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Adducts of Tetracoordinate Cobalt(II) Complexes and 1-(Pyridin-2-yl)methanimine: Computational Search for Valence Tautomeric Systems

A. G. Starikov[a,b], A. A. Starikova[b], and V. I. Minkin[a,b]

[a] *Southern Scientific Center, Russian Academy of Sciences,*
pr. Chekhova 41, Rostov-on-Don, 344006, Russia
e-mail: andr@ipoc.sfedu.ru

[b] *Institute of Physical and Organic Chemistry, Southern Federal University, Rostov-on-Don, Russia*

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Abstract—A density functional theory method [B3LYP*/6-311++G(d,p)] was used to study mixed-ligand adducts of tetracoordinate cobalt(II) complexes and 1-(pyridin-2-yl)methanimines. Stability of the adducts with respect to dissociation into the initial components and the possibility of intramolecular electron transfer were explored. The calculated energy characteristics of the adduct of Co(II) bisacetylacetonate with a redox-active ligand functionalized by cyano groups suggest the possibility of valence tautomerism in this compound.

Keywords: quantum-chemical calculations, valence tautomerism, cobalt bischelates, 1-(pyridin-2-yl)methanimine, density functional theory

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Transition metal complexes with redox-active ligands have attracted increased interest due to their ability to undergo heat- and light-induced intramolecular rearrangements involving electron transfer and referred to as redox isomerism or valence tautomerism. These processes are accompanied with a change in the spin state of the system, which makes the complexes possessing such a property candidates for molecular electronics, spintronics, and quantum computation applications [1, 2].

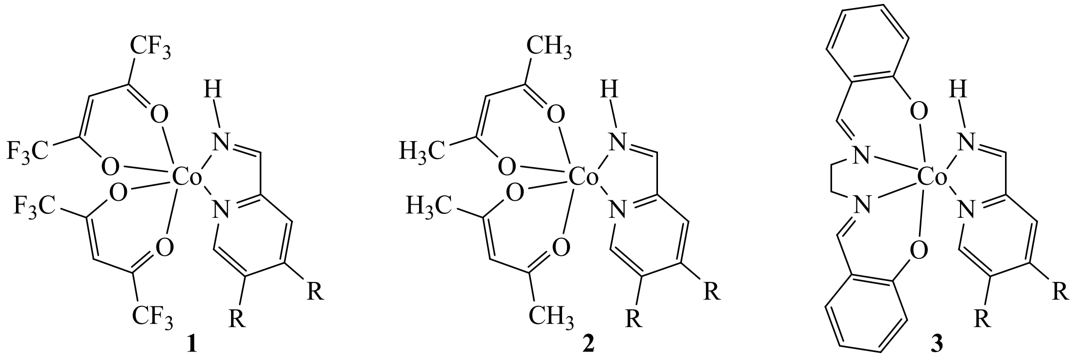
Among the most widely studied valence tautomeric systems are cobalt complexes with one or two *o*-benzoquinone ligands, where the interconversions of the radical monoanion semiquinone form and the dianion catecholate form are accompanied with a change in magnetic properties [3–5].

We recently suggested a different approach to the design of valence tautomeric compounds, involving the formation of cobalt bichelate adducts with electroneutral bidentate redox-active ligands (phenoxybenzoquinone imine, 1,4-diazabutadiene, and benzoquinone and its imino derivatives [6–8]. As shown in [9], the relative stability of isomers (electromers [10]) of such adducts can be controlled by varying substituents.

Aiming at extending the range of redox-active ligands for valence tautomeric systems, we focused on the adducts of 1-(pyridin-2-yl)methanimine (α-iminopyridines) with tetracoordinate Co^{II} complexes comprising hexafluoroacetylacetone (**1**), acetylacetone (**2**), and *N,N'*-ethylenebis(salicylaldimine) (**3**) ligands (Scheme 1). Lu et al. [11] in their research on homoleptic transition metal complexes with α-iminopyridine demonstrated that the possibility to stabilize different oxidation states of the ligand could be attained by varying the charge of the complex but found no evidence of the valence tautomerism [11].

The adduct of cobalt bis(hexafluoroacetylacetonate) $Co(hfac)_2$ with α-iminopyridine was first synthesized in 2010 [12]. However, the redox properties of this compound have never been studied. The calculated ground-state geometry of adduct **1** (R = H) (Fig. 1) is in a good agreement with the X-ray diffraction data in [12]; an exception is the Co–N distance, which is accounted for by the steric strain caused by the aromatic substituent at the imino nitrogen in the synthesized compound. The calculated bond lengths in

Scheme 1.



R = H, CN.

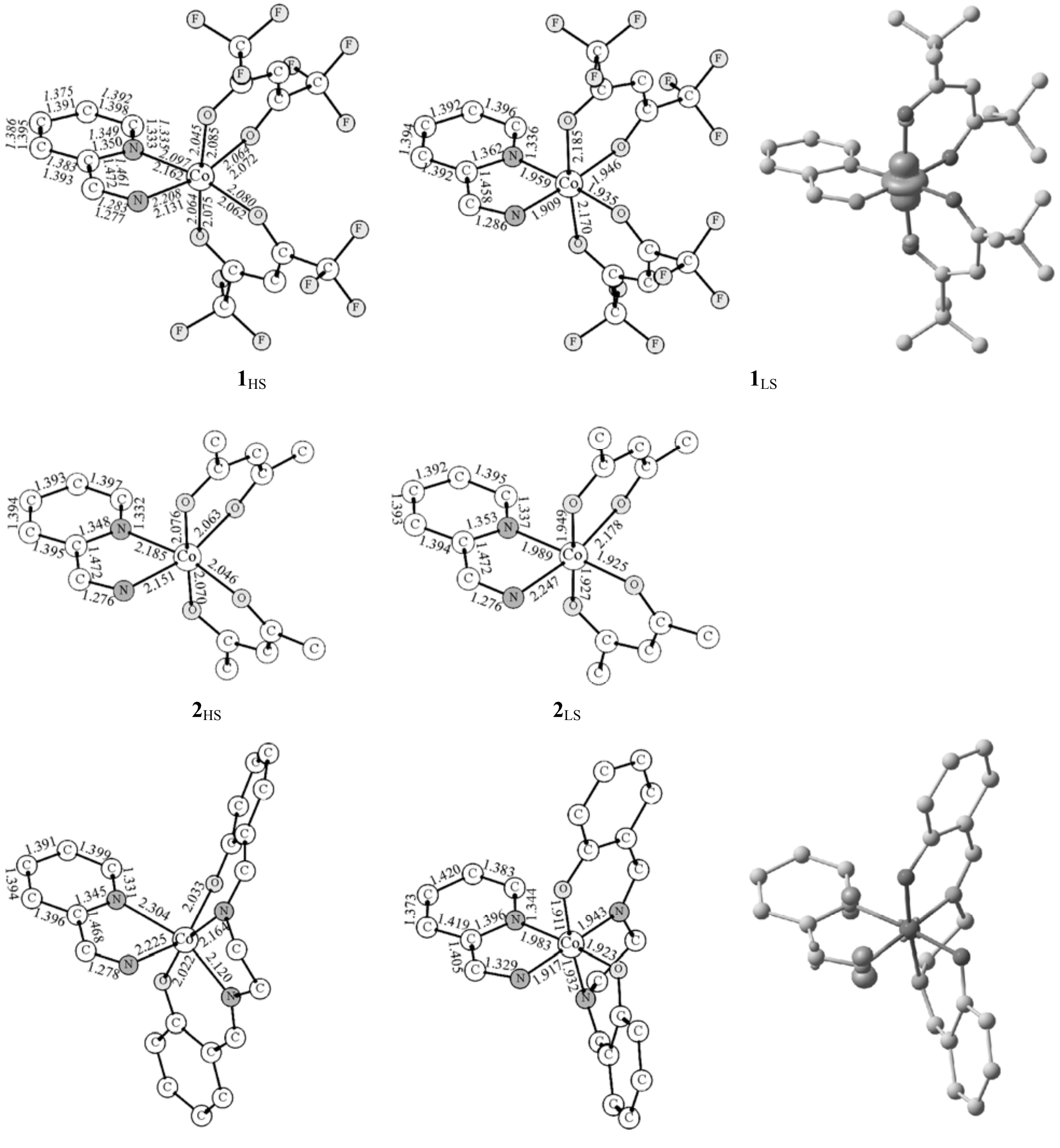
the iminopyridine ligand (L) correspond to its neutral form [13], and the spin density distribution suggests that the metal atom contains three unpaired electrons. This result allows us a conclusion that the adduct is a molecular complex stabilized with respect to the isolated bischelate and α-iminopyridine molecules by 30.9 kcal/mol (see the table).

The low-spin isomer of compound **1** (R = H), structure $\mathbf{1}_{\mathrm{LS}}$ (R = H) on the doublet potential energy surface, is higher in energy than the ground-state structure $\mathbf{1}_{\mathrm{HS}}$ (R = H) by 6.2 kcal/mol. The coordination site in structure $\mathbf{1}_{\mathrm{LS}}$ (R = H) is a tetragonal bipyramid having in its vertices the imino nitrogen and one of the oxygens, which are separated from the metal atom by 2.25 and 2.18 Å, respectively. These distances are much longer than the coordination bonds with other donor atoms (1.93–1.99 Å). The fact that the only unpaired electron in structure $\mathbf{1}_{\mathrm{LS}}$ (R = H) is localized on the metal atom (Fig. 1) and the bond distribution in the α-iminopyridine ligand is characteristic of the neutral form provide an evidence for the low-spin state of Co(II) in this isomer. Consequently, transitions between the spin states of adduct **1** (R = H) will not be accompanied by intramolecular electron transfer.

In a recent study on mixed-ligand complexes of cobalt with *o*-benzoquinone derivatives, we found the ability of the electron-acceptor trifluoromethyl groups to block valence tautomeric rearrangements [9]. Presumably, the same effect is characteristic of adduct **1** (R = H). To find out whether the CF_3 substituent can affect the tendency of such compounds to undergo intramolecular redox processes, we studied adduct **2** (R = H) of cobalt bis(acetylacetonate) $Co(acac)_2$. Like in adduct **1** (R = H), the most stable isomer is structure $\mathbf{2}_{\mathrm{HS}}$ (R = H) including $_{\mathrm{HS}}\mathrm{Co}^{\mathrm{II}}$ and an electroneutral α-iminopyridine. The stabilization energy of this structure relative to the isolated molecules is 13.5 kcal/mol (see table), which implies that the adduct is thermodynamically stable. The low-spin isomer $\mathbf{2}_{\mathrm{LS}}$ (R = H) is destabilized with respect to the high-spin isomer by 7.2 kcal/mol and has an unpaired electron localized on the metal atom. Consequently, both forms of complex **2** (R = H) contain a divalent cobalt, which makes valence tautomerism impossible.

In the search for α-iminopyridine complexes whose low-spin isomers contain $\mathrm{Co}^{\mathrm{III}}$ and a radical anion form of the ligand, we considered adduct **3** of *N,N'*-ethylenebis(salicylideneiminato)cobalt(II) Co(salen). The calculations showed that the high-spin isomer $\mathbf{3}_{\mathrm{HS}}$ (R = H) is preferred over the low-spin isomer $\mathbf{3}_{\mathrm{LS}}$ (R = H) by 5.8 kcal/mol. The low stability of adduct **3** (see the table) makes it impossible to isolate it on a preparative scale. However, the stabilization of the monoanion form of the redox-active ligand and $_{\mathrm{LS}}\mathrm{Co}^{\mathrm{III}}$ in the low-spin isomer $\mathbf{3}_{\mathrm{LS}}$ (R = H) makes it expectable that by targeted modification of α-iminopyridine we will find compounds capable of valence tautomerism.

Presumably, the results for adducts **1**–**3**, which show that electromers with the redox-active α-iminopyridine ligand in the radical monoanion form are either destabilized (**3**) or impossible to exist (**1**, **2**), point to an insufficient electron affinity of the ligand. Earlier we showed by an example of adducts with α-diimine ligands [14] that the electron-acceptor cyano substituents shift the equilibrium to radical anion forms. To find out whether adducts with α-iminopyridine complexes are fundamentally able to undergo valence tautomerism, we have modeled complexes with a CN-substituted α-iminopyridine ligand.



$\mathbf{1}_{\mathrm{HS}}$ $\mathbf{1}_{\mathrm{LS}}$

$\mathbf{2}_{\mathrm{HS}}$ $\mathbf{2}_{\mathrm{LS}}$

$\mathbf{3}_{\mathrm{HS}}$ $\mathbf{3}_{\mathrm{LS}}$

Fig. 1. Geometric parameters of the isomers of adducts **1–3** (R = H) calculated by the DFT B3LYP*/6-311++G(d,p) method. Spin density distribution is presented for structures $\mathbf{1}_{\mathrm{LS}}$ (R = H) and $\mathbf{3}_{\mathrm{LS}}$ (R = H). Italics in structure $\mathbf{1}_{\mathrm{HS}}$ (R = H) show experimental bond lengths [12]. Here and hereinafter the bond lengths are in Å and hydrogen atoms are omitted for clarity.

The ground state of adduct **1** (R = CN) of Co(hfac)$_2$ and α-iminopyridine with two CN substituents is a high-spin structure $\mathbf{1}_{\mathrm{HS}}$ (R = CN) which is preferable by 6.2 kcal/mol over the low-spin structure $\mathbf{1}_{\mathrm{LS}}$ (R = CN) (Fig. 2). As seen from the data in the table, spin density on the metal atom is present in both isomers. Thus it can be concluded that transitions between states of different multiplicity will not involve

Spins (*S*), total energies without (E_{tot}) and with (E_{tot}^{ZPE}) taking account of zero-point vibrational energy, relative energies without (ΔE) and with (ΔE^{ZPE}) taking account of zero-point vibrational energy, spin density on the metal atom (q_sM), stabilization energies without (E_{stab}) and with (E_{stab}^{ZPE}) taking account of zero-point vibrational energy of the isomers of the adducts **1–3** calculated by the DFT B3LYP*/6-311++G(d,p) method

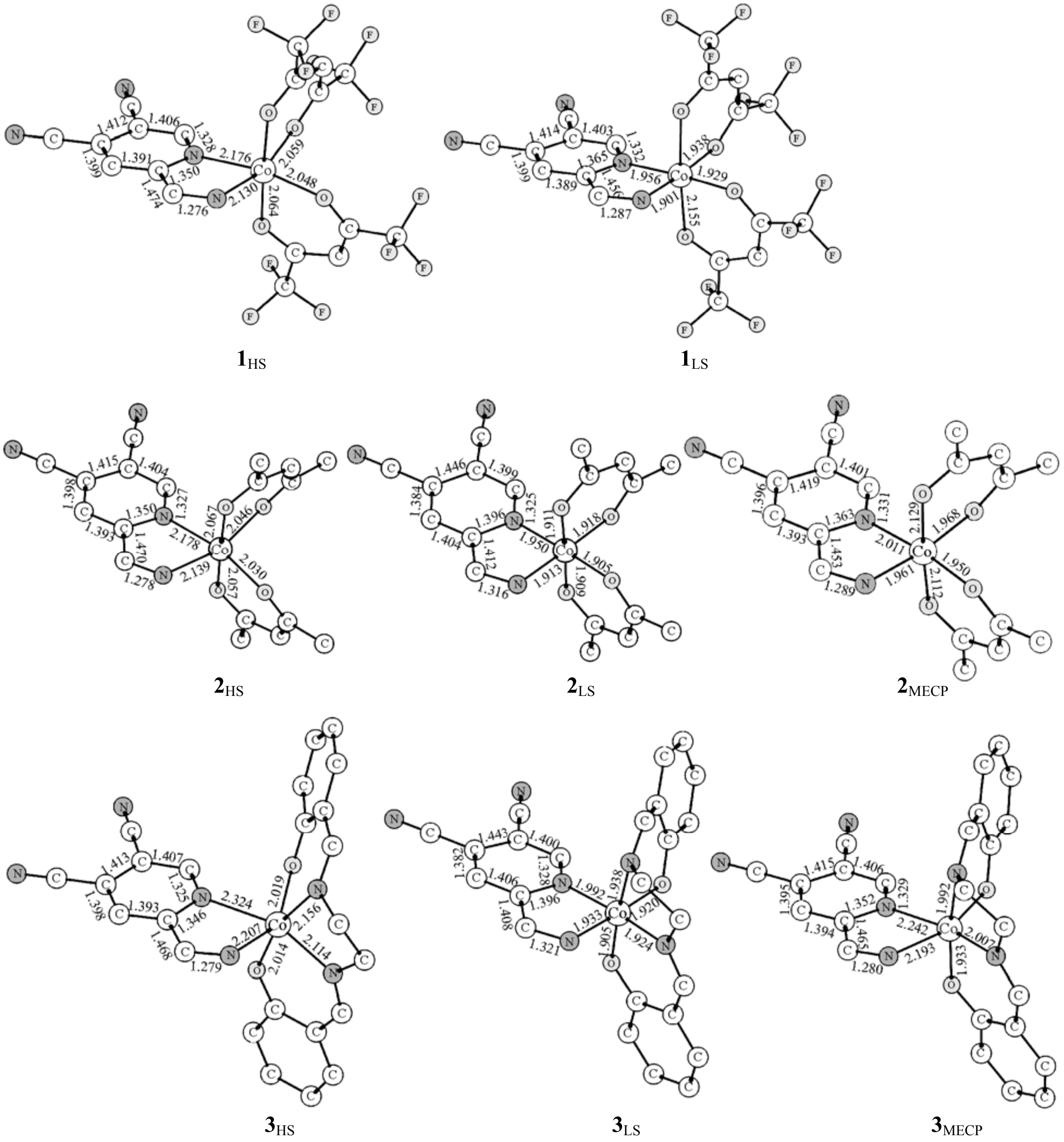
Structure	*S*	E_{tot}	E_{tot}^{ZPE}	ΔE	ΔE^{ZPE}	q_sM	E_{stab}[a]	E_{stab}^{ZPE}
		at. units		kcal/mol			kcal/mol	
L (R = H)	0	–341.59625	–341.48718					
L (R = CN)	0	–526.00983	–525.90399					
Co(hfac)$_2$	3/2	–3263.63635	–3263.50515					
Co(acac)$_2$	3/2	–2072.89123	–2072.66825					
Co(salen)	1/2	–2260.45676	–2260.18818					
1$_{LS}$ (R = H)	1/2	–3605.27404	–3605.03021	6.2	7.1	0.97	26.0	23.8
1$_{HS}$ (R = H)	3/2	–3605.28385	–3605.04153	0.0	0.0	2.65	32.2	30.9
2$_{LS}$ (R = H)	1/2	–2414.49868	–2414.16441	7.2	7.9	0.97	7.0	5.6
2$_{HS}$ (R = H)	3/2	–2414.51016	–2414.17701	0.0	0.0	2.64	14.2	13.5
3$_{LS}$ (R = H)	1/2	–2602.04955	–2601.67003	5.8	7.3	0.09	–2.2	–3.3
3$_{HS}$ (R = H)	3/2	–2602.05885	–2601.68172	0.0	0.0	2.63	3.7	4.0
1$_{LS}$ (R = CN)	1/2	–3789.67688	–3789.43651	6.2	7.2	0.99	19.3	17.2
1$_{HS}$ (R = CN)	3/2	–3789.68681	–3789.44795	0.0	0.0	2.62	25.5	24.4
2$_{LS}$ (R = CN)	1/2	–2598.92637	–2598.59352	0.0	0.0	0.06	15.9	13.4
2$_{HS}$ (R = CN)	3/2	–2598.92077	–2598.59093	3.5	1.6	2.64	12.4	11.7
2$_{MECP}$ (R = CN)		–2598.90984		10.4				
3$_{LS}$ (R = CN)	1/2	–2786.47838	–2786.10114	0.0	0.0	0.09	7.4	5.6
3$_{HS}$ (R = CN)	3/2	–2786.46963	–2786.09590	5.5	3.3	2.64	1.9	2.3
3$_{MECP}$ (R = CN)		–2786.45945		11.9				

[a] The stabilization energies were calculated with respect to isolated molecules of the cobalt complex and redox-active ligand.

a change in the oxidation level of the central atom and, consequently, intramolecular redox processes.

The calculation of adduct **2** (R = CN) of Co(acac)$_2$ and CN-substituted α-iminopyridine showed that the ground state of this compound is a low-spin structure **2**$_{LS}$ (R = CN) in which spin density is mostly localized on the redox-active ligand and is almost absent on the metal atom (see the table). Consequently, the formation of complex **2** is accompanied with the metal-to-ligand electron transfer and the stabilization of the radical anion form of the ligand. The high-spin isomer **2**$_{HS}$ (R = CN) is destabilized with respect to the ground state **2**$_{LS}$ (R = CN) by 3.5 kcal/mol, which allows us expecting the valence tautomerism in adduct **2**. The MECP (Minimum Energy Crossing Point) search aimed at finding energy characteristics of the suggested spin-forbidden process gave structure **2**$_{MECP}$ (R = CN). The energy gap between the latter structure and the most stable isomer **2**$_{LS}$ (R = CN) is 10.5 kcal/mol. This value falls in the range of valence tautomeric rearrangements.

The adduct formation between Co(salen) with functionalized α-iminopyridine, like with the above-considered complex **2** (R = CN), leads to stabilization of the low-spin isomer **3**$_{LS}$ (R = CN) containing the radical anion of the redox-active ligand and $_{LS}Co^{III}$. The high-spin isomer **3**$_{HS}$ (R = CN) is a molecular complex destabilized with respect to the low-spin isomer **3**$_{LS}$ (R = CN) by 5.5 kcal/mol. The energy barrier to interconversions between the electromers of



$\mathbf{1}_{\mathrm{HS}}$ $\mathbf{1}_{\mathrm{LS}}$

$\mathbf{2}_{\mathrm{HS}}$ $\mathbf{2}_{\mathrm{LS}}$ $\mathbf{2}_{\mathrm{MECP}}$

$\mathbf{3}_{\mathrm{HS}}$ $\mathbf{3}_{\mathrm{LS}}$ $\mathbf{3}_{\mathrm{MECP}}$

Fig. 2. Geometric parameters of the isomers of adducts **1–3** (R = CN), calculated by the DFT B3LYP*/6-311++G(d,p) method.

adduct **3** (R = CN) is 11.9 kcal/mol, which allows us to expect valence tautomerism in this adduct. However, the fact that structure $\mathbf{3}_{\mathrm{MECP}}$ (R = CN) is destabilized with respect to the isolated cobalt complex and the ligand makes this intramolecular process unlikely, because decomposition of adduct **3** (R = CN) is energetically preferred over its valence tautomeric rearrangement.

Thus, the quantum-chemical modeling [B3LYP*/6-311++G(d,p)] of the adducts of tetracoordinate cobalt complexes with 1-(pyridin-2-yl)methanimine showed that the latter ligand can change its oxidation state due to an intramolecular redox process. The conditions necessary for this effect [9], specifically, preference of low-spin form, small energy gaps between electromers, and low barriers to isomerization, as well as stability against the dissociation into the constituent components, are best met in the adduct of cobalt bis-(acetylacetonate) with α-iminopyridine with such strong electron-acceptor substituents as CN groups.

EXPERIMENTAL

All calculations were performed using GAUSSIAN 09 [15] by the DFT B3LYP*/6-311++G(d,p) method which correctly reproduces the structures [16] and mechanisms of intramolecular rearrangements [17, 18] of complexes with redox-active ligands. Full geometry optimization and subsequent vibrational analysis were performed to locate and identify stationary points on the potential energy surface. Spin-forbidden reactions were studied by searching for minimum energy crossing points between potential energy surfaces (MECPs) by the algorithm proposed in [19].

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