Electronic Structures and Related Properties of Complexes $M(bpy)_3^{n+}$(M = Re, Os, and Ir; n = 1, 2, and 3, Respectively)

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The theoretical studies on a series of isoelectronic complexes $M(bpy)_3^{n+}$ (M = Re, Os, and Ir; n = 1, 2, and 3, respectively) are carried out with DFT method at B3LYP/LanL2DZ level. The electronic structures and related chemical properties of complexes $M(bpy)_3^{n+}$, in particular, the regularities of the center ionic effects on the spectral properties, the chemical stabilities, and the atomic net charge populations, have been investigated. The results show that, for the complexes $Re(bpy)_3^{1+}$ and $Os(bpy)_3^{2+}$, the main components of HOMO and NHOMO come from d orbitals of the center ion, but for the LUMO and NLUMO, the main components come from p orbitals of the atoms C and N in ligands. Therefore, the ground bands and the next ground bands of their electronic spectra are designed as a typical spectrum band of the singlet metal-to-ligand charge transfer (^{1}MLCT). Whereas for the complex $Ir(bpy)_3^{3+}$, whether HOMO and NHOMO or LUMO and NLUMO, their main components come from the p orbitals of C and N in ligands, so the ground band and the next ground band of its electronic spectra are designed as a typical band of the singlet ligand-to-ligand transition ($^1L\pi-\pi^*$). With increase of the atomic number of the center atom M, the energy interval between HOMO and LUMO increases, the wavelength of the corresponding spectrum decreases, and the chemical stability of the complex increases. In addition, for three complexes, there are more negative charge populations on C6 in the ligands, and then C6 can be expected as an active site in electrophilic reactions. The computational results can be better used to explain some experimental phenomena and regularities.

Introduction

In the past 20 years, the octahedral Ru(II) polypyridyl complexes have been studied in detail because of their extensive applications to the fields of photochemistry, photophysics, photocatalysis, electrochemistry, biochemistry, and so on. In particular, they become a study focus of the related and the intersect subjects because of their important applications to the structural recognization of DNA, electrochemical luminescence, and solar energy battery material.[1−3] The excellent functions of the complexes derive from their special structural features. Each of them is an octahedral bidentate complex, which is composed of a transition metal ion as a center and three polypyridyl ligands with conjugation π bondings, and there are two N atoms as coordination points in every ligand, so that the whole complex becomes a very big conjugated molecule. Recently, many transition metal polypyridyl complexes have been synthesized. To modify the ligands or to change the central atoms can create interesting differences in the properties of the resulting complexes. So a logical extension of these studies is to pay great attention to the polypyridyl complexes of other d^6 transition metal systems, such as Os(II),[4] Co(III),[5] Rh(III),[6] Ir(III),[7] Re(I),[8] Tc(I),[9] etc., in which $Re(bpy)_3^{1+}$, $Os(bpy)_3^{2+}$, and $Ir(bpy)_3^{3+}$ are isoelectronic systems (bpy = 2,2′-bipypridyl), but their properties are dramatically different. Therefore, it is very significant to investigate the electronic structures and the related chemical properties of the series of the complexes.

Before the 1990s, a few quantum chemical investigations of ruthenium complexes had been published, and for most of them, the semiempirical calculation methods, such as EHMO, INDO, SINDO, MNDO, AM1, etc. were applied.[10] One of the problems in applying an ab initio quantum chemistry method to the polypyridyl complexes of second- or third-row transition metals is that such systems are too large to computations, and the other one is the considerable effects of electron correlations on binding energies, which is usually not accounted for in a traditional Hartree−Fock calculation, except for applying configuration interaction (CI) methods and Møller−Plesset perturbation theory[11] needing a terrible computational expense. Since the 1990s, in particular, recently, with the high-speed development of computer technology and the wide applications of G94/G98 program packages,[12,13] it becomes possible to calculate strictly some bigger transition metal complexes. Some computations applying density functional theory (DFT) method[11,14] and using LanL2DZ basis set[15] have been reported,[16] because of their accounting better for electron correlation energies and reducing greatly the computation expenses. However, so far, the reports of studies on transition metal polypyridyl complexes(especially those of second-row and third-row transition metals) with DFT method are still less found, and maybe some computational works on this field have escaped our attentions. When quantum chemical computations are applied to transition metal polypyridyl complexes with a relatively large size, undoubtedly the computations of energies and spectrum properties of complexes in an absolute meaning still have some disparities, but we think that the most important thing is to obtain some regularities on the electronic structures and related properties of the complexes with similar structures. For this purpose, the DFT method may be the most suitable. We have reported the computational results on $M(bpy)_3^{2+}$ (M = Fe, Ru, and Os)[16d], as well as the

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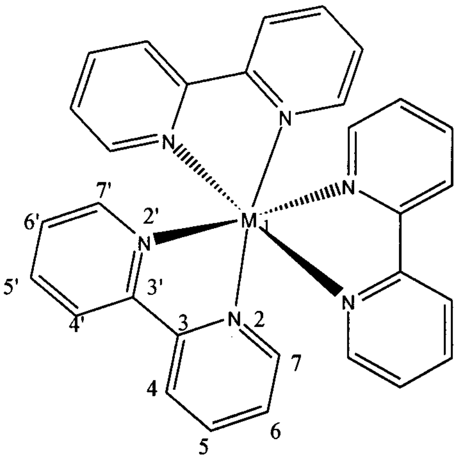


Figure 1. Computation model of $M(bpy)_3^{n+}$ complexes (M = Re, Os, and Ir; $n = 1$, 2, and 3, respectively).

TABLE 1: Main Bond Lengths (nm) and Bond Angles (Degrees) of $M(bpy)_3^{n+}$ Used in the Computations

$M(bpy)_3^{2+}$	M−N	C−C (C−N)	N−M−N	M−N−C	ref
I (M = Re)	0.2060	0.136	77.1	111.5	(8)
II (M = Os)	0.2056	0.136	77.8	111.1	(4)
III (M = Ir)	0.2021	0.136	78.8	110.6	(7)

disubstitutive derivatives on the three bpy of $Ru(bpy)_3^{2+}$ with DFT method,[16e] etc.

In this paper, the theoretical computational results of the series of complexes $M(bpy)_3^{n+}$ (M = Re, Os, and Ir; $n = 1$, 2, and 3, respectively) as isoelectronic systems are reported. The electronic structures and related chemical properties of the complexes, in particular, the regularities of the center ionic effects on the spectral properties, the chemical stabilities, and the atomic net charge populations of $M(bpy)_3^{n+}$, have been investigated. The results obtained may be useful as references for the synthesis of the complexes; the mechanism analysis on photochemistry, electrochemistry, and biochemistry of the complexes, etc.

Computation Section

The octahedral bidentate complexes $M(bpy)_3^{n+}$ (M = Re, Os, and Ir; $n = 1$, 2, and 3, respectively) belong to D_3 symmetry. To simplify the tedious computations and pay attention to the study on the regularities of the electronic structures and related chemical properties for the series of the complexes, the approximate computation model was taken as follows: (1) For the coordination bond lengths and bond angles of each complex, their mean experimental values[4,7,8] were used respectively; For C−C (C−N) bond lengths and C−C−C and C−N−C bond angles of all bpy ligands, the mean values[1] of the experimental bond lengths and bond angles of aromatic skeletons in the $Ru(bpy)_3^{2+}$ were used respectively, listed in Table 1. (2) For the H−C bond lengths and the related angles (e.g., H−C−C in ligands), the standard geometry data[17] were used. According to the approximate model, shown in Figure 1, the single-point energy computations on a series of complexes $M(bpy)_3^{n+}$ (M = Re, Os, and Ir; $n = 1$, 2, and 3, respectively) were carried out with DFT method at B3LYP/LanL2DZ level,[13,14] and the natural orbital population analysis (NPA)[13] were performed. In these computations, the singlet states were taken because of the low electronic spin for the complexes, 61 atoms are involved, and all computations were performed with G98 programs.[12]

Results and Discussion

Center Atomic Effects on Frontier Molecular Orbital Energies and Spectral Properties of the Complexes. The occupied frontier molecular orbital energies are related to photoelectronic energy spectra, and the intervals of frontier molecular orbital energy levels are related to UV spectra. Some frontier molecular orbital energies and the corresponding intervals of energy levels are listed in Table 2. For a simple comparison, the schematic representation of the energy levels of the NHOMO, HOMO, LUMO, and NLUMO and the related electronic energy transitions are shown in Figure 2. Meanwhile, to compare them with the series of $M(bpy)^{2+}$ (M = Fe, Ru, and Os) (belonging to the VIII-group and different periods), the schematic representation of energies of some frontier MO in $M(bpy)_3^{2+}$ (M = Fe, Ru, and Os) and the related electronic energy transitions, which were reported by us in Chinese,[16d] are also shown in Figure 3.

Table 2 and Figure 2 show the following: (1) HOMO and NHOMO orbitals of $M(bpy)_3^{n+}$ (M = Re, Os, and Ir; $n = 1$, 2, and 3, respectively) are all $2a_1$ and $2e(e')$, whereas LUMO and NLUMO orbitals are all $1a_2$ and $3e(e')$. The ground electronic configurations of the complexes are all $(2e)^4(2a_1)^2$. When the center atom M changes, both the orbital symmetry and the energy order do not change, but the corresponding orbital energies decrease greatly with the increase in the atomic number of the center metal atoms. It is a common characteristic for such a type of isoelectronic complexes. They differ from the other series of complexes with the VIII-group metal atoms, i.e., $M(bpy)^{2+}$ (M = Fe, Ru, and Os),[16d] in which changing the center ion makes some of their corresponding molecular orbital energy levels reverse (e.g., $1a_2$ and 3e in Figure 3). Such a difference may be explained as follows: For the $M(bpy)_3^{n+}$ (M = Re, Os, and Ir; $n = 1$, 2, and 3, respectively) complexes, the center atoms of which belong to the same period, their electronic structures are identical, but their nuclear charge numbers differ from each other. With the increase of the positive charges of the metal ion, the nuclear attractions for electrons increase; as a result, the corresponding molecular orbital energies greatly decrease in order, and then an order reverse of some molecular orbital energy levels cannot appear. Whereas for the complexes $M(bpy)^{2+}$ (M = Fe, Ru, and Os), although the electronic structures in the outer shells are the same, the whole electronic structures are different, so that there are complicated interactions between the atomic nucleus and electrons and between electrons and electrons; as a result, the order reverse of some orbital energy levels would happen. (2) With the increase of the atomic number and the positive charge of the metal ion, the energy intervals $\Delta\epsilon_{L-H}$ between LUMO and HOMO, $\Delta\epsilon_{L-NH}$ between LUMO and NHOMO, or $\Delta\epsilon_{NL-H}$ between NLUMO and HOMO increase dramatically in order, which are closely related to the ground bands and the next ground bands of electronic spectra. Therefore, it can firmly be predicted that the wavelength order of their ground bands and next ground bands are both $\lambda_I > \lambda_{II} > \lambda_{III}$. This regularity is consistent with the experimental results in which the wavelengths of the electronic ground bands are 823, 480, and 311 nm and those of the next ground bands are 506, 446 nm and far UV wave length,[8,18,19] respectively.

Center Ionic Effects on Frontier Molecular Orbital Components. To further study the center ionic effects on spectral properties of the complexes, some frontier molecular orbital components (or atomic orbital populations) have been analyzed. The atomic orbital populations for a varied type of atomic orbitals (e.g., s, p, or d orbitals) in specific molecular

TABLE 2: Some Frontier Molecular Orbital Energies (ϵ_i/a.u.) of M(bpy)$_3{}^{n+}$

	O[a]	O[a]	O[a]	O[a]	NHOMO	HOMO	LUMO	NLUMO	$\Delta\epsilon_{L-H}$	$\Delta\epsilon_{L-NH}$	$\Delta\epsilon_{NL-H}$
I	1a1	1 e	1e′	2e	2e′	2a1	1a2	3e(e′)			
	−0.3439	−0.3410	−0.3410	−0.2608	−0.2608	−0.2388	−0.1857	−0.1616	0.0531	0.0751	0.0772
II	1a1	1 e	1e′	2e	2e′	2a1	1a2	3e(e′)			
	−0.4614	−0.4570	−0.4570	−0.4077	−0.4077	−0.3963	−0.3001	−0.2870	0.0962	0.1076	0.1093
III	1a1	1 e	1e′	2e	2e′	2a1	1a2	3e(e′)			
	−0.5898	−0.5867	−0.5867	−0.5721	−0.5721	−0.5691	−0.4209	−0.4160	0.1482	0.1512	0.1531

[a] O expresses the occupied molecular orbital. A pair of e (e.g., 1e and 1e′) expresses a pair of degenerate orbitals.

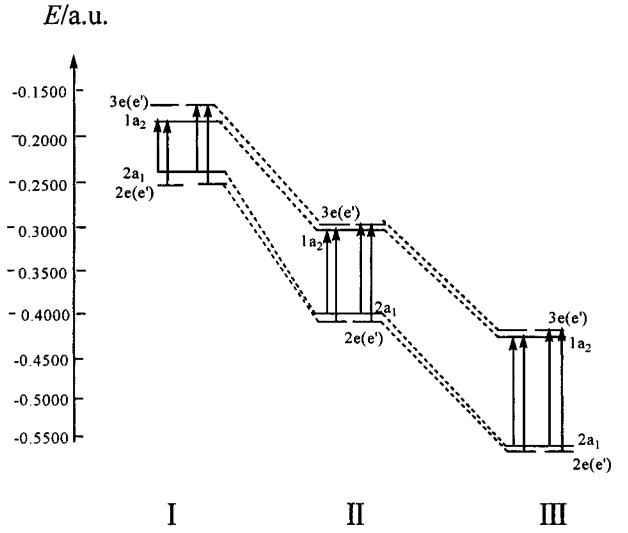


Figure 2. Schematic representation of energies of some frontier MO in M(bpy)$_3{}^{n+}$ (M = Re, Os, and Ir; $n = 1$, 2, and 3, respectively) and the related electronic energy transitions.

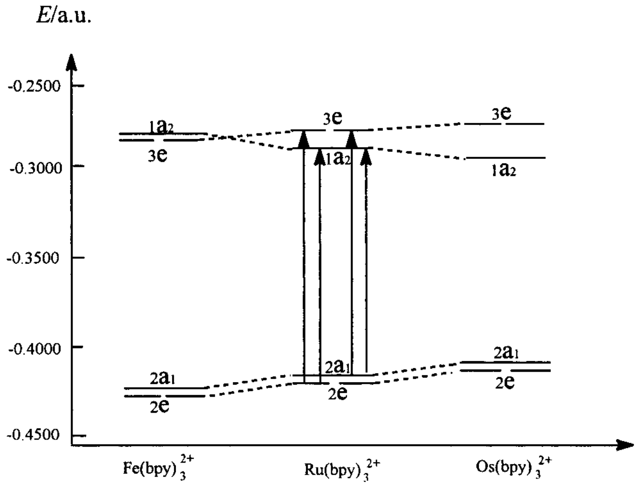


Figure 3. Schematic representation of energies of some frontier MO in M(bpy)$_3{}^{2+}$ (M = Fe, Ru, and Os) and the related electronic energy transitions.[16d]

TABLE 3: Main Atomic Orbital Populations (%) of Some Frontier Molecular Orbitals in Complexes M(bpy)$_3{}^{n+}$ (M = Re, Os, and Ir; *n* = 1, 2, 3, respectively)

atom orb./	M			N		C		H
mole. orb.	s	p	d	s	p	s	p	s
I								
NHOMO	0.0	0.3	43.2	0.2	5.4	3.4	47.4	0.1
HOMO	0.1	0.0	60.7	0.1	2.7	10.4	25.8	0.2
LUMO	0.0	0.2	0.0	0.5	30.7	0.6	68.0	0.0
NLUMO	0.0	0.2	14.2	0.4	14.6	1.3	69.1	0.1
II								
NHOMO	0.0	0.1	61.2	0.2	2.5	3.1	32.8	0.1
HOMO	0.1	0.0	67.0	0.0	5.4	6.9	20.4	0.1
LUMO	0.0	0.2	0.1	0.5	31.0	0.5	67.7	0.0
NLUMO	0.0	0.2	10.1	0.7	26.1	0.9	62.0	0.1
III								
NHOMO	0.0	0.0	9.4	0.1	8.6	0.5	81.3	0.0
HOMO	0.1	0.0	26.5	0.0	14.0	1.6	57.9	0.0
LUMO	0.0	0.4	0.0	0.6	31.7	0.5	66.8	0.0
NLUMO	0.0	0.3	4.9	0.9	30.8	0.6	62.5	0.1

orbitals (e.g., NHOMO, HOMO, LUMO, and NLUMO) are expressed as the atomic orbital coefficient square sum in the type of atomic orbitals and corrected by normalizing the certain molecule orbitals. The results are shown in Table 3. The stereographs of the HOMO and LUMO of the complexes are also shown in Figure 4 (drawn with Molden v3.6 program).

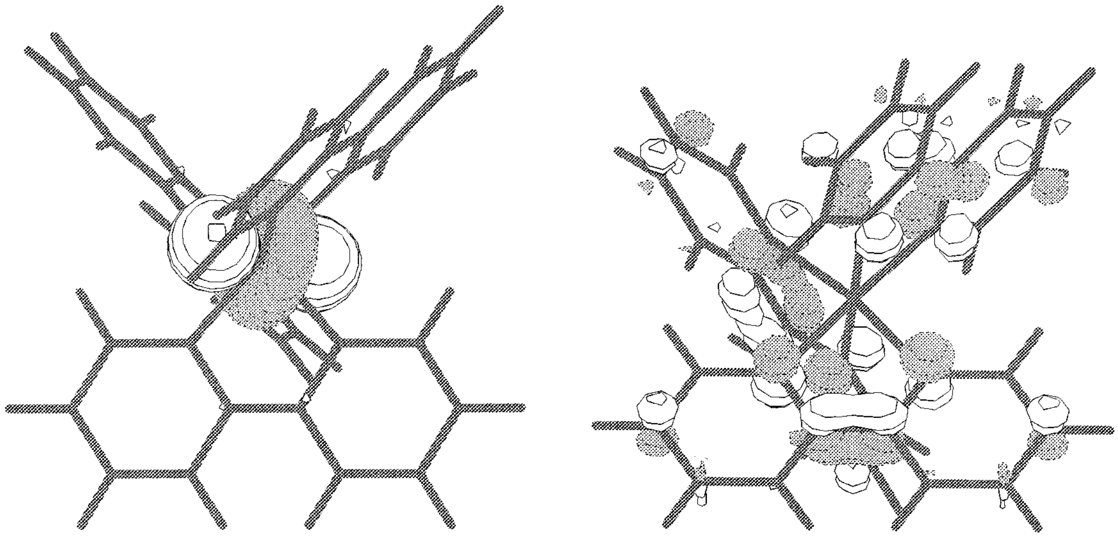
Some component regularities of the froniter molecular orbitals of M(bpy)$_3{}^{n+}$ can be seen from Table 3: First, for complexes **I** and **II**, the components of HOMO and NHOMO come mainly from d orbitals of the metal atoms, i.e., they may be characterized by d orbitals of the metal ions, but the components of LUMO and NLUMO come mainly from p orbitals of C and N atoms in ligands, i.e., they may be characterized by p orbitals of the ligands, and consequently, the electronic ground bands and the next ground bands are assigned as the bands of singlet metal-to-ligand charge transfer (^{1}MLCT). Second, for complex **III**, the components of the above four orbitals all come mainly from the p orbitals of C and N in ligands (the d orbital of the Ir ion still makes some contributions). The electronic ground bands and the next ground bands are assigned as the bands of singlet ligand-to-ligand transitions (^{1}Lπ−π*). The difference between **III** and **I** (or **II**) has been explained in that the additional nuclear proton for Ir^{3+} (in complex **III**) makes the energy of the d-orbital manifold of the metal ion lower than the energy of the π-orbital manifold of ligands in HOMO.[19] The regularities are consistent with the experimental results.[8,16,17]

Center Ionic Effects on the Chemical Stabilities of M(bpy)$_3{}^{n+}$. To carry on the theoretical computation studies on the stability regularity of the complexes, we define the coordination energy ΔE of a complex by the following:[20]

$$\Delta E = 3E_{\mathrm{bpy}} + E_{\mathrm{M}}{}^{n+} - E_{\mathrm{comp}}$$

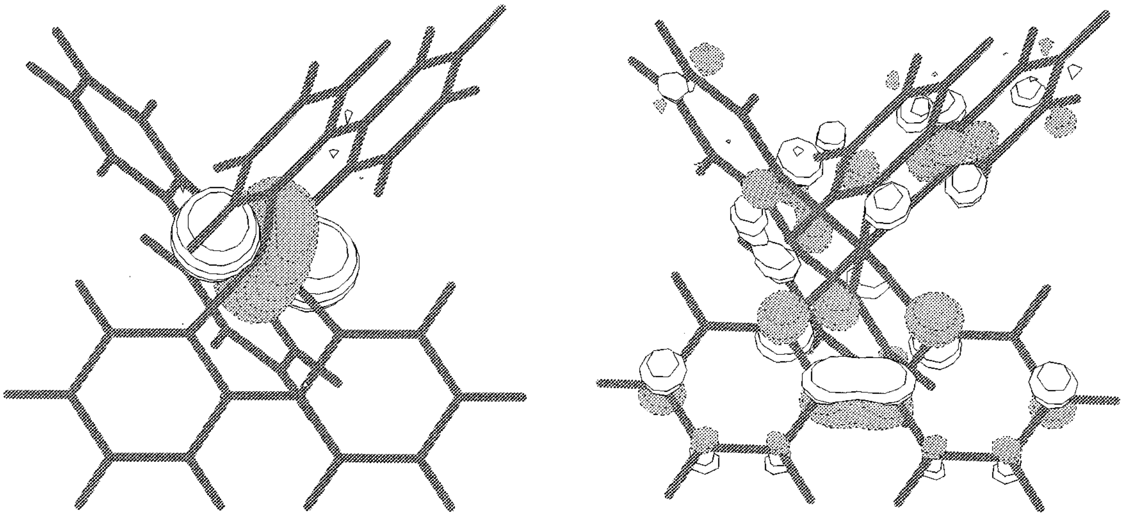
where E_{bpy}, $E_{\mathrm{m}}{}^{n+}$, and E_{comp} are the energies of ligand (bpy), center ion M^{n+}, and the complex, respectively, and the abovementioned quantum chemistry computation method is also used for center ion and ligand. Apparently, the more the coordination energy is, the more stable the complex is. The computation results are shown in Table 4.

Table 4 shows the coordination energies of M(bpy)$_3{}^{n+}$ (M = Re, Os, and Ir; $n = 1$, 2, and 3, respectively) to be 0.0519, 0.4442, and 1.0622 (a.u.), respectively. They indicate that M (M = Re, Os, and Ir)$^{n+}$ and bpy can form stable octahedral bidentate complexes, respectively, and the regularity of their chemical stabilities is in order $S_{\mathrm{III}} > S_{\mathrm{II}} > S_{\mathrm{I}}$. It can be easily explained as follows: Because M(bpy)$_3{}^{n+}$ (M = Re, Os, and



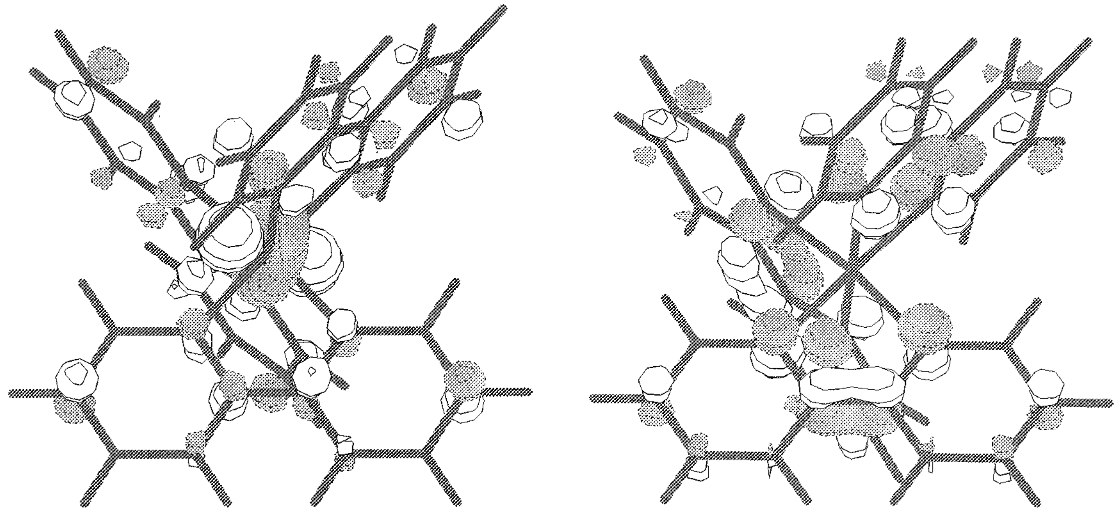
HOMO of complex **I (M=Re)**

LUMO of complex **I (M=Re)**



HOMO of complex **II (M=Os)**

LUMO of complex **II (M=Os)**



HOMO of complex **III (M=Ir)**

LUMO of complex **III (M=Ir)**

Figure 4. Stereographs of HOMO and LUMO of complexes (**I**−**III**).

Ir; $n = 1$, 2, and 3, respectively) are isoelectronic systems and their ligands are the same and the positive charges on center ion increase with the increase of the metal atomic number, the interaction between center ion and ligands must be strengthened, and then their chemical stabilities must also be increased in the above order.

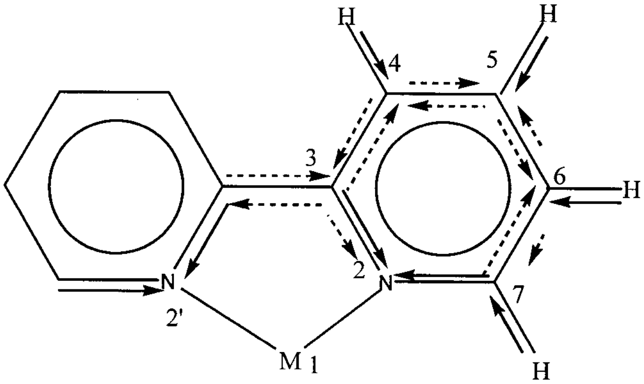


Figure 5. Sketch of the alternating-polarity and the polarity interferences on ligands of the complexes.

TABLE 4: Coordination Energies (ΔE/a.u.) of $M(bpy)_3^{n+}$

complexes	$E_{M^{n+}}$	E_{bpy}	E_{comp}	ΔE
I ($n = 1$)	−78.4840	−495.3750	−1564.6609	0.0519
II ($n = 2$)	−89.8258	−495.3750	−1576.3950	0.4442
III ($n = 3$)	−102.4041	−495.3750	−1589.5913	1.0622

TABLE 5: Net Charge Populations of Some Main Atoms in the Complexes (|*e*|)

	M1	$\Delta q_m{}^a$	N2	C3	C4	C5	C6	C7
I	0.8980	0.1020	−0.4840	0.1283	−0.1546	−0.1960	−0.2263	0.0600
II	0.8553	1.1447	−0.4695	0.1459	−0.1474	−0.1533	−0.2091	0.0747
III	1.0782	1.9218	−0.4796	0.1453	−0.1300	−0.1189	−0.1917	0.0894

[a] Δq_m is the transferred negative charges from ligands to center ions M^{n+}.

Atomic Net Charge Populations of $M(bpy)_3^{n+}$. According to the natural orbital population analysis (NPA), the net charge populations on some main atoms in the $M(bpy)_3^{n+}$ are shown in Table 5.

Two net charge population characteristics of the series of complexes are shown in Table 5:

(1) With an increase of the valence numbers of the center ions, the transferred negative charges from ligands to center ions (Δq_m) increase, and simultaneously, the negative charges on almost all corresponding C atoms of the ligands decrease (i.e., the positive charges on those increase) in the three complexes. This is a result of the negative charges transfer from all of the atoms in ligands to the center ion in order of $Re^{1+} < Os^{2+} < Ir^{3+}$. In addition, we had expected the negative charges on coordination N atoms to increase in the above order. However, in fact, those increase in the other order of $Os^{2+} < Ir^{3+} < Re^{1+}$. It can be explained by metal-to-ligand π back bonding.[8] The attraction of nucleuses for coordination atom N with negative charges is in the order of $Re^{1+} < Os^{2+} < Ir^{3+}$. So metal-to-ligand π back bonding would be more significant from Re^{1+} to N (or ligand) than from Os^{2+} or Ir^{3+} to N (or ligand), and then negative charges on coordination atom N of $Re(bpy)_3{}^{1+}$ are more than those of $Os(bpy)_3{}^{2+}$ or $Ir(bpy)_3{}^{3+}$.

(2) For the three complexes, the atomic charge populations obey to the law of polarity alternation and the idea polarity interference[21].To explain the regularity of the charge populations, we first draw a sketch of the polarity interference as Figure 5, where a solid arrowhead toward a greater electronegative atom represents primary bond polarity and two series of the alternately directional and gradually shortened dotted arrowheads represent the gradually reduced polarity caused by two N atoms (the sum of conjugative and inductive effects), but that caused by each H atom is neglected. The direction of arrowheads is determined according to the law of polarity alternation. The direction of an arrowhead shows the one of the move of negative charges. Because the quantity of charge transfer between the two directly adjoining atoms should be larger than that between the two indirectly adjoining atoms, the quantity of charge transfer represented by a solid arrowhead should be larger than that represented by a dotted arrowhead. Therefore, the relative size and sign of atomic charges can be predicted according to the directions, lengths, and number of solid arrowheads and dotted arrowheads. For example, the most negative charges are populated on the N2 atom because of two solid arrowheads toward the N2 atom, the next most negative charges are populated on the C6 atom because of one solid arrowheads and two longer dotted toward it, the most positive charges are populated on the C3 atom because of one solid and one longest dotted heads departing from it, and so on.

So it can be predicted from both the qualitative analysis by the idea of the polarity interference and the theoretical computational results on the charge populations that the most active site in electrophlic reactions should be C6.

Summary

In the series of isoelectronic complexes $M(bpy)_3^{n+}$ (M = Re, Os, and Ir; n = 1, 2, and 3, respectively), the components of HOMO and NHOMO of $Re(bpy)_3{}^{1+}$ and $Os(bpy)_3{}^{2+}$ come mainly from d orbitals in center ions, whereas the components of their LUMO and NLUMO come mainly from p orbitals of C and N atoms in ligands, and then related electronic ground bands and the next ground bands are assigned as the bands of singlet metal-to-ligand charge-transfer (^{1}MLCT). In contrast, the components of the above four orbitals of $Ir(bpy)_3{}^{3+}$ all come mainly from the p orbitals of C and N atoms in ligands, and then the electronic ground bands and the next ground bands are assigned as the bands of singlet ligand-to-ligand transition ($^1L\pi-\pi^*$). With the increase of the atomic number, the energy interval between HOMO and LUMO increases, the wavelength of the corresponding spectrum decreases, and the chemical stability of complex increases. In addition, there are more negative charge populations on C6 of the ligands, and then C6 can be expected as an active site in electrophilic reactions.

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