A molecular modelling study of the effects of pivalate ligand substitutions on the magnetic properties of chromium-wheels host complexes

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ABSTRACT

In our recent article, we had a successful experience in applying binuclear chromium (III) model ($[Cr_2F(tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$) instead of real chromium-wheel host complex ($[Cr_8F_8(tBuCO_2)_{16}]$) to calculate the effect of bridged-ligands substitution on the exchange coupling constants (J) values of the complexes. In this work our experienced procedure was used to evaluate the effect of pivalate ($tBuCO_2$) ligands substitution on the J values of the complexes. For this, at first two new groups of complexes were designed based on the replacement of pivalate by $X\text{-}tBuCO_2$ and $X\text{-}iPrCO_2$ anionic ligands (where X represents F, Cl, Br and I halogens) and then their J values were calculated. Since the existence of two halogen atoms in the structures of complexes leads to form different conformers, at first step a conformational analysis was carried out to identify the stable conformers of each complex. In $X\text{-}tBuCO_2$-containing complexes four stable conformers were recognized, while $X\text{-}iPrCO_2$-containing complexes had three stable conformers. At next step the J values of each of these conformers were calculated for all complexes. It was found that depending on which conformer was formed, the effect of these substitutions in each complex could be different, leading to a decrease or increase in the antiferromagnetic property of the complex. In both types of complexes, the formation of the least stable conformer, Conf1, led to the strengthening of the antiferromagnetic property of the complex but the impacts of the substitutions in other conformers were diverse. These new designed complexes could be considered as novel synthetic targets with different magnetic properties.

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1. Introduction

The effects of bridged ligand substitution on the magnetic properties of $[Cr_8F_8 (tBuCO_2)_{16}]$ [1] and $[Cr_8OH_8(tBuCO_2)_{16}]$ [2] chromium-wheel host complexes were evaluated using DFT molecular modeling in our recent study [3]. Three different binuclear chromium (III) models were designed and a broken symmetry approach [4] together with several levels of theories were used to calculate their exchange coupling constant. For modelling the magnetic behaviour of a polynuclear transition-metal complex the Heisenberg-Dirac Hamiltonian is used

$$\widehat{H} = -\sum_{i<j} J_{ij} \overrightarrow{S}_i \cdot \overrightarrow{S}_j, \tag{1}$$

in which $\overrightarrow{S}_i$ and $\overrightarrow{S}_j$ are spin operators of atoms located at sites i and j respectively and J_{ij} coefficient is their magnetic exchange coupling constant [5]. For systems with two spin-centres, Eq. (1) is reduced to (for more details see Ref. [6] p. 52):

$$\widehat{H} = -J \overrightarrow{S}_1 \cdot \overrightarrow{S}_2. \tag{2}$$

By applying the B3LYP [7,8]/TZV [9] level of theory and using the following equation [10].

$$J = \frac{2(E_{BS} - E_{HS})}{\langle S^2 \rangle_{HS} - \langle S^2 \rangle_{LS}}, \tag{3}$$

wherein E_{BS} and E_{HS} are the energies of the broken symmetry (or the low-spin) and high-spin states respectively, and $\langle S^2 \rangle_{HS}$ and $\langle S^2 \rangle_{LS}$ are total spin angular momentum of highest and lowest spin states respectively, the J values of complexes have been calculated. In our previous work, a BS-DFT molecular modelling approach was used to evaluate the effect of bridged-ligand substitution on magnetic properties of complexes. For this, three 3-positive, 1-positive and 1-negative charge binuclear chromium (III) complexes were utilized as models of the $[Cr_8F_8(tBuCO_2)_{16}]$ and $[Cr_8OH_8(tBuCO_2)_{16}]$ host complexes. The J values of these model complexes were calculated using different procedures and were compared with experimental values of real complexes to evaluate the accuracy of the results. It was found that imposing the B3LYP/TZV level of theory together with using Equation (3) yielded the J values which were closest to the experimental data. So this procedure was chosen for the following calculations. Our findings indicated that bridged-ligands substitutions changed the antiferromagnetic properties of the new designed complexes such that they would be attractive synthetic targets [3]. However, it is necessary to mention that our approach has some limitations. We used a binuclear molecular model instead of real chromium-wheel host complexes, which led to some approximations. In spite of using approximate equations and approximate methods such as BS-DFT methodology, the results of our approach were in good agreement with the experimental data and also reduced the calculations cost.

In Ref. [3], only the effects of the Fluoro-bridged substitutions on the magnetic properties of complexes were investigated and the effects of the substitutions of two pivalate ligands were not considered (Fig. 1(a)). Based on the usefulness of our proposed procedure, in this article we have used it to evaluate the effects of substitutions of the two pivalate ligands with halogenated pivalate ligands on the magnetic properties of complexes. Before choosing these new ligands, we first checked if any of them had been synthetized experimentally. We found that two types of halogenated pivalate anions were synthesized [11]. In the first type, one of methyl groups were halogenated, namely one of its hydrogens were replaced with halogen atom (3-Halogeno-2,2-dimethylpropanoate) while in the second type, one of the methyl groups was entirely substituted with the halogen atom (2-Halogeno-2-methylpropanoate) (Fig. 1(b)). These two types of ligands are called by abbreviations of X-tBuCO$_2$ and X-iPrCO$_2$ respectively, wherein the X represents the halogen atoms including F, Cl, Br and I.

In this article, two pivalate ligands of $[Cr_2F(tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$ modeled complex were replaced with the two mentioned types of anions and two new groups of complexes, i.e. $[Cr_2F(X\text{-}tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$ and $[Cr_2F(X\text{-}iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$, were designed (Fig. 1(c)). After that, the molecular modelling approach presented in our recent article [3] was used to calculate the J values of these new designed complexes and investigate the effects of halogenated pivalate ligands replacement on their antiferromagnetic properties. The details of calculations have been presented in the following section.

2. Computational details

To design new complexes, the initial geometric parameters were taken from optimized structure of $[Cr_2F(tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$ modeled complex at B3LYP/TZV level of theory (See Ref. [3]) and the pivalate ligands were changed to X-tBuCO$_2$ (in $[Cr_2F(X\text{-}tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$) and X-iPrCO$_2$ (in $[Cr_2F(X\text{-}iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$) ligands using GaussView 5.0.8 software [12,13]. These initial structures of $[Cr_2F(X\text{-}tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$ and $[Cr_2F(X\text{-}iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$ complexes, which X represents F, Cl, Br and I atoms, have been presented in Fig. 2. Geometrical structure analysis of these designed structures showed that in X-tBuCO$_2$-containing complexes rotation around two bonds, a and b (or a' and b') in Fig. 2(a), could lead to different conformers while in X-iPrCO$_2$- containing complexes rotation around one bond, a (or a') in Fig. 2(b), could make different conformers. Since the main
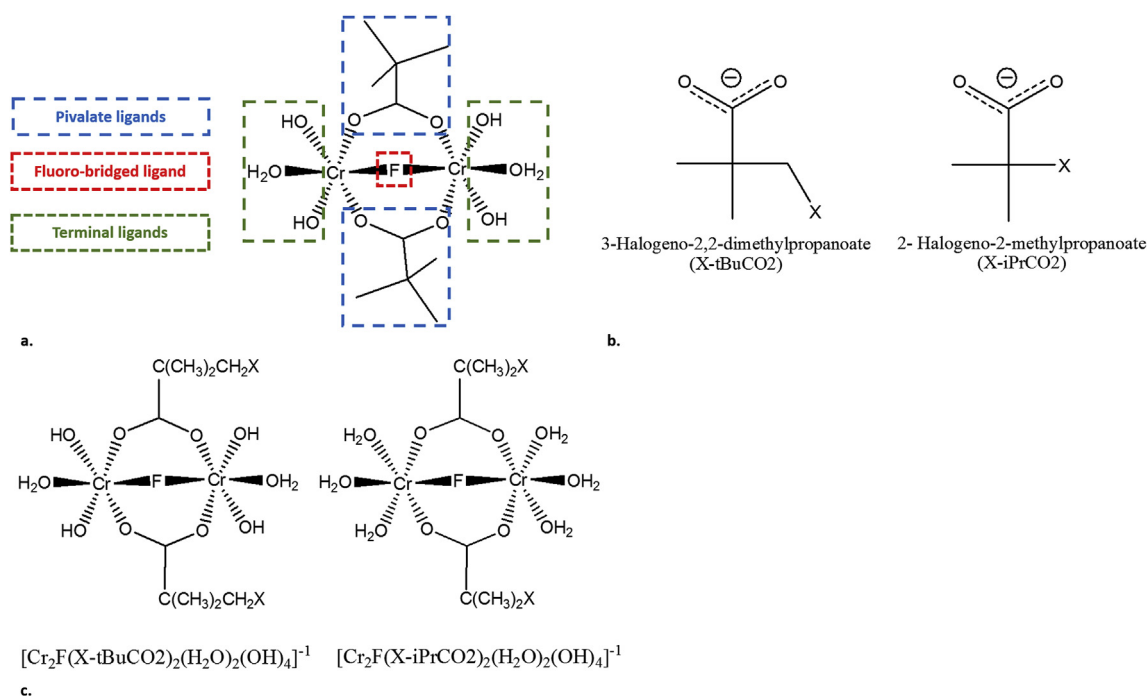

Fig. 1. (a) Schematic representation of modeled complex with three types of ligands. (b) Two new halogenated ligands that are substituted instead of pivalate ligands. (c) Two new types of modeled complexes, $[Cr_2F(X\text{-}tBuCO2)_2(H2O)_2(OH)_4]^{-1}$ and (c) $[Cr_2F(X\text{-}iPrCO2)_2(H2O)_2(OH)_4]^{-1}$ that were designed using replacement of pivalate ligands by halogenated ligands.
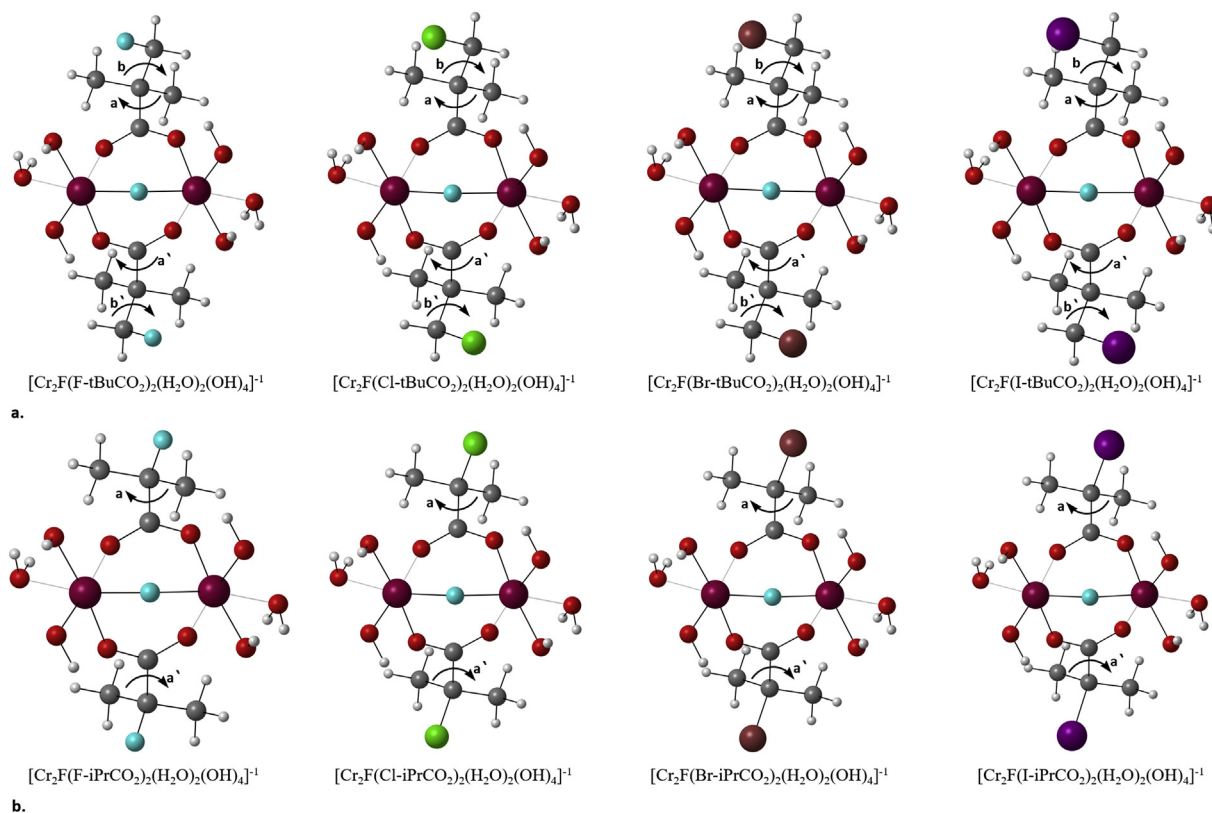
Fig. 2. Initial designed geometrical structures for new two types of complexes that are designed based on the optimized structure of $[Cr_2F(tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$ modeled complex. Rotation along arrows leads to form different conformers for these two types of complexes.

skeletons of the models due to the wheel-like structure of the main clusters ($[Cr_8F_8 (tBuCO_2)_{16}]$ and $[Cr_8O_8H_8 (tBuCO_2)_{16}]$ were almost rigid, possible conformers were only caused by rotation around these specified bonds.

At next step, it was necessary to determine all possible stable conformers for each complex. For this purpose, two procedures were selected and applied. First, the conformational energy surfaces of complexes were analyzed using Avogadro software [14], and applying GAFF force field [15] and genetic algorithm (GA) optimization method [16]. The GA as a stochastic conformer generator is a reliable and acceptable method for conformational analysis of chemical systems [17–22]. The GA options for conformational searching were children = 5, mutability = 5 and convergence = 25 with the scoring method of Energy. Since the GAFF is well parameterized for organic molecules including C, N, O, H, S, P, F and halogen atoms, and the rotator parts of our complexes contain C, H and halogen atoms (the inorganic core of the complexes are essentially rigid and therefore not influencing the conformer searching), this force field was used for conformational analysis. This methodology generated 9 and 50 conformers for X-iPrCO$_2$-containing and X-tBuCO$_2$-containing complexes respectively. These Avogadro generated conformers were converted to Gaussian inputs using GaussView and then their structural optimization was done at B3LYP/6-31g (d) [23] level of theory. Since the number of created conformers was too many and the structural optimization of all of them for all complexes could considerably increase the computations cost, so optimizations were done only for F-iPrCO$_2$-containing and F-tBuCO$_2$-containing complexes, and the results were extrapolated to the other halogen-containing complexes.

Secondly, the relaxed potential energy surface (PES) scan of involved dihedral angles in redundant internal coordinates were performed. For F-tBuCO$_2$-containing complex O_6-C_{13}-C_{14}-C_{16} and C_{13}-C_{14}-C_{16}-F_{49} dihedral angles were scanned separately for two states; the F_{48} atom located 1) in front and 2) behind the complex (Fig. 3 (a)). While in F-iPrCO$_2$-containing complex, the O_6-C_{12}-C_{13}-F_{42} dihedral was scanned for these two states of F_{43} atom (Fig. 3(b)). All potential energy surface scanning calculations were done at B3LYP/6-31g (d) level of theory. The purpose of choosing this computational level, besides of its reasonable accuracy, was its relatively low computational cost, which helped us to get a preliminary estimate of the possible stable conformers of these complexes. Computations for F-iPrCO$_2$-containing and F-tBuCO$_2$-containing complexes were also performed here, and the results were extrapolated to other halogens.

After obtaining the initial structures of possible stable conformers at lower level of theory, these conformers were optimized at our main computational level. For this, structural optimization of high-spin state followed by stability examination of the wavefunction and frequency calculations were done at B3LYP/TZV level of theory in the gas phase for all conformers. Then, the initial structures of low-spin or broken symmetry state were selected from the optimized structures of high-spin state and the fragment guess calculations of them were done at the same level of theory. These calculations as high-spin state were followed by checking the stability of the low-spin wavefunction and frequency calculations to approve the nature of the stationary point [8], [24–26]. It should be noted that in the iodine-containing complexes calculations, the 6−311g (d,p) basis set for iodine atoms was created, using the Basis Set Exchange (BSE) software and the EMSL Basis Set Library [27,28]. Other more advanced basis sets were also examined, but 6−311g (d, p) was the only cost effective and applicable basis set to iodine-containing models. All of these calculations were carried out using the Gaussian 09 program package [29]. Furthermore, the atoms in molecules (AIM) theory [30] was used to detect hydrogen bonds
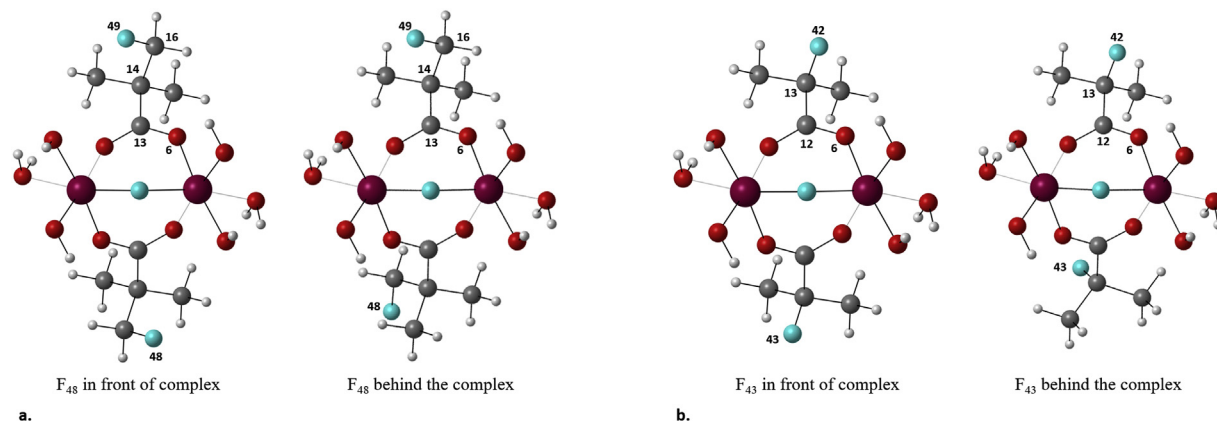
Fig. 3. Scanned dihedrals for two states of (a) F-tBuCO₂-containing and (b) F-iPrCO₂-containing complexes. Second fluorine atom could place in front or behind the complex, which leads to two states.

in the complexes structures. All the QTAIM properties were calculated by the AIMQB program within the AIM Studio [31] suite, using the PROAIM basin integration method [32]. Applying DFT-D functionals [33] could improve the results because non-bonded interactions could be considered efficiently by them [34,35]. But since the complexes under our study are covalent systems and the effects of non-bonded interactions are not dominated, B3LYP method without empirical dispersion corrections could provide acceptable results. Since the effectiveness of B3LYP methods for these systems were previously confirmed [36–39], this method was used for our calculations.

3. Results and discussion

3.1. Conformational analysis

At first step of the calculation, it was necessary to determine the stable conformers for each complex. As it was mentioned at pervious section, two procedures were used to determine all stable conformers of complexes. Findings presented 4 stable conformers for X-tBuCO₂-containing complexes, which were dubbed Conf1 to Conf4, and 3 stable conformers for X-iPrCO₂-containing complexes which were called Conf1 to Conf3. The details of calculations and the structure of stable conformers have been described in section I of Supporting Information and the obtained results have been gathered in Figs. S1–S8 and Tables S1 and S2.

3.2. Conformational relative energy

After determining the initial structures of stable conformers at the lower computational level, their final structures and relative energies (REs) were calculated at the desired computational level. Optimized structures and absolute energy values of $[Cr_2F(X\text{-}tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$ complexes (X = F, Cl, Br, I) for septet and singlet states of each of four stable conformers calculated at high level of theory, have been reported in section II of Supporting Information (see Figs. S8–S11 and Table S1). After structural optimization the relative energies of these conformers were examined to identify the order of conformational stability. By implying zero-point energy correction, the modified relative energy value of each conformer was calculated for each conformer of $[Cr_2F(X\text{-}tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$ complexes in high and low spin states which the results have been reported in Table 1. Based on these results, in all complexes the Conf4 was the most stable conformer for both spin. The second and third most stable conformer were Conf3 and Conf2 respectively for all stable conformers of complexes. The least stable conformer was Conf1, which had the relative energy values between 4.2 and 5.3 kcal mol⁻¹ in different complexes. A deeper investigation of the results revealed an interesting fact that the energy difference between the most and least stable conformers in various complexes were nearly the same; this difference in $[Cr_2F(F\text{-}tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$ complex for high-spin sate was 4.3 kcal mol⁻¹, while it increased to 5.3 kcal mol⁻¹ in chlorine-containing complex for the same spin state. In two other complexes, i.e. $[Cr_2F(Br\text{-}tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$ and $[Cr_2F(I\text{-}tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$ complexes this value became

Table 1
Modified Relative energy values for different conformers of $[Cr_2F(X\text{-}tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$ complexes at high level of theory for high and low spin states. The most stable conformer is considered as the reference state.

Conformer	$\Delta E_{\text{High-spin}}$			
	$[Cr_2F(F\text{-}tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(Cl\text{-}tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(Br\text{-}tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(I\text{-}tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$
Conf1	4.3	5.3	4.6	4.6
Conf2	2.6	3.1	2.7	2.5
Conf3	0.7	1.8	1.5	1.9
Conf4	0.0	0.0	0.0	0.0
Conformer	$\Delta E_{\text{Low-spin}}$			
	$[Cr_2F(F\text{-}tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(Cl\text{-}tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(Br\text{-}tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(I\text{-}tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$
Conf1	4.2	5.2	4.6	4.6
Conf2	2.6	3.1	2.7	2.5
Conf3	0.7	1.8	1.5	1.9
Conf4	0.0	0.0	0.0	0.0

Table 2
Modified Relative energy values for different conformers of $[Cr_2F(X-iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$ complexes at high level of theory for high and low spin states. The most stable conformer is considered as the reference state.

Conformer	$\Delta E_{High-spin}$			
	$[Cr_2F(F-iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(Cl-iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(Br-iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(I-iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$
Conf1	3.4	3.9	3.5	3.2
Conf2	1.8	1.0	1.0	0.6
Conf3	0.0	0.0	0.0	0.0
Conformer	$\Delta E_{Low-spin}$			
	$[Cr_2F(F-iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(Cl-iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(Br-iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(I-iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$
Conf1	3.4	3.9	3.5	3.1
Conf2	1.8	1.0	1.0	0.6
Conf3	0.0	0.0	0.0	0.0

4.6 kcal mol^{-1}.

Modified relative energies for 3 different conformers of X-iPrCO$_2$-containing complexes, which their optimized structures and absolute energy values at high level of theory have been reported in section II of Supporting Information (see Figs. S12–S15 and Table S2), have been gathered in Table 2. Examination of these results indicated that in both high-spin and low-spin states of these complexes the Conf3 and Conf1 were the most and least stable conformers respectively. In these complexes, the maximum difference between the most and least stable conformers have been observed in $[Cr_2F(Cl-iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$ complex while its minimum value occurred in $[Cr_2F(I-iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$ one.

3.3. Parameters affecting on the conformational relative energy

In continuation of our research, we investigated the parameters affecting on the conformational relative energy in the designed complexes. The first factor, which was realized to be effective in the stability order, was steric hindrances due to dihedral angle changes in different conformers. To determine the impact of this factor, the conformational energy changes (ΔE) versus dihedral angle variations ($\Delta\omega$) were investigated for both types of complexes (see Figs. S16 and S17). Based on obtained results, there was found an inverse linear relationship between the ΔE and $\Delta\omega$ in all complexes so that with $\Delta\omega$ increasing the relative energy of the conformer decreases and system becomes more stable. The second factor that was recognized to be effective in the conformational stability order, was the formation of hydrogen bonds due to the existence of halogen atoms in the structure. Doing atoms in molecules (AIM) analysis indicated that no clear relationship between hydrogen

bonds and the stability order can be recognized, and the presence of hydrogen bonds in some conformers just have led to their greater stability (See section III of Supporting Information for more details and Figs. S18 and S19). It must be noticed that B3LYP functional seems to be not adequately efficient for quantitative evaluation of non-bonded interactions. So the results of this section must be understood qualitatively and just be used in qualitative comparisons.

3.4. Effect of halogenated ligands-bridged substitutions on the J values

After determining the stable conformers of each of new designed complexes, we were ready to study the effect of substitution of pivalate ligands with halogenated X-tBuCO$_2$ and X-iPrCO$_2$ ligands on the magnetic properties of complexes; with a focus on their exchange coupling constants. For this purpose, exchange coupling constant (J) of each complex was calculated using our approved computing procedure presented in Ref. [3]. The obtained J values for $[Cr_2F(X-tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$ complexes have been reported in Table 3. Furthermore, ΔJ values, i.e. the J value changes compared to $[Cr_2F(tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$ complex, as a reference, have been presented in Table 3. Based on obtained results, J has acquired values from -12.1 to -10.5 cm^{-1} for different conformers of $[Cr_2F(F-tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$ complex. The maximum absolute value of J (12.1 cm^{-1}) belongs to the least stable conformer, namely Conf1, which shows 0.2 cm^{-1} increase in the absolute value of J compared to the reference complex. However in other conformers of this complex, a decreasing trend in their J values is observed such that Conf2, Conf3 and Conf4 of this

Table 3
Calculated absolute and relative J values (in cm^{-1}) for different conformers of $[Cr_2F(X-tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$ (X = F, Cl, Br, and I) complexes using our computational methodology.

Conformer	J			
	$[Cr_2F(F-tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(Cl-tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(Br-tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(I-tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$
Conf1	-12.1	-12.2	-12.1	-12.1
Conf2	-11.0	-9.8	-9.9	-7.3
Conf3	-11.1	-11.2	-11.4	-11.5
Conf4	-10.5	-10.6	-10.7	-10.7
Conformer	$\Delta|J|$			
	$[Cr_2F(F-tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(Cl-tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(Br-tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(I-tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$
Conf1	0.2	0.3	0.2	0.2
Conf2	-0.9	-2.1	-2.0	-4.6
Conf3	-0.8	-0.7	-0.5	-0.4
Conf4	-1.4	-1.3	-1.2	-1.2

These values were corrected by applying the zero-point energy correction.
The J value of $[Cr_2F(tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$ complex (-11.9 cm^{-1}) was taken as a reference to calculate the $\Delta|J|$ values (See Ref. [3]).

Table 4
Calculated absolute and relative J values (in cm^{-1}) for different conformers of $[Cr_2F(X\text{-}iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$ complexes using our computational methodology.

Conformer	J			
	$[Cr_2F(F\text{-}iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(Cl\text{-}iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(Br\text{-}iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$	$[Cr_2F(I\text{-}iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$
Conf1	−12.1	−13.8	−13.6	−13.2
Conf2	−11.0	−12.5	−12.3	−8.9
Conf3	−11.9	−11.7	−11.7	−11.6
Conformer	**$\Delta|J|$**			
	$[Cr_2F(F\text{-}iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$	**$[Cr_2F(Cl\text{-}iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$**	**$[Cr_2F(Br\text{-}iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$**	**$[Cr_2F(I\text{-}iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$**
Conf1	0.2	1.9	1.7	1.3
Conf2	−0.9	0.6	0.4	−3.0
Conf3	0.0	−0.2	−0.2	−0.3

These values were corrected by applying the zero-point energy correction.
The J value of $[Cr_2F(tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$ complex ($-11.9\ cm^{-1}$) was taken as a reference to calculate the $\Delta|J|$ values (See Ref. [3]).

complex, show 0.9, 0.8 and 1.4 cm^{-1} drops compared to the reference complex respectively. In $[Cr_2F(Cl\text{-}tBuCO_2)_2(H_2O)_2(OH)_4]^{-1}$ complex, Conf1 has also the highest absolute J value (12.2 cm^{-1}) showing a 0.3 cm^{-1} increase in the antiferromagnetic property of the complex and Conf2, Conf3 and Conf4 show 2.1, 0.7 and 1.3 cm^{-1} decreases in the absolute value of J respectively, compared to the reference complex.

A similar behavior can be seen in bromine and iodine-containing complexes, such that Conf1, i.e. the least stable conformer, has the highest absolute J value showing an increase of 0.2 cm^{-1} compared to the referenced complex while, Conf2, Conf3 and Conf4 showed in Br-containing complex 2.0, 0.5 and 1.2 cm^{-1} and in I- containing complex 4.6, 0.4 and 1.2 cm^{-1} decreases in the absolute value of J respectively. Based on these results, it can be inferred that in these complexes, depending on which conformer has been formed, the J value will differ and the complex show different antiferromagnetic behavior. If the least stable conformer, i.e. Conf1, has been formed, the antiferromagnetic property of the complex would strengthened while if any other conformers has been formed, the value of J will decrease and the antiferromagnetic property of the complex will weakened.

An identical investigation was performed for $[Cr_2F(X\text{-}iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$ complexes, which their results are reported in Table 4. Analysis of these results for $[Cr_2F(F\text{-}iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$ complex indicated that Conf1 and Conf2 has the strongest and weakest antiferromagnetic coupling with the J values of -12.1 and $-11.0\ cm^{-1}$ respectively and Conf4 took the J value between them. Comparing of these calculated values with J value of reference complex shows that the substitution of pivalate ligand with F-iPrCO2 ligand has strengthened the antiferromagnetic property of the complex in Conf1 (up to 0.2 cm^{-1}) while has weakened it in Conf2 (up to 0.9 cm^{-1}). However in Conf3 of this complex, this substitution has made no change in the J value.

In $[Cr_2F(Cl\text{-}iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$ complex, Conf1 with an absolute value of 13.8 cm^{-1} has the highest value of J, which is 1.9 cm^{-1} stronger compared to the reference complex. The Conf2 and Conf3 of this complex with J values of $-12.5\ cm^{-1}$ and -11.7 cm^{-1} respectively, show a 0.6 cm^{-1} increase and 0.2 cm^{-1} decrease with respect to the reference complex. Similar behavior has been observed for bromine-containing complex such that the absolute J values reduces from Conf1 to Conf3, which means that the antiferromagnetic property of the complex has been diluted. In this complex, Conf1 and Conf4 with J value of -13.6 and $-11.7\ cm^{-1}$ show an increase of 1.7 cm^{-1}, and a decrease of 0.2 cm^{-1} respectively compared to the reference complex. This behavior is also observed in $[Cr_2F(I\text{-}iPrCO_2)_2(H_2O)_2(OH)_4]^{-1}$ complex such that Conf1 and Conf2 has the strongest and weakest antiferromagnetic coupling, with the J values of -12.9 and $-8.9\ cm^{-1}$ respectively. So

the J value in Conf1 is 1.3 cm^{-1} greater and in Conf2 -3.0 cm^{-1} lesser than that of the reference complex. Conf3 with the value of $-11.6\ cm^{-1}$ locates between the other two conformers, and shows the minimum difference of J value (0.3 cm^{-1}) compared to the reference complex.

Deep investigation of obtained results indicates that in the second type of complexes, as in the first one, the substitution of pivalate ligands with X-iPrCO2 ligands has diverse effects on the exchange coupling constants values. Based on these results, this substitution in each complex can strengthen or weaken the antiferromagnetic property of the complex, depending on which conformer has been formed.

4. Conclusion

Following our previous work in which the effect of substitutions of the halogen ligands on the magnetic properties of the Chromium-Wheel host complexes were studied [3], in this study the effect of pivalate ligands substitutions on the properties of these complexes have been investigated. For this, a definite 1-negative charged binuclear chromium (III) complex was utilized as a model of the $[Cr_8F_8(tBuCO_2)_{16}]$ host complexes and two pivalate (tBuCO2) ligands were replaced by two types of halogenated anionic ligands including 3-halogeno-2,2-dimethylpropanoate (X-tBuCO2) and 2-halogeno-2-methylpropanoate (X-iPrCO2). Since the presence of halogen atoms in the structure led to form different conformers, a conformational analysis was done using two different procedures including conformational energy surfaces scanning with GAFF force field and relaxed potential energy surface (PES) scanning with DFT methods, to identify the possible stable conformers for each complex. It was found that, X-tBuCO2-containing complexes had four stable conformers, while for X-iPrCO2-containing complexes only three stable conformers were obtained. Subsequently, the conformational relative energies of stable conformers at desired computational level (B3LYP/TZV) were determined and the effective factors on the conformational energy changes were investigated. Structural and hydrogen bonding analysis showed that there was an inverse linear relationship between conformational energy and steric hindrances caused by dihedral angle rotation, but no trace of hydrogen bonding effect was observed.

After completing these steps, we evaluated the effect of halogenated pivalate ligands substitutions on magnetic properties of designed complexes at the B3LYP/TZV level of theory using a broken-symmetry molecular modelling approach. The Obtained results showed that in X-tBuCO2-containing complexes, if the least stable conformer i.e. Conf1 was formed, the antiferromagnetic property of the complex would be strengthened. But if any other

conformers was formed, the absolute value of J would decrease and the antiferromagnetic property of the complex would be weakened. In the case of X-iPrCO$_2$-containing complex, the replacement of pivalate ligands by X-iPrCO$_2$ ligands had similar effects on the J values. Based on these results, depending on which conformer was formed, the antiferromagnetic property of the complex could be strengthened or weakened.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jmgm.2018.11.005.

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