ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 5, pp. 919–924. © Pleiades Publishing, Ltd., 2008.
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A DFT Study of Transition Metal Complexes with 1,10-Phenanthroline, C–C-Dimeric 2,2'-Bi-1,10-phenanthroline, and Its Tetraaza Chromophore Anion

N. S. Panina, V. N. Demidov, and S. A. Simanova

St. Petersburg State Institute of Technology (Technical University),
Moskovskii pr. 26, St. Petersburg, 190013 Russia
e-mail: natali@AP2707.spb.edu

Received October 29, 2007

Abstract—Quantum-chemical calculations of the 1,10-phenanthroline complexes $[M(en)(1,10\text{-phen})]^{2+}$ (M = Pt, Pd, Ni; en = $NH_2C_2H_4NH_2$) were performed by the DFT B3LYP method in the 6-31G** basis set using the GAMESS-2006 program package. The calculations were also performed for the nickel complexes with 2,2'-bi-1,10-phenanthroline, $[Ni(2,2'\text{-bi-}1,10\text{-phen})]^{2+}$, and with its electron-excessive analog, $[Ni(2,2'\text{-bi-}1,10\text{-phen})]^{0}$, and also for the octahedral complex cation $[Ni(2,2'\text{-bi-}1,10\text{-phen})Cl(H_2O)]^{+}$ characterized by single crystal X-ray diffraction. For the Ni(II) complexes, the stabilities of their high- and low-spin isomers were evaluated, and the structural features were revealed. The barriers to mutual transformations of the low- and high-spin Ni(II) complexes are low.

DOI: 10.1134/S1070363208050149

Interest in coordination compounds with C–C dimers of 1,10-phenanthroline and of its derivatives, i.e., in bi-1,10-phenanthrolines in which the 1,10-phenanthroline fragments are linked not through a bridging group but directly by an interfragment C–C bond, arose relatively recently. Among a few complexes characterized in the literature, we should note the octahedral complex of Ni(II) with 2,2'-bi-1,10-phenanthroline, $[Ni(2,2'\text{-bi-}1,10\text{-phen})Cl(H_2O)]Cl$, examined by single crystal X-ray diffraction [1], in which the heterocyclic ligand in the *cis* conformation is coordinated in the planar fashion, luminescent redox-active binuclear complexes of Ir(III), Ru(II), and Os(II) with 5,5'-bi-1,10-phenanthroline as a bridging ligand [2], and the complex of Ru(II) with 2,2'-bi-1,10-phenanthroline coordinated to the metal ion via only one of the two 1,10-phenanthroline fragments [3]. Bi-1,10-phenanthrolines in the electron-excessive form enter as ligands into the composition of tetraaza chromophore complexes of *d* elements of the novel 1,10-phenanthrocyanine class [4–12]. Some of these complexes exhibit redox sensitivity and high affinity for polymeric biological substrates and are of interest as potential biocides. Therefore, comprehensive chemical and physicochemical study of such systems becomes extremely urgent.

Here we report on a quantum-chemical study of the coordination compounds of *d*-element ions with 1,10-phenanthroline, 2,2'-bi-1,10-phenanthroline (L), and its electron-excessive reduced derivative (L^{2-}). The objects of the study were low-spin complexes of Pt(II) and Pd(II) and high- and low-spin complexes of Ni(II) with the bidentate ligands ethylenediamine (en) and 1,10-phenanthroline (1,10-phen), with 2,2'-bi-1,10-phenanthroline (2,2'-bi-1,10-phen) and its electron-excessive analog $(2,2'\text{-bi-}1,10\text{-phen})^{2-}$, and also the octahedral complex cation of Ni(II) with 2,2'-bi-1,10-phenanthroline $[Ni(2,2'\text{-bi-}1,10\text{-phen})Cl(H_2O)]^{+}$, characterized previously by X-ray diffraction [1].

The electronic structures of the compounds were calculated by the DFT B3LYP method in the 6-31G** basis set for nontransition element atoms and with the HW pseudopotentials for the *d*-element atoms [13], using the GAMESS-2006 program complex [14].

The bond lengths in the complex cation $[Pt(en)(1,10\text{-phen})]^{2+}$, obtained by geometry optimization, are well consistent with the experimental values for $[Pt(en)(1,10\text{-phen})]Cl_2\cdot 2H_2O$ [15] (see table). The metal–ligand bond lengths in the diamagnetic square-planar cationic complexes $[M(en)(1,10\text{-phen})]^{2+}$ (M = Ni, Pd, Pt) are given in Figs. 1 and 2a. Analysis of the electron

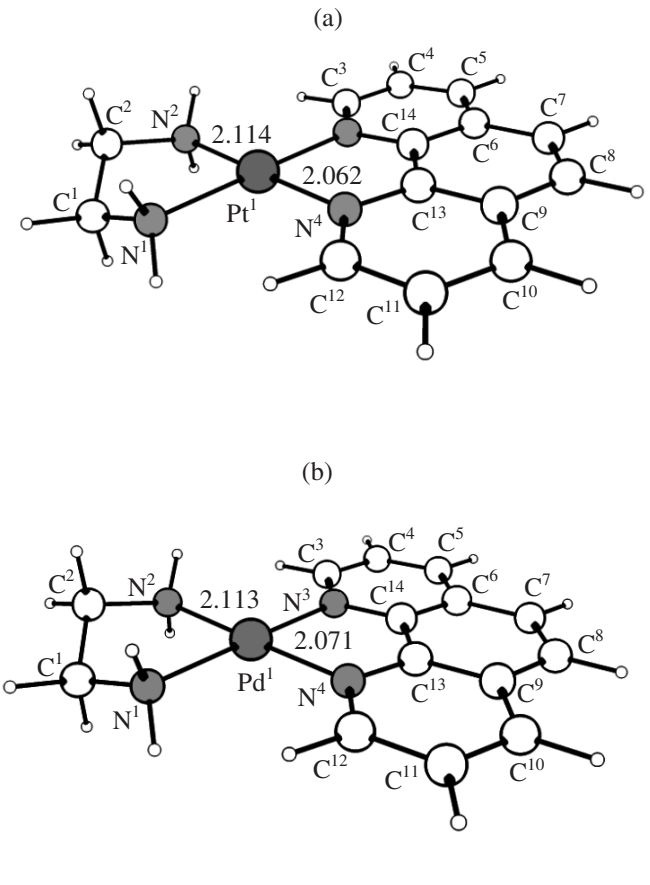

Fig. 1. Geometries of the complexes $[M(en)(1,10\text{-phen})]^{2+}$: (a) M = Pt^{2+} and (b) M = Pd^{2+} (bond lengths in Å; the same for Figs. 2–6).

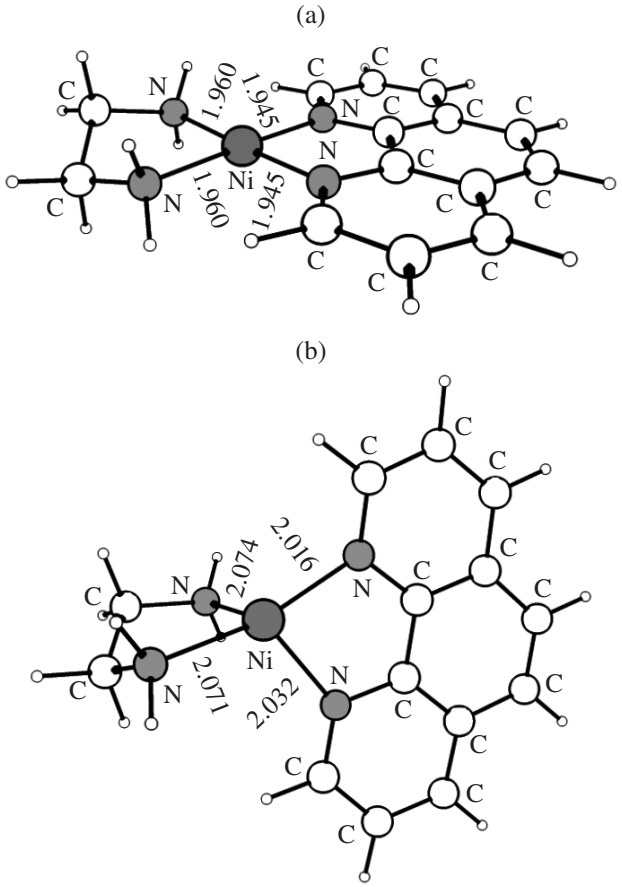

Fig. 2. Geometry of the complex $[Ni(en)(1,10\text{-phen})]^{2+}$: (a) low-spin and (b) high-spin.

density redistribution in this series of complexes shows that the largest total transfer of the electron density from the nitrogen-containing ligands to metal (N → M) is observed in the nickel complex, and the smallest, in the platinum complex: 1.42 *e* (Ni) > 1.38 *e* (Pd) > 1.04 *e* (Pt). The data obtained are consistent with the Pearson's concept of hard and soft acids and bases [16], according to which a hard N-donor π-electron-deficient

Calculated and experimental bond lengths (Å) in the complex $[Pt(en)(1,10\text{-phen})]^{2+}$

Bond	Calculation	Experiment [15]	Bond	Calculation	Experiment [15]
$Pt–N^1$	2.114	2.043	$C^3–C^4$	1.400	1.399
$Pt–N^2$	2.114	2.037	$C^4–C_5$	1.380	1.376
$Pt–N^3$	2.062	2.017	$C^5–C^6$	1.411	1.415
$Pt–N^4$	2.062	2.031	$C^6–C^7$	1.435	1.429
$N^1–C^1$	1.507	1.492	$C^6–C^{14}$	1.409	1.405
$N^2–C^2$	1.501	1.492	$C^8–C^9$	1.435	1.430
$C^1–C^2$	1.515	1.505	$C^9–C^{10}$	1.411	1.415
$N^3–C^3$	1.335	1.335	$C^9–C^{13}$	1.409	1.396
$N^3–C^{14}$	1.367	1.360	$C^{10}–C^{11}$	1.380	1.364
$N^4–C^{12}$	1.335	1.334	$C^{11}–C^{12}$	1.400	1.404
$N^4–C^{13}$	1.367	1.370	$C^{13}–C^{14}$	1.421	1.427

base prefers to form bonds with the nickel ion, which in the examined series is the least soft (i.e., harder) Lewis acid.

Nickel(II) forms numerous complexes having a square-planar (D_{4h}), tetrahedral (T_d), or octahedral (O_h) structure. These types of structures often occur in a complex equilibrium depending on the temperature and sometimes also on concentration [17]. Low-spin (singlet) four-coordinate complexes of this metal ion have, as a rule, a square-planar configuration, whereas high-spin (triplet) complexes are tetrahedral. The type of the spin state depends on the relationship between the difference in the energies of the two highest occupied *d* orbitals and the energy of the electron pairing. The difference of the energies of these orbitals is determined by the nature of the four ligands and by the contribution of the surrounding molecules to the ligand field. The decisive role can be played by the solvent molecules in solutions and by adjacent molecules in the crystal lattice.

The results of our DFT calculations showed that, for the complexes $[Ni(en)(1,10\text{-phen})]^{2+}$ in the gas phase, the low-spin square-planar configuration (D_{4h}) is only slightly more stable than the high-spin tetrahedral configuration (T_d): $\Delta E(D_{4h} - T_d) = -10.2$ kJ mol^{-1}. This difference can be readily compensated by the effect of temperature or medium. In this case, one can speak of a low barrier to transformation of a low-spin square complex into a high-spin tetrahedral complex. In the four-coordinate low-spin complex of approximate D_{4h} symmetry $[Ni(en)(1,10\text{-phen})]^{2+}$ (Fig. 2a), the Ni–N bond lengths are equal in pairs: 1.960 (en) and 1.945 Å (1,10-phen). The tetrahedral high-spin complex has a somewhat more distorted structure (Fig. 2b): The Ni–N bond lengths are 2.071 (en) and 2.074 (en), 2.016 (1,10-phen) and 2.032 Å (1,10-phen).

According to [17], on introduction of two additional ligands L' that are good donors and do not create strong fields, the difference of the energies of the two highest occupied d orbitals becomes small, and a paramagnetic complex $NiL_4L'_2$ is formed.

As additional ligands to the four-coordinate complex $[Ni(en)(1,10\text{-phen})]^{2+}$ we chose chloride anions. They are good σ donors and weak-field ligands. Furthermore, the two Cl^- ions do not affect the increase in the number of basis functions so strongly as do branched organic ligands, which is important for performing quantum-chemical calculations of extended systems.

According to the DFT calculations of octahedral high- and low-spin nickel chloride complexes [Ni(en)·(1,10-phen)Cl_2] without taking into account the effect of the medium, the high-spin triplet state in this case is considerably more stable (by 132.9 kJ mol^{-1}) than the singlet state. However, this difference in the stability of the spin isomers can also be controlled by introducing, instead of chloride anions, ligands with other characteristics of ligand field strength and other donor–acceptor properties. Donor solvent molecules creating medium-strength fields such as, e.g., ethylenediamine, ammonia, or pyridine can also decrease the barrier of mutual transformations of the octahedral high-spin triplet and low-spin singlet complexes.

The calculation results obtained for the complexes [Ni(en)(1,10-phen)Cl_2] show that, upon introduction of two additional good donor ligands such as chloride anions, the structure of the nickel–nitrogen bonds in the high- and low-spin polyhedra changes essentially. In the slightly distorted six-coordinate octahedral high-spin complex obtained, the Ni–N bond lengths are as follows: 2.135 (en) and 2.136 (en), 2.137 (1,10-phen) and 2.138 Å (1,10-phen) (Fig. 3a). In its less stable low-spin analog, one pair of *trans* Ni–N bonds becomes shorter, 1.930 (1,10-phen) and 1.941 Å (en), and the other pair, longer, 2.574 (1,10-phen) and 2.872 Å (en), so that the latter bonds become actually broken (Fig. 3b). This allows the structure of the low-spin complex obtained to be represented in the form of a new four-coordinate square-planar formation with *trans* Ni–N and Ni–Cl bonds.

The C–C-dimeric tetradentate ligand 2,2'-bi-1,10-phenanthroline can fully realize its coordination capacity with a single metal ion only in the *cis* configuration. Because of the rigid structure, without introducing additional ligands it can form only square-planar complexes, irrespective of their spin state. The DFT calculations of the complex cations $[Ni(2,2'\text{-bi-}1,10\text{-phen})]^{2+}$, as in the case of $[Ni(en)(1,10\text{-phen})]^{2+}$, gave a somewhat more stable optimized structure for the low-spin isomer (Fig. 4a): ΔE 34.4 kJ mol^{-1}. When introduced into the cavity formed by the four nitrogen atoms, the Ni^{2+} cation in the low-spin state withdraws the electron density from the ligand, 2,2'-bi-1,10-phenanthroline, more strongly (1.30 *e*) than does its high-spin analog (1.09 *e*). The Ni–N bond lengths in the more stable diamagnetic isomer (1.864 and 2.006 Å) appear to be shorter than those in the paramagnetic isomer (2.003 and 2.116 Å) (Fig. 4b).

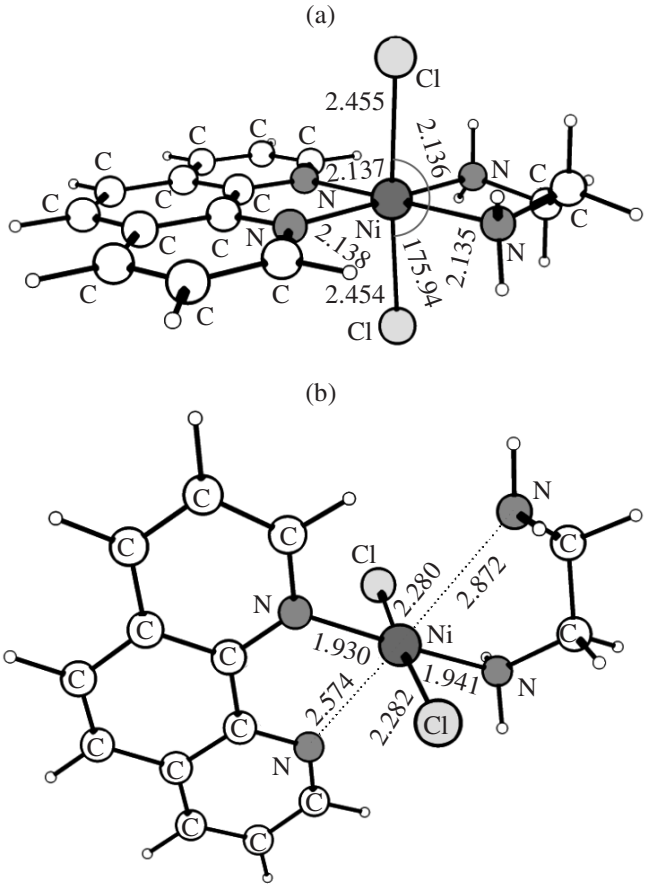

Fig. 3. Geometry of the complex [Ni(en)(1,10-phen)Cl_2]: (a) high-spin and (b) low-spin (angles in degrees; the same for Figs. 5 and 6).

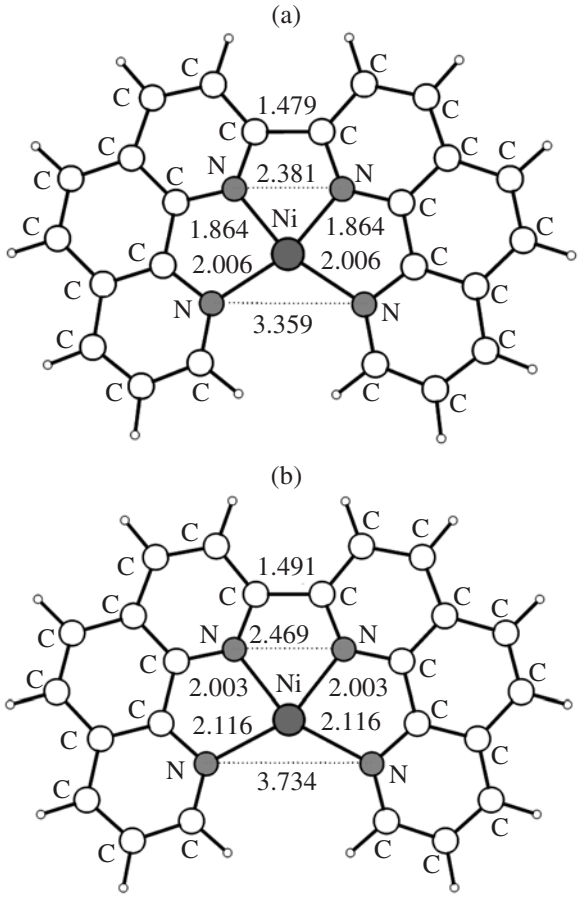

Fig. 4. Geometry of the complex $[Ni(2,2'\text{-bi-}1,10\text{-phen})]^{2+}$: (a) low-spin and (b) high-spin.

A DFT calculation of the six-coordinate cation [Ni(2,2'-bi-1,10-phen)Cl(H_2O)]$^+$ characterized by single crystal X-ray diffraction [1] gave a stable high-spin structure with the geometric parameters reasonably consistent with the corresponding experimental data: R_{calc} (Ni–N) = 2.270, 2.268, 2.063, 2.062; R_{exp} (Ni–N) = 2.200, 2.172, 2.026, 2.060 Å; $\angle NNiN_{calc}$ = 131.77°, 75.77°; $\angle NNi_{exp}$ = 128.01°, 77.41° (Fig. 5a). In the low-spin state, this compound in one case takes the tetragonal bipyramidal structure with the loss of the Ni–O bond (H_2O molecule). In the other case, a new square-planar complex species is formed, in which the nickel atom loses bonds with two nitrogen atoms of 2,2'-bi-1,10-phenanthroline (Fig. 5b). Both these structures have higher total energies than the octahedral high-spin structure.

In view of the above-mentioned possibility of using the $[2,2'\text{-bi-}1,10\text{-phen}]^{2-}$ ligand as a component of novel tetraaza chromophore complexes, their electronic structure is of particular interest. A DFT calculation of the $(2,2'\text{-bi-}1,10\text{-phen})^{2-}$ anion [18] revealed an increase in the length of the interfragment C–C bond and in the size of the cavity formed by the four nitrogen atoms and suitable for insertion of a transition metal ion. We also noted in [18] an increase in the negative charges q_{N10} and q_{N20} on the nitrogen atoms that are the closest to the interfragment C–C bonds, compared to the charges in the unreduced *cis* form, and a decrease in the energy of the electron removal from the highest occupied molecular orbital. These factors should favor an increase in the donor power of the reduced anionic form of 2,2'-bi-1,10-phenanthroline compared to the neutral ligand and insertion of complexing ions in its cavity.

The calculations of various spin states of the neutral [Ni(2,2'-bi-1,10-phen)] molecules showed that,

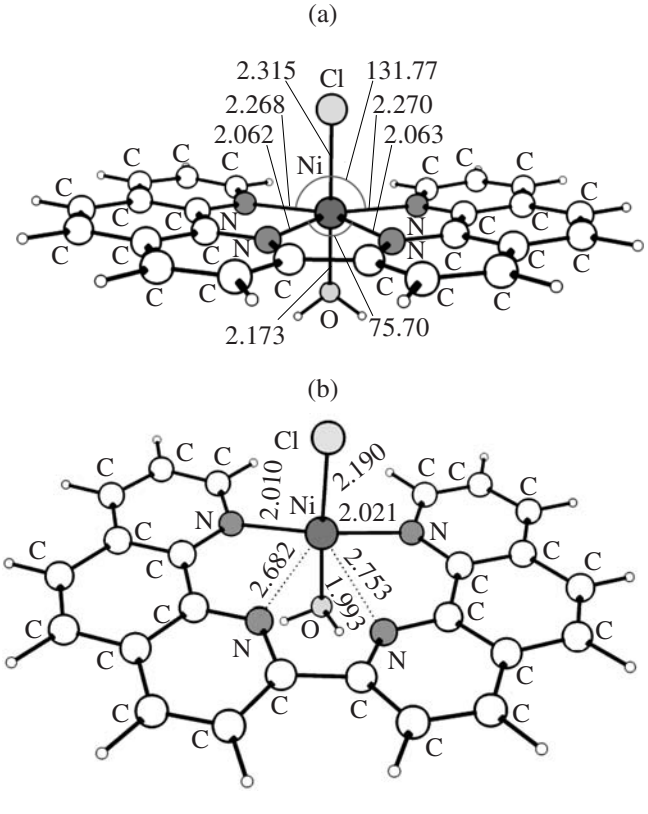

Fig. 5. Geometry of the complex [Ni(2,2'-bi-1,10-phen)·$Cl(H_2O)]^+$: (a) high-spin and (b) low-spin.

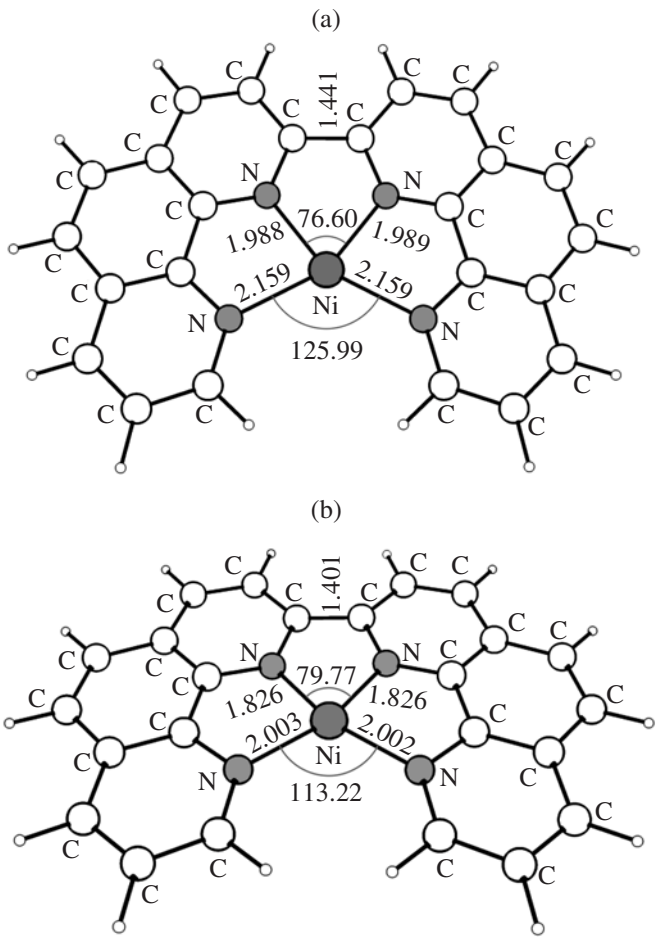

Fig. 6. Geometry of the molecular complex [Ni(2,2'-bi-1,10-phen)]: (a) high-spin and (b) low-spin.

in the anionic ligand, the structure of the high-spin state of the four-coordinate complex is slightly more stable than that of the low-spin state (ΔE 24.3 kJ mol^{-1}). In the high-spin state, the anionic ligand donates more electron density to the Ni^{2+} ion than does neutral 2,2'-bi-1,10-phen: 1.56 *e* in the high-spin and 1.43 *e* in the low-spin analogs. In the neutral high-spin complex [Ni(2,2'-bi-1,10-phen)], as in the previously described triplet cation $[Ni(en)(1,10\text{-phen})]^{2+}$, the presence of two unpaired electrons in the nickel ion leads to elongation of its bonds with the nitrogen atoms (1.986 and 2.159 Å) compared to the related bonds (1.826 and 2.003 Å) in the singlet low-spin complex (Figs. 6a, 6b).

Our study showed that, for preparing coordination compounds with preset properties that can vary depending on conditions, of the greatest interest are nickel(II) 1,10- and 2,2'-bi-1,10-phenanthroline complexes characterized by low barriers of the mutual transformations of the low-spin and high-spin complexes. Introduction of additional ligands with various field strengths and various donor properties can lead to stabilization of the required coordination polyhedron with the preset spin characteristics, and also can cause cleavage of the required Ni–N bonds. The tetradentate ligand 2,2'-bi-1,10-phen in the reduced electron-excessive form creates more favorable geometric and electronic conditions for insertion of complexing ions than does the neutral ligand.

ACKNOWLEDGMENTS

The study was supported by the Russian Foundation for Basic Research (project no. 04-03-32932) and by the Departmental Target Program "Development of the Scientific Potential of the Higher School" (project no. RNP.2.1.1.1277).

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