variant (IEF-PCM), as implemented in the Gaussian 16 package [12].

(ii) PW91/STO-TZ2P: Scalar-relativistic DFT using the gga PW91 (Perdew-Wang 1991) functional with the all-electron STO (Slater-Type Orbitals) triple \(\zeta\) basis set with two polarization functions (TZ2P) was applied, as implemented in the ADF 2018 package [14]. The geometry optimizations procedure in ADF is based on a quasi Newton approach, with an approximate Hessian. The Hessian is updated in the process of optimization. By default delocalized coordinates are used. The default convergence criteria were used, namely \(10^{-3}\) Hartree for the energy and \(10^{-3}\) Hartree/Å for the nuclear gradients. Solvent effects were taken into account for selected structures reported here, using the COSMO (Conductor like Screening Model) model of solvation, as implemented [15] in ADF. The type of cavity used was Esurf and the solvent used was CH\(_3\)CN (\(\varepsilon_0 = 37.5\)).

(iii) OLYP/STO-TZ2P: The gga OLYP functional was applied, with the TZ2P basis set and COSMO solvent model, as implemented in the ADF 2018 package [14].

(iv) OPBE0/STO-TZ2P: The hybrid OPBE0 functional was applied, with the TZ2P basis set and COSMO solvent model, as implemented in the ADF 2018 package [14].

(v) B3LYP/STO-TZ2P: The hybrid B3LYP functional was applied, with the TZ2P basis set and COSMO solvent model, as implemented in the ADF 2018 package [14].

The \([\text{Ru}(\beta\text{-diketonato})_3]\) compounds were calculated as doublets (with \(S = \frac{1}{2}\)) [11]. The input coordinates for the compounds were constructed using the program ChemCraft [16], and ChemCraft was also used to visualize the output files. The optimized coordinates, as well as an example input file, are provided in the supplementary information.
The DFT highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies \( E_{\text{HOMO}} \) and \( E_{\text{LUMO}} \) were obtained from the output file of the DFT computations. These energies were used to further calculate both the electron affinity (EA) and ionization potential (IP) of each of the fourteen compounds, according to Koopman’s theorem \([17,18]\):

\[
\text{IP} = -E_{\text{HOMO}}
\]

and

\[
\text{EA} = -E_{\text{LUMO}}
\]

The Mulliken electronegativity \( (\chi) \) \([19,20]\) was computed for each compound, by application of the following formulae:

\[
\chi = (\text{IP} + \text{EA})/2
\]

For the unsymmetrically substituted compounds \( 2 - 6 \) and \( 8 \) where \( R \neq R' \), an effective calculated energy \( E_{\text{HOMO}} \) and \( E_{\text{LUMO}} \) was determined by using the ratio of the relative population of the fac and mer isomers \( (n_i \text{ or } n_j) \), as determined by the Boltzmann equation at \( T = 298.15 \text{ K} \):

\[
\ln \frac{n_j}{n_i} = -\frac{(E_j - E_i)}{kT}
\]

where \( n_i \) is the number of molecules with energy \( E_i \) (fac or mer in this case), with the Boltzmann’s constant, \( k = 1.38066 \times 10^{23} \text{ JK}^{-1} \). \( E_i \) are provided in the supplementary information.

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**Conflict of Interest**

The author declares that there is no conflict of interest regarding the publication of this article.

**Supplementary materials**

Supplementary material associated with this article, electronic energies, example input and output files, as well as the optimized coordinates of DFT calculations, can be found in the online version, at doi:10.1016/j.dib.2020.105617.

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