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Computational study of exchange coupling in homo- and heterometallic oxo- and carboxylato bridged trinuclear complexes with triangular $\{Fe_2^{III}M(\mu_3\text{-}O)\}$ ($M = Fe^{III}$, Ni^{II}, Co^{II}) core

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ABSTRACT

Using broken symmetry approach (DFT-BS, 6-311G(d)/B3LYP level of theory) the structure and magnetic exchange interactions in homo- and heterometallic oxo-centered trinuclear carboxylate complexes $[Fe_2M(\mu_3\text{-}O)(RCO_2)_6(H_2O)_3]^{n+}$ ($M = Fe^{III}$, $n = 1$; Ni^{II}, Co^{II}, $n = 0$; $R = C(CH_3)_3$, CH_3, CCl_3, CF_3) were evaluated. The influence of metal ion and the nature of the carboxylate bridging ligand on the structure and magnetic properties of trinuclear complex is discussed. It was shown, that antiferromagnetic exchange interactions in both Fe^{III}–Fe^{III} and Fe^{III}–M^{II} (M = Ni, Co) pairs weakens in the row trimethylacetate > acetate > trichloroacetate ≈ trifluoroacetate.

1. Introduction

Discrete complexes and coordination polymers of high spin metal ions are considered as the basis for new magnetic materials, in particular, such compounds can be potentially used for creation of memory elements [1,2], active bodies for application in spintronics [3–5], etc). Magnetic properties of such system (molar magnetic susceptibility, type of magnetic ordering or ordering temperature) can change upon interaction with guest molecules, which opens ways for creation of magnetic sensors [6–9]. Linking of polynuclear complexes by bridging ligands allows to create porous coordination polymers or supramolecular assemblies with desired magnetic properties, which are in significant extent predetermined by the properties of “building blocks” [10–12]. Also, some polynuclear complexes show unique single molecule magnetic behavior (SMMs) [13–15] (for example, hysteresis of the magnetization curve, magnetization lag, slow relaxation of single molecule’s magnetization). The effects, attributed to SMM behavior, can occur in compounds, in which exchange interactions between metal ions are ferro- or antiferromagnetic [16,17], and depends on total spin of the ground state and magnetic anisotropy [16]. Thus, study of exchange interactions in polynuclear complexes, determination of the influence of electronic characteristics of bridging ligands on the nature and energy of the exchange interactions between paramagnetic centers, as well as development of approaches for theoretical evaluation of magnetic properties of polynuclear systems are actual problems of modern magnetochemistry, inorganic and physical chemistry.

Trinuclear oxo-centered homo- and heterometallic basic carboxylate complexes with triangular $(\mu_3\text{-}O)M_3$ core are well known [18–20] and have been attracting attention due to their ability to serve as building blocks for assembling of compounds of higher nuclearity or coordination polymers [10,21–23], including porous metal–organic frameworks [10–12,24]. It was found that magnetic properties of such systems are governed by exchange coupling within trinuclear fragments [10–12]. Even discrete trinuclear carboxylates were reported to possess not trivial magnetic behavior [25]. However, despite large quantity of works, devoted to determination of exchange coupling parameters in such systems [21,22,26–28], the dependency of exchange coupling parameter values (J) on the structure of such compounds (in particular, the nature of substituent in carboxylate moiety) is not clear. There are several reasons for such situation. First, determination of J was ambiguous in some cases and fitting of

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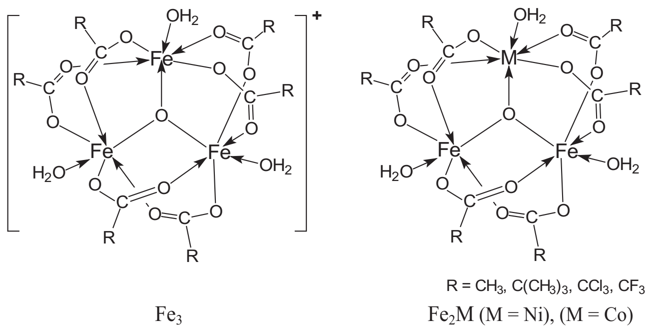
χ (or χT) *versus* T curve produced several sets of possible parameters, which were very different from each other but equally satisfied the requirement of R^2 minimum [19,29,30]. Second, in some cases data fitting was possible within different models, for example, Hamiltonians corresponding to equilateral or isosceles triangles were applied for Fe_3 systems, expected to be highly symmetric [29,31]. These reasons result in uncertainty in J values determination from experimental data, and the method for evaluation of "expected J" can be helpful for choosing proper set of parameter in curve fitting or choosing of an adequate model. It is also worth to note that some trinuclear carboxylates cannot be directly compared to close analogues, because they were not studied. For example, magnetic properties of $Fe_2CoO(CH_3CO_2)_6$(3-Cl-py)$_3$ complex (3-Cl-py is 3-chloropyridine) were studied and analyzed in details [32], but these data cannot be directly compared with other results because of the lack of similar complexes, containing 3-Cl-py ligand, as well as due to lack of data, obtained using the same theoretical model.

In many cases it was shown that action of electrono-accepting substituents led to decrease of J (in absolute value) in polynuclear complexes [33,34]. Similar situation is expected for trinuclear carboxylates and, as expected, it was found that $|J|$ in trifluoroacetates $Fe_2MO(CF_3CO_2)_6(H_2O)_3$ (M^{II} = Ni, Co, Mn) [26,35] were significantly lower compared to $|J|$ in analogous acetates [27,36] or pivalates [10–12,37,38]. Surprisingly, we could not see any correlation between $|J|$ for Fe^{III} complexes $Fe_3O(RCO_2)_6^+$ (R = $C(CH_3)_3$, CH_3, CCl_3) and some physical property related to electrono-accepting action of R (like pK of acids RCO_2H or chemical shifts in ^{13}C NMR spectra of these acids; see Supporting information for details). Thus, a question arose if exchange coupling in trinuclear carboxylates should depend on electrono-accepting action of the substituent R, and which influence can be expected at all for such systems.

The aim of this study was to develop theoretical approach for evaluation of J values in trinuclear μ_3-oxocentered carboxylates with Fe_3^{III} or $Fe_2^{III}M^{II}$ cores (M = Co, Ni) and to see, which values of J are predicted by theory (in the frames of the method, used in this work) and how significant is the predicted influence of electron-donating or electron-accepting groups on J values. Despite large quantity of works, devoted to different aspects of chemistry and physics of trinuclear carboxylates, the quantity of studies dealing with quantum-chemical modeling of such systems is limited [21,38].

In the present paper we report the results of theoretical study on the influence of the substituent in the bridging carboxylate groups on the exchange interactions in the series of compounds: homotrinuclear iron complexes $[Fe_3O(O_2CR)_6(H_2O)_3]^+\cdot RCO_2^-$ (R = $C(CH_3)_3$, CH_3, CCl_3, CF_3; Fe_3 core) and heterotrinuclear complexes $[Fe_2MO(O_2CR)_6(H_2O)_3]$ (R = CH_3, CCl_3, CF_3; M = Ni (Fe_2Ni core); M = Co (Fe_2Co core)) (see Scheme 1).



R = CH_3, $C(CH_3)_3$, CCl_3, CF_3

Fe_3 Fe_2M (M = Ni), (M = Co)

Scheme 1.

2. Computational details

All calculations in the present study were performed in the frames of density functional theory (DFT). It is well understood and was many times demonstrated by benchmark studies [39–41] that functionals with exact Hartree–Fock exchange contribution are superior over pure DFT ones for calculation of magnetic properties, that's why hybrid exchange correlation functional B3LYP [42] was employed with exchange part proposed by Bekke [43] and Lee–Yang–Parr [44] correlation. 6-311G(d) extended split-valence basis set with triple-zeta quality for valence orbitals was used for all atoms. Gaussian'03 code was employed for calculations [45]. Visualization and data preparation were carried out using Chemcraft software [46].

Parameters of exchange interactions were calculated within broken symmetry approach (DFT-BS) proposed by Ginsberg and Noodleman [47,48]. Thorough decryption and critical discussion of DFT-BS which is *de facto* considered mainstream method for the "real world" exchange interaction modeling approach can be found elsewhere [39,49–53].

For two interacting spin centers with total spins S_1 and S_2 exchange parameter can be calculated by the formula (1) that is readily derived using spin-projection operator on the broken symmetry (BS) determinant [47,48]:

$$2J_{12}^{SP} = \frac{E_{BS} - E_{HS}}{2S_1 \cdot S_2} \qquad (1)$$

where HS is high spin state with parallel orientation of electron's spins on centers 1 and 2, and BS is the broken symmetry state corresponding to their antiparallel alignment. Broken-symmetry solution for this state is obtained for the case when the symmetry of electronic density distribution was allowed to be lower than the actual spatial symmetry of the molecule. Eq. (1) is approximately valid in case of non-overlapping magnetically active single occupied molecular orbitals (SOMOs).

The non-spin projected formula (2) was obtained by Ruiz group [54] in proposition of strongly overlapping SOMOs:

$$2J_{12}^{nSP} = \frac{E_{BS} - E_{HS}}{2S_1 \cdot S_2 + S_2} \quad S_2 < S_1 \qquad (2)$$

In the current study we employed both expressions (1) and (2), because J^{SP} and J^{nSP} can be considered as estimation of the upper and lower limits of the exchange coupling parameter value [51].

Several methods were proposed and successfully applied for evaluation of exchange spin coupling in polynuclear metal clusters by DFT-BS method [21,51,55–63]. In the present study we employ so called minimal cluster approach (MCA) [51] in which minimum number of BS wavefunctions (equal to the number of independent magnetic coupling constants required by the symmetry) and the highest spin determinant are computed. Energies of two spin states for compounds with Fe_3 core and three for compounds with Fe_2Ni and Fe_2Co cores were calculated (Fig. 1).

In the case of the complexes with Fe_3 core these states are Fe_3-HS with total spin $S = 15/2$ (high spin), Fe_3-LS with $S = 5/2$ (low spin). For the complexes with Fe_2Ni core these states are: Fe_2Ni-HS with $S = 6$, Fe_2Ni-IS with $S = 4$ ("intermediate spin", spin orientation of electrons on Ni center is inverted) and Fe_2Ni-LS with $S = 1$ (low spin, spin orientation of the electrons on one of Fe ions is inverted). For the complexes with Fe_2Co core these states are Fe_2-Co-HS, Fe_2Co-IS and Fe_2Co-LS with S = 6½, 3½ and 1½, respectively.

Spin Hamiltonians (3) and (4) were used for the compounds with Fe_3, Fe_2Ni and Fe_2Co cores, respectively.

$$\hat{H}_{I} = -2J_{FeFe} \cdot [\hat{S}_{Fe1} \cdot \hat{S}_{Fe2} + \hat{S}_{Fe1} \cdot \hat{S}_{Fe3} + \hat{S}_{Fe2} \cdot \hat{S}_{Fe3}] \qquad (3)$$

$$\hat{H}_{II,III} = -2J_{MFe} \cdot [\hat{S}_{M} \cdot \hat{S}_{Fe1} + \hat{S}_{M} \cdot \hat{S}_{Fe2}] - 2J_{FeFe}\hat{S}_{Fe1} \cdot \hat{S}_{Fe2} \qquad (4)$$