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Magnetic interactions in oxide-bridged dichromium(III) complexes. Computational determination of the importance of non-bridging ligands

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ABSTRACT

The magnetic susceptibility of the dinuclear chromium(III) complex$[(CH_3CN)_5CrOCr(NCCH_3)_5](BF_4)_4\cdot 2CH_3CN$ has been measured and analyzed. With a fitted value of the triplet energy $J = 650\ cm^{-1}$, the antiferromagnetic coupling is the strongest hitherto determined for an unsupported linear oxide-bridged dinuclear Cr(III) system. The applicability of DFT for computational prediction of exchange in strongly coupled chromium(III) dimers was examined and an optimal and accurate modeling approach was devised. By such modeling it was shown possible to reproduce experimental exchange coupling constants with small relative errors typically of less than 10% ranging from the strongest coupled systems to systems with moderately strong couplings. A significant influence (>20%) of the chemical nature of the peripheral, non-bridging ligands on the exchange coupling was found and rationalized.

1. Introduction

Di- and polynuclear transition metal complexes attract much attention because of their occurrence in active centers of proteins, their use in catalysts and in molecule-based magnetic materials [1,2]. Consequently, the last decades have witnessed broad interest in the magnetic properties of polynuclear systems. Among the vast range of bridging ligands employed in polynuclear magnetic systems, oxide is ubiquitous and probably the most efficient mediator of exchange interactions. Accordingly, understanding of exchange across oxide bridges and establishment of magneto-structural correlations for oxide-bridged systems has been an important goal in molecular magnetism [3–6]. However, the extreme donor properties of oxide promotes ligand interactions and makes the assumption of additivity in ligand-field descriptions of oxide-ligated systems questionable. Likewise, magnetic interactions via oxide bridges are likely to be susceptible to the auxiliary ligand sphere, but this aspect has not been addressed in any systematic way. Semi-empirical models have been forwarded, that relate different quantities such as the distance between the metal centers [7,8] or the pK_a values of ligands [9] to the exchange coupling. Also, models based on the Anderson theory of exchange have been used for establishing magneto-structural correlations of oxide-bridged systems [10]. In recent years computational methods have become sufficiently powerful to be used on larger systems of experimental relevance, see Refs. [11,12] for examples. Despite the many advances achieved in computational modeling of exchange splittings, numerically accurate prediction of exchange coupling constants is not trivial and no methodology can be said to safely cover all possible systems. However, for the practically oriented chemist targeting systems with specific magnetic properties, tools for accurate prediction of exchange coupling constants can be of great value, even if their scope of applicability is limited.

Herein, the exchange interaction is described with the spin Hamiltonian:

$$\hat{H} = JS_A \cdot S_B \tag{1}$$

where J is the phenomenological exchange coupling constant and S_A and S_B are the localized spin operators for centers A and B, respectively. Few computational methodologies are capable of mapping this kind of Hamiltonian well, as it requires a large amount of both static and dynamic correlation [13]. DFT in combination with the broken-symmetry (BS) approach has become the method of choice in computation of exchange coupling constants for transition metal complexes. This computational methodology has been used extensively for a large number of molecules with good results, provided suitable choices for exchange–correlation functional and basis sets are made [12–15].

In this paper, we provide an analysis of exchange in dinuclear oxide-bridged chromium(III) systems. These systems are accessible with a range of auxiliary ligands and have physical properties deviating pronouncedly, from those of mononuclear chromium(III) systems due to the strong coupling via the oxo-bridge. The magnetic susceptibility of the newly characterized acetonitrile complex, μ-oxo-bis[pentakis(acetonitrile)chromium(III)]-ion (**1**) [16,17], is determined and found to corroborate the conclusion based on spectroscopy, that this system is the strongest coupled dinuclear

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chromium(III) system. However, the value of J obtained from the susceptibility data, is significantly different from that obtained in the solution experiment, but in good agreement with the computational results which reproduce the exchange coupling constants of known oxide-bridge dichromium(III) systems. A detailed investigation of DFT–BS computed coupling constants for the archetypical μ-oxo-bis[penta(ammine)chromium(III)]-ion (**2**) (known as "basic rhodo") [18] is presented. We have examined the influence of DFT exchange correlation functional and of the choice of one-electron basis set on the computed coupling constant. By this analysis we arrive at a combination of functional and basis set, which reproduces coupling constants not only over the full range observed for oxide-bridged chromium(III) dimers, but also for less strongly coupled systems with combinations of anionic bridging ligands. It is well known [19,20] that the bridge bond lengths have a strong influence on the coupling. Importantly, we find that the computational modeling of the Cr–O bond length dependence for different auxiliary ligands shows the nature of the auxiliary ligands also to be significant in determining the magnitude of the coupling.

2. Computational and experimental methods

All calculations were carried out using the ORCA 2.7 program package [21] using DFT with the TightSCF, Grid4 and NORI keywords. Even very small changes in the molecular geometry can lead to large changes in the coupling constant. Therefore, calculations with optimized geometries are not a viable approach for obtaining theoretical values of J. The accuracy by which experimental geometries of oxide-bridged systems is modeled by DFT, makes the errors in the geometries dominate the calculated exchange coupling constants. We have, thus, used experimental geometries for all calculations, which allows for a quantitative comparison with experimental values. The employed geometries were based on crystal structures obtained by Barra et al. [17] for **1** and by Uryshiyama [22] for **2**. Both compounds have rigorously linear oxide-bridges.

2.1. The broken symmetry approach

The BS approach was first proposed by Noodleman [14] and has been used extensively both for calculations of exchange coupling constants [12,13,15,23] and for making pseudo multi configurational calculations of bond cleavage [23,24]. A thorough review of the broken symmetry method as used in ORCA has been published by Neese [25]. The exchange coupling constant has been calculated by the expression in Eq. (2) proposed by Yamaguchi [26], which is valid for all coupling strengths:

$$J = \frac{E_F - E_{BS}}{\langle S^2\rangle_F - \langle S^2\rangle_{BS}} \tag{2}$$

2.2. Choice of basis set and functional

A basis set study was carried out on the X-ray geometry of the μ-oxo-bis[penta(ammine)chromium(III)]-ion **2** with the PBE0 functional, since it is known [25] to be a good functional for broken symmetry evaluations of exchange coupling constants and, as shown below, is the best performing for the present systems. The results from this study are given in Table 1. From these data, it is seen that, there is no difference between the VxZ(*d*) and VxZ(*2d*) basis sets for all three series, double (D), triple (T) and quadruple (Q) zeta. The VxZ(*2d*) basis sets add *f* polarization functions to the chromium atoms, and one would expect a better description of the magnetic orbitals on the chromium atoms and therefore some change in the coupling constant, but this is not the case. The only difference in going from the VxZ(*2d*) to the VxZ(*2df*) basis set is the inclusion of a set of *f* functions on the nitrogen and oxygen atoms which has a large effect on the coupling constant (for the full composition of the basis sets, see Supplementary materials, Table 2). This effect is almost solely due to the *f* function added to the oxygen between the two coupled chromium sites. To confirm this, a calculation was carried out with the VTZ(*2df*) basis on the oxygen and VTZ(*2d*) on the rest of the molecule, with a resulting J = 441.2 cm^{-1}. This is identical to the value of 441.2 cm^{-1} for using the VTZ(*2df*) basis set on all atoms.

Table 1
Basis set study performed on **2** with the PBE0 functional. All basis sets are Ahlrichs types, either double- [27], triple- [27] and quadruple- [28] zeta, with the corresponding polarization functions. [54].

Basis Set	$\langle S^2\rangle_F$	$\langle S^2\rangle_{BS}$	J (cm^{-1})
VDZ(*d*)	12.0378	2.9443	461.7
VDZ(*2d*)	12.0360	2.9434	462.0
VDZ(*2df*)	12.0362	2.9447	454.9
VDZ(*d/p*)	12.0380	2.9445	461.3
VDZ(*2d/2p*)	12.0361	2.9458	453.4
VDZ(2df/2pd)	12.0361	2.9473	445.3
VTZ(*d*)	12.0350	2.9474	447.6
VTZ(*2d*)	12.0339	2.9469	447.0
VTZ(*2df*)	12.0340	2.9479	441.2
VTZ(*d/p*)	12.0353	2.9469	449.9
VTZ(*2d/2p*)	12.0338	2.9469	446.0
VTZ(2df/2pd)	12.0339	2.9479	439.9
TZVP	12.0356	2.9481	442.7
TZVPP	12.0342	2.9489	435.4
VQZ(*d*)	12.0354	2.9498	436.5
VQZ(*2d*)	12.0342	2.9490	436.6
VQZ(*2df*)	12.0343	2.9498	432.1
VQZ(*d/p*)	12.0357	2.9494	438.6
VQZ(*2d/2p*)	12.0341	2.9492	435.8
VQZ(2df,2pd)	12.0342	2.9500	431.0
QZVP	12.0331	2.9511	422.0
QZVPP	12.0330	2.9510	421.5

While there is a great difference between the total energies of the system going from double to triple zeta basis sets, the differences in going from triple to quadruple are negligible, so with respect to the total energy of the system there is almost convergence in the basis sets. However, this is not the case with respect to J, which is essentially the difference between the total energy of the high spin and the broken symmetry state.

We find that both of the basis sets VTZ(*2df*) or VQZ(*2df*) perform well as they accurately reproduce the experimental data, and there is not much difference between them. However, complete convergence of the exchange coupling constant with respect to the valence split level is not observed cf. Fig. 2 in the Supplementary material. In the following, the VTZ(*2df*) basis has been employed.

The importance of the employed exchange correlation functional was examined for **2** and the results are summarized in Table 2. The GGA functionals describe this system poorly, by greatly overestimating the strength of the coupling by 290–400 cm^{-1} relative to the experimental value of J = 450 cm^{-1}.

All of the hybrid functionals, however, perform quite well, as shown in Fig. 1, with the B1LYP, B1P86, PWP1 and PBE0 functionals doing best, and giving almost identical results (see values in Table 2). We have chosen to use the PBE0 functional in further calculations as it is optimized for transition metal complexes (unlike the B1LYP functional), and it is newer than, but very similar to, the B1P86 and PWP1 functionals.

The findings obtained here for Cr(III) systems concerning optimal functionals are in line with those obtained by Neese et al. [43] on a large number of mixed oxidation state Mn(III)/Mn(IV)-dimers.