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Structure and magnetic properties of di-*o*-semiquinone complexes of alkali metals with a bischelate linker: a quantum chemical study

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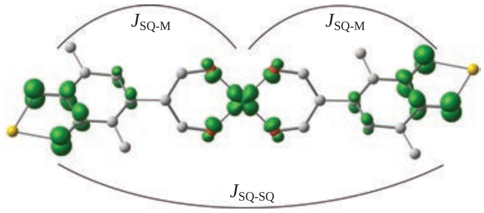
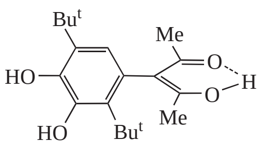
The DFT calculations reveal a possibility of controlling the magnetic properties of di-*o*-semiquinone complexes *via* coupling radical-anion moieties with a transition metal bischelate linker.



Transition metal complexes based on *o*-quinone ligands can undergo intramolecular redox processes accompanied by changes in their spin states. This effect termed as valence tautomerism[1] (VT) and most typical of cobalt and manganese compounds[2] has a significant potential for the use in molecular electronics and spintronics.[3] Recently, the occurrence of two-step VT rearrangements of the dinuclear adducts of cobalt diketonates with di-*o*-quinones was demonstrated by means of quantum chemical calculations.[4] The variation of hydrocarbon linker groups between the quinone fragments of these complexes allowed one to reveal systems possessing the properties of logical elements of quantum computers (qubits).[5]

It has been shown earlier that polynuclear clusters coupled by linkers based on transition metal complexes providing for the quantum 'entanglement' of paramagnetic centers can serve as suitable basic elements for spin qubits.[6] The goal of this study was to extend this approach to the di-*o*-quinone complexes exhibiting a VT behavior. The suitable compounds can be designed by involving recently prepared catechol-containing acetylacetone[†] **1** in complexation with metal ions (M) to form bischelates **2**,



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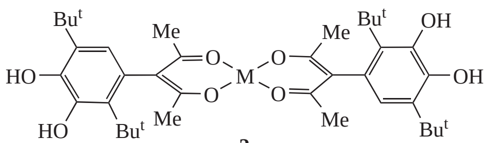

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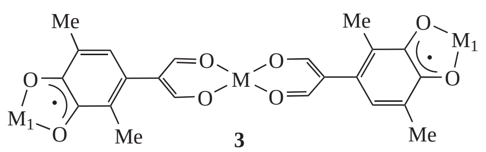

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[†] N. O. Druzhkov, M. V. Arsenyev, S. A. Chesnokov, V. K. Cherkasov and G. A. Abakumov, unpublished results.

whose oxidation to quinones and the subsequent reduction with alkali metals give rise to complexes with two radical-containing semiquinone (SQ) fragments. Then, these complexes can act as reactants for the synthesis of magnetoactive trinuclear transition metal coordination compounds.

Here, we report a computational modeling of the structure and magnetic properties of complexes **3** (M = Be, Co, Ni, Cu, Zn; M_1 = Na, K), aimed at getting insight into the influence of the origin of a metal and the coordination site geometry of a bischelate linker on the strength and character of exchange interactions between the unpaired electrons of semiquinone fragments. Sodium and potassium ions were selected as the counterions of radical-containing fragments. Distinctions in their ionic radii may lead to different orientations of metal atoms M_1 relative to semiquinone fragments and affect the magnetic properties of complexes.

The calculations were performed using the Gaussian 09 program package[7] by a density functional theory (DFT) method in UB3LYP*/6-311++G(d,p) approximation,[8] well reproducing the geometries and energy characteristics of complexes with redox-active ligands.[9] The exchange spin coupling parameters were estimated in the framework of a 'broken symmetry' (BS) formalism[10] using approaches suggested by Yamaguchi[11] and Ruiz.[12]

Figure 1 shows that complexes **3** (M = Be, Co, Ni, Cu, Zn; M_1 = Na, K) bearing sodium and potassium counterions have similar geometry characteristics. Both of the counterions form planar five-membered chelate rings by coordination to the oxygen atoms of quinone fragments. The main distinction is predicted for distances of 2.18 and 2.49 Å between the alkali metal atoms and oxygen atoms in sodium and potassium compounds, respectively, as conditioned by differences in the ionic radii of these metals. The calculated bond lengths in quinone fragments and the presence of spin density at the oxygen atoms and adjoined carbon atoms (see Figure S1, Online Supplementary Materials) are in accordance with the semiquinone form.[13] The semiquinone fragments of complexes **3** are turned around the central chelate rings by 52–58°.

An ability of diamagnetic bischelates to form an exchange channel between the unpaired electrons of semiquinone fragments was studied for complexes **3** (M = Be, Zn), which have similar

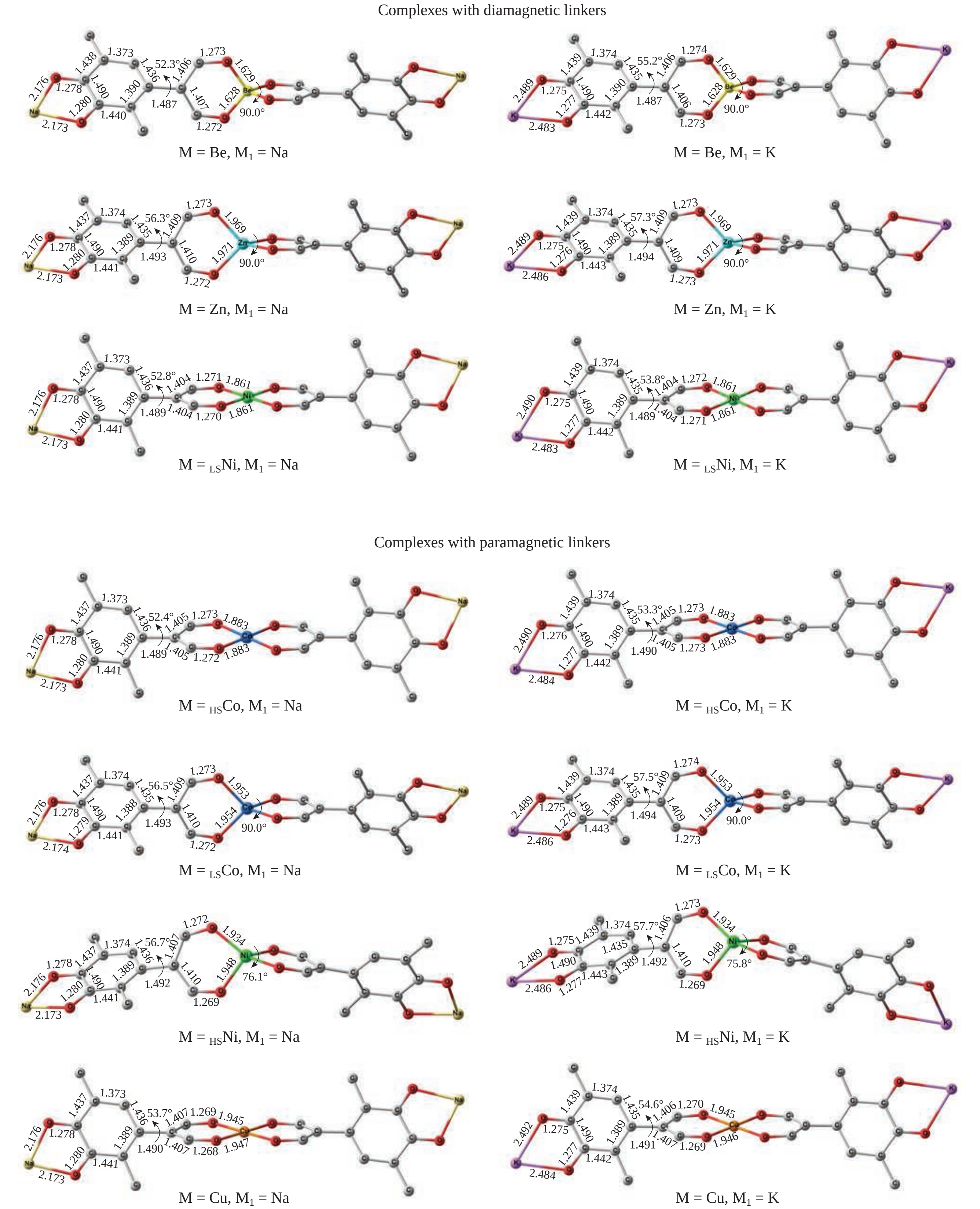

Figure 1 Optimized geometries of complexes **3** (M = Be, Co, Ni, Cu, Zn; M_1 = Na, K) calculated by the DFT UB3LYP*/6-311++G(d,p) method. Hydrogen atoms are omitted for clarity. Distances are given in Å.

tetrahedral coordination sites but differ in their M–O bond lengths, and for low-spin nickel complexes **3** (M = $_{LS}$Ni) with a planar coordination site. By the computation of exchange coupling parameters, it was established that, regardless of the stereochemistry of a coordination site (tetrahedron or square) and the nature of a central atom in the bischelate linker (M = Be, Zn, $_{LS}$Ni) and counterions (Na, K), the exchange interactions between unpaired electrons in these complexes are almost absent (Table 1). Therefore, a significant distance between the paramagnetic centers localized at the semiquinone parts of the complexes ensures the stabilization of their triplet biradical electronic configurations.

Table 1 Spin state (*S*), exchange spin coupling constants between semiquinone fragment and metal center ($J_{SQ\text{-}M}$) and exchange spin coupling constants between semiquinone fragments ($J_{SQ\text{-}SQ}$) of complexes **3** (M = Be, Co, Ni, Cu, Zn; M_1 = Na, K) calculated by the DFT UB3LYP*/6-311++G(d,p) method.

M	M_1	*S*	$J^a_{SQ\text{-}M}$/cm^{-1}	$J_{SQ\text{-}SQ}$/cm^{-1}
Be	Na	2/2	–	0.0 (0.0)
Zn	Na	2/2	–	0.0 (0.0)
$_{LS}$Ni	Na	2/2	–	–0.8 (–0.8)
$_{HS}$Co	Na	5/2	–12 (–19)	20 (10)
$_{LS}$Co	Na	3/2	–22 (–22)	2 (2)
$_{HS}$Ni	Na	4/2	–21 (–16)	–7 (–40)
Cu	Na	3/2	9 (9)	–0.4 (–0.4)
Be	K	2/2	–	–0.1 (–0.1)
Zn	K	2/2	–	0.0 (0.0)
$_{LS}$Ni	K	2/2	–	–0.7 (–0.7)
$_{HS}$Co	K	5/2	–9 (–13)	15 (8)
$_{LS}$Co	K	3/2	–23 (–23)	2 (2)
$_{HS}$Ni	K	4/2	–22 (–20)	–16 (–38)
Cu	K	3/2	8 (8)	–0.4 (–0.4)

[a] Exchange spin coupling constants were calculated using the Yamaguchi formula.[11] Values in brackets were calculated using the Ruiz approach.[12]

Cobalt bischelates can exist in a high-spin state with the tetrahedral geometry of the coordination site and in a low-spin state with the planar coordination site. According to the calculations, the high-spin isomers are 5.4 kcal mol^{-1} energy preferred compared to the low-spin ones (see Table S1, Online Supplementary Materials). The calculations predict weak antiferromagnetic interactions (*J* –9 to –12 cm^{-1}) between the semiquinone fragments and a high-spin cobalt ion, while exchange coupling between unpaired electrons localized at semiquinones is of ferromagnetic nature (*J* 15–20 cm^{-1}). In the low-spin isomers (M = $_{LS}$Co), the calculations predict weak antiferromagnetic SQ-M exchange coupling and negligible or even absent interactions between the unpaired electrons of semiquinones. The structures of complexes with a central high-spin nickel ion (M = $_{HS}$Ni) are 5.6 kcal mol^{-1} destabilized compared to those of the low-spin nickel (M = $_{LS}$Ni) planar isomers. In spite of significant distortion of the tetrahedral coordination site of the high-spin nickel compounds, exchange interactions here are rather weak and bear an antiferromagnetic character ($J_{SQ\text{-}Ni}$ –21 to –22 cm^{-1} and $J_{SQ\text{-}SQ}$ –7 to –16 cm^{-1}). Small exchange coupling constants predicted for this group of complexes **3** (M = $_{HS}$Ni, Co; M_1 = = Na, K) allow for their paramagnetism in a wide temperature range.

According to the results of calculations of exchange spin coupling constants in complexes with a central copper ion, the magnetic ordering of unpaired electrons centered at semiquinones and metal M is weak and bears a ferromagnetic character ($J_{SQ\text{-}Cu}$ 8–9 cm^{-1}). At the same time, exchange interactions between semiquinone fragments are virtually absent ($J_{SQ\text{-}SQ}$ –0.4 cm^{-1}). This finding correlates with analogous parameters found for complexes with the low-spin nickel ion also having a planar bischelate linker. Predicted ferromagnetic exchange coupling in complexes **3** (M = Cu) allows us to consider these compounds as a suitable basis for the design of molecules possessing the properties of spin qubits.

Thus, the DFT [UB3LYP*/6-311++G(d,p)] quantum chemical study of model complexes **3** (M = Be, Co, Ni, Cu, Zn; M_1 = Na, K) has shown the possibility of controlling magnetic properties of trinuclear compounds built on their basis *via* variation of bischelate linker metal atoms. Complexes comprising Be, Zn and low-spin Ni atoms with diamagnetic linker groups have triplet biradical electronic configurations with no exchange interactions between the unpaired electrons of semiquinone fragments. Complexes **3** with high-spin nickel ions and cobalt compounds are characterized by weak antiferromagnetic exchange coupling between the unpaired electrons of semiquinone and metal M. Ferromagnetic SQ-M ordering is predicted only for copper complexes, which may be suitable for the use as spin qubits due to small exchange coupling parameters.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.09.020.

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