Ab Initio Configuration Interaction Calculation of the Exchange Coupling Constant in Hydroxo Doubly Bridged Cr(III) Dimers

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Ab initio difference-dedicated configuration interaction (DDCI) calculations have been carried out on the exchange coupling constant of the hydroxo doubly bridged Cr(III) complex $[Cr_2(\mu\text{-}OH)_2(NH_3)_8]^{4+}$, and the magneto-structural dependence on the bridge angle, Cr−O−Cr, and on the OH out-of-plane distortion have been analyzed. The complex is antiferromagnetic for all the geometries calculated. For the planar structure of the $(CrOH)_2$ unit, the magnitude of the coupling constant calculated for a Cr−O−Cr bridge angle of $100°$, -10.6 cm^{-1}, is in good agreement with the experimental values found in complexes having almost planar structure of this unit and comparable bridge angles and external ligands such as ethylenediamine. When the geometry of the complex is defined according to the crystallographic data of $[Cr_2(\mu\text{-}OH)_2(NH_3)_8](S_2O_6)_24H_2O$ (**I**) and $[Cr_2(\mu\text{-}OH)_2(NH_3)_8]Cl_44H_2O$ (**II**), with OH out-of-plane distortions of 24 and 41°, respectively, the antiferromagnetic character decreases as the distortion increases. The DDCI calculated J, -6.1 cm^{-1} for the dithionate **I** geometry and -4.2 cm^{-1} for the chloride **II** one, are in very good agreement with experiment: -2.9 and -2.1 cm^{-1}, respectively. The influences of the basis set and of the counterions are also discussed.

1. Introduction

In the last two decades, a legion of compounds with weak interactions between transition-metal centers have been synthesized and their structure and magnetic behavior characterized. Among the transition-metal binuclear compounds, many bridged complexes of transition metals with a wide variety of bridge ligands have been described—chloro,[1,2] azido,[3,4] oxo,[5−8] hydroxo,[9−10] oxalato,[11,12] or more complex bridges[13]—whose magnetic behavior depends on the ligands, the metal coordination, and the geometrical structure of the bridge region. For some of these complexes, e.g., dihalide bridged Cu(II) dimers, magneto-structural correlations have been well-established.

However, when going to metals with a greater number of unpaired electrons or to bridges of a more complex electronic structure, the information is less easy to rationalize. Many papers[10] have been devoted to chromium (III) dimers with a double hydroxo bridge $[Cr_2(\mu\text{-}OH)_2L_x]^{4+}$, where L is an external ligand that can be multidentate, and have shown that the exchange coupling constant, J, depends on the metal−oxygen distance, the in-plane bridge angle, ϕ, as well as the out-of-plane distortion of the hydroxo ligand, θ (see Figure 1). Most

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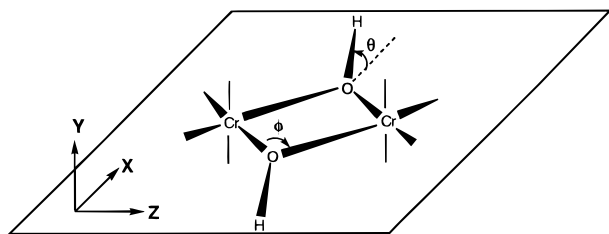
Figure 1. Simplified view of the structure of the $[Cr_2(\mu\text{-OH})_2(NH_3)_8]^{4+}$ complex.

of these compounds are reported to be antiferromagnetic. Correlations between the bridge angle and the exchange coupling constant have been discussed by Scaringe et al.[14,10] The decrease of the antiferromagnetic character with the out-of-plane OH distortion has also been analyzed, and correlations with ϕ and θ as well as the Cr–O distance have been given.[15] The aim of the present work is to show that ab initio calculations, including electron correlation, can give the correct trend of the magneto-structural dependencies in these systems and provide quantitative estimations of the coupling constant.

The spin interaction in these metal binuclear complexes is usually described using the phenomenological Heisenberg Hamiltonian

$$H = -2JS_1S_2 \tag{1}$$

which leads to an expression of the energy as a function of the exchange coupling constant. J is evaluated from the experiment by fitting the magnetic susceptibility to the temperature curve. In this formulation, a negative value of the coupling constant indicates antiferromagnetic coupling through the superexchange mechanism, as interpreted by Anderson.[16] For dimers with $S_1 = S_2$ total spin at each magnetic center, the possible states have total spin $S = 0, 1, ..., 2S_1$ and the energy difference between states of different multiplicity is given by

$$E(S) - E(S-1) = -2JS \tag{2}$$

Other terms such as biquadratic exchange terms may be added to (1) to obtain better data fitting. When the weight of these additional terms becomes important, the energy transitions may deviate from expression (2).

Calculations using Noodleman's[17] formalism based on broken symmetry calculations coupled to density functional methods[18] on this type of system have become frequent in recent years, but ab initio calculations which explicitly include multireference electron correlation are much less frequent: calculations with multireference Coupled Electron Pair Approximation (MR-

CEPA) on oxygen-bridged binuclear complexes of Ni(II)[19] and of Ti(III), V(III), and Cr(III)[20] have been reported.

On the basis of an early second-order perturbative treatment proposed by de Loth et al. for biradicals,[21] in previous papers[22–25] we presented a variational method especially conceived to determine the exchange coupling constant in molecular systems. This DDCI2 method is the version of the more general difference-dedicated configuration interaction method (DDCI)[26] which is specifically suited for magnetic systems. The method starts by giving a simple multireference zeroth-order description of the energy difference. Differential second-order contributions are then added to the CI space and treated variationally. DDCI2 has been applied to organic biradicals[24] and to Cu(II)[22] and Ni(II)[25] dimers with different types of bridges to analyze the dependence of J on the structural parameters. In all cases, the results have been in good agreement with the experimental values in sign, magnitude, and trend of the variation. A brief summary of the DDCI2 method is given in Section 2.

The DDCI2 method has been applied here to the reference complex bis(μ-hydroxo)bis[tetramminechromium(III)] cation, $[Cr_2(\mu\text{-OH})_2(NH_3)_8]^{4+}$, present in salts such as dithionate, $[Cr_2(\mu\text{-OH})_2(NH_3)_8](S_2O_6)_24H_2O$ (**I**), and chloride, $[Cr_2(\mu\text{-OH})_2(NH_3)_8]Cl_44H_2O$ (**II**),[27] in order to analyze the structural dependence of the coupling constant. The experimental structural parameters of both salts have been taken as a reference, and J has been calculated as a function of the Cr–O–Cr bridging angle, ϕ, and of the out-of-plane OH distortion, θ. Three basis sets of increasing quality have been used to verify their influence on the results. To take into account the effect of the counterions, some calculations have also been performed where the anions have been modeled first by negative point charges and then with chloride anions described with our smallest basis set. All these results are reported in Section 3.

2. The DDCI2 Method To Evaluate the Exchange Coupling Constant. The DDCI2 method, the reduced version of DDCI specifically designed for magnetic systems, is based on the early perturbative work by De Loth et al.[21] It was first

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derived to evaluate singlet−triplet gaps in biradicals[22] and was then generalized for problems with n unpaired electrons in n orbitals.[23] To analyze the contributions to the energy spectrum, the original perturbative method[21] uses a valence bond (VB) description, where the "magnetic orbitals" are orbitals localized on the magnetic center. These localized orbitals have an almost atomic nature and may be obtained from the molecular calculation, for instance, by performing a $\pi/2$ rotation of the symmetry-adapted molecular orbitals (MO). The DDCI2 method is based on the definition of a minimal model space which is generated by the neutral determinants, in the VB terminology built from the n singly occupied magnetic orbitals, i.e., a subspace of the complete active space (CAS) generated from the n localized orbitals and the n electrons. In the framework of the quasidegenerate perturbation theory, it has been demonstrated[22a,23] that of the double excitations which contribute to the second-order development of the corresponding effective Hamiltonian, only those with at most two inactive orbitals (occupied or virtual) are significant for the spectrum. The model space and these double excitations which contribute to the energy differences define the DDCI2 space, which is a subspace of the CAS single double configuration interaction (CAS*SDCI). To include higher orders of perturbation, the DDCI2 space is then treated variationally. The value of the coupling constant is determined from the difference between two roots through expression 2. The physical effects that are considered in the DDCI2 treatment include all the contributions up to the second order as discussed by de Loth et al.[21]—potential exchange, kinetic exchange, dynamic spin polarization, and charge transfer. The variational treatment, however, introduces higher order effects among which the contributions enabling the relaxation of the ionic determinants, in the VB terminology, that appear only at the fourth order. As discussed in ref 21a, this last effect is important because the magnetic orbitals are well-adapted to describe the neutral forms, where they are singly occupied, but not the ionic determinants whose energy is largely overestimated.

Complementary determinants are added to ensure that the wave functions are eigenfunctions of S^2 and space symmetry is taken into account. Unitary transformations of the active MOs keep the wave function unchanged and the magnetic orbitals are only needed for a formal purpose since the selection criteria are based on a VB formalism. The DDCI2 space thus includes: (1) the CAS generated from the n unpaired electrons and the n active symmetry-adapted MOs, which are essentially bonding and antibonding combinations of atomic orbitals centered on the magnetic center, with small contributions of the neighbor ligands; and (2) all singles and doubles on the CAS involving at most two inactive orbitals. The main characteristics of the DDCI2 method may be summarized in four points: (i) it is a variational method and for this reason (ii) it is an uncontracted method which allows the external correlation to modify the coefficients of the CAS; (iii) the DDCI2 matrix is invariant under rotations of the molecular orbitals in the active, doubly occupied, or virtual subsets, and therefore, the method takes advantage of working with symmetry adapted MOs; and (iv) the number of determinants in the DDCI2 space is proportional to the square of the dimension of the MO set, instead of to the fourth power of it as it would be in a CAS single and doubles configuration interaction (CAS*SDCI) calculation. A conventional Davidson diagonalization, with disk storage of the nonzero CI matrix elements, is possible provided that the basis set is medium-sized. However, when large molecular basis sets are considered, disk requirements become prohibitive and direct

algorithms are suitable alternatives.[26b,28] Truncations of the MO set are also possible, provided that a reliable criterion is used. It has been shown[25,29] that the MO set can be efficiently truncated after performing a transformation of the MOs which is specific to the magnetic systems. The exchange coupling dedicated MOs (EC-DMOs) are obtained from a perturbative estimation of differential contributions to the density matrix. The advantage of this transformation is that it avoids a complete transformation of two-electron integrals, since only a few of them are needed. Experience has shown that a reduction of around 30% of the molecular set, which represents a reduction of 50% of the DDCI2 space and 70% of the file of two-electron molecular integrals, keeps the J value unchanged. Since the dimensions of the DDCI2 spaces in the present work are still tractable, the MO basis set had to be truncated only in the last calculation reported in section 3.4.

It is worth mentioning that the results may be dependent on the set of active MOs. A procedure has been described[26c] to iteratively improve the active orbitals and obtain transitions independent of the starting MOs at self-consistency (IDDCI procedure). However, as will be shown in the next section, although the zeroth-order results are dramatically changed by the choice of active MOs, this has little influence on the coupling constant when dynamic correlation is added.

3. Results

3.1. Computational Details. Figure 1 gives a simplified view of the $[Cr_2(\mu\text{-OH})_2(NH_3)_8]^{4+}$ complex. The structural parameters of this cation were taken from the crystallographic data[27] of the dithionate, $[Cr_2(\mu\text{-OH})_2(NH_3)_8](S_2O_6)_2 \cdot 4H_2O$, **I**, and of the chloride, $[Cr_2(\mu\text{-OH})_2(NH_3)_8]Cl_4 \cdot 4H_2O$, **II**. These structures of the cation will be referred to hereafter as **C1** and **C2**, respectively. Among the variety of compounds with the $(CrOH)_2$ unit, the choice of **I** and **II** is not arbitrary since in this case the external NH_3 ligands need not be modeled in the calculation. The external ligands have little influence on the J value, provided that the coordination of the metal and the electronegativity are preserved. NH_3 can substitute amine-type ligands in the calculation without introducing appreciable errors, but the model may be a matter of discussion for other ligands. An idealized structure **M1**, of D_{2h} symmetry, was also considered to analyze the dependence of the coupling constant on the Cr−O−Cr bridge angle, ϕ, keeping the OH group in the plane. Table 1 shows the most important structural parameters of the $[Cr_2(\mu\text{-OH})_2(NH_3)_8]^{4+}$ cation in **C1**, **C2**, and **M1**. The **C1** and **C2** experimental geometries were used to determine the dependence of the coupling constant on the out-of-plane distortion, θ, since this angle increases from $\theta = 24°$ in **I** to $\theta = 41°$ in **II**. The symmetry point group for both structures was C_{2h}. Finally, the effect of the counterion charge on the coupling constant was also analyzed by including four negative point charges in symmetric positions which are nearly equivalent to the experimental chlorine positions in the chloride **II** in the **M2** model, $[Cr_2(\mu\text{-OH})_2(NH_3)_8]^{4+} \cdot (-1)_4$, and in a less crude **M3** model where chlorine ions were included, $[Cr_2(\mu\text{-OH})_2(NH_3)_8]Cl_4$. Because of the dependence of the geometry of the $(CrOH)_2$ unit on the external ligands and counterions, and the strong sensitivity of J to the changes in geometry, no optimization was performed.

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Table 1. Most Important Structural Parameters (Distances in Ångstroms, Angles in Degrees) of the $[Cr_2(\mu\text{-OH})_2(NH_3)_8]^{4+}$ Complex

parameter	C1[a]	C2[a]	M1[b]
d(Cr−Cr)	3.045	3.023	$2d(\text{Cr−O})\sin(\phi/_2)$
d(Cr−O)	1.968	1.980	1.969
	1.962	1.969	
d(O−H)	0.730	0.800	0.765
d(Cr−N)	2.078	2.074	2.082
	2.081	2.089	
	2.082	2.084	
	2.081	2.083	
d(N−H)[c]	1.09	1.09	1.09
ϕ	101.5	99.9	90−120
θ	24.0	41.0	0.0
H−H−H[c]	106	106	106

[a] **C1** and **C2** structures are obtained from the crystallographic data[27] in the dithionate, **I**, and in the chloride salts, **II**. [b] Mean distances and angles for the planar D_{2h} structure, **M1**. [c] Assumed.

Core potentials[30] were used for second-row atoms and for chromium, with a small Ne core, $[1s^2 2s^2 2p^6]$, in the last case. Three atomic basis sets were used in the calculations: (i) the A basis set, consisting of [4s,4p,3d] for Cr, valence double ζ (DZ) for O and H atoms of the OH groups, and a minimal basis set for the NH_3 external ligands; (ii) the B basis set, which is the same as A plus one f polarization function on Cr; (iii) the C basis set, which is the same as B plus polarization functions on bridge atoms O and H. The small basis set for the external ligands is justified by the fact that, as mentioned, the external ligands have little influence on J, provided that the electronegativity of the ligand and the coordination of the metal are preserved.

All the calculations started with an SCF calculation for the highest multiplet, a septet state, of the complex. After the transformation of the two-electron integrals, the DDCI2 space was generated.[31] According to expression 2, the coupling constants can be obtained by the difference of the energies of the septet, the quintet, the triplet or the singlet states: $E(S=2) - E(S=3) = 6J$, $E(S=1) - E(S=2) = 4J$, etc. Because of the much smaller size of the highest multiplet spaces, J was determined in all cases from the septet and the quintet states. The triplet state was only calculated for the D_{2h} symmetry to verify if Landé's rule is fulfilled. In fact, the fitting of the magnetic susceptibility curve for the chloride **II** shows a very small deviation from a pure Heisenberg behavior, while for the dithionate **I** the variation in the value of J is around 10% when quadratic terms are considered.

3.2. Dependence of the Exchange Coupling Constant on the Bridge Angle ϕ in the Planar $[Cr_2(\mu\text{-OH})_2(NH_3)_8]^{4+}$ Complex. The experimental works which study the dependence of magnetic behavior on the bridge angle M−X−M, where X is the bridge ligand, in doubly bridged binuclear complexes show a near-parabolic dependence of the coupling constant if the range of the experimental values is sufficiently wide. This is the case for Cu(II) dimers[32] whose behavior was interpreted from orbital energies in the early theoretical work by Hay, Thibeault, and

Table 2. Calculated Values (cm^{-1}) of the Exchange Coupling Constant, J, for the Complex $[Cr_2(\mu\text{-OH})_2(NH_3)_8]^{4+}$ in the D_{2h} Symmetry (**M1**) and the Bridging Angle $\phi = 100°$, Zeroth-Order (CASCI) and DDCI2 Results for the Basis Sets A, B, and C, and the Type of MOs and Dimension of the Corresponding DDCI2 Space (S)

basis set	MOs	J_{CASCI}	J_{DDCI2}	$S[^7B_{1u}]$	$S[^5A_g]$
A	SCF	60.9	−8.7	27 665	231 888
	IDDCI	1.2	−6.4	27 665	231 888
B	SCF	55.8	−9.4	33 233	280 314
C	SCF	58.2	−10.6	40 032	340 138

Hoffmann,[33] who showed that the antiferromagnetic contribution to J is minimum for a bridge angle of around 90°. DDCI2[22b] and other similar[34] calculations on this family of complexes correctly described this trend. A number of dihydroxo-bridged Cr(III) complexes show a similar magneto-structural correlation,[10] although it is less easy to interpret because of the great variety of external ligands as well as other coupled structural differences such as OH out-of-plane distortion. Hodgson et al.,[10,14] however, gave an explanation of this trend using a generalized Hay et al.[33] analysis. The following results on the **M1** complex were obtained by varying the Cr−O−Cr angle in a wide range, $90° \geq \phi \geq 120°$, and keeping the bridge core $(CrOH)_2$ planar, i.e., $\theta = 0°$. Since this structure belongs to the D_{2h} symmetry point group, the open-shell SCF calculation gave six singly occupied MOs belonging to the b_{3g}, a_u, a_g, b_{1u}, b_{2u}, and b_{1g} irreducible representations (IR), as already reported.[35] These orbitals correspond mainly to the bonding and antibonding combinations of the d atomic orbitals of the Cr atoms: a_g and b_{1u}, $(d_{z^2}, d_{x^2-y^2})_1 \pm (d_{z^2}, d_{x^2-y^2})_2$, b_{2u} and b_{3g}, $(d_{yz})_1 \pm (d_{yz})_2$, and a_u and b_{1g}, $(d_{xy})_1 \pm (d_{xy})_2$, where the subscripts 1 and 2 refer to each Cr center, with a small participation of the ligand orbitals. The lowest septet, quintet, and triplet states are, respectively, $^7B_{1u}$, ^5A_g, and $^3B_{1u}$. From these six active orbitals, two different symmetry and spin-adapted DDCI2 subspaces were generated: the $^7B_{1u}$ and the ^5A_g DDCI2 spaces. As Table 2 shows, there is ∼1 order of magnitude difference between the dimensions of both subspaces, which remain of moderate size. The diagonalization of each DDCI2 subspace provides the DDCI2 energies of the $^7B_{1u}$ and ^5A_g states. To verify Landé's rule (eq 2), the energy of the $^3B_{1u}$ state can also be computed. By diagonalizing this subspace, both triplet $^3B_{1u}$ and septet $^7B_{1u}$ roots are obtained. Since the $^3B_{1u}$ DDCI2 subspace includes 711 845 determinants with the A basis set, this calculation was performed only with this basis set and for one geometry, $\phi = 100°$. The influence of the choice of the MOs used was also verified for the same structure and basis set, by comparing the results obtained with SCF MOs and with MOs improved by the IDDCI[26c] procedure.

Table 2 shows the zeroth-order (labeled CASCI) and the DDCI2 calculated values of the coupling constant for the D_{2h} geometry with $\phi = 100°$ and the three basis sets. At the zeroth-order level (J_{CASCI}), all the coupling constants are positive, indicating ferromagnetic character, although IDDCI improved orbitals[26c] give nearly zero coupling. When dynamic correlation is added (J_{DDCI2}), all the calculated coupling constants become

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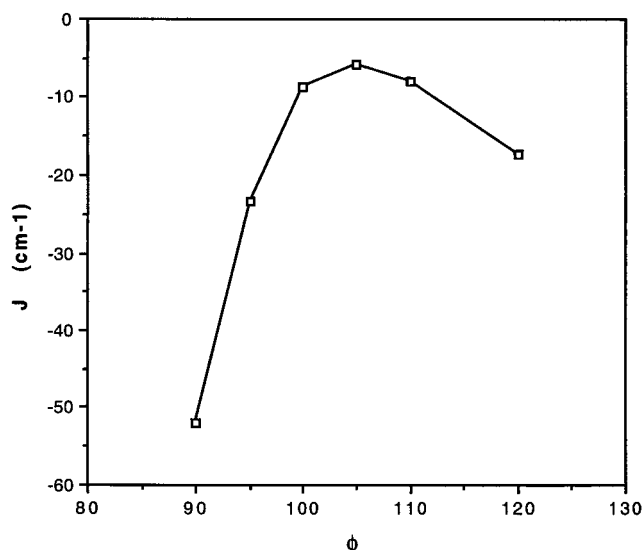
Figure 2. Dependence of the exchange coupling constant on the bridge angle, ϕ, with A basis set, at the DDCI2 level, in the planar structure of the $[Cr_2(\mu\text{-}OH)_2(NH_3)_8]^{4+}$ complex, **M1**.

Table 3. Calculated Values (cm^{-1}) of the Exchange Coupling Constant, J, for the Complex $[Cr_2(\mu\text{-}OH)_2(NH_3)_8]^{4+}$ in the Experimental Geometries **C1** and **C2** in the Dithionate and Chloride Salts, Respectively, Zeroth-Order (CASCI) and DDCI2 Results for the A and B Basis Sets, and Dimension of the Corresponding DDCI2 Space (S)

structure	basis set	J_{CASCI}	J_{DDCI2}	J_{exp}	$S[^7B_u]$	$S[^5A_g]$
C1	A	89.5	−5.7		54 372	463 792
				−2.9		
	B	81.9	−6.1		65 435	560 716
C2	A	82.1	−3.6		54 372	463 792
				−2.1		
	B	75.5	−4.2		65 435	560 716

negative ($|J|$ < 11 cm^{-1}), according to the observed antiferromagnetic behavior. The use of IDDCI improved active MOs does not significantly change the results when the correlation is included, since the DDCI2 coupling constant only differs by 2 cm^{-1} from the value calculated with open-shell SCF orbitals. The basis set also has little influence on the results, since the most extreme results differ by 2 cm^{-1}. When the coupling constant is determined from the energy difference between the quintet and the triplet states, ^5A_g and $^3B_{1u}$, it differs from the value obtained from the septet $^7B_{1u}$ and the quintet states by only 0.2 cm^{-1}. This indicates that when correlation is included, the system does not deviate substantially from the Landé's rule.

Some complexes have been described[36] in which the (CrOH)$_2$ unit remains almost planar, as $[Cr_2(\mu\text{-}OH)_2(en)_4]^{4+}$ in the tetrachloride−, tetrabromide−, or dichloride−diperchlorate salts. In all these complexes, the out-of-plane distortion is small and the Cr−O distance, which is also expected to influence the value of J,[10,15] is comparable to d(Cr−O) in **M1**. The coupling constant in these compounds ranges from −11 to −15 cm^{-1} for bridging angles of around 102°. The result obtained for ϕ = 100° with the best C basis set, −10.6 cm^{-1}, is thus in agreement with these experimental values.

Since the influence of the basis set and of the MOs is quite small, the influence on J of the Cr−O−Cr bridge angle was determined only with the A basis set with SCF MOs. Only the septet and quintet states were calculated. Figure 2 shows this variation when ϕ ranges between 90 and 120°. Throughout this range, the coupling constant is antiferromagnetic. The dependence is near-parabolic with a maximum of −5 cm^{-1}, corresponding to an angle of about 105°. The behavior is thus common to different bridged transition-metal binuclear complexes. In Cu(II) dimers, according to Hay et al.,[33] a simple one-electron analysis of the variation of the overlap between the d orbitals of the metal atoms facing the orbitals of the bridge ligands and the effect on the energies of the bonding and the antibonding orbitals allowed to interpret this trend. This argument was extended by Hodgson and co-workers[10,14] to Cr(III) dimers. On the other hand, Leuenberger and Güdel[35] showed that in this family of complexes, the overlap between the d$_{xy}$ orbitals in

the a$_u$ and b$_{1g}$ MOs was highly responsible for the antiferromagnetic coupling. This argument is consistent with the increasing of the antiferromagnetic character when the Cr−O−Cr angle is decreased.

3.3. Dependence of the Exchange Coupling Constant on the Out-of-Plane Angle θ in the $[Cr_2(\mu\text{-}OH)_2(NH_3)_8]^{4+}$ Complex. The influence of the out-of-plane distortion of the bridging OH ligands on J was analyzed by performing calculations on the $[Cr_2(\mu\text{-}OH)_2(NH_3)_8]^{4+}$ complex in the experimental geometries[27] **C1** and **C2**, where θ = 24 and 41°, respectively. In both cases, the chromium coordination is roughly octahedral with only slight differences between the Cr−N bond lengths (see Table 1). The out-of-plane distortion of the OH bridging groups reduces the symmetry of the complex to the C_{2h} point group.

The set of MOs was obtained from an open-shell calculation for the septet state, with both A and B basis sets. The six active orbitals belong now to the a$_g$, a$_u$(2), b$_g$(2) and b$_u$ IR. The lowest septet and quintet are thus the ^7B_u and ^5A_g states, respectively. There were twice as many determinants in the DDCI2 spaces for each IR as there were for the D_{2h} symmetry (see Table 3) for A and B basis sets. As shown in the table, the zeroth-order (CASCI) and the DDCI2 calculated values of the coupling constant for **C1** and **C2** geometries of the complex using both basis sets are all antiferromagnetic, with a small coupling ($|J|$ < 6 cm^{-1}), in good agreement with the experimental results. The effect of the basis set is less than 1 cm^{-1}. The calculated values show the same trend as the experimental ones and confirm that the magnitude of the coupling constant decreases when the out-of-plane distortion increases, in agreement with the correlation of Glerup et al.[15] which was based on perturbative estimations in the ligand field framework. Other compounds such as Na$_4$[Cr$_2(\mu\text{-}OH)_2(C_2O_4)_4$]·6H$_2$O,[37] [Cr$_2(\mu\text{-}OH)_2(H_2O)_2$-(chel)$_2$]·4H$_2$O,[38] where chel is chelidamate, and [Cr$_2(\mu\text{-}OH)_2$-(Cl-dipic)$_2(H_2O)_2$]·H$_2$O,[38] where Cl-dipic is 4-chlorodipicolinate, have out-of-plane distortions of the OH group that are about 40° and small coupling constants of −2 and −5 cm^{-1}. Even a weakly ferromagnetic structure is known,[39] Na$_4$[Cr$_2(\mu\text{-}OH)_2$-(mal)$_4$]·5H$_2$O, where mal is malonate, which presents a very strong out-of-plane distortion, 54°, which confirms the calculated trend. This result is also in agreement with a recent DFT study[18c] on Cu(II) dihidroxo-bridged binuclear complexes in which the same trend was observed.

3.4. Effect of the Counterion on the Calculation of the Coupling Constant. Since all the above calculations were performed on the cation, without taking into account the possible

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Table 4. Calculated DDCI2 Values (cm^{-1}) of the Exchange Coupling Constant, J, with A Basis Set for **M2**, $[Cr_2(\mu\text{-OH})_2(NH_3)_8]^{4+}\cdot(-1)_4$, and **M3**, $[Cr_2(\mu\text{-OH})_2(NH_3)_8]Cl_4$, in the **C2** Geometry

structure	M2	M3	C2
J_{DDCI2}	−3.7	−5.1	−3.6

role of the counteranion, two additional structures were calculated with the A basis set at the DDCI2 level including the effect of the four negative charges. In the first model, **M2**, four negative point charges were added, $[Cr_2(\mu\text{-OH})_2(NH_3)_8]^{4+}\cdot(-1)_4$. In the second model, **M3**, the four chloride ions were included, $[Cr_2(\mu\text{-OH})_2(NH_3)_8]Cl_4$. Since the size of the DDCI2 space increases with the square of the basis set, for **M3** the set of MOs was truncated after the EC-DMO transformation[25] mentioned in the first subsection of this paper. The experimental **C2** structure of the cation was used, and the negative charges were located at the positions of the chloride anions in $[Cr_2(\mu\text{-}OH)_2(NH_3)_8]Cl_4\cdot4H_2O$. As shown by the results of the exchange-coupling constants for both models reported in Table 4, the introduction of the four negative point charges has a negligible effect on the value of the coupling constant. The effect of the chloride groups' presence is slightly more significant, 1.5 cm^{-1}, but does not introduce changes in the sign or in the order of magnitude of the calculated constant. A similar conclusion was obtained in a recent DFT analysis[18b] of the influence on J of neglecting the bromide counterions in the closely related Cu(II) complex $[Cu_2(\mu\text{-OH})_2(tmeen)_2]Br_2$.

4. Conclusions

The results show that the DDCI2 method that had proved to give results in agreement with the experiment on systems with one or two unpaired electrons on each metal center, like Cu(II) and Ni(II) dimers, also provides accurate estimations of the magnetic exchange coupling constant in systems of increasing electronic complexity such as Cr(III) dimers. Compared with the reported experimental values, the magnitude of the coupling is quantitatively predicted, even for very weak couplings such as those of the dithionate and chloride salts discussed here. The trend of J with structural modifications is also well reproduced. Since the size of the CI space increases only with the square of the dimension of the basis set, the method appears to be less expensive than other high-level CI treatments.