Exchange interactions in $\text{Ti}_2\text{Cl}_9^{3-}$: a critical analysis

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Abstract

The electronic nature of the exchange interactions in $\text{Ti}_2\text{Cl}_9^{3-}$ is investigated from a theoretical point of view, using two different methods: (i) a parametric model Hamiltonian acting in the space of the $(t_{2g})^1-(t_{2g})^1$ pair states of the ground configuration; (ii) detailed ab initio calculations of the CASSCF and CASPT2 type. Comparison of the results allows the hopping integrals between the trigonal components of the t_{2g} shells, as well as in intercentre Coulomb integrals, to be determined. Both 'through-bond' and 'through-space' exchange interactions appear to be present. The conclusions are compared with existing exchange models and with experimental results.

Keywords: Electronic structure; Exchange interactions; Titanium complexes; Chloride complexes

1. Introduction

Dinuclear complexes of transition-metal ions are of great importance as molecular models for magnetic materials [1,2]. In particular, dimers of orbitally degenerate ions have attracted attention as they may exhibit a rich variety of exchange interactions. Several rival models have been proposed to incorporate the effect of orbital degeneracies in the standard Heisenberg–Dirac–Van Vleck Hamiltonian for magnetic exchange [3–6]. In the present contribution we attempt to evaluate the validity of these proposals. To this aim a general phenomenological Hamiltonian is constructed in the space of active spin orbitals. This model is worked out in detail for the case of $\text{Ti}_2\text{X}_9^{3-}$ dimers ($\text{X}=\text{Cl}, \text{Br}$), which represent an ideal high-symmetry example of two interacting ions with a $(t_{2g})^1$ ground state. The resulting parametric expressions for the dimer multiplet energies are compared with ab initio calculations of the CASPT2 type. This allows the relative importance of Coulomb and exchange interactions to be gauged, and provides a framework for a critical discussion of existing effective Hamiltonian models.

2. The effective Hamiltonian for $\text{Ti}_2\text{X}_9^{3-}$

2.1. Basis orbitals and states

$\text{Ti}_2\text{Cl}_9^{3-}$ has a face-shared bioctahedral structure, with a short intermetallic distance of 3.0–3.2 Å [7]. Chains based

on face-shared biocahedra are typical of hexagonal perovskite lattices. The symmetry of $\text{Ti}_2\text{Cl}_9^{3-}$ is D_{3h} . Trigonal forms of the t_{2g} orbitals on each centre are described in Eq. (1).

$$\begin{aligned} |a^A\rangle &= d_{xz}^A \\ |\theta^A\rangle &= \frac{1}{\sqrt{3}}(d_{xx}^A + \sqrt{2}d_{yz}^A) \\ |\epsilon^A\rangle &= \frac{1}{\sqrt{3}}(d_{yz}^A - \sqrt{2}d_{xx}^A) \\ |a^B\rangle &= d_{yz}^B \\ |\theta^B\rangle &= \frac{1}{\sqrt{3}}(-d_{xz}^B + \sqrt{2}d_{xy}^B) \\ |\epsilon^B\rangle &= \frac{1}{\sqrt{3}}(-d_{xy}^B - \sqrt{2}d_{xz}^B) \end{aligned} \quad (1)$$

The d-orbital functions in this expression refer to the local Cartesian (x^A, y^A, z^A) and (x^B, y^B, z^B) frames shown in Fig. 1. The labels a, θ, ϵ correspond to standard trigonal symmetry functions as defined by Griffith [8]. The θ and ϵ functions are components of a trigonal e representation. They are respectively symmetric and antisymmetric with respect to a vertical symmetry plane through the x and z directions. The relative phases of the orbitals are chosen in such a way that the A and B partners of a given type are mapped onto

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Fig. 1. Cartesian frames used in the text.

each other under the action of the horizontal symmetry plane, $\hat{\sigma}_h$,

$$\hat{\sigma}_h |a^A\rangle = |a^B\rangle$$

$$\hat{\sigma}_h |\theta^A\rangle = |\theta^B\rangle$$

$$\hat{\sigma}_h |\epsilon^A\rangle = |\epsilon^B\rangle$$

(2)

The twelve spin orbitals of two t_{2g} shells form the orbital basis of our effective Hamiltonian. From the start it will be required that this basis be orthonormal. This can easily be achieved by transforming all orbitals in Eq. (1) to Wannier type functions. Interactions in this space will be expressed in terms of creation and annihilation operators, such as $a_{\theta\alpha}^\dagger$, which creates an electron with α spin in $|\theta^A\rangle$, or $b_{\alpha\beta}$, which annihilates an electron with β spin in $|a^B\rangle$ [9]. Because of the orthonormality of the basis, these operators will obey the standard anticommutation rules for fermions. The $(t_{2g})^1-(t_{2g})^1$ configuration gives rise to some 36 states. The corresponding determinant functions are given in Table 1. In addition there are 30 so-called ionic states of the $(t_{2g})^0-(t_{2g})^2$ type. In the subsequent treatment these ionic states will be removed from the active space by a unitary transformation of the effective Hamiltonian.

2.2. The Hamiltonian

The total Hamiltonian in the space of twelve orbitals consists of several parts which will be denoted in the following way:

$$H = H_0^A + H_0^B + H_0^{AB} + V \quad (3)$$

where H_0^A and H_0^B represent all single-centre contributions, H_0^{AB} is the interelectronic repulsion between electrons on different centres and V contains the transfer terms. This latter term is the only term in H that is able to mix covalent and ionic states.

Table 1

Determinant functions for the $(t_{2g})^1-(t_{2g})^1$ configuration (for the E-type functions only the θ component is written)

$(a \times a)$	${}^3A_2'' = a^A a^B $ ${}^1A_1' = \frac{1}{\sqrt{2}}(a^A \bar{a}^B - \bar{a}^A a^B)$
$(a \times e)$	${}^3E' = \frac{1}{\sqrt{2}}(\theta^A \theta^B - \theta^A a^B)$ ${}^1E' = \frac{1}{2}(\theta^A \bar{\theta}^B - \bar{a}^A \theta^B - \theta^A \bar{a}^B + \bar{\theta}^A a^B)$ ${}^3E'' = \frac{1}{\sqrt{2}}(a^A \theta^B + \theta^A a^B)$ ${}^1E'' = \frac{1}{2}(a^A \bar{\theta}^B - \bar{a}^A \theta^B + \theta^A \bar{a}^B - \bar{\theta}^A a^B)$
$(e \times e)$	${}^3A_2'' = \frac{1}{\sqrt{2}}(\theta^A \theta^B + \epsilon^A \epsilon^B)$ ${}^1A_1' = \frac{1}{2}(\theta^A \bar{\theta}^B - \bar{\theta}^A \theta^B + \epsilon^A \bar{\epsilon}^B - \bar{\epsilon}^A \theta^B)$ ${}^3A_2' = \frac{1}{\sqrt{2}}(\theta^A \epsilon^B - \epsilon^A \theta^B)$ ${}^1A_1'' = \frac{1}{2}(\theta^A \epsilon^B - \bar{\theta}^A \epsilon^B - \epsilon^A \bar{\theta}^B + \bar{\epsilon}^A \theta^B)$ ${}^3E'' = \frac{1}{\sqrt{2}}(\theta^A \theta^B - \epsilon^A \epsilon^B)$ ${}^1E' = \frac{1}{2}(\theta^A \bar{\theta}^B - \bar{\theta}^A \theta^B - \epsilon^A \bar{\epsilon}^B + \bar{\epsilon}^A \epsilon^B)$

2.2.1. Single-centre contributions

The characteristic ingredients of a single-centre Hamiltonian for a transition-metal ion are discussed in ligand field theory [8] and comprise interelectronic repulsion between the d electrons, ligand field splittings and spin-orbit coupling. Leaving aside spin-orbit coupling we will write H_0^A (and similarly H_0^B) as follows:

$$\begin{aligned}
 H_0^A = & U_1 \sum_i n_{i\sigma}^A n_{i\bar{\sigma}}^A + U_\perp \sum_{i < j} \sum_{\sigma \sigma'} n_{i\sigma}^A n_{j\sigma'}^A \\
 & - J \sum_{i < j} \sum_{\sigma \sigma'} (n_{i\sigma}^A n_{j\sigma'}^A - a_{i\sigma}^{\dagger} a_{j\sigma'}^{\dagger} a_{i-\sigma}^{\dagger} a_{j-\sigma} - a_{i\sigma}^{\dagger} a_{j\sigma'}^{\dagger} a_{i-\sigma}^{\dagger} a_{j-\sigma}) \\
 & + \Delta \sum_{\sigma} (n_{\epsilon\sigma}^A + n_{\theta\sigma}^A)
 \end{aligned} \quad (4)$$

Here i and j are orbital indices denoting the a , θ and ϵ orbitals in Eq. (1); σ and σ' are spin labels for α and β . The $n_{i\sigma}^A$ quantities are the number operators $a_{i\sigma}^{\dagger} a_{i\sigma}$ that count the population of the $(i\sigma)$ spin orbital in t_{2g}^A . The U parameters are Coulomb repulsion integrals between two electrons in the same t_{2g} orbital (U_1) or in different t_{2g} orbitals ($U_\perp$). J represents the exchange integral and Δ measures the trigonal splitting of the t_{2g} shell. In a d-only formalism the repulsion integrals are subject to the relationship in Eq. (5) which allows $U_\perp$ to be eliminated.

$$U_1 - U_\perp = 2J \quad (5)$$

As we have explained elsewhere [10], eigenfunctions of H_0 may be characterized by pseudo-angular momentum labels, which refer to the degeneracy group of a t_{2g} shell. In this scheme the $(t_{2g})^2$ configuration gives rise to 1S , 1D , 3P states. When H_0 operates on these it produces the crystal field levels given in Table 2.

2.2.2. Intercentre repulsion integrals

Two-body intercentre matrix elements are of two different kinds: U integrals describing the repulsion between electron clouds on different centres, and B integrals, which represent exchange interactions. In its most general form the corresponding Hamiltonian is written as follows:

$$H_0^{AB} = \frac{1}{2} \sum_{\sigma\sigma'} \sum_{ijkl} (U_{ijkl} (a_{i\sigma}^\dagger b_{j\sigma'}^\dagger b_{l\sigma} a_{k\sigma} + b_{i\sigma}^\dagger a_{j\sigma'}^\dagger a_{l\sigma} b_{k\sigma}) + B_{ijkl} (a_{i\sigma}^\dagger b_{j\sigma'}^\dagger a_{l\sigma} b_{k\sigma} + b_{i\sigma}^\dagger a_{j\sigma'}^\dagger b_{l\sigma} a_{k\sigma})) \quad (6)$$

Taking into account the equivalence of centres A and B, the permutational symmetry of the two-particle interaction, and the trigonal site-symmetry of the orbital basis, one can rewrite this Hamiltonian more explicitly as follows:

$$\begin{aligned} H_0^{AB} = & \sum_{\sigma\sigma'} (U_{aaad} n_{a\sigma}^\dagger n_{a\sigma'}^\dagger + U_{\theta\theta\theta\theta} (n_{\theta\sigma}^\dagger n_{\theta\sigma'}^\dagger + n_{\epsilon\sigma}^\dagger n_{\epsilon\sigma'}^\dagger + n_{\theta\sigma}^\dagger n_{\epsilon\sigma'}^\dagger + n_{\epsilon\sigma}^\dagger n_{\theta\sigma'}^\dagger) + U_{aa\theta\theta} (a_{a\sigma}^\dagger a_{\theta\sigma}^\dagger b_{a\sigma'}^\dagger b_{\theta\sigma'}^\dagger + a_{a\sigma}^\dagger a_{\epsilon\sigma}^\dagger b_{a\sigma'}^\dagger b_{\epsilon\sigma'}^\dagger \\ & + a_{\theta\sigma}^\dagger a_{a\sigma}^\dagger b_{\theta\sigma'}^\dagger b_{a\sigma'}^\dagger + a_{\epsilon\sigma}^\dagger a_{a\sigma}^\dagger b_{\epsilon\sigma'}^\dagger b_{a\sigma'}^\dagger + a_{a\sigma}^\dagger a_{\theta\sigma}^\dagger b_{a\sigma'}^\dagger b_{\theta\sigma'}^\dagger + a_{\theta\sigma}^\dagger a_{a\sigma}^\dagger b_{\theta\sigma'}^\dagger b_{a\sigma'}^\dagger + a_{\epsilon\sigma}^\dagger a_{a\sigma}^\dagger b_{\epsilon\sigma'}^\dagger b_{a\sigma'}^\dagger + a_{a\sigma}^\dagger a_{\epsilon\sigma}^\dagger b_{a\sigma'}^\dagger b_{\epsilon\sigma'}^\dagger \\ & + U_{a\theta a\theta} (n_{a\sigma}^\dagger n_{\theta\sigma'}^\dagger + n_{\theta\sigma}^\dagger n_{a\sigma'}^\dagger + n_{\theta\sigma}^\dagger n_{\epsilon\sigma'}^\dagger + n_{\epsilon\sigma}^\dagger n_{\theta\sigma'}^\dagger) + U_{\theta\theta\epsilon\epsilon} (a_{\theta\sigma}^\dagger a_{\epsilon\sigma}^\dagger b_{\theta\sigma'}^\dagger b_{\epsilon\sigma'}^\dagger + a_{\epsilon\sigma}^\dagger a_{\theta\sigma}^\dagger b_{\epsilon\sigma'}^\dagger b_{\theta\sigma'}^\dagger + a_{\theta\sigma}^\dagger a_{\epsilon\sigma}^\dagger b_{\theta\sigma'}^\dagger b_{\epsilon\sigma'}^\dagger \\ & + a_{\epsilon\sigma}^\dagger a_{\theta\sigma}^\dagger b_{\epsilon\sigma'}^\dagger b_{\theta\sigma'}^\dagger - 2n_{\theta\sigma}^\dagger n_{\epsilon\sigma'}^\dagger - 2n_{\epsilon\sigma}^\dagger n_{\theta\sigma'}^\dagger) - B_{aaaa} \sum_{\sigma} (n_{a\sigma}^\dagger n_{a\sigma}^\dagger + a_{a\sigma}^\dagger a_{a-\sigma}^\dagger b_{a-\sigma}^\dagger b_{a\sigma}) \\ & - B_{\theta\theta\theta\theta} (\sum_{\sigma} (n_{\theta\sigma}^\dagger n_{\theta\sigma}^\dagger + a_{\theta\sigma}^\dagger a_{\theta-\sigma}^\dagger b_{\theta-\sigma}^\dagger b_{\theta\sigma} + n_{\epsilon\sigma}^\dagger n_{\epsilon\sigma}^\dagger + a_{\epsilon\sigma}^\dagger a_{\epsilon-\sigma}^\dagger b_{\epsilon-\sigma}^\dagger b_{\epsilon\sigma}) + \sum_{\sigma\sigma'} (a_{\theta\sigma}^\dagger a_{\epsilon\sigma'}^\dagger b_{\theta\sigma}^\dagger b_{\epsilon\sigma'}^\dagger + a_{\epsilon\sigma}^\dagger a_{\theta\sigma'}^\dagger b_{\epsilon\sigma}^\dagger b_{\theta\sigma'}^\dagger) \\ & - B_{a\theta a\theta} (\sum_{\sigma} (n_{a\sigma}^\dagger n_{\theta\sigma}^\dagger + a_{a\sigma}^\dagger a_{a-\sigma}^\dagger b_{a-\sigma}^\dagger b_{a\sigma} + n_{\epsilon\sigma}^\dagger n_{\epsilon\sigma}^\dagger + a_{\epsilon\sigma}^\dagger a_{\epsilon-\sigma}^\dagger b_{\epsilon-\sigma}^\dagger b_{\epsilon\sigma} + n_{\theta\sigma}^\dagger n_{a\sigma}^\dagger + a_{\theta\sigma}^\dagger a_{\theta-\sigma}^\dagger b_{\theta-\sigma}^\dagger b_{a\sigma} + n_{\epsilon\sigma}^\dagger n_{a\sigma}^\dagger \\ & + a_{a\sigma}^\dagger a_{\epsilon-\sigma}^\dagger b_{a-\sigma}^\dagger b_{\epsilon\sigma}) + \sum_{\sigma\sigma'} (a_{a\sigma}^\dagger a_{\theta\sigma'}^\dagger b_{a\sigma}^\dagger b_{\theta\sigma'}^\dagger + a_{a\sigma}^\dagger a_{\epsilon\sigma'}^\dagger b_{a\sigma}^\dagger b_{\epsilon\sigma'}^\dagger + a_{\theta\sigma}^\dagger a_{a\sigma'}^\dagger b_{\theta\sigma}^\dagger b_{a\sigma'}^\dagger + a_{\epsilon\sigma}^\dagger a_{a\sigma'}^\dagger b_{\epsilon\sigma}^\dagger b_{a\sigma'}^\dagger) \\ & - B_{a\theta a\theta} \sum_{\sigma\sigma'} (a_{a\sigma}^\dagger a_{\theta\sigma'}^\dagger b_{a\sigma}^\dagger b_{\theta\sigma'}^\dagger + a_{a\sigma}^\dagger a_{\epsilon\sigma'}^\dagger b_{a\sigma}^\dagger b_{\epsilon\sigma'}^\dagger + a_{\theta\sigma}^\dagger a_{a\sigma'}^\dagger b_{\theta\sigma}^\dagger b_{a\sigma'}^\dagger + a_{\epsilon\sigma}^\dagger a_{a\sigma'}^\dagger b_{\epsilon\sigma}^\dagger b_{a\sigma'}^\dagger) \\ & - B_{\theta\theta\epsilon\epsilon} (\sum_{\sigma} (n_{\theta\sigma}^\dagger n_{\epsilon\sigma}^\dagger + a_{\theta\sigma}^\dagger a_{\theta-\sigma}^\dagger b_{\theta-\sigma}^\dagger b_{\epsilon\sigma} + n_{\epsilon\sigma}^\dagger n_{\theta\sigma}^\dagger + a_{\epsilon\sigma}^\dagger a_{\epsilon-\sigma}^\dagger b_{\epsilon-\sigma}^\dagger b_{\theta\sigma}) \\ & + \sum_{\sigma\sigma'} (a_{\theta\sigma}^\dagger a_{\epsilon\sigma'}^\dagger b_{\theta\sigma}^\dagger b_{\epsilon\sigma'}^\dagger + a_{\epsilon\sigma}^\dagger a_{\theta\sigma'}^\dagger b_{\epsilon\sigma}^\dagger b_{\theta\sigma'}^\dagger - 2a_{\theta\sigma}^\dagger a_{\epsilon\sigma}^\dagger b_{\theta\sigma}^\dagger b_{\epsilon\sigma} - 2a_{\epsilon\sigma}^\dagger a_{\theta\sigma}^\dagger b_{\epsilon\sigma}^\dagger b_{\theta\sigma})) \end{aligned} \quad (7)$$

An important trigonal symmetry relation which is incorporated in this expression reads:

$$U_{\theta\theta\theta\theta} = 2U_{\theta\theta\epsilon\epsilon} + U_{\epsilon\epsilon\theta\theta} \quad (8)$$

and similarly for $B_{\theta\theta\theta\theta}$.

A simplified form of the Hamiltonian, which will be useful in the subsequent unitary transformation, can be obtained by neglecting all exchange integrals and overlap-type Coulomb integrals, while replacing all remaining genuine Coulomb integrals by an average isotropic repulsion parameter U' . This yields

$$H_0^{AB} \approx \sum_{i,j} \sum_{\sigma\sigma'} U' (n_{i\sigma}^\dagger n_{j\sigma'}^\dagger) \quad (9)$$

U' may be approximated by the repulsion between point charges at the metal centres.

2.2.3. The transfer term

Finally H contains the transfer term contribution V which results from overlap between equisymmetric orbitals on both centres. It may be written as follows:

$$V = t_a \sum_{\sigma} (a_{a\sigma}^\dagger b_{a\sigma} + b_{a\sigma}^\dagger a_{a\sigma}) + t_e \sum_{\sigma} (a_{\theta\sigma}^\dagger b_{\theta\sigma} + a_{\epsilon\sigma}^\dagger b_{\epsilon\sigma} + b_{\theta\sigma}^\dagger a_{\theta\sigma} + b_{\epsilon\sigma}^\dagger a_{\epsilon\sigma}) \quad (10)$$

Table 2
Crystal field levels generated by H_0^A acting on the various $(t_{2g})^2$ states

M_L	M_S	Function	Energy
3P	1	$ \theta\bar{e} $	$U_1 - 3J + 2\Delta$
	0	$\frac{1}{\sqrt{2}}(\theta\bar{e} - \bar{e}\theta)$	
	-1	$ \bar{\theta}\bar{e} $	
	1	$ \theta a $	$U_1 - 3J + \Delta$
	0	$\frac{1}{\sqrt{2}}(a\bar{\theta} - \bar{\theta}a)$	
	-1	$ \bar{\theta}a $	
1D	1	$ \bar{e}a $	$U_1 - J + \Delta$
	0	$\frac{1}{\sqrt{2}}(- \bar{e}a + a\bar{e})$	
	-1	$ \bar{e}a $	
	0	$\frac{1}{\sqrt{6}}(\theta\bar{\theta} + \bar{e}\bar{e} - 2 a\bar{a})$	$U_1 - J + \frac{2}{3}\Delta$
	θ	$\frac{1}{\sqrt{2}}(\theta\bar{a} + a\bar{\theta})$	
	θ	$\frac{1}{\sqrt{2}}(\theta\bar{a} + a\bar{\theta})$	
1S	0	$\frac{1}{\sqrt{2}}(\bar{e}a + a\bar{e})$	$U_1 - J + 2\Delta$
	θ	$\frac{1}{\sqrt{2}}(\bar{e}\bar{e} - \theta\bar{\theta})$	
	θ	$\frac{1}{\sqrt{2}}(\bar{e}\bar{e} - \theta\bar{\theta})$	
	0	$\frac{1}{\sqrt{2}}(\theta\bar{\theta} + \bar{e}\bar{e} + a\bar{a})$	$U_1 + 2J + \frac{4}{3}\Delta$
	ϵ	$\frac{1}{\sqrt{2}}(\theta\bar{\theta} + \bar{e}\bar{e} + a\bar{a})$	
	ϵ	$\frac{1}{\sqrt{2}}(\theta\bar{\theta} + \bar{e}\bar{e} + a\bar{a})$	

Here t_a and t_e are one-body interaction elements connecting a -type and e -type orbitals on the two centres, as indicated in Scheme 1. Such interactions may be caused by direct overlap between the orbitals but may also involve contributions of bridging ligand orbitals.

2.3. Energy expressions

Energy expressions for the t_{2g} states of the $Ti_2Cl_9^{3-}$ dimer may be obtained by diagonalizing H in the space of all covalent and ionic states. In actual calculations however the contribution of the ionic states is incorporated into an effective operator, using a second-order perturbational formalism.

2.3.1. The transformed Hamiltonian

All existing models of exchange interactions in dinuclear metal complexes have one important point in common. They all assume that the hopping integrals t_a and t_e are much smaller than the repulsion between electrons on the same centre. This criterion ranges the dimeric complexes in the so-called Heisenberg limit, where electrons tend to localize on different

Scheme 1.

centres, as opposed to the Hückel or band limit, where electrons are occupying delocalized molecular orbitals. In the Heisenberg regime the zeroth-order Hamiltonian H_0 corresponds to $H_0^A + H_0^B + H_0^{AB}$, while V acts as the perturbation. Let $|\phi_k^0\rangle$ represent an eigenstate of H_0 with energy E_k . As we have indicated before, H_0 has 36 eigenstates belonging to the $(t_{2g})^1-(t_{2g})^1$ configuration (see Table 1), and 30 eigenstates of the $(t_{2g})^2-(t_{2g})^0$ type (see Table 2). We now define an operator S in the space of H_0 eigenstates:

$$S = \sum_{k,l} \frac{V_{kl}}{E_k - E_l} |\phi_k^0\rangle \langle \phi_l^0| \quad (11)$$

where V_{kl} is a matrix element $\langle \phi_k^0 | V | \phi_l^0 \rangle$. The commutator of S and H_0 is equal to $-V$:

$$\begin{aligned} [S, H_0] &= \sum_{k,l} \frac{V_{kl}}{E_k - E_l} (|\phi_k^0\rangle \langle \phi_l^0 | H_0 - H_0 | \phi_k^0\rangle \langle \phi_l^0|) \\ &= - \sum_{k,l} V_{kl} |\phi_k^0\rangle \langle \phi_l^0| = -V \end{aligned} \quad (12)$$

The unitary transformation of H by S is given by [11]:

$$\begin{aligned} \tilde{H} &= e^S H e^{-S} = (1 + S + \frac{1}{2}S^2 + \dots)(H_0 + V) \\ &\times (1 - S + \frac{1}{2}S^2 - \dots) \\ &\approx H_0 + V + [S, H_0] + [S, V] + \frac{1}{2}[S, [S, H_0]] \end{aligned} \quad (13)$$

Upon substitution this result simplifies to:

$$\tilde{H} \approx H_0 + \frac{1}{2}[S, V] \quad (14)$$

with

$$[S, V] = \sum_{k,n} \left\{ \left(\frac{1}{E_k - E_l} + \frac{1}{E_n - E_l} \right) V_{kl} V_{ln} \right\} |\phi_k^0\rangle \langle \phi_n^0|$$

The unitary transformation by S thus results in a second-order perturbational expression, which describes the effect of the transfer terms in the space of H_0 eigenfunctions. When working out this expression explicitly we have approximated H_0^{AB} by the simplified isotropic repulsion expression in Eq. (9). We further assume Eq. (5) to hold.

One then obtains for the transfer term in $\tilde{H}$:

$$\begin{aligned}
 \frac{1}{2}[S, V] = & \left(-\frac{4t_a^2}{3(U_{\parallel} - U' - J + \frac{2}{3}\Delta)} - \frac{2t_a^2}{3(U_{\parallel} - U' + 2J + \frac{4}{3}\Delta)} \right) \times \sum_{\sigma} (n_{a\sigma}^A n_{a-\sigma}^B - a_{a\sigma}^{\dagger} b_{a-\sigma}^{\dagger} b_{a\sigma} a_{a-\sigma}) \\
 & - \left(\frac{t_e^2}{3(U_{\parallel} - U' - J - \frac{4}{3}\Delta)} + \frac{t_e^2}{U_{\parallel} - U' - J} + \frac{2t_e^2}{3(U_{\parallel} - U' + 2J - \frac{2}{3}\Delta)} \right) \times \sum_{i=\theta, \epsilon} \sum_{\sigma} (n_{i\sigma}^A n_{i-\sigma}^B - a_{i\sigma}^{\dagger} b_{i-\sigma}^{\dagger} b_{i\sigma} a_{i-\sigma}) \\
 & - \left(\frac{t_e^2}{3(U_{\parallel} - U' - J - \frac{4}{3}\Delta)} - \frac{t_e^2}{U_{\parallel} - U' - J} + \frac{2t_e^2}{3(U_{\parallel} - U' + 2J - \frac{2}{3}\Delta)} \right) \times \sum_{\sigma} (a_{\theta\sigma}^{\dagger} b_{\theta-\sigma}^{\dagger} b_{\epsilon-\sigma} a_{\epsilon\sigma} - a_{\theta\sigma}^{\dagger} b_{\theta-\sigma}^{\dagger} b_{\epsilon\sigma} a_{\epsilon-\sigma}) \\
 & + a_{\epsilon\sigma}^{\dagger} b_{\epsilon-\sigma}^{\dagger} b_{\theta-\sigma} a_{\theta\sigma} - a_{\epsilon\sigma}^{\dagger} b_{\epsilon-\sigma}^{\dagger} b_{\theta\sigma} a_{\theta-\sigma} + \left(\frac{t_a t_e}{3(U_{\parallel} - U' - J + \frac{2}{3}\Delta)} + \frac{t_a t_e}{3(U_{\parallel} - U' - J - \frac{4}{3}\Delta)} \right. \\
 & \left. - \frac{t_a t_e}{3(U_{\parallel} - U' + 2J + \frac{4}{3}\Delta)} - \frac{t_a t_e}{3(U_{\parallel} - U' + 2J - \frac{2}{3}\Delta)} \right) \times \sum_{i=\theta, \epsilon} \sum_{\sigma} (a_{i\sigma}^{\dagger} b_{i-\sigma}^{\dagger} b_{i-\sigma} a_{i\sigma} - a_{i\sigma}^{\dagger} b_{i-\sigma}^{\dagger} b_{i\sigma} a_{i-\sigma}) \\
 & + a_{i\sigma}^{\dagger} b_{i-\sigma}^{\dagger} b_{a-\sigma} a_{a\sigma} - a_{i\sigma}^{\dagger} b_{i-\sigma}^{\dagger} b_{a\sigma} a_{a-\sigma} + \sum_{i=\theta, \epsilon} \sum_{\sigma} \left[-\frac{t_a^2 + t_e^2}{U_{\parallel} - U' - 3J} (n_{i\sigma}^A n_{i\sigma}^B + n_{i\sigma}^A n_{a\sigma}^B) + \frac{2t_a t_e}{U_{\parallel} - U' - 3J} \right. \\
 & \times (a_{a\sigma}^{\dagger} b_{i\sigma}^{\dagger} b_{a-\sigma} a_{i\sigma} + a_{i\sigma}^{\dagger} b_{a\sigma}^{\dagger} b_{i\sigma} a_{a\sigma}) - \frac{1}{2} \left(\frac{t_a^2 + t_e^2}{U_{\parallel} - U' - 3J} + \frac{t_a^2 + t_e^2}{U_{\parallel} - U' - J} \right) (n_{a\sigma}^A n_{i-\sigma}^B + n_{i\sigma}^A n_{a-\sigma}^B) \\
 & + \left(\frac{t_a t_e}{U_{\parallel} - U' - 3J} + \frac{t_a t_e}{U_{\parallel} - U' - J} \right) (a_{a\sigma}^{\dagger} b_{i-\sigma}^{\dagger} b_{a\sigma} a_{i-\sigma} + a_{i\sigma}^{\dagger} b_{a-\sigma}^{\dagger} b_{i\sigma} a_{a-\sigma}) - \frac{1}{2} \left(\frac{t_a^2 + t_e^2}{U_{\parallel} - U' - 3J} - \frac{t_a^2 + t_e^2}{U_{\parallel} - U' - J} \right) \\
 & \times (a_{a\sigma}^{\dagger} b_{i-\sigma}^{\dagger} b_{i\sigma} a_{a-\sigma} + a_{i\sigma}^{\dagger} b_{a-\sigma}^{\dagger} b_{a\sigma} a_{i-\sigma}) + \left(\frac{t_a t_e}{U_{\parallel} - U' - 3J} - \frac{t_a t_e}{U_{\parallel} - U' - J} \right) (a_{a\sigma}^{\dagger} b_{i-\sigma}^{\dagger} b_{a-\sigma} a_{i\sigma} + a_{i\sigma}^{\dagger} b_{a-\sigma}^{\dagger} b_{i-\sigma} a_{a\sigma}) \left. \right] \\
 & + \sum_{\sigma} \left[-\frac{2t_e^2}{U_{\parallel} - U' - 3J} (n_{\theta\sigma}^A n_{\epsilon\sigma}^B + n_{\epsilon\sigma}^A n_{\theta\sigma}^B) + \frac{2t_e^2}{U_{\parallel} - U' - 3J} (a_{\theta\sigma}^{\dagger} b_{\epsilon\sigma}^{\dagger} b_{\theta\sigma} a_{\epsilon\sigma} + a_{\epsilon\sigma}^{\dagger} b_{\theta\sigma}^{\dagger} b_{\epsilon\sigma} a_{\theta\sigma}) \right. \\
 & - \left(\frac{t_e^2}{U_{\parallel} - U' - 3J} + \frac{t_e^2}{U_{\parallel} - U' - J} \right) (n_{\theta\sigma}^A n_{\epsilon-\sigma}^B + n_{\epsilon\sigma}^A n_{\theta-\sigma}^B - a_{\theta\sigma}^{\dagger} b_{\epsilon-\sigma}^{\dagger} b_{\theta\sigma} a_{\epsilon-\sigma} - a_{\epsilon-\sigma}^{\dagger} b_{\theta\sigma}^{\dagger} b_{\epsilon-\sigma} a_{\theta\sigma}) \\
 & \left. - \left(\frac{t_e^2}{U_{\parallel} - U' - 3J} - \frac{t_e^2}{U_{\parallel} - U' - J} \right) (a_{\theta\sigma}^{\dagger} b_{\epsilon-\sigma}^{\dagger} b_{\epsilon\sigma} a_{\theta-\sigma} + a_{\epsilon\sigma}^{\dagger} b_{\theta-\sigma}^{\dagger} b_{\theta\sigma} a_{\epsilon-\sigma} - a_{\theta\sigma}^{\dagger} b_{\epsilon-\sigma}^{\dagger} b_{\theta-\sigma} a_{\epsilon\sigma} - a_{\epsilon\sigma}^{\dagger} b_{\theta-\sigma}^{\dagger} b_{\epsilon-\sigma} a_{\theta\sigma}) \right] \quad (15)
 \end{aligned}$$

2.3.2. Energies

Armed with the effective Hamiltonian we can now express the energies of the Heisenberg states in Table 1 as a function of the crystal field, hopping and bielectronic interactions. The results are listed in Table 3. $\tilde{H}$ is found to connect some equisymmetric states by off-diagonal matrix elements. These are also given in the table for completeness.

The results in Table 3 will form the basis for the subsequent analysis of ab initio work and rival model descriptions.

3. Ab initio calculations

In the ab initio calculations a complete active space (CAS) SCF wavefunction constitutes the zeroth-order wavefunction in a perturbation treatment of the electron correlation. The CASSCF wavefunction is constructed by distributing two electrons in

Table 3

Parametric energy expressions for the $(t_{2g})^1-(t_{2g})^1$ configuration

$(a \times a)$	${}^3A_2''$	$U_{aaaa} - B_{aaaa}$
	${}^1A_1'$	$U_{aaaa} + B_{aaaa} - \frac{8t_a^2}{3(U_1 - U' - J + \frac{2}{3}\Delta)} - \frac{4t_a^2}{3(U_1 - U' + 2J + \frac{4}{3}\Delta)}$
$(a \times e)$	${}^3E'$	$\Delta + U_{aebg} - U_{aebg} - B_{aebg} + B_{aebg} - \frac{t_a^2 + t_e^2 + 2t_a t_e}{U_1 - U' - 3J}$
	${}^1E'$	$\Delta + U_{aebg} + U_{aebg} + B_{aebg} + B_{aebg} - \frac{t_a^2 + t_e^2 + 2t_a t_e}{U_1 - U' - J}$
	${}^3E''$	$\Delta + U_{aebg} + U_{aebg} - B_{aebg} - B_{aebg} - \frac{t_a^2 + t_e^2 - 2t_a t_e}{U_1 - U' - 3J}$
	${}^1E''$	$\Delta + U_{aebg} - U_{aebg} + B_{aebg} - B_{aebg} - \frac{t_a^2 + t_e^2 - 2t_a t_e}{U_1 - U' - J}$
$(e \times e)$	${}^3A_2''$	$2\Delta + U_{eeeg} + U_{eeeg} - B_{eeeg} - B_{eeeg}$
	${}^1A_1'$	$2\Delta + U_{eeeg} + U_{eeeg} + B_{eeeg} + B_{eeeg} - \frac{4t_e^2}{3(U_1 - U' - J - \frac{4}{3}\Delta)} - \frac{8t_e^2}{3(U_1 - U' + 2J - \frac{2}{3}\Delta)}$
	${}^3A_2'$	$2\Delta + U_{eeeg} - 3U_{eeeg} - 3B_{eeeg} + B_{eeeg} - \frac{4t_e^2}{U_1 - U' - 3J}$
	${}^1A_1''$	$2\Delta + U_{eeeg} - 3U_{eeeg} + 3B_{eeeg} - B_{eeeg}$
	${}^3E''$	$2\Delta + U_{eeeg} - U_{eeeg} + B_{eeeg} - B_{eeeg}$
	${}^1E'$	$2\Delta + U_{eeeg} - U_{eeeg} - B_{eeeg} + B_{eeeg} - \frac{4t_e^2}{U_1 - U' - J}$
	${}^3A_2''$	$\sqrt{2}U_{aebg} - \sqrt{2}B_{aebg}$
$(a \times a) - (e \times e)$	${}^1A_1'$	$\sqrt{2}U_{aebg} + \sqrt{2}B_{aebg} + 2\sqrt{2}\left(\frac{t_a t_e}{3(U_1 - U' - J - \frac{2}{3}\Delta)} + \frac{t_a t_e}{3(U_1 - U' - J - \frac{4}{3}\Delta)} - \frac{t_a t_e}{3(U_1 - U' + 2J + \frac{4}{3}\Delta)} - \frac{t_a t_e}{3(U_1 - U' + 2J - \frac{2}{3}\Delta)}\right)$

the titanium 3d derived active orbitals. The remaining dynamical electron correlation energy is obtained from second-order perturbation theory (CASPT2) [12,13]. Two sets of CASPT2 calculations were performed. In the first set, denoted as CASPT2(v) only the valence electrons, originating from Ti 3d and Cl 3s, 3p were correlated. However, in a CASSCF/CASPT2 study [14] of the lowest excited states in the transition-metal series $Ti^{2+}-Ni^{2+}$ and $V^{3+}-Cu^{3+}$ it was shown that correlation of the metal 3s, 3p electrons thoroughly affects the energy difference between different terms belonging to the d^n configuration. Therefore we decided to include also the Ti 3s, 3p electrons in a second set of calculations, denoted as CASPT2(c).

All states originating from the octahedral ${}^2T_{2g}$ state were included in the calculations. An active space of six molecular orbitals, consisting of the symmetric and antisymmetric combination of the octahedral t_{2g} orbitals, was used in these calculations. The results are shown in Table 4. In addition, a number of ligand field excited states, corresponding to the octahedral 2E_g state, were also considered. In order to do so, the active space was enlarged to 10 orbitals, including now all Ti 3d type orbitals. In a recent investigation of the possibilities of the CASSCF/CASPT2 method in transition-metal chemistry it was shown [15] that an active space consisting of only the metal 3d orbitals includes all important non-

dynamical correlation effects in ionic-type transition-metal compounds like the $Ti_2Cl_9^{3-}$ molecule considered here. For the electric dipole allowed ligand field transitions, oscillator strengths were also calculated. They were obtained using the CASSCF state interaction (CASSI) method [16] for the calculation of the transition dipole moments, in combination with CASPT2 results for the excitation energies appearing in the expression of the oscillator strengths. The results are summarized in Table 5. Of the $e(t_{2g}) \times e(e_g)$ excited configuration only those states are included that can be reached by dipole allowed transitions from ${}^1A_1'$ or ${}^1E''$ ground states.

All calculations were performed with generally contracted basis sets of the atomic natural orbital (ANO) type [17]. The primitive sets are (17s12p9d4f) for Ti and (13s10p4d) for Cl. Three different contraction schemes were used. In basis A the contractions [6s4p3d1f] for Ti and [4s3p] on Cl were applied. Since the ANO contraction scheme used is not designed to treat 3s, 3p correlation on Ti accurately, the CASPT2(c) calculations were repeated with an enlarged set on Ti (in combination with [4s3p] on Cl), obtained by uncontracting three s, three p and two d primitives in the core-valence region. This basis set is denoted as B. Finally, in basis C the [6s4p3d1f] contracted set on Ti was used in combination with a larger [4s3p1d] set on Cl.

Table 4

Calculated energy spectrum ^a of Ti₂Cl₉³⁻

	CASSCF			CASPT2(v)		CASPT2(c)		
	A	B	C	A	C	A	B	C
¹ A ₁ '	0	0	0	0	0	0	0	0
³ A ₂ "	269	279	297	657	735	746	780	827
¹ E"	1673	1657	1566	718	639	-799	-839	-903
³ E"	1682	1682	1591	823	673	-674	-804	-868
³ E'	1739	1722	1621	850	744	-652	-704	-787
¹ E'	1773	1772	1672	962	793	-523	-661	-739
³ A ₂ '	2408	2411	2210	1690	1501	405	268	154
¹ A ₁ "	2422	2424	2219	1711	1510	424	279	160
³ E"	2469	2471	2265	1745	1531	456	310	179
¹ E'	2472	2475	2272	1741	1531	450	412	183
³ A ₂ "	2519	2521	2313	1775	1546	480	333	189
¹ A ₁ '	2530	2533	2328	1782	1561	487	346	203

^a Three different basis sets were used: A: 6s4p3d1f on Ti, 4s3p on Cl. B: 8s7p5d1f on Ti, 4s3p on Cl. C: 6s4p3d1f on Ti, 4s3p1d on Cl.

Table 5

Calculated excited state spectrum performed with basis A

		CASSCF		CASPT2(v)		CASPT2(c)	
		ground state $^1A_1'$		ground state $^1A_1'$		ground state $^1E''$	
		ΔE	Osc. str.	ΔE	Osc. str.	ΔE	Osc. str.
		(cm^{-1})	(10^4)	(cm^{-1})	(10^4)	(cm^{-1})	(10^4)
			$\perp$ $\parallel$		$\perp$ $\parallel$		$\perp$ $\parallel$
$a(t_{2g}) \times e(e_g)$	$^3E''$	13329		13104		12743	
	$^1E''$	13334		13120		12763	0.32
	$^3E'$	13387		13267		12925	
	$^1E'$	13460	2.13	13327	2.12	12980	1.29
$e(t_{2g}) \times e(e_g)$	$^1A_2''$	14385	0.00	13677	0.00	12881	0.28
	$^1E''$	14453		13725		12915	0.66
	$^1E'$	14470	0.04	13770	0.04	12992	0.00
	$^1A_1''$	14584		13900		13089	0.27

Calculations were performed on the Ti₂Cl₉³⁻ cluster embedded in a Madelung potential representing the Cs₃Ti₂Cl₉ crystal [18]. Only the Ti₂Cl₉³⁻ cluster was directly included in all ab initio calculations, using the following structural parameters [7] (with Cl₁ and Cl₂ standing for bridging and terminal ligands, respectively): Ti–Cl₁ = 2.503 Å, Ti–Cl₂ = 2.328 Å, Ti–Ti = 3.191 Å, Cl₁TiCl₁ = 83.7°, Cl₂TiCl₂ = 95.2°. The crystal environment was simulated by a number of point charges, obtained by the following method. First, point charges are assigned to each atomic location in the crystal. The values of the point charges are assumed to be those corresponding to the formal oxidation state. The field of these charges in the region of the Ti₂Cl₉³⁻ cluster is calculated by an infinite Ewald summation in a preselected set of grid points. Finally, this potential is represented by a finite number of point charges at crystallographic positions. The charges are determined by a least-squares fit. Thus the following 80 point charges were used: 14 charges representing Cs, with a value of +0.40 (3), +1.00 (3), +0.98 (8), 18

charges representing Ti, with a value of +2.51 (12) and 1.96 (6), and 48 charges representing Cl, with a value of -0.98 (6), -0.76 (6), -0.90 (12), -0.95 (12) and -0.94 (12) respectively, the charges depending on the crystallographic position.

All calculations were performed on IBM RS/6000 workstations using the MOLCAS-3 quantum chemistry software [19].

4. Information from experiment

Before starting a discussion of the theoretical results, we present a brief overview of what is known from experiment. Although the chloride compound, and to a lesser extent also the bromide compound, has been the subject of several spectroscopic and magnetic studies, the actual knowledge of the system remains poor and indecisive.

The most detailed study is due to Briat et al. [7] and was performed on crystalline samples of $\text{Cs}_3\text{Ti}_2\text{Cl}_9$. The spectral measurements reveal the presence of broad featureless absorption bands in the IR region between 800 and 3000 cm^{-1} which are apparently due to electronic excitations within the $t_{2g}^3-e_g^2$ system. In contrast Leuenberger and Güdel [6] mention weak and broad signals between 450 and 900 cm^{-1} , on the basis of IR reflectivity measurements. There are no attempts to propose detailed assignments in this frequency region. In the visible spectrum one can clearly delineate the first ligand field band system, at about 14 000 cm^{-1} . Polarized spectra show two components, one at 12 900 cm^{-1} in parallel polarization (π), and one at 14 200 cm^{-1} in perpendicular polarization (σ). Both components are of comparable intensity.

Magnetic susceptibility data indicate that the states populated below 100 K carry no or very small magnetic moments. Detailed measurements of the magnetic anisotropy at low temperatures showed strong interference from magnetic impurities, probably due to Fe^{3+} contamination. For this reason the interpretation of the magnetic studies remains highly uncertain. Nonetheless on the basis of the observed diamagnetism several authors have proposed a $^1A_1'$ ($a \times a$) ground state assignment, with a large $^1A_1' \rightarrow ^3A_2''$ gap in the order of 400–600 cm^{-1} [3,6,7]. The problem with this assignment is that it cannot explain why the first ligand field band carries intensity in both polarizations. Indeed one expects the parallel component to be forbidden since the corresponding $^1A_1' \rightarrow ^1A_2''$ excitation would involve a two-orbital jump, from $a(t_{2g}) \times a(t_{2g})$ to $e(t_{2g}) \times e(e_g)$ (see Table 5). Hence the nature of the ground state cannot really be decided experimentally.

A comparison of the experimental data with the ab initio results in Tables 4 and 5 leads to the following conclusions: (i) the CASPT2 calculations reproduce a large antiferromagnetic coupling in the ($a \times a$) configuration with a gap of 650–800 cm^{-1} ; (ii) the first ligand band is calculated at about 13 000 cm^{-1} , which is in good agreement with experiment; (iii) the ab initio calculations fail to resolve the ambiguity over the ground state assignment; at the CASSCF and CASPT2(v) levels a $^1A_1'$ ground state is obtained, but there is a change to a $^1E''$ ground state at the CASPT2(c) level; (iv) the calculated oscillator strengths confirm that excitation from $^1A_1'$ indeed only carries dipole strength in perpendicular polarization; in contrast the alternative $^1E''$ ground state does not give rise to a pronounced linear dichroism.

5. Analysis of the ab initio results

The parameters which describe the interaction between the metal ions can be obtained by fitting the model expressions in Table 3 to the CASPT2 energies in Table 4. As will be shown in the present section such a model analysis of a computed spectrum provides an interesting insight into the nature of the exchange interaction in $\text{Ti}_2\text{Cl}_9^{3-}$ clusters.

5.1. Configurational energies

The ab initio results in Table 4 can conveniently be grouped together in multiplets belonging to the trigonal configurations ($a \times a$), ($a \times e$), ($e \times e$). As we have already indicated, the relative position of these configurations strongly depends on the computational level. At the CASSCF level the configurations are well separated with average energies of 223 ($a \times a$), 1609 ($a \times e$) and 2266 ($e \times e$) cm^{-1} , respectively (basis C). However upon introducing more correlation, there is a dramatic change of relative energies, leading to a configurational cross-over of ground states from $^1A_1'$ ($a \times a$) to $^1E''$ ($a \times e$). These results immediately suggest that the correlation energy contents of these configurations are quite different, so that their relative energies will be very susceptible to correlation energy corrections.

From the model point of view the energy differences between the configurations can easily be analysed by neglecting the J and Δ contributions to the denominators in the transfer terms. One then obtains the following configurational averages:

$$\begin{aligned} E(a \times a) &= -\frac{2t_a^2}{U_1 - U'} + U_{aaaa} \\ E(a \times e) &= \Delta - \frac{t_a^2 + t_e^2}{U_1 - U'} + U_{a0a0} \\ E(e \times e) &= 2\Delta - \frac{2t_e^2}{U_1 - U'} + U_{0000} - U_{00ee} \end{aligned} \quad (16)$$

Note that spin degeneracies were not taken into account while calculating these averages. As far as the crystal field and exchange interactions are concerned, the results in Eq. (16) may be described by an effective $a \rightarrow e$ promotion energy, equal to $\Delta - (t_e^2 - t_a^2)/(U_1 - U')$. Hence on the configurational level the transfer interaction corresponds to an effective one-electron operator that contributes to the trigonal splitting of the t_{2g} shells. The CASSCF results seem to suggest that this trigonal splitting is positive and rather large, in the order of 1000 cm^{-1} . Obviously this conclusion is in sharp contrast to the CASPT2(c) results. In fact the ($a \times e$) ground state of the CASPT2(c) calculation cannot be reproduced by the crystal field and transfer terms, whatever their signs or magnitudes, since these terms will always place the ($a \times e$) states halfway between ($a \times a$) and ($e \times e$).

Independent estimates of the crystal field and transfer term contributions suggest that they do not introduce a large trigonal splitting. First, from the subsequent analysis of the multiplet separations we could deduce that the exchange interaction $-(t_e^2 - t_a^2)/(U_1 - U')$ in the $a \rightarrow e$ promotion energy is approximately 200 cm^{-1} (vide infra Eqs. (19) and (21)). Second, the crystal field splitting can be estimated from a simple AOM treatment of the first coordination sphere. According to the X-ray structure each Ti^{3+} ion is surrounded by a trigonally distorted octahedron elongated at the side of the bridging ligands (with an azimuthal angle $\theta = 50.4^\circ$) and

compressed at the side of the terminal ligands (with $\theta = 58.5^\circ$) [7]. Clearly these opposite distortions will yield an exceedingly small trigonal splitting: using $e_{\sigma}^{\text{Cl}} = 6750 \text{ cm}^{-1}$, and $e_{\pi}^{\text{Cl}} = 1/4 e_{\sigma}^{\text{Cl}}$, one obtains by standard AOM methods $\Delta_{\text{t}_{2g}} = -300 \text{ cm}^{-1}$. Crystal field and transfer term contributions thus tend to cancel.

In principle the model (Eq. (16)) offers an alternative way to cope with the configurational ordering, by fitting the energies to the U parameters. At large internuclear distances these parameters do not discriminate between configurations since they converge to the isotropic Coulomb repulsion between two separated electrons (cf. Eq. (9)), except for the $U_{\theta\theta\theta\theta}$ parameter which becomes vanishingly small. However at shorter distances it can be expected that there will be appreciable differences between U_{aaaa} , $U_{a\theta a\theta}$ and $U_{\theta\theta\theta\theta}$ due to the anisotropy of the charge distribution in the a and θ orbitals. To evaluate this hypothesis we have performed d-only calculations at the observed Ti–Ti distance of 3.2 Å, using optimized d-functions for atomic Ti. The calculated values for the U integrals are:

$$\begin{aligned} U_{aaaa} &= 38737 \text{ cm}^{-1} \\ U_{a\theta a\theta} &= 36863 \text{ cm}^{-1} \\ U_{\theta\theta\theta\theta} &= 35372 \text{ cm}^{-1} \\ U_{\theta\theta\theta\theta} &= 571 \text{ cm}^{-1} \end{aligned} \quad (17)$$

These results probably overestimate the actual interaction, since they were calculated for zerovalent Ti in the absence of molecular screening effects. Nor were corrections for orbital overlap taken into account. Nonetheless they clearly show that the intercentre Coulomb repulsion has a differential destabilizing effect on the configurations, in the order $(a \times a) > (a \times e) > (e \times e)$. The $(a \times e)$ configuration thereby remains intermediate between the other two, which implies that the U interaction will not be able to favour the $(a \times e)$ ground state. On these grounds we consider it likely that the CASPT2(c) calculation produces an anomalous ground state.

Fortunately, as we will show in the subsequent sections, the intraconfigurational splitting are far less dependent on the computational method. This is undoubtedly due to constant correlation errors within a given configuration.

5.2. $(a \times a)$ multiplets

The $(a \times a)$ configuration offers a typical example of two interacting spins in equivalent non-degenerate orbitals. The gap between the resulting triplet and singlet state is given by:

$${}^3A_2'' - {}^1A_1' = \frac{4t_a^2}{3} \left(\frac{2}{U_1 - J + \frac{2}{3}\Delta - U'} + \frac{1}{U_1 + 2J + \frac{4}{3}\Delta - U'} \right) - 2B_{aaaa} \quad (18)$$

Fig. 2. Contour plots of the symmetric (A) and antisymmetric (B) molecular orbital combinations of the a orbitals.

This result essentially corresponds to the Anderson expression [20], where the first term describes the kinetic part of the exchange while B_{aaaa} is the potential part. The ab initio calculations yield a positive gap, the size of which strongly depends on the extent of correlation — from 297 cm^{-1} for CASSCF to not less than 827 cm^{-1} for CASPT2(c). The large gap points to strong antiferromagnetic coupling between the centres in the ${}^1A_1' (a \times a)$ state. This can be attributed to direct overlap between d_{xz}^A and d_{xz}^B , as is readily demonstrated by comparing the contour plots of symmetric and antisymmetric combinations of the orbitals (see Fig. 2).

The large overlap and the considerable spin pairing it induces probably also explain why correlation corrections have such an important effect on the ab initio results. For the strong coupling case Eq. (18) may be simplified to yield the following approximate expression for the transfer term parameters of the $(a \times a)$ configuration:

$$\frac{4t_a^2}{(U_1 - U')} \approx 827 \text{ cm}^{-1} \quad (19)$$

5.3. $(a \times e)$ multiplets

The $a \times e$ configuration contains four states. At all levels of calculation the two lowest states are ${}^1E'$ and ${}^3E''$. Both are antisymmetric with respect to the horizontal plane of symmetry. In contrast the upper two levels are ${}^1E'$ and ${}^3E'$, i.e. states that are symmetric with respect to σ_h . The separation between the average single and double prime states is given by:

$$\begin{aligned} \frac{1}{2}({}^1E' + {}^3E') - \frac{1}{2}({}^1E'' + {}^3E'') = \\ -2t_a t_e \left(\frac{1}{U_1 - 3J - U'} + \frac{1}{U_1 - J - U'} \right) + 2B_{a\theta a\theta} \end{aligned} \quad (20)$$

This expression again resembles the Anderson result of Eq. (18). For the highest level of calculation the separation amounts to 123 cm^{-1} . This is a fairly substantial exchange

Fig. 3. Contour plot of the symmetric (A) and antisymmetric (B) molecular orbital combinations of the e_g orbitals. Note the π antibonding Ti–Cl interaction in A.

splitting which points to a predominance of the transfer term. Neglecting J and $B_{aa\theta\theta}$, Eq. (20) may be simplified to:

$$-\frac{4t_a t_e}{U_1 - U'} \approx 123 \text{ cm}^{-1} \quad (21)$$

A comparison of the $(a \times a)$ and $(a \times e)$ multiplets thus allows estimation of the ratio of transfer integrals as $t_a/t_e \approx -6.5$. Hence not only is the transfer integral between e orbitals on the two centres much smaller than the transfer integral between a orbitals, but moreover — and quite remarkably so — t_a and t_e have different signs! Clearly t_a must be negative, as it represents a bonding interaction between two orbitals that overlap directly through space (see Fig. 2). Hence t_e must be positive, which implies that the e orbitals on the two centres interact with each other through bonds involving the bridging ligands. This is indeed borne out by orbital drawings of the symmetric and antisymmetric combinations of the e orbitals, as shown in Fig. 3. More specifically the symmetric combination is found to contain a p orbital of the bridging chloride ligand forming Ti–Cl π antibonds. This feature is typical for the superexchange pathway leading to a positive t_e integral [21–23].

The remaining fine structure of the $(a \times e)$ manifold can conveniently be analysed by expressing the difference between the average singlet and triplet state energies by means of model parameters:

$$\frac{1}{2}({}^1E' + {}^1E'') - \frac{1}{2}({}^3E' + {}^3E'') = 2B_{aa\theta\theta} + (t_a^2 + t_e^2) \left[\frac{1}{(U_1 - 3J - U')} - \frac{1}{(U_1 - J - U')} \right] \quad (22)$$

The $B_{aa\theta\theta}$ parameter and the J integral in the denominators of the transfer terms are seen to act in the same way: they both tend to stabilize the high-spin states. Their effect is rather small though since the average singlet is only 6.5 cm^{-1} above

Scheme 2.

the average triplet. As it is impossible to deconvolute both contributions we will absorb the transfer terms into an effective $B_{aa\theta\theta}$ parameter. The resolution of the single and double prime averages by the remaining $U_{aa\theta\theta}$ and $B_{aa\theta\theta}$ parameters is represented in Scheme 2.

From the energies in the table one immediately obtains:

$$\begin{aligned} 2U_{aa\theta\theta} &= 41.5 \text{ cm}^{-1} \\ 2B_{aa\theta\theta} &= 6.5 \text{ cm}^{-1} \end{aligned} \quad (23)$$

These results certainly represent acceptable values for overlap type Coulomb and exchange integrals between the two centres.

5.4. $(e \times e)$ multiplets

To evaluate the exchange interaction in the $(e \times e)$ configuration we start by comparing the symmetric and antisymmetric states:

$$\begin{aligned} \frac{1}{4}({}^1A_1' + {}^3A_2' + 2{}^1E') - \frac{1}{4}({}^1A_1'' + {}^3A_2'' + 2{}^3E'') = \\ 2B_{\theta\theta\theta\theta} - 2B_{\theta\theta ee} - \frac{4t_e^2}{U_1 - U'} \end{aligned} \quad (24)$$

where again we have neglected the J and Δ parameters in the denominators. Note that the ${}^1E'$ and ${}^3E'$ states coincide with the centres of the respective single prime and double prime manifolds. At the CASPT2(c) level the difference between both is extremely small, only 4 cm^{-1} . Apparently the exchange coupling between the e orbitals is mainly determined by the potential exchange parameter $B_{\theta\theta\theta\theta}$, since this is the only positive contribution in Eq. (24). If we extrapolate the results in Eqs. (18) and (20), the kinetic part of the exchange amounts to: $4t_e^2/(U_1 - U') = 18 \text{ cm}^{-1}$, which is indeed much smaller than the exchange between a orbitals. By absorbing this part into an effective $B_{\theta\theta\theta\theta}$ parameter we end up with three formal repulsion parameters to fit five energy differences. The splitting can be represented as in Scheme 3.

Here we did not take into account the off-diagonal matrix elements given in Table 3, that could affect the position of ${}^1A_1'$ and ${}^3A_2''$. On the basis of estimates for $U_{aa\theta\theta}$ and $B_{aa\theta\theta}$ parameters involved (see Eq. (23)) these elements are

indeed likely to be rather small. In the proposed splitting scheme the U_{00cc} interaction puts the ${}^1E'$ and ${}^3E''$ states in the middle of a mirror relation between ${}^1A_1'$, ${}^3A_2''$ and ${}^1A_1''$, ${}^3A_2'$. This is indeed almost exactly what is found for the CASSCF result. It is less well obeyed at the correlated level with intervals 24 and 15 cm^{-1} , respectively. However the further resolution of the three pair states can exactly be fitted by only two B parameters. The best model parameters for the CASPT2(c) calculations thus read:

$$\begin{aligned} 2U_{00cc} &= 20\text{ cm}^{-1} \\ 2B_{0000} &= 9\text{ cm}^{-1} \\ 2B_{00cc} &= 5\text{ cm}^{-1} \end{aligned} \quad (25)$$

A simple first-order Hamiltonian is thus entirely capable of rationalizing the complex fine structure of the trigonal t_{2g} – t_{2g} problem.

6. Rival models into perspective

As pointed out by Kahn [2], $\text{Ti}_2\text{Cl}_6^{3-}$ is a relatively simple example of a highly-symmetric binuclear complex with only one electron on each centre, and yet both experimental evidence and theoretical interpretation turn out to be ambiguous and controversial. Although the present ab initio calculations are not able to remove the uncertainties related to the configurational energies, they do yield stable and definite results regarding the multiplet structure, which will form the basis of our analysis of rival models.

6.1. The generalized Heisenberg Hamiltonian

The spin Hamiltonian formalism for the exchange between two electrons on different centres was introduced by Heisenberg [24], and is written as:

$$H = J\hat{S}_A \cdot \hat{S}_B \quad (26)$$

where $\hat{S}_A$ and $\hat{S}_B$ are local spin operators for electrons in orbitals on centres A and B, respectively. This Hamiltonian separates the dimer states as singlet and triplet, which, in the case of non-degenerate orbitals, correspond to eigenstates of

the exchange interaction. In the case of degenerate shells a straightforward generalization of the Heisenberg Hamiltonian was proposed by simply introducing exchange interactions between all orbital pairs [25,26]:

$$H = \sum_{r,s} J_{rs} \hat{S}_{A_r} \cdot \hat{S}_{B_s} \quad (27)$$

where r and s run over the orbitals on centres A and B, respectively. An early application of this model to the magnetism in $\text{Ti}_2\text{Cl}_6^{3-}$ is due to Barraclough and Gregson [3]. Later on Kahn [27] argued that the Hamiltonian was not invariant with respect to a unitary transformation of the degenerate orbital basis. In spite of this serious criticism generalized Heisenberg models of this type continue to be used [28].

The energetic effect of the multi-orbital Heisenberg Hamiltonian is to separate the singlet and triplet states of all rs configurations. When comparing this results with the expressions in Table 3, it is clear that in general our model parameters do not have a similar energetic effect, except for the $(a \times a)$ configuration (see Eq. (18)). To analyse this result in more detail we first convert the Heisenberg Hamiltonian to its second quantized form. The components of the local spin operators can easily be expressed as follows [20]:

$$\begin{aligned} 2S_{A_r}^z &= n_{ra}^{\uparrow} - n_{ra}^{\downarrow} \\ 2S_{A_r}^x &= a_{ra}^{\dagger} a_{r\beta} + a_{r\beta}^{\dagger} a_{ra} \\ 2S_{A_r}^y &= -ia_{ra}^{\dagger} a_{r\beta} + ia_{r\beta}^{\dagger} a_{ra} \end{aligned} \quad (28)$$

and similarly for $\hat{S}_{B_s}$. Upon substitution in Eq. (27) one obtains:

$$H = \frac{1}{4} \sum_{r,s} J_{rs} \sum_{\sigma} (n_{ra}^{\uparrow} n_{s\sigma}^{\uparrow} - n_{ra}^{\downarrow} n_{s\sigma}^{\downarrow} + 2a_{ra}^{\dagger} a_{r-\sigma} b_{s\sigma}^{\dagger} - a_{ra}^{\dagger} a_{r-\sigma} b_{s\sigma}^{\dagger}) \quad (29)$$

Let the total number of electrons in orbital r on A and orbital s on B be counted by $n_r^{\uparrow}$ and $n_s^{\uparrow}$, respectively. Eq. (29) may then be written in either of the following forms:

$$H = \frac{1}{4} \sum_{r,s} J_{rs} (n_r^{\uparrow} n_s^{\uparrow} + 2 \sum_{\sigma} (n_{ra}^{\uparrow} n_{s\sigma}^{\uparrow} + a_{ra}^{\dagger} a_{r-\sigma} b_{s\sigma}^{\dagger} - a_{ra}^{\dagger} a_{r-\sigma} b_{s\sigma}^{\dagger})) \quad (30)$$

$$H = \frac{1}{4} \sum_{r,s} J_{rs} (n_r^{\uparrow} n_s^{\uparrow} - 2 \sum_{\sigma} (n_{ra}^{\uparrow} n_{s\sigma}^{\uparrow} - a_{ra}^{\dagger} a_{r-\sigma} b_{s\sigma}^{\dagger} - a_{ra}^{\dagger} a_{r-\sigma} b_{s\sigma}^{\dagger})) \quad (30')$$

In these expressions the first part is a constant for a given configuration, while the second part represents the true second quantized Heisenberg exchange operator. Inspection of the model Hamiltonian in Eqs. (8) and (15) immediately reveals that the Heisenberg operators are indeed included both in the potential exchange and in the kinetic exchange expressions. However there are only two cases where the operators show exact coincidence. One is the $(a \times a)$ configuration, which exemplified the trivial single orbital exchange (see Eq. (18)). The other is the B_{aa00} interaction in the

($a \times e$) configuration. The operator part of the latter interaction is given by:

$$H(B_{aa\theta\theta}) = \sum_{\sigma} (n_{a\sigma}^A n_{\theta\sigma}^B + a_{a\sigma}^{\dagger} a_{\theta-\sigma} b_{\theta-\sigma}^{\dagger} b_{a\sigma} + n_{\theta\sigma}^A n_{a\sigma}^B + a_{\theta\sigma}^{\dagger} a_{\theta-\sigma} b_{a-\sigma}^{\dagger} b_{\theta\sigma}) + \sum_{\sigma\sigma'} (a_{a\sigma}^{\dagger} a_{\theta\sigma'} b_{a\sigma'}^{\dagger} b_{\theta\sigma} + a_{\theta\sigma}^{\dagger} a_{a\sigma'} b_{\theta\sigma'}^{\dagger} b_{a\sigma}) \quad (31)$$

and similarly with θ replaced by ϵ . The first summation in this expression corresponds to the $J_{a\theta}$ and $J_{\theta a}$ Heisenberg exchange, while the second part connects ($a \times a$) and ($e \times e$) configurations. So within the ($a \times e$) configuration $B_{aa\theta\theta}$ indeed exactly parametrizes the singlet–triplet separation, as is borne out by the expressions in Table 3. It is clear though that this is only a weak interaction which is of marginal importance as compared to the effect of the transfer terms. In conclusion the generalized Heisenberg Hamiltonian completely fails to describe the relevant exchange operators in multi-orbital dimers.

6.2. The Anderson model

The fundamental reason why the Heisenberg Hamiltonian fails to quantize the important kinetic pathway to the exchange is of course because hopping not only exchanges spins but also orbitals of the two centres. The symmetry group of the $\text{Ti}_2\text{Cl}_9^{3-}$ cluster contains an element which precisely acts in this way, viz. the horizontal plane of symmetry. This can easily be demonstrated by rewriting the $[S, V]$ commutator (Eq. (15)) under the simplifying assumptions: $J = \Delta = 0$, $t = t_a = t_e$. One then obtains:

$$\frac{1}{2}[S, V] = \frac{-2t^2}{(U_1 - U')} [n^A n^B + \sum_{i,j} \sum_{\sigma\sigma'} a_{i\sigma}^{\dagger} b_{j\sigma'}^{\dagger} b_{i\sigma} a_{j\sigma'}] \quad (32)$$

where n^A and n^B count the total number of electrons on A and B. In the summations i and j run independent over a, θ and ϵ . The second part in Eq. (32) is seen to permute the spin orbitals between the two centres, and precisely corresponds to the action of $\hat{\sigma}_h$ on pair states. Eq. (32) may thus be written as:

$$\frac{1}{2}[S, V] = \frac{-2t^2}{(U_1 - U')} [1 + \hat{\sigma}_h] \quad (33)$$

This Hamiltonian will separate the $36 (t_{2g})^1 - (t_{2g})^1$ states of Table 1 into 21 double prime states at energy zero, and 15 single prime states at energy $-4t^2/(U_1 - U')$. Drillon and Georges [4] have shown that this result may be expressed in a spin Hamiltonian formalism, by including local orbital momentum operators $\hat{L}_A$ and $\hat{L}_B$. These act on the components of the t_{2g} shell in the same way as the angular momentum operator transforms the states of a spherical p-shell. When we confront this Anderson type spin Hamiltonian with our present results, it is clear that it completely ignores the important difference, in magnitude and in sign, between the t_e and

t_a hopping integrals. Hence by imposing pseudo-spherical symmetry, one has missed the principal characteristic of the exchange coupling in clusters of this type.

In a further development Drillon and Georges also considered a refinement of the exchange parameter, by discriminating exchange pathways involving singlet and triplet ionic states. This extension is deficient as well since it fails to recognize that the $(t_{2g})^2$ configuration contains two singlet repulsion states with widely differing energies.

6.3. The model by Leuenberger and Güdel

Leuenberger and Güdel [6] proposed a model that is much closer to reality than the approaches discussed so far. This model still neglected all contributions of U and B integrals, as well as the differential repulsion effects in the denominators, but it did take into account the correct trigonal symmetry of the hopping integrals and also included the ligand field splitting Δ and even spin–orbit coupling on the metal centres.

The influence of all these parameters was discussed by means of correlation diagrams, but few conclusions could be reached in the absence of ab initio results. The $^1A_1'$ ($a \times a$) ground state was adopted in order to explain the strong depression of the magnetic moment with decrease in temperature. This required a strong antiferromagnetic coupling between the d_{z^2} orbitals and hence $t_a^2 \gg t_e^2$, in agreement with our own conclusion. The relative sign of the integrals could not be determined though. Parenthetically we note that the authors also presented results from Extended Hückel calculations from which it can be inferred that t_a and t_e indeed have opposite signs.

In the perspective of our present results the treatment by Güdel and Leuenberger appears to be in qualitative agreement with the CASSCF calculations, at least in the lower energy part of the spectrum (see Table 4). It obviously fails to account for the multiplet splittings at higher energies, which were shown to be due to interelectronic repulsion effects.

Recently Weihe [29] used a similar approach to discuss the magnetic coupling in μ -oxo bridged dimeric complexes of D_{4h} symmetry. Explicit parameters were included to describe the term energies of the ionic states involved in the exchange paths. Under this latter assumption the model was found to offer a satisfactory rationalization of CASSCF ab initio calculations by Staemmler and co-workers [30]. Apparently in complexes such as $\text{L}^-\text{Ti}-\text{O}-\text{TiL}_5$, the two metal centres are too far apart for two-electron intercentre repulsion interactions to play any determining role.

7. Conclusions

In the present article we have attempted to advance the theoretical understanding of the complex electronic structure of $\text{Ti}_2\text{Cl}_9^{3-}$. To this aim we first constructed a model Hamiltonian which offers a description of the space of pair states. This Hamiltonian is essentially complete as far as the inter-

centre contributions are concerned, but its single-centre part could still be refined by including spin-orbit coupling. As it stands it allows the ab initio spectrum to be analysed and also provides a convenient framework to discuss existing model treatments.

The CASSCF method and its perturbational corrections are shown to produce a reliable description of the multiplet structures within a given configuration. The relative energies of the configurational averages remain uncertain due to differences in electronic correlation. It is further demonstrated that the exchange interactions are highly anisotropic, and that interelectronic repulsion effects are not negligible.

In the end we feel we have reached a point where we tend to agree with the authors of Ref. [6] that further progress in the understanding of exchange interactions in $A_3Ti_2Cl_9$ will have to come from experiment.

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References

- [1] D. Gatteschi, *Adv. Mater.*, **6** (1994) 635.
- [2] O. Kahn, *Molecular Magnetism*, VCH, New York, 1993.
- [3] C.G. Barraclough and A.K. Gregson, *J. Chem. Soc., Faraday Trans. II*, (1972) 177.
- [4] M. Drillon and R. Georges, *Phys. Rev. B*, **26** (1982) 3882.
- [5] O. Kahn, *Mol. Phys.*, **31** (1976) 957–965.
- [6] B. Leuenberger and H.U. Güdel, *Mol. Phys.*, **51** (1984) 1.
- [7] B. Briat, O. Kahn, I. Morgenstern-Badarau and J.C. Rivoal, *Inorg. Chem.*, **20** (1981) 4193.
- [8] J.S. Griffith, *The Theory of Transition-metal Ions*, Cambridge University Press, Cambridge, 1961.
- [9] B.R. Judd, *Second Quantization and Atomic Spectroscopy*, The Johns Hopkins Press, Baltimore, MD, 1967.
- [10] A. Ceulemans, *Top. Curr. Chem.*, **171** (1994) 27.
- [11] A.S. Davydov, *Quantum Mechanics*, Pergamon, Oxford, 1976.
- [12] K. Andersson, P.-Å. Malmqvist, B.O. Roos, A.J. Sadlej and K. Wolinski, *J. Phys. Chem.*, **94** (1990) 5483.
- [13] K. Andersson, P.-Å. Malmqvist and B.O. Roos, *J. Chem. Phys.*, **96** (1992) 1218.
- [14] K. Pierloot, E. Tsokos and B.O. Roos, *Chem. Phys. Lett.*, **214** (1993) 583.
- [15] B.O. Roos, K. Andersson, M.P. Fülscher, P.-Å. Malmqvist, L. Serrano-Andrés, K. Pierloot and M. Merchán, *Advances in Chemical Physics*, Vol. XCIII, Wiley, New York, 1996, p. 219.
- [16] P.-Å. Malmqvist and B.O. Roos, *Chem. Phys. Lett.*, **155** (1989) 189.
- [17] K. Pierloot, B. Dumez, P.-O. Widmark and B.O. Roos, *Theor. Chim. Acta*, **90** (1995) 87.
- [18] G.J. Wessel and D.J.W. Ijdo, *Acta Crystallogr.*, **10** (1957) 466.
- [19] K. Andersson, M.P. Fülscher, G. Karlström, R. Lindh, P.-Å. Malmqvist, J. Olsen, B.O. Roos, A.J. Sadlej, M.R.A. Blomberg, P.E.M. Siegbahn, V. Kellö, J. Noga, M. Urban and P.-O. Widmark, *MOLCAS Version 3*, Dept. of Theor. Chem., Chem. Center, Univ. of Lund, P.O.B. 124, S-22100 Lund, Sweden, 1994.
- [20] P.W. Anderson, *Solid State Phys.*, **14** (1963) 99.
- [21] M.A. Atanasov and H.-H. Schmidtke, *Chem. Phys.*, **124** (1988) 205.
- [22] J. Glerup, *Acta Chem. Scand.*, **26** (1972) 3775.
- [23] A. Bencini and D. Gatteschi, *Mol. Phys.*, **56** (1985) 97.
- [24] W. Heisenberg, *Z. Phys.*, **49** (1928) 619.
- [25] P.A.M. Dirac, *Proc. R. Soc. London, Ser. A*, **123** (1929) 714.
- [26] J.H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, Oxford, 1932.
- [27] O. Kahn, *Mol. Phys.*, **29** (1975) 1039.
- [28] T. Schönher, *J. Mol. Struct. (Theochem.)*, **161** (1992) 203.
- [29] H. Weihe, unpublished results.
- [30] K. Fink, W. Fink and V. Staemmler, *Inorg. Chem.*, **33** (1994) 6219.