Russian Journal of General Chemistry, Vol. 71, No. 7, 2001, pp. 995–1000. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 7, 2001, pp. 1057–1063.

Chemistry of Electronically Excited Ruthenium Polypyridine Complexes: III.[1] Electronic Structure of Complexes *cis*-$[Ru(2,2'\text{-}bpy)_2(4,4'\text{-}bipy)(X)]^q$

O. V. Sizova, V. V. Sizov, A. Yu. Ershov, A. B. Nikol'skii, V. I. Baranovskii, and A. D. Shashko

St. Petersburg State University, St. Petersburg, Russia

Received March 23, 2000

Abstract — The results of *ab initio* quantum-chemical calculations of isolated ruthenium(II) complexes *cis*-$[Ru(bpy)_2(bipy)(X)]^q$ (bpy is 2,2'-bipyridyl, bipy is 4,4'-bipyridyl; X = NH_3, Cl^-, Br^-, CN^-, NO_2^-, ONO^-, MeCN, and NO^+) are presented. Analysis of the charge distributions and the orbital structures of the complex ions points to absence of strong π-acceptor bonds Ru–bpy, Ru–bipy, and Ru–X (X = NO^+), to delocalization of π-electron density under the action of strong donors X, to localized nature of lowest unoccupied molecular orbitals, and to special position of the nitrosyl complexes in this series.

Analysis of the electronic structures of molecules constitutes an integral part of modern theoretical inorganic chemistry, as the elucidation of composition–electronic structure–properties correlations makes it possible not only to interpret available experimental data, but also to direct further investigations. It is not incidentally that results of quantum-chemical calculations find increasing use as equitable characteristics of new chemical compounds.

In this work we present the results of nonempirical calculations of complexes *cis*-$[Ru(bpy)_2(bipy)(X)]^q$ (X = NH_3, Cl^-, Br^-, CN^-, NO_2^-, ONO^-, MeCN, NO^+). The Cl^- and NO_2^- complexes were described earlier [2, 3] and the others were recently synthesized by A.D. Shashko and A.Yu. Ershov. The previous publications of this series [1, 4] were devoted to the complex *cis*-$[Ru(bpy)_2(bipy)(NH_3)]^{2+}$. The listed compounds were synthesized with a view to their prospective use as building blocks of photoactivated electron transport circuits. Therefore, data on the charge distribution and the relative arrangement of energy levels of fragments in the complexes with various ligands X are of prime importance. It is quite natural to accept the results of quantum-chemical calculations for isolated species in the ground states as a starting point for subsequent analysis of the electronic structure of excited complex ions in solutions. To obtain such data was the aim of the present work.

The electronic structures of related ruthenium complexes have been calculated by various quantum-chemical methods [5–12] but none of these methods could be relied on in our work. In fact, *ab initio* calculations with large basis sets are hardly extended on polynuclear systems, whereas semiempirical methods (as a rule, for pertinent systems various versions of the INDO approximation are used) inevitably introduce effects not involved in the Hartree–Fock formalism and depending on parametrization. To consider the whole *cis*-$[Ru(bpy)_2(bipy)(X)]^q$ series from a common viewpoint and to avoid using empirical parameters, we addressed to *ab initio* calculations.

All the calculations were carried out by the GAMESS program [13] by the restricted Hartree-Fock (RHF) method with fixed geometry taken from experimental data for similar bonds in known ruthenium(II) organometallic complexes. The same bonds in different complexes were assigned equal lengths *r* (Å): Ru–N(bpy) 2.055, Ru–N(bipy) 2.01, Ru–Cl 2.37, Ru–Br 2.56, Ru–CN 2.03, Ru–NO_2 2.09, Ru–ONO 2.055, Ru–NH_3 2.15, Ru–N(MeCN) 2.02, and Ru–NO 1.77. The electronic structures of the complexes were described in terms of commonly accepted calculated characteristics related to the most important concepts of theoretical chemistry: effective charges (*q*) of atoms and fragments, populations (*n*) of separate atomic orbitals (AO) (first of all *d* AOs of the metal and π orbitals of ligands), valences of atoms (*V*), multiplicities of bonds (*W*), and diagrams of molecular orbitals (MO). These characteristics depend on basis set and can not directly be compared with experimental values. Therefore, first of all, on an example of two representative structural units of polynuclear

---

[1] For communication II, see [1].

Table 1. Results of calculations of the $[Ru(NH_3)_5(pyz)]^{2+}$ complex with various basis sets: effective charges on ruthenium and pyrazine (q, e), charges transfered from ruthenium d_π AOs (δd_π, e) and on pyrazine π orbitals ($\delta\pi_{pyz}$, e), energy gaps between HOMO and LUMO ($\Delta\varepsilon$, eV), valences of atoms (V), and bond multiplicity indices (W)[a]

Parameter	STO–3G (103)	SBK/STO–3G (108)	MINI (100)	SBK (160)	3-21G (176)	MIDI (170)
q(Ru)	1.00	0.24	1.13	0.42	0.98	1.22
q(pyz)	–0.32	0.28	0.15	0.21	0.07	0.10
δd_π	0.80	–0.04	0.05	0.05	0.09	0.07
$\delta\pi_{pyz}$	0.68	–0.07	0.03	0.08	0.02	0.02
$\Delta\varepsilon$, eV	6.95	10.74	13.10	11.54	11.43	11.64
V(Ru)	4.00	2.96	1.63	2.67	2.24	1.58
$V(N^1)$	3.38	3.38	3.27	2.71	2.79	2.86
$V(N^2)$	3.01	3.01	3.02	2.88	2.73	2.80
$W(Ru–N^1)$	1.00	0.52	0.32	0.16	0.32	0.25
$W(Ru–NH_3)$	0.46	0.48	0.26	0.39	0.36	0.25

[a] Values in parentheses indicate basis size.

chains of the cationic complex $[Ru(NH_3)_5(pyz)]^{2+}$ (pyz is pyrazine) and the anionic complex $[Ru(bpy)\cdot(CN)_4]^{2-}$, we analyzed the results of calculations with several basis sets: the most known minimal basis set STO–3G, the well-optimized minimal basis set MINI [14], the popular valence-split basis set 3–21G, the basis set MIDI comparable with 3–21G in size [14], the basis set SBK with core pseudopotential [15], and the combined basis set SBK/STO–3G with core pseudopotential for Ru and the minimal basis set STO–3G for light atoms (Table 1). Combined basis sets, such as SBK/STO–3G and SBK/6–31G [9] or MIDI/STO–3G [10], were earlier repeatedly used for calculation of ruthenium complexes.

As follows from the data for $[Ru(NH_3)_5(pyz)]^{2+}$ in Table 1, the STO–3G results contradict all the other results: The π-acceptor power of pyrazine (0.68 *e* in excess of six electrons in the free molecule), resulting from STO–3G calculations, is notably higher than that obtained with the other basis sets, and the population of the d_π AO of ruthenium is lower owing to $d_\pi \rightarrow \pi^*$(pyz) charge transfer; the highest occupied molecular orbital (HOMO) lies too high and consists basically of pyrazine orbitals, whereas the *d* AOs of Ru, not involved in bonding with pyrazine, lie much lower (by 2.5 eV). Naturally, the multiplicity of the Ru–pyz bond and the valence of ruthenium are therewith overestimated. The overestimated energies of ruthenium d_π AOs and the underestimated populations of these orbitals show that the STO–3G basis is unsuitable for Ru. Our attempts to improve the situation by using the combined SBK/STO–3G basis failed: Disbalacing the basis resulted in underpopulated orbitals of the organic ligand and lack of π-acceptor properties in pyrazine. As compared to the 3–21G basis, in the SBK basis the valence of ruthenium is overestimated because of increased $Ru–NH_3$ and Ru–C(pyz) bond multiplicities; therewith, the ratio of the Ru–pyz $Ru–NH_3$ bond multiplicities seems improbable. Moreover, the lower valence of the pyrazine nitrogen atom (N^1) bound to ruthenium compared with the terminal nitrogen atom (N^2) seems strange. The MINI and MIDI results for $[Ru(NH_3)_5(pyz)]^{2+}$ are similar to each other and close to those obtained with the 3–21G basis set, though they give underestimated V(Ru) values are at the expense of underestimation of the $Ru–NH_3$ bond multiplicity. Note, however, the atomic charges in the organic ligands are notably different: The 3–21G and MIDI calculations result in higher bond polarities, in particular, the charges on nitrogen atoms have high negative values (–0.8 and –0.5 *e* on N^1 and N^2, respectively).

In the case of the anionic complex $[Ru(bpy)\cdot(CN)_4]^{2-}$, the STO–3G and SBK/STO–3G valences of ruthenium were 5.6 and the effective charges, 0.9 and –1.1, respectively, which is hardly correlated with the commonly accepted chemical notion of Ru(II) complexes. A more reasonable value of 2.9 for V(Ru) was obtained with the 3–21G and MINI basis sets. While overestimated compared to the “classical” value of 2, it can be accounted for by a rather high multiplicity of Ru–C bonds W(Ru–C) of 0.5, the charge on the ruthenium atom in this case being close to unit: q(Ru) 1.1 (3–21G) and 0.8 (MINI). Therefore, for calculation of complexes *cis*-$Ru(bpy)_2(bipy)(X)]^q$ we chosed two basis sets: 3–21G and MINI, which provide rather realistic valence structures. Comparative analysis of the total energies showed that MINI

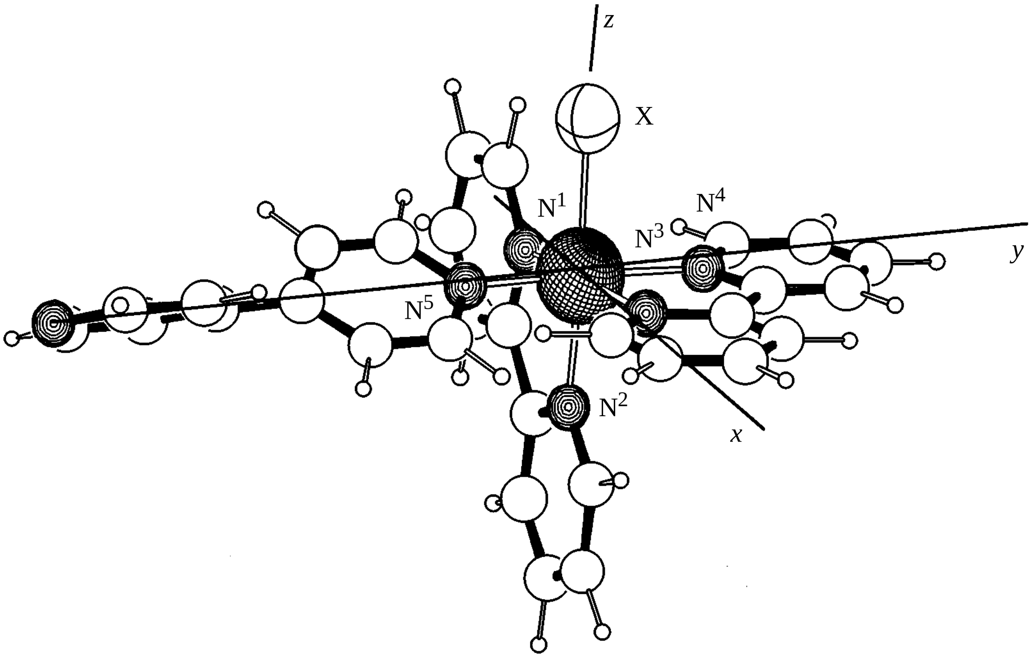

Fig. 1. Structure of complexes $[Ru(bpy)_2(bipy)(X)]^q$, atom numbering, and coordinate axes.

is somewhat inferior to 3–21G in the description of orbitals of light atoms but considerably surpasses it in the description of ruthenium orbitals. Taking account of the "economy" of the MINI basis set, we tried it with a view to its prospective feasibility for subsequent calculations of more extended fragments of photoactivated electron transport circuits.

The structure of complexes *cis*-$[Ru(bpy)_2(bipy)(X)]^q$ in Cartesian coordinates and the numbers of nitrogen atoms in the bipyridyl ligands are shown in Fig. 1. The calculated characteristics of charge distribution and valence structure of the complexes are given in Table 2, and the diagrams of frontier MOs and the contributions of ruthenium and ligand orbitals, obtained with the MINI basis set, are shown in Fig. 2. The MO energies in Fig. 2 were counted from the HOMO energy for each complex, which allowed us

Table 2. MINI calculation results for complexes $[Ru(bpy)_2(bipy)(X)]^q$: effective charges of fragments [Ru, X, bpy, py^1 (the pyridine ring of bipy, closest to the metal), and py^2 (remote pyridine ring of bipy)] (q, e), valence of ruthenium [V(Ru)], multiplicities (W) of the bonds Ru–N and Ru–X (to an atom in ligand X, closest to the metal), and HOMO energies [ε(HOMO), eV]

Parameter	Br^-	Cl^-	NO_2^-	ONO^-	CN^-	NH_3	MeCN	NO^+
q(Ru)	1.10	1.11	1.14	1.12	1.06	1.16	1.18	1.35
q(X)	–0.71	–0.71	–0.74	–0.71	–0.61	0.14	0.10	0.32
$q(bpy^1)$	0.24	0.23	0.22	0.21	0.20	0.28	0.28	0.53
$q(bpy^2)$	0.24	0.24	0.24	0.24	0.22	0.27	0.28	0.50
$q(py^1)$	0.09	0.09	0.09	0.08	0.08	0.07	0.08	0.15
$q(py^2)$	0.05	0.05	0.05	0.05	0.05	0.08	0.08	0.14
V(Ru)	1.92	1.93	1.92	1.94	2.10	1.80	1.86	3.30
W(Ru–X)	0.43	0.44	0.35	0.42	0.62	0.24	0.27	0.97
$W(Ru–N^1)$	0.27	0.27	0.27	0.27	0.27	0.28	0.28	0.36
$W(Ru–N^2)$	0.26	0.26	0.24	0.24	0.20	0.30	0.29	0.41
$W(Ru–N^3)$	0.28	0.28	0.28	0.28	0.28	0.29	0.29	0.37
$W(Ru–N^4)$	0.27	0.27	0.27	0.27	0.27	0.28	0.28	0.35
$W(Ru–N^5)$	0.30	0.30	0.30	0.30	0.30	0.31	0.31	0.40
ε(HOMO), eV	–9.50	–9.85	–9.96	–9.78	–10.8	–14.2	–19.1	–16.3

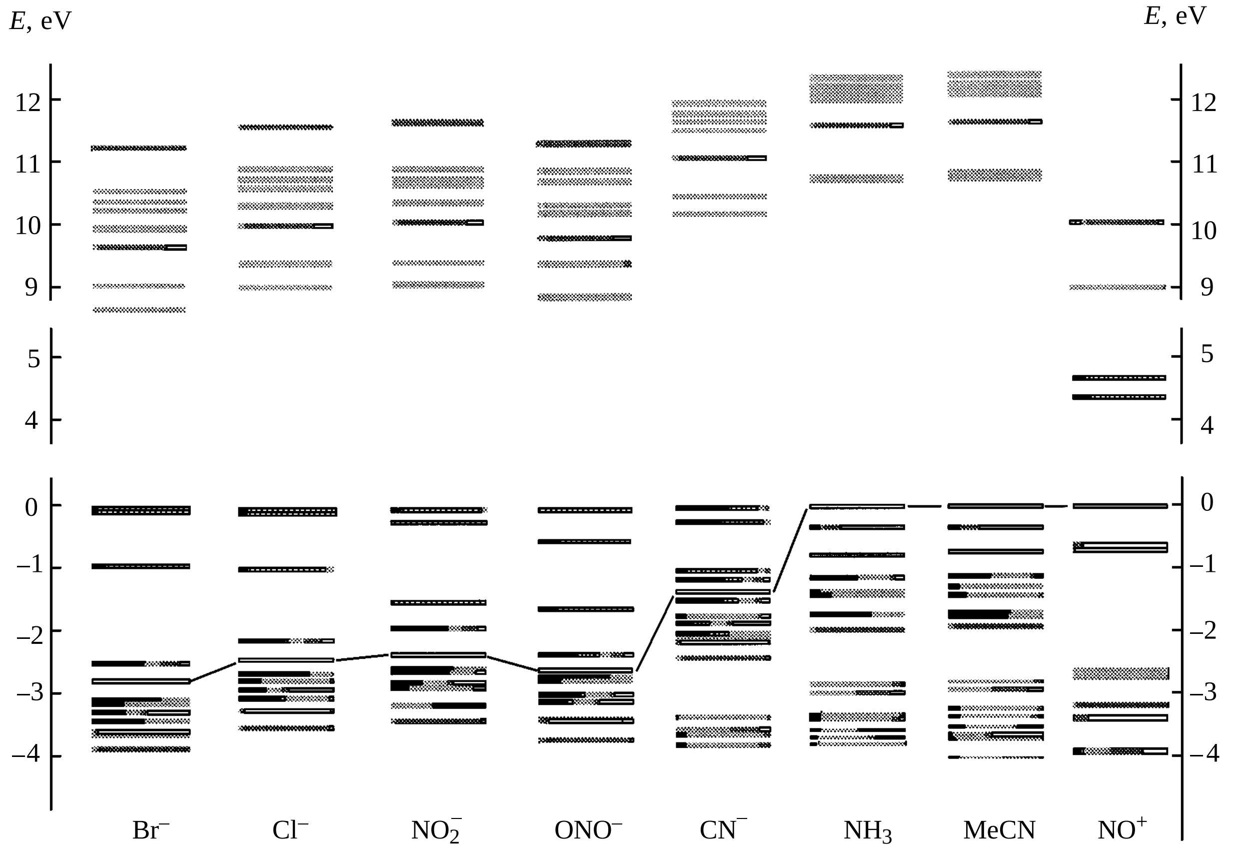

Fig. 2. Diagrams of frontier MOs for complexes $[Ru(bpy)_2(bipy)(X)]^q$ and contributions to the MOs of separate fragments of the complexes: (black lines) Ru, (transversal shading) X, (light gray lines) bpy, (dark gray lines) py^2, and (unpainted lines) py^1. The MO energies are counted from HOMO for each complex.

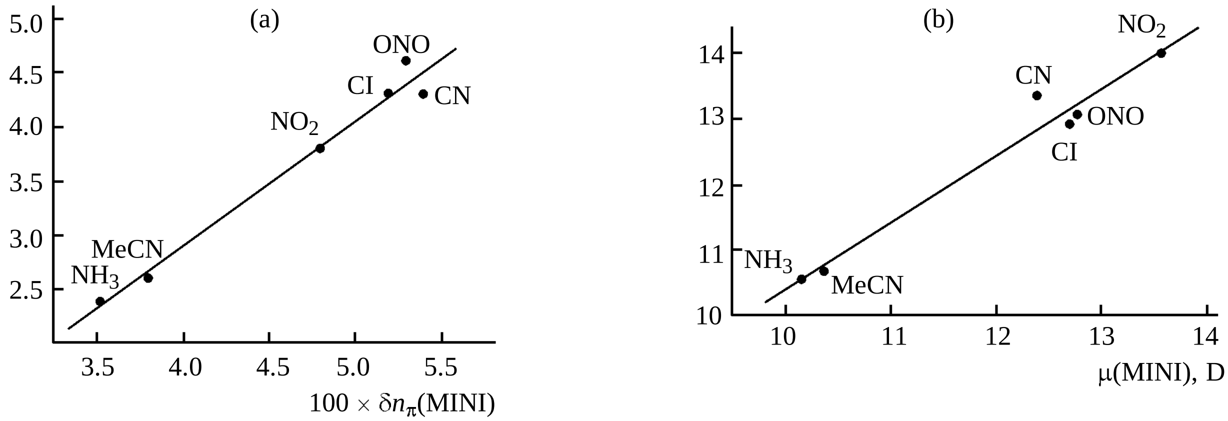

Fig. 3. Correlation of the MINI and 3–21G calculation results for complexes $[Ru(bpy)_2(bipy)X]^q$: (a) π-charge transfer (δn_π, eV) and (b) dipole moment (μ, D).

to reduce all the MO diagrams to a unified energy scale (the HOMO energies are given in Table 2). Figure 3 correlates the 3–21G and MINI estimates for the Ru → bpy π-charge transfer (δn_π, Fig. 3a) and the dipole moments of the complexes (μ, Fig. 3b). As seen, the 3–21G and MINI π-charge transfers vary in parallel; an unexpectedly good correlation was also obtained for the dipole moments of $[Ru(bpy)_2(bipy)\cdot(X)]^q$. As would be expected, the greatest discrepancies between the 3–21G and MINI results relate to trends in variation of such characteristics as the charge and valence of the ruthenium atom, the multiplicity of the Ru–X bond, and the charge on ligand X along the group of equally charged compounds in the series of complexes. The charges on the 4,4'-bipyridyl molecules in the complexes with equal q values vary too slightly for any trends to be revealed, whereas the charges on the 2,2'-bipyridyl molecules in both bases vary in a similar way.

As follows from the RHF results, the nitrosyl complex represents an exception from the $[Ru(bpy)_2 \cdot (bipy)(X)]^q$ series. This complex is the only, where the π-orbital population of ligand X (n_π 4.82) points to a strong π-dative interaction $Ru \rightarrow NO^+$: Apart from the π-bonding MO (four electrons), the π^* MO of the free ligand is also populated on coordination. In all the complexes, except for $[Ru(bpy)_2(bipy) \cdot (NO)]^{3+}$, the total decrease in the population of the three t_{2g} d AOs of ruthenium is close to 0.15, due to weak π-acceptor interactions with bipyridyl molecules. For example, upon the coordination with 2,2'-bipyridyl the charge transfer on orbitals perpendicular to the molecular plane (δn_π) in all the complexes under discussion is no higher than 0.06, whereas at X = NO^+ it is completely wiped out. The cyano ligand does not exhibit noticeable π-acceptor properties: The excess electron density on its π orbitals in $[Ru(bpy)_2 \cdot (bipy)(CN)]^+$ is as low as 0.03. In this case, as well as at X = NO_2^-, ONO^-, and MeCN, the π-orbital population of an atom closest to ruthenium increases, and that of a remote atom or atoms decreases. The coordination with acetonitrile increases the π-electron density on the N≡C group (q ~0.06) to a somewhat greater extent than on the CN^- anion, on account of the absence of negative charge in MeCN.

In the complexes with anionic ligands (X = Cl^-, Br^-, CN^-, NO_2^-, and ONO^-) the charge transfer from the *transC*-partner of X (pyridyl bound through N^2) is suppressed. The bpy ligand coordinated through N^3 and N^4 (bpy^2) has the highest positive charge, and the bpy ligand coordinated through N^1 and N^2 (bpy^1) is next. The positive charge on 4,4'-bipyridyl is insignificant. The lowest positive charge on bpy^1 with both the basis sets was obtained at X = CN^-. At X = NH_3 or MeCN, the bpy^1 and bpy^2 ligands have almost equal charges. The effect of ligand X on the charges of *cis*-oriented fragments is not so evident.

The Wyberg indices which are used as a measure of bond multiplicity are fully consistent with the commonly accepted notion of bonds in such compounds. The most strongly bonded ligands X are those capable of π-dative bonding with the metal (NO^+ and CN^-) or are strong donors (Cl^-, Br^-, and ONO^-) (Table 2). The multiplicities of the bonds between ruthenium and the N^1–N^5 atoms, both *trans* and *cis* to ligand X (Fig. 1), vary only slightly in the series of equally charged complexes; the W(Ru–N) values are the highest for X = NO^+ and the lowest, for anionic ligands X. This fact suggests that bipyridyl (bpy and bipy) first exhibits donor properties on bonding with ruthenium(II): The weaker the competing charge transfer from ligand X, the higher the Ru–N bond multiplicity.

The 3–21G calculations result in slightly greater contributions of ruthenium d_π AOs into the HOMOs compared with the MINI calculations, which is primarily attributable to fact that the 3–21G basis set, not MINI, is not quite suitable for ruthenium. The following regularities are reproduced with both the basis sets. A large group of HOMOs and a group of LUMOs in complexes $[Ru(bpy)_2(bipy)(X)]^{q+}$ are π-type orbitals, bonding or antibonding with respect to particular pairs of atoms. The mixed nature of the HOMOs suggests that the π-electron density is appreciably delocalized over the whole inner coordination sphere. The delocalization is the strongest in the complexes, where all ligands are involved in π bonding (donors or acceptors). Within this group of ligands, only one, namely, the remote pyridine ring of 4,4'-bipyridyl (py^2), capable of coordinating another metal ion through its nitrogen atom, exhibits a high degree of localization.

For isolated complexes the most noticeable distinctions in the order of occupied MOs (Fig. 2) are determined first by the charge q, i.e., by the formal charge of ligand X. The MO diagrams for the group of complexes with equal total charges q are rather similar; however, the above-mentioned features of the valence structure of the complexes with different ligands X are also traced when examining the molecular orbitals. If X is an uncharged ligand or NO^+, the HOMO of the complex is a π orbital consisting of π AOs of carbon atoms of the remote pyridine ring (py^2) of 4,4'-bipyridyl. This π orbital is nonbonding with respect to the remaining part of the complex. The HOMOs of the complexes with X = Cl^-, Br^-, and NO_2^- consistes of orbitals of ligand X with a small admixture of ruthenium d AOs. The HOMO of the complex $[Ru(bpy)_2(bipy)(ONO)]^+$ is the π^* orbital of ONO^-, and lower in energy are antibonding orbitals with respect to the Ru–O bond (HOMO-1 and HOMO-2), mostly contributed by the nonbonding π MO of ONO^-. The HOMO of the complex $[Ru(bpy)_2 \cdot (bipy)(CN)]^+$ which is distinguished by the greatest degree of delocalization of Ru d AOs over occupied MOs is antibonding with respect to the Ru–CN^- bond and represent a combination of Ru d_π AOs and the π-bonding MO of the cyano group.

Among MOs with a considerable contribution of d_π(Ru), orbitals involving d_{yz} (oriented between bpy, bipy, and X) are higher in energy. In the complexes with the charge +2 (X = NH_3 and MeCN), orbitals mostly contributed by d_π AOs lie 1–2 eV lower than HOMO, whereas in the complexes with charge +1, by 2.5–3 eV. However, it is hardly necessary to exaggerate significance of this distinction, since it was obtained for isolated ions, and it will undoubtedly be smoothed out by electrostatic interactions with solvent.

The order of virtual orbitals is of interest for understanding spectral properties of $[Ru(bpy)_2 \cdot (bipy)(X)]^q$ complexes. For all the complexes (except for X = NO^+) LUMO do not contain noticeable Ru or X contributions and, as a rule, are localized on one of the fragments: bpy, py^1, and py^2. These vacant orbitals (LUMO and the following LUMO+1) are orbitals of the two 2,2'-bipyridyl molecules. For the complexes with X = Cl^-, Br^-, CN^-, NO_2^-, and ONO^- the MO localized on bpy^2 coordinated through N^3 and N^4 is lower in energy, and for X = NH_3 and MeCN the LUMO and LUMO+1 almost coincide in energy. The π^* MO (LUMO+2) of 4,4'-bipyridyl (py^1) lies higher than LUMO by approximately 1 eV, and the following (higher by ~0.3–0.5 eV) are again 2,2'-bipyridyl orbitals. A distinctive feature of the orbital structure of the nitrosyl complex is the presence of two low-lying unoccupied MOs consisting predominantly of π^* MOs of the nitrosyl group with a noticeable (up to 30 %) contribution of Ru d_π AOs, which lie between the HOMO (π MO of py^2) and vacant π^* MOs of bpy (Fig. 2). Antibonding σ MOs mostly contributed by Ru d_σ AOs lie higher than LUMO by 5–6 eV, the gap increasing in the order $NH_3 \sim MeCN < Br^- < Cl^- < NO_2^- \sim ONO^- < CN^-$.

Thus, the calculations of complexes $[Ru(bpy)_2 \cdot (bipy)(Œ)]^q$ point to (1) relatively weak Ru → bpy, Ru → bipy, and Ru → X π-charge transfer (for X ≠ NO^+), (2) *trans*-effect of ligand X, which, however, can hardly noticeably labilize the bond between the bidentate ligand (bpy) and ruthenium atom; (3) absence of noticeable static *cis*-effect of ligand X; (4) delocalization of the electron density over higher occupied MOs under the action of strong π donors; (5) localized nature of lower unoccupied MOs; and (6) special position of the nitrosyl complex in this series.

It is necessary to point out that these conclusions concern the electronic structure of isolated complexes, which only predetermines a number of properties of the complexes in solution. However, we are not always able to predict the effect of macroscopic interactions on these features. This question deserves further investigation.

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation of Basic Research (project no. 99-03-32685) and the *Universitety Rossii* Program (project no. 992757).

REFERENCES

1. Ershov, A.Yu., Shashko, A.D., Sizova, O.V., Ivanova, N.V., Grigor'ev, Ya.M., and Nikol'skii, A.B., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 11, pp. 1761–1765.
2. Adeyemi, S.A., Johnson, E.C., Miller, F.I., and Meyer, T.J., *Inorg. Chem.*, 1973, vol. 12, no. 10, pp. 2371–2374.
3. Ershov, A.Yu., Veletskii, N.I., Dement'ev, I.A., Sokolova, N.I., and Nikol'skii, A.B., *Zh. Obshch. Khim.*, 1994, vol. 64, no. 8, pp. 1233–1242.
4. Ershov, A.Yu., Sizova, O.V., Shashko, A.D., Ivanova, N.V., and Nikol'skii, A.B., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 6, pp. 908–913.
5. Daul, C., Baerends, E.J., and Vernooijs, P., *Inorg. Chem.*, 1994, vol. 33, no. 16, pp. 3538–3543.
6. Maruyama, M., Matsuzava, H., and Kaizu, Y., *Inorg. Chem.*, 1955, vol. 34, no. 12, pp. 3232–3240.
7. Metcalfe, R.A. and Lever, A.B.P., *Inorg. Chem.*, 1997, vol. 36, no. 21, pp. 4762–4771.
8. Gorelsky, S.I., Dodsworth, E.S., Lever, A.B.P., and Vlcek, A.A., *Coord. Chem. Rev.*, 1998, vol. 174, no. 3, pp. 469–494.
9. Broo, A. and Lincoln, P., *Inorg. Chem.*, 1997, vol. 36, no. 12, pp. 2544–2553.
10. Broo, A. and Larsson, S., *J. Chem. Phys.*, 1992, vol. 161, no. 3, pp. 363–378.
11. Baranovski, V.I. and Sizova, O.V., *Chem. Phys. Lett.*, 1999, vol. 315, no. 1/2, pp. 130–134.
12. Reimers, J.R. and Hush, N.S., *J. Phys. Chem. A*, 1999, vol. 103, no. 16, pp. 3066–3072.
13. Schmidt, M.W., Baldridge, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.H., Koseki, S., Matsunaga, N., Nguyen, K.A., Su, S.J., Windus, T.L., Dupuis, M., and Montgomery, J.A., *J. Comput. Chem.*, 1993, vol. 14, no. 5, pp. 1347–1363.
14. Sakai, Y., Tatewaki, H., and Huzinaga, S., *J. Comput. Chem.*, 1982, vol. 3, no. 2, pp. 6–13.
15. Stevens, W.J., Basch, H., Krauss, M., and Jasien, P., *Can. J. Chem.*, 1992, vol. 70, no. 2, pp. 612–630.