

# Inversion of spin levels in exchange-coupled pairs under combined time reversal

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**Abstract.** The method for transforming antiferromagnetic exchange interaction into the ferromagnetic one has been proposed for binuclear coordination compounds, which contain dimers consisting of iron or rare earth ions with arbitrary spins and having identical electronic configurations. The method is based on the time-reversal symmetry violation at isomorphic substitution of one of dimer's ions by a "time-reversed" ion, when the spin projection operators of only one of dimer's ions are reversed. Restoration of broken symmetry accompanied by its transformation into combined time-reversal symmetry is caused by sign reversing of exchange interaction constant  $J$  at isomorphic substitution. Experimental data confirm the proposed way of inverting the sign of  $J$ . The method for controlled synthesis of binuclear coordination compounds using specific isomorphic substitutions with "time-reversed" ions allows extending the class of coordination compounds characterized by ferromagnetic exchange interaction.

**Keywords:** binuclear complex, dimer, exchange interaction, time-reversal symmetry, isomorphic substitution, inversion of spin levels.

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## 1. Introduction

In all coordination compounds that include clusters (in particular, dimers) consisting of paramagnetic ions, there is exchange interaction between ions. The main contribution into exchange interaction occurring in dimer magnetic clusters of binuclear coordination compounds is provided by the indirect exchange interaction through neighboring anions.

The exchange interaction constant values, determined from EPR data and magnetic susceptibility measurements for a large number of  $3d-3d$  dimers, show that antiferromagnetic exchange interaction occurs in dimers containing paramagnetic ions with the same electron configuration [1-28]. In this case, the absolute value of the constant  $J$  is equal to hundreds, tens and, in rare cases, unities of  $\text{cm}^{-1}$ . A similar situation is typical for  $4f-4f$  clusters. The only feature of these clusters is the value of constant  $J$  being of 2 to 3 orders of magnitude smaller [29-54]. This is due to the screening effect of the filled electron shell of the rare earth ion, following after the unfilled  $4f$ -shell. The screening of Coulomb interaction leads to weakening indirect exchange interaction between the ions of the dimer through closely spaced anions. It should be noted that in the case of half-filled  $3d$ - and  $4f$ -shells, both ferromagnetic and

antiferromagnetic exchange interactions occur with the same probability in homonuclear  $3d-3d$  and  $4f-4f$  dimers.

Thus, in most of binuclear coordination compounds containing  $3d-3d$  or  $4f-4f$  dimers antiferromagnetic exchange interaction occurs. Here, we propose the method to transform these binuclear compounds into compounds with ferromagnetic exchange interaction. First, we will illustrate the method efficiency on simplest  $3d^1-3d^1$  and  $3d^9-3d^9$  dimers, after that the obtained results will be generalized to the case of  $3d^n-3d^m$  ( $n+m=10$ ) and  $4f^n-4f^m$  ( $n+m=14$ ) dimers.

In Section 2, the time-reversal symmetry of dimer clusters, its violation and subsequent restoration will be discussed. It will be shown that at isomorphic substitution of one dimer's ion of the same electronic configuration by the "time-reversed" ion, violation of the time-reversal symmetry occurs. In this context, the "time-reversed" ion means an ion which electron spin wave function is exposed to the time-reversal operator action, resulting in transforming the electron spin wave function into a spin wave function of arising hole. This isomorphic substitution of the dimer ion by a "time-reversed" ion is accompanied by changing the sign of exchange interaction constant. Thereby, the broken time-reversal symmetry is restored becoming a combined time-reversal symmetry. In Subsection 2.4, the developed approach is generalized to the case of dimers consisting of ions with spins  $S_1 = S_2 > 1/2$ .

In Section 3, we present classification of binuclear coordination compounds, containing dimers formed of  $3d$ - or  $4f$ -ions, by types of intracluster exchange interaction.

Experimental data confirming the proposed method for controlled synthesis of binuclear coordination compounds are given in Section 4. In Section 5, the obtained results are discussed, and a number of conclusions are drawn.

## 2. Time-reversal symmetry, its violation and restoration in dimeric clusters. New method for controlled synthesis of binuclear coordination compounds

The time-reversal symmetry is one of the fundamental concepts in physics. The chemical synthesis is the dynamic crystallization process and, at first glance, it has nothing in common with this symmetry. However, as it will be shown, time-reversal symmetry violation along with its restoration by inverting the exchange interaction constant sign in magnetic dimers enables the controlled synthesis of binuclear coordination compounds. It permits to predict, before the synthesis, the type of intradimeric exchange interaction (ferro- and antiferromagnetic).

### 2.1. Invariance of exchange interaction Hamiltonian of $S_1 = S_2 > 1/2$ dimers relative to time-reversal transformation

In absence of a crystal field of lower than cubic symmetry, from the four wave spin functions  $\alpha\alpha$ ,  $\beta\alpha$ ,  $\alpha\beta$ ,  $\beta\beta$  of the  $3d^1-3d^1$  dimer (where  $\alpha = |1/2, 1/2\rangle$ ,  $\beta = |1/2, -1/2\rangle$ ) one antisymmetric function

$$|0,0\rangle = (1/\sqrt{2})(\alpha\beta - \beta\alpha) \quad (1)$$

corresponding to the singlet spin level and three symmetric functions

$$\begin{aligned} |1,1\rangle &= \alpha\alpha \\ |1,0\rangle &= (1/\sqrt{2})(\alpha\beta + \beta\alpha) \\ |1,-1\rangle &= \beta\beta \end{aligned} \quad (2)$$

corresponding to the triplet spin level can be formed [4]. Here, the first and the second factors in products of the spin wave functions refer, respectively, to the first and the second ions of the dimer. Whether the ground state of the dimer is singlet or triplet, it depends on the sign of the constant  $J_{12} \equiv J$  of exchange interaction between the dimer ions.

The Hamiltonian of isotropic exchange interaction between electrons of the dimer ions can be presented as [55]:

$$H = -J S_1 S_2. \quad (3)$$

Note that this is not the only form of the Hamiltonian  $H$  as given in various publications. Along with the constant  $-J$  [55-57], in (3) it is used  $J$  [4, 58] or  $-2J$  [27, 40, 46, 51, 59]. Therefore, the singlet or triplet ground states of the magnetic dimer can be differently described, depending on the constant ( $-J$ ,  $J$ , or  $-2J$ ) used in the Hamiltonian (3). Moreover, at the same numerical value of the constant  $J$ , the singlet-triplet splitting due to exchange interaction may differ twice in the papers of different authors. Therefore, caution should be observed when comparing the values and signs of the constant  $J$  obtained by different authors on the basis of experimental data.

In the case of dimer consisting of ions with electron spins  $S_1 = S_2 = 1/2$ , the antiunitary time-reversal operator has the following form [60]:

$$T = i\sigma_{1y}K \cdot i\sigma_{2y}K, \quad (4)$$

where  $\sigma_{1y}$  and  $\sigma_{2y}$  are imaginary Pauli operators related to the spins  $S_1$  and  $S_2$  ( $S_1 = (1/2)\sigma_1$ ,  $S_2 = (1/2)\sigma_2$ ), and  $K$  is the operator of complex conjugation.

For further discussion, it is convenient to represent the time-reversal operator  $T$  as a product of two operators:

$$T = T_1 \cdot T_2, \quad (5)$$

where

$$T_n = i\sigma_{ny} K, \quad n = 1, 2. \quad (6)$$

Due to time-reversal symmetry, the Hamiltonian  $H$  from (3) must be invariant under the time-reversal operator  $T$ :

$$THT^+ = T_1 T_2 H T_2^+ T_1^+ = T_2 T_1 H T_1^+ T_2^+ = H, \quad (7)$$

where  $T^+$ ,  $T_1^+$  and  $T_2^+$  are Hermitian conjugated operators. In (7),  $T_1$  and  $T_2$  are commuting operators ( $T_1 T_2 = T_2 T_1$ ).

## 2.2. Time-reversed symmetry violation in magnetic dimers with $S_1 = S_2 = 1/2$ at isomorphic substitution of an ion by a “time-reversed” one

By definition of the time-reversal operator, there is a reversal of signs of all three spin projections operators under action of the operator  $T_n$  ( $n = 1, 2$ ):

$$T_n S_{nx} T_n^+ = -S_{nx}, \quad T_n S_{ny} T_n^+ = -S_{ny}, \quad T_n S_{nz} T_n^+ = -S_{nz}. \quad (8)$$

In this case, along with (7), we have the relation:

$$T_1 H T_1^+ = -J [i\sigma_{1y} K S_{1x} K^+ (i\sigma_{1y})^\dagger S_{2x} + i\sigma_{1y} K S_{1y} K^+ (i\sigma_{1y})^\dagger S_{2y} + i\sigma_{1y} K S_{1z} K^+ (i\sigma_{1y})^\dagger S_{2z}] = -H. \quad (9)$$

The relation (9) arises due to relationships:

$$\begin{aligned} i\sigma_{1y} K S_{1x} K^+ (i\sigma_{1y})^\dagger &= -S_{1x}, \\ i\sigma_{1y} K S_{1y} K^+ (i\sigma_{1y})^\dagger &= -S_{1y}, \\ i\sigma_{1y} K S_{1z} K^+ (i\sigma_{1y})^\dagger &= -S_{1z}. \end{aligned} \quad (10)$$

Similarly, one can find

$$T_2 H T_2^+ = -J [S_{1x} i\sigma_{2y} K S_{2x} K^+ (i\sigma_{2y})^\dagger + S_{1y} i\sigma_{2y} K S_{2y} K^+ (i\sigma_{2y})^\dagger + S_{1z} i\sigma_{2y} K S_{2z} K^+ (i\sigma_{2y})^\dagger] = -H, \quad (11)$$

because relations similar to (10) are valid for operators  $S_{2x}$ ,  $S_{2y}$ , and  $S_{2z}$ . It can be seen from (9) and (11) that the operator  $T_1$  or  $T_2$  acting separately on the exchange interaction Hamiltonian  $H$  changes its sign leading to violation of time-reversal symmetry.

Thus, the Hamiltonian of the isotropic exchange interaction  $H$  from (3) remains invariant under the time-reversal operator  $T = T_1 T_2 = T_2 T_1$ , but it is not invariant under operators  $T_1$  and  $T_2$  acting separately. In this context, the operators  $T_1$  and  $T_2$  can be conventionally referred to as “incomplete” time-reversal operators.

In order to restore the invariance of the Hamiltonian  $H$  under time-reversal operator, violated by the operator  $T_1$ , it is necessary to subject it to further transformation,

which consists in changing the sign of operators  $S_{2x}$ ,  $S_{2y}$ , and  $S_{2z}$  under operator  $T_2$ . By analogy, in order to restore the invariance of  $H$  under the time-reversal operator, which was violated by the operator  $T_2$ , it is necessary to subject it to further transformation, which consists in changing the sign of  $S_{1x}$ ,  $S_{1y}$ , and  $S_{1z}$  operators under  $T_1$  operator. However, this restoration of the time-reversal invariance of the Hamiltonian  $H$  violated by  $T_1$  or  $T_2$  operators is trivial and doesn't lead to any new results.

## 2.3. Time-reversal symmetry restoration in $S_1 = S_2 = 1/2$ binuclear clusters by reversing the sign of the exchange interaction constant

Let us consider the change of the sign of the exchange interaction constant  $J$ , on the second step of the Hamiltonian transformation, by introducing the operator  $I_J$  [61]:

$$I_J J = -J, \quad I_J^2 = 1. \quad (12)$$

The transformation (12) is essentially formal, as the constant  $J$  is a characteristic of the substance, and in order to change its sign it would be necessary to change the substance itself. Since the energy of the exchange interaction is part of the Coulomb energy, one can assume that  $J$  is an electrical characteristic of the substance. On the other hand, different signs of the constant  $J$  correspond to ferromagnetic or anti-ferromagnetic exchange interaction. Therefore, one could assume that  $J$  is a magnetic characteristic of the substance.

It is easy to see that  $T_1$ ,  $T_2$ , and  $I_J$  are commuting operators. Taking into account (7)-(12), it can be shown that Hamiltonian  $H$  from (3) remains invariant under  $T_1 I_J$  and  $T_2 I_J$  operators:

$$T_1 I_J H I_J^+ T_1^+ = -(I_J J) [i\sigma_{1y} K S_{1x} K^+ (i\sigma_{1y})^\dagger S_{2x} + i\sigma_{1y} K S_{1y} K^+ (i\sigma_{1y})^\dagger S_{2y} + i\sigma_{1y} K S_{1z} K^+ (i\sigma_{1y})^\dagger S_{2z}] = H, \quad (13)$$

$$T_2 I_J H I_J^+ T_2^+ = -(I_J J) [S_{1x} i\sigma_{2y} K S_{2x} K^+ (i\sigma_{2y})^\dagger + S_{1y} i\sigma_{2y} K S_{2y} K^+ (i\sigma_{2y})^\dagger + S_{1z} i\sigma_{2y} K S_{2z} K^+ (i\sigma_{2y})^\dagger] = H. \quad (14)$$

As it was shown in Subsection 2.2, action of the operator  $T_1$  or  $T_2$  from (6) on the Hamiltonian  $H$  from (3) leads to violation of its time-reversal invariance. In each of these cases, the Hamiltonian time-reversal invariance can be restored by changing the sign of the exchange interaction constant  $J$  ( $J \rightarrow -J$ ). Formally, this can be done simply. However, as it was mentioned above,  $J$  is a characteristic of the material (binuclear coordination compounds containing  $3d-3d$  or  $4f-4f$  dimers, in our case). Therefore, the method of changing the sign of this constant requires a special discussion.

As it results from (13) or (14), the time-reversal symmetry violated by  $T_1$  or  $T_2$  operators will be restored, if  $I_J$  operator (12) acts on Hamiltonian  $H$  simultaneously

with  $T_1$  or  $T_2$  operators. Thus,  $T_1 I_J = i\sigma_{1y} I_J$  and  $T_2 I_J = i\sigma_{2y} I_J$  are symmetry operators, and their separate action leaves the Hamiltonian  $H$  invariant. Therefore, these operators may be termed as combined time-reversal operators.

Here, it is important to note that action of operators  $T_1$  or  $T_2$  on  $H$  leads to inversion of the spin projection operators sign, respectively  $S_{1x}$ ,  $S_{1y}$ , and  $S_{1z}$  or  $S_{2x}$ ,  $S_{2y}$ , and  $S_{2z}$ . Indeed, the calculations show that the transition from the matrix of the Hamiltonian  $H$  determined in the spinor basis  $\{|0,0\rangle, |1,1\rangle, |1,0\rangle, |1,-1\rangle\}$  to the  $H$  matrix determined in the spinor basis  $\{T_1|0,0\rangle, T_1|1,1\rangle, T_1|1,0\rangle, T_1|1,-1\rangle\}$ , where

$$T_1|0,0\rangle = (1/\sqrt{2})(\alpha\alpha + \beta\beta), T_1|1,1\rangle = -\alpha\beta,$$

$$T_1|1,0\rangle = (1/\sqrt{2})(\alpha\alpha - \beta\beta), T_1|1,-1\rangle = \beta\alpha$$

leads to transformation of the operators  $S_{1x}$ ,  $S_{1y}$ , and  $S_{1z}$  into  $-S_{1x}$ ,  $-S_{1y}$ , and  $-S_{1z}$ .

The same result can be obtained at transition from  $H$  matrix determined in the spinor basis  $\{T_1 T_2|0,0\rangle, T_1 T_2|1,1\rangle, T_1 T_2|1,0\rangle, T_1 T_2|1,-1\rangle\}$ , where

$$T_1 T_2|0,0\rangle = (1/\sqrt{2})(\alpha\beta - \beta\alpha), T_1 T_2|1,1\rangle = \beta\beta,$$

$$T_1 T_2|1,0\rangle = (-1/\sqrt{2})(\alpha\beta + \beta\alpha), T_1 T_2|1,-1\rangle = \alpha\alpha$$

to the  $H$  matrix determined in the spinor basis  $\{T_1|0,0\rangle, T_1|1,1\rangle, T_1|1,0\rangle, T_1|1,-1\rangle\}$ .

Analogically, the transition to  $H$  matrix, determined in the spinor basis  $\{T_2|0,0\rangle, T_2|1,1\rangle, T_2|1,0\rangle, T_2|1,-1\rangle\}$ , where

$$T_2|0,0\rangle = (-1/\sqrt{2})(\alpha\alpha + \beta\beta), T_2|1,1\rangle = -\beta\alpha,$$

$$T_2|1,0\rangle = (1/\sqrt{2})(\alpha\alpha - \beta\beta), T_2|1,-1\rangle = \alpha\beta$$

leads to transformation of the operators  $S_{2x}$ ,  $S_{2y}$ , and  $S_{2z}$  into  $-S_{2x}$ ,  $-S_{2y}$ , and  $-S_{2z}$ . In both cases, this transformation is equivalent to changing the  $J$  sign, because  $J$  is the common factor for  $S_{1\xi}$  and  $S_{2\xi}$  ( $\xi = x, y, z$ ) in Eq. (3). Here, the results of action of operators  $T_1$  and  $T_2$  from (6) on the spin wave functions (1) and (2) have been taken into consideration.

Thus, the time-reversal symmetry violation is accompanied by inversion of the exchange interaction constant sign. It restores symmetry, and the Hamiltonian  $H$  becomes invariant again, this time in relation to combined time-reversal operators  $i\sigma_{1y} K I_J$  and  $i\sigma_{2y} K I_J$ .

On the other hand, under action of  $T_1$  operator, the electron wave function of one ion of the  $3d^1 - 3d^1$  dimer is transformed into the wave function of the hole in the electronic shell. The same is valid for  $T_2$  operator acting on the other dimer ion. Each of these transformations is equivalent to isomorphic substitution of dimer's ion of  $3d^1$  electronic configuration by an ion of  $3d^9$  electronic configuration. Thus,  $T_1$  operator transforms the  $3d^1 - 3d^1$  dimer with antiferromagnetic exchange interaction ( $J < 0$ ) into the  $3d^9 - 3d^1$  dimer (or the equivalent  $3d^1 - 3d^9$  dimer) with a ferromagnetic exchange interaction ( $J > 0$ ).

Similarly, under the action of  $T_1$ , the spin wave function of the hole in the electronic shell of one of  $3d^9 - 3d^9$  dimer' ion is transformed into the  $3d^1$  electron spin wave function of the same dimer's ion. Thus, the  $3d^9 - 3d^9$  dimer with antiferromagnetic exchange interaction ( $J < 0$ ) turns into  $3d^1 - 3d^9$  (or  $3d^9 - 3d^1$ ) dimer with ferromagnetic exchange interaction ( $J > 0$ ). This transformation  $J \rightarrow -J$  by isomorphic substitution is admissible, because it ensures restoration of the Hamiltonian  $H$  invariance relative to time-reversal symmetry.

These results obtained for  $3d^n - 3d^n$  ( $n = 1, 9$ ),  $3d^9 - 3d^1$  and  $3d^1 - 3d^9$  dimers extend without any change to  $4f^m - 4f^m$  ( $n = 1, 13$ ),  $4f^{13} - 4f^1$ , and  $4f^1 - 4f^{13}$  dimers.

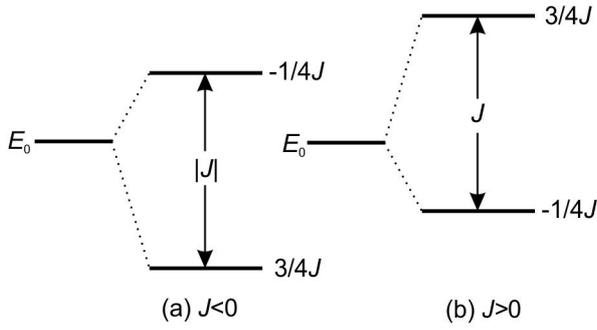
#### 2.4. Spin levels inversion of $3d^n - 3d^n$ ( $n = 1, 9$ ) and $4f^m - 4f^m$ ( $m = 1, 13$ ) dimers

Let us calculate the energy values for the singlet and triplet spin levels of  $3d^n - 3d^n$  ( $n = 1, 9$ ),  $3d^9 - 3d^1$ , and  $3d^1 - 3d^9$  dimers in the first order of perturbation theory. In order to do this, it is necessary to build a secular determinant and solve a 4-th degree secular equation, the roots of which are easily to find.

As a result of diagonalization of the Hamiltonian (3) matrix in the spinor basis  $\{|0,0\rangle, |1,1\rangle, |1,0\rangle, |1,-1\rangle\}$ , the following values are obtained for the spin singlet energy level  $E^{(s)}$  and the spin triplet level  $E^{(t)}$  of the  $3d^1 - 3d^1$  cluster ( $J < 0$ ):

$$E^{(s)}(3d^1 - 3d^1) = 3/4J, E^{(t)}(3d^1 - 3d^1) = -1/4J. \quad (15)$$

If diagonalization is performed in the spinor basis  $\{T_1 T_2|0,0\rangle, T_1 T_2|1,1\rangle, T_1 T_2|1,0\rangle, T_1 T_2|1,-1\rangle\}$ , then the same values are obtained for the spin singlet energy level,  $E^{(s)}$ , and the spin triplet energy level,  $E^{(t)}$ , of the  $3d^9 - 3d^9$  cluster. Similarly, by diagonalizing the Hamiltonian matrix in the spinor basis  $\{T_1|0,0\rangle, T_1|1,1\rangle, T_1|1,0\rangle, T_1|1,-1\rangle\}$  or in the spinor basis  $\{T_2|0,0\rangle, T_2|1,1\rangle, T_2|1,0\rangle, T_2|1,-1\rangle\}$  one obtains the same result but for the case  $J > 0$ .



**Fig. 1.** Diagram of two lowest spin energy levels for a binuclear cluster with antiferromagnetic (a) and ferromagnetic (b) exchange interactions: (a)  $E^{(s)} = (3/4)J$ ,  $E^{(t)} = -(1/4)J$ ; (b)  $E^{(s)} = (3/4)J$ ,  $E^{(t)} = -(1/4)J$ . The singlet-triplet splitting is equal to  $|J|$  in (a) and  $J$  in (b).

In the case of dimers consisting of  $3d$ - or  $4f$ -ions, the isomorphic substitution of one of dimer's ions by a "time-reversed" ion leads not only to inversion of spin levels, but also to shifting  $E^{(s)}$  ( $S = 0$ ) and  $E^{(t)}$  ( $S = 1$ ) levels by  $|J|/2$  towards higher energy values (Fig. 1).

Obviously, at transition from electron wave functions to the hole ones, both the coordinate and spin parts of the wave function are exposed to the action of the time-reversal operator. However, for finding the eigenvalues of the Hamiltonian (3), one needs to know only the spin wave functions, therefore, we do not consider here the coordinate part of wave functions of  $3d$ - and  $4f$ -electrons.

Fig. 1 shows inversion of the singlet and triplet spin levels of  $3d^n - 3d^n$  ( $n = 1, 9$ ) and  $4f^m - 4f^m$  ( $m = 1, 13$ ) clusters at isomorphic substitution of one of the  $3d^1$ -ions by a  $3d^9$ -ion or of one of  $3d^9$ -ions by a  $3d^1$ -ion, and, correspondingly, at isomorphic substitution of one of the  $4f^1$ -ions by a  $4f^{13}$ -ion, or of one of the  $4f^{13}$ -ions by a  $4f^1$ -ion.

The initial  $3d^n - 3d^n$  ( $n = 1, 9$ ) and  $4f^m - 4f^m$  ( $m = 1, 13$ ) clusters (before the isomorphic substitution) are characterized by antiferromagnetic exchange interaction ( $J < 0$ ). After isomorphic substitutions, these clusters are transformed into  $3d^1 - 3d^9$  or equivalent  $3d^9 - 3d^1$  clusters and, respectively, into  $4f^1 - 4f^{13}$  or equivalent  $4f^{13} - 4f^1$  clusters. These clusters are characterized by a ferromagnetic exchange interaction ( $J > 0$ ).

All dimers with ferromagnetic exchange interaction, as a rule, are heteronuclear, excepting the case when the ions of heteronuclear, as well as those of homonuclear dimers, have half-filled electron shells. In this case, both ferro- and antiferromagnetic exchange interactions ( $J > 0$  and  $J < 0$ ) occur with the same probability.

## 2.5. Generalization to the case of dimers consisting of ions with $S_1 = S_2 > 1/2$ spins

In order to find out what happens at isomorphic substitution of a dimer's high spin ion by a "time-reversed" ion, the Hamiltonian (3) must be diagonalized in both spinor bases  $\{|S_n, S_n\rangle, |S_n, S_n - 1\rangle, \dots, |S_n, 1 - S_n\rangle, |S_n, -S_n\rangle\}$  and  $\{T_n|S_n, S_n\rangle, T_n|S_n, S_n - 1\rangle, \dots, T_n|S_n, 1 - S_n\rangle, T_n|S_n, -S_n\rangle\}$ , where  $n = 1, 2$ . In this case, comparison of the obtained results would allow drawing conclusions similar to those that have been made in case of dimers consisting of ions with spins  $1/2$ . However, these calculations (which become increasingly cumbersome with increasing the magnitude of the spin  $S$ ) are no longer necessary, if one notes that the action of  $T_n$  operator on the basis spin functions leads to changing the sign of the operators  $S_{nx}$ ,  $S_{ny}$ , and  $S_{nz}$  independently of the spin value. In particular, it is easy to see that, for a particle with the spin  $S = 1/2$ , the matrices of  $S_{1x}$ ,  $S_{1y}$ , and  $S_{1z}$  operators in the basis of functions  $\{T_1\alpha = -\beta, T_1\beta = \alpha\}$  have the following form:

$$\begin{aligned} S_{1x} &= (-1/2) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \\ S_{1y} &= (-1/2) \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \\ S_{1z} &= (-1/2) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \end{aligned} \quad (16)$$

which differ only in sign from the matrices of the same operators written in the standard basis  $\{\alpha, \beta\}$ . In the case of systems with the spin  $S > 1/2$ , the situation is similar.

For a system with an arbitrary spin  $S$ , action of the time-reversal operator  $T$  (which is different from the operator  $T$  from (4) for the  $3d^1 - 3d^1$  dimer) is

$$T|S, m\rangle = (-1)^{S+m}|S, -m\rangle \quad (17)$$

in the case when the operator matrices  $S_x$ ,  $S_y$ , and  $S_z$  are given in the basis  $\{|S, S\rangle, |S, S - 1\rangle, \dots, |S, 1 - S\rangle, |S, -S\rangle\}$ . Some caution should be exercised when (17) is used.

If the matrices of  $S_x$ ,  $S_y$ , and  $S_z$  operators are defined in the basis  $\{|S, S\rangle, |S, S - 1\rangle, \dots, |S, 1 - S\rangle, |S, -S\rangle\}$ , then the formula

$$T|S, m\rangle = (-1)^{S-m}|S, -m\rangle \quad (18)$$

should be used [60, 63] instead of (17).

The non-zero matrix elements of  $S_{1x}$ ,  $S_{1y}$ , and  $S_{1z}$  operators in the standard basis are well known [62, 63].

Going to the “time-reversed” basis  $\{(-1)^{2S_1}|S_1, -S_1\rangle, (-1)^{2S_1-1}|S_1, 1-S_1\rangle, \dots, -|S_1, S_1-1\rangle, |S_1, S_1\rangle\}$  and comparing the results of calculations of the matrix elements of these operators with those from [62], we find that the matrices of the  $S_{1x}$ ,  $S_{1y}$ , and  $S_{1z}$  operators in the original basis and in the “time-inverted” basis differ only in sign. Thus, the time-reversal operator that transforms the spin basis functions causes a change of the sign of spin projection operators. It is equivalent to changing the sign of the exchange interaction constant, which is a common factor in these operators. So, in order to change the sign of  $J$  in case of arbitrary spin, it is necessary to provide an isomorphic substitution of one of the ions of homonuclear dimer by a “time-reversed” ion.

### 3. Classification of dimers formed from 3d- or 4f-ions by exchange interaction type

As a result of the analysis, a classification of all possible dimers formed of 3d- or 4f-ions by types of exchange interaction has been made. Table 1 shows 3d–3d dimeric clusters with antiferromagnetic and ferromagnetic exchange interactions.

The 4f–4f dimers with antiferromagnetic and ferromagnetic exchange interactions are listed in Table. 2.

As for the  $\text{Fe}^{3+}\text{--Fe}^{3+}$ ,  $\text{Mn}^{2+}\text{--Mn}^{2+}$  and  $\text{Fe}^{3+}\text{--Mn}^{2+}$  dimers, it is impossible to specify the type of exchange interaction, since they are formed from ions with half-filled 3d-shells. The same refers to the  $\text{Gd}^{3+}\text{--Gd}^{3+}$  dimer. In all of these dimers with half-filled electron shells, the probability to realize ferromagnetic or antiferromagnetic exchange interaction is close to 1/2.

The proposed classification of dimer clusters by types of the exchange interaction (Tables 1 and 2) is based on the following reasons:

1. There are firmly established experimental data proving that in the 3d–3d and 4f–4f dimeric clusters, ions of which contain the same number of electrons, the antiferromagnetic exchange interaction is realized (with some exceptions).
2. Transformation of any of 3d–3d or 4f–4f dimers with antiferromagnetic exchange interaction into a dimer with ferromagnetic exchange interaction can be accomplished experimentally by isomorphic substitution of dimer’s ion by a “time-reversed” ion. The feasibility of such a transformation is proved for homonuclear dimers containing high spin ions ( $S > 1/2$ ).

Our classification of dimers by types of exchange interaction does not apply to mixed dimers such as 3d–4f.

### 4. Experimental confirmation of the new approach in controlled synthesis of binuclear coordination compounds

We found that the ground state of the dimers  $3d^1\text{--}3d^1$  and  $3d^9\text{--}3d^9$  is a singlet one, if the exchange interaction constant  $J < 0$ . Just this situation takes place in the case of the binuclear coordination compound  $\text{Cu}_2(\text{fsa})_2\text{enCH}_3\text{COOH}$  containing the dimers  $\text{Cu}^{2+}\text{--Cu}^{2+}$ , where  $(\text{fsa})_2\text{en}^{4-}$  denotes the bichelating ligand derived from the Schiff base bis(2'-hydroxy-3'-carboxybenzilidene)-1,2-diaminoethane [21]. The exchange interaction constant value determined in [21], based on experimental data, is  $J = -650 \text{ cm}^{-1}$ .

On the other hand, in [22, 23] experimental studies have been performed on magnetic properties of the binuclear coordination compound  $\text{CuVO}(\text{fsa})_2\text{enCH}_3\text{COOH}$ , which differs from the coordination compound  $\text{Cu}_2(\text{fsa})\text{enCH}_3\text{COOH}$  only in the fact that one of the ions  $\text{Cu}^{2+}$  of the dimer  $\text{Cu}^{2+}\text{--Cu}^{2+}$  is substituted by the ion  $(\text{VO})^{2+}$ . Since the electronic configuration of the ion  $\text{Cu}^{2+}$  is  $3d^9$ , and the electronic configuration of the ion  $(\text{VO})^{2+}$  is  $3d^1$ , the situation theoretically analyzed in Subsection 2.4 occurs: isomorphic substitution of one of the 3d-ions of the dimer by a “time-reversed” 3d-ion. As a result of this isomorphic substitution, the wave function of the 3d-hole in one of 3d-ions transforms into the wave function of the 3d-electron of the same ion under action of the operator  $T_1$  or  $T_2$ , this transformation being accompanied by the constant  $J$  sign inversion. In such a way, the time reversal symmetry violation (changing the sign of the Hamiltonian  $H$  under the action of  $T_1$  or  $T_2$  operators) is restored, because  $H$  operator is now invariant relative to  $T_1I_J$  or  $T_2I_J$  operators (the combined time-reversal symmetry). The exchange interaction constant for the dimer  $\text{Cu}^{2+}\text{--}(\text{VO})^{2+}$ , determined in [22, 23] on the basis of experimental data, is  $J = +118 \text{ cm}^{-1}$ . Thus, as a result of the isomorphic substitution of  $\text{Cu}^{2+}$  ion by the  $(\text{VO})^{2+}$ , not only the inversion of spin levels, but also reduction of the absolute value of  $J$  occurs. This result is not surprising, taking into account that  $(\text{VO})^{2+}$  and  $\text{Cu}^{2+}$  ions are not equivalent: the  $(\text{VO})^{2+}$  ion is polar, while the  $\text{Cu}^{2+}$  ion is non-polar. At isomorphic substitution of one of the homonuclear cluster ions by a “time-reversed” ion, a change of the constant  $J$  sign occurs. It is accompanied by a transition from the antiferromagnetic exchange interaction to the ferromagnetic one. Therefore, we can consider that at  $J > 0$  the orthogonality of magnetic orbitals exists (for example, in the case of heteronuclear  $3d^n\text{--}3d^{10-n}$  dimers). This conclusion is confirmed experimentally for  $(\text{VO})^{2+}\text{--Cu}^{2+}$  cluster in heterobinuclear complexes  $\text{CuV}(\text{fsa})_2\text{enCH}_3\text{COOH}$  ( $J = +118 \text{ cm}^{-1}$ ) [22-24] and in  $\text{LCuVO}$  complex, which were synthesized using an unsymmetrical dinucleating ligand L based on 1,8-naphthalenediol ( $J = +46 \text{ cm}^{-1}$ ) [24]. In

**Table 1.** The types of exchange interactions in  $3d-3d$  clusters.

Dimer clusters $3d-3d$ with antiferromagnetic exchange interaction		Dimer clusters $3d-3d$ with ferromagnetic exchange interaction
$Ti^{3+}-Ti^{3+}$	$Cr^{3+}-V^{2+}$	$Ti^{3+}-Cu^{2+}$
$V^{4+}-V^{4+}$	$Mn^{3+}-Mn^{3+}$	$V^{4+}-Cu^{2+}$
$(VO)^{2+}-(VO)^{2+}$	$Cr^{2+}-Cr^{2+}$	$(VO)^{2+}-Cu^{2+}$
$Ti^{3+}-V^{4+}$	$Mn^{3+}-Cr^{2+}$	$V^{3+}-Ni^{2+}$
$Ti^{3+}-(VO)^{2+}$	$Fe^{2+}-Fe^{2+}$	$Cr^{3+}-Co^{2+}$
$(VO)^{2+}-V^{4+}$	$Co^{2+}-Co^{2+}$	$V^{2+}-Co^{2+}$
$V^{3+}-V^{3+}$	$Ni^{2+}-Ni^{2+}$	$Mn^{3+}-Fe^{2+}$
$Cr^{3+}-Cr^{3+}$	$Cu^{2+}-Cu^{2+}$	$Cr^{2+}-Fe^{2+}$
$V^{2+}-V^{2+}$		

**Table 2.** The types of exchange interactions in  $4f-4f$  clusters.

Dimer clusters $4f-4f$ with antiferromagnetic exchange interaction		Dimer clusters $4f-4f$ with ferromagnetic exchange interaction
$Ce^{3+}-Ce^{3+}$	$Tb^{3+}-Tb^{3+}$	$Ce^{3+}-Yb^{3+}$
$Pr^{3+}-Pr^{3+}$	$Dy^{3+}-Dy^{3+}$	$Pr^{3+}-Tb^{3+}$
$Nd^{3+}-Nd^{3+}$	$Ho^{3+}-Ho^{3+}$	$Nd^{3+}-Er^{3+}$
$Pm^{3+}-Pm^{3+}$	$Er^{3+}-Er^{3+}$	$Pm^{3+}-Ho^{3+}$
$Sm^{3+}-Sm^{3+}$	$Tu^{3+}-Tu^{3+}$	$Sm^{3+}-Dy^{3+}$
$Eu^{3+}-Eu^{3+}$	$Yb^{3+}-Yb^{3+}$	$Eu^{3+}-Tb^{3+}$

particular, the magnetic orbital around the copper(II), constructed from the  $d_{x^2-y^2}$  metallic orbital, transforms as the  $a''$  irreducible representation of the  $C_s$  point group of symmetry, whereas the magnetic orbital around vanadium(IV), constructed from the  $d_{xy}$  magnetic orbital, transforms as  $a'$ . The overlap integral  $\langle a''/a' \rangle$  between the magnetic orbitals is identically zero [22].

The experimental data presented in this section were obtained many years ago without being interpreted in terms of time-reversal symmetry, excepting [61], where the basic results were obtained with account of the symmetry properties, without the energy levels calculation carried out in this paper.

The reference [22] is the first experimental paper, where transformation of the antiferromagnetic exchange interaction into ferromagnetic one by isomorphous substitution of a  $3d$ -ion by the same "time-reversed"  $3d$ -ion in binuclear clusters has been accomplished. This study has not lost its relevance and remains a classic experimental work, confirming the possibility of carrying out the controlled synthesis of binuclear coordination compounds by isomorphous substitution of one of the ions in different dimers by "time-reversed" ions. The use of the proposed method in synthesis processes will allow to obtain new binuclear coordination compounds with ferromagnetic exchange interaction.

## 5. Discussion and conclusions

The proposed method for controlled synthesis of binuclear coordination compounds is a semi-empirical one, because it is based on the analysis of experimental data on a large number of binuclear coordination compounds. As it was ascertained, if these compounds contain dimers formed of paramagnetic ions with the

same electron configuration, then the exchange interaction between the ions of dimers is usually antiferromagnetic. On the other hand, once the ground state of these dimers was determined to be non-spin degenerated, the developed regular procedure of transformation of antiferromagnetic exchange interaction into ferromagnetic one can be carried out. This procedure reduces to the isomorphous substitution of one of the dimer ions by an ion with time-reversed electronic states. Thus, if the dimer ions are characterized each by the  $3d^n$  (or  $4f^m$ ) electronic configuration, then after reversing the constant  $J$  sign, one of dimer's ions will be found already in the electronic configuration  $3d^{10-n}$  (or  $4f^{14-m}$ ).

The transition from electron wave functions to the wave functions of holes in the electronic shell leads to violation of time reversal symmetry, which is restored when the sign of the constant  $J$  is inverted, it being transformed into the combined time-reversal symmetry. In its turn, this symmetry justifies the referred isomorphous substitution as a method for controlled synthesis of binuclear coordination compounds, taking into account the Hamiltonian invariance with respect to the combined time-reversal operators  $T_1I_J$  and  $T_2I_J$ .

Experimental data concerning substitution of one of the  $Cu^{2+}$  ions by  $(VO)^{2+}$  in the  $Cu^{3+}-Cu^{3+}$  dimer [22, 23] confirm our proposed method of  $J$  sign changing by using  $T_1$  or  $T_2$  operators of "incomplete" time reversal. The use of our new method for synthesis of binuclear coordination compounds based on the invariance of the Hamiltonian with respect to the combined transformations  $T_1I_J$  and  $T_2I_J$  will expand the class of substances with ferromagnetic exchange interaction.

If the filling of electron shells of ions forming the homonuclear dimer is different from  $1/2$ , weak ferromagnetic exchange interaction is also possible, in rare cases, when it exists really, an accidental orthogonality of the magnetic orbital centered on metallic ions. It occurs, for example, in the  $Cu^{2+}-Cu^{2+}$  dimer with  $J = +4.8 \text{ cm}^{-1}$  in the homonuclear complex having a bridging  $\beta$ -diketimineamid unit [24]. It was also found in [25] a rare case of ferromagnetic exchange interaction in homonuclear  $Cu^{2+}-Cu^{2+}$  dimers. In the tetraazido dinuclear  $Cu(II)$  complex of the polyaza-polyoxa macrocyclic ligand [24]ane- $N_2O_6$ , which crystallizes in the monoclinic system with the spatial group  $P2_1/n$  ( $a = 1.7780(2) \text{ nm}$ ,  $b = 0.9719(1) \text{ nm}$ ,  $c = 1.7361(2) \text{ nm}$ ,  $\beta = 109.32(5)^\circ$ ,  $Z = 4$ ), two  $Cu(II)$  centers are doubly bridged by two azide ions bound end-on, and each  $Cu(II)$  displays octahedral coordination with four equatorial nitrogens and two axial oxygens (the  $Cu-Cu$  distance is  $0.3162 \text{ nm}$ ). The copper(II) ions are coupled in a ferromagnetic manner with the ground-spin triplet stabilized by  $70 \pm 20 \text{ cm}^{-1}$  with regard to the singlet excited state. The intracluster ferromagnetic coupling is caused by nearly accidental orthogonality of magnetic orbitals centered on the metal ions.

For the same reason, binuclear copper helates, based on tridentate azomethines containing  $N_4$ ,  $N_2S$ , and  $N_2OS$  ligand environments with aromatic coordination unit  $CuN_2S_2$  or heterocyclic coordination fragments  $CuN_4$  and  $CuNOS_2$ , exhibit the intradimer  $Cu^{2+}-Cu^{2+}$  ferromagnetic exchange interaction [26]. As it was shown in [27], the dimeric nickel(II)-ethylendiamine complexes containing  $X = Cl, Br, \text{ or } NCS$  exhibit a ferromagnetic intradimeric exchange interaction with  $J(X = Cl) = +10 \text{ cm}^{-1}$ ,  $J(X = Br) = +8 \text{ cm}^{-1}$ , and  $J(X = CNS) = +5 \text{ cm}^{-1}$ , having the analogical origin. These data have been interpreted using the exchange interaction Hamiltonian  $H = -2JS_1S_2$ .

The following conclusions are derived from this study:

1. Isomorphous substitution of one of the ions with the spin  $S \geq 1/2$  and the same electron configuration of the  $3d-3d$  or  $4f-4f$  binuclear cluster by a "time-reversed" ion is accompanied by inverting the sign of the exchange interaction constant  $J$ .
2. A "time-reversed" ion is obtained under the  $T_1$  or  $T_2$  time reversal operator action on the state vector of electrons or holes in its electronic shell.
3. Isomorphous substitution of one of the ions of the  $3d-3d$  or  $4f-4f$  binuclear clusters of the same electron configuration by a "time-reversed" ion leads to time-reversal symmetry violation (inverting the sign of the exchange interaction spin-Hamiltonian,  $H$ , under action of the  $T_1$  or  $T_2$  operators). It is restored due to inversion of the sign of the constant  $J$ . Thus, from the chemical point of view, the referred isomorphous substitution is the method to control synthesis of binuclear coordination compounds by inverting the constant  $J$  sign in the synthesis process.
4. A classification of the coordination compounds containing  $3d-3d$  or  $4f-4f$  binuclear clusters by exchange interaction type between the paramagnetic ions of the clusters has been made.
5. The practical application of the proposed method for controlled synthesis of binuclear coordination compounds would increase the number of binuclear coordination compounds with ferromagnetic exchange interaction that is now much smaller than the number of antiferromagnetic exchange interaction compounds.

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