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Cobalt diketonate adducts with redox-active diiminosuccinonitriles

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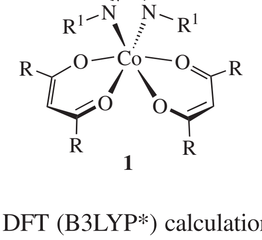
The DFT calculations predict that adducts of cobalt diketonates with diiminosuccinonitriles can exhibit a valence tautomeric behavior.

Transition metal complexes with redox-active (noninnocent) ligands, in which interconversion between high-spin and low-spin states is caused by the intramolecular electron transfer between the metal and the ligand externally tuned by temperature, light, or applied pressure, have significant promise for the design of magnetically responsive molecular switches and sensors.[1,2] The reversible rearrangements of these coordination compounds, termed as valence tautomerism (VT), have now been extensively studied and amply reviewed.[2–4] Since the first report on a VT transition,[5] attention has been focused on studying octahedral mononuclear Co and Mn 1 : 2 complexes with benzoquinone ligands.[6,7] We have recently noted that the area of prospective VT coordination compounds can be substantially extended by turning attention to the adducts of tetracoordinate transition metal complexes with redox-active ligands in the case when the energy barrier to the VT rearrangement of the adduct is less than the energy required for its thermal dissociation. The density functional theory (DFT) calculations performed on the adducts of Co diketonates with *o*-benzoquinone and its imines[8] and diimines of glyoxal[9] have shown that these adducts meet the necessary requirements. The recently synthesized mixed-ligand adducts of redox-active 2,4,6,8-tetra-*tert*-butylphenoxazin-1-one with cobalt bis(salicylaldiminates) demonstrate temperature-dependent magnetic properties related to the Co^{II}/Co^{III} transitions.[10]

Here, we report a computational study of the molecular and electronic structures of adducts **1** of Co^{II} acetylacetonate (acac) and hexafluoroacetylacetonate (hfacac) with redox-active diimines of glyoxal containing electron-withdrawing cyano groups – diiminosuccinonitriles,[11] aimed at the search for new coordination compounds capable of VT rearrangements. Bis-chelate Ni^{II} and Pt^{II} complexes with semidiiminosuccinonitrile anions (R = H) were previously synthesized.[12]



1

R = Me, CF_3
R^1 = H, Me

The unrestricted DFT (B3LYP*) calculations were performed using the Gaussian 03 program package[13] with the 6-311++G(d,p) basis set. As has been previously shown,[14,15] the modified B3LYP* functional[16] and the employed basis set generally well reproduce the energy parameters of VT rearrangements in transition metal complexes. For all the geometry-optimized structures, force constants were calculated and the stability of wave functions was checked.

Table 1 Stabilization energies (E_{stab}), relative energies without (E_{rel}) and with (E_{rel}^{ZPE}) the energies of the zero harmonic vibrations taken into account, spin densities at the metal centers (q_{sM}) and spin state (S) of adducts **1** (R = Me, CF_3; R^1 = H, Me), calculated by the DFT B3LYP*/6-311++G(d,p) method.

Structure	E_{stab}^{a}/ kcal mol^{-1}	E_{rel}/ kcal mol^{-1}	E_{rel}^{ZPE}/ kcal mol^{-1}	q_{sM} (a.u.)	S
$\mathbf{2}_{HS}$	6.8	12.9	10.8	2.75	3/2
$\mathbf{2}_{LS}$	19.7	0.0	0.0	0.01	1/2
$\mathbf{3}_{HS}$	8.1	6.7	4.4	2.67	3/2
$\mathbf{3}_{LS}$	14.8	0.0	0.0	0.03	1/2
$\mathbf{3}_{MECP}$	4.0	10.8	–		–
$\mathbf{4}_{HS}$	14.9	2.0	0.2	2.69	3/2
$\mathbf{4}_{LS}$	16.9	0.0	0.0	0.07	1/2
$\mathbf{5}_{HS}$	19.3	–5.7	–7.8	2.65	3/2
$\mathbf{5}_{LS}$	13.6	0.0	0.0	0.00	1/2

[a]As calculated relative to the isolated molecules of diketonate and α-diimine (see Online Supplementary Materials, Table S1).

Figure 1 illustrates the results of the calculations of electrically neutral α-diimine ligands **L** in the most energetically preferred *trans*-form. The calculated geometry of parent ligand **L** (R^1 = H) is consistent with the experimental data.[11] The replacement of hydrogen atoms by methyl groups negligibly affects the ligand geometry. According to the calculations of the complexes of diiminosuccinonitriles (Table 1), the ground states of the adducts of $Co^{II}(acac)_2$ are represented by low-spin structures $\mathbf{2}_{LS}$ and $\mathbf{3}_{LS}$, in which spin density is mainly localized at the ligands. This finding points to the occurrence of electron transfer from the metal to the redox-active ligand as a result of complexation. Small energy difference between low-spin isomer $\mathbf{3}_{LS}$ and compound $\mathbf{3}_{HS}$ with its Co^{II} centre in a high-spin state makes it possible to expect the VT behavior of adduct **1** (R = R^1 = Me).

In order to evaluate the energy barrier to the expected VT rearrangement, the minimal energy crossing point (MECP) on the seam of the intersecting doublet and quartet potential energy surfaces has been located. Corresponding compound $\mathbf{3}_{MECP}$ is energetically disfavored, as compared with low-spin isomer $\mathbf{3}_{LS}$, by 10.8 kcal mol^{-1}. This result is consistent with the experimental energy barriers of valence tautomeric rearrangements.[17,18]

As follows from Table 1, $\mathbf{3}_{MECP}$ is stabilized with respect to the isolated molecules of $Co^{II}(acac)_2$ and the diimine (R^1 = Me), which indicates that the intramolecular spin-forbidden VT rearrangement reaction can proceed without interference with a competitive process, the dissociation of the complex into the initial components.

The results of the calculations on the adducts containing electron-withdrawing substituents in both the redox-active ligand and the diketonate (hfacac) (Figure 2) showed that the low-spin

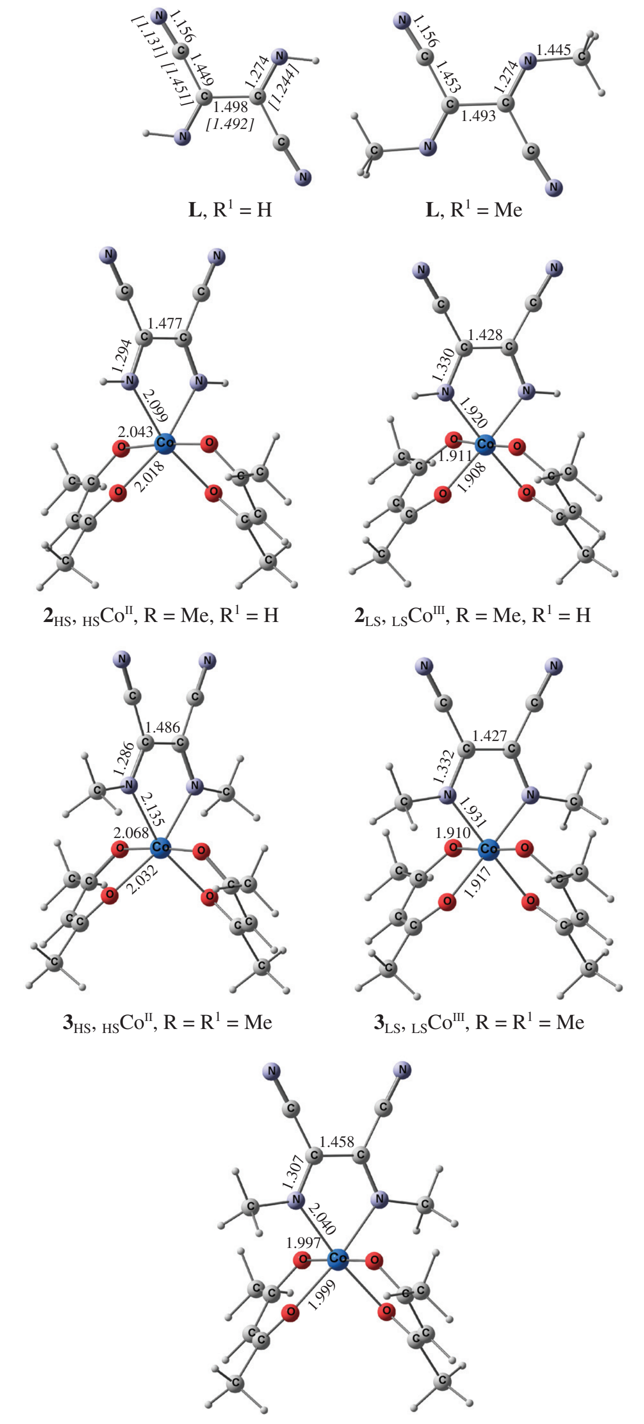


Figure 1 Optimized geometries of ligands **L** (R^1 = H, Me) and adducts **1** (R = Me; R^1 = H, Me), calculated by the DFT B3LYP*/6-311++G(d,p) method. Italicized figures given in brackets refer to X-ray determined parameters.[11] Hereinafter, the bond lengths are given in Å.

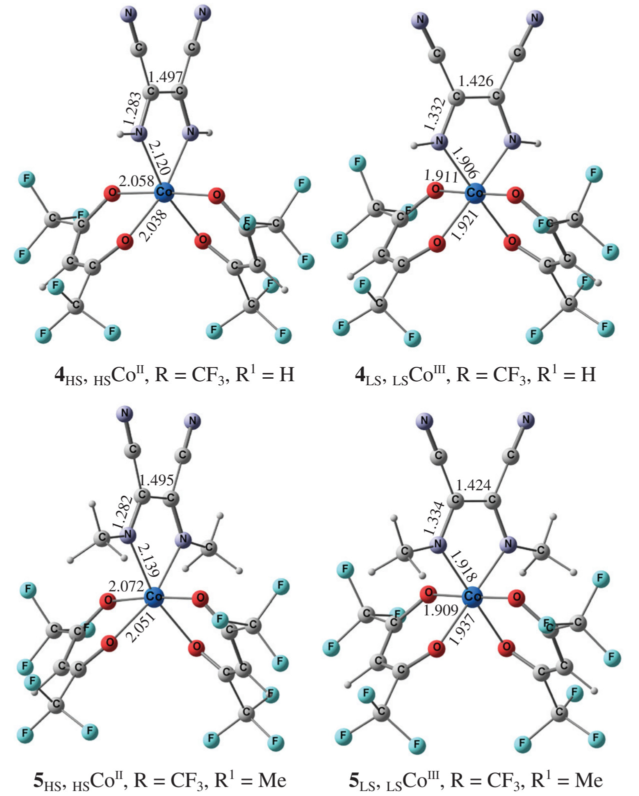


Figure 2 Optimized geometries of adducts **1** (R = CF$_3$; R^1 = H, Me), calculated by the DFT B3LYP*/6-311++G(d,p) method.

structure of $\mathbf{4}_{LS}$ (R = CF$_3$, R^1 = H) is by only 2 kcal mol^{-1} energy preferred compared with the high-spin electromeric form. Such a low energy difference between the two electronic isomers allows one to expect that, in a solution, these complex species occur in equilibrium, which would complicate the detection of valence tautomerism. The replacement of NH hydrogens in diimine **L** by methyl groups (R = CF$_3$, R^1 = Me) leads to a 5.7 kcal mol^{-1} energy preference of high-spin form $\mathbf{5}_{HS}$ over the low-spin one. Therefore, we concluded that the steric hindrances induced by the alkyl groups destabilize the low-spin state forms and obstruct VT processes in the test adducts.

The DFT UB3LYP*/6-311++G(d,p) calculations showed that the interaction of Co^{II} diketonates with diiminosuccinonitriles leads to the formation of thermodynamically stable adducts due to intramolecular metal to ligand electron transfer. The pseudo-octahedral structure of the coordination site of all the adducts has been predicted. Changeable magnetic properties, manifested as a result of intramolecular redox processes, are expected in the adduct of Co^{II}(acac)$_2$ with methyl-substituted diiminosuccinonitrile. The insertion of electron-withdrawing CF$_3$ groups into the diketonate increases the stability of the high-spin forms and inhibits valence tautomeric rearrangements.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2014.11.003.

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