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Light-controlled spin-state-switching rearrangements of transition metal complexes with photochromic ligands

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Abstract: New families of the transition metal complexes with photochromic ligands manifesting photoswitchable magnetic properties determined by the light-induced spin-crossover and configurational isomerization rearrangements are theoretically designed by means of DFT calculations of electromeric forms of the complexes.

Keywords: configurational isomerization; magnetic properties; Mendeleev XX; photochromic ligands; spin-crossover; spin-state-switching; transition metal complexes.

Introduction

The magnetically bistable compounds [1] comprise the basis for engineering of high-capacity nonvolatile molecular memories, molecular magnets, pressure and optical sensors, flexible displays, switchable MRI agents and other useful technical applications [2–5]. Rational design of compounds with switchable magnetic properties must be based on their impregnation with a certain molecular mechanism responsible for the transformation of the spin state of a system. Therefore, it seems advisable in the beginning to specify the underlying mechanisms providing for changes of magnetic characteristics of metal coordination compounds.

Magnetically active transition metal complexes can be conventionally divided into two groups differing in type of transformation leading to changes of magnetic characteristics. The first one comprises compounds exhibiting spin-crossover (SCO) [6–8] and redox-isomerism (valence tautomerism, VT) rearrangements [9–12], which are not accompanied by alteration in coordination polyhedrons. Whereas SCO involves the rearrangement of electrons within a metal ion shell between low-spin and high-spin states, the mechanism of redox-isomerism of metal coordination compounds is based on the intramolecular electron transfer that occurs between a metal ion and a redox-active (so-called non-innocent) ligand [13]. Photochemical controlling of these processes can be realized by means of light-induced excited state spin trapping (LIESST) [14] initiated via metal-to-ligand electron transitions and ligand driven light-induced spin change (LD LISC) [15] originated

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from modulation of the ligand field strength of an appropriate SCO complex. While the first effect occurs predominately at low (helium) temperatures, the second one can be observed under ambient conditions. SCO rearrangement inverting spin state of a metal center under transfer from low-spin (LS) to high-spin (HS) electronic configuration results in significant elongation of bonds between the central metal atom and donor centers of the ligand, but does not practically affect the rest of the molecular geometry. Redox-isomerism implies changes of structural parameters of both metal–ligand and intraligand bonds. Common to SCO and VT rearrangements is that the structural variation of the interconverting electronic isomers (electromers [16]) is relatively low [17], which makes them realizable in crystals.

Complexes undergoing configurational isomerization of coordination site of the central metal atom compose another group of magnetically bistable compounds. Photoinduced controlling of magnetic characteristics via the mechanism of reversible changes of the coordination number of a metal center [ligand driven coordination-induced spin-state-switching (LD-CISSS) mechanism] was demonstrated by the example of nickel porphyrin complexes [18, 19]. In contrast with SCO and VT transformations, these rearrangements are associated with rather significant structural variation of the isomeric forms which complicates their occurrence in crystals. However, the goal of switching magnetic properties in crystalline state can be achieved through appropriate structural modifications of the complexes (insertion of bulky counter-ions or inclusion of solvate molecules).

Spin-crossover

The most general approach to the synthesis of the transition metal complexes capable of light-controlled spin-state switching is, undoubtedly, associated with implication of spin-crossover effects. In the framework of the LD LISC photoswitching scheme, the main problem consists in finding the photoactive ligands, whose light-induced isomerizations would significantly modify the ligand field to induce a sufficiently high, well detected change in spin state of a coordinated metal ion. It has been shown [20] that the effects exerted by *cis-trans* isomerizations of ligand moieties distantly located with respect to the metal center do not exceed more that 2 %. Much stronger can be those produced by electrocyclic isomerizations of photochromic ligands directly attached to the coordination site. This trend has been nicely evidenced by the recent results simultaneously and independently presented by two research groups in Germany [21] and Japan [22]. Khusniyarov et al. have shown that UV – irradiation of acetonitrile solution of an open high-spin (HS) form of the bis(pyrazolyl)borate iron complex containing the photochromic diarylethene ligand functionalized by a phenanthroline (phen) moiety for 42 h at room temperature results in the reversible conversion (about 40 %) to low-spin (LS) closed form and is accompanied by the change in the value of μ_{eff} from 5.37 to 3.16 μ_B (Fig. 1). In a parallel work of the Japanese group of researchers the same compound was studied in the microcrystalline state. Along with the LD LISC behavior, they were also able to detect the LIESST properties of the compound, that is to trap its metastable HS state upon light irradiation at 637 nm, which corresponds to the excitation energy of the metal-to-ligand charge transfer (MLCT) band in the UV/Vis absorption spectrum of the LS form.

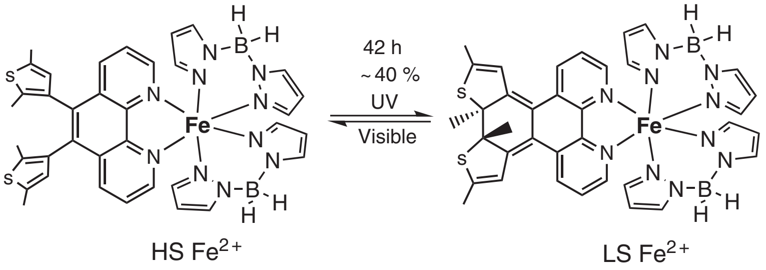


Fig. 1: Light-induced spin-state switching of iron(II) complex **1** with a photochromic diarylethene moiety.

These findings encouraged us to consider a possibility to implement another class of photochromic compounds – spiropyrans, spirooxazines and chromenes [23]. A distinguishable feature of the diarylethene photochromic ligands is their very high fatigue resistance and thermal stability of the photo-isomeric forms, but a drawback of this photochromic system is the long irradiation time needed to reach the photostationary state. In this connection, the LD LISC complexes with spirocyclic photochromic ligands may have certain preferences.

By means of density functional theory (DFT) quantum-chemical calculations we checked [24] the possibility of reversible photo-controlled switching of spin states of Fe(II) complexes with another phenanthroline-containing spirooxazine ligand **2** (Fig. 2), the photochromic properties of which and its ruthenium complex had been previously revealed [25, 26] and tris(chelate) complexes of the first row transition metals preparatively obtained [27]. The significant structural changes caused by photochromic rearrangement occurring in the immediate proximity to the coordination site allow one to expect considerable alteration of the ligand field strength and, as a consequence, magnetic properties of complexes **3** and **4** (Fig. 3) on the basis of ligand **2**.

The calculations performed with various functionals (B3LYP*, TPSSh and OLYP) well reproduce geometry characteristics of the phen iron complex [28] with the reaction site similar to the compounds under study, while energy difference between the low-spin and the high-spin forms is best reproduced by the B3LYP* functional [29], the efficiency of which for estimation of relative stability of electromers of photochromic metal complexes with spiropyran ligands has been earlier demonstrated [30]. The structure ${}_{LS}$**3a**, a minimum on the singlet potential energy surface (PES), corresponds to the ground state of complex **3** with the ring-closed spirooxazine fragment (Fig. 4). The high-spin isomer ${}_{HS}$**3a**, in which ferrous iron ion comprises four unpaired electrons, is by 4.0 kcal/mol destabilized as compared to the structure ${}_{LS}$**3a**. This value is in complete agreement with the energy gap $\Delta E_{HS\text{-}LS}$ predicted for the parent phenanthroline complex [28] and points to the possibility of spin-crossover phenomenon in compound **3**.

Ring-opening of the spirocycle is accompanied by significant elongation (exceeding 0.1 Å) of the C–C bond conjugated with the photochromic fragment and also the Fe–N bonds (by 0.03 Å). The low-spin structure ${}_{LS}$**3b** is 3.9 kcal/mol energy preferred compared to the high-spin one ${}_{HS}$**3b**, which is compatible with possible SCO behavior. According to the calculations, the energy of the low-spin form of the complex with the ring-closed spirooxazine ${}_{LS}$**3b** is equivalent to the energy of the high-spin isomer with open spirocyclic moiety ${}_{HS}$**3b**. This result enables the prediction of switching magnetic properties induced by exposure of the complex

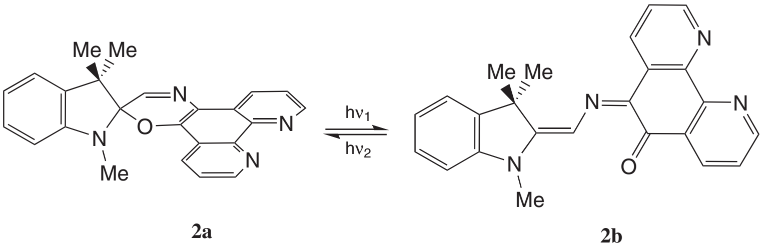


Fig. 2: Photoisomerization of the ligand **2**.

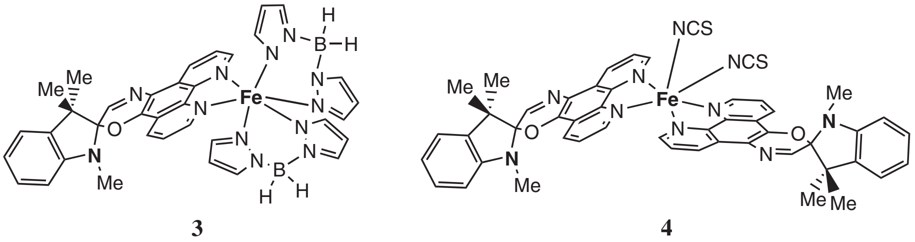
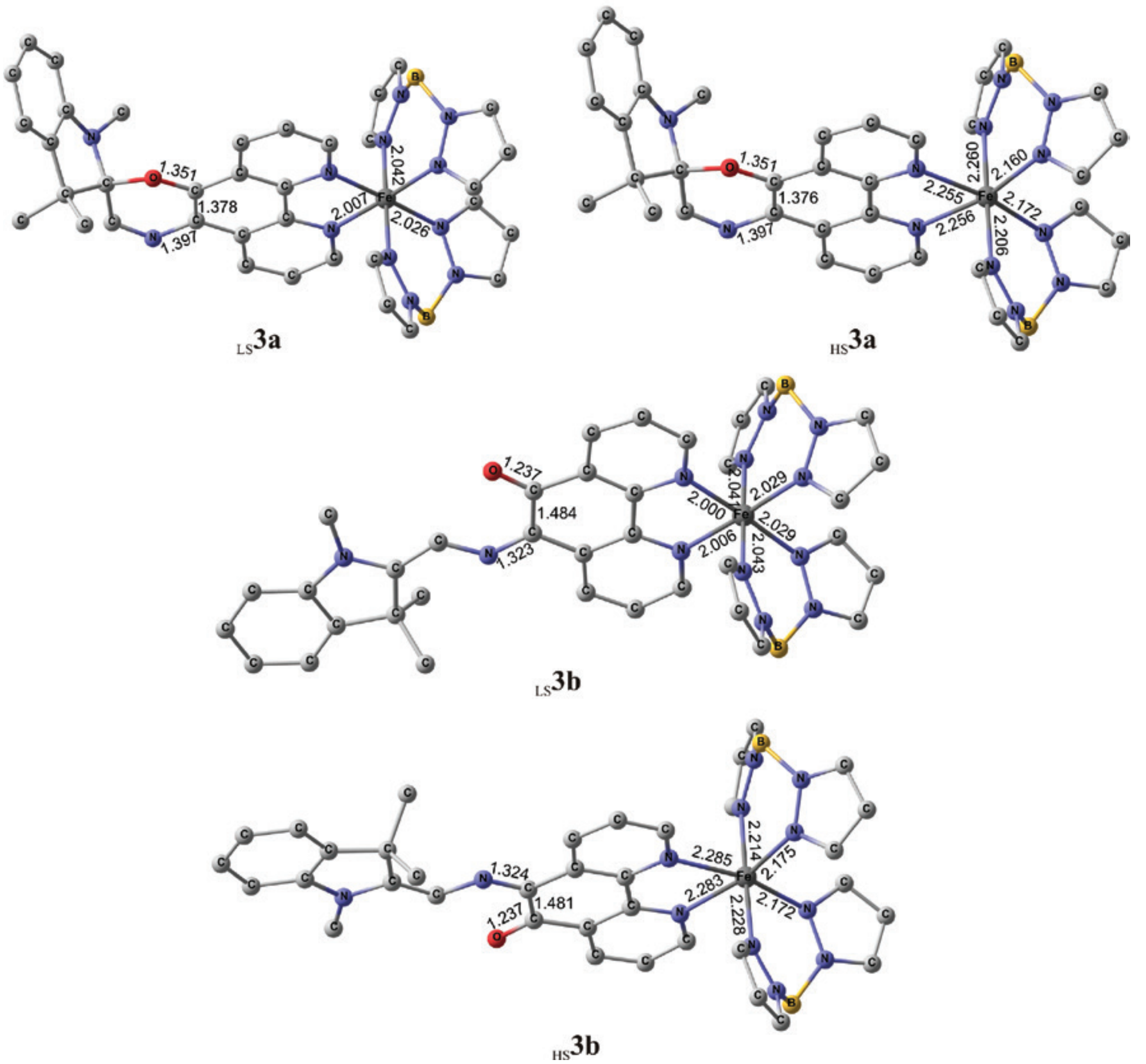


Fig. 3: Complexes with one (**3**) and two (**4**) phenanthroline-containing spirooxazine ligands.



$_{\text{LS}}$**3a** $_{\text{HS}}$**3a**

$_{\text{LS}}$**3b**

$_{\text{HS}}$**3b**

Fig. 4: Optimized geometries of the structures $_{\text{LS}}$**3a**, $_{\text{HS}}$**3a**, $_{\text{LS}}$**3b** and $_{\text{HS}}$**3b** calculated by the DFT B3LYP*/6-311++G(d,p) method [24]. Here and in Figs. 5, 8, 9, 12, 19, 21, 22, 25 hydrogen atoms are omitted for clarity. Hereinafter bond lengths are given in Å.

to the light of an appropriate wavelength, i.e. the occurrence of LD LISC effect. The calculations of complex **4** comprising two modified phenanthroline ligands witness the energy preference (by 1.4 kcal/mol) of the low-spin form $_{\text{LS}}$**4a** relative to the high-spin structure $_{\text{HS}}$**4a** (Fig. 5). This finding is in agreement with the calculated value ($\Delta E_{\text{LS-HS}} = 0.9$ kcal/mol) for the original complex containing two non-substituted phen ligands [31] and, consequently, is indicative of possible SCO rearrangements. The isomer with the ring-opened spirocycle is characterized by elongation (by 0.12 Å) of the C–C bond annulated to the phenanthroline moiety. The energy difference between the high-spin $_{\text{HS}}$**4b** and the low-spin $_{\text{LS}}$**4b** structures with the ring-opened spirooxazine form is equal to 1.7 kcal/mol, which allows to predict the occurrence of spin crossover in complex **4**.

Based on the DFT [B3LYP*/6-311++G(d,p)] calculations it may, thus, be concluded that the compounds **3** and **4** comprising one or two phenanthroline ligands with an annulated photochromic spirooxazine moiety are capable of manifestation of SCO, which is observed in the parent non-functionalized phenanthroline complexes [28, 31]. Low energy gaps between the low-spin isomer with the ring-closed form of the spirocycle and the high-spin structure with the ring-opened spirooxazine moiety allow the prediction of controlling magnetic properties of the considered Fe(II) complexes under irradiation by the LD LISC mechanism. Similar conclusion has been reached on the basis of calculations of complexes with phenanthroline-functionalized spiropyrans.

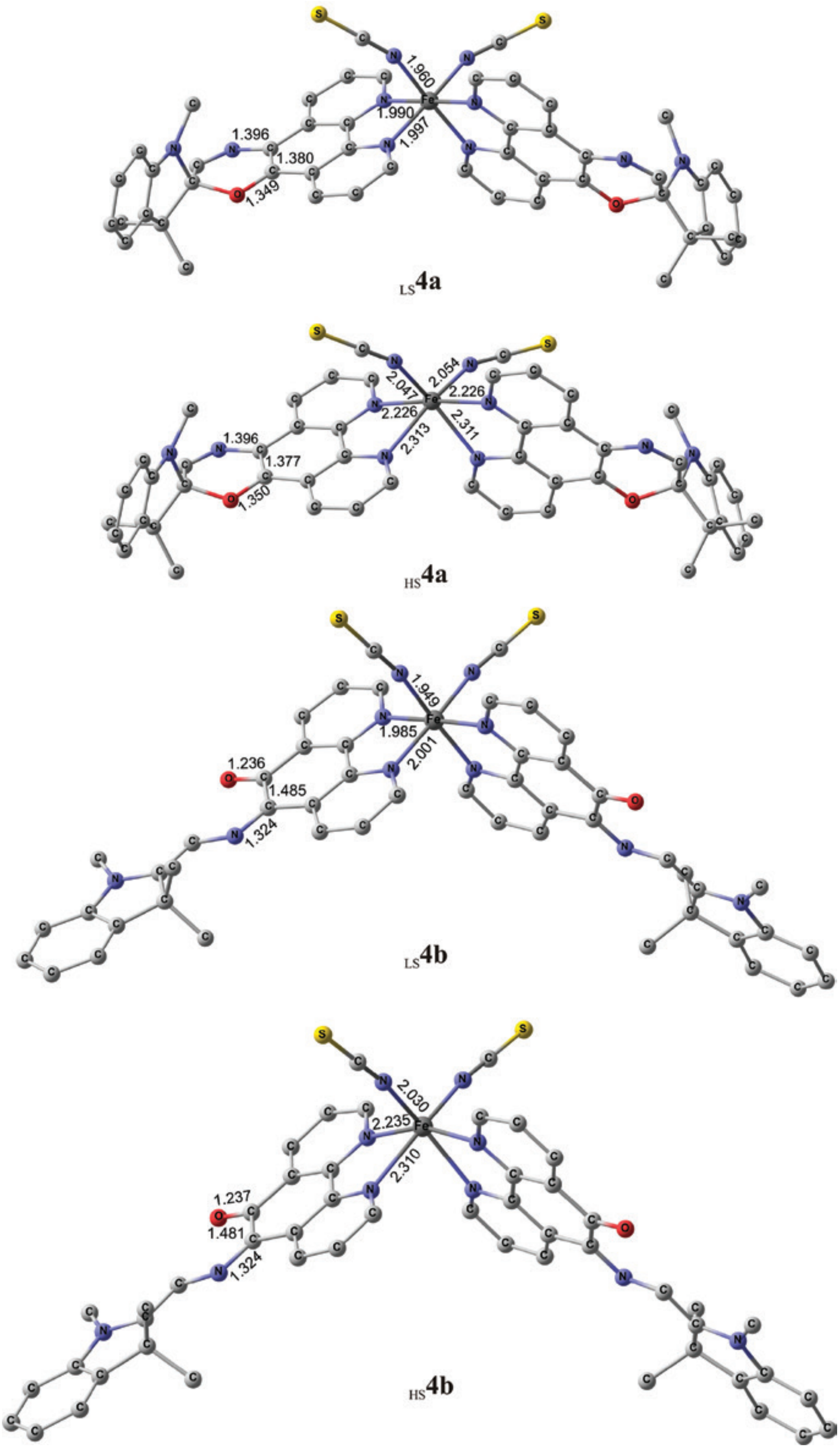


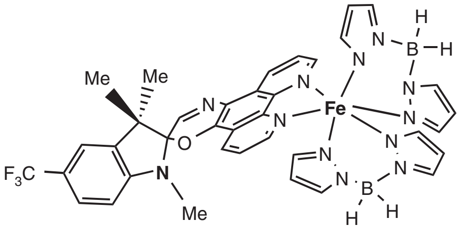
Fig. 5: Optimized geometries of the structures $_{LS}$**4a**, $_{HS}$**4a**, $_{LS}$**4b** and $_{HS}$**4b** calculated by the DFT B3LYP*/6-311++G(d,p) method [24].

We have previously shown that the HS electromeric forms of magnetically bistable systems can be substantially stabilized relative to the LS forms and the energy gap between them diminished through appropriate functionalization of the ligands with electron-withdrawing groups [32]. In order to estimate the effect of such type substituents in the indoline fragment of the spirocyclic moiety on the energy characteristics of the isomeric forms of complex **3**, calculations have been carried out on a compound **3** (**CF_3**) containing a trifluoromethyl group in the position 5 of indoline ring (Fig. 6). It has been found that the energy gap between the corresponding isomers with the ring-opened and ring-closed forms of spirooxazine fragment was lowered to 2.5 kcal/mol. It may, therefore, be expected that by introduction of proper substituents into the indoline ring it can be possible to substantially affect relative energies of the ring-closed and ring-opened electromeric forms and even invert, as desirable, the ground state energy levels of the ring-closed and ring-opened LS electromers.

As was shown by the calculations [33], the number of groups of photochromic ligands, isomerization of which is accompanied by spin-state switching of metal centers in coordination compounds, can be complemented with 2*H*-chromenes fused to a phenanthroline moiety (Fig. 7).

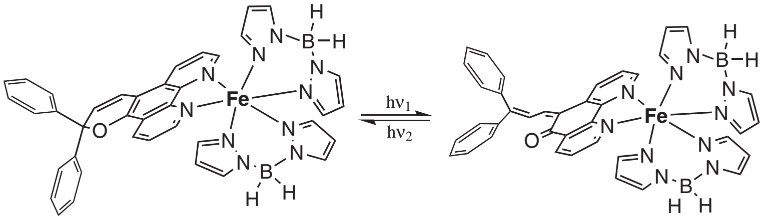
The ground state of the iron complex **5** is given by its low-spin electromer $_{LS}$**5a** with ring-closed phenanthrolinochromene fragment (Fig. 8). The high-spin structure $_{HS}$**5a** having elongated Fe–N bonds is 4.2 kcal/mol disfavored compared to the low-spin one $_{LS}$**5a**. This value is close to that calculated for an analogous complex with phenanthroline ligands [24] known to exhibit SCO behavior. For **5**, the expected spin-state-switching process can be initiated by photoirradiation of the complex at low temperature to produce at the initial stage the isomer with an excited singlet spin state of the metal center, which then relaxes *via* intermediate metastable triplet spin state to the final HS quintet form. This stepwise mechanism plays an important role in realization of the LIESST effect [34, 35].

Geometry optimization of the complex on the triplet PES leads to the structure $_{IS}$**5a** characterized by the presence of two unpaired electrons at metal ion (Fig. 8). Destabilization of this isomer compared to the ground state $_{LS}$**5a** is equal to 12.8 kcal/mol of energy, which is indicative of low probability of its thermal population. To elucidate the mechanism of intramolecular photo-initiated isomerization, the search for minimum energy crossing point (MECP) [36] between the isomers with different spin states was performed. The structure $_{MECP}$**5a**$_{LS\text{-}IS}$ (which is 13.0 kcal/mol destabilized relative to $_{LS}$5a) corresponds to the minimum energy point on the seam lying on the intersection of singlet and triplet PESs (Fig. 8). Gradient descent from the MECP along the corresponding PESs leads to the isomers $_{LS}$**5a** and $_{IS}$**5a**, which points to residing the structure $_{MECP}$**5a**$_{LS\text{-}IS}$ at the intrinsic reaction path of the thermal rearrangement. The energy barrier of the transition between the high-spin and the intermediate-spin states is determined by the energy of $_{MECP}$**5a**$_{IS\text{-}HS}$,



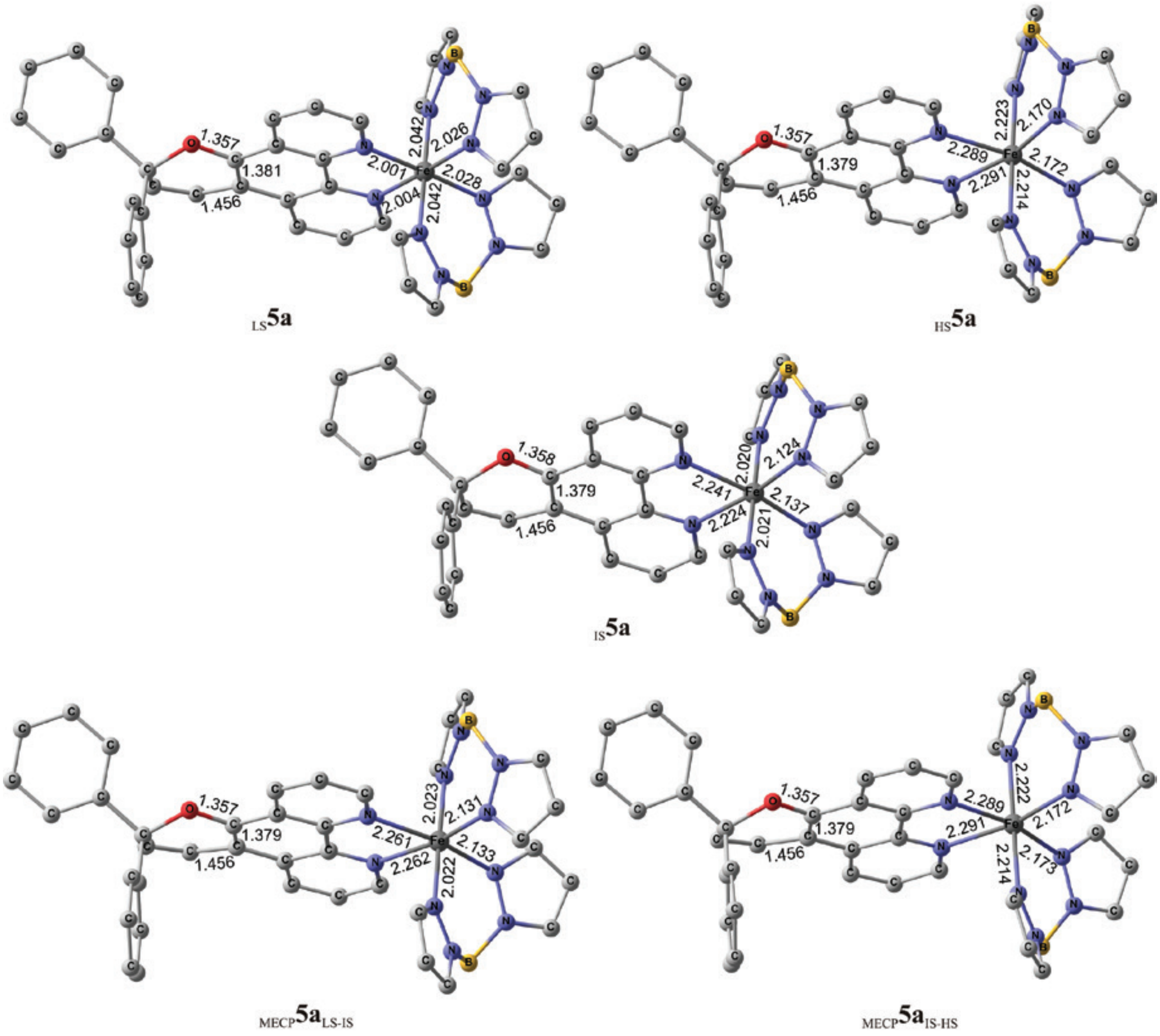
3 (CF_3)

Fig. 6: Complex **3** (**CF_3**) containing a trifluoromethyl group in the position 5 of indoline ring.



5a **5b**

Fig. 7: Photoisomerization of the complex **5**.



${}_{\mathrm{LS}}\mathbf{5a}$ ${}_{\mathrm{HS}}\mathbf{5a}$

${}_{\mathrm{IS}}\mathbf{5a}$

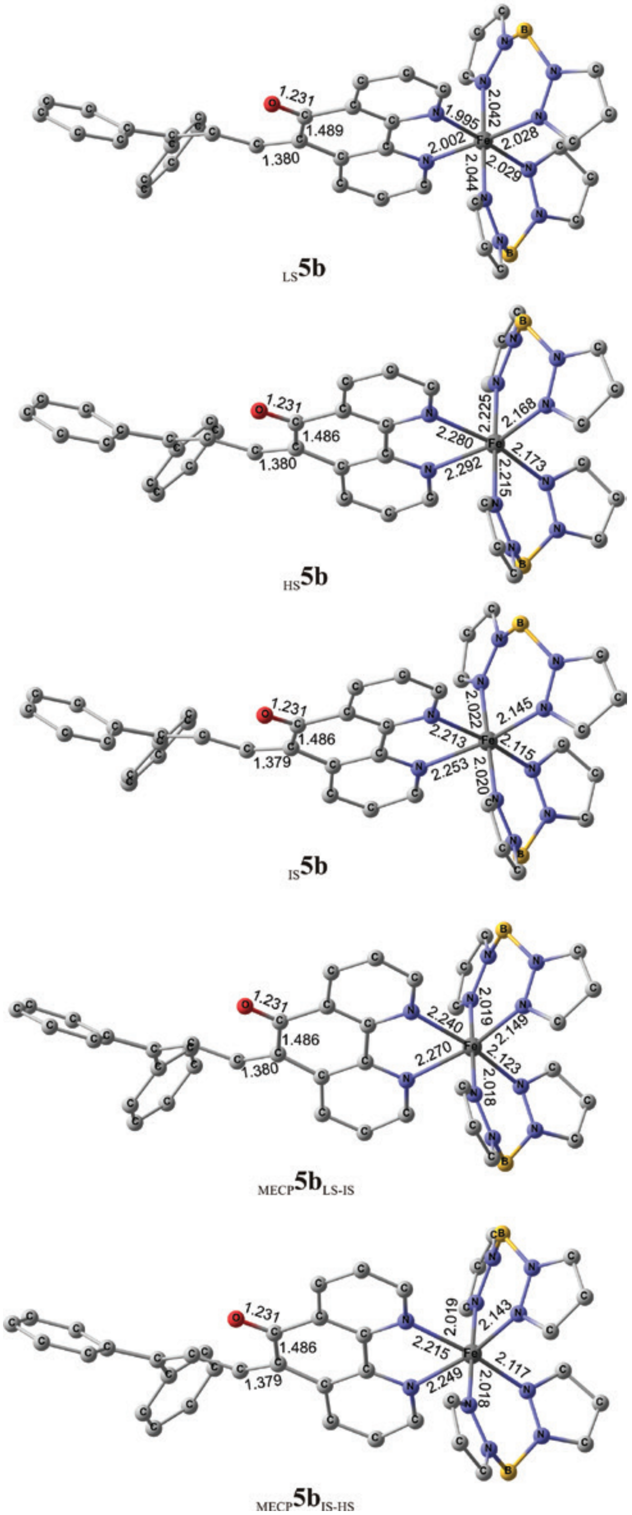
${}_{\mathrm{MECP}}\mathbf{5a}_{\mathrm{LS\text{-}IS}}$ ${}_{\mathrm{MECP}}\mathbf{5a}_{\mathrm{IS\text{-}HS}}$

Fig. 8: Optimized geometries of the structures ${}_{\mathrm{LS}}\mathbf{5a}$, ${}_{\mathrm{HS}}\mathbf{5a}$, ${}_{\mathrm{IS}}\mathbf{5a}$, ${}_{\mathrm{MECP}}\mathbf{5a}_{\mathrm{LS\text{-}IS}}$ and ${}_{\mathrm{MECP}}\mathbf{5a}_{\mathrm{IS\text{-}HS}}$ calculated by the DFT B3LYP*/6-311++G(d,p) method [33].

which is 13.1 kcal/mol destabilized relative to the ground state isomer ${}_{\mathrm{LS}}\mathbf{5a}$. Close values of total energies of structure with the intermediate-spin state ${}_{\mathrm{IS}}\mathbf{5a}$ and two MECPs (${}_{\mathrm{MECP}}\mathbf{5a}_{\mathrm{LS\text{-}IS}}$, ${}_{\mathrm{MECP}}\mathbf{5a}_{\mathrm{IS\text{-}HS}}$) and also smooth evolution of geometry parameters of the coordination site when passing from the ground state ${}_{\mathrm{LS}}\mathbf{5a}$ to the high-spin isomer ${}_{\mathrm{HS}}\mathbf{5a}$ enable one to expect manifestation of the LIESST effect in complex **5**.

Ring-opening of the spirocycle in compound **5** is accompanied by elongation of the C–C bond conjugated with photochromic moiety from 1.38 Å in the ring-closed form to 1.49 Å (Fig. 9). The ring-opened isomers are by 2 kcal/mol energy preferred than their ring-closed counterparts. The low-spin structure ${}_{\mathrm{LS}}\mathbf{5b}$, which is 4.2 kcal/mol energy favored over the high-spin ${}_{\mathrm{HS}}\mathbf{5b}$ structure, corresponds to the ground state of the complex. Destabilization of the intermediate-spin structure ${}_{\mathrm{IS}}\mathbf{5b}$ is equal to 12.8 kcal/mol; similar energy values are predicted for ${}_{\mathrm{MECP}}\mathbf{5b}_{\mathrm{LS\text{-}IS}}$ and ${}_{\mathrm{MECP}}\mathbf{5b}_{\mathrm{IS\text{-}HS}}$. These findings are in a good accordance with the possibility of controlling spin states of complex **5** by means of external stimuli.

Thus, the theoretical study of iron complexes with phenanthroline ligands comprising annulated photochromic fragments leads to the conclusion that such type compounds can undergo SCO rearrangements induced by UV-Vis light irradiation at low temperatures (LIESST). Light-driven ring opening/closing rearrangements of the spirocyclic and 2*H*-chromene ligands proceeding under ambient temperatures will be accompanied by changes of the ligand field strength and will, therefore, influence the ratio between the



$_{LS}$**5b**

$_{HS}$**5b**

$_{IS}$**5b**

$_{MECP}$**5b**$_{LS\text{-}IS}$

$_{MECP}$**5b**$_{IS\text{-}HS}$

Fig. 9: Optimized geometries of the structures $_{LS}$**5b**, $_{HS}$**5b**, $_{IS}$**5b**, $_{MECP}$**5b**$_{LS\text{-}IS}$ and $_{MECP}$**5b**$_{IS\text{-}HS}$ calculated by the DFT B3LYP*/6-311++G(d,p) method [33].

low-spin and the high-spin isomeric species of complex, thus giving rise to the occurrence of LD LISC transformations. The principal features of the complexes capable of photo-controlled spin-crossover include: (1) low energy gaps between LS and HS electromers for both ring-closed and ring-opened ligand forms; (2) energy preference of the electromer containing LS ring-opened isomeric form of ligand, which being irradiated with the light of appropriate wavelength can be converted to its ring-closed form energy equivalent to the HS ring-opened form. The combined LD LISC – thermal SCO process can result in switching magnetic properties.

Configurational isomerization

Bischelate complexes

In the above considered coordination compounds, light-induced changes of their magnetic characteristics are conditioned by transformations of the photochromic spirocyclic fragments of the ligands not directly coupled to the coordination site. It may be expected that a greater effect can be achieved in metal complexes, in which donor centers of the photochromic fragment take part in the formation of the coordination site. In this case photoinduced transformation of spin state of the complex may be accomplished as the result of reconfiguration of the coordination site, i.e. configurational isomerization [37]. If the spirocyclic form of the ligand of complexes **4**, **5** can be involved into complexation with transition metal ions like cobalt or nickel, the interconversion between their planar and tetrahedral configurational isomers may lead to switching spin states of the complexes. An advantage of configurational modulation of spin states is the extremely high speed of spin-forbidden rearrangements of this type reaching and overcoming the rates of electron transfers [38].

The ability of spirocyclic compounds to form complexes with metal ions was first reported by Phillips et al. [39]. In the course of the later study of ionochromism of quinoline-containing spiropyrans [40, 41] it was shown that insertion of additional donor centers into spiropyran molecules **6** facilitates the formation of complexes **7** due to involvement of the carbonyl oxygen of the isomeric merocyanine structure into coordination with metal ions (Fig. 10).

At the same time, no experimental data were reported on stabilization of bischelate structures formed by transition metal complexes with ring-closed forms of spiropyrans, which is necessary for realization of switching spin states via the mechanism of configurational isomerization. It was expected that this mechanism can operate in the case of complexes of tetracoordinated nickel, which depending on stereochemistry of the chelate coordination site may possess either low- or high-spin states [42]. In the search for compounds capable of formation of bischelate structures with both ring-closed and ring-opened forms of spirocyclic moieties we have computationally studied Ni(II) complexes **9** with spiro[indoline-2,2′-pyrano[3,2-*h*]quinoline] **8** (Fig. 11) [30]. Due to steric hindrances created by the indoline fragment no LS (with planar coordination site) or HS (with *pseudo*-tetrahedral site) structures with the ring-closed ligand ($_{\mathrm{LS}}$**9a** and $_{\mathrm{HS}}$**9a**) were found to exist on the potential energy surfaces. The complexation is accompanied by opening the spiropyran ring. The most energy preferred *cis*-structure of the ring-opened form is presented by the low-spin isomer $_{\mathrm{LS}}$**9c** with square-planar geometry of coordination site (Fig. 12). Its high-spin *pseudo*-tetrahedral electromer $_{\mathrm{HS}}$**9c** is 14.5 kcal/mol of energy destabilized compared to the $_{\mathrm{LS}}$**9c**.

The isomers of **9** with *trans*-form of the ring-opened spirocycle are represented by low-spin structure $_{\mathrm{LS}}$**9b** and high-spin structure $_{\mathrm{HS}}$**9b** disfavored relative to the ground state by 8.4 kcal/mol. Comparison of

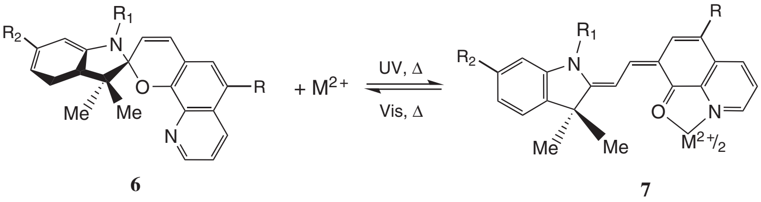
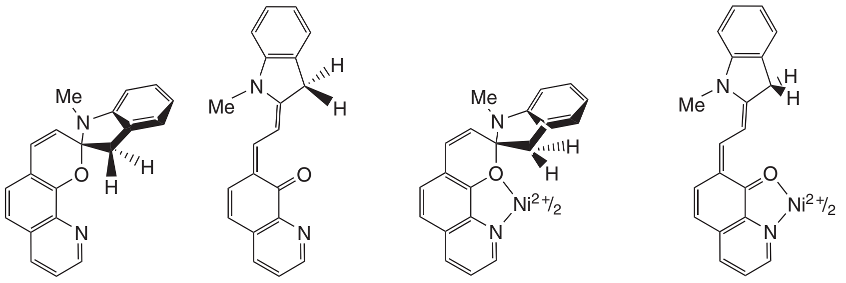


Fig. 10: Photoinduced ionochromism of spiropyrans: $M^{2+}=Zn^{2+}$, Co^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}.



8a **8b** **9a** **9b**

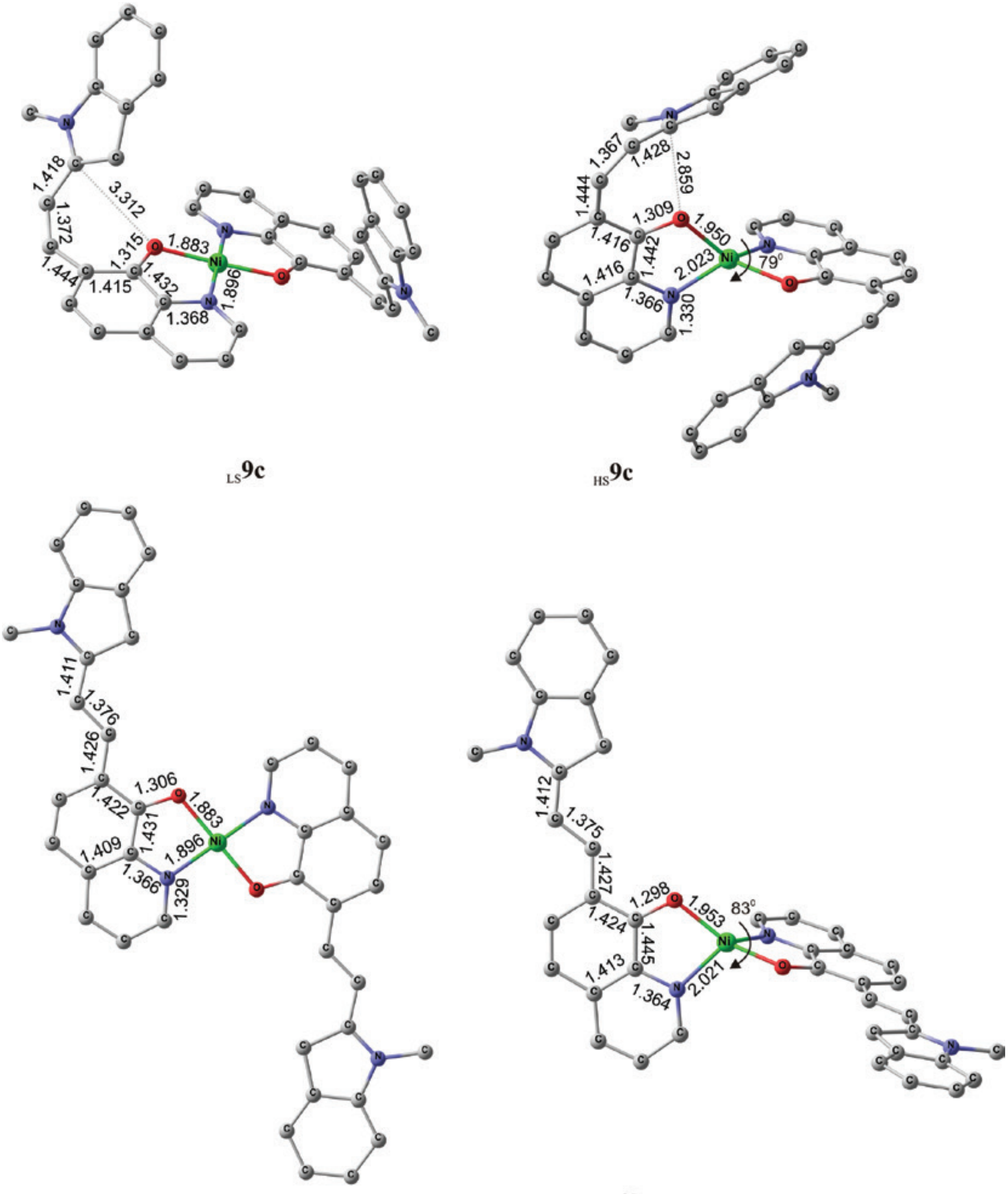
Fig. 11: Spiropyran **8** and its complex with Ni^{2+} **9**. Index **a** corresponds to the structure with the ring-closed form of the ligand, while index **b** – to the ring-opened isomer.

total energies of the structures ${}_{\mathrm{LS}}$**9c** and ${}_{\mathrm{LS}}$**9b** corresponding to the most stable isomers of nickel complex with *cis*- and *trans*-forms of the spirocyclic moiety, respectively, points to the energy preference of the latter ($\Delta E = 22.1$ kcal/mol). The calculations showed that complexation of nickel ions with spiro[indoline-2,2′-pyrano[3,2-*h*]quinoline] leads to the formation of bichelate structures with only ring-opened forms of spirocyclic ligands, that is completely shifts the equilibrium observed in solutions of initial spiropyrans [43]. Therefore, due to the steric hindrances created by the indoline heterocycle complexes **9** cannot exhibit ligand-driven spin-state-switching behavior. To avoid this undesirable effect we turned attention to the computational modeling of a series of metal complexes with structurally similar to spiropyrans, but sterically unhindered properly functionalized 2*H*-chromenes (2*H*-1-benzopyrans). The chosen ligands **10–14** (Fig. 13) comprising two donor centers for coordination of metal ions in both ring-closed and ring-opened forms were found to be capable of undergoing light-induced electrocyclic rearrangements [23] resulted in spin-state switching of bischelate metal complexes (Fig. 14).

The most promising results were obtained for Ni(II) and Co(II) complexes with 2*H*-chromene-8-amine **10** and 2*H*-pyrano[3,2-*h*]quinoline **14** [44, 45] characterized by the formation of a five-membered chelate cycle, which provides with the best steric conditions for stabilization of isomers with ring-closed form of the ligands.

According to the calculations, the interaction of Co(II) ions with chromene **10** in the ring-closed form leads to the formation of bichelate structure ${}_{\mathrm{HS}}$**Co10a** on the quartet PES (Fig. 15). The high-spin *pseudo*-tetrahedral structure ${}_{\mathrm{HS}}$**Co10b** and the low-spin structure ${}_{\mathrm{LS}}$**Co10b** with the planar coordination site correspond to the isomers with ring-opened form of the ligand **10b**. In this way, 2*H*-chromene-8-amine **10** forms with Co(II) ion stable ring-closed isomer ${}_{\mathrm{HS}}$**Co10a**, although energy disfavored ($\Delta E = 15$ kcal/mol) compared to the ring-opened isomers ${}_{\mathrm{LS}}$**Co10b** and ${}_{\mathrm{HS}}$**Co10b**. Nearly energy equivalent ring-opened isomers ${}_{\mathrm{LS}}$**Co10b** and ${}_{\mathrm{HS}}$**Co10b** ($\Delta E = 0.5$ kcal/mol) may coexist in a dynamic equilibrium in solution. The calculated MECP ${}_{\mathrm{MECP}}$**Co10b** for the rearrangement of these electronic isomers found on the intersection of the doublet and quartet PESs lies only 6.8 kcal/mol higher than the energy level of the high-spin ring-opened structure ${}_{\mathrm{HS}}$**Co10b**. It may, thus, be concluded that the considered system is capable of demonstrating fast interconversion "square-tetrahedron" in solution, while the exposure of the complex to light will promote electrocyclic rearrangement of the photochromic ligand and, as a consequence, transitions between the high-spin ${}_{\mathrm{HS}}$**Co10a** and the low-spin ${}_{\mathrm{LS}}$**Co10b** isomers accompanied by switching magnetic properties.

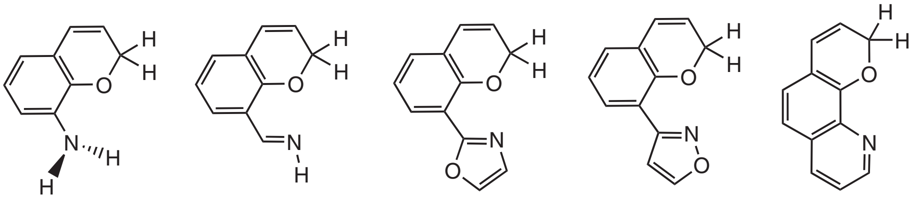
Coordination of 2*H*-chromene-8-amines **10a** in the ring-closed form to nickel center stabilizes the high-spin structure ${}_{\mathrm{HS}}$**Ni10a** characterized by *pseudo*-tetrahedral coordination site (Fig. 16). Structure ${}_{\mathrm{LS}}$**Ni10b** on the singlet PES corresponds to the ground state of the complex. Another isomer with the ring-opened form of the ligand **10b** is represented by the high-spin structure ${}_{\mathrm{HS}}$**Ni10b** on the triplet PES, which is by 9.7 kcal/mol destabilized compared to ${}_{\mathrm{LS}}$**Ni10b**. Thus, nickel(II) complex with the ring-closed form of 2*H*-chromene **10** possesses the high-spin state structure ${}_{\mathrm{HS}}$**Ni10a**, while the complex with the ring-opened form is stabilized in the low-spin state (structure ${}_{\mathrm{LS}}$**Ni10b**), which makes possible to switch magnetic properties of the compound by irradiation of its solution or crystals.



$_{LS}$**9c** $_{HS}$**9c**

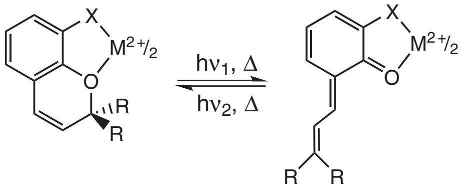
$_{LS}$**9b** $_{HS}$**9b**

Fig. 12: Optimized geometries of the structures $_{LS}$**9c**, $_{HS}$**9c**, $_{LS}$**9b** and $_{HS}$**9b** calculated by the DFT B3LYP*/6-311++G(d,p) method [30].



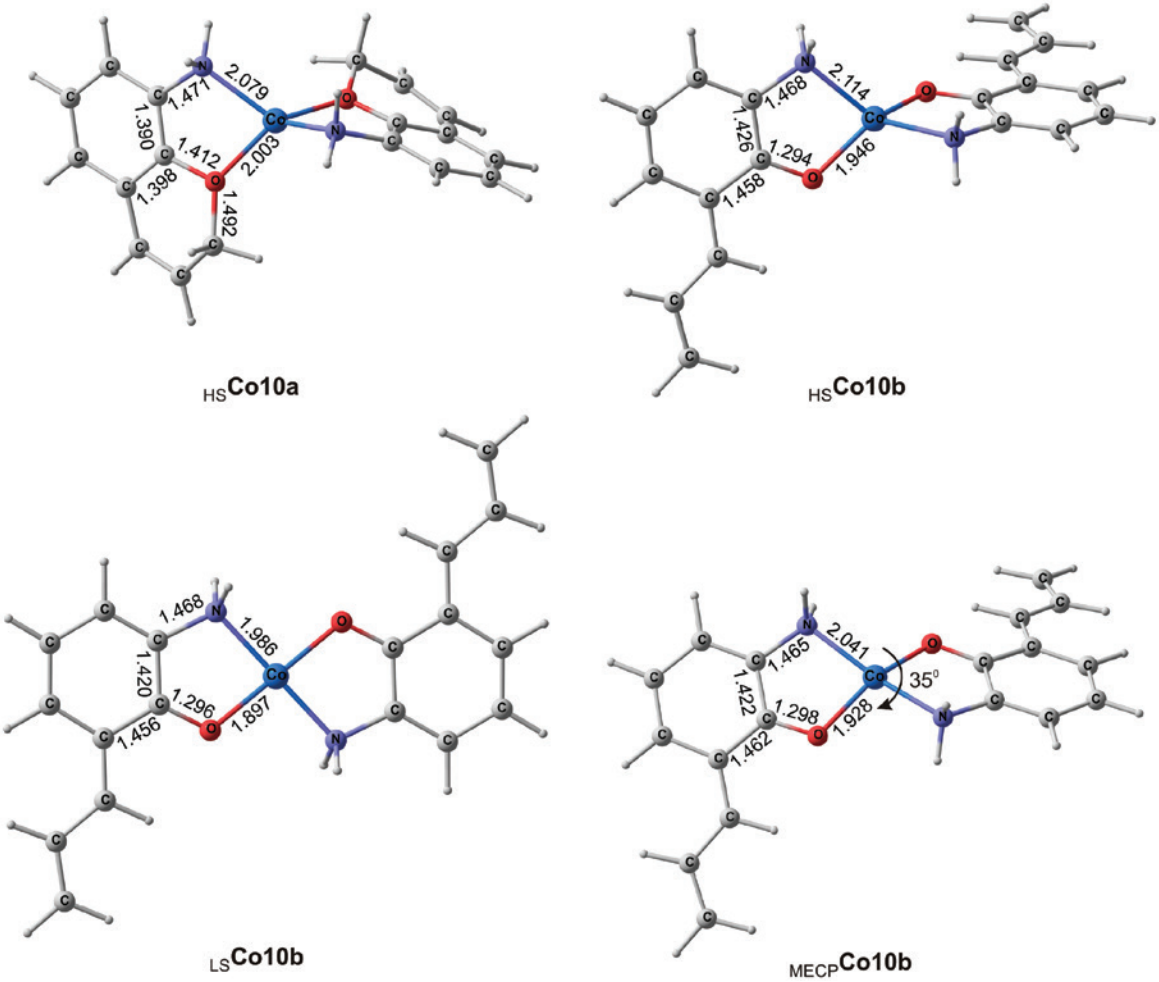
10 **11** **12** **13** **14**

Fig. 13: 2*H*-chromenes **10–14**.



M = Co, Ni, Cu, Zn; X = NR_1R_2, OR'

Fig. 14: Light-controlled rearrangements of metal bischelates with 2*H*-chromenes **10–14**. Index **a** corresponds to the structure with the ring-closed form of the ligand, while index **b** – to the ring-opened isomer.

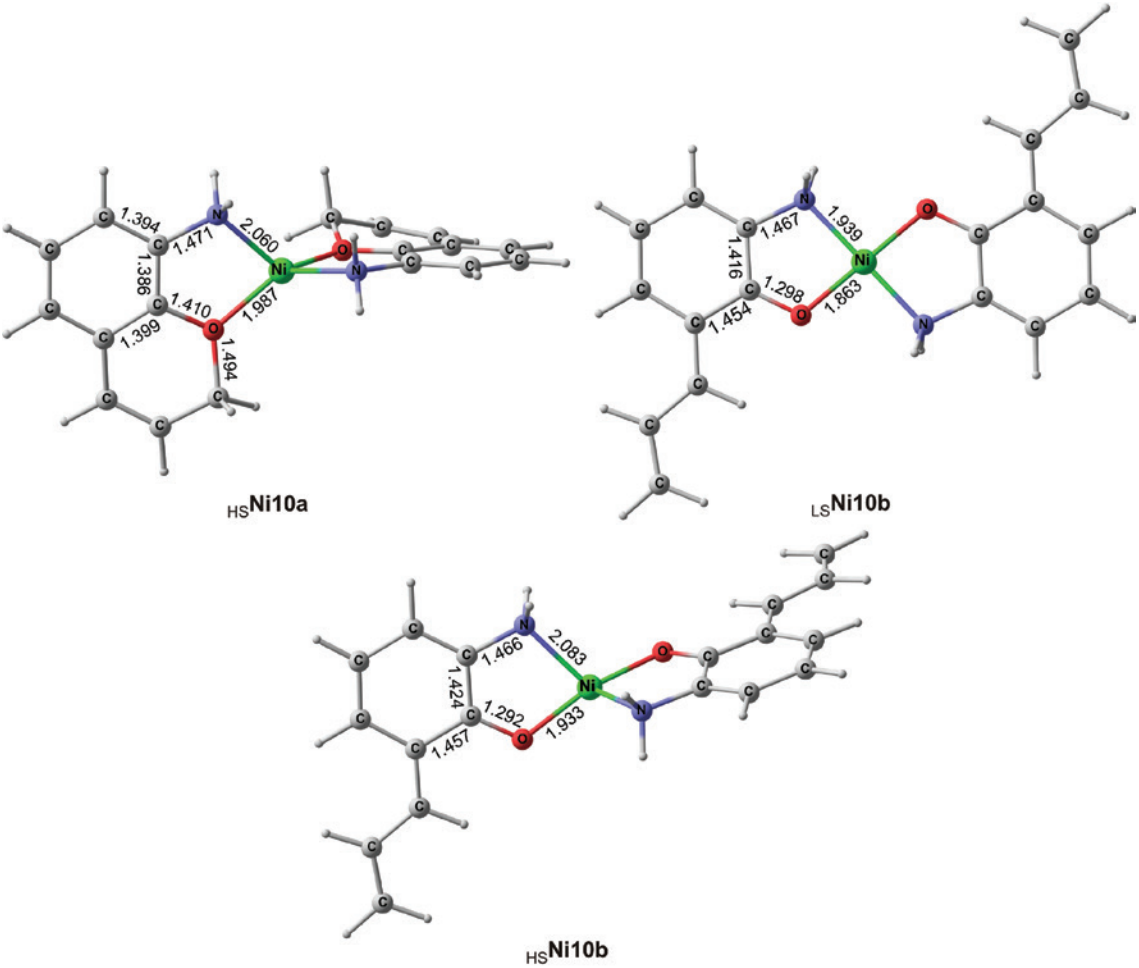


$_{\mathrm{HS}}$**Co10a** $_{\mathrm{HS}}$**Co10b**

$_{\mathrm{LS}}$**Co10b** $_{\mathrm{MECP}}$**Co10b**

Fig. 15: Optimized geometries of the isomeric forms and MECP structure of Co(II) complex with 2*H*-chromene-8-amine **10** calculated by the DFT B3LYP*/6-311++G(d,p) method [45]. Here and in Figs. 16–18 all the structure are dicationic.

Co^{2+} ion forms *pseudo*-tetrahedral high-spin structure $_{\mathrm{HS}}$**Co14a** with the ring-closed form of 2*H*-pyrano[3,2-*h*]quinoline **14**, and also more energy favorable (by 6.8 kcal/mol) high-spin ($_{\mathrm{HS}}$**Co14b**) and low-spin ($_{\mathrm{LS}}$**Co14b**) electromeric structures with the ring-opened form of the ligand (Fig. 17). Energy equivalence of these two structures points to their coexistence in solution. Interconversion of these isomers occurs via $_{\mathrm{MECP}}$**Co14b**, relative energy of which is equal to 6.4 kcal/mol. This finding is indicative of possible change of magnetic properties of cobalt(II) complex as a result of photoinitiated rearrangement.



$_{\mathrm{HS}}$**Ni10a**

$_{\mathrm{LS}}$**Ni10b**

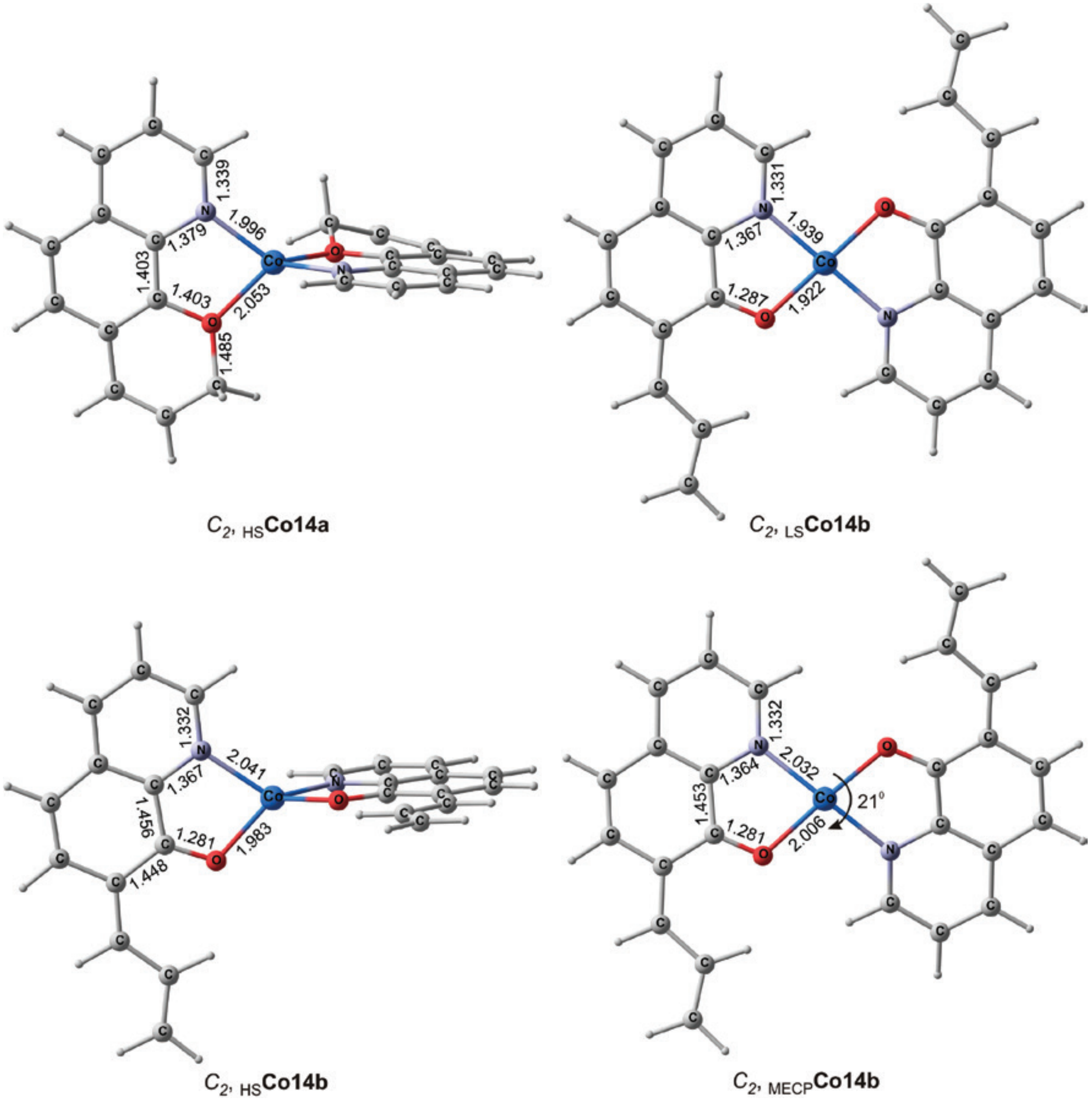
$_{\mathrm{HS}}$**Ni10b**

Fig. 16: Optimized geometries of the isomeric forms of Ni(II) complex with 2*H*-chromene-8-amine **10** calculated by the DFT B3LYP*/6-311++G(d,p) method [45].

Similar situation takes place in the case of 2*H*-pyrano[3,2-*h*]quinoline nickel complex. The high-spin structure $_{\mathrm{HS}}$**Ni14a** with the ring-closed form of the photochromic ligand corresponds to a minimum on the triplet PES (Fig. 18). The high-spin isomer $_{\mathrm{HS}}$**Ni14b** is 6.5 kcal/mol energy disfavored compared to the ground state *trans*-planar structure $_{\mathrm{LS}}$**Ni14b** with the ring-opened form of 2*H*-pyrano[3,2-*h*]quinoline. Structure MECP $_{\mathrm{MECP}}$**Ni14b** located on the intersection of singlet and triplet PESs is destabilized relative to the ground state by 12 kcal/mol. It may, thus, to predict that this complex can undergo light- and thermally-induced configurational rearrangements between the diamagnetic and paramagnetic states.

The calculations, results of which are illustrated in Figs. 15–18, have been performed on the double-charged cations to demonstrate the capacity of the compounds containing these structural units to the intramolecular light-controlled rearrangements leading to spin-state-switching effects. In order to clarify whether the properties inherent in the dications **Co10–Co14** and **Ni10–Ni14** can be retained when attaching these with proper counter-ions we have calculated the electrically neutral structures comprising dicationic complex **Ni14** and various anions (Cl^-, BF_4^- and BPh_4^-). It has been found that Cl^- and BF_4^- anions readily enter into the coordination sphere of the central nickel ion completing it to the six-coordinated form and stabilizing the high-spin state in all the isomers, which obstruct the occurrence of spin-state-switching mechanism [45].

The expansion of the coordination sphere can be obviated by coupling the dications **Co10–Co14** and **Ni10–Ni14** with bulky tetraphenylborate counter-ions. The optimized structures of the isomeric tight ion pairs $_{\mathrm{LS}}$**Ni14b**$(BPh_4)_2$ and $_{\mathrm{HS}}$**Ni14b**$(BPh_4)_2$ with ring-opened form of 2*H*-pyrano[3,2-*h*]quinoline **14** are depicted in Fig. 19. The low-spin structure is by 10.5 kcal/mol energy favored with respect to the high-spin one.



$C_{2,\,\mathrm{HS}}$**Co14a** $C_{2,\,\mathrm{LS}}$**Co14b**

$C_{2,\,\mathrm{HS}}$**Co14b** $C_{2,\,\mathrm{MECP}}$**Co14b**

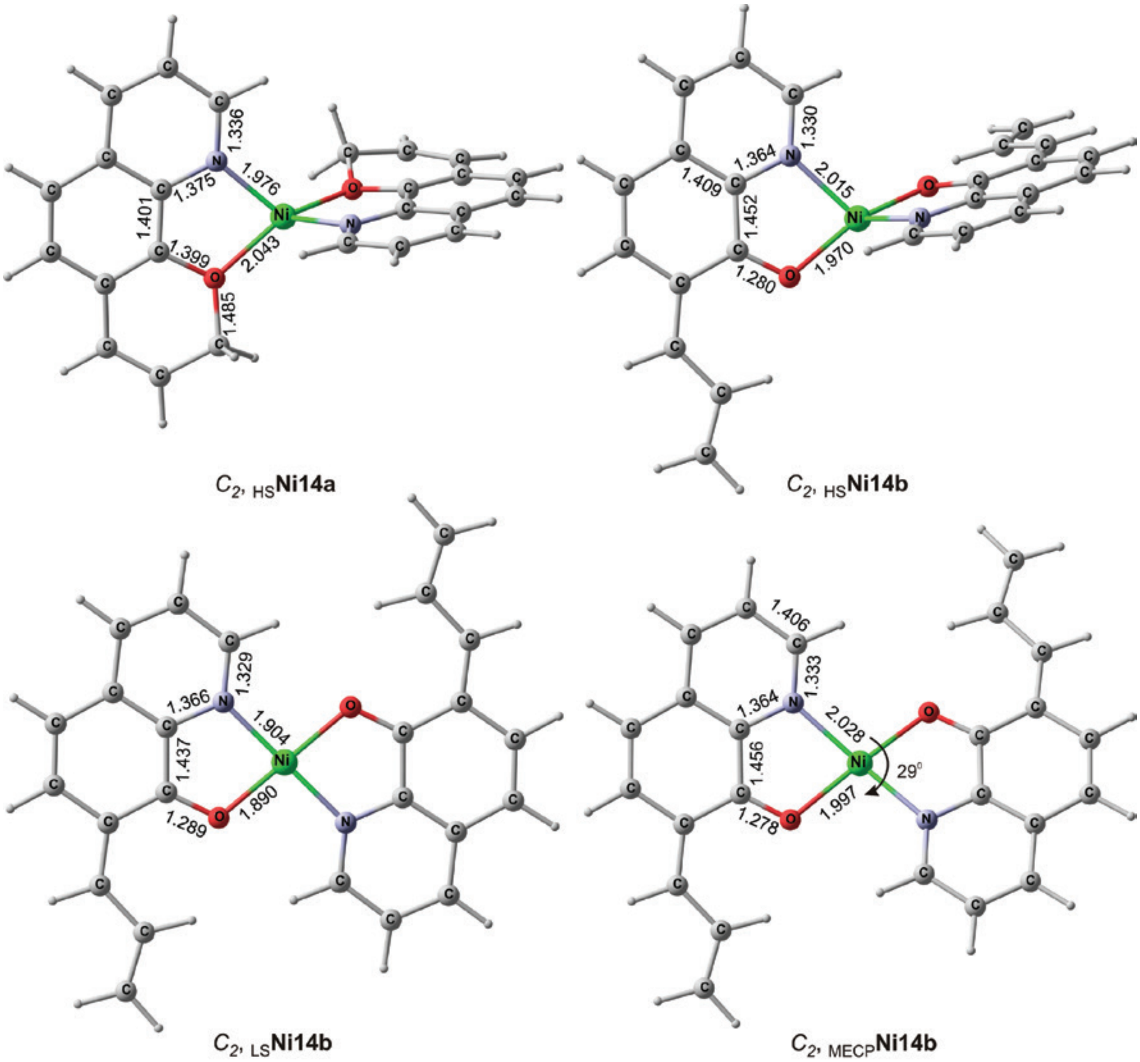
Fig. 17: Optimized geometries of the isomeric forms and MECP structure of Co(II) complex with 2*H*-pyrano[3,2-*h*]quinoline **14** calculated by the DFT B3LYP*/6-311++G(d,p) method [45].

This energy difference is close to the energy gap between the LS and HS isomeric forms of dication **Ni14** prone to low energy barrier spin-forbidden transition between them. This means that complex **Ni14**$(BPh_4)_2$ belongs to the species with thermally- or light-driven switchable spin states.

Compounds **Co10–Co14** and **Ni10–Ni14** represent a new family of the LD LISC systems in which the light-induced rearrangements of the photochromic ligands occur not in a part of the molecular space distant from the coordination site, but in the molecular fragment containing donor centers directly coordinated to the central metal ion. Another specific feature of these systems is that photoswitching of magnetic properties of the rearranged isomers is governed by the mechanism of configurational isomerization.

Monochelate complexes

A recent X-ray study of zinc complexes with a quinoline-containing spiropyran ligand [46] has shown that the properly functionalized spirocyclic ligands can form stable monochelate 1 : 1 complexes with halogen



C_2, $_{HS}$**Ni14a**

C_2, $_{HS}$**Ni14b**

C_2, $_{LS}$**Ni14b**

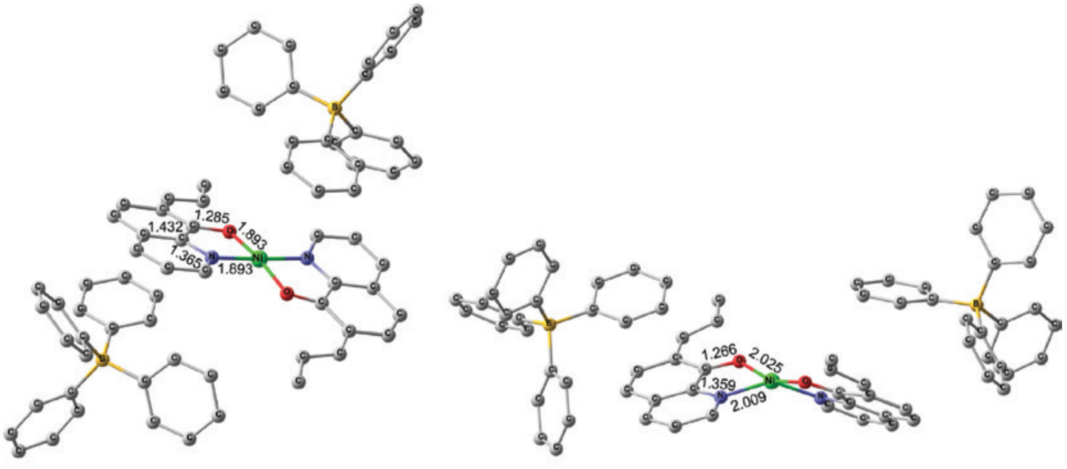
C_2, $_{MECP}$**Ni14b**

Fig. 18: Optimized geometries of the isomeric forms and MECP structure of Ni(II) complex with 2*H*-pyrano[3,2-*h*]quinoline **14** calculated by the DFT B3LYP*/6-311++G(d,p) method [44].

anions entering coordination sphere of the complex. This finding stimulated our study of possible spin-state-switching rearrangements of monochelate complexes **15** formed by quinoline-containing derivatives of 2*H*-chromenes with Ni(II) dihalogenides (Fig. 20).

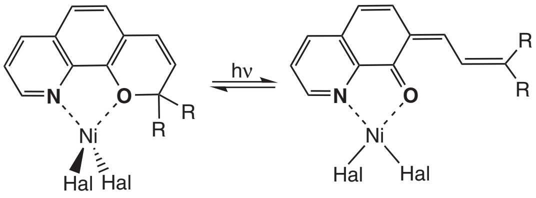
The calculations have shown that regardless of the isomeric form of the ligand the energy preferred state of complexes **15** (Hal=Cl; R=H, CH_3) is represented by the high-spin structures with *pseudo*-tetrahedral configuration of the coordination site [47]. In the fluoride complex **15** (Hal=F; R=CH_3), also stabilized is the high-spin state isomer with ring-closed chromene, $_{HS}$**15a** (Fig. 21). Ring-opening of the cycle leads to the formation of two energy nearly equivalent isomers appearing on the triplet ($_{HS}$**15b**) and singlet ($_{LS}$**15b**) PESs. It may be suggested that these isomers coexist in a solution. The energy level of MECP ($_{MECP}$**15b**) for their interconversion is spaced apart from the low-spin isomer by only 6.5 kcal/mol. This indicates to the possible dynamic equilibrium between the ring-opened forms of the complex possessing different spin states. Therefore, photo-induced ring-opening of the chromene ring in complex **15** (Hal=F; R=CH_3) will be accompanied by switching magnetic properties as the result of conversion of a portion of molecules from the high- to the low-spin state.

To sum up, it may be concluded that ring-closed and ring-opened isomers of 2*H*-chromenes create different conditions for the formation of low-spin planar and high-spin tetrahedral isomeric forms of transition metal complexes and their electrocyclic rearrangements can, thus, be associated with configurational



$_{LS}$**Ni14b**$(BPh_4)_2$ $_{HS}$**Ni14b**$(BPh_4)_2$

Fig. 19: Optimized geometries of the isomeric forms of Ni(II) complex with 2*H*-pyrano[3,2-*h*]quinoline **14** and two tetraphenylborate counter-ions calculated by the DFT B3LYP*/6-311++G(d,p) method [45].



15a **15b**

15, Hal=Cl, F; R=H, CH_3

Fig. 20: Photoisomerization of the complexes **15**.

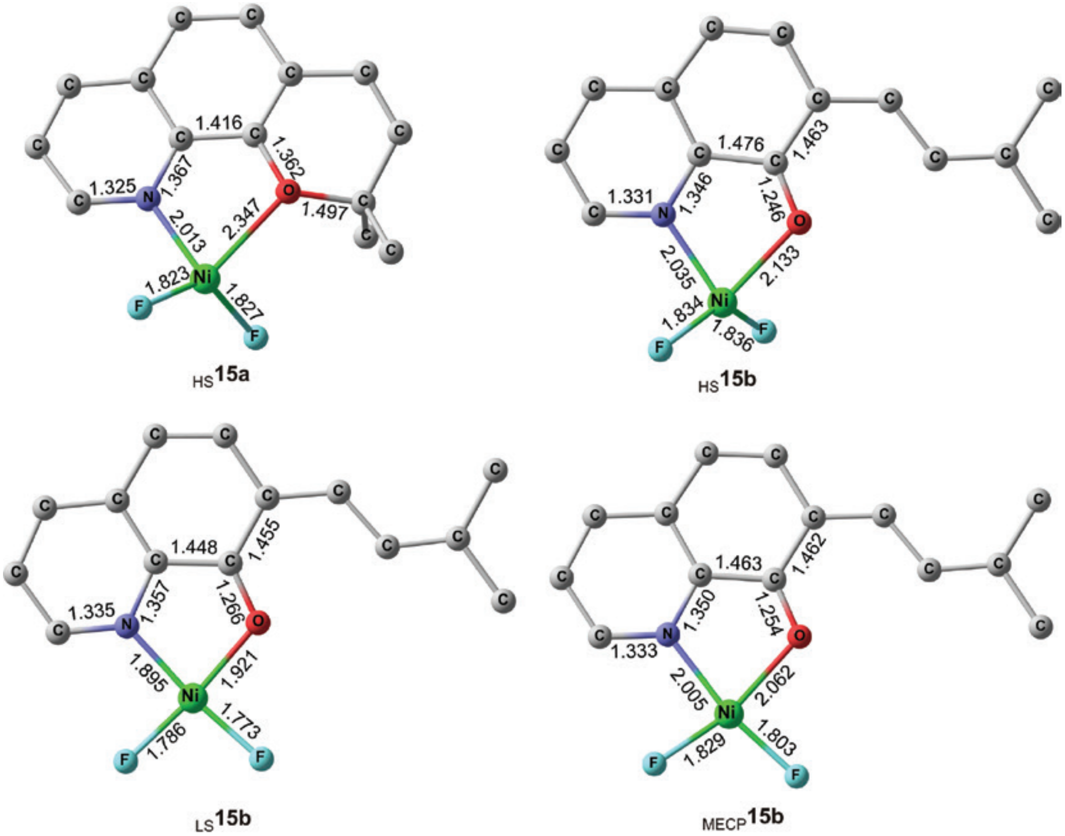
isomerizations of the complexes and sharp changes in their magnetic properties. The rational choice of photochromic ligands and transition metal ions provides for the occurrence of light-controlled rearrangements resulting in switching of spin states of magnetically active coordination compounds.

Ligand driven coordination-induced spin-state switching

The concept of light-controlled reconstruction of a ligand providing for switching spin state of the central metal ion was also used as the basis of a recently suggested new mechanism termed LD-CISSS [18, 19]. As in the case of LD LISC effect, the photochemical stage of the interconversion of magnetically active isomers implies *cis-trans* isomerization of the ligand designed in a special way for providing the possibility of the formation of a new bond with complexing agent as the result of light-induced reaction. This new bond changes the coordination polyhedron and spin state of the complex.

In the most structurally elegant way, the idea of association – recombination mechanism has been realized in the complexes with scorpionate ligands [18, 19] susceptible to the LD-CISSS effect. Under irradiation of toluene solution of Ni(II) **16**-*trans* complex by light of 500 nm a photo-stationary state achieved at ambient temperature contains 63 % of paramagnetic **16**-*cis* form (Fig. 22).

Following to the principle of the LD-CISSS mechanism a series of cobalt and nickel complexes **17** and **18** (Fig. 23) comprising ligands with photochromic arylazo group capable of coordination to the metal center have been synthesized and reversible changes in electronic absorption spectra of the compounds observed



$_{HS}$**15a** $_{HS}$**15b** $_{LS}$**15b** $_{MECP}$**15b**

Fig. 21: Optimized geometries of the isomeric forms and MECP structure of Ni(II) complex **15** (Hal=F; R=CH_3) calculated by the DFT B3LYP*/6-311++G(d,p) method [47].

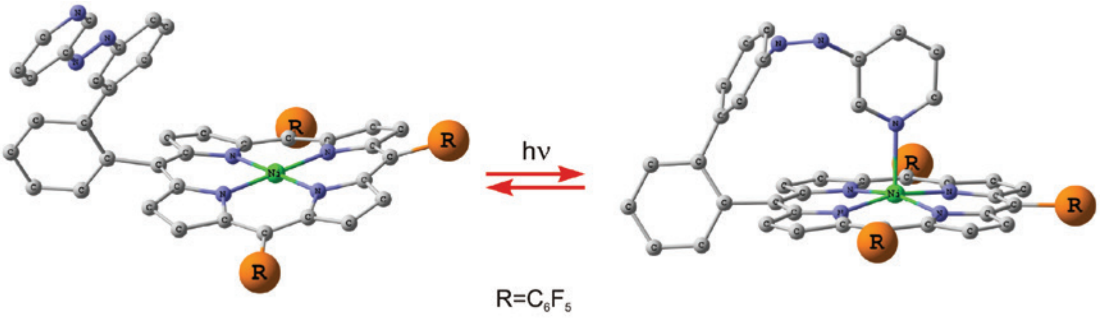
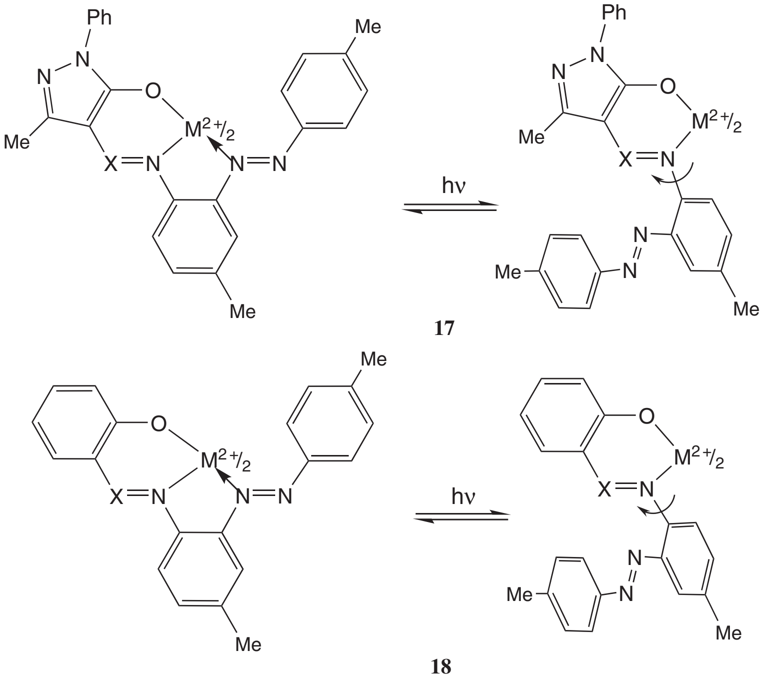


Fig. 22: Photoisomerization of complex **16** (R=C_6F_5).

under temperature variation of their solutions [48, 49]. Although the calculations [DFT B3LYP/6-311++G(d,p)] well reproduced the experimental X-ray geometry of **17** and confirmed that the detected spectral changes were due to the process of dissociation–recombination of the Co–N, they also showed that the energy gap between the ground state isomer of **17** (M=Co, X=CH) with *pseudo*-octahedral geometry of coordination and its low-spin isomer form having *pseudo*-tetrahedral coordination site was too large (8.2 kcal/mol) for the occurrence of a thermal SCO rearrangement. Exposure of solutions of complex **18** to UV- light of 400 nm wave length results in evolution of the spectral picture characteristic for *cis-trans*-isomerization of the azobenzene fragment. However, the calculations showed that regardless of orientation of the photochromic group in complex **18** (M=Co, X=CH) the cobalt ion retains its *pseudo*-tetrahedral environment, which means that



M=Co, Ni; X=CH, N

Fig. 23: Photoisomerization of the complexes **17** and **18**.

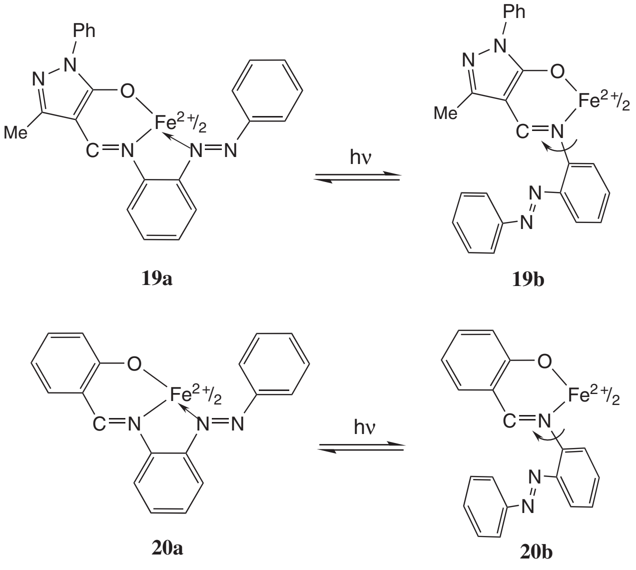
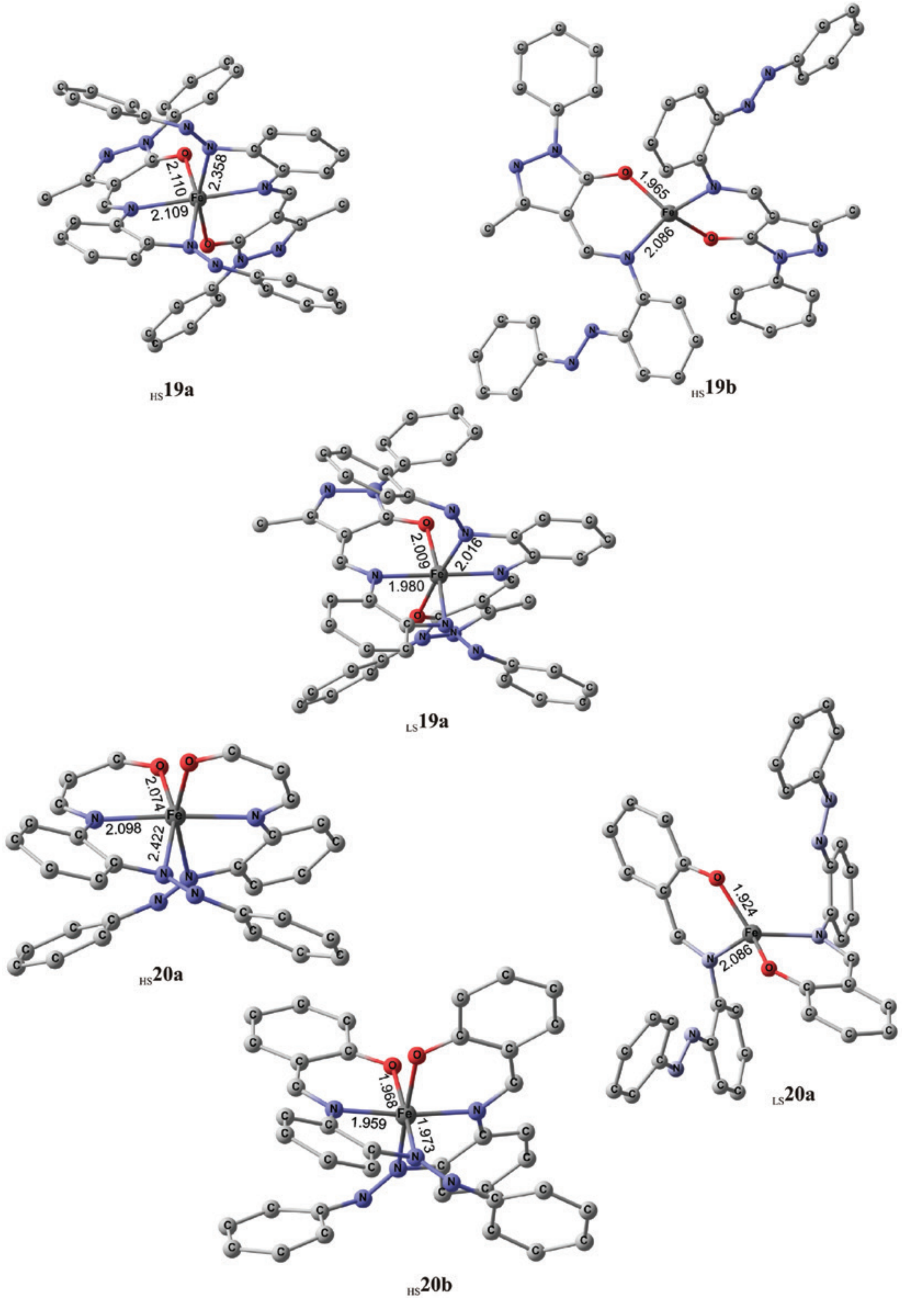


Fig. 24: Photoisomerization of the complexes **19** and **20**.

the light-induced rearrangement of the ligand fragment cannot notably change magnetic properties of the complex.

More promising light-controlled magnetic properties have been predicted for the analogous iron complexes **19** and **20** (Fig. 24). The B3LYP*/6-311++G(d,p) calculations predict that the ground state isomeric form of **19** is represented by the high-spin structure $_{HS}$**19a** with hexacoordinated Fe(II) central atom (Fig. 25), which is by 4.3 kcal/mol energy preferred to the corresponding low-spin isomer $_{LS}$**19a.** The isomer $_{HS}$**19b** with



$_{\text{HS}}$**19a** $_{\text{HS}}$**19b** $_{\text{LS}}$**19a** $_{\text{HS}}$**20a** $_{\text{LS}}$**20a** $_{\text{HS}}$**20b**

Fig. 25: Optimized geometries of the isomeric forms of Fe(II) complexes **19** and **20** calculated by the DFT B3LYP*/6-311++G(d,p) method.

the tetrahedral coordination site also possesses the high-spin state. Therefore, the light-induced dissociation of Fe–N_{azo} bonds will not result in significant changes of magnetic characteristics of complex **19**. By contrast with **19**, the hexacoordinated iron complex **20** with salicylaldiminate ligands has the low-spin structure

$_{LS}$**20a**, which is by 0.8 kcal/mol of energy preferred to the high-spin isomeric form $_{HS}$**20a**, which makes possible occurrence of thermally initiated SCO rearrangements between these isomers. The light-induced conversion into the isomer with tetracoordinated iron center will lead to the high-spin structure $_{HS}$**20b** representing the ground state of the complex ($\Delta E_{HS\mathbf{20b}\text{-}LS\mathbf{20a}} = -2.4$ kcal/mol). Therefore, magnetic properties of Fe(II) compound **20** can be controlled by means of two effects – spin-crossover and photo-induced dissociation–recombination of the Fe–$N_{arylazo}$ bond.

Conclusion

The use of photochromic ligands for the formation of transition metal complexes potentially prone to manifestation of the effects of spin-crossover (SCO) provides a convenient technically adaptable way for controlling magnetic properties of the complexes through the light-induced rearrangements of the ligands. The DFT calculations performed on the series of the first row transition metal complexes based on the phenanthroline-functionalized photochromic spirocyclic (spiropyrans, spirooxazines) and 2*H*-chromene ligands have shown that in the case of Fe(II) complexes photoisomerization of the ligand can lead to changes of ligand field strength sufficiently large to initiate SCO on condition of the appropriately low energy gap between the ground state LS and HS electromeric forms of the complexes.

Another spin-state-switching mechanism that includes configurational isomerizations of the tetracoordinated coordination sites operates in the case Ni(II) and Co(II) complexes. The computationally designed Ni(II) and Co(II) complexes with quinoline-functionalized 2*H*-chromenes **10–14** represent a new family of the LD LISC systems, in which the light-induced rearrangements of the photochromic ligands initiating planar-to-tetrahedral isomerization of the coordination site occur within the molecular fragment containing donor centers directly linked to the central metal ion.

With the proper choice of the molecular platform of Fe(II), Co(II) and Ni(II) compounds **17–20** with a photochromic arylazo group capable of coordination to the metal center, a promising system (**20**) has been predicted for the occurrence of LD-CISSS mechanism combining the effects of SCO and photo-induced dissociation–recombination of the Fe–$N_{arylazo}$ bond.

It may, thus, be concluded that computational modeling of transition metal complexes capable of spin-state-switching rearrangements aimed at tuning molecular structure to the electronic and steric requirements of the basic molecular mechanisms driving these processes represents an important and reliable tool for rational design of novel magnetically active compounds.

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