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Adducts of transition metal complexes with redox-active ligands: the structure and spin-state-switching rearrangements †

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The currently available literature data on the synthesis, molecular and electronic structure of mixed-ligand complexes (adducts) of transition metals (chromium, manganese, iron, cobalt, ruthenium) with organic redox-active ligands are systematically considered for the first time. The possibility of manifestation of magnetic bistability by adducts of tetracoordinate Co^{II} and Fe^{II} complexes and the potential for their application as molecular switches are studied in detail by means of quantum chemical modelling of thermally initiated rearrangements controlled by the spin crossover and valence tautomerism mechanisms. Special attention is given to dinuclear adducts of Co^{II} and Fe^{II} complexes with linearly bonded and polycyclic di-*o*-quinones and their imines, which can operate as thermally switchable elements of quantum computers suitable for practical implementation of two-qubit gates.
The bibliography includes 183 references.

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1. Introduction

Transition-metal coordination compounds possessing photo- and thermally switchable magnetic properties are considered as potential basis of the molecular electronics and spintronics [1–22] and building blocks for next-generation electronic devices.[3,23–33] Generally, transitions between different spin states of magnetically bistable complexes are controlled *via* the spin crossover (SCO) mechanism involving electronic rearrangements within the valence shell of a coordinated metal ion (for transition metals, these are d^4-d^7 ions).[34] On the molecular level, SCO is governed by the dependence of the ligand field strength on the chemical composition and structure of the coordination site of the complex. The necessary conditions for realization of the SCO effect include meeting of criterion (1) for the electron pairing energy (Π) and the splitting parameter ($10Dq$) for the low- (LS) and high-spin (HS) states and a rather narrow energy gap between these states (2).

$$10Dq^{HS} < \Pi < 10Dq^{LS} \quad (1)$$

$$\Delta E_{HS-LS} \simeq k_B T \quad (2)$$

where k_B is the Boltzmann constant and T is temperature.

Transitions between different spin states of transition metal complexes with redox-active (non-innocent [35]) ligands can also occur by the mechanism called valence tautomerism (VT).[36] Like SCO, the VT effect is due to intramolecular electron transfer; however, now one deals with electron transfer between the metal d-electrons and electrons from the close-lying frontier molecular orbitals (MOs) of the ligand rather than intra-d-shell transfer. A necessary condition for a thermally initiated VT rearrangement to occur

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is to meet criterion (2). Transitions between the ground low-spin state and energetically less favourable high-spin states of the complexes occurring by the SCO and VT mechanisms belong to reactions driven by the increase in entropy, which is due to the increased density of vibrational states of the HS-forms with elongated metal – ligand bonds.[25] The magnetic properties of transition metal complexes with redox-active ligands capable of spin transitions are usually determined by valence tautomerism.[36] At the same time, iron[37–41] and cobalt compounds[42,43] can simultaneously undergo VT and SCO rearrangements including light-driven ones.

Iron, cobalt, manganese and other metal complexes with redox-active ligands are of considerable interest not only as molecular switches with magnetic response, but also since they play a decisive role in many key metabolic, biosynthetic and catalytic processes.[44–51] Interest in methods of synthesis of this type of complexes and establishment of correlations between their chemical composition, structure and energies of intramolecular rearrangements accompanied by changes in the spin states and switching of magnetic properties is also quite understandable. The most common synthetic approach to transition metal complexes with redox-active ligands is based on the ability of these ligand molecules to readily undergo transition to ionic form (*viz.*, semiquinonate form in the case of most widely used *o*-quinone ligands) with subsequent formation of stable chelate structures.[44,45,48] Donor centres in the *o*-quinone and certain other redox-active ligand molecules also allow them to react with metal ions (in both free and ligand-coordinated forms) to give adducts where the redox-active ligand is in its initial nonreduced form. The main goal of this review is to systematize data on electrically neutral adducts of transition metal complexes with bi- and polydentate redox-active ligands in which the structure of a possible isomeric form contains the initial nonreduced form of the ligand, which is consistent with the description of a coordination compound as adduct of two electrically neutral molecules. In the literature, the notion 'adduct' is also often applied to metal complexes with redox-active ligands containing outer-sphere counterions;[52–57] however, an analysis of this type of compounds goes beyond the scope of this review.

Here we report the first attempt to collect and systematically analyze the results of studies carried out in the title field and to assess the potential of its development. In Section 2, we will consider the results of experimental research into the synthesis and properties of the adducts in question. Sections 3 – 6 are devoted to thorough analysis of the results of theoretical studies on the electronic structure, magnetic properties, as well as the thermodynamic and kinetic parameters of rearrangements of both known and previously unknown (theoretically predicted) transition metal complexes with redox-active ligands. Besides, we will offer methods for structure modification of the compounds of interest, aimed at revealing stable complexes with switchable magnetic properties.

Notations used in the review are as follows:

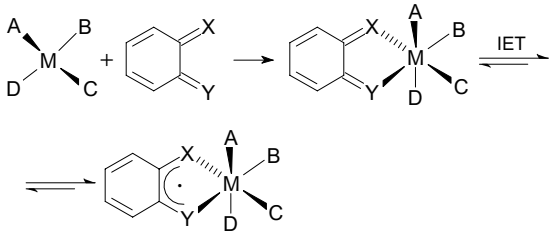
acac — acetylacetonate;
acacen — *N*,*N*′-ethylenebis(acetylacetoneiminate);
acNac — aminovinyl ketonate;
BIAN — bis(arylimino)acenaphthene;
bpz — bis(pyrazolyl)borate;
BS — broken symmetry (state);
Cat — catecholate ligand form;
CTIST — charge-transfer-induced spin transition(s);
DAD — diazabutadiene;
DFT — density functional theory;
diketo — diketonate;
PES — potential energy sufrace;
hfac — hexafluoroacetylacetonate;
HS — high-spin state;
IET — intramolecular electron transfer;
IS — intermediate spin state;
LS — low-spin state;
mal — malonate;
MECP — minimum energy crossing point;
NBO — natural bond orbital;
Q — quinone ligand form;
sal — salicylaldiminate;
salen — *N*,*N*′-ethylenebis(salicylideneiminate);
saldien — *N*,*N*′-diethyleneaminebis(salicylideneiminate);
saloph — *N*,*N*′-phenylenebis(salicylideneiminate);
salpren — *N*,*N*′-propylenebis(salicylideneiminate);
salprenOH — *N*,*N*′-2-hydroxypropylenebis(salicylideneiminate);
SCO — spin crossover;
SOMO — singly occupied molecular orbital;
SQ — semiquinone ligand form;
TD-DFT — time-dependent DFT;
tfac — trifluoroacetylacetonate;
Tol — tolyl;
VT — valence tautomerism.

2. Adducts of transition metal complexes with redox-active ligands: the synthesis, structure and magnetic properties

2.1. Complexes of Cr, Co, Fe, Mn

The most common method of synthesis of magnetoactive adducts is to conduct direct reactions between redox-active *o*-quinones and their imine derivatives with tetracoordinate metal complexes. The reaction is accompanied by metal-to-ligand intramolecular electron transfer (IET) and results in compounds (Scheme 1) that can exist in at least two oxidation states. Usually, IET provides significant additional stabilization of reaction products.

Scheme 1



X, Y = O, NR; M = Cr, Mn, Fe, Co, Ru; A – D are ligands

Figure 1 presents the most widely used redox-active ligands ($^{L}\boldsymbol{n}$) that will be considered below. Additional stabilization of a complex is achieved through expansion of its coordination sphere using so-called ancillary ligands, *e.g.*, 2,2′-bipyridine, phenanthroline and their derivatives that complete the coordination site of the complex to

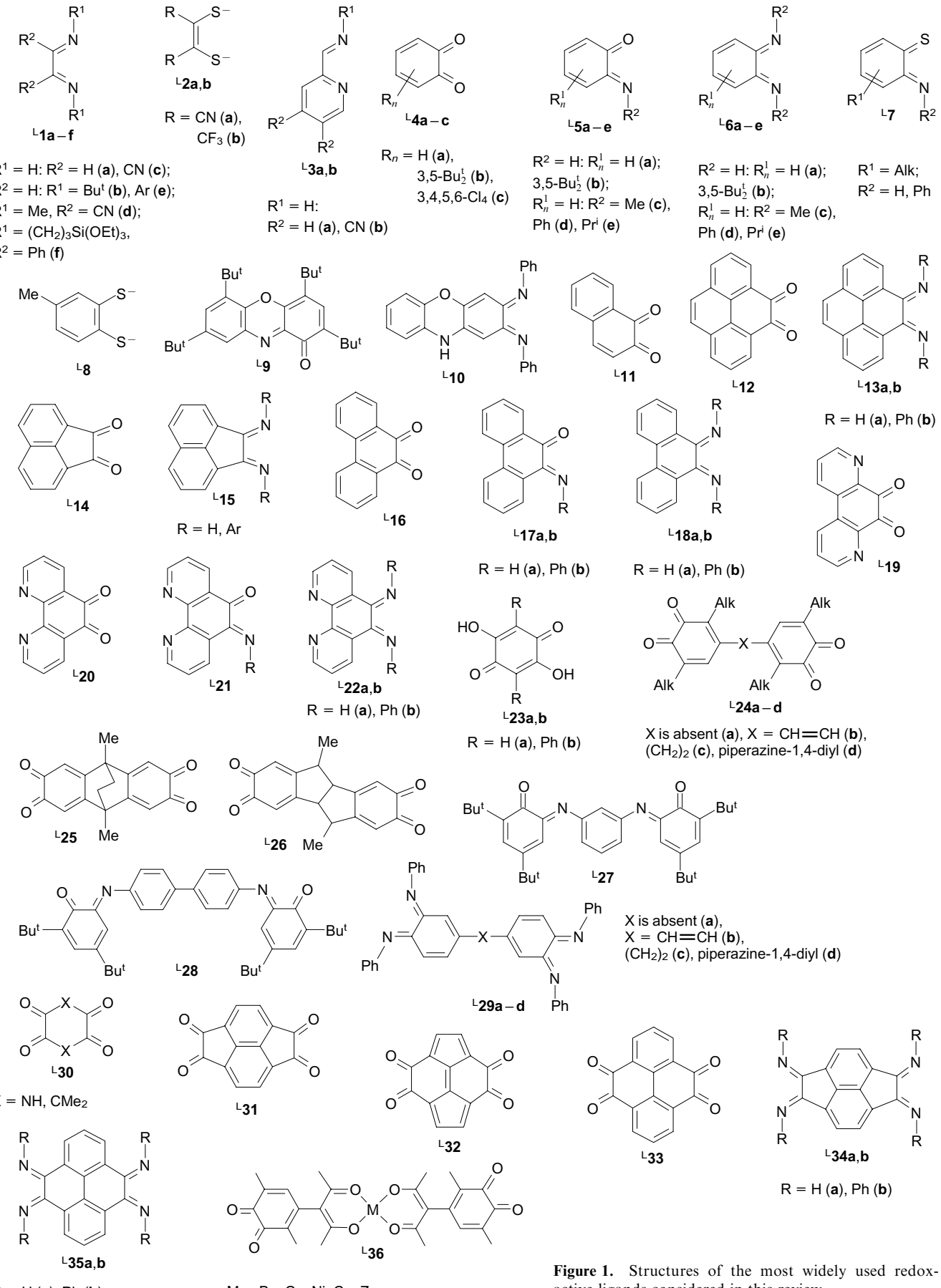


Figure 1. Structures of the most widely used redox-active ligands considered in this review.

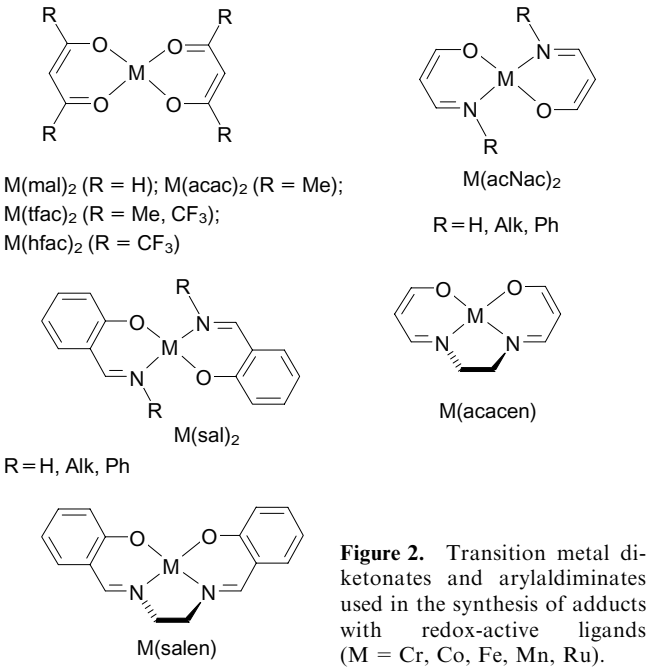


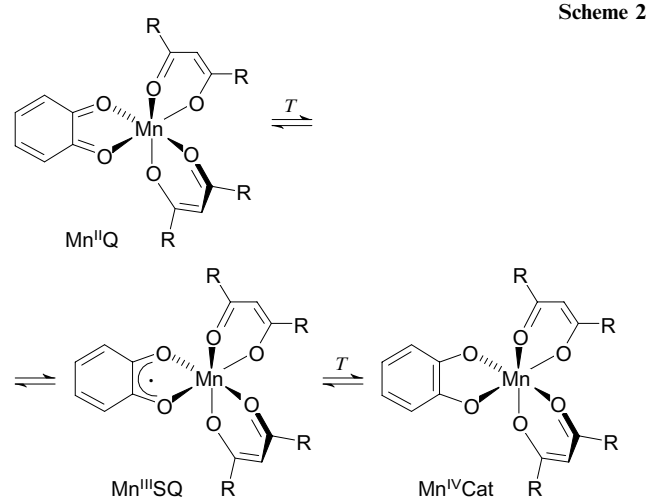
Figure 2. Transition metal diketonates and arylaldiminates used in the synthesis of adducts with redox-active ligands (M = Cr, Co, Fe, Mn, Ru).

octahedron. The ancillary ligands manifest redox-active properties under conditions of electrochemical reactions or upon chemical oxidation (reduction) involving these ligands of the complex.[45,47] The largest groups of ancillary ligands include diketones, bi- and tetradentate Schiff bases since there is a convenient synthetic route to the adducts involving the reaction of transition metal diketonates and arylaldiminates (Fig. 2) with the redox-active ligands.

The general Scheme 1 of the redox transformations of the adducts can be detailed and best demonstrated in relation to rearrangements of mixed-ligand complexes of manganese diketonates with *o*-benzoquinone (Scheme 2, from this point on the symbol '*T*' above the arrow denotes heating). Manganese has three oxidation states (+2, +3 and +4), while the redox-active ligand can exist in electrically neutral (Q), radical anion (semiquinone, SQ) and dianionic (catecholate, Cat) forms.

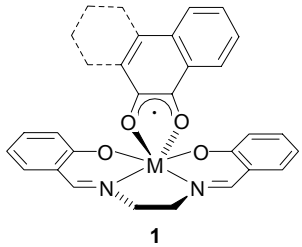
o-Quinones and their imine derivatives form adducts with certain transition metal (Cr, Co, Fe, Mn and Ru)

Scheme 2



diketonates and arylaldiminates. These systems can exist in different oxidation states. One of the first studies[58] includes the description of the synthesis of 1 : 1 adducts of Co^{II} and Fe^{II} *N*,*N*′-ethylenebis(salicylideneiminates) (salen) with 9,10-phenanthrenequinone (^{L}**16**) and 1,2-naphthoquinone (^{L}**11**) (Structures **1**). According to data of magnetochemical studies, the effective magnetic moment of these compounds is 4.8 μ_B at room temperature. It is believed[58] that this value corresponds to the Fe^{III}SQ-type structure and results from antiferromagnetic exchange interactions between the unpaired electrons of the monoanionic form of the redox-active ligand and electrons of the high-spin Fe^{III} with d^5 configuration.

Structures 1



1

M(salen)(^{L}**11**), M(salen)(^{L}**16**)
(M = Fe, Co)

A similar structure, Co^{III}SQ, was proposed[59] for adducts of Co^{II} acetylacetonate with *o*-benzoquinones based on EPR data. According to EPR and magnetochemical data, reactions of Co(salen) and *N*,*N*′-ethylenebis(acetylacetoneiminato)cobalt [Co(acacen)] with *o*-benzoquinone (^{L}**4**) derivatives[60] and sulfur-containing redox-active ligands ^{L}**2** and ^{L}**8** (see Ref. 61) are also accompanied by the oxidation of the metal to Co^{III} and transition of the ligand to the radical anion form.

The set of *o*-quinones and tetracoordinate complexes M(salen) involved in the adduct formation was significantly extended by using complexes with M = Mn, Co, Fe, as well as *o*-quinones ^{L}**4b**, ^{L}**4c**, ^{L}**11**, ^{L}**16** and vicinal acenaphthenequinone ^{L}**14**.[62] Mössbauer spectroscopy studies showed that in the iron complexes the metal ions are in the high-spin Fe^{III} state, while the results of magnetic susceptibility measurements[58–62] suggest a strong antiferromagnetic exchange between the unpaired electrons of the radical anion form of the *o*-quinone ligand and the metal ion. Manganese adducts exhibit similar magnetic properties. An adduct of Co(salen) with 3,5-di(*tert*-butyl)-*o*-benzoquinone (^{L}**4b**) bears one unpaired electron and has effective magnetic moments of 1.86 and 1.74 μ_B at 286 and 4.2 K, respectively.[62] The room-temperature EPR spectrum in a chloroform – toluene mixture demonstrates a hyperfine splitting on the cobalt and hydrogen atoms. The ^{1}H hyperfine coupling constant is 3.50 Œ, being somewhat different from that in uncoordinated semiquinone (3.20 Œ).[62] Based on these results, it was concluded[62] that the complex being formed comprises a low-spin Co^{III} ion and a coordinated semiquinonate ligand. Attempts to obtain adducts with acenaphthenequinone (^{L}**14**) failed owing to a relatively low reduction potential of ligand ^{L}**14**.

Further progress in this investigation line is associated with research into adducts of Fe(salen) derivatives (Fig. 3) with *o*- and *p*-quinones.[63] It was shown that the temperature

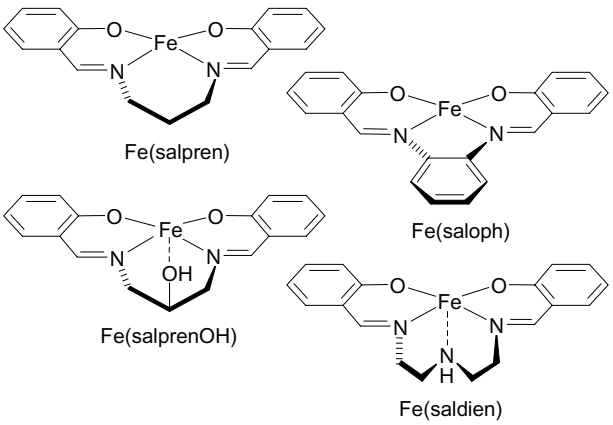
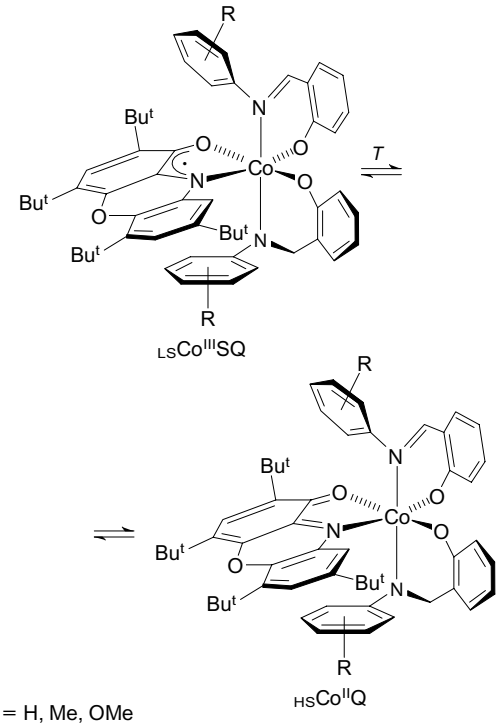


Figure 3. Fe(salen) derivatives and analogues used for the synthesis of adducts with *o*- and *p*-quinones.

dependence of the magnetic susceptibility of the complexes with *o*-quinones is well described assuming strong antiferromagnetic exchange interaction between the semiquinone moiety and the Fe^{III} ion. A slight decrease in the effective magnetic moment (μ_{eff}) on lowering the temperature was explained by the influence of intermolecular interactions. A crystal structure study[64] of the Fe(salen) complexes with phenanthrenequinone (^{L}**16**) and *o*-quinone ^{L}**4b** revealed that the former contains the radical anion form of phenanthrenequinone molecule (^{L}**16**) coordinated in bidentate fashion while the latter contains the catecholate form of the ligand and an outer-sphere potassium cation. This is in excellent agreement with the results of Mössbauer spectroscopy and magnetic susceptibility studies.

The first examples of adducts of tetracoordinate transition metal complexes with the redox-active ligands capable of undergoing VT rearrangements are provided by the

Scheme 3

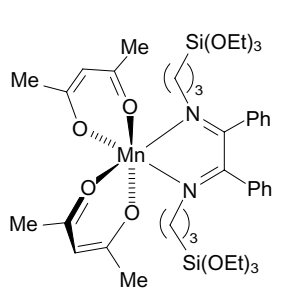


mixed-ligand complexes of Co^{II} salicylaldiminates with 2,4,6,8-tetra(*tert*-butyl)phenoxazin-1-one (^{L}**9**).[65–67] The crystal structures of these compounds were determined by X-ray diffraction analysis. The results of magnetochemical studies suggest that the adducts obtained have a low-spin ground state $_{LS}Co^{III}SQ$ (Scheme 3). Although the magnetic properties of polycrystalline complex Co(N-(*p*-Tol)-sal)(^{L}**9**) remain unchanged in the temperature interval of 77 – 298 K (μ_{eff} = 1.93 μ_B), the magnetic susceptibility measurements of a solution of this complex in toluene demonstrated a change in μ_{eff} from 1.89 μ_B (263 K) to 2.67 μ_B (333 K), probably, as a result of partial shift of the equilibrium towards the high-spin form.[65,66] This assumption was confirmed by the evolution of the EPR spectrum, *viz*., weakening of the signal corresponding to the radical anion form of the ligand with increasing the solution temperature. However, the dynamics observed is complicated by a side process, *viz*., reversible dissociation of the complex to the initial components, which was detected from the appearance of free phenoxazinone bands in the electronic absorption spectrum.

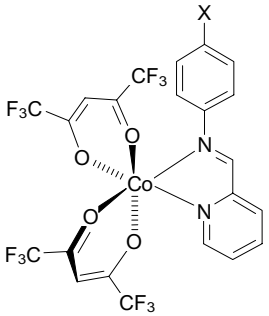
To date, a mixed-ligand complex of chromium acetylacetonate with the diazabutadiene ligand ^{L}**1e** containing 2,6-diisopropylphenyl groups at nitrogen atoms[68] is the one and only chromium compound that can be treated as adduct of Cr bis(chelate). Based on X-ray diffraction data, the complex has the structure $Cr^{III}(acac)_2(^{L}\mathbf{1e}^{-\bullet})$. The magnetic moment of the complex is 2.75 μ_B in the temperature range of 5 – 295 K, thus being indicative of triplet ground state (S = 1) originating from strong antiferromagnetic exchange interaction ($J < -450$ cm^{-1}) between spins of the unpaired electrons of the metal ion and the redox-active ligand.[68] Electrochemical or chemical oxidation of the complex leads to the structure $[Cr^{III}(acac)_2(^{L}\mathbf{1e}^{0})](PF_6)$ containing an electrically neutral ligand. The crystal and electronic structure of the oxidized form of the complex was confirmed by X-ray diffraction and by the results of magnetochemical measurements and quantum chemical calculations.

A complex obtained[69] by the reaction of manganese tris(acetylacetonate) with functionalized diazabutadiene ^{L}**1f** [Ph-DAD-$(CH_2)_3Si(OEt)_3$] can be described as adduct of manganese diketonate with the redox-active ligand. Although no X-ray quality crystals were grown, the results of magnetic susceptibility measurements and density functional theory (DFT) calculations of different electromers of the complex suggest stabilization of the high-spin state

Structures 2, 3



2 [Mn(acac)$_2$(^{L}**1f**)]



3 [Co(hfac)$_2$(^{L}**3c**)]

X = H, Me, Et, OMe, F, Cl, Br, I

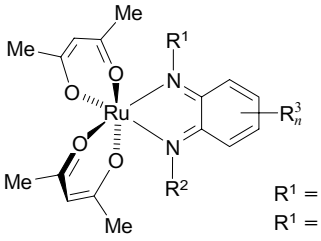
($S = 5/2$). Based on these data, the metal ion in $Mn(acac)_2(^{L}\mathbf{1f})$ (Structure **2**) is high-spin Mn^{II} ion and, therefore, the ligand in this system is in its electrically neutral form.

The structure of adduct of manganese bis(acetylacetonate) $Mn(acac)_2$ with redox-active *N*,*N*′-bis(2-pyridylmethylene)cyclohexane-1,2-diamine (^{L}**37**) was established by X-ray diffraction.[70] The magnetic properties of $Mn(acac)_2(^{L}\mathbf{37})$ were not studied; however, the complex was tested as catalyst of asymmetric oxidation of sulfides by hydrogen peroxide. Adducts of cobalt and nickel diketonates with (4-X-phenyl)-2-pyridylmethaneimines (X = H, Me, Et, OMe, F, Cl, Br, I) ^{L}**3c** were obtained earlier.[71 – 73] According to X-ray diffraction data, the ground state of the complexes[72,73] corresponds to molecular adducts of metal bis(hexafluoroacetylacetonate) with electrically neutral redox-active ligand $M(hfac)_2(^{L}\mathbf{3c})$ (structure **3**), *i.e.*, the reaction is not accompanied by electron transfer from the metal ion to the redox-active ligand.

2.2. Ruthenium complexes

Greater attention has been paid to those adducts of ruthenium complexes with redox-active ligands that efficiently catalyze various redox and polymerization reactions.[74 – 96] Among the first representatives of this type of compounds, there is a hexacoordinate complex of ruthenium acetylacetonate with unsymmetrical *o*-diiminobenzoquinone (structures **4**, $R^1 = R^3_n = H$, $R^2 = Ph$) synthesized by dimerization of aniline promoted by Ru^{III} acetylacetonate.[74]

Structures 4



4 [$Ru(acac)_2(^{L}\mathbf{6})$]

$R^1 = R^3_n = H$, $R^2 = Ph$;
$R^1 = R^2 = H$, R^3_n = 4,5-Me_2, 4-Cl, 4-NO_2; $R^1 = R^2 = SO_2Me$, $R^3_n = H$

More recently, this approach was used to obtain a series of $Ru(acac)_2$ complexes with various *N*-aryl-1,2-diiminobenzoquinones Ar-^{L}**6**.[75] The C – N and C – C bond lengths in the diiminoquinone ligand in the complex best correspond to the electrically neutral form of the ligand. Therefore, compounds $Ru(acac)_2$(Ar-^{L}**6**) contain ruthenium in the oxidation state +2, which is in good agreement with diamagnetic properties of the adduct. In principle, ruthenium complexes can undergo four successive one-electron transfer steps (Scheme 4). Two of them occur upon applying a positive potential and are metal-centred, whereas the other two steps occurring at negative potentials are ligand-centred.

Scheme 4

$$[(acac)_2Ru^{IV}(L^0)]^{2+} \rightleftharpoons [(acac)_2Ru^{III}(L^0)]^{+} \rightleftharpoons$$
$$\rightleftharpoons [(acac)_2Ru^{II}(L^0)] \rightleftharpoons [(acac)_2Ru^{II}(L^{-\bullet})] \rightleftharpoons$$
$$\rightleftharpoons [(acac)_2Ru^{III}(L^{2-})]$$

Lever and co-workers[76] synthesized a series of $Ru(acac)_2$(R-^{L}**6**) complexes with various substituents (see structures **4**, $R^1 = R^2$) and carried out a detailed study of charge distribution in the bis(acetylacetonato)ruthenium adducts with *o*-diiminobenzoquinones. Using a combination of experimental methods (UV, IR and Raman spectroscopies, electrochemical measurements) and theoretical approaches (DFT, TD-DFT), a detailed picture of the bonding between the metal and the redox-active ligand was obtained and correlations were established between the nature of the substituents and the extent of σ-forward and π-back donation. Considering the available interpretations of the electronic structure of the adducts of ruthenium complexes $Ru^{II}Q$ (Ref. 77), $Ru^{III}SQ$ (Ref. 97) and their superposition,[98] it was concluded[76] that these compounds contain the central Ru^{II} ion and electrically neutral *o*-diiminobenzoquinone, which has strong π-back donation effect on the metal centre. An alternative synthetic route to adducts of ruthenium diketonates with *o*-diiminobenzoquinones ^{L}**6** involving the reaction of ionic complex $[Ru^{III}(acac)_2(MeCN)_2]^{+}ClO_4^{-}$ with aniline was proposed.[77] In this case, perchlorate anion acts as oxidizing agent that converts aniline to *o*-semiquinonediimine.

The oxidation states of the metal and redox-active ligand in the adducts $Ru(acac)_2$(R-^{L}**6**) (Ref. 76) were determined by varying the ancillary ligands (phenylazopyridine, 2,2′-bipyridine and acetylacetone).[78] Based on the available X-ray diffraction and spectroelectrochemical data and on the results of quantum chemical calculations, it was concluded that two forms, $Ru^{II}Q$ and $Ru^{III}SQ$, are present simultaneously and that their content varies depending on the nature of the substituents and ancillary ligands. Mention was made that the electronic structure of such complexes should be described using the concept of continuum between the alternative formulations.

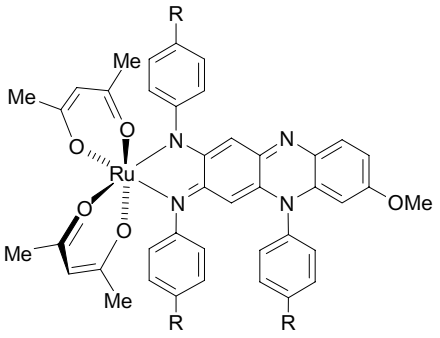
Yet another adduct with the diimine ligand was reported.[79] The effective magnetic moment of complex $Ru(acac)_2(^{L}\mathbf{38})$ (Structures **5**) is 1.69 μ_B,[79] which corresponds to one unpaired electron localized on the Ru^{III} ion, as follows from the characteristic EPR spectrum. The structure of the complex was confirmed by X-ray diffraction; the coordination site is formed by three (two acetylacetonato and one aminoiminophenazine) chelate monoanionic ligands and has a distorted octahedral geometry.

Reactions of $Ru(acac)_2(MeCN)_2$ with 2-aminophenols and 2-aminobenzenethiols afforded diamagnetic adducts of iminoquinones and iminothioquinones with ruthenium diketonates $Ru(acac)_2(^{L}\mathbf{5})$ and $Ru(acac)_2(^{L}\mathbf{7})$ (Structures 6).[80] Based on X-ray diffraction data, it was concluded that the adducts contain the Ru^{III} ion and the *o*-iminosemiquinone ligand and are characterized by strong antiferromagnetic exchange interaction between the unpaired electrons of the ion and ligand.

A series of complexes with variable number of iminobenzoquinone ligands $Ru(acac)_2(^{L}\mathbf{5})$, $Ru(acac)(^{L}\mathbf{5})_2$ and $Ru(^{L}\mathbf{5})_3$ was studied.[81] Based on the results of spectroelectrochemical studies, it was concluded that all these compounds contain the Ru^{III} central atom and exhibit multiple electron transfer behaviour under conditions of electrochemical reactions.

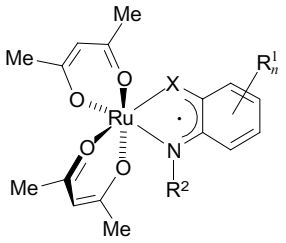
Adducts of ruthenium bis(acetylacetonate) with *o*-benzoquinones ^{L}**4** (Structures **7**) were for the first time synthesized in 2011.[82] These complexes also contain the Ru^{III} ion

Structures 5 – 9



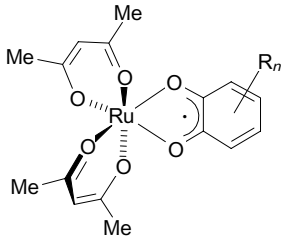
5 [Ru(acac)$_2$(L**38**)]

R = H, Cl, OMe



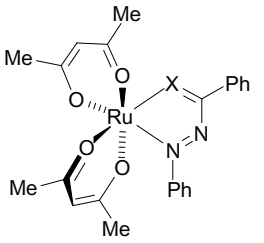
6 [Ru(acac)$_2$(L**5**), Ru(acac)$_2$(L**7**)]

X = O, S; R^1_n = H, 4,6-Bu$^t_2$; R^2 = H, Ph



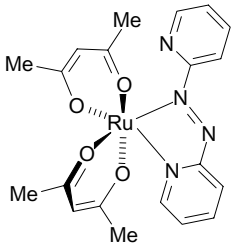
7 [Ru(acac)$_2$(L**4**)]

R_n = 4-Me, 3-OMe, 3,5-Bu$^t_2$



8 [Ru(acac)$_2$(L**39**), Ru(acac)$_2$(L**40**)]

X = O, S



9 [Ru(acac)$_2$(L**41**)]

and the SQ form of the redox-active ligand. Unlike diamagnetic adducts with imino- (L**5**) and diiminoquinones (L**6**), the adduct with *o*-benzoquinone has the triplet ground state ($S = 1$), as follows from the data of magnetochemical studies and from the results of quantum chemical calculations. This was explained by the qualitatively different type of metal – ligand interactions in the adducts with donor oxygen atoms. In this case, spin pairing appears to be less favourable, which leads to a complex pattern of paramagnetism.

Recently, adducts of ruthenium bis(acetylacetonates) with diazabutadiene (DAD) derivatives Ru(acac)$_2$(L**1**) were synthesized.[83] Based on X-ray diffraction data and negative solvatochromism of charge transfer bands, it was established that the complexes consist of Ru^{III} and the radical anion form of the α-diimine ligand, *viz.*, $DAD^{-\bullet}$. The oxidation of compounds mainly occurs in the radical ligand and results in the spectroelectrochemically detectable Ru^{III} form of the complex.

Like the mixed-ligand complexes with DAD, adducts of ruthenium bis(acetylacetonates) with *N*-benzoyl-*N′*-phenyldiazene (L**39**) and *N*-thiobenzoyl-*N′*-phenyldiazene (L**40**) (Structures **8**) contain the radical anion form of the ligand and are characterized by antiferromagnetic exchange between the unpaired electrons of the metal and ligand.[84] The EPR spectra and the results of spectroelectrochemical studies and TD-DFT calculations are indicative of multiple ligand-centred electron transfer steps:

$$[(acac)_2Ru^{III}(L^0)]^+ \rightleftharpoons [(acac)_2Ru^{III}(L^{-\bullet})] \rightleftharpoons$$
$$\rightleftharpoons [(acac)_2Ru^{III}(L^{2-})]^- / [(acac)_2Ru^{II}(L^{-\bullet})]^-.$$

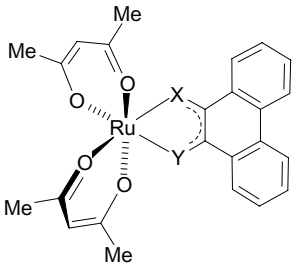
The mononuclear adduct of Ru(acac)$_2$(L**41**) (Structure **9**) with polydentate 2,2′-azobispyridine (L**41**) was described as Ru^{II} complex with electrically neutral redox-active ligand (N – N distance of 1.32 Å matches the length of the N = N double bond).[85]

To compare the effect of the nature of the oxygen and nitrogen donor atoms in the redox-active ligands based on phenanthrene on the electronic structure of ruthenium bis(acetylacetonate) adducts, complexes $Ru^{II}(acac)_2$(L**16**), $Ru^{II}(acac)_2$(L**17**) and $Ru^{II}(acac)_2$(L**18**) (Structures **10**) were synthesized and characterized structurally, electrochemically and spectroscopically.[86] A joint analysis of the bond lengths, ^{1}H NMR and EPR spectra, electrochemical data and results of DFT calculations revealed a large scatter of the contributions of the electromers $[Ru^{III}(acac)_2(L^-)]$ and $[Ru^{II}(acac)_2(L^0)]$ depending on the type of the donor atoms. The reduced ability of NH-containing systems to undergo reduction is due to the $Ru^{II}(L^0)$ state being preferred over $Ru^{III}(L^-)$ in the electrically neutral systems. Besides, the $Ru^{II}(L^-)$ electromer is energetically more favourable than $Ru^{III}(L^{2-})$ in the monoanionic derivatives.

Mondal *et al.*[87] synthesized diamagnetic adducts of ruthenium bis(diketonates) with bis(arylimino)acenaphthenes (BIAN) L**15** (Ar = Ph, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-O$_2$NC$_6$H$_4$) (Structures **11**). The lengths of the CN and CC bonds in the chelate ring of the redox-active ligand fall in the range of 1.304 – 1.334 and 1.425 – 1.449 Å, respectively, thus indicating a high degree of metal-to-ligand charge transfer in the ground state of the complex, which can be described as $Ru^{III}(acac)_2(BIAN^{-\bullet})$. However, DFT calculations and EPR studies of Ru^{III}-containing cations and $(BIAN^{-\bullet})$-containing anions suggest that the electronic structure of the complex cannot be represented by a single electromeric form and, following Lever and coworkers,[76] it is more appropriate to describe it as resonance hybrid $Ru^{III}(acac)_2(BIAN^{-\bullet}) \leftrightarrow Ru^{II}(acac)_2(BIAN^0)$.

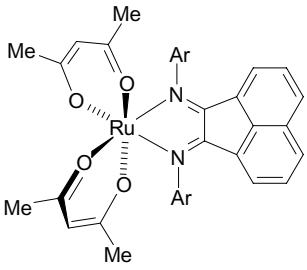
Studies on dinuclear adducts of ruthenium diketonates with redox-active ligands began in 2001.[88] A dinuclear adduct **12** of ruthenium bis(acetylacetonate) with redox-

Structures 10 – 14



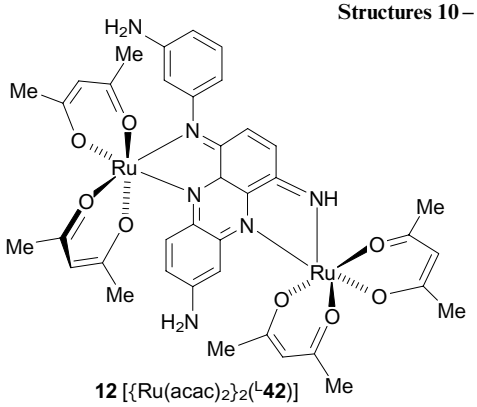
10 [Ru(acac)$_2$(L)]

X, Y = O, NH; L = ^{L}**16** – ^{L}**18**

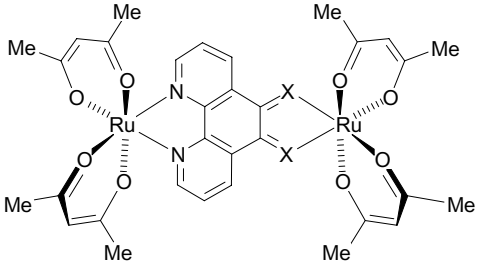


11 [Ru(acac)$_2$(^{L}**15**)]

Ar = Ph, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-O$_2$NC$_6$H$_4$

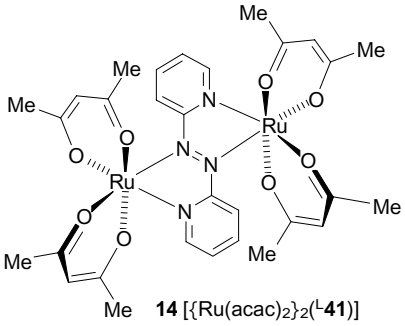


12 [{Ru(acac)$_2$}$_2$(^{L}**42**)]



13 [{Ru(acac)$_2$}$_2$(^{L}**20**), {Ru(acac)$_2$}$_2$(^{L}**22a**)]

X = O, NH



14 [{Ru(acac)$_2$}$_2$(^{L}**41**)]

active *p*-quinonediimine — 2-amino-6-(3-aminophenyl)-imino-9-iminophenazine (^{L}**42**) — was obtained by the reaction of Ru^{III}(acac)$_3$ with molten 1,3-diaminobenzene. The structure of compound **12** was established by X-ray diffraction and confirmed by physicochemical methods including ^{1}H NMR spectroscopy, mass spectrometry, IR spectroscopy and electronic absorption spectroscopy. Adduct **12** is diamagnetic and, therefore, it is a complex containing two Ru^{II} ions.

Adducts of ruthenium diketonates with redox-active bifunctional derivatives of 1,10-phenanthrolines were studied[89] by elemental analysis, EPR spectroscopy and mass spectrometry. Although no X-ray data for the complexes with the redox-active ligands ^{L}**20** and ^{L}**22a** are available, these structures were described as {Ru(acac)$_2$}$_2$(L) (Structures **13**). The electronic structure of the complex with the quinone ligand ^{L}**20** is described as Ru^{II}(^{L}**20**$^{-\bullet}$)Ru^{III} with partially coupled paramagnetic semiquinone and Ru^{III} centres. The difference between the oxidation and reduction potentials of the complex {Ru(acac)$_2$}$_2$(^{L}**22a**) is as large as 580 mV, and the temperature dependence of the magnetic susceptibility of this compound is governed by weak antiferromagnetic exchange interaction ($J = -1.14$ cm^{-1}).[89] Compound {(Ru(acac)$_2$}$_2$(^{L}**22a**) exhibits a strong Ru^{III}-type EPR spectrum ($g_1 = 2.36$, $g_2 = 2.21$, $g_3 = 1.82$) complemented by a half-field signal at $g = 4.28$.[89] Based on the data listed above and on the differences between the complexes {Ru(acac)$_2$}$_2$(^{L}**20**) and {(Ru(acac)$_2$}$_2$(^{L}**22a**), the structure of the latter was described as Ru^{III}(^{L}**22a**$^{2-}$)Ru^{III}.

Strong antiferromagnetic exchange interaction between the unpaired electrons of the radical anion form of the ligand and the metal ion was detected in stereoisomeric dinuclear complexes of Ru(acac)$_2$ with 2,2′-azobispyridine (^{L}**41**) (Structure **14**).[90] Based on the results of spectroelectrochemical study and X-ray data, it was concluded that these compounds contain mixed-valence metal ions and can be described as systems [Ru$^{2.5}$(^{L}**41**$^{-\bullet}$)Ru$^{2.5}$]. A detailed study on the influence of electrochemically controlled redox processes on the charge distribution in such complexes and mononuclear adducts with 2,2′-azobispyridine ligands ^{L}**41** was carried out by Kaim and co-workers.[91]

Electrically neutral dinuclear complex **15** synthesized by the reaction of ruthenium bis(acetylacetonate) with 1,4-diamino-2,5-hydroquinone (^{L}**43**) contains metal ions stabilized in the oxidation state +3.[92] The structure of the complex was established by X-ray diffraction analysis. The effective magnetic moment of complex **15** decreases as temperature decreases. Weak antiferromagnetic exchange coupling ($J = 4$ cm^{-1}) between the unpaired electrons of the metal centres was found.[92] Electrochemical reduction of the complex stabilizes the radical form of the ligand and the Ru^{II} state of the central ion.

A dinuclear complex of ruthenium bis(diketonate) with diiminoquinone exhibits similar properties.[93] According to X-ray data and results of magnetochemical studies, the complex contains two weakly coupled Ru^{III} ions. Oxidation of this compound produces mixed-valence Ru^{III} – Ru^{IV} derivatives while reduction leads to stabilization of the structure containing the radical form of the redox-active ligand and two Ru^{III} ions. As in the case of complex **15** (see above),[92] no intramolecular charge transfer was observed.

Dinuclear complexes **16** with dioxidobenzoquinones ^{L}**23a** and ^{L}**23b** contain ruthenium ions in the oxidation state +3 and the dianionic form of the redox-active linker ligand.[94] The effective magnetic moment of adduct {Ru(acac)$_2$}$_2$(^{L}**23a**) is (2.66 μ_B),[94] being close to the expected value for two isolated ruthenium ions. The effective magnetic moment of compound {Ru(acac)$_2$}$_2$(^{L}**23b**) is somewhat overestimated. As temperature decreases, the magnetic moment also decreases due to weak antiferromagnetic coupling [$J = -13.5$ cm^{-1} for {Ru(acac)$_2$}$_2$(^{L}**23a**); $J = -15.5$ cm^{-1} for {Ru(acac)$_2$}$_2$(^{L}**23b**)].[94] Weak ferromagnetism of the complexes observed at high temperatures

suggests not only intramolecular antiferromagnetic exchange, but also intermolecular ferromagnetic coupling that strengthens with increasing temperature. An analysis of spectroelectrochemical data showed that changes in the charge of the complex from 2+ to 2− do not cause ruthenium ions to go to the oxidation state +2.

Yet another dinuclear adduct of $Ru(acac)_2$ (Structure **17**) was synthesized by the reaction with 1,2,4,5-tetraimino-3,6-diketocyclohexane (^{L}**44**).[95] This compound exhibits diamagnetic properties. Its chemical composition was determined by mass spectrometry and the structure was confirmed by X-ray diffraction data. The oxidized and reduced forms of the complex were studied spectroelectrochemically and by EPR spectroscopy.

Like mononuclear complex **4** of ruthenium bis(acetylacetonate) with *N*-aryl-1,2-diiminobenzoquinone (Ar-^{L}**6**),[75] dinuclear adduct **18** of ruthenium bis(acetylacetonate) based on 3,3′,4,4′-tetraimino-3,3′,4,4′-tetrahydrobiphenyl (^{L}**45**) is diamagnetic.[96] The compound contains metal ions in the oxidation state +2. A spectroelectrochemical study of paramagnetic intermediates revealed an unpaired electron on one quinone fragment of the monoanion, whereas the monocationic complex contains mixed-valence metal centres Ru^{II}/Ru^{III}.

3. Theoretical modelling of the structure of adducts and the dynamics of SCO and VT rearrangements

Although there is a variety of redox-active and ancillary ligands used for the synthesis of adducts of transition metal complexes (see Section 2), all of them cannot undergo IET under the action of external factors and subsequent spin transitions. The only exception are adducts of cobalt bis(salicylaldiminates) with phenoxazinone ^{L}**9**;[65–67] however, their thermal stability is not high, so these adducts dissociate to the initial components at elevated temperatures. It seems likely that, despite a huge amount of experimental data, the potential of readily available adducts of transition metal complexes with redox-active ligands is far from being exhausted. In this connection, a new line of theoretical research into magnetoactive adducts of transition metals aimed at revealing mono- and dinuclear complexes (potentially) capable of undergoing thermally (probably, photochemically and pressure) initiated spin-state switching transitions emerged recently. Complexes exhibiting the ability to undergo VT and SCO rearrangements should meet the following requirements:[99, 100]

1. The adduct should be stable (total energy of the adduct molecule should be lower than the sum of the total energies of its components).

2. Low-spin (LS) electronic state of the complex should be energetically more preferable than the high-spin (HS) state.

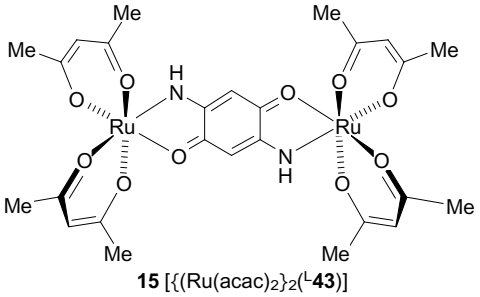
3. The relative energies of the isomers being rearranged (electromers) should not go beyond the limits specified by expression (2).

4. The energy barrier between different electromers should be lower than the stabilization energy of the adduct (10 – 12 kcal mol^{-1} for a thermally initiated rearrangement).

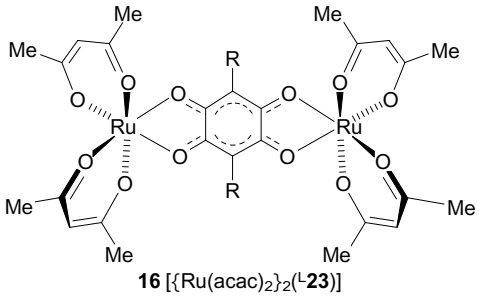
Evaluation of the energies of the predicted rearrangements accompanied by changes in the spin states of the reactants is complicated by the fact that these processes belong to spin-forbidden reactions, and the barrier to rearrangement is defined as the relative energy of the minimum energy crossing point (MECP). The energy of the MECP is a nonadibatic equivalent of the activation energy, being its upper limit. Figure 4 illustrates the results of MECP calculations of VT-controlled thermal rearrangement of an adduct of cobalt bis(salicylaldiminate) with phenoxazinone Co(N-(*p*-Tol)-sal)(^{L}**9**) using a software program developed by Harvey *et al.*[102]

It is a challenge to choose an appropriate computational scheme for quantum chemical prediction of the properties and reactivity of magnetoactive transition metal complexes. High lability of the electronic structure of mixed-ligand complexes, which in some cases[75, 76, 97, 98] excludes the possibility of simple characterization of the oxidation state

Structures 15 – 18

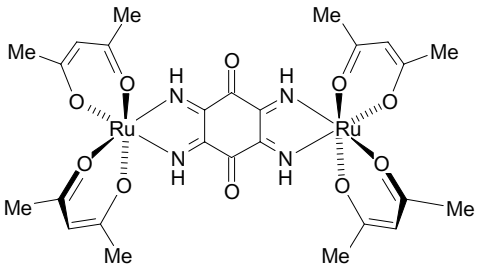


15 [{(Ru(acac)$_2$}$_2$(^{L}**43**)]

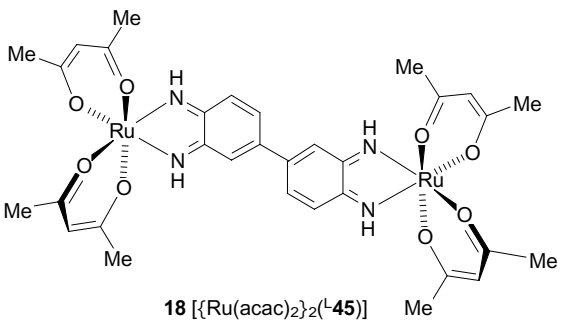


16 [{Ru(acac)$_2$}$_2$(^{L}**23**)]

R = H, Ph



17 [{Ru(acac)$_2$}$_2$(^{L}**44**)]



18 [{Ru(acac)$_2$}$_2$(^{L}**45**)]

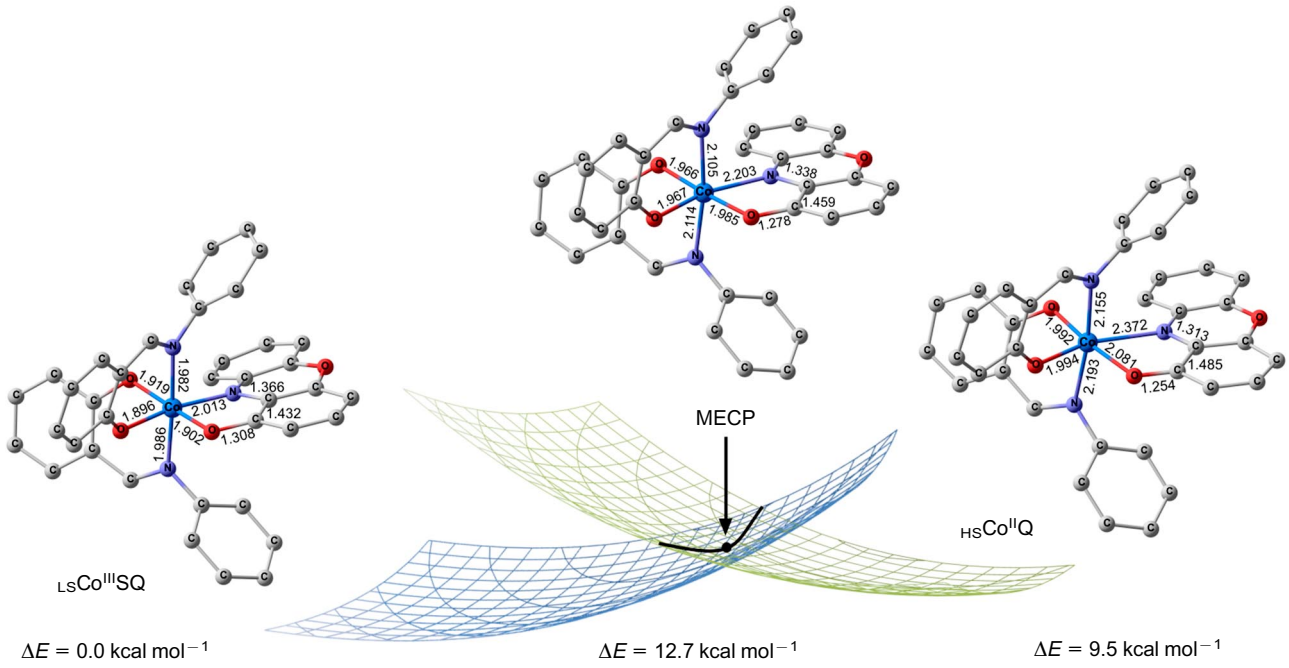


Figure 4. Energy profile of spin-forbidden rearrangement of the mixed-ligand complex Co(N-(*p*-Tol)-sal)(L**9**) obtained from DFT B3LYP*/6-311 + + G(d,p) calculations.[66]
Hydrogen atoms and alkly groups are omitted for clarity. Here and in Figs 5 – 17 and 21 the graphical images of the molecular structures were obtained using the ChemCraft software;[101] the bond lengths are given in Å.

of metal ions, and the existence of several potential energy surfaces (PESs) of the same multiplicity necessitate the use of multideterminant approximations. At the same time, complexes with redox-active ligands that possess switchable magnetic properties usually represent polyatomic structures containing 100 and more atoms or structures containing more than one paramagnetic centre. At present, geometry optimization of such compounds by the CASSCF and CASPT2 (NEVPT2) methods using relevant active spaces is nonrealistic. A fair trade-off is to use DFT computations. However, strong dependence of the results of calculations on the functional and orbital basis set requires thorough evaluation and testing of a certain approximation in relation to the closest analogues to the compounds of interest provided that reliable experimental data for these analogues are available. This can be exemplified by calculations of complexes of cobalt salicylaldiminates with phenoxazin-1-one.[66] The energy profile in Fig. 4 characterizes the dynamics of intramolecular rearrangements of these complexes. It was obtained by correlating the results of calculations using different types of functionals and basis sets with experimental data for complexes that are structurally similar to Co(N-(*p*-Tol)-sal)(L**9**). It was found[66] that the thermodynamic, kinetic, structural and magnetic parameters of the electromers involved in the rearrangements are best reproduced using the modified B3LYP* functional[103] and the 6-311 + + G(d,p) basis set of triple-zeta quality. Almost all results of calculations presented in Sections 4 – 6 were obtained in this approximation. Since neither Mulliken charges nor the charges calculated using the natural bond orbitals (NBO) scheme provide a correct value of the oxidation state of cobalt in the complexes with redox-active ligands, it seems appropriate to evaluate this parameter in terms of the number of unpaired electrons per metal atom.[104] Parameters of exchange interaction (J/cm^{-1}) are calculated within the framework of the broken symmetry (BS) formalism[105] using Yamaguchi's formula.[106] Methodological aspects of calculations of transition metal complexes with redox-active ligands taking account of dispersion, solvation effects, steric effect of substituents, counterions, *etc.* were considered in detail in a recent review[107] using a number of typical examples.

4. Mononuclear adducts of Co^{II}, Mn^{II} and Fe^{II} complexes

The conditions for occurrence of thermally initiated VT rearrangements of mixed-ligand complexes (adducts) specified in the previous Section can be represented in the form of expressions (2) – (4), where E_{stab} is the stabilization energy of an adduct relative to its dissociation to initial components.

$$E_{stab} > \text{MECP} \quad (3)$$

$$\text{MECP} \leqslant 10 - 12 \text{ kcal mol}^{-1} \quad (4)$$

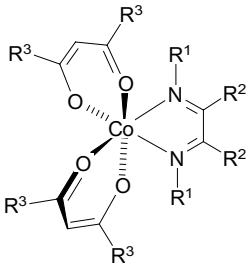
Now we will consider theoretical studies aimed to reveal (i) novel adducts of tetracoordinate metal complexes with redox-active ligands capable of undergoing VT rearrangements and (ii) structural factors that facilitate meeting conditions (2) – (4).

4.1. Adducts of Co^{II} and Mn^{II} complexes with α-diimines

4.1.1. Cobalt(II) complexes

The first attempt of theoretical prediction of VT-adducts, *viz.*, a DFT study[108] of mixed-ligand complexes of cobalt bis(diketonates) (malonates, acetylacetonates and hexafluoroacetylacetonates) Co(diketo)$_2$ with α-diimines, the

Structures 19



L = ^{L}**1a**–**d**;
R^3 = H, Me, CF_3

19 (Co(diketo)$_2$(L))

simplest diazabutadiene ligands ^{L}**1a**—^{L}**1d**, was reported in 2011. The cobalt bis(chelate) complexes of these ligands were studied earlier.[109,110] The adducts in question are presented as Structures **19**.

The adduct of diazabutadiene with cobalt bismalonate Co(mal)$_2$(^{L}**1a**) is more stable than its isolated components (E_{stab} = 14.8 kcal mol^{-1}).[108] The calculated spin density distribution suggests three unpaired electrons on the metal ion (q_s^M = 2.68), which is typical of the high-spin state of Co^{II}. The low-spin isomer of the complex, located on doublet PES, has the same energy and represents the electromer with the radical anion form of the redox-active ligand. The upper limit of the barrier to IET, defined as the MECP, is 6.3 kcal mol^{-1}, which allows one to expect VT in the adduct Co(mal)$_2$(^{L}**1a**) (Fig. 5). Similar results were obtained for Co(acac)$_2$(^{L}**1a**) with ancillary acetylacetonate ligands. Complexation of diazabutadiene with cobalt diketonate containing electron-withdrawing trifluoromethyl groups results in stable adduct Co(hfac)$_2$(^{L}**1a**) with the high-spin isomer (E_{stab} = 27.9 kcal mol^{-1}) as the ground state,[108] which limits the possibility of valence tautomeric equilibrium.

The model complexes considered above can only partially reflect the electronic structure of the complexes of Co(acac)$_2$ with diazabutadiene derivatives containing bulky groups at nitrogen atoms. The impact of steric factors on the formation of mixed-ligand cobalt complexes was analyzed in the calculations of adducts of cobalt diketonates with *N*,*N*′-bis(*tert*-butyl)-1,4-diazabuta-1,3-diene (^{L}**1b**) (Fig. 6).

It was shown that *tert*-butyl groups do not preclude stabilization of the high-spin forms of the complexes; however, the calculated spin density distribution suggests that the low-spin isomers bear an unpaired electron on the metal atom and, therefore, contain a Co^{II} ion. Nonequlvalence of Co—N bonds in these structures suggests that mono-coordination of the nitrogen-containing ligand is more preferable. It follows that VT in the complexes containing bulky *tert*-butyl groups is impossible. These substituents produce steric hindrances. As a consequence, unlike the adduct with ligand ^{L}**1a**, the redox-active ligand in the adduct Co(salen)(^{L}**1b**) adopts the *trans*-conformation (Structures **20a**,**b**) and only one donor centre of this ligand is involved in coordination with the central ion.

According to calculations of the adduct of cobalt bismalonate with iminosuccinonitrile Co(mal)$_2$(^{L}**1c**),[111] the energy difference between the ground state of the complex containing the low-spin Co^{III} ion and the high-spin structure exceeds a value of 11 kcal mol^{-1}. Replacement of hydrogen atoms in iminosuccinonitrile by methyl groups in the adduct Co(mal)$_2$(^{L}**1d**) causes the energy gap to narrow to 4.7 kcal mol^{-1} and thus to meet the necessary condition for VT specified by expression (2). The introduction of electron-withdrawing substituents into the redox-active and diketone ligands in the adduct Co(hfac)$_2$(^{L}**1c**) also favours narrowing of the energy gap between the HS and LS electromeric forms to meet condition (2); however, the

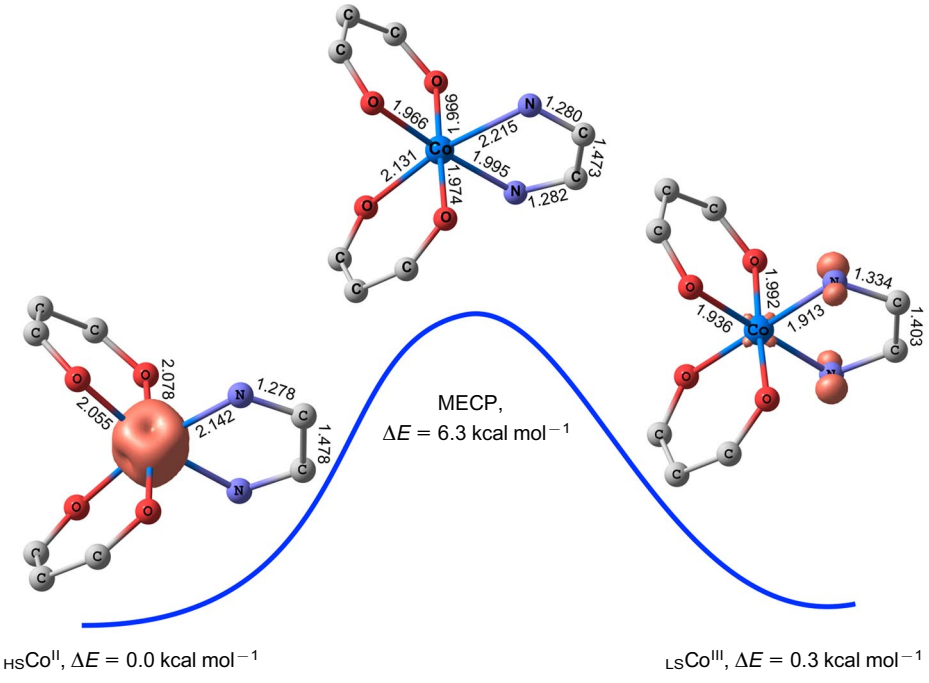


Figure 5. Optimized structures of electromers of adduct Co(mal)$_2$(^{L}**1a**) and the MECP for their VT rearrangement.[108]

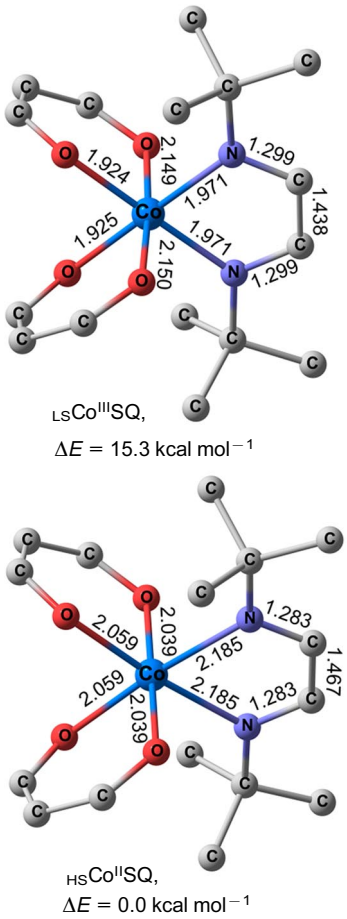
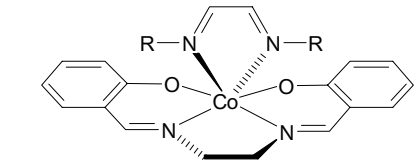


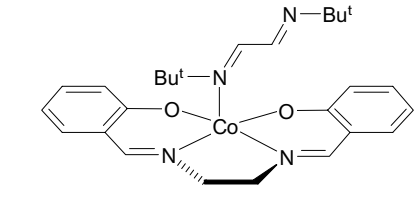
Figure 6. Optimized structures of isomers of adduct Co(mal)$_2$(^{L}**1b**).[108]

Structures 20



20a [Co(salen)(^{L}**1a**)]

R = H, Me



20b [Co(salen)(^{L}**1b**)]

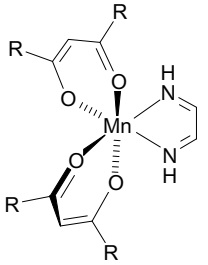
low-spin isomer becomes destabilized relative to the high-spin one, which makes VT impossible.

Calculations of adducts of diiminosuccinonitriles ^{L}**1c** and ^{L}**1d** with Co(salen) having a more rigid structure compared to diketonates showed that the ground state of these complexes corresponds to low-spin structures. Non-zero spin density on α-diimine is indicative of metal-to-ligand electron transfer upon complexation. The finding that the unpaired electrons in the high-spin structures are localized solely on the cobalt atom is indicative of the electrically neutral form of the DAD ligand. The incorporation of methyl groups into diiminosuccinonitrile causes the energy difference between the high- and low-spin isomers of the adduct to decrease to 9.8 kcal mol^{-1}, which allows one to expect VT in this system. However, destabilization of the high-spin form by 7 kcal mol^{-1} relative to the initial molecules suggests a highly probable dissociation of the adduct Co(salen)(^{L}**1d**) to the initial molecules, *viz*., Co(salen) and diiminosuccinonitrile ^{L}**1d**.

4.1.2. Manganese(II) complexes

Experimental studies[112–115] showed that VT transitions in manganese complexes are unambiguously detected by electron spectroscopy and not accompanied by switching of the magnetic properties of the molecules. Slight variations of the magnetic properties of the isomers with different charges and number of redox-active ligands are due to strong antiferromagnetic exchange interaction between the unpaired electrons of the metal ion and the radical forms of the ligands. According to calculations, the ground state of the adduct of Mn(acac)$_2$(^{L}**1a**) (Structure **21**) with α-diimine is represented by the structure in which four unpaired electrons on the metal ion are antiferromagnetically coupled with one unpaired electron on the redox-active ligand.[116] Therefore, this isomer of the complex contains the high-spin Mn^{III} ion and the radical anion form of α-diimine.

Structures 21



21 [Mn(acac)$_2$(^{L}**1a**), Mn(hfac)$_2$(^{L}**1a**)]

R = Me, CF_3

A structure located on the quartet PES contains three unpaired electrons on the metal ion. This may correspond to the Mn^{II} ion in the intermediate spin state (IS) and to the Mn^{IV} ion in the high-spin state (Fig. 7). An analysis of the bond lengths in the α-diimine ligand[116] suggests its dianionic form and, correspondingly, the oxidation state +4 of manganese. Destabilization of this isomer relative to the ground state (ΔE_{HS-LS} = 11.1 kcal mol^{-1})[116] practically excludes the possibility of redox transitions between these forms of the adduct. The electromer with five unpaired electrons on the manganese ion and electrically neutral ligand corresponds to the molecular complex Mn(acac)$_2$ and α-diimine ^{L}**1a**. Small energy difference between the isomer Mn^{II}Q and the ground state Mn^{III}SQ (4 kcal mol^{-1}) and rather low barrier separating them (ΔE_{MECP} = 8.7 kcal mol^{-1}) allow one to expect thermally induced electron transfer in the adduct Mn(acac)$_2$(^{L}**1a**) accompanied by the changes in the spin of the system from 3/2 to 5/2.[116]

Replacement of methyl groups by trifluoromethyl ones in the diketonate ligands leads to inversion of the electromeric forms of the adduct Mn(hfac)$_2$(^{L}**1a**). As a result, the

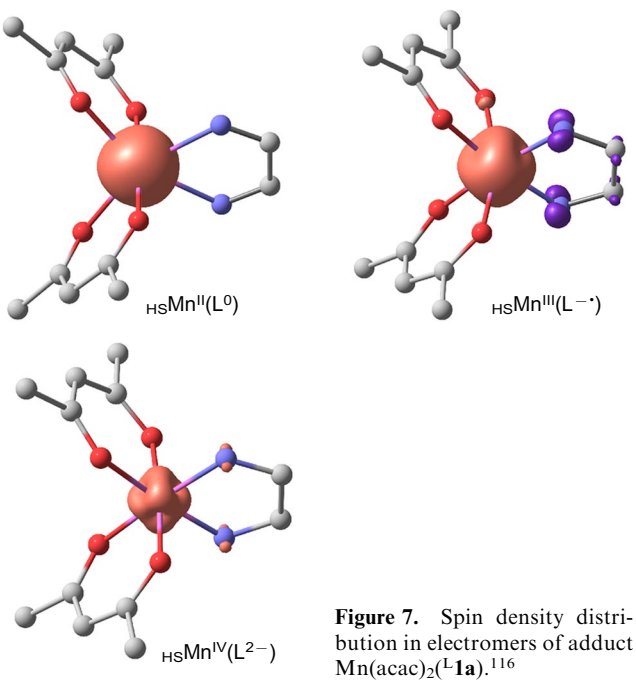


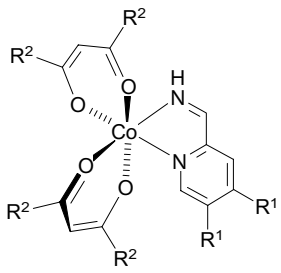
Figure 7. Spin density distribution in electromers of adduct Mn(acac)$_2$(L**1a**).[116]

ground state complex is represented by the structure containing the high-spin Mn^{II} ion and electrically neutral redox-active ligand. Destabilization (ΔE = 2.9 kcal mol^{-1})[116] of the isomer containing the high-spin Mn^{III} ion and the radical anion form of the α-diimine ligand makes VT in this system hardly probable. Calculations failed to locate the electromer containing the Mn^{IV} ion since the electron-withdrawing trifluoromethyl groups preclude transfer of the second electron from the metal to the redox-active ligand.

4.2. Adducts of Co^{II} complexes with 2-pyridylmethanimines

The synthesis of the adduct of cobalt bis(hexafluoroacetylacetonate) Co(hfac)$_2$(L**3a**) (Structure **22**) with α-iminopyridine was reported earlier;[117] however, the redox properties of this compound were not studied. Calculations[118] of adducts of 2-pyridylmethanimines L**3** with tetracoordinate Co^{II} complexes with the diketonate and *N*,*N*′-ethylenebis(salicylideneiminate) ligands revealed stabilization of the HSCo^{II}Q isomer containing the high-spin metal ion and electrically neutral diimine ligand. The low-spin isomer of compound Co(hfac)$_2$(L**3a**) is 6.2 kcal mol^{-1} higher on the energy scale. Localization of the only unpaired electron on the metal atom (Fig. 8) and the bond lengths typical of the electrically neutral form of the α-iminopyridine ligand[118]

Structure 22



L = L**3a**,**b**;
R^2 = Me, CF_3

22 [Co(diketo)$_2$(L)]

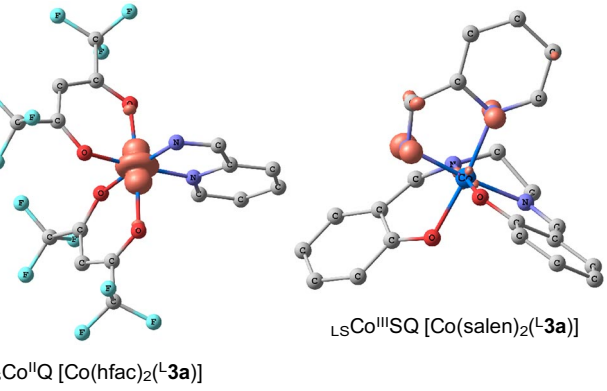
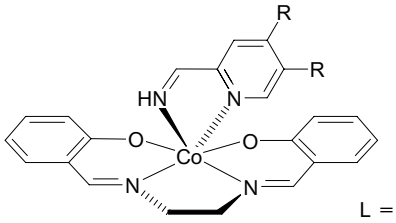


Figure 8. Spin density distribution in low-spin states of adducts Co(hfac)$_2$(L**3a**) and Co(salen)(L**3a**).[118]

point that this form of the complex contains the low-spin Co^{II} ion (LSCo^{II}Q).

The stability of the isomers containing electrically neutral ligands can be due to the electron-withdrawing properties of trifluoromethyl groups.[108, 111] Like in the case of compound Co(hfac)$_2$(L**3a**) considered above, the low-spin isomer LSCo^{II}Q of the adduct of cobalt bis(acetylacetonate) Co(acac)$_2$(L**3a**) is destabilized relative to the high-spin isomer and contains the unpaired electron localized on the metal atom. The adduct Co(salen)(L**3a**) (Structure **23**) is also stabilized in the high-spin state (ΔE = 5.8 kcal mol^{-1}),[118] but, unlike the complexes with diketonates, the low-spin isomer of this adduct contains the radical anion form of the iminopyridine ligand and the LSCo^{III} central ion. Low stability of Co(salen)(L**3a**) (E_{stab} = 3.7 kcal mol^{-1}) makes preparative-scale isolation of this compound little probable; however, stabilization of the low-spin isomer LSCo^{III}SQ containing the radical anion form of the redox-active ligand allows one to expect that targeted design of the ligand through functionalization of α-iminopyridine can lead to compounds possessing valence tautomerism.[118]

Structure 23



L = L**3a**,**b**

23 [Co(salen)(L)]

It was shown for adducts with the α-diimine ligands[111] that the introduction of electron-withdrawing substituents (*e.g.*, cyano groups) into the redox-active ligand stabilizes the structures containing the radical anion forms of the ligand. To search for α-iminopyridine based complexes capable of undergoing VT rearrangements, compounds with ligands containing two CN groups were studied. However, calculations of the adduct Co(hfac)$_2$(L**3b**) revealed no fundamental changes in the electronic structure and energy parameters of the isomers. Like in the case of compound Co(hfac)$_2$(L**3a**), the high-spin structure is energetically more preferable than the low-spin one, and both

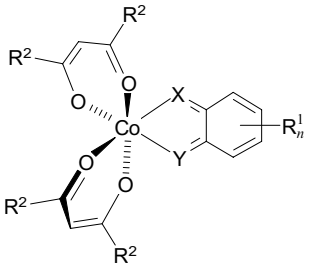
electromers contain the Co^{II} ion and electrically neutral ligand. However, the presence of electron-withdrawing groups only in α-iminopyridine leads to stabilization of the adduct of cobalt bis(acetylacetonate) $Co(acac)_2(^{L}\mathbf{3b})$ in the low-spin state $_{LS}Co^{III}SQ$ where the spin density is localized on the redox-active ligand. Small energy difference (3.5 kcal mol^{-1}) between the isomers of the adduct $Co(acac)_2(^{L}\mathbf{3b})$ allows one to expect a VT rearrangement with a barrier of at most 10.5 kcal mol^{-1} (Ref. 118). The $_{LS}Co^{III}SQ$ isomer of the adduct Co(salen)(^{L}**3b**) containing α-iminopyridine functionalized with cyano groups is also energetically more favourable than the high-spin isomer $_{HS}Co^{II}Q$.

4.3. Adducts of Co^{II}, Mn^{II} and Fe^{II} complexes with *o*-benzoquinone and its imino derivatives

4.3.1. Adducts of Co^{II} diketonates with *o*-benzoquinone

As mentioned above (see Section 2.1), the formation of adducts of *o*-benzoquinones with tetracoordinate cobalt ion complexes (Structure **24**) always stabilizes the low-spin isomer containing the SQ form of the ligand and Co^{III}.[58–62]

Structures 24



24 [Co(diketo)$_2$)(L)]

L = ^{L}**4**–^{L}**6**;
X, Y = O, NH;
R^1_n = H (^{L}**4a**–^{L}**6a**),
3,5-Bu^t_2 (^{L}**4b**–^{L}**6b**);
R^2 = H, Me, CF_3

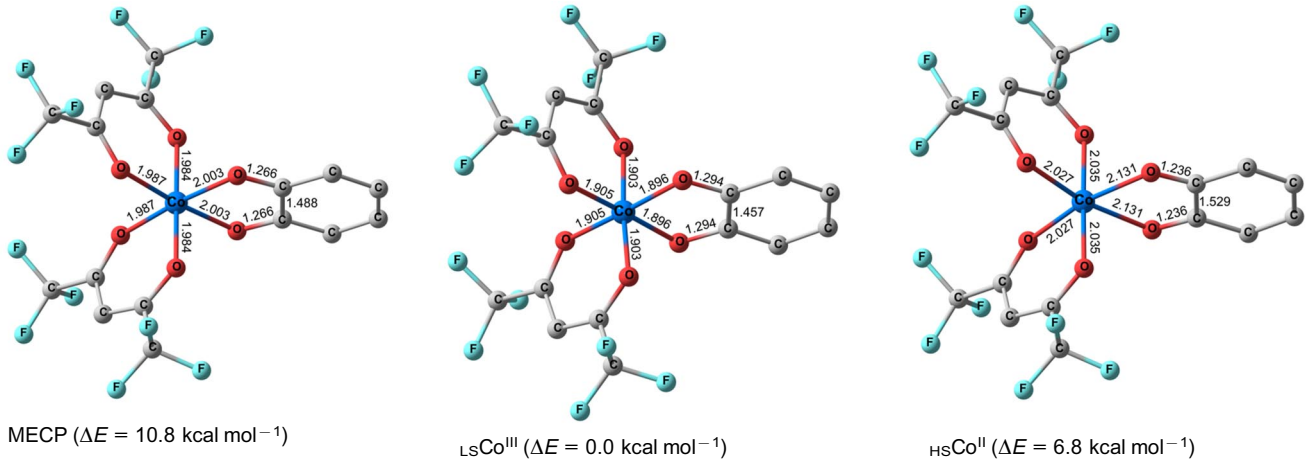
Calculations[119] showed that the low-spin electromer, $_{LS}Co^{III}SQ$, of the adduct of cobalt bis(acetylacetonate) with *o*-benzoquinone $Co(acac)_2(^{L}\mathbf{4a})$ is 15 kcal mol^{-1} energetically more preferable than the high-spin isomer $_{HS}Co^{II}Q$. This makes thermally initiated VT rearrangements in the system in hand impossible [see Eqn (2)]. However, the mixed-ligand complex $Co(hfac)_2(^{L}\mathbf{4a})$ is characterized by a narrower energy gap between the electromers (6.8 kcal mol^{-1}) and by lower barrier to transition (less than 11 kcal mol^{-1}, Fig. 9); taking into account high stabilization energy of this compound, one can expect the occurrence of VT.[119]

4.3.2. Adducts of Co^{II} diketonates with *o*-iminobenzoquinone and *o*-diiminobenzoquinone

According to calculations,[119] adducts of cobalt diketonates with *o*-iminobenzoquinone ^{L}**5a** (see Structures **24**) are also characterized by pronounced stabilization of the isomer $_{LS}Co^{III}SQ$ relative to $_{HS}Co^{II}Q$, while compound $Co(hfac)_2(^{L}\mathbf{5a})$ can undergo VT rearrangements. The low-spin isomer of the adduct of $Co(acac)_2$ with *o*-diiminobenzoquinone ^{L}**6a** is 12.2 kcal mol^{-1} energetically more favourable than the high-spin isomer; this should inhibit thermally initiated VT rearrangement. Using hexafluoroacetylacetonate as ancillary ligand leads to the most stable mixed-ligand complex $Co(hfac)_2(^{L}\mathbf{6a})$ with a stabilization energy of 34 kcal mol^{-1} (the highest value for all complexes considered above). A combination of the similar energies of the high- ($_{HS}Co^{II}Q$) and low-spin ($_{LS}Co^{III}SQ$) forms with the low energy barrier to the rearrangement (ΔE_{MECP} = 5.1 kcal mol^{-1}) (Ref. 119) makes the adduct of bis(hexafluoroacetylacetonato)cobalt with *o*-diiminobenzoquinone a candidate for the design of a stable thermally controlled VT system.

4.3.3. Adducts of Co^{II} diketonates with 3,5-di(*tert*-butyl)-*o*-benzoquinone and its imine derivatives

Substituents introduced into redox-active ligand molecules can significantly influence the energy parameters of VT-systems.[99,107] A study of adducts of 3,5-di(*tert*-butyl)-*o*-benzoquinone (^{L}**4b**) and its imine derivatives with bis(hexafluoroacetylacetonato)Co^{II} (Structures **24**) showed that bulky substituents at the *o*-benzoquinone ring decrease the energy difference between the low- and high-spin electromeric forms by more than 4 kcal mol^{-1}. As a result, VT in adducts of cobalt diketonates with quinone derivatives was predicted only for the complex with *o*-benzoquinone $Co(hfac)_2(^{L}\mathbf{4b})$. Compound $Co(hfac)_2(^{L}\mathbf{5b})$ is less promising since its high-spin isomer is 0.5 kcal mol^{-1} energetically more preferable than the low-spin isomer.[119] Calculations of adduct $Co(hfac)_2(^{L}\mathbf{6b})$ revealed stabilization of the high-



MECP (ΔE = 10.8 kcal mol^{-1})

$_{LS}Co^{III}$ (ΔE = 0.0 kcal mol^{-1})

$_{HS}Co^{II}$ (ΔE = 6.8 kcal mol^{-1})

Figure 9. Optimized structures of electromers of adduct $Co(hfac)_2(^{L}\mathbf{4a})$ and the MECP for their VT rearrangement.[119]

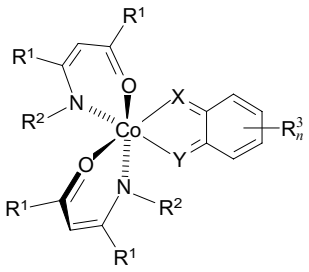
spin isomer relative to the low-spin one by 2.5 kcal mol^{-1}, which precludes manifestation of VT-properties in this system.[119] These results confirm an important role of bulky *tert*-butyl groups in the formation of the redox properties of coordination compounds of metals.

4.3.4. Adducts of azomethine complexes of Co^{II} with *o*-quinones and their derivatives

Adduct of *o*-benzoquinone (^{L}**4a**) with *N*,*N*′-ethylenebisacetylacetoneiminato)cobalt Co(acacen) is most stable in the $_{LS}$Co^{III}SQ form.[61] The results of DFT calculations [107] agree with experimental data and predict destabilization of the next-in-energy isomer ($_{IS}$Co^{III}SQ) by more than 12 kcal mol^{-1} (Fig. 10). The energy of the expected VT-electromer $_{HS}$Co^{II}Q is more than 18 kcal mol^{-1} higher than that of the ground state. Replacement of the *o*-quinone ligand by its diimine derivative causes inversion of the relative stability of the electromers $_{IS}$Co^{III}SQ and $_{HS}$Co^{II}Q, but does not facilitate VT.

An attempt was made to find VT-complexes among adducts of cobalt aminovinyl ketonates with *o*-benzoquinones and their imine derivatives ^{L}**4** – ^{L}**6** (Structures **25**).[120] According to calculations of complexes of *o*-benzoquinone (^{L}**4a**) with cobalt aminovinyl ketonates, the energetically favourable states include low-spin electronic ones, $_{LS}$Co^{III}SQ. No stationary points corresponding to the $_{HS}$Co^{II}Q isomers were located on the quartet PES; however, local minima were found corresponding to isomers containing a Co^{III} ion in the intermediate spin state and semiquinonate $_{IS}$Co^{III}SQ. Electron-withdrawing trifluoromethyl groups introduced into the aminovinyl ketone ligand stabilize the high-spin isomer with an energy of 17.7 kcal mol^{-1} relative to the low-spin isomer.[120] The large energy difference also makes manifestation of the SCO effect in the isomers containing the Co^{III} ion in different spin states impossible [see Eqn (2)].

Structures 25



25 [Co(acNac)$_2$(L)]

L = ^{L}**4a**, ^{L}**5a**,**c** – **e**, ^{L}**6a**,**c** – **e**;
X, Y = O, NR^3;
R^1 = H, Me, CF$_3$;
R^2 = R^3 = H, Me, Pr^i, Ph

The equilibrium between different electromeric forms can be shifted by replacing oxygen atoms in the *o*-quinone ligand by imino groups that create additional steric hindrances to formation of low-spin structures. Adducts with *o*-iminobenzoquinone ^{L}**5** have isomers containing Co^{II} ions in the high-spin state. Replacement of hydrogen atom by methyl group in iminoquinone (ligand ^{L}**5c**) does not narrow the energy gap between electromers; however, the stabilization energy decreases to 4.6 kcal mol^{-1}.[120] The introduction of phenyl group into iminoquinone (ligand ^{L}**5d**) causes the energy levels of the electromers to draw together; however, the stabilization energy of the $_{HS}$Co^{II}Q isomer is close to zero. Even bulkier isopropyl substituent (R^2 = Pr^i) at nitrogen atom completely destabilizes the high-spin electromer. The energy difference between the high-spin isomer and the low-spin ground state of adducts of diiminobenzoquinones ^{L}**6** containing phenyl (^{L}**6d**) and isopropyl (^{L}**6e**) groups at nitrogen atoms decreases to 8.6 – 7.5 kcal mol^{-1}; however, bulky substituents decrease the stabilization energies to 1 – 3 kcal mol^{-1}.[120] This is similar to the case for phenoxazinone complexes with cobalt salicylaldiminates,[65,66] namely, these compounds can exhibit VT in the crystalline state but dissociate to initial bis(chelate) and redox-active ligand in solutions.

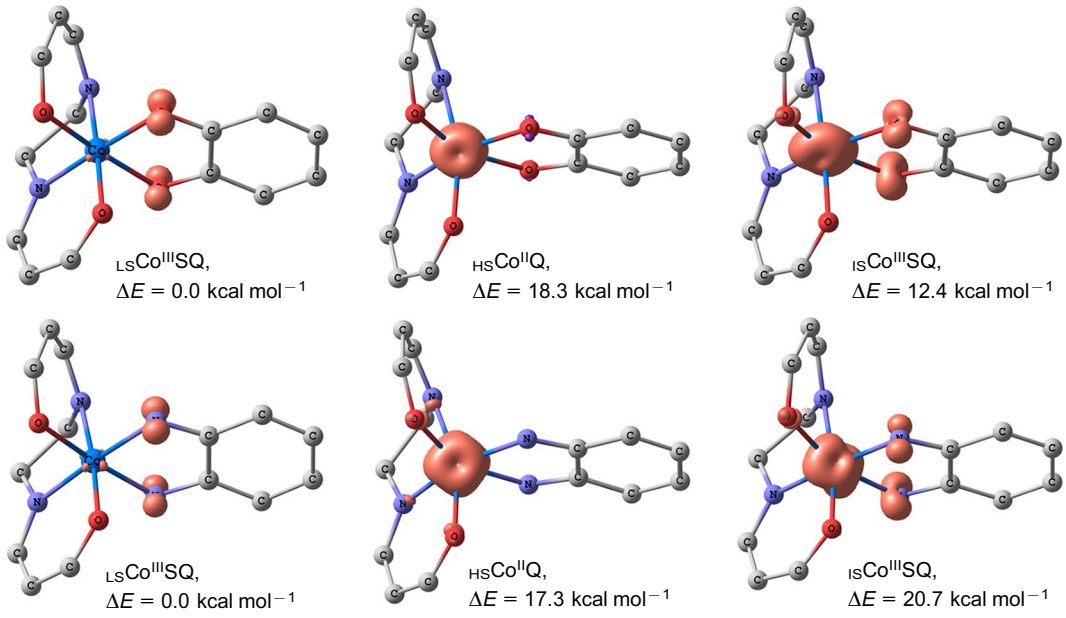


Figure 10. Spin density distribution in electromeric forms of adducts Co(acacen)(^{L}**4a**) and Co(acacen)(^{L}**6a**).[107]

4.3.5. Adducts of Mn^{II} diketonates

Theoretical modelling of the drawing together of the *o*-benzoquinone and Mn^{II} bis(malonate) molecules separated by distances longer than 3.5 Å revealed the absence of pre-reaction complexes on the path of formation of adduct.[121] At a distance of 2.2 Å between the metal ion and quinonoid oxygen atom, electron transfer from the metal to the redox-active ligand occurs and the ligand undergoes rearrangement to the radical anion SQ form. Therefore, the adduct formation is not accompanied by the formation of the $_{HS}Mn^{II}Q$ isomer corresponding to the molecular complex. The ground state of complex $Mn(mal)_2(^{L}\mathbf{4a})$ is represented by the electromer $_{HS}Mn^{III}SQ$ (Fig. 11) for which calculations predicted a strong antiferromagnetic exchange interaction between the unpaired electrons of the metal and ligand resulting in the state with $S = 3/2$. An analysis of the electronic structure of the electromer located on the quartet PES suggests three unpaired electrons on the metal ion and slight alternation of bonds in the six-membered ring,[113] which allows one to describe this system as $_{HS}Mn^{IV}Cat$.

Similar results were obtained for the adduct $Mn(acac)_2(^{L}\mathbf{4a})$ [121] characterized by the absence of the electromeric form $Mn^{II}Q$. The reaction of *o*-benzoquinone with $Mn^{II}(hfac)_2$ results in the system $_{HS}Mn^{III}SQ$ with strong antiferromagnetic exchange interaction ($J = -340$ cm^{-1}). Although the geometry of the electromer located on the quartet PES does not exactly match that of the catecholate form of the redox-active ligand, the spin density on the metal ($q_s^{Mn} = 2.29$) (Ref. 121) suggests that the minimum located on this PES corresponds to $_{HS}Mn^{IV}$-Cat. The most stable electromer of complex $Mn(mal)_2(^{L}\mathbf{5a})$ for which calculations predicted a strong antiferromagnetic coupling ($J = -467$ cm^{-1}) can be described as $_{HS}Mn^{III}SQ$.[121] The electromer containing the catecholate form of the ligand has short Mn–O and Mn–N bonds (1.88 and 1.91 Å, respectively), which favours partial spin density transfer from the metal atom ($q_s^{Mn} = 2.31$) to the ligand. Destabilization of the $_{HS}Mn^{IV}Cat$ isomer relative to the ground state of adduct $Mn(mal)_2(^{L}\mathbf{5a})$ makes VT in this compound impossible.

The interaction of *o*-iminoquinone with $Mn^{II}(hfac)_2$ results in molecular complex $Mn(hfac)_2(^{L}\mathbf{5a})$ containing the Q form of the ligand and bis(diketonate) $Mn^{II}Q$; a total of five unpaired electrons ($q_s^{Mn} = 4.58$) are localized on the metal atom.[121] Strong antiferromagnetic exchange interaction stabilizes the electromer $_{HS}Mn^{III}SQ$ by 7.6 kcal mol^{-1} relative to the high-spin form of the complex. Therefore, one can expect a thermally induced transition between these electromers. Like in the complexes with *o*-quinones and *o*-iminoquinones (see above), the ground state of the adduct $Mn(mal)_2(^{L}\mathbf{6a})$ is represented by the electromer $_{HS}Mn^{III}SQ$ with antiferromagnetic exchange between the unpaired electrons of the metal and ligand. No isomer described as $_{HS}Mn^{II}Q$ was located, while the structure corresponding to the $_{HS}Mn^{IV}Cat$ electromer has an energy of 6.7 kcal mol^{-1} relative to the ground state. Electron-withdrawing properties of trifluoromethyl groups favour stabilization of two isomers of the adduct $Mn(hfac)_2(^{L}\mathbf{6a})$, namely, $_{HS}Mn^{III}SQ$ and $_{HS}Mn^{II}Q$. The energy preferableness of the former isomer and the height of the barrier to transition between them (8.0 kcal mol^{-1}) do not exclude the possibility of VT.[121]

Thus, for all adducts considered the electromers containing the Mn^{IV} ion and the catecholate form of the redox-active ligand do not correspond to the ground electronic state. Therefore, thermally initiated transitions between the tautomers containing Mn^{IV} and Mn^{III} are impossible. The most stable isomers correspond to the structures containing the $_{HS}Mn^{III}$ ion and the SQ form of the redox-active ligand. There is strong antiferromagnetic exchange between the unpaired electrons of the metal ion and the ligand. Electromers representing molecular complexes of divalent metal ($_{HS}Mn^{II}$) diketonates and electrically neutral redox-active ligand were found only for adducts of manganese hexafluoroacetylacetonate with imine- and diimine-*o*-benzoquinone. Destabilization of the structures corresponding to these forms by 7–8 kcal mol^{-1} relative to the ground states allows one to expect a VT transition $_{HS}Mn^{III}SQ \rightleftharpoons {}_{HS}Mn^{II}Q$ in the adducts $Mn(hfac)_2(^{L}\mathbf{5a})$ and $Mn(hfac)_2(^{L}\mathbf{6a})$.[121] It should be noted that the redox-isomeric rearrangements predicted by calculations will be accompanied by changes in the magnetic properties in contrast to the known VT-complexes of manganese.[112–115]

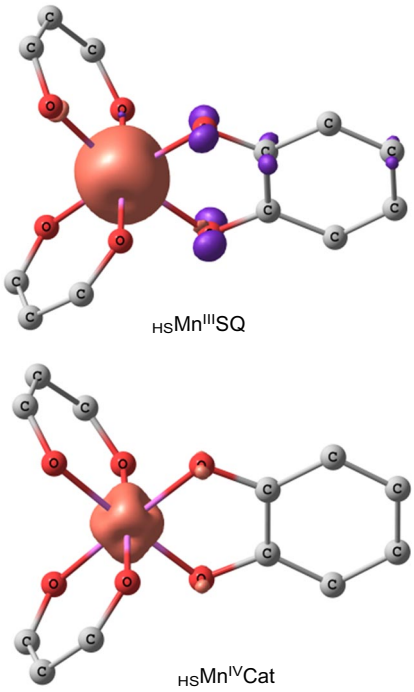
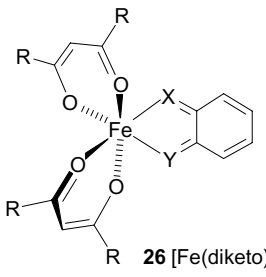


Figure 11. Spin density distribution in electromers of adduct $Mn(mal)_2(^{L}\mathbf{4a})$.[121]

4.3.6. Adducts of Fe^{II} complexes

According to DFT calculations, the formation of adducts of iron(II) diketonates with *o*-benzoquinones and their mono- and diimine derivatives (Structure **26**) is accompanied by

Structures 26



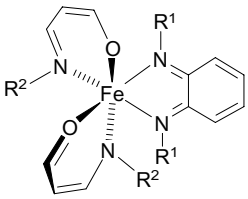
26 [Fe(diketo)$_2$(L)]

L = ^{L}**4**–^{L}**6**;
X, Y = O, NH;
R = Me, CF_3

electron transfer from the metal to the redox-active ligand and emergence of two paramagnetic centres, one on the Fe^{III} ion and the other on the radical anion form of the redox-active ligand. A lack of isomers containing divalent iron suggests that VT in this group of complexes is impossible.

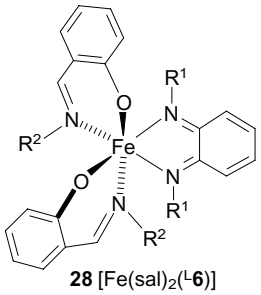
A feature of the electronic structure of the high-spin isomers consists in spin density transfer from the metal ion to the donor atoms of the diketonate ligands. The spin density at iron ion is nearly 4 a.u., being much smaller than the value expected for five unpaired electrons. The calculated stabilization energies of the adducts (21 – 25 kcal mol^{-1}) point to high thermodynamic stability of these systems. The strength of exchange interaction between paramagnetic centres increases in the order *o*-benzoquinone < *o*-iminobenzoquinone < *o*-diiminobenzoquinone. The high-spin isomers of all adducts considered are characterized by antiferromagnetic exchange (from −161 to −751 cm^{-1}). The low-spin structures based on *o*-benzoquinones are characterized by ferromagnetic exchange. These results agree with the data of magnetochemical studies of the iron complexes with the *o*-benzoquinone ligand.[122, 123] The broken symmetry states used as models for antiparallel orientation of the spins of paramagnetic centres and $_{HS}Fe^{III}SQ$ isomers are energetically more preferable than corresponding low-spin isomers $_{LS}Fe^{III}SQ$; this indicates stabilization of the high-spin states of all adducts considered. The energy gap between isomers narrows from 7.5 – 5.1 to 1.4 – 0.8 kcal mol^{-1} on going to the complexes of *o*-diiminoquinones. One can expect manifestation of the SCO effect on Fe^{III} ions in the adducts of bis(chelates) with high ligand field strength. Although most SCO-complexes represent Fe^{II} compounds with the coordination site FeN_6,[124] there is also a large number of Fe^{III} SCO-complexes with the FeN_4O_2 coordination site.[125, 126] The latter coordination site is formed in the adducts of azomethine complexes of iron with *o*-diiminoquinones. Probably, the corresponding ligand field is strong enough for SCO on Fe^{III} ions to occur.

Structures 27 – 30



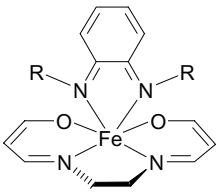
27 [Fe(acNac)$_2$(L**6**)]

R^1 = H, Ph; R^2 = H, Me, Ph



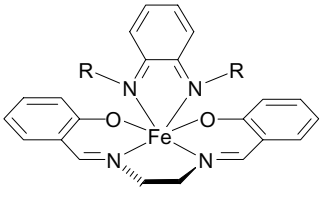
28 [Fe(sal)$_2$(L**6**)]

R^1 = H, Ph; R^2 = H, Me, Ph



29 [Fe(acacen)(L**6**)]

R = H, Ph



30 [Fe(salen)(L**6**)]

R = H, Ph

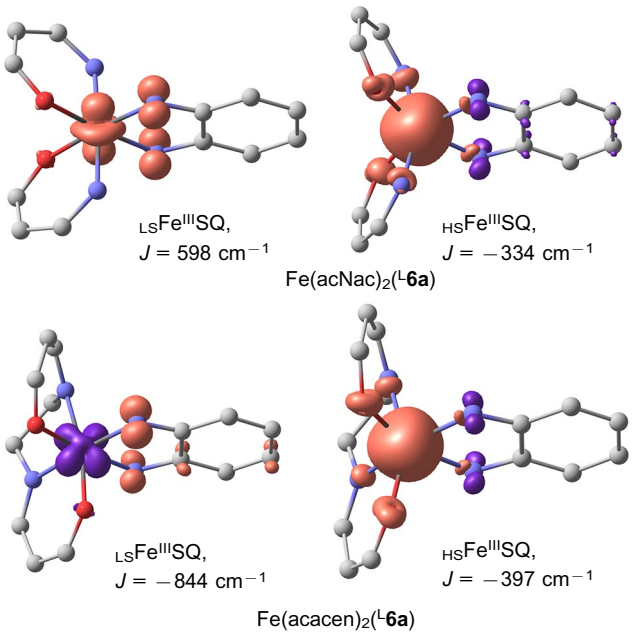


Figure 12. Spin density distribution in electromers of adducts Fe(acNac)$_2$(L**6a**) and Fe(acacen)(L**6a**).[127]

The results of calculations of adducts Fe(acNac)$_2$(L**6a**) and Fe(sal)$_2$(L**6a**) (structures **27** and **28**, respectively) point to little effect of annelation of six-membered rings to the aminovinyl ketone ligands on the choice of the ground electronic state and geometric parameters of the coordination site of the stable adducts (E_{stab} > 13 kcal mol^{-1}) being formed.[127] An analysis of exchange interactions suggests a strong antiferromagnetic exchange (J is from −334 to −406 cm^{-1}) in the high-spin forms $_{HS}Fe^{III}SQ$, which stabilizes the state with $S = 4/2$.[127] Ferromagnetic coupling of the low-spin isomers of adducts Fe(acNac)$_2$(L**6a**) and Fe(sal)$_2$(L**6a**) allows one to expect that the complexes are paramagnetic in a wide temperature range (Fig. 12). The energy parameters of the complexes show that thermally induced SCO in compounds Fe(N-Me-acNac)$_2$(L**6a**) and Fe(N-Me-sal)$_2$(L**6a**) is possible irrespective of the substituent at nitrogen atoms of the diimine ligands.

Calculations of adducts of Fe^{II} *N*,*N*′-ethylenebis(aminovinyl ketonates) and Fe^{II} *N*,*N*′-ethylenebis(salicylideneiminates) also predict stabilization of the electromers containing Fe^{III} and the radical anion form of diimine. Unlike complexes Fe(acNac)$_2$(L**6**) and Fe(sal)$_2$(L**6**), antiferromagnetic ordering of unpaired electrons in the low-spin isomers Fe(acacen)(L**6**) and Fe(salen)(L**6**) (structures **29** and **30**, respectively) is expected, *viz*., the parameter J is in the range from −470 to −844 cm^{-1}; this should lead to diamagnetism of the complexes.[127] Changes in the character of exchange interaction in the low-spin isomers of the adducts Fe(acacen)(L**6**) and Fe(salen)(L**6**) can be due to the low degree of biradical component (39% – 46%, Ref. 128) and to differences in the overlap of magnetic orbitals.

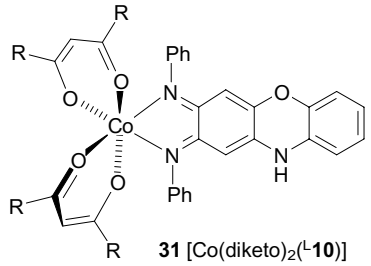
4.4. Adducts of Co^{II} complexes with diiminophenoxazine

Derivatives of recently synthesized (*Z*)-6,8-di(*tert*-butyl)-*N*-(4-methoxyphenyl)-3-[(4-methoxyphenyl)imino]-3*H*-phenox-

azine-2-amine[129] may appear to be promising redox-ligands.

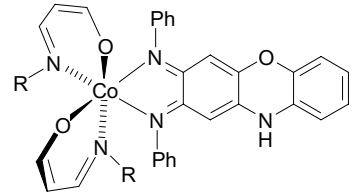
According to calculations,[130] the ground state of adduct of cobalt bis(acetylacetonate) with *N*,*N*-diphenyldiimino-phenoxazine Co(acac)$_2$(^{L}**10**) (Structures **31**) is $_{LS}$Co^{III}SQ containing low-spin Co^{III} ion and the radical anion SQ form of the redox-active ligand. The high-spin isomer $_{HS}$Co^{II}Q representing a molecular complex is destabilized by 4.5 kcal mol^{-1} relative to the low-spin isomer; this allows one to expect a thermally initiated VT rearrangement. Replacement of methyl groups by trifluoromethyl ones in the diketonate ligands of complexes Co(tfac)$_2$(^{L}**10**) and Co(hfac)$_2$(^{L}**10**) is followed by inversion of the electromer energy levels. As a consequence, the VT rearrangement in these complexes becomes impossible. As to adducts of ^{L}**10** with cobalt bis(aminovinyl ketonates) and cobalt bis(salicylaldiminates) (Structures **32** and **33**, respectively), complexation is also accompanied by metal-to-ligand electron transfer and results in $_{LS}$Co^{III}SQ electromers on the doublet PES irrespective of substituents at azomethine nitrogen atoms. The energy difference between the low- and high-spin isomers of adducts Co(acNac)$_2$(^{L}**10**), Co(N-Me-acNac)$_2$(^{L}**10**) and Co(N-Ph-acNac)$_2$(^{L}**10**) monotonically decreases from 14.4 to 3.3 kcal mol^{-1} as the volume of the substituent at nitrogen atoms of aminovinyl ketonate ligand increases.[130] The energy differences between the $_{LS}$Co^{III}SQ and $_{HS}$Co^{II}Q isomers of adduct Co(N-Ph-acNac)$_2$(^{L}**10**) facilitate VT in the crystalline state; however, VT in solution will compete with dissociation of the adduct to the initial azomethine complex and redox-active ligand owing to the low stabilization energy of the compound. Similar results were obtained for adducts based on salicylaldiminates.[130]

Structures 31 – 33



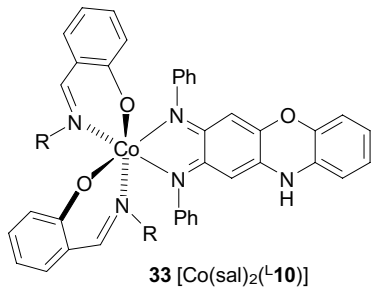
R = Me, CF$_3$

31 [Co(diketo)$_2$(^{L}**10**)]



R = H, Me, Ph

32 [Co(acNac)$_2$(^{L}**10**)]



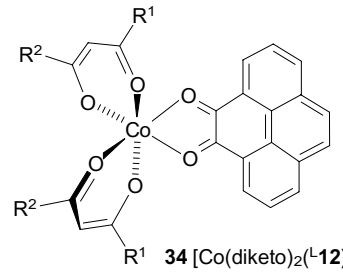
R = H, Me, Ph

33 [Co(sal)$_2$(^{L}**10**)]

4.5. Adducts of Co^{II} complexes with pyrene-4,5-dione

The molecule of pyrene-4,5-dione[131, 132] contains four fused six-membered rings that can significantly influence the redox properties of the quinone moiety. The calculated energy difference (9.7 kcal mol^{-1}) between electromers of the adduct Co(acac)$_2$(^{L}**12**) (Structures **34**) allows one to expect the VT behaviour; however, low stabilization energy of the high-spin isomer relative to isolated cobalt diketonate and redox-active ligand molecules (3.8 kcal mol^{-1}) and high barrier to IET (MECP > 16 kcal mol^{-1}) will facilitate dissociation of the adduct at elevated temperatures.[133] The introduction of two electron-withdrawing trifluoromethyl groups into the diketonate ligands leads to formation of stable (ΔE_{stab} = 18.7 kcal mol^{-1}) high-spin electromer of adduct Co(hfac)$_2$(^{L}**12**). The low-spin structure bears one unpaired electron on the redox-active ligand. Its energy is 3.9 kcal mol^{-1} higher than that of the high-spin electromer; as a consequence, VT in this system is impossible.[133] From the results of calculations of adducts Co(acac)$_2$(^{L}**12**) and Co(hfac)$_2$(^{L}**12**) it follows that methyl groups in the diketonate fragment of the complexes stabilize the low-spin electromer, whereas trifluoromethyl groups favour stabilization of the high-spin one. One would expect that combination of the effects produced by these substituents will lead to a compound that can undergo thermally induced VT rearrangements.[134] According to calculations, the most stable form of adduct Co(tfac)$_2$(^{L}**12**) is represented by the low-spin structure located on the doublet PES, which comprises the low-spin Co^{III} ion and the SQ form of the redox-active ligand. The high-spin isomer is sufficiently stable towards dissociation (ΔE_{stab} = 10.4 kcal mol^{-1}) and the energy difference between the electromers is 3.1 kcal mol^{-1}.[133] The energy of the MECP structure is 9.3 kcal mol^{-1} relative to the ground state, being lower than the stabilization energy of the adduct. It follows that the energy parameters of compound Co(tfac)$_2$(^{L}**12**) meet the conditions (2) – (4) for thermally induced VT rearrangement.[133]

Structure 34



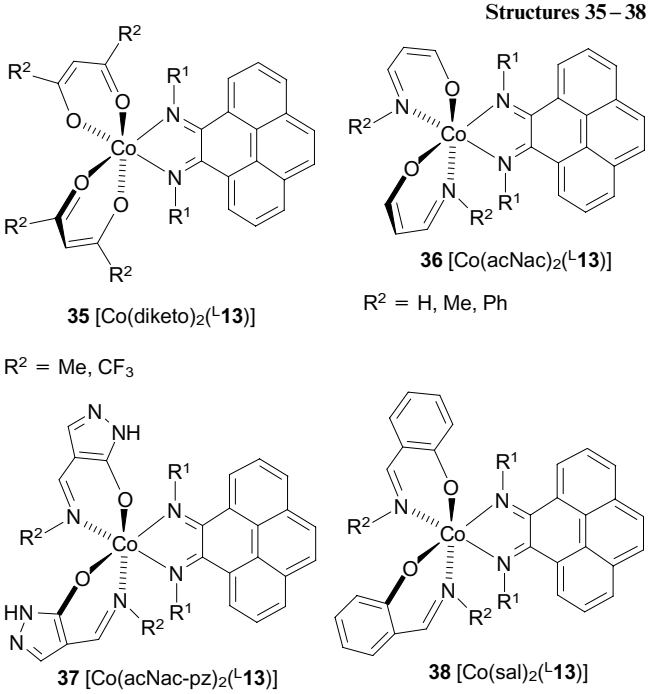
R^1, R^2 = Me, CF$_3$

34 [Co(diketo)$_2$(^{L}**12**)]

4.6. Adducts of Co^{II} complexes with pyrene-4,5-diimines

According to calculations,[135] pyrene-4,5-diimine (^{L}**13a**) forms stable (E_{stab} = 10 – 35 kcal mol^{-1}) adducts with various Co^{II} bis(chelate) complexes (Structures **35** – **38**). Adducts of pyrene-4,5-diimines ^{L}**13** with cobalt diketonates are characterized by higher stabilization energies compared to their analogues based on pyrene-4,5-dione (^{L}**12**) (see Section 4.5). Nitrogen-containing donor centres in the redox-active ligand favour stabilization of the high-spin isomers of the complexes, which can be explained by lower

Structures 35 – 38



electron affinity of the pyrenediimine ligands as compared to their oxygen-containing analogues.

Numerical values of the energy differences between the low- and high-spin isomers as well as the MECP values allow one to expect the occurrence of VT rearrangements in the adducts with cobalt bis(acetylacetonate) $Co(acac)_2(^{L}\mathbf{13a})$ and with azomethine complexes $Co(N\text{-}Ph\text{-}acNac)_2(^{L}\mathbf{13a})$, $Co(N\text{-}Me\text{-}acNac\text{-}pz)_2(^{L}\mathbf{13a})$, $Co(N\text{-}Ph\text{-}acNac\text{-}pz)_2(^{L}\mathbf{13a})$ and $Co(N\text{-}Ph\text{-}sal)_2(^{L}\mathbf{13a})$. The introduction of bulky phenyl groups at the donor atoms of the diimine ligand leads to steric overcrowding of the coordination site in the adducts and subsequent destabilization of these systems. Calculations predicted the possibility for VT transitions to occur in the mixed-ligand complexes $Co(acac)_2(^{L}\mathbf{13b})$, $Co(N\text{-}Ph\text{-}acNac\text{-}pz)_2(^{L}\mathbf{13b})$ and $Co(N\text{-}Ph\text{-}sal)_2(^{L}\mathbf{13b})$.

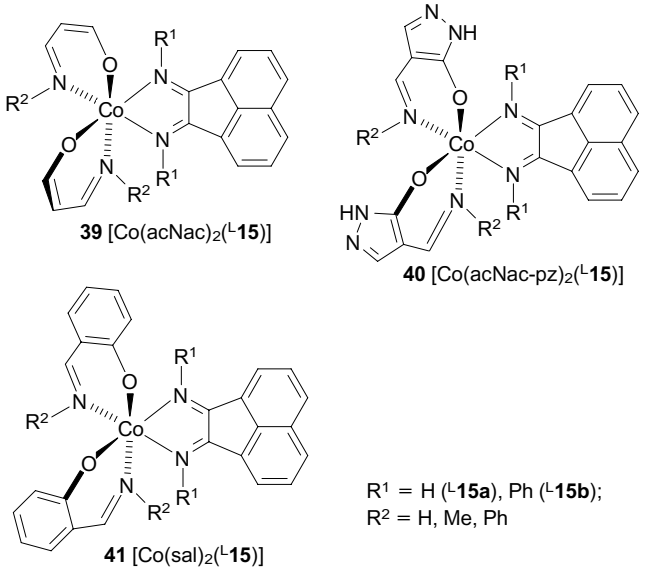
4.7. Adducts of Co^{II} complexes with acenaphthene-1,2-diimine

The ability of diiminoacenaphthene ligands to undergo redox-isomeric rearrangements was demonstrated for complexes of rare-earth elements.[136–138] The possibility of manifestation of this effect in adducts of cobalt bis(chelates) was considered in a recent study.[139]

The ground electronic state of acenaphthene-1,2-diimine complexes with cobalt bis(aminovinyl ketonate) $Co(acNac)_2(^{L}\mathbf{15a})$ (Structure **39**) is represented by the low-spin form which contains one unpaired electron localized on the radical anion form of BIAN. The high-spin electromer is destabilized by 8.5 kcal mol^{-1} relative to the low-spin one and contains three unpaired electrons on the metal ion.[139] This allows one to expect manifestation of thermally induced VT in the adduct $Co(acNac)_2(^{L}\mathbf{15a})$. Phenyl groups at nitrogen atoms of the azomethine ligand preclude stabilization of the low-spin isomer. As a result, the high-spin structure appears to be the more stable form of complex $Co(N\text{-}Ph\text{-}acNac)_2(^{L}\mathbf{15a})$. Further increase in steric hindrances in the coordination site owing to the influence of phenyl groups in the BIAN ligand causes destabilization of the high-spin forms of adducts $Co(acNac)_2(^{L}\mathbf{15b})$, $Co(N\text{-}Ph\text{-}acNac)_2(^{L}\mathbf{15b})$, $Co(N\text{-}Me\text{-}acNac)_2(^{L}\mathbf{15b})$ with respect to the initial components. Consequently, thermally initiated transitions from the low-spin forms of such compounds to the high-spin ones will be accompanied by dissociation to isolated cobalt bis(aminovinyl ketonate) and acenaphthene-1,2-diimine ligand.

Incorporation of pyrazole (pz) rings into the structure of ancillary azomethine ligand causes the thermal stability of the adducts to decrease. The calculated energy parameters of isomers of the adducts $Co(acNac\text{-}pz)_2(^{L}\mathbf{15a})$ and $Co(acNac\text{-}pz)_2(^{L}\mathbf{15b})$ (structures **40**) (E_{stab} = 3.3 – 5.8 kcal mol^{-1}, ΔE_{LS-HS} = 2.2 – 3.1 kcal mol^{-1})[139] allow thermally induced VT rearrangements to occur in these systems; however, dissociation of the complexes to initial components is also possible. Methyl and phenyl substituents at nitrogen atoms of the azomethine ligand facilitate inversion of the relative stabilities of the electromeric forms, *viz.*, the high-spin structures become the energetically more preferable isomers of the complexes $Co(N\text{-}Me\text{-}acNac\text{-}pz)_2(^{L}\mathbf{15a})$, $Co(N\text{-}Ph\text{-}acNac\text{-}pz)_2(^{L}\mathbf{15a})$ and the VT rearrangements are thus inhibited. Mixed-ligand complexes $Co(N\text{-}Me\text{-}acNac\text{-}pz)_2(^{L}\mathbf{15b})$ and $Co(N\text{-}Ph\text{-}acNac\text{-}pz)_2(^{L}\mathbf{15b})$ containing bulky substituents at nitrogen atoms of the azomethine and redox-active ligands are destabilized with respect to the initial bis(chelate) and BIAN molecules.

Structures 39 – 41



The predicted energy differences (ΔE_{HS-LS}) between the low- and high-spin structures of the adducts of cobalt salicylaldiminates $Co(sal)_2(^{L}\mathbf{15a})$ and $Co(N\text{-}Me\text{-}sal)_2(^{L}\mathbf{15a})$ (structures **41**) allow one to expect VT rearrangements. The introduction of phenyl group at nitrogen atoms of the acenaphthene-1,2-diimine ligand reduces the stability of the corresponding adducts $Co(sal)_2(^{L}\mathbf{15b})$ and $Co(N\text{-}Me\text{-}sal)_2(^{L}\mathbf{15b})$ by 3 – 5 kcal mol^{-1}.[139] In the case

of complex Co(N-Me-sal)$_2$(^{L}**15b**), this inhibits the intramolecular redox process owing to the expected dissociation of the high-spin structure to initial molecules. Destabilization of the low-spin isomers with respect to the ground states by more than 2 kcal mol^{-1} excludes the possibility for VT to occur in the adducts of cobalt salicylaldiminate Co(N-Ph-sal)$_2$)(^{L}**15**) containing phenyl substituents at nitrogen atoms of the azomethine ligand.[139]

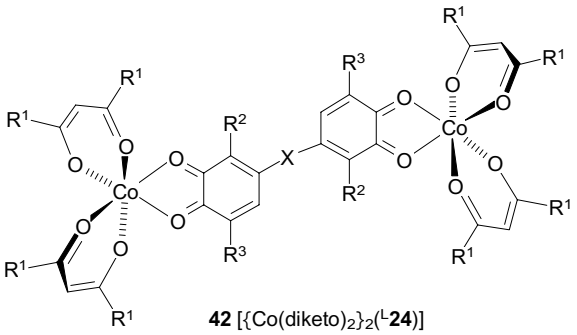
5. Dinuclear adducts of Co^{II} and Fe^{II} complexes

5.1. Adducts with di-*o*-quinones containing various linkers

Promising development of structural design of mixed-ligand complexes with switchable magnetic properties is associated with the possibility to utilize the VT mechanism for processing of quantum information. Using redox-active ligands capable of coordinating two transition metal complex, one can obtain adducts containing two magnetic metal centres separated by an organic bridge whose structure can be varied in order to tune the spin – spin interaction between these centres in targeted manner. It is spin – spin interaction that is responsible for quantum entanglement of the paramagnetic centres (qubit carriers), while the complexes themselves act as elements of a quantum computer, suitable for realization of two-qubit gates provided that the exchange interaction between the paramagnetic centres is relatively weak. To date, a number of single-molecule magnets assembled in this fashion are available and conditions (so-called DiVincenzo criteria [140]) to be met by such compounds [141 – 148] have been specified. Dinuclear adducts of tetracoordinate transition metal complexes with di-*o*-quinones can be treated as next steps of the evolution of the known design of molecular spin qubits M^1 – X – M^2. The adducts in question can impart two new properties to the M^1 – X – M^2 structures. First, VT rearrangements of dinuclear adducts provide the possibility of switching the characteristics of a logic gate of a quantum computer under the action of external factors (temperature, irradiation, pressure). Next, the necessary second paramagnetic centre can be localized not only on the metal atom, but also on the radical anion form of a fragment of the redox-active ligand.

Among the necessary conditions,[140] there is high coherency of the molecular system, *i.e.*, high indifference towards various types of intermolecular interaction. This dictates the need for a theoretical search for possible candidates for a role of molecular spin qubits M^1 – X – M^2 among nonionic electrically neutral structures. Research in this field began

Structures 42



42 [{Co(diketo)$_2$}$_2$(^{L}**24**)]

X = HC═CH, (CH$_2$)$_2$, piperazine-1,4-diyl or no linker;
R^1 = H, Me, CF$_3$; R^2, R^3 = H, Alk

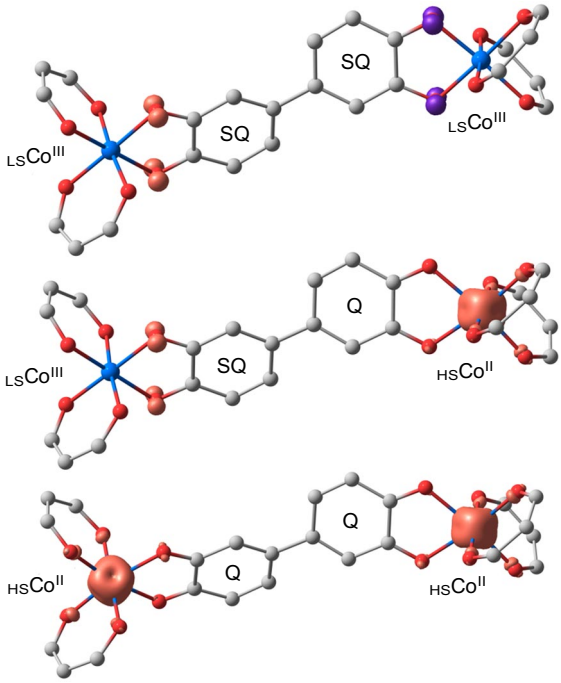


Figure 13. Spin density distribution in electromers of adducts of cobalt diketonates with di-*o*-quinone ligands ^{L}**24**.[149]

with a computational modelling study of a series of 2 : 1 dinuclear adducts of cobalt diketonates with tetradentate di-*o*-quinone ligands ^{L}**24** containing various linker fragments (Structures **42**).[149]

The ground-state structures of adducts {Co(acac)$_2$}$_2$(^{L}**24**) are described as $_{LS}$Co^{III}-(SQ-SQ)-$_{LS}$Co^{III}. They contain low-spin Co^{III} ions and the SQ form of the redox-active ligand (Fig. 13), which is indicative of electron transfer from the metal to the quinone rings. The spin density in these isomers is localized on the antiferromagnetically coupled SQ moieties.

A relatively low (< 10 kcal mol^{-1}) energy of the electronically excited isomer $_{LS}$Co^{III}-(SQ-Q)-$_{HS}$Co^{II} with respect to the ground state facilitates thermally initiated spin-state switching through IET from an SQ fragment to the metal ion.[149] Migration of paramagnetic centres predicted by calculations is accompanied by a change from antiferromagnetic to ferromagnetic exchange interaction. Further increase in temperature can initiate a similar electron transfer in the other fragment of the complex with the formation of the high-spin isomer $_{HS}$Co^{II}-(Q-Q)-$_{HS}$Co^{II} containing largely separated and therefore noninteracting paramagnetic metal centres. Targeted variation of the linker group X connecting the quinone rings and appropriate choice of substituents in the diketonate moieties allowed one to select adducts whose energy and magnetic parameters are suitable for making a two-qubit system. The parameters in question include (i) retention of paramagnetism of all electromers in a wide temperature range, (ii) weak coupling between paramagnetic centres, (iii) stability of the adduct towards dissociation to initial molecules and (iv) small energy differences between the spin states to provide the possibility for a thermally initiated two-step VT rearrangement to occur.

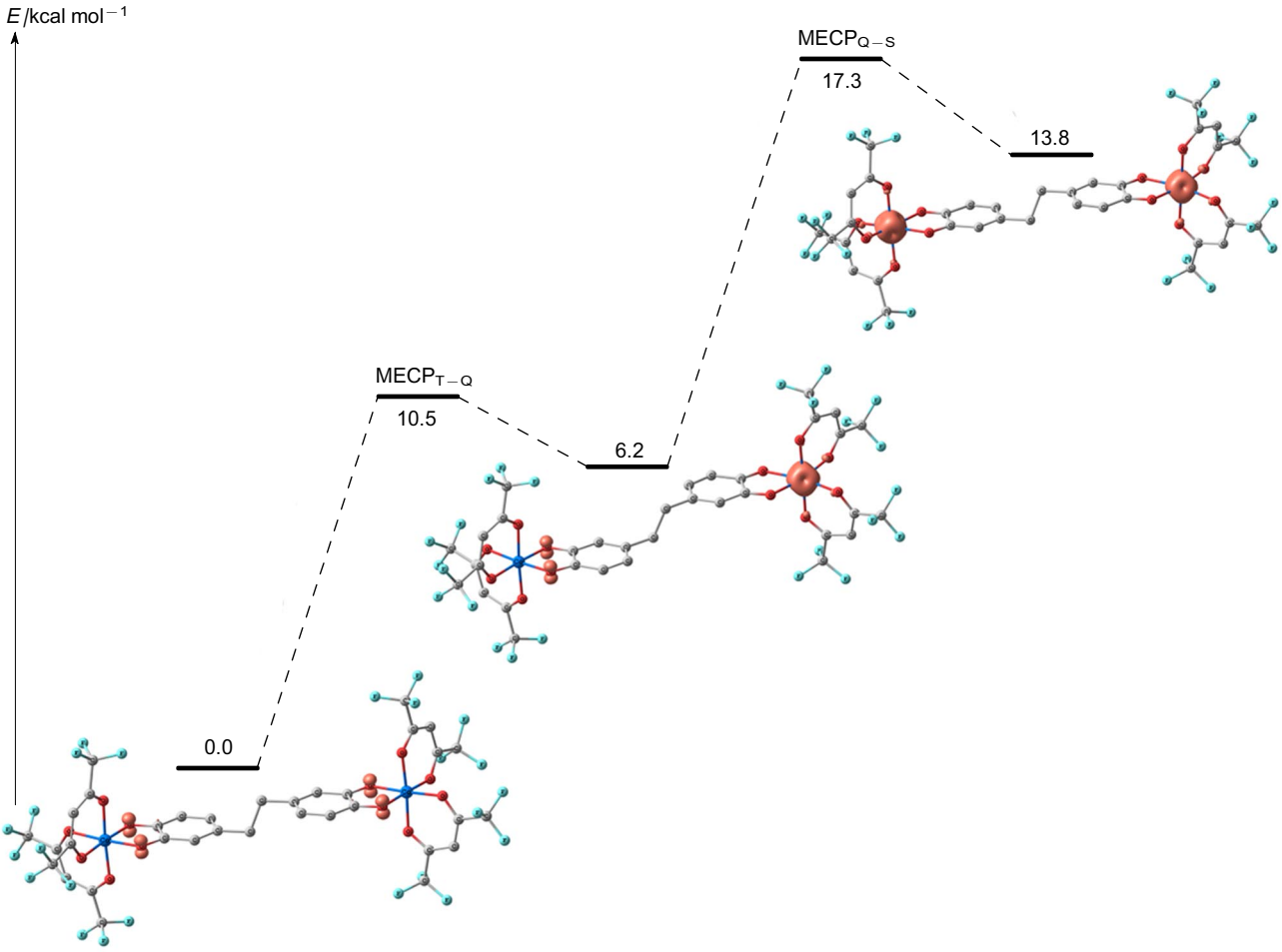


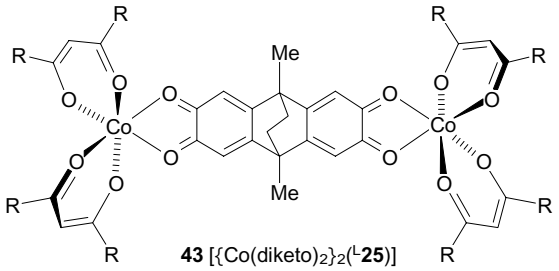
Figure 14. Energy profile of VT rearrangements of adduct $\{Co(hfac)_2\}_2(^{L}\mathbf{24c})$.[149]
Here and in Fig. 18 the subscripts T, Q and S denote the triplet, quintet and septet, respectively.

The energy diagram presented in Fig. 14 characterizes the reaction path of VT rearrangements of electromeric forms of the most promising adduct of Co^{II} bis(hexafluoroacetylacetonate) with di-*o*-quinone $\{Co(hfac)_2\}_2(^{L}\mathbf{24c})$ containing a dimethylene linker. The calculated relative MECP energies that specify the barriers to transitions between the corresponding PES are thermally accessible.

Unlike $\{Co(hfac)_2\}_2(^{L}\mathbf{24c})$, dinuclear complexes with dimethine linker HC═CH (ligand $^{L}\mathbf{24b}$) do not meet the requirements mentioned above since the conjugated system is characterized by violation of weak connectivity (entanglement) of fragments of the dinuclear complex. It follows that the linker X should be represented by an alkane or cycloalkane fragment. In this connection, dinuclear adducts **43** and **44** of cobalt diketonates with isomeric di-*o*-quinone ligands $^{L}\mathbf{25}$ and $^{L}\mathbf{26}$, respectively, were studied.

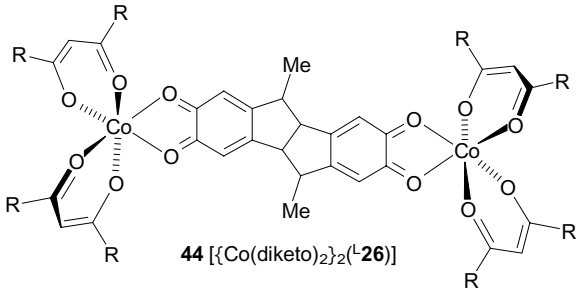
Calculations of adduct of cobalt(II) bis(malonate) with 9,10-dimethyl-9,10-ethanoanthracene-2,3,6,7(9*H*,10*H*)-tetraone ($^{L}\mathbf{25}$) revealed stabilization of the $_{LS}Co^{III}$-$(SQ)_2$-$_{LS}Co^{III}$ isomer with the predicted antiferromagnetic exchange ($J = -466$ cm^{-1}) leading to diamagnetism of the complex in the ground state.[150] The electromer $_{LS}Co^{III}$-(SQ-Q)-$_{HS}Co^{II}$ contains two paramagnetic centres, one on the high-spin Co^{II} ion and the other on the distant quinone moiety. Calculations predicted ferromagnetic interaction between these centres. The energy difference between

Structures 43, 44



43 [{Co(diketo)$_2$}$_2$(^{L}**25**)]

R = H, Me, CF_3



44 [{Co(diketo)$_2$}$_2$(^{L}**26**)]

R = H, Me, CF_3

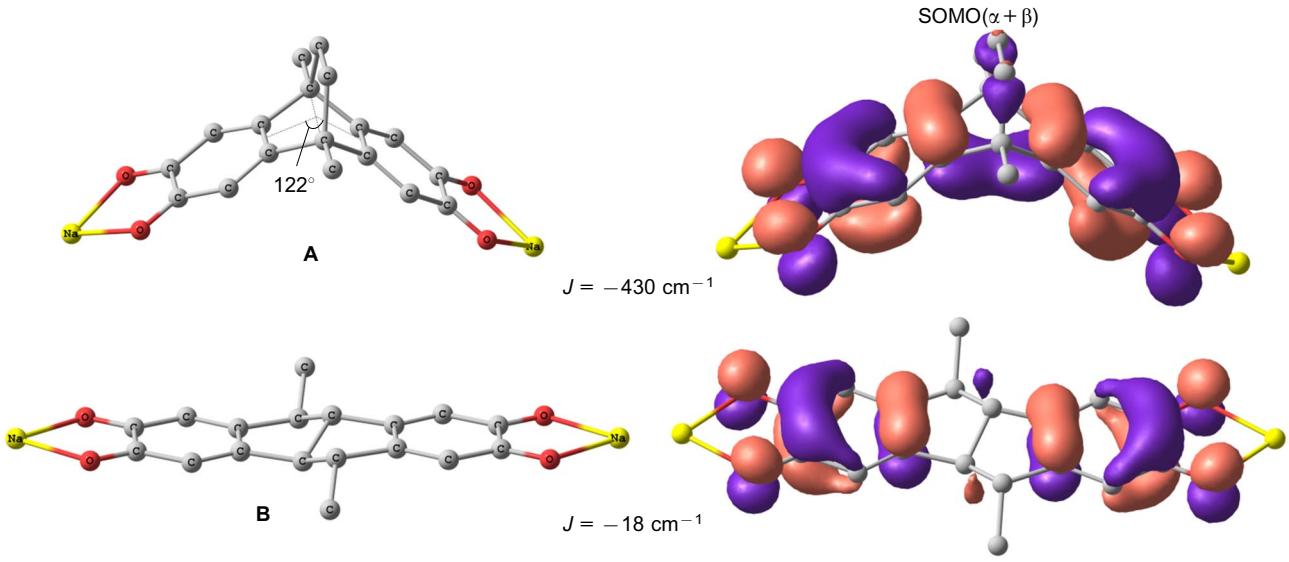


Figure 15. Shape of magnetic orbitals and magnetic exchange parameters of model complexes **A** and **B** containing sodium cations instead of transition-metal diketonates.[150]

this structure and the ground state $_{LS}Co^{III}$-$(SQ)_2$-$_{LS}Co^{III}$ is 9.1 kcal mol^{-1}, which falls in the energy range typical of VT rearrangements.[150] The introduction of trifluoromethyl groups into diketonate ligands favours a decrease in the energy difference between the isomers of the adduct $(Co(hfac)_2)_2(^L\mathbf{25})$ to values that allow one to expect a reversible stepwise transfer of two electrons.

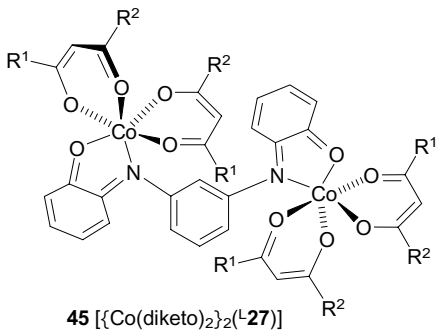
Calculations of the ground-state structure of the adduct of cobalt bis(malonate) with 5,10-dimethyl-4b,5,9b,10-tetrahydroindeno[2,1-*a*]indene-2,3,7,8-tetraone ($^L\mathbf{26}$) in which the quinone fragments are parallel to each other predicted weak antiferromagnetic exchange that provides paramagnetism in a wide temperature range. Destabilization of the $_{LS}Co^{III}$-(SQ-Q)-$_{HS}Co^{II}$ isomer by 10 kcal mol^{-1} allows one to expect intramolecular one-electron transfer.[150] A small energy difference between the ground-state form ($_{LS}Co^{III}$-$(SQ)_2$-$_{LS}Co^{III}$) of the complex $(Co(hfac)_2)_2(^L\mathbf{26})$ and other electromers is indicative of the possibility of two-step redox isomerism.

Factors determining the changes in the strength of the exchange interaction in the ground states of the adducts considered were established using the orbital analysis of the model compounds **A** and **B** (analogues to complexes **43** and **44**, respectively) in which the metal diketonates were replaced by sodium cations. From Fig. 15 it follows that complex **A** is characterized by significant overlap of the magnetic orbitals, which leads to strong antiferromagnetic exchange. No such overlap was found in compound **B**; as a consequence, one deals with weak interaction between the unpaired electrons. Therefore, the key factor responsible for the strength of exchange interaction is the degree of overlapping of the orbitals of the SQ fragments.

5.2. Adducts with di-*o*-iminoquinones and di-*o*-diiminoquinones

Complexes $\{Co(acac)_2\}_2(^L\mathbf{27})$ (structures **45**) and $\{(Co(acac)_2\}_2(^L\mathbf{28})$ are characterized by significant destabilization of electronic-excited isomers with respect to the ground state (13 – 26 kcal mol^{-1}).[151] This makes VT rearrangements impossible. The introduction of electron-withdrawing CF_3 groups into the diketonate moiety causes the energy difference between electromers of the complexes based on trifluoroacetylacetonates to decrease, so one can expect one-step VT rearrangements in the adducts $\{Co(tfac)_2\}_2(^L\mathbf{27})$ and $\{Co(tfac)_2\}_2(^L\mathbf{28})$. Similar values of the total energies of the isomers of complex $\{Co(hfac)_2\}_2(^L\mathbf{27})$ imply a possible equilibrium of all three forms of the adduct in solution, while the adduct of cobalt(II) bis(hexafluoroacetylacetonate) with di-*o*-iminoquinone $\{Co(hfac)_2\}_2(^L\mathbf{28})$ containing a biphenylene linker can be treated as a system undergoing a two-step VT rearrangement.

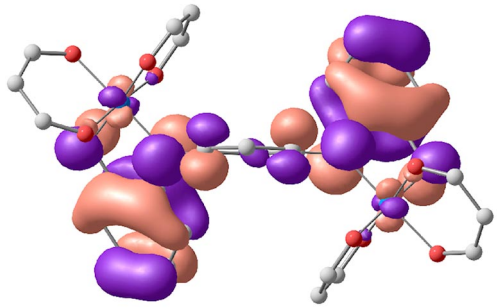
Structure 45



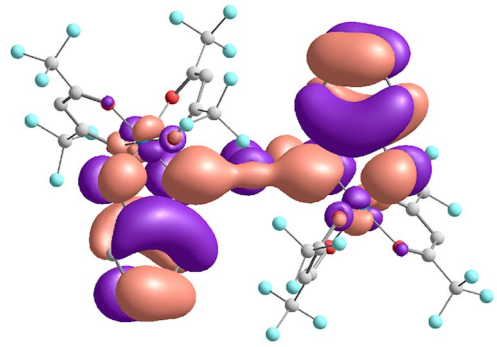
45 [{Co(diketo)$_2$}$_2$(^{L}**27**)]

R^1, R^2 = Me, CF_3

Calculations predicted weak ferromagnetic exchange interactions in the low-spin electromer of adduct $\{Co(acac)_2\}_2(^L\mathbf{27})$ and negative sign of exchange parameters *J* of the mixed-ligand complexes $\{Co(tfac)_2\}_2(^L\mathbf{27})$ and $\{(Co(hfac)_2\}_2(^L\mathbf{27})$. These results can be explained by different orientations of the SQ fragments in the compounds in hand and, as a consequence, by different shapes of the α-SOMO + β-SOMO orbitals, *viz.*, π-orbitals of the nitrogen centres in the iminoquinone moiety and a carbon atom in the linker in $\{Co(acac)_2\}_2(^L\mathbf{27})$ do not overlap, whereas the magnetic behaviour of the adduct $\{Co(hfac)_2\}_2(^L\mathbf{27})$ is



{Co(acac)$_2$}$_2$(L**27**)



{Co(hfac)$_2$}$_2$(L**27**)

Figure 16. Shape of magnetic orbitals of complexes {Co(diketo)$_2$}$_2$(L**27**).[151]

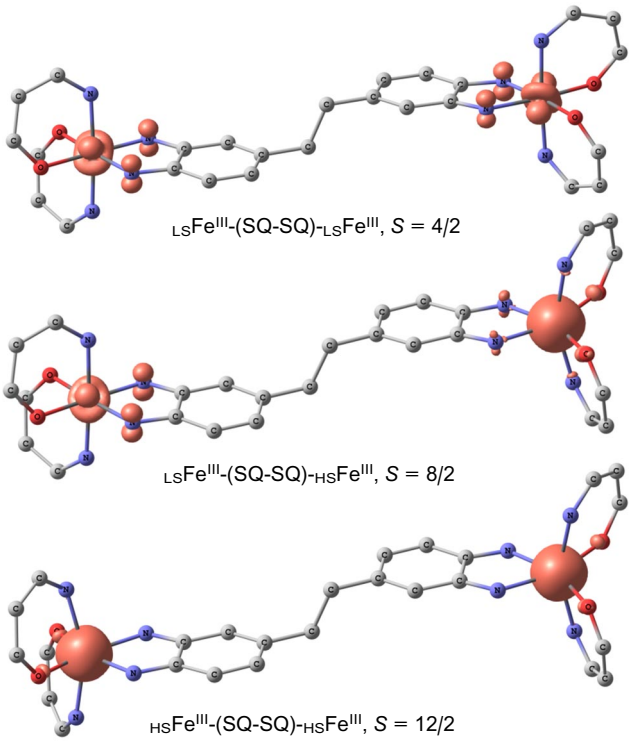
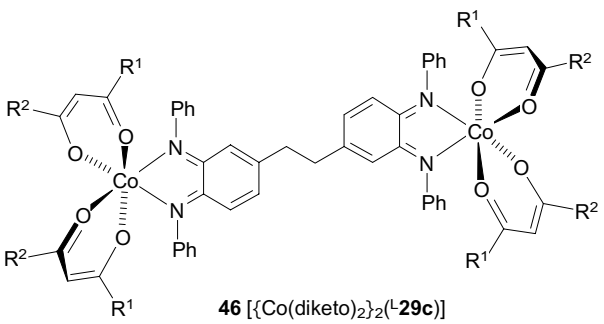


Figure 17. Spin density distribution in electromers of adducts of iron azomethine complexes with di-*o*-diimine L**29c**.[152]

determined by the presence of the antiferromagnetic exchange channel (Fig. 16).

The spin density distribution in the isomers of the adducts of cobalt diketonates with di-*o*-diimines L**29** is analogous to that found for dinuclear cobalt complexes with di-*o*-quinones.[149,150] Calculations of complex {Co(acac)$_2$}$_2$(L**29c**) (Structures **46**) predict only one VT transition to the LSCoIII-(SQ-Q)-HSCoII isomer with an intermediate spin state.[152]

Structures 46



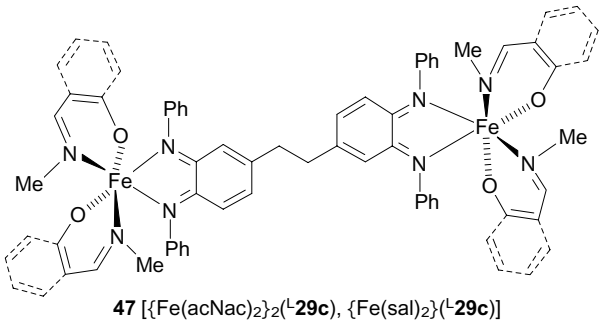
46 [{Co(diketo)$_2$}$_2$(L**29c**)]

R^1, R^2 = Me, CF$_3$

Replacement of a methyl group by trifluoromethyl one in the diketonate ligands favours a decrease in the energy differences between electromeric forms down to values corresponding to two-step VT. Weak exchange interaction between paramagnetic centres ($< |20|$ cm^{-1}) allows the adduct {Co(tfac)$_2$}$_2$(L**29c**) to be considered as potential spin qubit.[152] Stabilization of the high-spin isomer of adduct {Co(hfac)$_2$}$_2$(L**29c**) inhibits thermally initiated IET.

Unlike cobalt complexes, all isomers of adducts with iron bis(chelates) (Structures **47**) contain Fe^{III} ions (Fig. 17).

Structures 47



47 [{Fe(acNac)$_2$}$_2$(L**29c**), {Fe(sal)$_2$}(L**29c**)]

The ground-state structures of iron complexes contain low-spin metal ions, are described as LSFeIII-(SQ)$_2$-LSFeIII and can undergo transformation to HSFeIII-(SQ)$_2$-HSFeIII as a result of two successive spin transitions. Calculations predicted ferromagnetic exchange between the low-spin metal ions and adjacent redox-active ligand and antiferromagnetic interaction of high-spin iron ions with diimines. The Fe^{III}SQ paramagnetic centres almost do not interact irrespective of the spin state of the metal.

The calculated energy differences between the electromeric forms of adduct {Fe(N-Me-acNac)$_2$}$_2$(L**29c**) are 3.7 and 4.8 kcal mol^{-1} and thus fall in the range typical of

SCO, which allows one to expect a thermally induced two-step spin transition.

Summing up, the results of calculations demonstrate the potential ability of adducts of transition metal bis(chelates) with *N*-phenyl-di–*o*-diiminobenzoquinone ^{L}**29c** to exhibit two effects accompanied by stepwise switching of magnetic properties, namely, VT in cobalt complexes and SCO in iron compounds. The predicted magnetic properties of adducts based on di-*o*-diiminobenzoquinone are of interest for application of these compounds in various molecular electronics and spintronics devices.

5.3. Adducts with pyrene-4,5,9,10-tetraone, its imines and acenaphthene-1,2,5,6-tetraimine

The tetraone structures ^{L}**30** – ^{L}**33** and their imine derivatives contain quinone moieties embedded into the ligand. As a consequence, adducts with the Co^{II} complexes (Structures **48** – **51**) have an integrated π-system. Although the π-conjugated linker should enhance the interaction between paramagnetic centres and preclude their entanglement, the low-spin electromers $_{LS}Co^{III}$-$(SQ)_2$-$_{LS}Co^{III}$ of the complexes based on pyrene-4,5,9,10-tetraone ^{L}**33**, in contrast to the diamagnetic isomers of compounds with ligands ^{L}**30** – ^{L}**32**, exhibit ferromagnetic coupling of the unpaired electrons of the diradical-dianion and, according to calculations, can possess the properties suitable for making spin qubits.[153] Isomers with the intermediate spin state $_{LS}Co^{III}$-(SQ-Q)-$_{HS}Co^{II}$ are characterized by weak antiferromagnetic exchange interaction.

By varying substituents in the terminal diketonate fragments of the mixed-ligand complexes of cobalt bis(chelates) with tetraone ^{L}**33**, the energy differences between electromeric forms and the energy barriers to their interconversions can be tuned to fall in the ranges typical of thermally initiated VT rearrangements. The introduction of strong electron-withdrawing trifluoromethyl groups favours stabilization of high-spin states of the complexes and causes the energy gap between electromers to narrow. According to calculations, all parameters of adduct $\{Co(tfac)_2\}_2(^{L}$**33**$)$ meet the conditions for occurrence of thermally controlled two-step VT rearrangement involving all three paramagnetic electromeric forms (Fig. 18).

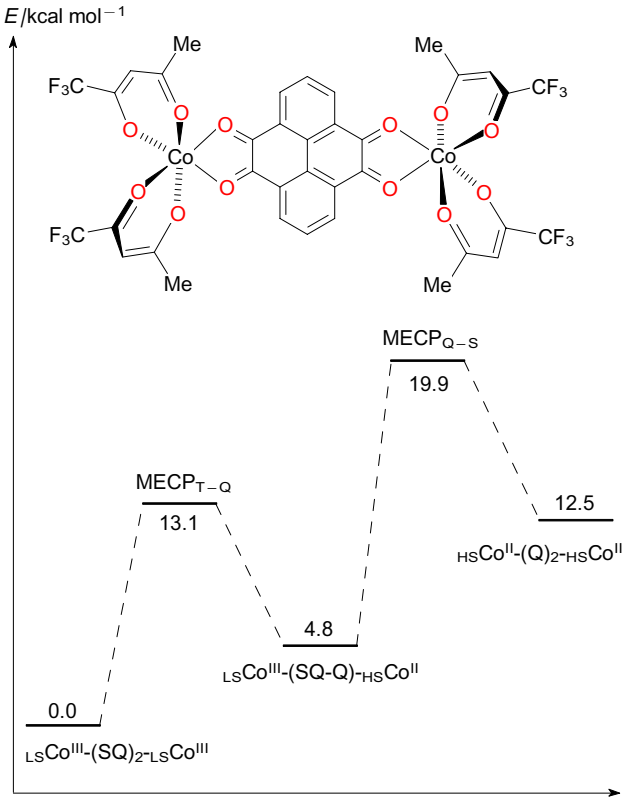
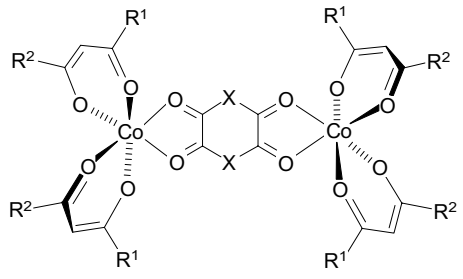


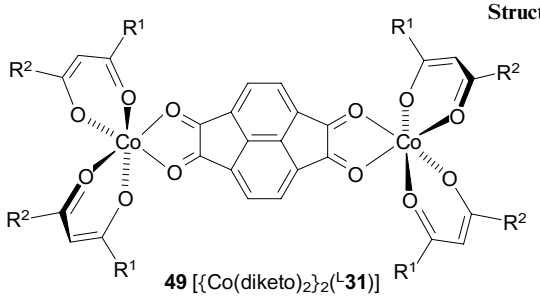
Figure 18. Energy profile of VT rearrangements of adduct $\{Co(tfac)_2\}_2(^{L}$**33**$)$.[153]

Structures 48 – 51

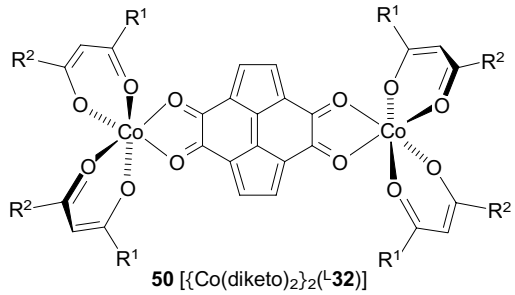


48 $[\{Co(diketo)_2\}_2(^{L}$**30**$)]$

X = NH, CMe_2

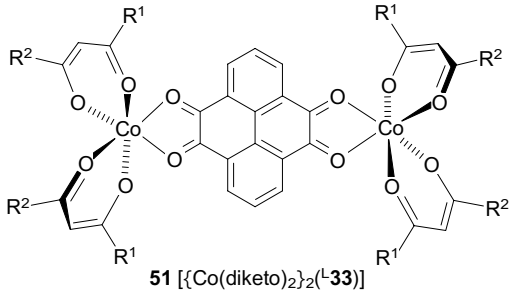


49 $[\{Co(diketo)_2\}_2(^{L}$**31**$)]$



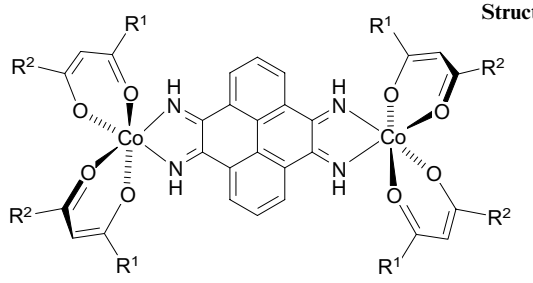
50 $[\{Co(diketo)_2\}_2(^{L}$**32**$)]$

R^1, R^2 = Me, CF_3



51 $[\{Co(diketo)_2\}_2(^{L}$**33**$)]$

Structures 52



52 [{Co(diketo)$_2$}$_2$(^{L}**35**)]

R^1, R^2 = Me, CF_3

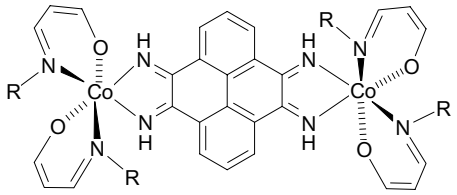
Dinuclear adducts of cobalt diketonates with pyrene-4,5,9,10-tetraimine ^{L}**35** (Structures **52**) have been studied recently.[154]

The most stable electromer $_{LS}Co^{III}$-$(SQ)_2$-$_{LS}Co^{III}$ of complex {Co(acac)$_2$}$_2$(^{L}**35**) is characterized by ferromagnetic exchange (J_{SQ-SQ} = 234 cm^{-1}).[154] The electromer $_{LS}Co^{III}$-(SQ-Q)-$_{HS}Co^{II}$ formed upon IET from one SQ moiety to the metal ion exhibits weak antiferromagnetism (J_{Co-SQ} = −22 cm^{-1}). Small destabilization of this structure relative to the ground state (6.8 kcal mol^{-1}) allows one to expect the thermally induced redox process; however, the energy difference between the low-spin ground state and high-spin sate $_{HS}Co^{II}$-$(Q)_2$-$_{HS}Co^{II}$ of complex exceeds 16 kcal mol^{-1} and thus shows that the second VT transition in this adduct is impossible.[154] The complex with cobalt trifluoroacetylacetonate {Co(tfac)$_2$}$_2$(^{L}**35**) is characterized by smaller energy differences between electromers and can undergo a two-step IET. The MECP energies for transitions between the ground-state ($_{LS}Co^{III}$-(SQ-Q)-$_{HS}Co^{II}$) and high-spin ($_{HS}Co^{II}$-$(Q)_2$-$_{HS}Co^{II}$) forms are 7.7 and 12.2 kcal mol^{-1}, respectively.[154] Thus, the predicted energy parameters (high stabilization energy, low relative energies of electromeric forms and thermally accessible barriers to VT rearrangements) and magnetic properties (paramagnetism of all isomers) of the mixed-ligand complex {Co(tfac)$_2$}$_2$(^{L}**35**) meet the spin qubit criteria. The adduct based on cobalt hexafluoroacetylacetonate is characterized by inversion of the energy characteristics of the isomers, which excludes the possibility of VT rearrangements.

Adducts of pyrene-4,5,9,10-tetraimines ^{L}**35** with azomethine ligands (Structures **53**, **54**) are stable towards dissociation. Their stabilization energies are higher than 10 kcal mol^{-1}.[155] The ground states are represented by the isomers $_{LS}Co^{III}$-$(SQ)_2$-$_{LS}Co^{III}$ for which calculations predicted ferromagnetic exchange interaction. The structures with intermediate spin state $_{LS}Co^{III}$-(SQ-Q)-$_{HS}Co^{II}$ are expected to possess weak antiferromagnetic coupling between spins of the unpaired electrons, while no exchange interaction was predicted for the high-spin electromers $_{HS}Co^{II}$-$(Q)_2$-$_{HS}Co^{II}$.

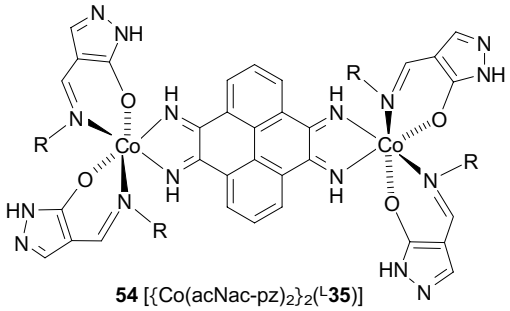
An increase in steric strain in the coordination sites of the compounds under study upon replacement of hydrogen atoms at nitrogen atoms of the azomethine ligand by methyl or phenyl groups, as well as annelation of the five-membered heterocycle to the aminovinyl ketonate moiety favours a decrease in the energy difference between electromers to the range typical of redox-isomeric cobalt complexes. Based on analysis of the energy characteristics of electromers, one can expect thermally induced one-step redox-isomeric process in the adducts

Structures 53 – 57



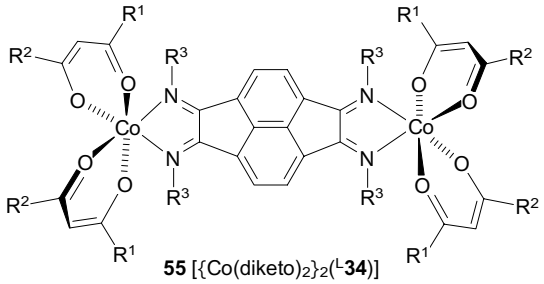
53 [{Co(acNac)$_2$}$_2$(^{L}**35**)]

R = H, Me, Ph



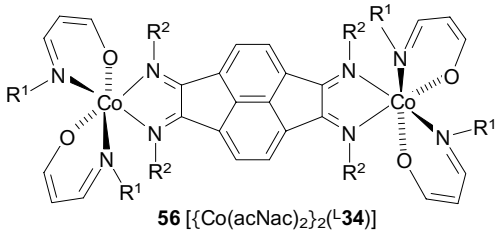
54 [{Co(acNac-pz)$_2$}$_2$(^{L}**35**)]

R = H, Me, Ph



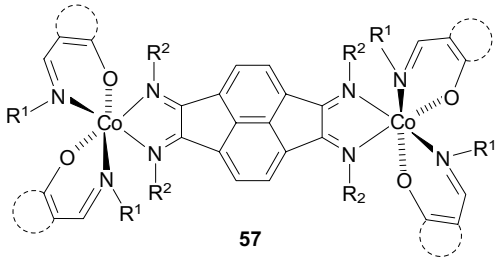
55 [{Co(diketo)$_2$}$_2$(^{L}**34**)]

R^1, R^2 = H, Me, CF_3; R^3 = H, Ph



56 [{Co(acNac)$_2$}$_2$(^{L}**34**)]

R^1 = H, Me, Ph; R^2 = H, Ph



57

{Co(acNac-pz)$_2$}$_2$(^{L}**34**) (= HC═N–NH)

{Co(sal)$_2$}$_2$(^{L}**34**) (= HC═CH–CH═CH)

R^1 = H, Me, Ph; R^2 = H, Ph

{Co(N-Ph-acNac)$_2$}$_2$(^{L}**35**), {Co(N-Me-acNac-pz)$_2$}$_2$(^{L}**35**). High stability towards dissociation to isolated components

(ΔE = 17.8 kcal mol^{-1}), small energy differences between isomers (2.8 and 5.7 kcal mol^{-1}, see Ref. 155) and paramagnetism of the isomeric forms of complex {Co(N-Ph-acNac-pz)$_2$}$_2$(^{L}**35**) meet the requirements for the molecular two-qubit system.

Unlike compounds {Co(acac)$_2$}$_2$(^{L}**35**) and {Co(tfac)$_2$}$_2$(^{L}**35**), the ground states of the adducts of cobalt bis(diketonates) with acenaphthene-1,2,5,6-tetraimines ^{L}**34** (Structures **55** – **57**) correspond to the high-spin electromers $_{HS}$Co^{II}-(Q)$_2$-$_{HS}$Co^{II}; consequently, thermally initiated VT rearrangements are impossible. However, calculations predicted that one- and two-step VT rearrangements can occur upon replacement of diketonate complexes by aminovinyl ketonate and salicylaldiminate ones.

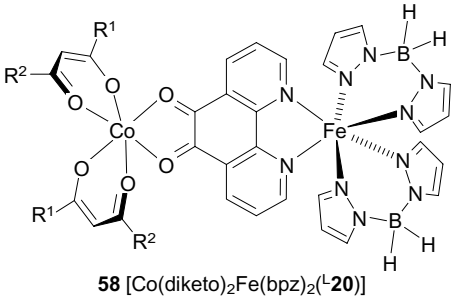
Strong antiferromagnetic exchange interaction between the SQ moieties in the electromers $_{LS}$Co^{III}-(SQ)$_2$-$_{LS}$Co^{III} stabilize the singlet (S = 0) structures of the complexes {Co(acNac)$_2$}$_2$(^{L}**34**), {Co(sal)$_2$}$_2$(^{L}**34**) and {Co(acNac-pz)$_2$}$_2$(^{L}**34**). Therefore, the expected VT-rearrangements on going from diamagnetic to paramagnetic structures will be accompanied by significant changes in the spin of the system, which allows one to consider adducts of azomethine cobalt complexes with ligands ^{L}**34** as potential molecular switches.

5.4. Adducts with 1,10-phenanthroline-5,6-dione

As mentioned above, the most common mechanisms of spin rearrangements in transition metal complexes include SCO and VT. Certain bimetallic complexes can also undergo more rarely occurring charge-transfer-induced spin transitions (CTIST).[156 – 158] Recent DFT calculations [159] of dinuclear complexes of Co^{II} and Fe^{II} with 1,10-phenanthroline-5,6-dione (^{L}**20**) predicted the feasibility of all the three spin-state switching mechanisms. The ability of phenanthroline-dione ^{L}**20** (Ref. 160) to chelate metal ions as either a diimine or a catecholate has been well studied [161 – 164] while its quinone and bipyridyl fragments are ideal ligand structures for the formation of VT- and SCO-complexes, respectively. The quinone moiety of the ligand ensures the formation of adducts with Co^{II} bis(chelates), while the 2,2′-bipyridyl moiety is responsible for coordination of iron(II) to bis(pyrazolyl)borate [Fe(bpz)$_2$] (Structures **58**, **59**).

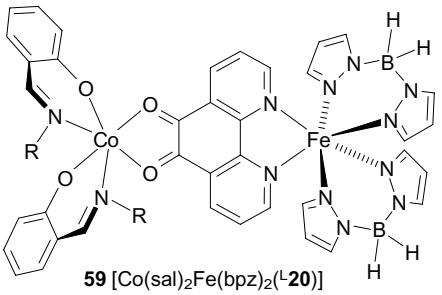
The results of recent calculations [159] revealed high sensitivity of parameters of the systems under study (relative stability of electromers, energetically preferred mechanism of their rearrangements and magnetic properties) to the choice of the Co^{II} bis(chelate) fragment. A rare, as applied to cobalt complexes, spin-state switching mechanism (SCO between the $_{LS}$Co^{III}-SQ-$_{LS}$Fe^{II} and $_{LS}$Co^{III}-SQ-$_{HS}$Fe^{II} electromers) was predicted for compounds Co(acac)$_2$Fe(bpz)$_2$(^{L}**20**) and Co(N-Ph-sal)$_2$Fe(bpz)$_2$(^{L}**20**). The full potential of polyfunctional ligand ^{L}**20** is achieved in the rearrangements of adduct of cobalt bis(trifluoroacetylacetonate) Co(tfac)$_2$Fe(bpz)$_2$(^{L}**20**). This complex has four electromeric forms with similar energies, which can readily undergo SCO on iron ion ($_{LS}$Co^{III}-SQ-$_{LS}$Fe^{II} ⇌ $_{LS}$Co^{III}-SQ-$_{HS}$Fe^{II}, $_{HS}$Co^{II}-Q-$_{LS}$Fe^{II} ⇌ $_{HS}$Co^{II}-Q-$_{HS}$Fe^{II}), low-barrier VT rearrangement due to electron transfer between the cobalt centre and the quinone fragment of the ligand ($_{LS}$Co^{III}-SQ-$_{LS}$Fe^{II} ⇌ $_{HS}$Co^{II}-Q-$_{LS}$Fe^{II}), as well as synchronized SCO and VT mechanisms ($_{LS}$Co^{III}-SQ-$_{LS}$Fe^{II} ⇌ $_{HS}$Co^{II}-Q-$_{HS}$Fe^{II}) (Fig. 19). Weak exchange interaction between paramagnetic centres and the spin-state switching processes accompanied by changes in the number of unpaired electrons from 1 to 7 make this compound a promising candidate for being used in the design of spin qubits. Unlike ionic systems studied previously,[165 – 180] electrical neutrality of the dinuclear systems proposed makes it possible to avoid undesired, coherency-destroying intermolecular motion of charges (electrons) in the materials built of ionic structures and consider them as a base for making spin qubits.

Structures 58, 59



58 [Co(diketo)$_2$Fe(bpz)$_2$(^{L}**20**)]

R^1, R^2 = Me, CF$_3$



59 [Co(sal)$_2$Fe(bpz)$_2$(^{L}**20**)]

R = Ph, 4-O$_2$NC$_6$H$_4$

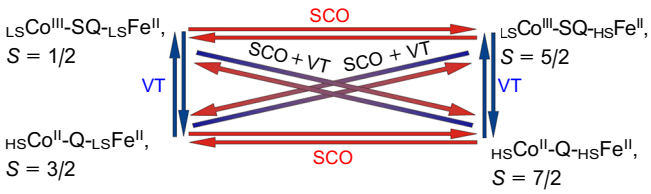


Figure 19. Spin crossover and valence tautomeric rearrangements of electromers of adduct Co(tfac)$_2$Fe(bpz)$_2$(^{L}**20**).[159]

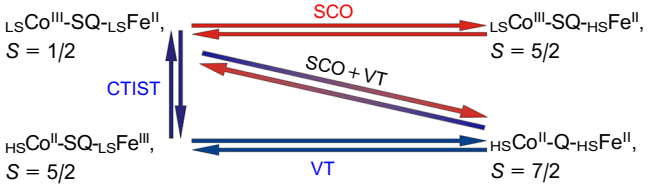


Figure 20. Rearrangements of electromers of adduct Co(hfac)$_2$Fe(bpz)$_2$(^{L}**20**).[159]

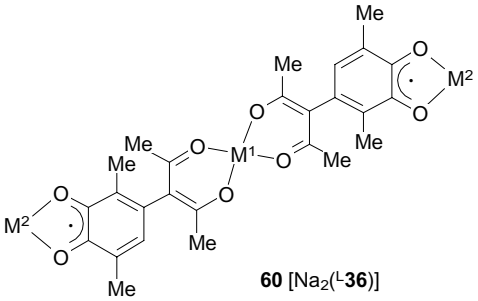
Introduction of additional trifluoromethyl substituents into the diketone fragment and nitro groups at salicylaldiminate nitrogen atoms facilitates manifestation of the CTIST effect originating from charge transfer between cobalt and iron ions ($_{LS}Co^{III}$-SQ-$_{LS}Fe^{II} \rightleftharpoons {}_{HS}Co^{II}$-SQ-$_{LS}Fe^{III}$) that causes changes in the oxidation state of both metal ions with retention of the oxidation state of the SQ ligand (Fig. 20). The adduct Co(hfac)$_2$-Fe(bpz)$_2$(^{L}**20**) can also undergo a VT rearrangement ($_{HS}Co^{II}$-SQ-$_{LS}Fe^{III} \rightleftharpoons {}_{HS}Co^{II}$-Q-$_{HS}Fe^{II}$) due to electron transfer between the redox-active ligand and the iron ion.[159]

6. Trinuclear adducts of Co^{II} complexes

The results presented in Section 5 demonstrate the critical impact of the structure of the linker connecting the fragments of the dinuclear complex on the properties of the complex considered as potential spin qubit. Three more recent studies [181–183] are concerned with bis(chelate) complexes of transition and main-group metals treated as linkers.

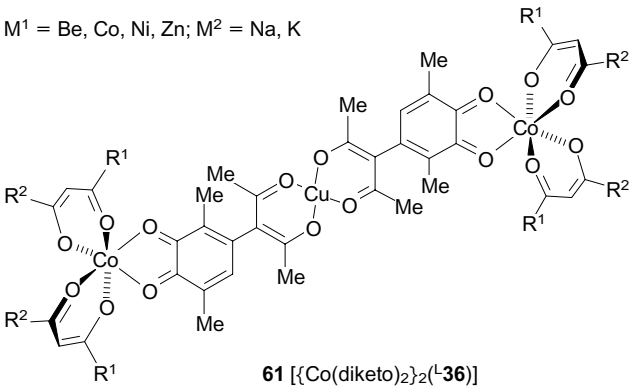
Calculations of model complexes of alkali metals with di-*o*-semiquinone ligands ^{L}**36** (Structures **60**) containing a bis(chelate) linker revealed the possibility of controlling the magnetic properties of these compounds by varying the central metal atom.[181] Weak ferromagnetic coupling between electron spins of radical anions and copper ion in the central bis(chelate) fragment of complex Na_2(^{L}**36**Cu) allowed one to choose di-*o*-quinone ^{L}**36**Cu as basic element for spin qubits. The ground state of adduct {Co(acac)$_2$}$_2$(^{L}**36**Cu) (Structures **61**) is represented by the low-spin electromer $_{LS}Co^{III}$-SQ-Cu^{II}-SQ-$_{LS}Co^{III}$. Significant destabilization of the isomers $_{LS}Co^{III}$-SQ-Cu^{II}-Q-$_{HS}Co^{II}$ and $_{HS}Co^{II}$-Q-Cu^{II}-Q-$_{HS}Co^{II}$ relative to $_{LS}Co^{III}$-SQ-Cu^{II}-SQ-$_{LS}Co^{III}$ makes the thermally induced intramolecular redox process hardly probable.[182]

Structures 60, 61



60 [Na_2(^{L}**36**)]

M^1 = Be, Co, Ni, Zn; M^2 = Na, K



61 [{Co(diketo)$_2$}$_2$(^{L}**36**)]

R^1, R^2 = Me, CF_3

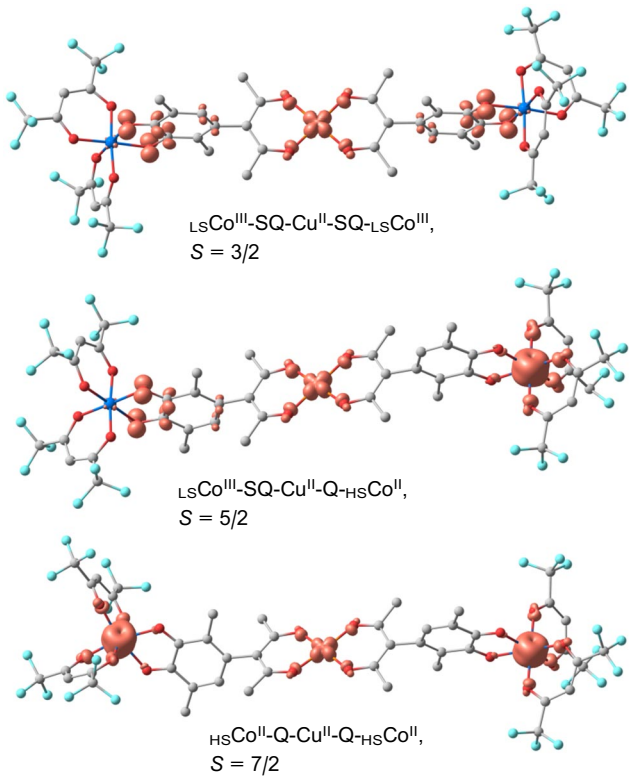


Figure 21. Spin density distribution in electromers of adduct {Co(hfac)$_2$}$_2$(^{L}**36**Cu).[183]

A quantum chemical study of complex {Co(hfac)$_2$}$_2$(^{L}**36**Cu) disclosed electromers similar to those of the adduct with cobalt acetylacetonates (Fig. 21). Replacement of methyl groups by trifluoromethyl ones in the diketonate fragment expectedly leads to narrowing of the energy gaps between isomers with different spin states of cobalt ions and stabilizes the mixed-ligand complex (E_{stab} = 36.2 kcal mol^{-1}).[182] The predicted decrease in the energy difference between the isomers $_{LS}Co^{III}$-SQ-Cu^{II}-Q-$_{HS}Co^{II}$ and $_{HS}Co^{II}$-Q-Cu^{II}-Q-$_{HS}Co^{II}$ and the ground-state structure $_{LS}Co^{III}$-SQ-Cu^{II}-SQ-$_{LS}Co^{III}$ to 3.0 and 7.2 kcal mol^{-1}, respectively, allows one to expect a VT rearrangement in the complex in hand. Based on the MECP values, the barriers to transition between the electromers are at most 12.1 and 13.0 kcal mol^{-1} (Ref. 182), which allows one to expect a two-step IET in the adduct {Co(hfac)$_2$}$_2$(^{L}**36**Cu).

Calculations predicted weak antiferromagnetic coupling (J_{SQ-Cu} = −31 to 32 cm^{-1}) between paramagnetic centres of the SQ fragments and copper ions of the electromers $_{LS}Co^{III}$-SQ-Cu^{II}-SQ-$_{LS}Co^{III}$ and $_{LS}Co^{III}$-SQ-Cu^{II}-Q-$_{HS}Co^{II}$, as well as weak exchange between the unpaired electrons of the metal centres (J_{Cu-Co} = 2 cm^{-1}) in the isomeric structures $_{LS}Co^{III}$-SQ-Cu^{II}-Q-$_{HS}Co^{II}$, and $_{HS}Co^{II}$-Q-Cu^{II}-Q-$_{HS}Co^{II}$.[182,183] These values are close to those calculated for the adduct with cobalt acetylacetonate {Co(acac)$_2$}$_2$(^{L}**36**Cu). It follows that electron-withdrawing trifluoromethyl groups have no effect on the character and strength of exchange coupling between paramagnetic centres in the compounds in question. The results of calculations of adducts {Co(acac)$_2$}$_2$(^{L}**36**Co), {Co(acac)$_2$}$_2$(^{L}**36**Ni) and {Co(acac)$_2$}$_2$(^{L}**36**Zn) containing

Co, Ni and Zn atoms in the bis(chelate) linker suggest that the nature of the central metal atom has little effect on the energy characteristics of electromeric forms of the adducts and on the exchange interaction between paramagnetic redox-active centres.[183] Adducts of cobalt bis(hexafluoroacetylacetonate) $\{Co(hfac)_2\}_2(^L\mathbf{36})$ can undergo a two-step VT rearrangement irrespective of the nature of the central metal atom.

Thus, trinuclear complexes $\{Co(hfac)_2\}_2(^L\mathbf{36}Cu)$ and $\{Co(hfac)_2\}_2(^L\mathbf{36}Co)$, which have two VT centres and are characterized by metal-containing-linker-controlled exchange interaction between the VT centres are suitable for making spin qubits.

7. Conclusion

Tetracoordinate transition metal complexes readily form stable adducts with bidentate organic redox-active ligands, thus completing their coordination spheres to octahedral environment of the central ion. Unlike conventional molecular complexes, stabilization of adducts containing redox-active ligands is governed by intramolecular electron transfer from the metal to the ligand that undergoes rearrangement to the radical anion form. These mixed-ligand complexes have extremely labile electronic structure. In some cases (typically, for ruthenium complexes), this precludes the assignment of a particular oxidation state to the metal ion. Lability of the electronic configurations of the complexes creates prerequisites for modulating their properties by varying external factors (temperature, irradiation, pressure). This also imparts the properties of molecular switches to the complexes. At the same time, the potential of the adducts of transition metal complexes in the field of molecular electronics and spintronics applications has almost not been studied. In spite of a large number of available adducts, there are only a few examples of compounds demonstrating low-barrier SCO or VT transitions with switching of magnetic parameters. In this review the discovery of systems capable of undergoing reversible spin-state switching is considered from the standpoint of theoretical modelling of the properties and dynamics of adducts of tetracoordinate transition metal complexes with various redox-active ligands.

The results of quantum chemical calculations presented above should be treated as substantiated R&D roadmap for the title field as a branch of coordination chemistry and as a challenge to chemists who can synthesize promising molecular switches based on transition metal complexes with redox-active ligands and thus to verify the reliability of theoretical predictions.

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