

Molecular design of the valence tautomeric mixed-ligand adducts of Co^{II} diketonates with redox-active ligands

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A new concept of the structural design of valence tautomeric (VT) systems involves a search for stable adducts of tetracoordinate transition metal complexes with bidentate redox-active ligands that meet the conditions of appropriate energy gaps and energy barriers between the electromeric forms of the complexes. A series of prospective VT systems has been found out based on the DFT/B3LYP*/6-311++G(d,p) theoretical modeling of their structures and properties. Intramolecular electron transfer between metal and ligand centers in the dinuclear VT 2:1 adducts of Co^{II} diketonates and redox-active tetradentate di-*o*-quinones is proposed as a new promising mechanistic paradigm for the design of 2-qubit molecular systems.

Introduction

During the last decades, considerable interest has grown in the synthesis and characterization of new functional materials on the basis of bistable molecular organic, organometallic and metal coordination compounds. This is due to the fact that the molecules and molecular systems existing in two stable (or metastable) electronic states under the control of an external stimulus can serve as the switching elements and key sub-structures of dynamic nanoscale materials for future technologies. For an efficient molecular switch, a rearrangement between its distinct states should be accompanied by a measurable and well-detected change of the properties. Among the bistable compounds,¹ metal coordination complexes are distinguished with the ability of responding to an external stimulus (temperature, light or pressure) by changes in their magnetic properties caused by spin-state transitions. This property of metal complexes and

the possibility of its proper modulation *via* a judicious choice of metal ions and ligands make these compounds especially promising for applications in molecular electronics and spintronics, data storage and display devices.² Another very exciting prospect in metal coordination chemistry is to manipulate electronic spins within magnetic complexes for performing quantum logic operations.

The most important mechanism that governs the magnetic bistability of transition metal complexes triggered by temperature, light irradiation, pressure or electric field relates to a spin crossover (SCO) phenomenon and implies an electron spin flip between a low-spin ground state and a high-spin excited state in d^4 – d^7 complexes of the first transition series.^{3–5} A number of ramifications of the intrinsic SCO mechanisms that include light-induced excited state spin trapping (LIESST),⁶ ligand driven light-induced spin change (LD LISC)⁷ and ligand driven coor-



Vladimir I. Minkin[†] received his Candidate (PhD) and Dr. Sci. (Chemistry) degrees from Rostov-on-Don State University. In 1967, he was appointed Professor at the same University and held the position of head of the Institute of Physical and Organic Chemistry (IPOC) at Rostov (since 2006 Southern Federal) University in 1981–2012. In 2012, he took the position of Research Adviser of Southern Federal University, while keeping the positions of head of a division of IPOC and deputy to the President of the Southern Research Center of the Russian Academy of Sciences (RAS). He was a visiting professor or visiting scientist at the Havana, Strathclyde, Queen's, Cornell, Florida, Regensburg, Marseille and Humboldt Universities, received his Dr.h.c. degrees from the Mediterranean University of Aix-Marseille and several Russian Universities. In 1990, he was elected a corresponding member and, in 1994, a full member of RAS. He is also a foreign member of Italian Academy of Sciences 'Gioennia'. Among his awards are the

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[†] The Editorial Board and Staff of Mendeleev Communications take an opportunity to congratulate Academician V. I. Minkin on the occasion of his 80th birthday and wish him all the very best.

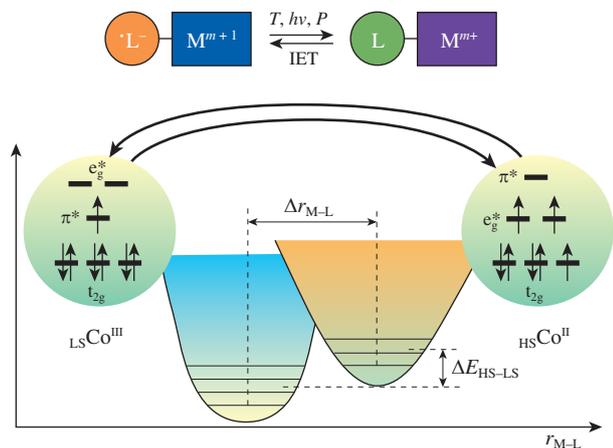
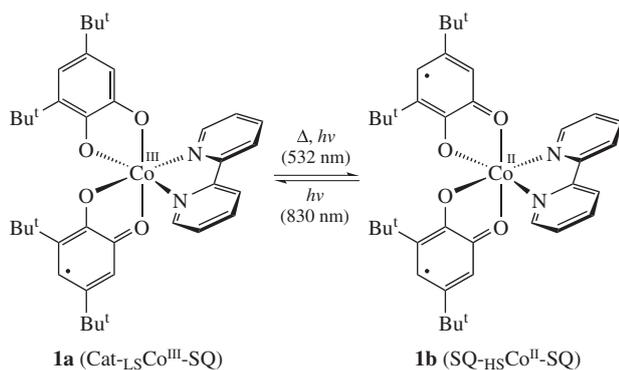
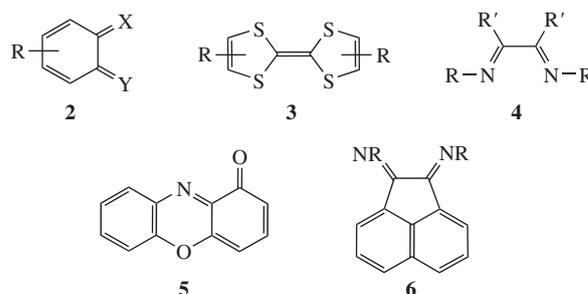


Figure 1 Schematic VT mechanism of spin-state switching as a consequence of reversible intramolecular electron transfer between a metal ion (exemplified by Co^{II}/Co^{III}) and redox-active ligand L.

dination-induced spin state switching (LD CISS)⁸ effects are known. Currently, more than a thousand metal complexes, particularly prevalent in iron chemistry, have been reported to display a magnetic behaviour regulated by external stimuli. Spin crossover is essentially a vibronic and typically solid-state phenomenon brought about by cooperative intermolecular interaction between a large number of spins. Electron transfer within a molecule as a purely intramolecular process is in the root of another general mechanism of the bistability of transition metal coordination compounds – valence tautomerism.^{9–12} Valence tautomeric (VT) rearrangements occur between the isomers of complexes formed by redox-active [so-called non-innocent (ni)] ligands, and they are driven by electron transfer between a metal ion and the ligand. This process leads to cumulative changes in the spin state and the valence state (oxidation number) of the transition metal ions linked to the ligand, whereas in the course of SCO transformations, the transition metal ions attain different spin states while keeping the same oxidation number. To display the VT behaviour, the energy levels of the frontier molecular orbitals of the ligand and metal valence electronic levels must be particularly close in energy (Figure 1). Such an arrangement is specifically favorable for cobalt complexes with *o*-quinone ligands, for which the equilibrium between two redox isomeric forms had been observed for the first time in solution and in the solid state by Pierpont and Buchanan¹³ and then studied in detail by Abakumov and Cherkasov with co-authors.¹⁴ For this complex, low-spin (LS) tautomer **1a** favored at low temperature displays a thermally induced VT transition to the high-spin (HS) form with $T_{1/2}$ values (temperature at which equal amounts of the two tautomers exist) of 275 K in solution and 325 K in the solid state. The effective magnetic moment of the complex, $\mu_{\text{eff}} = 1.73\mu_{\text{B}}$ (5 K) characteristic of the LS form increases up to $4.60\mu_{\text{B}}$ when heating a solid sample to 400 K. The rearrangement in both directions can also be driven by illumination with visible light.¹⁵



Apart from *o*-quinones and their imines, which remain the most frequently employed redox ligands, other organic, organometallic and even inorganic compounds are known to form redox-isomeric pairs of complexes with the appropriate metal ions, thus creating ambiguity as to the oxidation state descriptions. Some of the most actively employed redox-active organic ligands, for which the term ‘noninnocent’ as explained by way of contradiction has been coined by Jørgensen,¹⁶ are compounds **2–6**. In many biologically important systems, such as hemoglobin and nitric oxide synthase, the noninnocent ligands serve as the redox-active cofactors cooperating with metal centres in electron transfer and substrate activation processes.^{17–19}



Note that the use of the term ‘valence tautomerism’ when applied to transition metal compounds is ambiguous. According to the IUPAC Gold Book²⁰ the term ‘valence tautomerism’ is reserved for organic chemistry and determined as ‘rapid and reversible isomerizations involving the formation and rupture of single and/or double bonds’. No making and breaking bonds take place in the fast and reversible rearrangements of VT transition metal complexes caused by intramolecular electron transfer (IET) between a metal centre and a ligand. The interconverting species are, therefore, not classical constitutional, but electronic isomers for which case the terms electromers and electromerism have been recently proposed and already widely accepted.

As associated with large variations in the optical and magnetic properties of bistable metal complexes, the VT phenomenon has attracted considerable interest as a potential basis for molecular electronic and spintronic²¹ devices, because of which the synthesis and VT behaviour of complexes with transition metals (V, Mn, Fe, Co, Ni, Cu, Ru and Yb) and redox-active ligands were extensively studied and amply reviewed.^{9–12,22} The general and most usable way of the construction of VT complexes consists in the coordination of a transition metal ion to two bidentate redox-active ligands. It is realized in the 1:2 structures of cobalt complexes **1**, in which the bipyridine molecules serve as ancillary ligands completing the coordination sites of the central atoms to an octahedral environment. Another less common approach to the VT systems implies the preparation of 1:1 complexes as stable adducts of a paramagnetic tetracoordinate transition metal complex with a sterically suitable electrically neutral bidentate redox-active ligand. Whereas the VT behaviour of 1:2 complexes with bidentate ligands is due to electronic transfers between the catecholate (Cat) and semiquinone (SQ) forms of the ligands, in the mixed-ligand adducts, the electron transfer occurs between the semiquinone and the electrically neutral quinone (Q) isomeric forms. The two versions of the structural design of VT complexes are shown in Figure 2. This review systematizes the results of our computational studies of the structures, rearrangements and possible applications of 1:1 mixed-ligand cobalt complexes with various redox-active ligands aimed at finding novel VT systems and elucidation of the electronic and structural factors responsible for their VT behaviour.

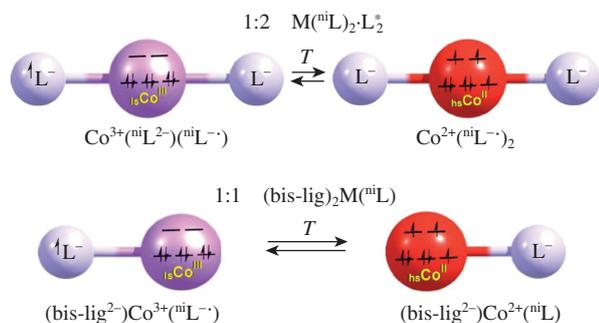


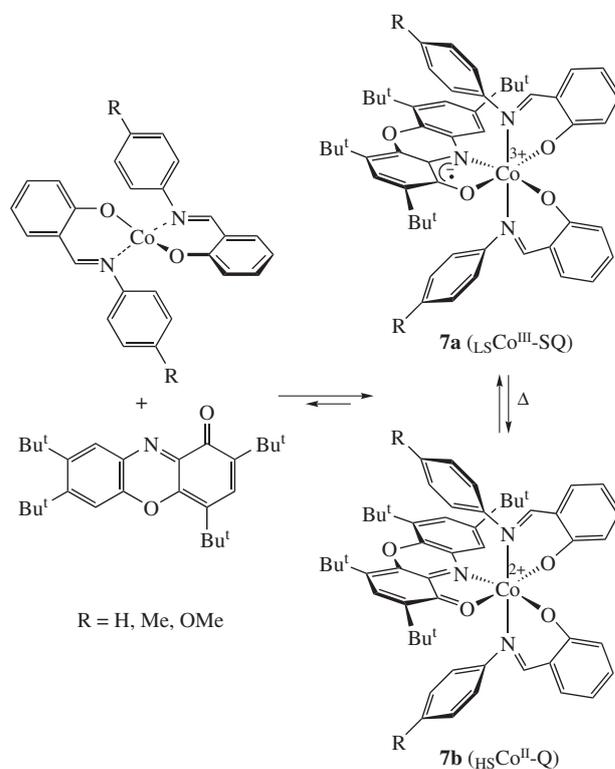
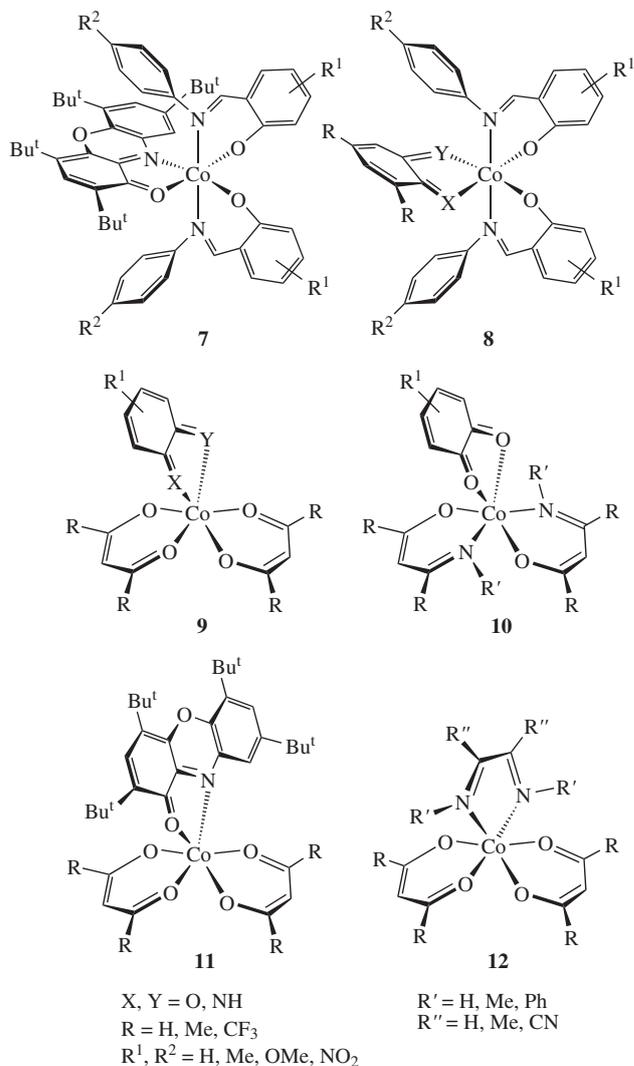
Figure 2 Two structural designs and mechanisms of the intramolecular electron transfer of the VT complexes of cobalt.

As distinct from a broad variety of 1:2 VT complexes, the assortment of 1:1 complexes is mostly confined to the ionic $[\text{Co}(\text{N}_4\text{L})(\text{diox})]^+$ compounds, in which diox is an *o*-quinone derivative and N_4L is a tetradentate ancillary ligand.²³ A possibility of the practically unlimited expansion of the array of potentially VT 1:1 complexes consists in the preparation of the adducts of redox-active ligands and tetracoordinate bis-chelate complexes of d^4 – d^7 metals. The first examples of such structures, whose important advantage is their electric neutrality, were given by the adducts of Co^{II} and Fe^{II} salicylalethylenediamines with *o*-benzoquinone, 1,2-naphthoquinone and 9,10-phenanthroquinone.²⁴ The formation of these and later studied associates of the square-planar Co^{II} complexes with *o*-quinones²⁵ is accompanied by intramolecular electron transfer from the metal ion to the redox-active ligand yielding ${}_{\text{LS}}\text{Co}^{\text{III}}\text{-SQ}$ structures. The IET reactions determine the formation of adducts of Ru^{II} diketonates with *o*-quinones, their imines and thioimines^{26–28} and with 1,4-diazabuta-1,3-diene.²⁹ The structures of the prepared mixed-ligand complexes were thoroughly studied in a solid state and solution by X-ray diffraction, ESR and magnetic measurements. In no case the coexistence of another electromeric form conjugated with the ground state low-spin form was observed and valence tautomerism was reported for none of the synthesized adducts.

Mixed-ligand adducts of tetracoordinate transition metal complexes with redox-active ligands. Design of valence tautomeric 1:1 systems

The inability of the above adducts to exhibit VT properties is explained by the excessive stabilization of their low-spin SQ electromeric forms with respect to their partnership high-spin forms. Therefore, we have formulated the task of a search for the mixed-ligand transition metal complexes with the energy close low-spin and high-spin electromeric forms divided by thermally surmountable energy barriers. To evaluate these parameters determining the possible VT behaviour of complexes, systematic density functional theory (DFT) calculations of the critical parts of the potential energy surfaces (PESs) of the ground and lowest excited electronic states were performed for a series of adducts **7–12** formed by cobalt diketonates, bis(aminovinylketonates) and bis(salicylaldiminates) with the following redox-active ligands: *o*-benzoquinones and their imines, α -diimines and phenoxazinone.^{30–34} Based on the predictions made on the properties of these compounds and their other metal analogues, systematic studies have been commenced on the preparation and investigation into their possible and dynamic behaviour.^{35–37}

The interaction of Co^{II} bis(salicylaldiminates) with redox-active 2,4,6,8-tetra(*tert*-butyl)phenoxazin-1-one gives rise to well crystallized adducts **7** which are stable in air; low-spin radical-anions **7a** were characterized using X-ray crystallography and magnetic measurements.^{36,37} In the solid state, the effective mag-



netic moment of **7a** is $1.93\mu_{\text{B}}$, and it remains almost unchanged in the temperature range of 77–298 K. In a toluene- d_6 solution,

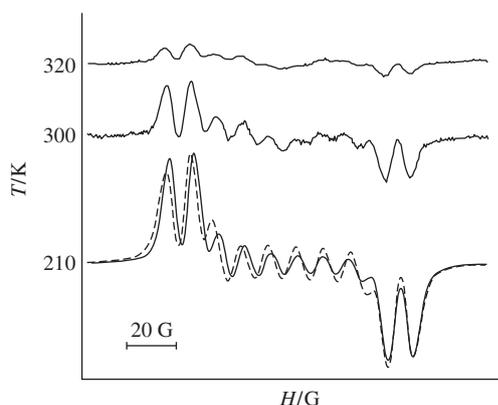


Figure 3 ESR spectra of complex **7a** ($R = \text{Me}$) in a toluene solution at different temperatures ($a^N = 15.4 \text{ G}$, $a^{\text{Co}} = 12.0 \text{ G}$, $g = 1.9936$) and the simulated ESR spectrum at 210 K (dashes).

raising the temperature from 263 to 333 K leads to reversible changes in the magnetic moment from $1.89\mu_B$ to $2.67\mu_B$, which is indicative of the formation of ~20% high-spin electromeric form **7b** at the elevated temperature. This tendency is also reflected by the temperature-variable ESR spectrum of the complex (Figure 3), which exhibits a gradual decrease in the concentration of radical anion **7a** with temperature.³⁷ The qualitative interpretation of the dynamic processes is complicated by the occurrence of an interfering reaction of adduct dissociation to the starting components at higher temperatures, detected by the appearance of the characteristic bands of phenoxazinone in the electronic absorption spectrum (Figure 4).³⁷ To eliminate this undesired reaction, it is necessary to substantially increase the stabilization energy of the adduct. Since the VT rearrangements belong to spin-forbidden reactions, their kinetics is evaluated on the basis of the energy and position of minimum energy crossing points (MECPs), which are the lowest energy points on the seam of two intersecting PESs of differing multiplicity. MECP values should be considered as the nonadiabatic equivalents of energy barriers, for which these are the upper limit values.³⁸ The DFT calculations performed for the **7a** \rightleftharpoons **7b** rearrangement resulted in the structure of MECP lying by $12.4 \text{ kcal mol}^{-1}$ higher than the ground state low-spin structure of **7a**. This value nearly matches the range of the experimentally determined values for the VT rearrangement of cobalt complexes,^{23,39–41} but in the case of **7a** \rightleftharpoons **7b** rearrangement the corresponding thermal energy barrier cannot be attained because the stabilization energy of an electromeric form of adduct

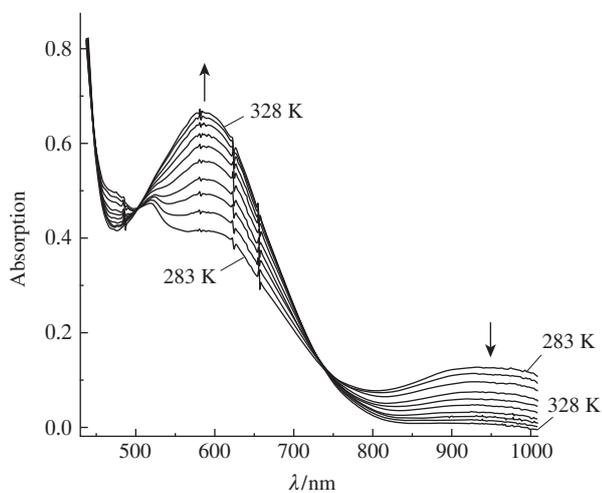


Figure 4 Electronic absorption spectra of complex **7** ($R = \text{Me}$) in a toluene solution ($C = 8.3 \times 10^{-5} \text{ mol dm}^{-3}$) in a temperature range from 283 to 328 K with an increment of 5 K. Phenoxazinone has a maximum at 950 nm.

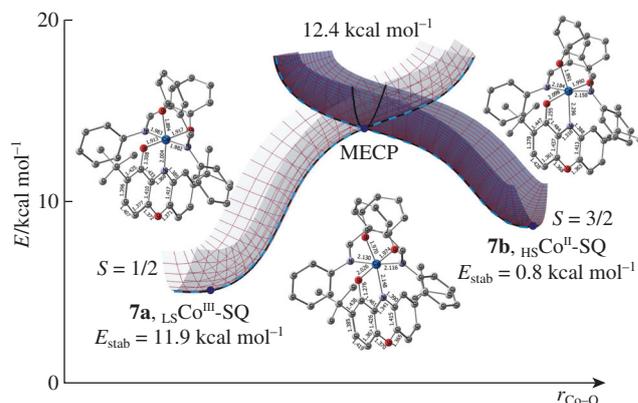


Figure 5 Energy profile of the spin-forbidden rearrangement of mixed-ligand complex **7** ($R^1 = R^2 = \text{H}$). The calculations were carried out by the DFT/B3LYP*/6-311++G(d,p) method for the structure stripped of 4- and 6-*tert*-butyl groups. The structure of MECP is shown in the seam of the intersecting doublet and quartet PESs. For the sake of clarity, no hydrogen atoms are shown.

7 is much lower than the value needed for its overcoming. This situation is illustrated in Figure 5.³⁷

The results of the experimental and computational study of the **7a** \rightleftharpoons **7b** rearrangement clarify a necessary condition for the mixed-ligand complexes with the expected VT behaviour: they should be stable with respect to dissociation into the components. This and other requirements, which define the extreme values of the thermally attainable energy barrier and energy gap between the interconverting electromers and should be met by the adducts of tetracoordinate transition metal complexes with redox-active ligands possessing the properties of molecular switches with changeable magnetic properties in various media environments, are given by the relationships

$$\begin{aligned} E_{\text{stab}} &> \text{MECP}; \\ \text{MECP} &\leq 10\text{--}12 \text{ kcal mol}^{-1}; \\ \Delta E_{\text{HS-LS}} &\approx k_B T. \end{aligned} \quad (1)$$

With the goal of the molecular modeling of mixed-ligand complexes meeting conditions (1) and having, thus, a potential to exhibit VT behaviour, we studied the adducts formed by cobalt diketonates with typical noninnocent ligands, *o*-benzoquinone and its mono- and diimines **9**³² (Tables 1–3).

Table 1 shows that the stabilization energies of the adducts of Co^{II} bis(malonate) ($R = \text{H}$) and bis(acetylacetonate) ($R = \text{Me}$) are too small, whereas the energy gaps between the low- and

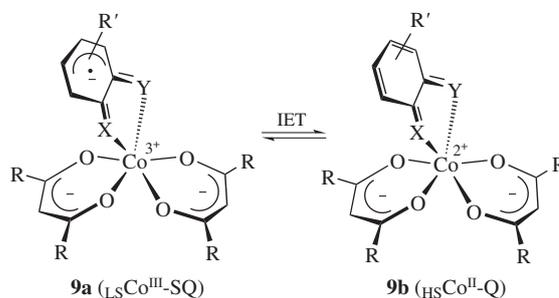


Table 1 The DFT/B3LYP*/6-311++G(d,p) evaluation³² of the influence of substituents R on the energy parameters of the **9a** \rightleftharpoons **9b** ($X = Y = \text{O}$, $R' = \text{H}$) rearrangement.

R	$^{\text{HS}}E_{\text{stab}}/\text{kcal mol}^{-1}$	$\Delta E_{\text{HS-LS}}/\text{kcal mol}^{-1}$	MECP/ kcal mol^{-1}
H	7.8	15.0	15.2
Me	7.4	15.0	15.3
CF_3	16.2	6.8	10.8

Table 2 The DFT/B3LYP*/6-311++G(d,p) evaluation³² of the influence of the ligating centres X and Y on the energy parameters of the **9a** \rightleftharpoons **9b** (R = CF₃, R' = H) rearrangement.

X, Y	^{HS} E _{stab} /kcal mol ⁻¹	ΔE _{HS-LS} /kcal mol ⁻¹	MECP/kcal mol ⁻¹
O, O	16.2	6.8	10.8
O, NH	25.5	3.5	9.5
NH, NH	34.1	0.6	13.9

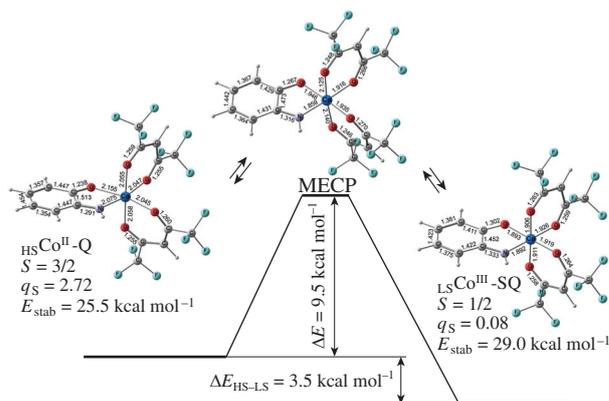
Table 3 The DFT/B3LYP*/6-311++G(d,p) evaluation³² of the influence of the bulky substituents R' = 3,5-Bu₂ on the energy parameters of the **9a** \rightleftharpoons **9b** (R = CF₃, R' = H) rearrangement.

X, Y	^{HS} E _{stab} /kcal mol ⁻¹	ΔE _{HS-LS} /kcal mol ⁻¹
O, O	19.4	2.5
O, NH	28.0	-0.5
NH, NH	37.3	-2.5

high-spin forms are too large. The excessive stabilization of the low-spin electromeric forms and the low stability of high-spin forms with respect to the thermally induced splitting of the redox-active ligand eliminated these adducts as candidates for the VT compounds. At the same time, the energy gap between the ground state low-spin and high-spin forms may be substantially narrowed by the introduction of electron-accepting trifluoromethyl groups capable of withdrawing a part of the electron density from the radical-anion semiquinonate form of the coordinated redox-ligand into the diketonate moieties. The relative energy (10.8 kcal mol⁻¹) calculated for the MECP structure of the adduct of bis(hexafluoroacetylacetonate) Co^{II}/Co^{III} with *o*-benzoquinone is very close to the activation energies reported for VT cobalt complexes^{23,39–41} and matches conditions (1). The further optimization of the energy parameters of adducts **9** in the direction dictated by relationships (1) is achieved *via* the replacement of ligating oxygen centers in the redox-active ligand by more electron donor nitrogen centres. Table 2 illustrates a drastic increase in the stabilization energy of the adducts and a sharp decrease in the energy gap between the low- and high-spin forms due to the relative stabilization of the latter in the mixed-ligand complexes formed by bis(hexafluoroacetylacetonate) Co^{II} with *o*-benzoquinone mono- and diimines. The values of E_{stab} calculated for these adducts are much greater than energy barriers (MECP) against their thermal rearrangements. Therefore, mixed-ligand adducts **9** (R = CF₃, X and/or Y = O, NH) may possess the properties inherent in thermally driven valence tautomeric systems including (i) stability against thermal dissociation, (ii) energy preference of the low-spin electromer and (iii) thermally attainable energy barrier to intramolecular electron transfer between the electromeric forms, which determines the mechanism of valence tautomeric rearrangements. The energy profile and geometries of the structures involved into the VT rearrangement of one of these systems are pictured in Figure 6.³²

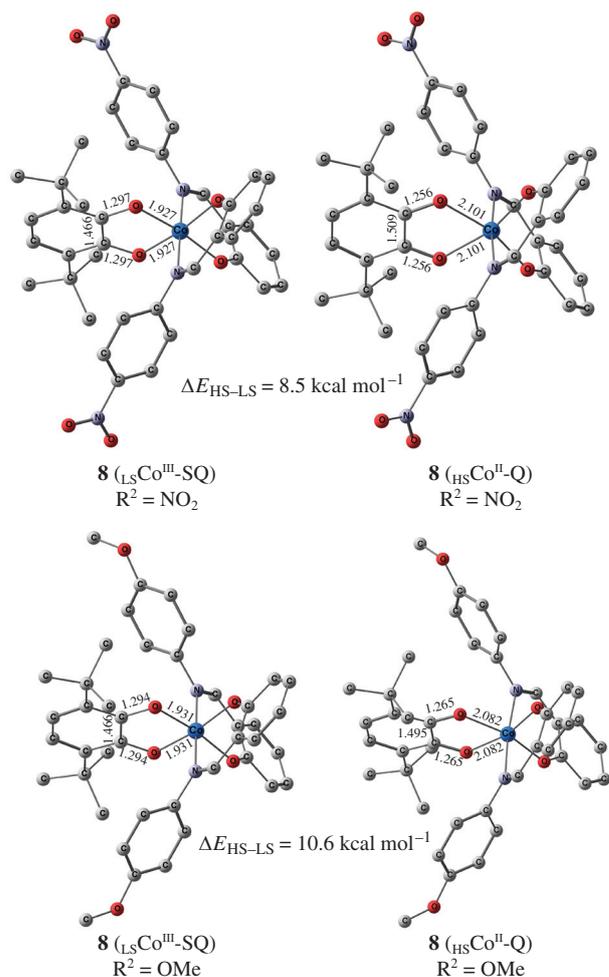
Table 3 indicates that even subtle structural modifications in the ancillary ligands may perceptibly affect the energy parameters of VT rearrangements in mixed-ligand adducts **9**. From a comparison with the data of Table 2, it follows that the bulky alkyl groups in the quinone fragments of the adducts may lower the energy level of the high-spin forms with respect to the low-spin ones by ~3 kcal mol⁻¹, which is sufficient for the inversion of their relative stability.

Other examples of the extreme sensitivity of the relative stability and magnetic properties of the electromeric forms of potentially VT systems have been found within the family of adducts **8** (Figure 7). The substituents in the aryl rings of the ancillary ligand, although far distant from the coordination site,

**Figure 6** Energy profile of the VT rearrangement of adduct **9** (R = CF₃, X = O, Y = NH), as calculated by the DFT/B3LYP*/6-311++G(d,p) method.

notably affect the energy gap between the electromers of the complexes.

By the introduction of electron-donor substituents R¹ and R² into the aryl rings, it becomes possible to notably vary the energy gap between the low- and high-spin states of the complexes. Much sharper is the effect of stripping two arene rings annulated to aminovinylketonate fragments in **8** when passing from adducts **8** to **10**. The DFT calculations performed for compounds **10**³³ have shown that, regardless of the ligating centres (O, NH) and substituents R, the ground state of the complexes is represented by their low-spin radical-anion forms separated from the corresponding high-spin forms by the energy gaps significantly greater

**Figure 7** Geometry parameters of electromeric forms of adducts **8** (R² = NO₂, OMe) according to the DFT/B3LYP*/6-311++G(d,p) calculations.

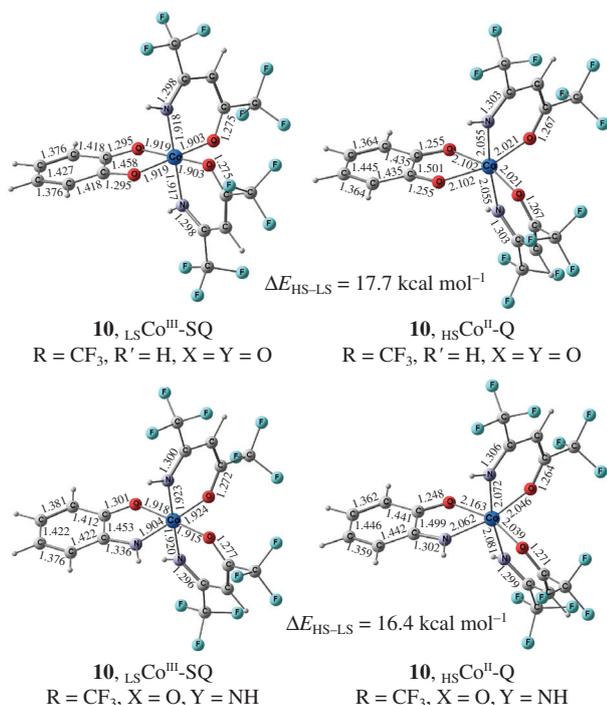


Figure 8 The DFT/B3LYP*/6-311++ G(d,p) calculated geometries and energy parameters of two complexes **10**.

than the critical value of $\Delta E_{\text{HS-LS}}$ (Figure 8).³³ It may be concluded that 1:1 mixed-ligand complexes **10** have no prospect as the VT systems. This conclusion is consistent with the results of an experimental study²⁵ of the structurally similar adducts of cyclic Co^{II} bis(aminovinylketonates) and *o*-quinones that occur only as low-spin electromeric forms.

A redox-active ligand serves as the principal component of the mixed-ligand adducts and is the main structural factor that determines the capability of an adduct to display the VT behaviour. By a judicious choice of redox-active and ancillary ligands, one can deliberately tune up the electronic configuration of the mixed-ligand complex to either low- or high-spin state structure. An illustrative example can be found within the series of adducts **11**. Whereas the complexes formed by cobalt diketonates with quinones **9** generally strongly prefer the low-spin structures with SQ ligands, phenoxazinone having a more negative reduction potential and Co^{II} bis(hexafluoroacetylacetonates) **11** (R = CF₃) form the high-spin adducts. The X-ray determined and DFT calculated structures of such an adduct are shown in Figure 9. In **11** (R = Me), the replacement of electron-withdrawing trifluoromethyl groups in the diketonate moiety by electron-releasing methyl groups inverts the energy levels of the low-spin and high-spin electromers: the calculated energy gap is $\Delta E_{\text{LS-HS}} = -6.0$ kcal mol⁻¹.

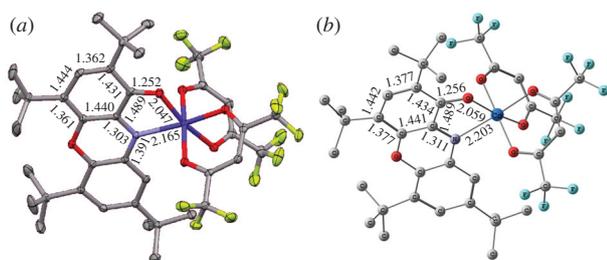


Figure 9 Molecular structure of a mixed-ligand adduct of Co^{II} bis(hexafluoroacetylacetonate) and 2,4,6,8-tetra(*tert*-butyl)phenoxazin-1-one **11** as determined by (a) X-ray crystallography and (b) DFT/B3LYP*/6-311++G(d,p) calculations. The electronic ground state is represented by the high-spin HS Co^{II}-Q form. $E_{\text{stab}} = 28.7$ kcal mol⁻¹; $\Delta E_{\text{HS-LS}} = 8.0$ kcal mol⁻¹.

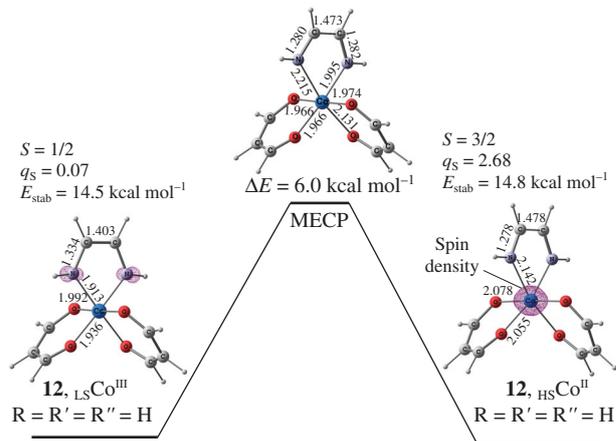


Figure 10 Energy profile of the VT rearrangement of adduct **12** (R = R' = R'' = H) as calculated by the DFT/B3LYP*/6-311++ G(d,p) method.

As found by the DFT/B3LYP*/6-311++G(d,p) calculations, a combination appropriate for the formation of the mixed-ligand cobalt complexes with VT properties can be constructed based on Co^{II} diketonates and the redox-active diimines of glyoxal³¹ and diiminosuccinonitriles.³⁴ The low- and high-spin electromers of stable adduct **12** (R = R' = R'' = H) are nearly energy equivalent ($\Delta E_{\text{HS-LS}} = -0.3$ kcal mol⁻¹) and the value of MECP is as low as 6.0 kcal mol⁻¹. Conditions (1) are totally satisfied; thus, it would be expected that this complex is prone to thermally driven VT rearrangements. Figure 10 shows the computed energy profile of this rearrangement.³¹ The necessary energy balance is very squeamish, and it can be easily affected by the effects of substitution. The results of the calculations for adducts **12** containing electron-withdrawing substituents in both redox-active ligand and diketonate showed that the low-spin structure of **12** (R = CF₃, R' = H and R'' = CN) is by 2 kcal mol⁻¹ energy favorable compared with the high-spin electromeric form, but the replacement of NH hydrogens in the diimine by methyl groups (R = CF₃, R' = Me and R'' = CN) leads to a 5.7 kcal mol⁻¹ energy preference of the corresponding high-spin form. The steric hindrances induced by the alkyl groups destabilize the low-spin state forms and obstruct VT processes in the adducts.

The central element of the mixed-ligand adducts is, certainly, the metal ion and, not surprisingly, the properties of these complexes most drastically depend on the metal. In this regard, especially promising switching properties might be expected in the Fe^{II} analogues of the above cobalt adducts. The reason for this is that Fe^{II}-based compounds have six *d*-electrons and one of the electromeric forms in the possible equilibrium has a closed

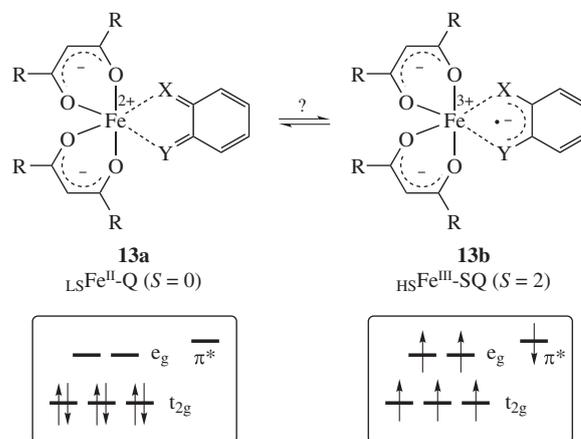


Figure 11 Theoretically envisaged Fe^{II}/Fe^{III} VT rearrangement of the adducts of iron diketonates with *o*-quinone derivatives.

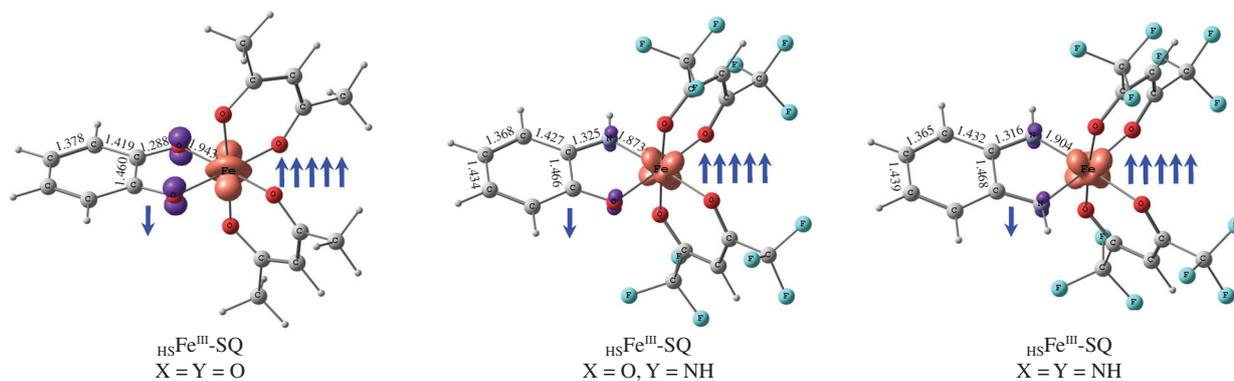


Figure 12 Ground state electromeric forms of Fe^{II} bis(hexafluoroacetylacetonate) adducts **13**: geometry parameters and distribution of spin density according to the data of DFT/B3LYP*/6-311++G(d,p) calculations.

electronic shell and is diamagnetic. It is well known that SCO transitions in Fe^{II} complexes are especially pronounced, abrupt and beneficial for robust and prompt switching.^{42,43} Therefore, Fe^{II} VT systems **13** may serve as molecular switches with a very sharp contrast of the magnetic parameters (Figure 11). However, the currently available information on the thermally induced VT rearrangements of Fe^{II} complexes is limited by a few cases of specific molecular systems comprised of ferrocene moieties and the perchlorotriphenylmethyl radical.⁴⁴ The calculations carried out for the iron analogues of cobalt complexes **9** demonstrated that the low-spin Fe^{II} form of the adducts is strongly destabilized with respect to the Fe^{III}-SQ form (Figure 12). The calculated energy gaps with low-spin forms **13a** leave no chance to observe the VT behaviour of iron(II) complexes **13**.

In contrast with the iron analogues, mixed-ligand ruthenium complexes formed as the adducts of *o*-quinones with ruthenium bis(acetylacetonates) were synthesized and studied in detail.^{26–28,45–48} Adducts **14** and **15** (Figure 13) occur in the SQ electromeric trivalent ruthenium form with an electron transferred from the metal centre to the noninnocent ligand. Note that the essential values for this assignment were not magnetic, but the geometry parameters of the complexes including the charac-

teristic bond alternancy within the nonaromatic six-membered rings and C–O bond lengths in the quinone moieties (~1.28 Å). In general, the combination of Ru^{III} with semiquinone-type radical ligands results in almost maximal spin-pairing and antiferromagnetic coupling, that is, to a singlet as the ground state.^{27,46} At the same time, the diminished propensity of NH-containing systems for reduction results in the preference for the ^{LS}Ru^{II}-Q⁰ configuration of complexes **15** relative to ^{LS}Ru^{III}-SQ.

We concluded that the preparation of the deliberately selected mixed-ligand 1:1 complexes of tetracoordinate transition metal with proper bidentate redox-active ligands may be regarded as a promising way to a new broad series of compounds with VT behaviour. To prepare such mixed-ligand complexes, one must carefully choose all the components to adjust (as in the jigsaw puzzle in Figure 14) the properties of the system to the narrow range of the energy parameters given by equations (1).

Dinuclear valence tautomeric adducts of Co^{II} diketonates with redox-active diquinones for the design of spin qubits

A challenging extension of the structural design of the mixed-ligand adducts with switchable magnetic properties is associated with an idea to employ the mechanism of intramolecular electron transfer between metal and ligand centres in the VT complexes formed as the electrically neutral 2:1 adducts of Co^{II} diketonates and redox-active tetradentate di-*o*-quinones for quantum information processing. The search for metal coordination compounds and their clusters containing weakly coupled (entangled) open-shell metal centres has currently drawn significant attention due to the attractive properties of electronic spins as quantum bits (qubits), primarily such as the true scalability guaranteed by the identity of molecular structures and possibilities of fine tuning spin coupling through the implication of suitable ligands.^{5,49} With regard to metal coordination compounds, the basic conditions

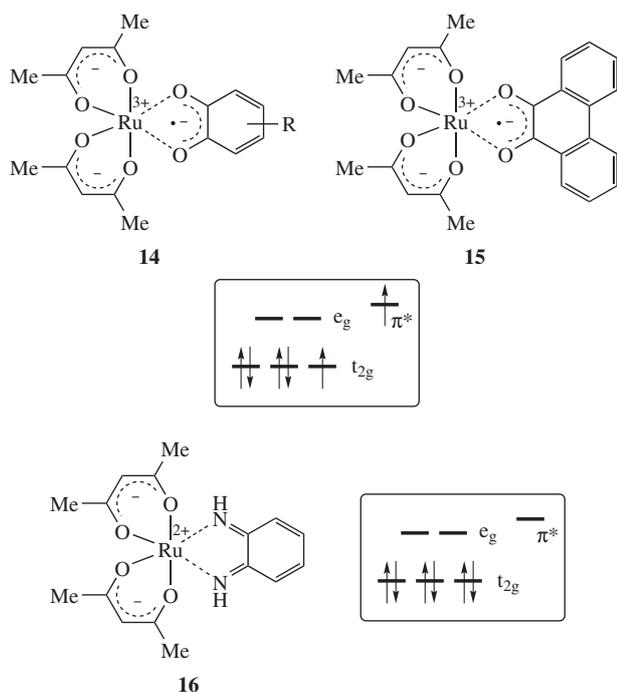


Figure 13 Stable electromeric forms and valence electronic shells of the adducts formed by ruthenium bis(acetylacetonates) as calculated by the DFT/B3LYP*/6-311++G(d,p) method.

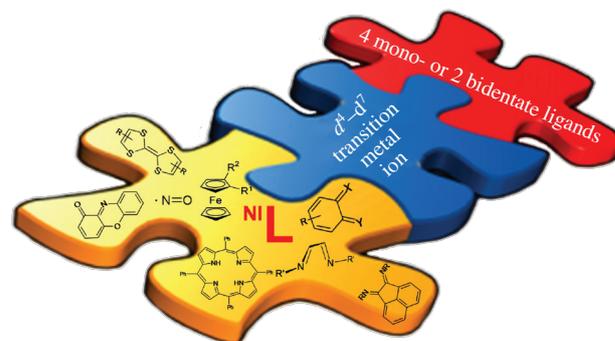
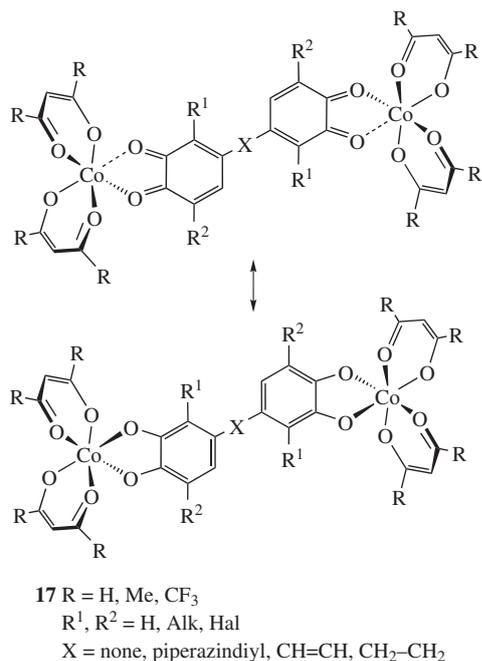


Figure 14 A picturesque (lego) representation of the layout of mixed-ligand adducts of the tetracoordinate metal complexes with redox-active ligands that should meet requirements (1) for the VT behaviour.

that a spin-based quantum gate system should fulfil known as the Di Vincenzo criteria⁵⁰ contain the following requirements: (i) the clear definition of spin states of a molecule; (ii) the rapid initialization of qubits by irradiation or cooling in an external magnetic field to convert a molecule into its ground state; (iii) a much longer decoherence time than the time needed for switching magnetic properties, whereas the coherence time should be longer than the time of switching logic gates; and (iv) the readability of spin states of each magnetic fragment of the molecule. These conditions can be met by molecular magnets formed by linking two units of transition metal cluster complexes or heterometallic rings together by proper organic or organometallic bridges.^{51–58} Such molecular assemblies contain a pair of well-defined paramagnetic metal units which can serve as prospective 2-qubit quantum gates on condition of generating weak coupling (a prerequisite for quantum entanglement) between their states.

We have suggested to consider another approach to the construction of spin qubits on the basis of multinuclear transition metal complexes, whose spin states and coupling between their paramagnetic centers can be varied in a wide range due to the externally controlled intramolecular electron transfer rearrangements of their electromeric forms. For this purpose, we computationally studied a series of dinuclear 2:1 adducts of diketonates with the derivatives of tetradentate di-*o*-quinones **17** as viable candidates for physical systems suitable for quantum computing.⁵⁹ It is desired to find the electrically neutral mixed-ligand complexes with the diminished exchange coupling to conduce to increase in the time of spin state coherence.



The most stable isomeric form of the 2:1 adducts is represented by the structures corresponding to minima on a triplet potential energy surface. Such a structure of the adduct of Co^{II} bis(malonate) with diphenyl-3,3',4,4'-diquinone **17** (X = none, R¹ = R² = H) is shown in Figure 15. The absence of spin densities at the metal atoms clearly points to the ${}_{LS}Co^{III}-(SQ-SQ)-{}_{LS}Co^{III}$ electromeric form of the adduct. The exchange coupling between the two unpaired electrons localized at the distant parts of the tetradentate ligand, $J = -1050\text{ cm}^{-1}$, is indicative of a strong antiferromagnetic interaction that should lead to the diamagnetic character of this complex. On the quintet PES, the calculations reveal a minimum corresponding to the ${}_{LS}Co^{III}-(SQ-Q)-{}_{HS}Co^{II}$ structure with differing geometries of its one-half fractions of the diquinone ligand

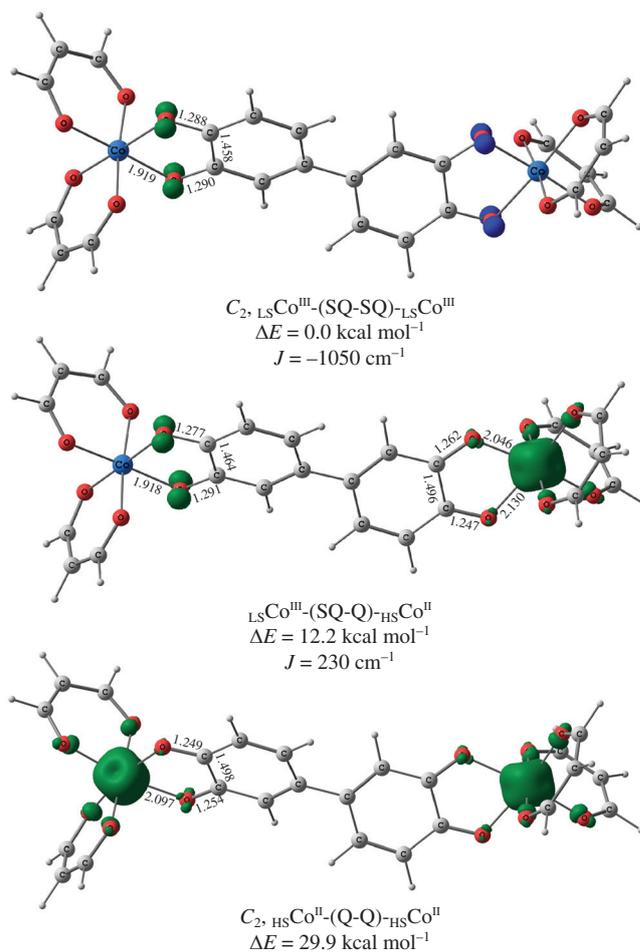


Figure 15 Optimized geometries and spin density distribution in the electromeric forms of adducts **17** (R = H, R¹ = R² = H, X = none).

(Figure 15).⁵⁹ Spin density is distributed over only one of the metal centres and the adjoined part of the ligand. The exchange coupling between the paramagnetic centres is of a ferromagnetic character ($J = 230\text{ cm}^{-1}$). The energy difference (9.3 kcal mol^{-1}) between the two electronic isomers falls into the range of values typical of dynamic VT complexes.^{23,39–41} The highest-spin ${}_{HS}Co^{II}-(Q-Q)-{}_{HS}Co^{II}$ electromer represents the most energy disfavored form of **17** (X = none, R¹ = R² = H), which is destabilized, as compared to the ground state, by $24.2\text{ kcal mol}^{-1}$. This energy gap is too large for the systems susceptible to the VT transformations. As shown above, it can be diminished by the introduction of electron-withdrawing trifluoromethyl groups into the ancillary diketonate ligands. Another problem is the strong antiferromagnetic exchange coupling of unpaired electrons in the ground state isomers and ferromagnetic coupling in the nearest excited states predicted for adducts **17** (X = none or CH=CH, R¹ = R² = H) that should lead to a very short time of coherence of the system. The reason is favorable conditions for the intermolecular communication of spin *via* π -conjugated molecular bridges in these compounds.

The ways proposed to control the strength of the interaction between paramagnetic centres incorporated into a conjugated chain in order to achieve weak magnetic communication between the spins^{56–58,60–63} are mainly based on the attenuation of the extent of conjugation between aromatic rings bridging the paramagnetic centres. We found that linkers such as X = CH₂-CH₂ and piperazindiy, which move the spin centres apart, provide for the necessary minimization of π -overlap between the two aromatic units of the diquinone ligands of complexes **17**. The rupture of a π -conjugated chain by the insertion of a dimethylene bridge into the diquinone ligand results in the sharp weakening of

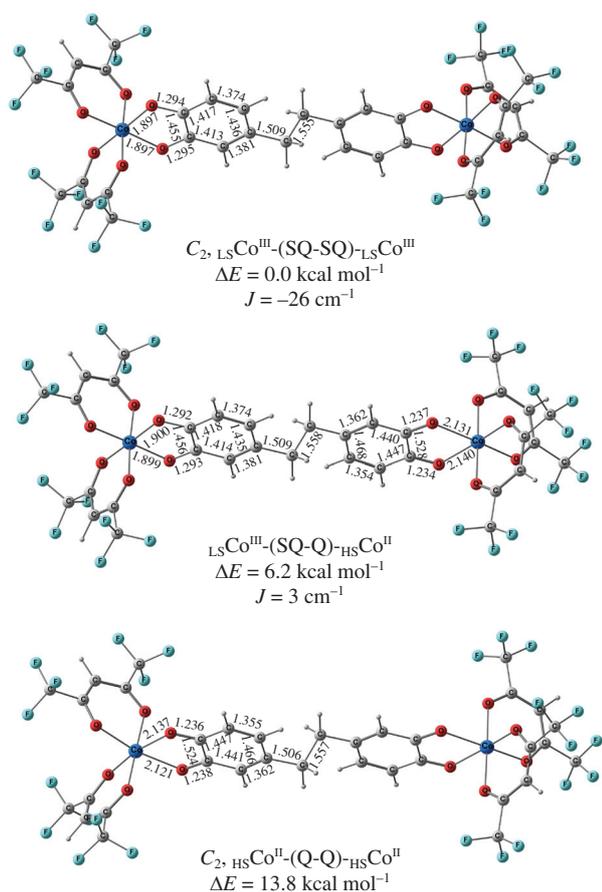


Figure 16 Optimized geometries of the isomeric forms of adduct **17** ($R = \text{CF}_3$, $R^1 = R^2 = \text{H}$, $X = \text{CH}_2\text{-CH}_2$) calculated by the B3LYP*/6-311++G(d,p) method.

exchange coupling between the paramagnetic centres of adduct **17** ($X = \text{CH}_2\text{-CH}_2$). The weak antiferromagnetic coupling of unpaired electrons ($J = -30 \text{ cm}^{-1}$) predicted for the ground state triplet $\text{LS Co}^{\text{III}}\text{-(SQ-SQ)-LS Co}^{\text{III}}$ structure (Figure 16)⁵⁹ should provide for the paramagnetic behaviour in a wide temperature range. Even weaker is the ferromagnetic character ($J = 3 \text{ cm}^{-1}$) between the spin centres in the quintet electromeric $\text{LS Co}^{\text{III}}\text{-(SQ-Q)-HS Co}^{\text{II}}$ structure. The low energy differences between the electromers of **17** ($X = \text{CH}_2\text{-CH}_2$, $R^1 = R^2 = \text{H}$, $R = \text{CF}_3$) (Figure 16) and the relative energy of the MECPs (Figure 17) corresponding to the theoretically estimated energy barriers of rearrangements between the triplet and quintet, and quintet and septet (10.5 and 17.3 kcal mol^{-1} , respectively) electromers make it possible to detect interconversion processes of these forms. The energy diagram portraying the reaction path of the VT rearrangements of these electromeric forms is shown in Figure 17.

Thus, the DFT calculations performed for the dinuclear adducts of Co^{II} diketonates with redox-active diquinones revealed that, under the proper structural tuning of the ligands, these paramagnetic complexes possess the properties required in a 2-qubit molecular system.

Conclusions

We demonstrated a rational molecular strategy for the structural engineering of VT spin state switchable systems, which is based on the DFT computational modeling of a series of mixed-ligand complexes – the adducts of paramagnetic tetracoordinate metal complexes and redox-active ligands. By adjusting structural and energy parameters of the three-component (a metal ion and ancillary and redox-active ligands) system to the electronic and steric requirements of the intrinsic IET mechanism, it becomes

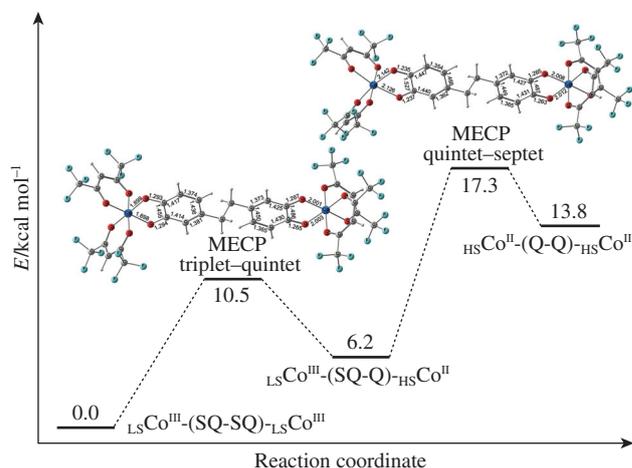


Figure 17 Energy profile of the spin-forbidden rearrangements of electro-meric forms of mixed-ligand adduct **17** ($R = \text{CF}_3$, $R^1 = R^2 = \text{H}$, $X = \text{CH}_2\text{-CH}_2$) according to the data of B3LYP*/6-311++G(d,p) calculations.

possible to find out the adducts with the targeted dynamic properties. The principal conditions to be met by the mixed-ligand complexes capable of thermal VT rearrangements include: (i) a sufficient stability of the adduct with respect to dissociation into the components, (ii) the energy preference of the low-spin electronic state over the high-spin state and (iii) a thermally achievable energy barrier to VT rearrangements. The calculations performed for a series of the adducts of Co^{II} diketonates, bis(aminovinylketonates) and bis(salicylaldiminates) with o -benzoquinones, their mono- and diimines and other redox-active ligands (phenoxazinone and α -diimine derivatives) showed that all conditions for the VT behaviour could be met by mixed-ligand complexes of Co^{II} bis(hexafluoroacetylacetonate).

Electrically neutral dinuclear cobalt complexes **17**, whose spins states and intramolecular migration of paramagnetic centres are controlled by the mechanism of valence tautomerism, were designed, and their properties as possible candidates for 2-qubit quantum gates were evaluated. The most promising thermodynamic, kinetic and magnetic properties are exhibited by adducts **17** containing electron-withdrawing trifluoromethyl groups in the diketonate fragments and nonconjugated dimethylene linker groups bridging the quinone rings in the redox-active diquinone ligand. The computational results give promise that, by the judicious choice of the components of dinuclear adducts **17**, the compounds possessing the properties of 2-qubit gates can be found out within this structural family.

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References

- 1 *Molecular Switches*, eds. B. L. Feringa and W. R. Browne, Wiley-VCH, Weinheim, 2011, vols. 1, 2.
- 2 J.-F. Letard, *J. Mater. Chem.*, 2006, **16**, 2550.
- 3 *Spin Crossover in Transition Metal Compounds. Topics in Current Chemistry*, eds. P. Gülich and H. A. Goodwin, Springer-Verlag, Berlin, 2004, vols. 233–235.
- 4 P. Gülich, *Eur. J. Inorg. Chem.*, 2013, 581.
- 5 *Spin-Crossover Materials: Properties and Applications*, ed. M. A. Halcrow, John Wiley & Sons, Oxford, 2013, p. 546.
- 6 S. Decurtins, P. Gülich, K. M. Hasselbach, A. Hauser and H. Spiering, *Inorg. Chem.*, 1985, **24**, 2174.
- 7 C. Roux, J. Zarembowitch, B. Gallois, T. Granier and R. Claude, *Inorg. Chem.*, 1994, **33**, 2273.
- 8 S. Venkataramani, U. Jana, M. Dommaschk, F. D. Sönnichsen, F. Tuczek and R. Herges, *Science*, 2011, **331**, 445.
- 9 D. N. Hendrickson and C. G. Pierpont, *Top. Curr. Chem.*, 2004, **234**, 63.

- 10 O. Sato, A. Cui, R. Matsuda, J. Tao and S. Hayami, *Acc. Chem. Res.*, 2007, **40**, 361.
- 11 E. Evangelio and D. Ruiz-Molina, *C. R. Chim.*, 2008, **11**, 1137.
- 12 T. Tezgerevska, K. G. Alley and C. Boskovic, *Coord. Chem. Rev.*, 2014, **268**, 23.
- 13 R. M. Buchanan and C. G. Pierpont, *J. Am. Chem. Soc.*, 1980, **102**, 4951.
- 14 G. A. Abakumov, V. K. Cherkasov, M. P. Bubnov, O. G. Ellert, Z. V. Dobrokhotova, L. N. Zakharov and Yu. T. Struchkov, *Dokl. Akad. Nauk*, 1993, **328**, 332 (in Russian).
- 15 A. Cui, K. Takahashi, A. Fujishima and O. Sato, *J. Photochem. Photobiol., A*, 2004, **161**, 243.
- 16 C. K. Jørgensen, *Coord. Chem. Rev.*, 1966, **1**, 164.
- 17 K. P. Butin, E. K. Beloglazkina and N. V. Zyk, *Russ. Chem. Rev.*, 2005, **74**, 531 (*Usp. Khim.*, 2005, **74**, 585).
- 18 W. Kaim and B. Schwederski, *Pure Appl. Chem.*, 2004, **76**, 351.
- 19 W. Kaim, *Eur. J. Inorg. Chem.*, 2012, 343.
- 20 IUPAC, *Compendium of Chemical Technology (the 'Gold Book')*, eds. A. D. McNaught and A. Wilkinson, Blackwell, Oxford, 1997 (<http://goldbook.iupac.org>).
- 21 A. Calzolari, Y. Chen, G. F. Lewis, D. B. Dougherty, D. A. Shultz and M. Buongiorno Nardelli, *J. Phys. Chem. B*, 2012, **116**, 13141.
- 22 A. I. Poddel'sky, V. K. Cherkasov and G. A. Abakumov, *Coord. Chem. Rev.*, 2009, **253**, 291.
- 23 A. Dei, A. Feis, G. Poneti and L. Sorace, *Inorg. Chim. Acta*, 2008, **361**, 3842.
- 24 C. Floriani, G. Fachinetti and F. Calderazzo, *J. Chem. Soc., Dalton Trans.*, 1973, 765.
- 25 F. Hartl and A. Vlček, Jr., *Inorg. Chim. Acta*, 1986, **118**, 57.
- 26 S. Patra, B. Sarkar, S. V. Mobin, W. Kaim and G. K. Lahiri, *Inorg. Chem.*, 2003, **42**, 6469.
- 27 D. Das, B. Sarkar, D. Kumbhakar, T. K. Mondal, S. M. Mobin, J. Fiedler, F. A. Urbanos, R. Jiménez-Aparicio, W. Kaim and G. K. Lahiri, *Chem. Eur. J.*, 2011, **17**, 11030.
- 28 D. Das, T. K. Mondal, A. D. Chowdhury, F. Weisser, D. Schweinfurth, B. Sarkar, S. M. Mobin, F. A. Urbanos, R. Jiménez-Aparicio and G. K. Lahiri, *Dalton Trans.*, 2011, **40**, 8377.
- 29 A. Grupp, M. Bubrin, F. Ehret, Q. Zeng, F. Hartl, H. Kvapilová, S. Zláliš and W. Kaim, *Eur. J. Inorg. Chem.*, 2014, 110.
- 30 V. V. Koval, A. G. Starikov, R. M. Minyaev and V. I. Minkin, *Dokl. Chem.*, 2010, **435**, 319 (*Dokl. Akad. Nauk*, 2010, **435**, 624).
- 31 A. G. Starikov, R. M. Minyaev, A. A. Starikova and V. I. Minkin, *Dokl. Chem.*, 2011, **440**, 289 (*Dokl. Akad. Nauk*, 2011, **440**, 646).
- 32 V. I. Minkin, A. A. Starikova and R. M. Minyaev, *Dalton Trans.*, 2013, **42**, 1726.
- 33 A. A. Starikova, R. M. Minyaev and V. I. Minkin, *Russ. Chem. Bull., Int. Ed.*, 2014, **63**, 812 (*Izv. Akad. Nauk, Ser. Khim.*, 2014, 0812).
- 34 A. A. Starikova, V. I. Minkin and A. G. Starikov, *Mendeleev Commun.*, 2014, **24**, 329.
- 35 E. P. Ivakhnenko, A. G. Starikov, V. I. Minkin, K. A. Lyssenko, M. Yu. Antipin, V. I. Simakov, M. S. Korobov, G. S. Borodkin and P. A. Knyazev, *Inorg. Chem.*, 2011, **50**, 7022.
- 36 E. P. Ivakhnenko, Yu. V. Koshchienko, P. A. Knyazev, M. S. Korobov, A. V. Chernyshev, K. A. Lyssenko and V. I. Minkin, *Dokl. Chem.*, 2011, **438**, 155 (*Dokl. Akad. Nauk*, 2011, **438**, 485).
- 37 M. Yu. Antipin, E. P. Ivakhnenko, Yu. V. Koshchienko, P. A. Knyazev, M. S. Korobov, A. V. Chernyshev, K. A. Lyssenko, A. G. Starikov and V. I. Minkin, *Russ. Chem. Bull., Int. Ed.*, 2013, **62**, 1744 (*Izv. Akad. Nauk, Ser. Khim.*, 2013, 1744).
- 38 J. N. Harvey, in *Computational Organometallic Chemistry*, ed. T. R. Cundari, Marcel Dekker, New York, 2001, p. 291.
- 39 C. G. Pierpont and O. S. Jung, *Inorg. Chem.*, 1995, **34**, 4281.
- 40 A. Caneschi, A. Cornia and A. Dei, *Inorg. Chem.*, 1998, **37**, 3419.
- 41 A. Dei and L. Sorace, *Appl. Magn. Reson.*, 2010, **38**, 139.
- 42 T. Saha-Dasgupta and P. M. Oppeneer, *MRS Bulletin*, 2014, **39**, 614.
- 43 S. V. Larionov, *Russ. J. Coord. Chem.*, 2008, **34**, 237 (*Koord. Khim.*, 2008, **34**, 243).
- 44 I. Ratera, D. Ruiz-Molina, F. Renz, J. Ensling, K. Wurst, C. Rovira, P. Gütllich and J. Veciana, *J. Am. Chem. Soc.*, 2003, **125**, 1462.
- 45 W. Kaim and B. Sarkar, *Coord. Chem. Rev.*, 2007, **251**, 584.
- 46 D. Das, A. K. Das, B. Sarkar, T. K. Mondal, S. M. Mobin, J. Fiedler, S. Zláliš, F. A. Urbanos, R. Jiménez-Aparicio, W. Kaim and G. K. Lahiri, *Inorg. Chem.*, 2009, **48**, 11853.
- 47 D. Kumbhakar, B. Sarkar, S. Maji, S. M. Mobin, J. Fiedler, F. A. Urbanos, R. Jiménez-Aparicio, W. Kaim and G. K. Lahiri, *J. Am. Chem. Soc.*, 2008, **130**, 17575.
- 48 A. Mandal, T. Kundu, F. Ehret, M. Bubrin, S. M. Mobin, W. Kaim and G. K. Lahiri, *Dalton Trans.*, 2014, **43**, 2473.
- 49 G. A. Timco, S. Carretta, F. Troiani, F. Tuna, R. J. Pritchard, C. A. Muryn, E. J. L. McInnes, A. Ghirri, A. Candini, P. Santini, G. Amoretti, M. Affronte and R. E. P. Winpenny, *Nat. Nanotechnol.*, 2009, **4**, 173.
- 50 D. Loss and D. P. Di Vincenzo, *Phys. Rev. A: At. Mol. Opt. Phys.*, 1998, **57**, 120.
- 51 L. Bogani and W. Wernsdorfer, *Nat. Mater.*, 2008, **7**, 179.
- 52 P. C. E. Stamp and A. Gaita-Arino, *J. Mater. Chem.*, 2009, **19**, 1718.
- 53 F. Troiani and M. Affronte, *Chem. Soc. Rev.*, 2011, **40**, 3119.
- 54 G. Aromí, D. Aguilà, P. Gamez, F. Luis and O. Roubeau, *Chem. Soc. Rev.*, 2012, **41**, 537.
- 55 R. Vincent, S. Klyatskaya, M. Ruben, W. Wernsdorfer and F. Balestro, *Nature*, 2012, **488**, 357.
- 56 T. B. Faust, V. Bellini, A. Candini, S. Carretta, G. Lorusso, D. R. Allan, L. Carthy, D. Collison, R. J. Docherty, J. Kenyon, J. Machin, E. J. L. McInnes, C. A. Muryn, H. Nowell, R. G. Pritchard, S. J. Teat, G. A. Timco, F. Tuna, G. F. S. Whitehead, W. Wernsdorfer, M. Affronte and R. E. P. Winpenny, *Chem. Eur. J.*, 2011, **17**, 14020.
- 57 G. A. Timco, T. B. Faust, F. Tuna and R. E. P. Winpenny, *Chem. Soc. Rev.*, 2011, **40**, 3067.
- 58 T. B. Faust, F. Tuna, G. A. Timco, M. Affronte, V. Bellini, W. Wernsdorfer and R. E. P. Winpenny, *Dalton Trans.*, 2012, **41**, 13626.
- 59 V. I. Minkin, A. A. Starikova and A. G. Starikov, *Dalton Trans.*, 2015, **44**, 1982.
- 60 A. M. W. Cargill Thompson, D. Gatteschi, J. A. McCleverty, J. A. Navas, E. Rentschler and M. D. Ward, *Inorg. Chem.*, 1996, **35**, 2701.
- 61 V. Á. Ung, A. M. W. Cargill Thompson, D. A. Bardwell, D. Gatteschi, J. C. Jeffery, J. A. McCleverty, F. Totti and M. D. Ward, *Inorg. Chem.*, 1997, **36**, 3447.
- 62 S. R. Bayly, E. R. Humphrey, H. de Chair, C. G. Paredes, Z. R. Bell, J. C. Jeffery, J. A. McCleverty, M. D. Ward, F. Totti, D. Gatteschi, S. Courric, B. R. Steele and C. G. Screttas, *J. Chem. Soc., Dalton Trans.*, 2001, 1401.
- 63 K. M. Stobie, Z. R. Bell, T. W. Munhoven, J. P. Maher, J. A. McCleverty, M. D. Ward, E. J. L. McInnes, F. Totti and D. Gatteschi, *Dalton Trans.*, 2003, 36.

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