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Studies on electronic structures and related properties of complexes $M(tap)_3^{2+}$ (M = Fe, Ru, Os) by the DFT method

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Studies on a series of complexes $M(tap)_3^{2+}$ (M = Fe, Ru, Os; tap = 1,4,5,8-tetraazaphenanthrene) are carried out using the DFT method at the B3LYP/LanL2DZ level. The electronic structures and related chemical properties of complexes $M(tap)_3^{2+}$, *e.g.* the energies and components of some frontier molecular orbitals, the spectral properties, and the net charge populations of some main atoms of the complexes, *etc.* have been investigated. In addition, computations on the complex $Ru(phen)_3^{2+}$(phen = 1,10-phenanthroline) are also performed for comparison. The computational results show some very interesting trends in electronic structures and related properties of complexes $M(tap)_3^{2+}$. First, the computational energies of some frontier molecular orbitals of $Ru(tap)_3^{2+}$ are all lower than those of $Ru(phen)_3^{2+}$. In particular, the energies of LUMOs of the complexes $Os(tap)_3^{2+}$ and $Ru(tap)_3^{2+}$ are all rather low and their electron affinities are rather high, leading to the prediction that an electron is very easily transferred from DNA guanine base to the LUMO of the complexes. This may be a major reason why these cations are excellent photoreagents for DNA. Second, the components of the HOMO of the four complexes all arise mainly from d orbitals of the central metal ions, and the components of the LUMO arise mainly from p orbitals of C and N atoms in the ligands, so their electronic ground state bands are theoretically all assigned to singlet metal-to-ligand charge-transfer (^{1}MLCT) transitions in absorption spectra, similar to those of $Ru(bpy)_3^{2+}$. Third, for $M(tap)_3^{2+}$, the most negative charges are populated on N1, with the next populated on N4. Fourth, the chemical stabilities (S) of the complexes are in order $S_{III} > S_{II} > S_I$, according to coordination energy computations. In addition, the central atom M has little effect on the coordination bond lengths and bond angles of the complexes. The obtained results should be important references for the synthesis of the complexes, mechanistic analysis of their photochemistry, electrochemistry and catalysis chemistry.

Introduction

An increasing number of octahedral Ru(II) polypyridyl complexes have been studied experimentally because of their extensive applications in the fields of photochemistry, photophysics, photocatalysis, electrochemistry and biochemistry, in particular, their very important applications to electrochemical luminescence, as solar energy battery materials and binding to DNA.[1–5] Many such complexes have been synthesized,[6–10] and related studies have been logically expanded to the polypyridyl or polypyridyl-like complexes of other transition metals,[11–15] *e.g.*, $Os(tap)_3^{2+}$ (tap = tetraazaphenanthrene) has been reported to be a novel metallic complex as a photoreagent for DNA guanine bases without the disadvantages caused by photoinstability as observed with $Ru(tap)_3^{2+}$ *etc.*[16–18] The excellent functions of the complexes undoubtedly derive from the characteristics of their electronic structures. In particular, the energies and compositions of frontier molecular orbitals as well as charge populations of the complexes play important roles in explaining the mechanism of their interactions with DNA, their spectroscopic properties, and electrochemical and photochemical behavior. Therefore, it is of importance to theoretically investigate the electronic structures and related properties of their series of complexes.

Quantum chemistry computations can aid in revealing electronic structures. Quantum chemical computations on ruthenium complexes have been published,[19–24] although semi-empirical calculation methods, such as EHMO, INDO, SINDO, MNDO and AM1 *etc.*, are usually applied,[25–30] and the DFT method has also been preliminarily used.[23] *Ab initio* quantum chemical methods are rarely applied to polypyridyl complexes of second- or third-row transition metals because (1) these complexes are rather large, and (2) electronic correlations have considerable effects on bonding energies, and traditional Hartree–Fock computations usually do not consider electron correlation energies, whereas H–F methods considering electron correction energies with configuration interaction (CI) or Møller–Plesset perturbation theory[31] require more computational expense. With the high speed development of computer technology and the wide applications of the G94/G98 program packages,[32] more and more quantum chemical computations on transition metal complexes, in particular, computations applying the density functional theory (DFT) method have been reported,[33–40] since they consider electron correlation energies and reduce greatly the computational expense. DFT has been proven to be especially useful to obtain more accurate molecular orbital energies and other properties of transition metal complexes.[19,37]

Recently, we have also reported the theoretical results on the complexes $M(bpy)_3^{2+}$(M = Fe, Ru, Os),[38] $[Ru(4,4'\text{-}2R\text{-}bpy)_3]^{2+}$,[39] and $[Ru(bpy)_2(5,6\text{-}2R\text{-}phen)]^{2+}$,[40] by the DFT method. Here, we report further the computational results for $M(tap)_3^{2+}$ (M = Fe, Ru, Os; tap = 1,4,5,8-tetraazaphenanthrene). Trends in the electronic structures and related properties of the complexes, *e.g.*, the compositions and the energies of some frontier molecular orbitals, spectral properties, atomic charge populations in complexes, *etc.*, have been investigated. The results should be important references for the synthesis or designs of functional molecules of the complexes, and for a mechanistic analysis of their photochemistry, electrochemistry and biochemistry.

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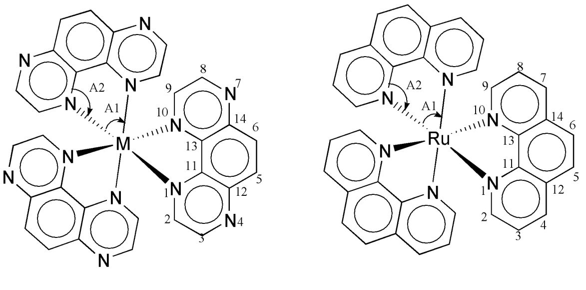
Table 1 Computational results of the main bond lengths (nm) and bond angles (°) of complexes $M(tap)_3^{2+}$ (Fe, Ru, Os) and $Ru(phen)_3^{2+}$

Compound		M–N	N–M–N	M–N–C	C–C(C–N)
I (M = Fe)		0.2021	83.1	111.2	0.1392
II (M = Ru)		0.2110	80.0	112.2	0.1394
III (M = Os)		0.2093	79.6	113.1	0.1394
IV $[Ru(phen)_3]^{2+}$	Calc.	0.2106	79.5	113.2	0.1405
	Expt.[42]	0.2067	79.8	—[a]	—[a]

[a] Data not provided.

Computational details

The octahedral bidentate complexes $[M(tap)_3]^{2+}$ (Fe, Ru, or Os) (tap = 1,4,5,8-tetraazaphenanthrene) are formed from M^{2+} and three tap ligands, and have D_3 symmetry. Full geometry optimizations of the complexes starting at D_3 symmetry are carried out with the DFT method at the B3LYP/LanL2DZ level. The computational model of $M(tap)_3^{2+}$ (M = Fe, Ru, Os) is shown in Fig. 1. In these computations, singlet states are assumed due to the low electronic spin for the analogous complex $Ru(bpy)_3^{2+}$.[1] 61 atoms are involved in each complex. For comparison, computations on complex $Ru(phen)_3^{2+}$ (phen = 1,10-phenanthroline) are also shown. All computations are performed with the G98 quantum chemistry program-package.[32]



(a) **I-III** (b) **IV**

Fig. 1 Calculation models of complexes $M(tap)_3^{2+}$ (M = Fe, Ru, Os) (a) and $Ru(phen)_3^{2+}$(b).

In order to discuss the central ion effects on the frontier molecular orbital energies and the spectral properties of the complexes, some frontier molecular orbital components (or atomic orbital populations in MO) in $M(tap)_3^{2+}$ (Fe, Ru, Os) should be analyzed. The orbital populations for various types of atomic orbitals (*e.g.*, s, p, d orbitals) in a specific molecular orbital (*e.g.*, NHOMO, HOMO, LUMO or NLUMO) are approximatively expressed as the atomic orbital coefficient square sums of the atomic orbitals and corrected by normalizing the specific molecule orbital. In order to vividly depict the detail of the frontier molecular orbital interactions, the stereographs of the HOMO and LUMO of the complexes are drawn with the Molden v3.6 program[41] based on the above computational results.

Results and discussion

A. Computational main bond lengths and bond angles of the complexes

Computational results of the main bond lengths and bond angles of complexes $M(tap)_3^{2+}$ (Fe, Ru, Os) and $Ru(phen)_3^{2+}$ and comparisons are shown in Table 1.

Reports on the crystal structures of the complexes $M(tap)_3^{2+}$ (M = Fe, Ru, Os) are not available although the ligands (tap) and $M(tap)_3^{2+}$ (M = Ru, Os) have been prepared and characterized.[16–18] Thus, we can not directly compare the computational results with experimental values. However, the computational results are reliable because they are nearly in agreement with the reported experimental values of the analogous complex (last row in Table 1).[42] The level of errors of the computational results from corresponding experimental values are about 2%. Those errors arise from two factors: the first is that theoretical computations do not consider the effects of the chemical environment (as a free molecule). The second is that the computational method and basis set are still approximate to some extent. However, these computational results are significant for discussion of trends in the properties of large systems, so that we can carry out a study of trends of the central atom effects on the structures and the related properties of the complexes.

From Table 1, we see only a small effect of the central atom M on coodination bond lengths and bond angles of the complexes. First, the order of computational coordination bond lengths is Ru–N (0.2110 nm) > Os–N (0.2093 nm) > Fe–N (0.2021 nm). *i.e.* the coordination bond lengths of the second-row transition metal complex is the longest in the group. The trend in $M(tap)_3^{2+}$ agrees with that in $M(bpy)_3^{2+}$(Fe, Ru, Os)[38] or $M(CO)_6$ (M = Cr, Mo, W).[31] Second, the order of the computational coordination bond angles is N–Fe–N (83.1°) > N–Ru–N(80.0°) ~ N–Os–N > (79.6°). Finally, the central ions have nearly no effect on the average bond lengths of the ligand skeletons (except for Fe for which they slightly shorten). Therefore, in terms of geometric structures, $Ru(tap)_3^{2+}$ and $Os(tap)_3^{2+}$ are similar, but they are rather different from $Fe(tap)_3^{2+}$.

B. Components and energies of the frontier molecular orbitals and related properties of the complexes

Frontier molecular orbitals, in particular, the HOMO and LUMO are very important because they are related not only to photoelectronic spectra and UV spectra, but also to reaction active sites and interaction mechanisms between the complexes and DNA. We should thus further discuss the components and energies of frontier molecular orbitals of the complexes. Computed results are shown in Tables 2 and 3 and schematic representation of the energy levels of the NHOMO, HOMO, LUMO and NLUMO and related electronic energy transitions of the complexes are shown in Fig. 2. Stereographs of the HOMO and LUMO orbitals of the complexes **I–III** are shown in Fig. 3.

Tables 2 and 3 and Figs. 2 and 3 show some very interesting trends in components and energies of the frontier molecular orbitals of $M(tap)_3^{2+}$ (M = Fe,Ru,Os).

(1) The components of HOMO and NHOMO of the three complexes $M(tap)_3^{2+}$ arise mainly from d orbitals of the central ions, *i.e.*, they may be characterized by d orbitals of the central ions, and the components of the LUMO and NLUMO arise mainly from p orbitals of C and N atoms in the ligands, *i.e.*, they may be characterized by p orbitals of the ligands, so their electronic ground state bands and the next ground state bands are all assigned to singlet metal-to-ligand charge-transfer (^{1}MLCT) transitions in absorption spectra. These spectral properties of $M(tap)_3^{2+}$ should also be similar to those [1,43–46] of $Ru(phen)_3^{2+}$ and $Ru(bpy)_3^{2+}$.

(2) The energies of the frontier molecular orbitals of $M(tap)_3^{2+}$ are all lower than those of $Ru(phen)_3^{2+}$. In particular, the LUMO energies of $Os(tap)_3^{2+}$ and $Ru(tap)_3^{2+}$ are all rather low [relative to the LUMO energy of $Ru(phen)_3^{2+}$], and so we can predict that an electron is very easily transfered from DNA guanine base to LUMOs of the two complexes.[16] Such a LUMO energy trend can easily be understood since their LUMO components arise mainly from the ligand p orbitals and the number

Table 2 Main atomic orbital populations (%) of NHOMO, HOMO, LUMO and NLUMO in $M(tap)_3{}^{2+}$ and $Ru(phen)^{2+}$

		M			N		C		H
Compound		s	p	d	s	p	s	p	s
I	NHOMO (2e)	0.0	0.8	70.2	0.1	8.8	0.8	19.2	0.0
	HOMO ($1a_1$)	0.0	0.0	85.9	0.0	4.5	1.4	8.2	0.0
	LUMO (3e)	0.0	0.1	4.4	0.7	51.9	0.5	42.4	0.0
	NLUMO ($2a_2$)	0.0	0.3	0.0	0.4	52.4	0.7	46.2	0.0
II	NHOMO (2e)	0.0	0.6	68.9	0.3	9.9	2.4	17.9	0.0
	HOMO ($1a_1$)	0.1	0.0	78.0	0.0	6.2	4.2	11.5	0.0
	LUMO ($2a_2$)	0.0	0.3	0.0	0.5	53.9	0.5	44.9	0.0
	NLUMO (3e)	0.0	0.1	7.1	0.7	50.4	0.8	40.9	0.0
III	NHOMO (2e)	0.0	0.4	64.1	0.4	11.3	2.8	21.1	0.0
	HOMO ($1a_1$)	0.2	0.0	71.9	0.0	7.4	5.6	14.8	0.0
	LUMO ($2a_2$)	0.0	0.5	0.0	0.7	54.2	0.5	44.1	0.0
	NLUMO (3e)	0.0	0.2	8.2	0.8	48.5	1.3	41.0	0.0
IV	NHOMO (2e)	0.0	0.5	69.3	0.2	2.4	3.0	24.7	0.0
	HOMO ($1a_1$)	0.1	0.0	77.6	0.0	3.5	4.6	14.1	0.0
	LUMO ($2a_2$)	0.0	0.2	0.0	0.4	29.7	0.6	69.1	0.0
	NLUMO (3e)	0.0	0.0	6.4	0.6	29.0	0.4	63.6	0.0

Table 3 Some frontier molecular orbital energies (ε_i/a.u.) of $M(tap)_3{}^{2+}$ (M = Fe, Ru, Os) and $Ru(phen)_3{}^{2+}$

Compound	Occ	Occ	Occ	Occ	Occ	HOMO	LUMO	Vir	Vir	$\Delta\varepsilon_{L\text{-}H}$	$\Delta\varepsilon_{L\text{-}NH}$
I	1e	1e′	$1a_2$	2e	2e′	$1a_1$	3e	3e′	$2a_2$		
	−0.4855	−0.4855	−0.4850	−0.4725	−0.4725	−0.4719	−0.3267	−0.3267	−0.3245	0.1452	0.1458
II	1e	1e′	$1a_2$	2e	2e′	$1a_1$	$2a_2$	3e	3e′		
	−0.4836	−0.4836	−0.4823	−0.4613	−0.4613	−0.4565	−0.3268	−0.3222	−0.3222	0.1297	0.1345
III	1e	1e′	$1a_2$	2e	2e′	$1a_1$	$2a_2$	3e	3e′		
	−0.4851	−0.4851	−0.4837	−0.4534	−0.4534	−0.4459	−0.3326	−0.3225	−0.3225	0.1133	0.1208
IV	1e	1e′	$1a_2$	2e	2e′	$1a_1$	$2a_2$	3e	3e′		
	−0.4444	−0.4444	−0.4421	−0.4056	−0.4056	−0.4016	−0.2750	−0.2709	−0.2709	0.1266	0.1306

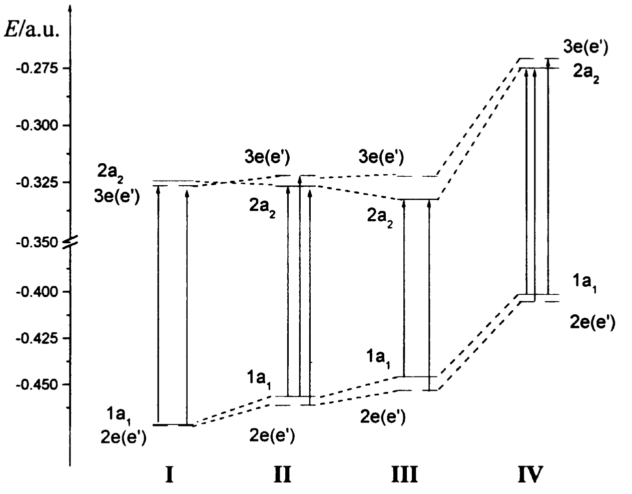


Fig. 2 Schematic representation of energies and related energy transitions of some frontier MO in $M(tap)_3{}^{2+}$ (M = Fe, Ru, Os) and $Ru(phen)_3{}^{2+}$.

of N atoms (having greater electronegativity, relative to C) in tap is twice that in phen. Thus the attraction of tap for electrons on corresponding orbitals is stronger than that of phen.

In order to test the reliability of the prediction of the trend in electron transfer in terms of the LUMO energies, computations of electron affinities of the complexes have also been performed, according to the definition[31] of eqn. (1).

$$\Delta E_A = E[M(tap)_3{}^{2+}] - E[M(tap)_3{}^{+}] \qquad (1)$$

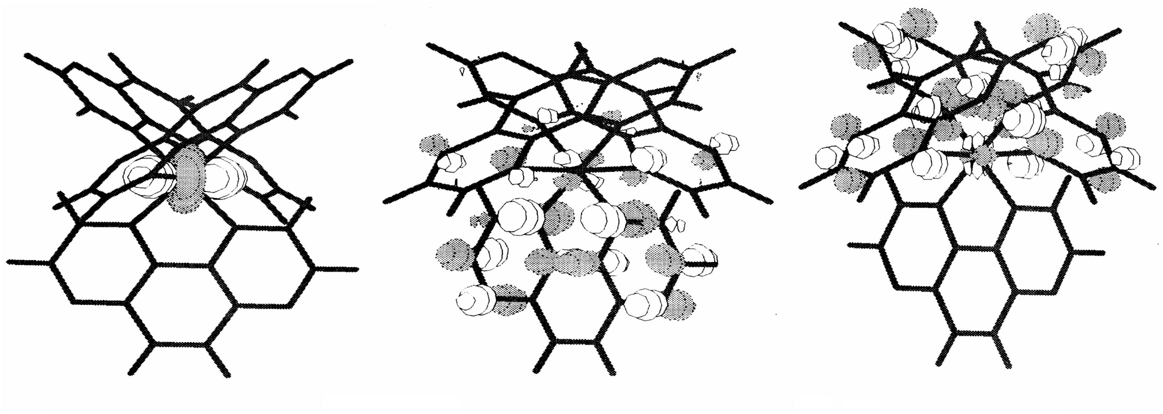
Here, $E[M(tap)_3{}^{2+}]$ (M = Fe, Ru or Os) is the total energy of $M(tap)_3{}^{2+}$ and $E[M(tap)_3{}^{+}]$ is that of $M(tap)_3{}^{+}$ (*via* unrestricted doublet state calculations). The computational results are shown in Table 4. The order of electron affinities of the complexes agrees well with that of the negative values of their LUMO orbital energies.

Table 4 Electron affinities (a.u.) of $M(tap)_3{}^{2+}$ (M = Fe, Ru, Os) and $Ru(phen)_3{}^{2+}$

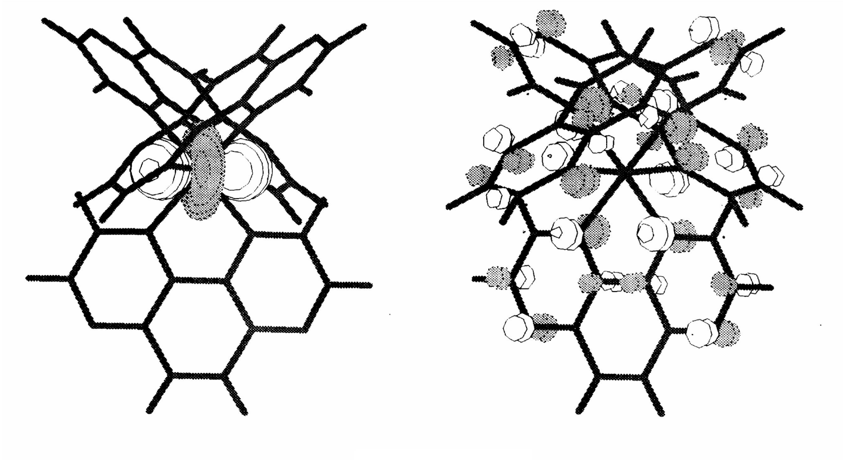
	I (M = Fe)	II (M = Ru)	III (M = Os)	IV
$E(+2)$	−1933.7707	−1904.2313	−1901.4026	−1808.1801
$E(+1)$	−1934.0528	−1904.5164	−1901.6935	−1808.4148
ΔE	0.2821	0.2851	0.2909	0.2347

(3) For the three complexes $M(tap)_3{}^{2+}$, with an increase of atomic number of M, the HOMO and NHOMO energies of the series of complexes obviously increase, and the LUMO energy slightly reduces and thus the energy difference between the LUMO and HOMO($\Delta\varepsilon_{L\text{-}H}$) is obviously reduced, *i.e.*, the wavelength (λ_1) of electronic ground state band obviously increases. This trend can be simply explained as follows: the HOMOs and NHOMOs of the three complexes are all formed mainly by d orbitals of the central metal ions (see Table 3 and Fig.3), therefore, their energies are mainly decided by the d-orbital energies of M, which follow the sequence obtained from our computations: $\varepsilon_{Fe}{}^{2+}(-1.094$ a.u) $< \varepsilon_{Ru}{}^{2+}$ $(-0.993$ a.u.) $<$ $\varepsilon_{Os}{}^{2-}(-0.921$ a.u.), so the HOMO and NHOMO energies follow the same sequence, *i.e.*, the HOMO and NHOMO energies of the complexes increase with an increase of the atomic number of M. By contract, the LUMOs of complexes are formed mainly by p_z orbitals of N and C atoms of the identical ligand skeletons far from the metal ions, so their energies should be expected to be only slightly influenced by these metal ions and are mainly influenced by the relative contributions of the p orbitals of C and N atoms, for example, the order of LUMO energies is $\varepsilon_{I} > \varepsilon_{II} > \varepsilon_{III}$, whereas the order of the N p-orbital contributions is **I** < **II** < **III**, *i.e.*, in general, the higher the contributions of the N p-orbitals, the lower the MO energy of the complex.

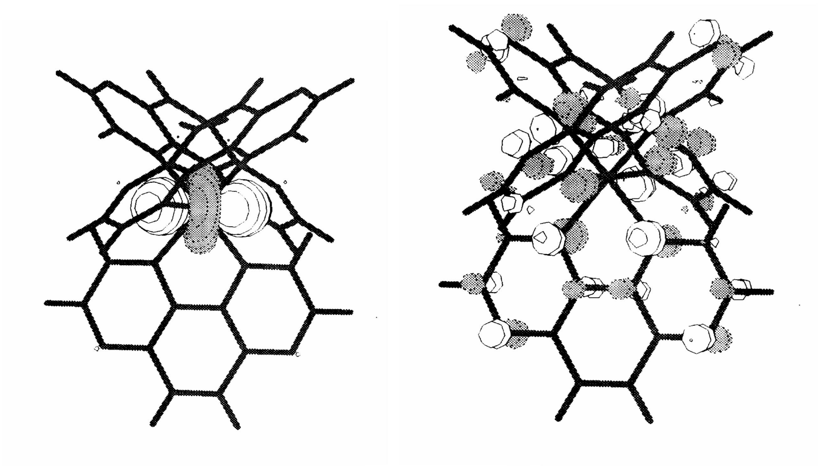
With an increase in M atomic number in $M(tap)_3{}^{2+}$, the energy difference between the LUMO and HOMO ($\Delta\varepsilon_{L\text{-}H}$), that between LUMO and NHOMO($\Delta\varepsilon_{L\text{-}NH}$), or that between NLUMO and HOMO ($\Delta\varepsilon_{NL\text{-}H}$) are all reduced. These energy



I (M=Fe, HOMO=$1a_1$) **I** (M=Fe, LUMO=3e) **I** ((M=Fe, LUMO=3e′)



II (M=Ru, HOMO=$1a_1$) **II** (M=Ru, LUMO=$2a_2$)



III (M=Os, HOMO=$1a_1$) **III** (M=Os, LUMO=$2a_2$)

Fig. 3 Stereographs of HOMOs and LUMOs of $M(tap)_3^{2+}$ (M = Fe, Ru, Os).

differences are closely related to the ground state bands and the next ground state bands of the electronic spectra of the complexes. Therefore, it can be predicted that the wavelength orders of their ground state bands and next ground state bands are $\lambda_I < \lambda_{II} < \lambda_{III}$. Such a trend is very similar to that found in $M(bpy)_3^{2+}$(M = Fe, Ru, Os).[38] For $Ru(tap)_3^{2+}$ and $Os(tap)_3^{2+}$, the trend is satisfactorily consistent with the experimental results in which the wavelengths of the electronic ground state bands are 437 and, 462 nm, respectively, and those of the next ground state bands are 408 and 416 nm, respectively,[16] although the experimental data for $Fe(tap)_3^{2+}$ have not been reported. In addition, $\Delta\varepsilon_{L-H}$ and $\Delta\varepsilon_{NL-H}$ for $Ru(tap)_3^{2+}$ are greater than those for $Ru(phen)_3^{2+}$. The trend in these computed results also agrees with that for the experimental data, in which the wavelengths of their ground state bands and next ground state bands are 437 and 408 nm, respectively, for $Ru(tap)_3^{2+}$,[16] and 447 and 423 nm, respectively, for $Ru(phen)_3^{2+}$.[43,44]

Trends in the frontier molecular orbital energies are very useful in analysis of DNA-binding, use of solar energy, and design of new photoreagents.

According to perturbation molecular orbital theory[47] and frontier molecular orbital theory,[48] for a reaction controlled by orbital interactions between reactant molecules, a higher HOMO energy of one reactant molecule and a lower LUMO energy of other are advantageous for reaction between the two molecules, since electrons more easily transfer from the HOMO of one reactant to the LUMO of another one in the orbital interaction, and reduces the total energy of the reaction system. Hence, from above-mentioned trends (the HOMO energy increases and the LUMO energy reduces and the electron

Table 5 Charge populations (unit: |*e*|) along path (a) from N1 to C5 of ligands of $M(tap)_3^{2+}$ and $Ru(phen)_3^{2+}$

	M	N1	C2	C3	N4(C4)	C12	C5
I	0.7122	−0.4729	0.0653	0.0636	−0.3938	0.1857	−0.1549
II	0.6287	−0.4521	0.0636	0.0636	−0.3969	0.1871	−0.1546
III	0.8234	−0.4791	0.0597	0.0624	−0.3983	0.1887	−0.1542
IV	0.6263	−0.4697	0.0979	−0.2194	−0.1297	−0.0615	−0.1632

affinity of the complex increases with an increase of metal atomic number in the three complexes), we can easily deduce that for groove binding mode and intercalative binding between the complexes and DNA, in particular, the intercalative binding mode (the main ligand of complex intervening with the base group pair of DNA), the affinity of the complex binding to DNA increases in the order, $[Fe(tap)_3{}^{2+}]$ < $[Ru(tap)_3{}^{2+}]$ < $[Os(tap)_3{}^{2+}]$. This should be the reason why $Ru(tap)_3^{2+}$ and $Os(tap)_3^{2+}$ are studied much more than $Fe(tap)_3^{2+}$ as binding agents to DNA. In particular, it was reported recently that $Os(tap)_3^{2+}$ is a novel metallic complex as a photoreagent for DNA guanine bases without the disadvantages caused by photoinstability as observed with $Ru(tap)_3^{2+}$. The main reason for this should be the rather lower LUMO energy or the higher electron affinity of $Os(tap)_3^{2+}$. In addition, the HOMO energy of $Fe(tap)_3^{2+}$ is much lower than that of $Ru(tap)_3^{2+}$ or $Os(tap)_3^{2+}$ and its LUMO energy (note doubly degenerate orbitals, i.e., 3e and 3e′) is slightly higher than that of $Ru(tap)_3^{2+}$ or $Os(tap)_3^{2+}$, and thus we can predict the wavelengths of the ground state band and next ground state band of $Fe(tap)_3^{2+}$ to be much shorter than that of $Ru(tap)_3^{2+}$ or $Os(tap)_3^{2+}$. According to the approximate correlation of reverse radio of the difference between the LUMO and the HOMO energies ($\Delta\varepsilon_{\text{L–}}$) to experimental wavelength (λ), using $\Delta\varepsilon_{\text{L–H}}$ data of the complexes in Table 3 and the experimental wavelength of the ground state band of $[Ru(tap)_3]^{2+}$ (**II**, λ = 437 nm)[16], we can evaluate the wavelength of the electronic ground band of the complex $Fe(tap)_3^{2+}$ to be ~390 nm. Therefore, we can deduce that if we make use of solar energy to excite $Fe(tap)_3^{2+}$, the efficiency will be rather low because only ultraviolet radiation of solar energy can be used. This may also be why the study on $Fe(tap)_3^{2+}$ for solar energy use is much less than that of $Ru(tap)_3^{2+}$ or $Os(tap)_3^{2+}$.

Approximation of the energy difference between the LUMO and HOMO to the transition energy from the ground state to the first excited state of the complex is based on frontier molecular orbital theory,[48] in which the HOMO and LUMO play predominant roles in many chemical reactions and related properties of compounds. Such an approximation is very advantageous to discuss some relative regularities or trends. With regard to the excited states, further computations require density-functional theory for excited states, in which a Kohn–Sham formalism of excited states with density-functional theory (DFT) is presented, and the differences of Kohn–Sham eigenvalues are also shown to be well-defined approximations for excitation energies.[49]

C. Atomic net charge populations of complexes

According to natural orbital population analysis (NPA), the net charge populations on some skeleton atoms in $[M(tap)_3]^{2+}$ and $Ru(phen)_3^{2+}$ are shown in Tables 5 and 6.

From Tables 5 and 6 the following characteristics of the atomic net charge populations on a ligand skeleton of $M(tap)_3^{2+}$ and $Ru(phen)_3^{2+}$ along path (a) and (b) can been seen.

(1) The atomic charge populations for $M(tap)_3^{2+}$ **I**–**III** are very similar to each other, and they do not show polarity alternation along the two paths (a) and (b), such charge populations are different from those for $Ru(phen)_3^{2+}$ **IV** which essentially shows polarity alternation (except for negative charges instead of positive charges on C4 and C5) along the two paths.

Table 6 Charge populations (unit: |*e*|) along path (b) from N1 to C5 of ligands of $M(tap)_3^{2+}$ and $Ru(phen)_3^{2+}$

Compound	M	N1	C11	C12	C5
I	0.7122	−0.4729	0.1631	0.1857	−0.1549
II	0.6287	−0.4521	0.1590	0.1871	−0.1546
III	0.8234	−0.4791	0.1565	0.1887	−0.1542
IV	0.6263	−0.4697	0.1966	−0.0615	−0.1632

Table 7 Computed coordination energies (ΔE/a.u.) of $M(tap)_3^{2+}$ and $Ru(phen)_3^{2+}$

Compound	$E_{\text{M}}{}^{2+}$	E_{tap}	$E_{\text{comp.}}$	ΔE
I	−122.4810	−603.5462	−1933.7707	0.6511
II	−92.8815	−603.5462	−1904.2313	0.7112
III	−89.9578	−603.5462	−1901.4026	0.8062
IV	−92.8815	−571.5020	−1808.1801	0.7926

(2) For $M(tap)_3^{2+}$**I**–**III**, the most negative charges are populated on N1 and the next are populated on N4 while the most negative charges are populated on C5 among the C atoms. By contrast for $Ru(phen)_3^{2+}$ **IV**, the most negative charges are populated on N1 and the next on C3.

The above atomic charge populations in the heterocyclic systems can not be explained with the traditional schematic representation expressed by a single series of winding arrow heads, which explains well the net charge populations on some unisubstituted benzenes. However they can be simply and satisfactorily interpreted applying a schematic map expressed by several series of arrow heads based on the law of polarity alternation[50,51] and the idea of polarity interference proposed by us.[52,53,40]

D. Center atomic effects on the chemical stabilities of $M(bpy)_3^{n+}$

In order to carry on the computation studies on the stabilities of the complexes, for process (2)

$$M^{2+} + 3\ \text{tap} \longrightarrow M(tap)_3^{2+} \qquad (2)$$

we define the coordination energy ΔE of the complex by eqn. (3).[54]

$$\Delta E = 3E_{\text{tap}} + E_{\text{M}}{}^{2+} - E_{\text{comp}} \qquad (3)$$

Here E_{tap}, $E_{\text{M}}{}^{2+}$ and E_{comp} are the energies of ligand (tap), central ion M^{2+} and the complex respectively. The same computation method is used for the central ion and ligand, and for the computations of free central ions M^{2+}, the quintet states (S = 2) are taken. The computed coordination energies are shown in Table 7. According to the above definition, the positive value of ΔE shows the corresponding complex to be stable, and the higer the coordination energy, the more stable the complex. The energies of $M(tap)_3^{2+}$ are 0.6511, 0.7112 and 0.8062 a.u., respectively. This indicates that the three metal ions and tap can form stable octahedral bidentate complexes, and the trend in their chemical stabilities (S) is in order $S_{\text{III}} > S_{\text{II}} > S_{\text{I}}$. With an increase of atomic number, the stability of the complex increases. The trend in the coordination energies of the complexes may depend on many factors such as coordination bond lengths, charges on N atoms and M ion σ-bonging and π back-bonding existing between the central ion and ligands. Detailed correlations among these retain to be solved in further studies.

Conclusions

From the computational studies using the DFT method, we have found some important trends in electronic structures and related properties of complexes $M(tap)_3^{2+}$ (M = Fe, Ru, Os) and $Ru(phen)_3^{2+}$. First, the computational energies of some frontier molecular orbitals of $Ru(tap)_3^{2+}$ are all lower than those of $Ru(phen)_3^{2+}$. In particular, the energies of LUMOs of the complexes $Os(tap)_3^{2+}$ and $Ru(tap)_3^{2+}$ are all rather low and their electron affinities are rather high, and thus we can predict that an electron will read its transfer from DNA guanine base to the LUMO of the complexes. This may be a primary reason why they are excellent photoreagents for DNA. Second, the components of the HOMO of the four complexes all arise mainly from d orbitals of the central metal ions, and the components of the LUMO arise mainly from p orbitals of C and N atoms in ligands, so their electronic ground bands in absorption spectra are theoretically all assigned to singlet metal-to-ligand charge-transfer (^{1}MLCT) transitions in absorption spectra, similar to those of $Ru(bpy)_3^{2+}$. Third, for $M(tap)_3^{2+}$, the most negative charges are populated on N1, followed by N4. Fourth, center atom M has only a small effect on the coordination bond lengths and bond angles of the complexes. In addition, the chemical stabilities (S) of the complexes are in order $S_{III} > S_{II} > S_{I}$, according to coordination energy computations. The obtained results should be important references for the synthesis of the complexes and mechanistic analysis on photochemistry, electrochemistry and catalysis chemistry.

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