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Modern magnetic chemistry of exchange clusters

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Abstract. The review concerns the state-of-the-art in studies on the magnetic chemistry of exchange clusters (polynuclear transition-metal complexes in which the unpaired electrons of particular sites are involved in magnetic exchange due to both direct or indirect, *via* bridging ligands, interactions of their wave functions). Particular emphasis is placed on (i) theoretical models that can be used to interpret experimental data in terms of the effective Hamiltonians and chemical bonding theory and (ii) molecular nanomagnets (complexes containing a large number of magnetic atoms and possessing unusual properties). The bibliography includes 158 references.

I. Introduction

Magnetic chemistry studies the interrelations between the magnetic properties of chemical compounds and their molecular and electronic structures. Creation of a theoretical basis for magnetic chemistry is intimately associated with the development of quantum mechanics.[1,2] Current progress in magnetic chemistry is due to improvement of its theoretical foundations and posing new problems of preparative chemistry.[3–25]

The first advances in magnetic chemistry were due to the discovery of correlations between the magnetic properties and the type of chemical bonding in diamagnetic crystals and organic molecules.[3] Studies on the splitting of transition-metal atomic orbitals (AOs) in mononuclear complexes[4–7] became even more important, because prediction of these effects belongs to the key results obtained using the ligand field theory, which is the main model in the theory of electronic structure of transition-metal compounds.

In 1952, it was found that the interactions between paramagnetic metal atoms in polynuclear complexes can cause a pronounced temperature dependence of the magnetic moment.[8] This class of compounds is called 'exchange clusters'. The spin–spin correlations in the exchange clusters are due to the same exchange interactions as in the magnetically ordered crystals; however, they occur within isolated molecules. Therefore, detailed interpretation of experimental data based on the conventional molecular orbital (MO) theory is an easy task in the case of clusters. In magnetically ordered crystals the microscopic nature of magnetic interactions is masked by a continuous spectrum of elementary excitations. Such continuum systems have been the subject of solid state physics,[2,26] which uses methods based on consideration of translational symmetry of crystals rather than specific features of pair atom–atom interactions in them to interpret the properties.

At the same time, the border between the physics of magnetic phenomena and magnetic chemistry is rather conventional. In particular, complexes containing a large number of paramagnetic atoms exhibit a magnetic memory effect,[22–25] which is characteristic of crystals. At the same time, computational methods based on division of crystals into small clusters proved their efficiency in the case of magnetics.[27]

Usually, the magnetic properties of exchange clusters smoothly depend on temperature and the corresponding curves can hardly be used to assess particular characteristics of the electronic structure. Because of this, interpretation of experimental data in magnetic chemistry is based on two related but clearly distinct divisions of theory.

The object of a phenomenological theory is to determine the form of model Hamiltonians and to develop relevant methods of solution in order to find the parameters of such Hamiltonians by comparing the calculated and experimental characteristics. Phenomenological theories are usually based on some general considerations. Therefore, treatment of experimental data as a set of parameters of the model Hamiltonian can be considered correct. Calculations of the parameters of the Hamiltonian using particular versions of the theory of electronic structure is the object of microscopic theory.

In accord with the aforesaid, in this review we will briefly outline the theoretical methods of modern magnetic chemistry, which are employed to interpret the experimental data, and then dwell on some applications of these methods to molecular nanomagnets, the most complex and promising class of polynuclear complexes.

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II. Phenomenological theory

1. Exchange effect and the exchange Hamiltonian

The simplest way of introducing the notion of exchange interaction is to consider the interaction between a pair of atoms containing one unpaired electron each. Using the spin functions of two electrons, $|\alpha\rangle$ and $|\beta\rangle$, it is possible to derive the following functions of the total spin S

$$|1\rangle = \left(\alpha\alpha, \frac{\alpha\beta+\beta\alpha}{\sqrt{2}}, \beta\beta\right)$$

and

$$|0\rangle = \frac{\alpha\beta-\beta\alpha}{\sqrt{2}}.$$

Then, the total wave functions can be written as

$$\psi(1) = \varphi_-|1\rangle, \qquad (1)$$
$$\psi(0) = \varphi_+|0\rangle,$$

where φ_- and φ_+ are the corresponding radial components.

The spin functions $|1\rangle$ and $|0\rangle$ are of different symmetry. According to the Pauli principle, the functions φ_- and φ_+ should also be of different symmetry and, hence, describe the states characterised by different Coulombic energies (E). The exchange effect consists of the appearance of energy difference (splitting), which is usually denoted as

$$-2J = E(S=1) - E(S=0), \qquad (2)$$

where J is the exchange parameter.

Depending on which has a lower energy, the magnetic triplet ($-2J<0$) or the non-magnetic singlet ($-2J>0$), one deals with ferromagnetic or antiferromagnetic exchange, respectively. As the temperature decreases, the magnetic moment increases in the former and decreases in the latter case. The rate of the change in the magnetic moment depends on the parameter $|-2J|$. This dependence serves as the basis for the determination of the parameters of exchange interactions in clusters.

Formally [see relation (2)], the exchange effect can be treated as some 'interaction', which causes orientation of the spins $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$. The corresponding spin Hamiltonian has the form

$$\widehat{H} = -2J\,\boldsymbol{S}_1\boldsymbol{S}_2. \qquad (3)$$

Since

$$-2J\boldsymbol{S}_1\boldsymbol{S}_2 = (\boldsymbol{S}_1+\boldsymbol{S}_2)^2 - \boldsymbol{S}_1^2 - \boldsymbol{S}_2^2 = \boldsymbol{S}^2 - \boldsymbol{S}_1^2 - \boldsymbol{S}_2^2, \qquad (4)$$

passing from operators to their eigenvalues, we get

$$E(S) = -J[S(S+1) - S_1(S_1+1) - S_2(S_2+1)]. \qquad (5)$$

From this it follows that

$$E(S=1) = -\frac{1}{2}J,$$

$$E(S=0) = \frac{3}{2}J,$$

$$E(S=1) - E(S=0) = -2J,$$

which coincides with relation (2).

Compared to the simple expression (2), relationship (3) for the spin Hamiltonian has advantage consisting of the possibility of generalisation to the multi-centre systems with arbitrary spins of the paramagnetic particles.

From general considerations [14, 20, 28] it follows that in the absence of orbital degeneracy the interaction between localised spins can be described using the spin Hamiltonian

$$\widehat{H} = -2\sum_{ij} J_{ij}\boldsymbol{S}_i\boldsymbol{S}_j + \sum_{ij}\boldsymbol{G}_{ij}[\boldsymbol{S}_i\times\boldsymbol{S}_j] + \sum_{\boldsymbol{k}\geqslant 2}\sum_{\gamma} J_{\gamma}^{(k)}\boldsymbol{O}_{\gamma}^{(k)} + \sum_{ij\alpha\beta} J_{ij}^{(d)}(\boldsymbol{S}_{\alpha i}\boldsymbol{S}_{\beta j} + \boldsymbol{S}_{\beta i}\boldsymbol{S}_{\alpha i}) + \sum_i \mu_B\boldsymbol{S}\boldsymbol{g}_i\boldsymbol{H}. \qquad (6)$$

Here, the subscripts i and j denote paramagnetic ions, α and β are the spin components; $-2J_{ij}$ are the Heisenberg isotropic exchange parameters; $\boldsymbol{S}_i$ and $\boldsymbol{S}_j$ are the spin operators of the magnetic atoms; $\boldsymbol{G}_{ij}$ are the vector parameters of antisymmetric exchange; and $J_{ij}^{(d)}$ are the anisotropic exchange parameters. All higher-order isotropic exchange operators $\boldsymbol{O}_{\gamma}^{(k)}$ can be derived by summing similar terms in the expressions $(\sum_{ij}\boldsymbol{S}_i\boldsymbol{S}_j)^k$. The last term in relationship (6) describes the Zeeman interaction with external magnetic field $\boldsymbol{H}$, $\boldsymbol{g}_i$ are the g-tensors and μ_B is the Bohr magneton. Usually, the Heisenberg term predominates.

2. General relations of theory of magnetism

In the approximation of isotropic g-factors the static magnetic susceptibility of orbitally non-degenerate exchange clusters is given by [20]

$$\chi_m = \chi'_m + N\alpha = \qquad (7)$$
$$= \frac{N_A\mu_B^2}{3kT}\frac{\sum_{\gamma,\boldsymbol{S}} g^2(\gamma,\boldsymbol{S})S(S+1)(2S+1)\exp[-E(\gamma,S)/kT]}{\sum_{\gamma,\boldsymbol{S}}(2S+1)\exp[-E(\gamma,S)/kT]}.$$

Here χ'_m is the magnetic susceptibility per mole of paramagnetic molecules, $N\alpha$ is the correction for temperature-independent paramagnetism of the metal ions and for diamagnetism of ligands, N_A is the Avogadro constant and $\sum_{\gamma,\boldsymbol{S}}$ denotes summation over all quantum numbers.[4, 13, 20]

Often, construction of temperature dependences of the magnetic properties of real clusters requires the inclusion of corrections for the monomer impurity

$$\chi = (1-\eta)\chi_m + \eta\chi_{mono}, \qquad (8)$$

(η is the monomer fraction and χ_{mono} is the magnetic susceptibility of the monomer) and for intermolecular exchange [29–31]

$$\chi_{cl} = \frac{\chi'_m}{1 - 2z'J'\chi'_m/Ng^2\mu_B^2}, \qquad (9)$$

where z' is the number of nearest neighbours and χ'_m and $2J'$ are the parameters of intermolecular exchange.

The magnetic susceptibilities of polyatomic clusters χ'_m can reach very high values, so that intermolecular exchange can strongly affect the magnetic properties even at rather small values of the intermolecular exchange parameters $-2z'J'$.

For mononuclear complexes characterised by the only spin state S and $E(\gamma,\boldsymbol{S})$ = const, Eqn (7) takes the form

$$\chi'_{mono} = \frac{N_A g^2\mu_B^2 S(S+1)}{3kT} \qquad (10a)$$

or

$$\chi'_{mono}T = \frac{N_A g^2\mu_B^2 S(S+1)}{3k}. \qquad (10b)$$

Hence, for such systems the right side of this equation is temperature independent.

In the high-temperature limit $|E(\gamma,\boldsymbol{S})| \ll kT$, Eqn (7) is the sum of the contributions of n paramagnetic atoms in a molecule

$$\chi'_m = \sum_i^n \chi'_{mono}(i), \qquad (11a)$$

or

$$\chi'_{\rm m}T = \sum_{i}^{n} \chi'_{\rm mono}(i)T\,. \qquad (11b)$$

Relationships (10b) and (11b) show the advantages of using the parameters $\chi'_{\rm m}T$ instead of $\chi'_{\rm m}$ in the analysis of experimental data. The high-temperature values $\chi'_{\rm m}T$ permit the spins of the metal ions to be determined by simple summation of n constant contributions (10b). If one knows the trend and rate of changes in $\chi'_{\rm m}T$ on lowering the temperature, it is possible to determine the sign and estimate the magnitude of exchange interactions. If, at low temperatures, the parameter $\chi'_{\rm m}T$ corrected for the monomer impurity and intermolecular exchange takes some nonzero value, relationship (10b) also allows the ground-state spin to be evaluated.

Often, the ratio

$$\chi'_{\rm a} = \frac{\chi'_{\rm m}}{n} \qquad (12)$$

is used instead of $\chi'_{\rm m}$ and $\chi'_{\rm m}T$ (here, n is the number of atoms; usually, $\chi'_{\rm a}$ is denoted as $\chi'_{\rm m}$!). Then, the effective magnetic moment is given by

$$\mu^2_{\rm ef} = \frac{3kT\chi'_{\rm a}}{N_{\rm A}\mu^2_{\rm B}} \approx 7.991\chi'_{\rm a}T. \qquad (13)$$

For mononuclear complexes, the parameter

$$\mu_{\rm ef} = g[S(S+1)]^{1/2} \qquad (14)$$

is temperature independent and can be used in analysing the experimental data in nearly the same way as the parameter $\chi'_{\rm m}T$. However, this is less convenient because $\mu_{\rm ef}$ (in contrast to $\chi'_{\rm m}T$) is a non-additive quantity.

The $\chi'_{\rm mono}T$ and $\mu_{\rm ef}$ values for all realistic S at $g = 2$ are as follows:

S_i	1/2	1	3/2	2	5/2	3	7/2
$\chi'_{\rm mono}T$ /cm^3 K	0.375	1.000	1.875	3.001	4.377	6.002	7.898
$\mu_{\rm ef}/\mu_{\rm B}$	1.732	2.828	3.873	4.899	5.916	6.928	7.937

3. The energy level and magnetic susceptibility calculations

The shape of the curves $\chi(T)$ is highly 'sensitive' to the magnitude and sign of the parameters $-2J_{ij}$, which mainly depend on the energies of the levels $E(\gamma,S)$.[32] Therefore, the parameters $-2J_{ij}$ can be determined using best-fit procedures for the experimental and calculated $\chi(T)$ values. Clearly, the reliability of a particular procedure depends on the correctness of the theoretical model employed. The formalism of deriving correct spin Hamiltonians has been well developed.[14] Because of this, the most important problem is to calculate the eigenvalues (energies) of such spin Hamiltonians.

A method of finding the simplest analytical solutions to the spin Hamiltonians of a large number of types of cluster structure was reported.[33]

a. Analytical solutions to the spin Hamiltonians

Theorem. Consider a system that can be divided into two subsystems, L and M, such that (1) the spin Hamiltonians of the subsystems L and M have the solutions $E_L(\gamma_L,S_L)$ and $E_M(\gamma_M,S_M)$, respectively; and (2) all particles of one subsystem interact with particles of the other subsystem in an identical manner. Then, the solution of the total spin Hamiltonian has the form

$$E = E_L + E_M - J_{LM}[S_{LM}(S_{LM}+1) - S_L(S_L+1) - S_M(S_M+1)], \qquad (15)$$

where S_L and S_M are the spins of the subsystems, $-2J_{LM}$ is the parameter of the exchange interaction between particles of the subsystems and S is the total spin, which can take the following values

$$S = S_L + S_M, S_L + S_M - 1, ..., |S_L - S_M|. \qquad (16)$$

In the simplest case (binuclear complexes) from Eqns (15) and (16) one gets

$$E = -J_{12}[S_{12}(S_{12}+1) - S_1(S_1+1) - S_2(S_2+1)], \qquad (17)$$

$$S_{12} = S_1 + S_2, S_1 + S_2 - 1, |S_1 - S_2|. \qquad (18)$$

Equation (5) is a particular case of Eqn (17).

The equilateral triangle (Fig. 1 *a*) meets the conditions of the theorem mentioned above. According to Eqns (15) and (16), here one has

$$E = -J_{12}[S_{12}(S_{12}+1) - 2S_1(S_1+1) - J_{123}[S_{123}(S_{123}+1) - S_{12}(S_{12}+1) - S_3(S_3+1)], \qquad (19)$$

where

$$S_1 = S_2,$$
$$J_{123} = J_{13} = J_{23},$$
$$S_{123} = S_{12} + S_3, S_{12} + S_3 - 1, ..., |S_{12} - S_3|. \qquad (20)$$

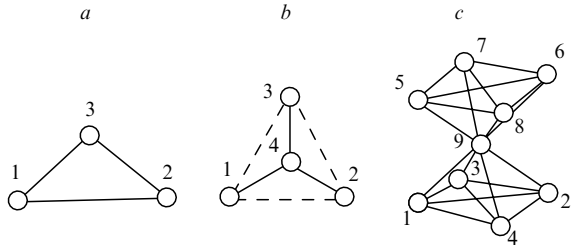


Figure 1. Schematic view of the structures of triangular (*a*), trigonal (*b*) and nonanuclear (*c*) clusters for which analytical solutions of the spin Hamiltonian exist.

Among tetramers, the theorem is applicable to, *e.g.*, a trigonal pyramid (Fig. 1 *b*), which can be represented as a combination of a regular triangle 123 and a mononuclear species 4. Therefore, taking into account Eqns (15) and (19), one has

$$E = -J_{123}[S_{123}(S_{123}+1) - 3S_1(S_1+1)] - J_{1234}[S_{1234}(S_{1234}+1) - S_{123}(S_{123}+1) - S_4(S_4+1)], \qquad (21)$$

where

$$S_1 = S_2 = S_3,$$
$$J_{1234} = J_{14} = J_{24} = J_{34}\,,$$
$$S_{1234} = S_{123} + S_4, S_{123} + S_4 - 1, ..., |S_{123} - S_4|.$$

Other solutions can be obtained using the next terms of the expansion. For instance, an analytical solution for the nonanuclear cluster shown in Fig. 1 *c* can be found by simply representing the system as a combination of two square fragments 'linked' by the interaction parameters $J_{ij} = 0$. Then, the eight-particle subsystem interacts with the symmetrically arranged central species. Solving this simple problem using general methods requires considerable efforts.[34]

To interpret the magnetic properties of various types of polynuclear complexes based on the theory outlined above, a software library was developed.[20]

b. Method of irreducible tensor operators and consideration of spatial symmetry

If the system under study does not meet the conditions formulated in the theorem given in Chapter II.3.a, one should numerically solve the corresponding spin Hamiltonian. For small molecules, the solutions can be obtained by diagonalisation of the matrix of the operator (6), written in the complete basis set of the product functions:

$$|S_1 m_1\rangle|S_2 m_2\rangle ... |S_n m_n\rangle. \tag{22}$$

However, the number of such functions,

$$N_f = \prod_{i=1}^{n}(2S_i + 1)$$

rapidly increases as the number and magnitude of the spins S_i increase. For instance, even for a relatively simple Fe(III) complex with $n = 8$ and $S_i = 5/2$ the order of the matrix in the basis set of the functions (22) is $N_f = 1\,679\,616$. Computer diagonalisation of matrices of so high an order is currently impossible.

The situation is significantly simplified if we take into account only the Heisenberg exchange, which usually predominates. Indeed, the first term in expression (6) can be represented as the sum of zero-rank irreducible tensor operators [35]

$$\sum X_{ij} = -2\sum J_{ij}\boldsymbol{S}_i\boldsymbol{S}_j = \tag{23}$$

$$= 2\sqrt{3}\sum J_{ij}\{...[(S_1^{(k_1)}S_2^{(k_2)})^{(k_{12})}S_3^{(k_3)}]^{(k_{123})}...S_n^{(k_n)}\}^{(0)},$$

where, *e.g.*, the contribution $-2J_{13}\boldsymbol{S}_1\boldsymbol{S}_3$ corresponds to the tensor operator with $k_1 = k_{12} = k_3 = 1$ (all other $k_\alpha = 0$). Other 'multiplication' schemes that obey the quantum vector addition rule [1,2] can also be applied to Eqn (23). Based on the Wiegner–Eckart theorem,[36] in the basis set of the total spin functions one can write

$$\langle ...SM|\sum X_{ij}|...S'M'\rangle = \delta(M, M')\delta(S, S') \times \tag{24}$$

$$\times\, 2\sqrt{3}(2S+1)^{-1/2} \times \sum J_{ij}\langle ...SM||X_{ij}||...SM\rangle,$$

where $\langle ...SM||X_{ij}||...SM\rangle$ are the reduced matrix elements, which can be calculated with ease.[35–37]

Thus, the method of irreducible tensor operators (ITO) involves division of the isotropic spin Hamiltonian matrices into blocks corresponding to particular S and M values. In particular, for the above-mentioned octanuclear complex of trivalent iron the maximum order of the matrix in the basis set of the functions $|...SM\rangle$ is only 16 576. This allowed the software library [20] to be extended by including some modules written to interpret the magnetic properties of rather large clusters ($n \leqslant 16$) possessing no particular symmetry.

More detailed analyses of applications of the ITO method to the phenomenological theory of magnetism are available.[7, 14, 20, 38]

The inclusion of spatial symmetry of molecules allows the orders of the matrices to be significantly reduced even in the case of low symmetry. To this end, it is sufficient to go from the basis set of the functions $|...SM\rangle$ to the functions $|...\Gamma^{(\alpha)}q_\alpha SM\rangle$, which are transformed by rows q_α of irreducible representations of the $\Gamma^{(\alpha)}$ point group.[39] For instance, in the case of an octanuclear Fe(III) complex [40] of a rather low symmetry (D_2), this passage causes the maximum order of the matrix to reduce from 16 576 down to 4170. This means that the required computer memory and the diagonalisation time are reduced by a factor of nearly 16.[41]

c. Cyclic clusters and linear chains

There is a large family of n-nuclear cyclic clusters, for which the Heisenberg spin Hamiltonian has the form

$$\widehat{H} = -2J\sum_i \boldsymbol{S}_i\boldsymbol{S}_{i+1},\ n+1 \equiv 1 \tag{25}$$

The most thoroughly studied uniform chains ($n \to \infty$) have the same spin Hamiltonian.

The J- and S-alternating chains with the spin Hamiltonian

$$\widehat{H} = -2J\sum_i \boldsymbol{S}_{2i}(\boldsymbol{S}_{2i-1} + \alpha\boldsymbol{S}_{2i+1}) \tag{26a}$$

(α is the alternation constant) and

$$\widehat{H} = -2J\sum_i \boldsymbol{S}_{2i}(\boldsymbol{s}_{2i-1} + \boldsymbol{s}_{2i+1}),\ s \neq S, \tag{26b}$$

($\boldsymbol{S}$ and $\boldsymbol{s}$ are the spins in the alternated chain), respectively, have also been studied.

There is an analogy between cyclic clusters and linear chains. In both cases, the spin Hamiltonians depend on the single parameter, $-2J$, so the theoretical curves once calculated can be then used for all chains of a given type. Besides, cyclic clusters and linear chains possess a translational symmetry, which corresponds to periodic boundary conditions $n + 1 \equiv 1$.

It should be noted that the magnetic properties of chains and other infinite systems are described using the quantity χ'_a [see Eqn (12)], because χ'_m is not defined in these cases.

In spite of considerable interest in linear chains as candidates for molecular magnets [19, 22–25] and models of superconducting cuprates,[42] there are few calculations of the magnetic properties of linear chains.

Numerical calculations of uniform chains with $S_i = 1/2$ and $n \leqslant 11$ were reported.[43] The possibility of approximation of infinite chains using finite ones was first demonstrated, the quality of approximation being significantly improved when using periodic boundary conditions. The effect of the chain length on the energy spectrum was first reported by Tsukerblat *et al.*[44] and on the magnetic properties by Hatfield *et al.*[38] Studies [45–48] in which exact numerical solutions of functions $\chi'_a(T)$ for antiferromagnetic and ferromagnetic chains with $S_i = 1/2$ were obtained deserve particular attention. The $\chi'_a(T)$ plots for uniform chains with $S_i = 1$ were reported.[49] Theoretical dependences $\chi'_a(T)$ were also obtained for all S_i values ranging from 1/2 to 7/2 obtained by the high-temperature expansion method [50] and in the classical spin approximation.[51] A review [52] provides a comprehensive consideration of theoretical results for uniform and J-alternated chains with $S_i = 1/2$. Based on these results, one can no longer use the popular theoretical Weng curves[53] the plotting of which is based on rather rough assumptions.[54]

The results of numerical calculations [17, 55–57] of J-alternated chains with $S_i = 1/2$ and 1 were presented in the form of fractional rational functions. For $S_i = 1$, the $\chi'_a = f(\alpha, J, T/J)$ plots were reported.[58] These calculations were performed for finite cycles; however, the results obtained must also correctly describe the magnetism of infinite chains, because the $\chi'_a(T, n)$ curves rapidly match the limiting $\chi'_a(T, n \to \infty)$ curves at $\alpha \neq 1$.[59]

The results of magnetic susceptibility calculations for S-alternated chains with $s_{2i} = 1/2$ and $S_{2i+1} \leqslant 5/2$ were briefly outlined.[60, 61] The case for $s_{2i} = 1/2$ and $S_{2i+1} = 5/2$ has been studied in more detail.[62] Analytical solutions for the systems with $s_{2i} \ll S_{2i+1}$ and the parameters S_{2i+1} approximated by classical spins were also reported.[18, 63]

The limited number of theoretical $\chi'_a(T)$ curves for cyclic and quasi-one-dimensional systems is to a great extent due to the little amount of attention paid to the possibilities of symmetrisation of the basis set. In particular, for a real cyclic cluster Fe_{10} (see Ref. 64) on going from the complete basis set to the $|...SM\rangle$-representation and then to the $|...\Gamma^{(\alpha)}q_\alpha SM\rangle$ functions symmetrised in the C_{10v} group, the maximum order of the secular equation is reduced from 60 466 176 to 484 155 and then down to 48 480, which seems to be quite acceptable for being solved with modern computers.

4. Non-Heisenberg exchange

Higher-order isotropic exchange operators in Eqn (6) cause insignificant modification of the intervals between the spin levels. They have little effect on the magnetic properties, the more so if the parameters $J_\gamma^{(k)}$ are small.[14, 20] Because of this, we will not dwell on them.

a. Antisymmetric exchange

The notion of antisymmetric (AS) exchange, $\sum \boldsymbol{G}_{ij}(\boldsymbol{S}_i \times \boldsymbol{S}_j)$, was phenomenologically introduced by Dzyaloshinskii.[65] The energy,

$$|\boldsymbol{G}| \sim \frac{J(g-2)}{2}$$

of this interaction estimated by Moria [66] was found to be relatively low. However, if isotropic exchange favours alignment of spins or their antiparallel orientation, the AS exchange favours a perpendicular alignment of spins. In crystals, this leads to formation of non-collinear magnetic structures, which was called 'weak ferromagnetism',[2,65] and in clusters, to manifestation of nontrivial magnetic and spectroscopic properties.[14] Magnetic measurements [67] carried out using a specially synthesised trinuclear complex of divalent copper seem to remain the most reliable confirmation of the Moria estimate as yet.

b. Anisotropic exchange. Molecular magnetic memory effect

If Z is the molecular axis of light magnetisation, the major contribution to the operator of anisotropic exchange has the form $D\boldsymbol{S}_Z^2$ (see Ref. 68). Because of this, in the magnetic field $H \parallel Z$ for any (in particular, for the lowest well separated level $|S\rangle$) the solution to the spin Hamiltonian has the form:

$$E = DM^2 - g\mu_B HM, \tag{27}$$

where $M = S, S-1, \ldots, -S$; $g \sim -g_e > 0$.

Consider the behaviour of the lowest energy level $|S\rangle$ of such a system with $D < 0$ in the magnetic field (Fig. 2 *a*). Application of an external $H > 0$ followed by slow reduction of temperature will make only the lowest level $M = -S$ populated. Let us reduce the field H down to zero. From Fig. 2 *a* it can be seen that at $H \to 0$ the levels $M = -S$ and $M = S$ become degenerate. However, no instantaneous equalisation of the level populations will occur because the transition $|-M\rangle \to |M\rangle$ is forbidden for $H \parallel Z$.[68] Hence, at $H = 0$ the system under study will retain its magnetisation corresponding to $M = -S$. This is the essence of the molecular magnetic memory effect.

An increase in the ground-state spin S is accompanied by an increase in the energy difference, $\Delta M = 2S$, between the two lowest-lying levels, a decrease in the transition probability between them and, hence, a slowing down of relaxation of the magnetisation.

Another mechanism of relaxation of the magnetisation involves successive thermal population of higher levels. The nearest of them, $|M = \pm(S-1)\rangle$, is separated from the ground-state energy level $|M = \pm S\rangle$ by an interval of $D(-2S+1)$. Therefore, slowing down relaxation of the magnetisation favours an increase in not only S but also $|D|$. Complete thermalisation of the system corresponds to the overcoming of the barrier between M_{max} and M_{min}

$$\Delta E \approx |D|S^2 ,$$

which confirms the conclusion drawn.

At rather large S values, not only the level $M = -S$ but also the levels $M = -S+1$, $-S+2$ can have long lifetimes. The latter levels can be individually populated by selective excitation. Thus, multilevel molecular magnetic memory is possible.

If $D \geqslant 0$, different levels with close M values cross one another at $H \to 0$ (see Fig. 2 *b*), which leads to unavoidable rapid thermalisation and the absence of magnetic memory effect. A similar situation is typical of systems with any D, if the ground state forms a group of spin levels: numerous crossings of the levels with close moments inevitably lead to fast relaxation of the magnetisation.

In all cases, acceleration of relaxation is also favoured by the anisotropic exchange operators of the type $E(\boldsymbol{S}_X^2 - \boldsymbol{S}_Y^2)$, which appear at symmetries lower than axial symmetry.[68]

The anisotropic exchange parameters are combinations of dipole–dipole, pseudodipole and single-ion contributions;[19,68] therefore, their estimates are usually based on experimental data.

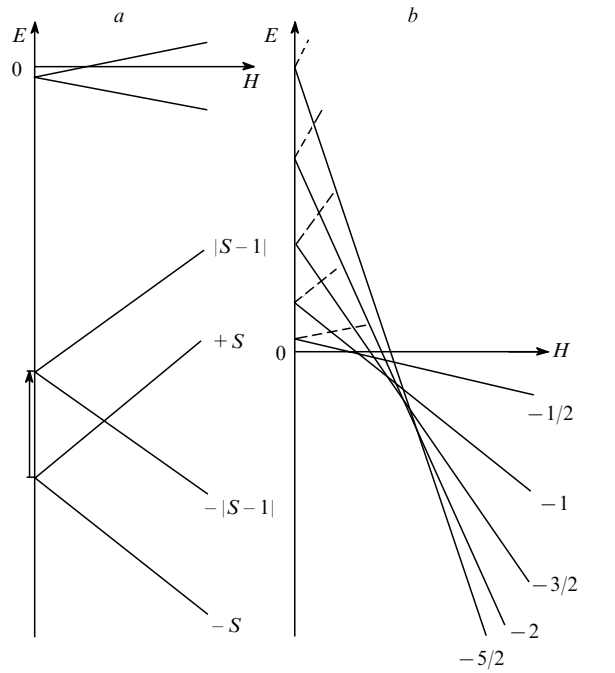


Figure 2. Splitting of the spin level S due to the action of the anisotropic exchange operator $D\boldsymbol{S}_Z^2$ and magnetic field at $D < 0$ (*a*) and $D > 0$ (*b*).

III. Microscopic theory

Targeted synthesis of compounds with predictable magnetic properties (design of molecular magnets) is mainly based on the calculated and experimentally confirmed 'structure–magnetic property' correlations.[15,19–21] Because of this, in this section the emphasis is placed on theoretical description of such correlations, the more so as this problem is somewhat simpler than calculations of numerical values of the exchange parameters.

Microscopic models in modern magnetic chemistry of exchange clusters are based on Anderson's theory of magnetism (see, *e.g.*, Refs 9 and 69). In particular, most models use the magnetic orbital approximation.[19] In essence, this approximation is the same as that used in the ligand field theory,[7,20,21] namely, only those nonbonding and antibonding orbitals are considered, which mainly belong to the metal atoms and can contain unpaired electrons.

1. Natural orbital approximation

The natural orbital approximation is based on the assumption that a polynuclear complex can be represented as a system composed of mononuclear fragments. Quantitatively, the validity of the natural orbital approximation is determined by the possibility of division of the system under study into weakly interacting mononuclear fragments. However, this approximation is convenient for qualitative analysis of exchange effects, because it allows well-known concepts of the ligand field theory [6,7,20,21] to be used.

a. Ferromagnetic and antiferromagnetic exchange

In Anderson's theory, the expression for the parameter of exchange interaction between the unpaired electrons localised in the natural orbitals, Φ_a and Φ_b, of two sites a and b has the form

$$-2J_{12} = -2\langle\Phi_a\Phi_b\left|\frac{e^2}{r_{12}}\right|\Phi_b\Phi_a\rangle - 4\delta\langle\Phi_a|V|\Phi_b\rangle. \tag{28}$$

Here $\langle\Phi_a\Phi_b|\, e^2/r_{12}|\Phi_b\Phi_a\rangle$ is the Coulombic energy of two-electron charge distribution (this energy is always positive; *i.e.*, it corresponds to the ferromagnetic contribution $-2J^f < 0$). In the

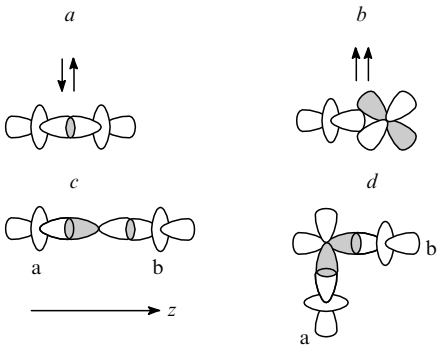


Figure 3. Schemes of direct and indirect electron–electron interactions favouring antiferromagnetism (*a*, *c*) and ferromagnetism (*b*, *d*).

second term δ is the overlap integral $\langle\Phi_a|\Phi_b\rangle$, and $\langle\Phi_a|V|\Phi_b\rangle < 0$ is the matrix element of effective one-electron Hamiltonian V. This term appears only in the case of non-orthogonal orbitals ($\delta \neq 0$). In the Heitler–London scheme, it is responsible for the formation of chemical bonds involving paired electrons. Therefore, $-2J_{12} < 0$ only at $\delta \sim 0$.

The aforesaid serves as the theoretical basis for the well-known Goodenough–Kanamori rules.[9] They can be exemplified in the simplest way by considering a direct interaction between d-orbitals of two neighbouring metal atoms. Figure 3 *a* presents a scheme of the formation of the metal–metal bond involving paired electrons in the case of strong antiferromagnetism. If, from symmetry considerations, $\delta = 0$ (Fig. 3 *b*), the resulting effect is ferromagnetism. A more complicated situation is observed when direct interaction is absent but a bridging ligand L is available. However, this can be simplified by considering that the predominant contribution to the antiferromagnetic exchange is due to the interaction of unpaired electrons on the bridge.[70] Indeed, in this case the natural orbitals (with inclusion of the bridging ligand only) take the form

$$|\Phi\rangle \sim \mathrm{d} + \alpha\varphi_L,$$

where α is the covalency. Figure 3 *c* illustrates the case where the orbital φ_L is common to both centres. Here, one has

$$\delta = \langle\Phi_a|\Phi_b\rangle \sim \langle\alpha\varphi_L|\alpha\varphi_L\rangle = \alpha^2 \neq 0,$$

which corresponds to indirect antiferromagnetic exchange. The case where

$$\delta \sim \langle\Phi_{La}|\Phi_{Lb}\rangle = 0$$

corresponds to indirect ferromagnetic exchange (Fig. 3 *d*).

b. The bond covalency and bond length effects

From the aforesaid it follows that an increase in the bond covalency (α) must cause an increase in the parameter $|-2J|$. Indeed, this holds for compounds with the F^-, O^{2-}, S^{2-} and Se^{2-} bridges.[11]

At long metal–bridging ligand distances (R), the site–site interactions vanish; therefore, the fact that the dependence $|J(R)|$ has a decreasing character is not in doubt. This dependence was revealed[71,72] by analysing experimental data for oxides and fluorides and a quantitative correlation was established

$$-2J \sim R^{-m},\ m = 10-12. \tag{29}$$

c. Angular dependence of superexchange

Using the natural orbital approximation, it is an easy matter to derive an expression for the angular dependence of superexchange on a monatomic ligand.

Let the sites a and b (Fig. 4) contain one unpaired electron in the orbitals d_{z^2}, the lobes of which are directed at the bridging ligand L and overlapped with its valence orbitals s and p. Then,

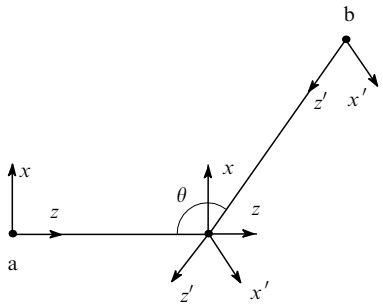


Figure 4. Directions of the local axes in the fragment M–L–M.

the natural orbitals in the local system of coordinates have the form

$$\Phi_a \sim d_{z^2} + \alpha p_z - \beta s, \tag{30a}$$

$$\Phi_b \sim d_{(z')^2} + \alpha p_{z'} - \beta s, \tag{30b}$$

where α and β are the covalency parameters. By substituting relations (30a) and (30b) into (28), we get the expression for the antiferromagnetic contribution with inclusion of the interaction on the ligand only[70]

$$-2J^{af} = -4\alpha^4 V_1 \cos^2\theta - 4\alpha^2\beta^2(V_1 + V_2)\cos\theta - 4\beta^4 V_2. \tag{31}$$

Here

$$V_1 = \langle p_z|V|p_z\rangle < 0,$$

$$V_2 = \langle s|V|s\rangle < 0$$

and it is considered that

$$p_{z'} = p_z\cos\theta - p_x\sin\theta.$$

Since α^2 is nearly an order of magnitude greater than β^2 (see Ref. 73), the major contribution to Eqn (31) comes from the first term at all angles except for the range $\theta \approx 90^\circ$. The presence of the angle independent term causes the minimum of $-2J^{af}$ to be attained at $\theta \approx 95-100^\circ$ rather than $\theta = 90^\circ$.

As for the ferromagnetic contribution, after substituting expressions (30a) and (30b) into the relationship

$$-2J^f = -2\langle\Phi_a\Phi_b\left|\frac{e^2}{r_{12}}\right|\Phi_b\Phi_a\rangle$$

one gets the sum of terms of the same order of magnitude, which only slightly depends on the angle θ. This conclusion was proved by direct numerical estimates (see, *e.g.*, Ref. 74). In addition, usually $|-2J^f| \leqslant -100\ \mathrm{cm}^{-1}$ (see Ref. 19), whereas $-2J^{af}(\theta)$ can take values ranging from 0 to $\sim 2000\ \mathrm{cm}^{-1}$ (see Refs 20 and 75). Thus, to an accuracy of relatively small and nearly constant contribution, the expression (31) provides a correct explanation for the angular dependence of superexchange. Usually, Eqn (31) is used in the parametric form

$$-2J = -2J_1\cos^2\theta - 2J_2\cos\theta - 2J_3, \tag{32}$$

where J_1, J_2 and J_3 are determined from the experimental data, the parameters also including the ferromagnetic contribution. Expression (32) correctly describes the angular dependence of superexchange for a broad class of oxide crystals[76–78] even without considering J_2, though the explanation for subtle effects similar to exchange striction in NiO (see Ref. 79) also requires the inclusion of a linear term.

d. Double exchange and heteronuclear complexes

Compounds containing paramagnetic ions of the same metal in close oxidation states can exhibit the so-called double exchange.[80] Physically, it is due to the fact that the 'extra' electron (or hole) migrates between two equivalent centres and alternately interacts

with the localised spins S_i. This causes the formation of spin levels with energies

$$E(S) = \pm bS, \qquad (33)$$

$$S = 2S_i + \frac{1}{2}, 2S_i - \frac{1}{2}, ..., \frac{1}{2},$$

so that the order of the lowest $2S_i$-levels corresponds to ferromagnetic non-Heisenberg exchange. Uisng the same notations as above, one gets

$$b \sim \alpha^2 V_1 \cos\theta + \beta^2 V_2.$$

Comparison of this expression with Eqn (31) shows that double exchange can result in strong ferromagnetism even in the case of a large antiferromagnetic contribution. This occurs in, *e.g.*, tetra(μ-1,8-naphthyridine-*N*,*N*′)bis(bromonickel)tetraphenyl borate.[81] Double exchange in this mixed-valence Ni(II)/Ni(I)-complex with structure similar to that of copper acetate is so significant that only the lowest level ($S = 3/2$) is populated even at $T \approx 400$ K.

There are only a few systems exhibiting double exchange, because in most mixed-valence complexes the 'extra' electron is trapped by one centre and the centres become inequivalent.[14] This is intrinsic in heteronuclear clusters in which the 'extra' electrons are localised on one centre. This causes the appearance of a ferromagnetic contribution due to transfer of the unpaired electron of one centre to the vacant orbital of the other centre and/or one of the electrons of the filled orbital of one centre to the half-filled orbital of the other centre due to direct or indirect interaction.[10, 11]

An example of the aforesaid is provided by heterobinuclear complex $CuVO(fsa)_2en \cdot CH_3OH$, where $H_4(fsa)_2en$ = *N*,*N*′-bis-(2-hydroxy-3-carboxybenzylidene)-1,2-diaminoethane, in which the Cu^{2+} and VO^{2+} ions are linked *via* an oxygen bridge.[82] The scheme of interaction between magnetic orbitals in this complex is shown in Fig. 5. The orbitals of the unpaired electrons of Cu(II) and vanadium monoxide ($|x^2 - y^2\rangle$ and $|xy\rangle$, respectively) are orthogonal from symmetry considerations; however, the metal atoms are separated by a monatomic oxygen bridge only. This should result in strong Anderson ferromagnetism. At the same time, the unpaired electron can be transferred from the $|x^2 - y^2\rangle$ orbital of Cu(II) to the vacant orbital $|x^2 - y^2\rangle$ of vanadium monoxide and from the filled orbital $|xy\rangle$ of Cu(II) to the half-filled orbital $|xy\rangle$ of vanadium monoxide. In this case, it is hard to determine which mechanism makes the predominant contribution to the experimental value $-2J = -118$ cm^{-1} (see Ref. 82). The exchange parameters in complexes with a linear magnetic fragment Cr(III)–O–Fe(III) were analysed.[83] Such complexes are characterised by shortened M–O bonds, which must favour the transfer mechanism. Nevertheless, no corresponding anomalies in the $-2J$ values were found.

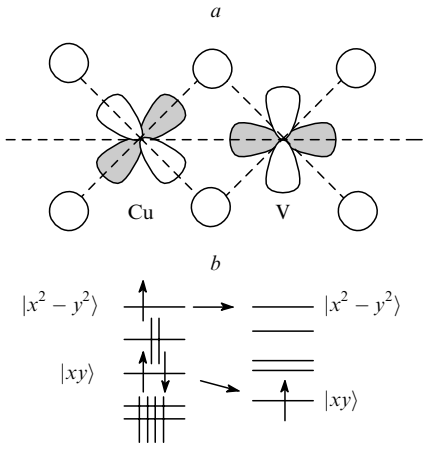


Figure 5. Scheme of interaction between magnetic orbitals in the complex $CuVO(fsa)_2en \cdot CH_3OH$ (*a*) and possible types of electron transfer mechanism (*b*).

2. The Hay – Thibeault – Hoffmann model

Within the molecular orbital (MO) method, more consistent is the Hay – Thibeault – Hoffmann (HTH) model.[84] According to this model, the parameter $-2J$ of homobinuclear complexes is given by

$$-2J = \frac{-2\sum_{ij} J_{ij}^f - \sum_\mu \Delta^2(\mu)/2K_{ab}}{4S_a S_b}. \qquad (34)$$

Here $-2J_{ij}^f$ are the ferromagnetic contributions due to the electrostatic interaction of the unpaired electrons occupying the orbitals $|i\rangle$ and $|j\rangle$ of two centres; the second term is the antiferromagnetic contribution $-2J^{af}$; $2K_{ab}$ = 5–10 eV (see Ref. 84) is the metal–metal charge transfer energy, which is stable for the atoms of the same transition-metal row; and S_a and S_b are the spins of the metal ions.[20] The parameters $\Delta(\mu)$ are the energy differences between the symmetric (s) and antisymmetric (as) MOs composed of combinations of orbitals of the unpaired electrons of the magnetic sites a and b, $\sim (d_\mu^a \pm d_\mu^b)$, and of the ligand orbitals. In Fig. 6, these orbitals and the parameter $\Delta(\mu)$ are shown for the triatomic linear fragment containing three orbitals and four electrons (for simplicity, the non-bridging ligands are not shown).

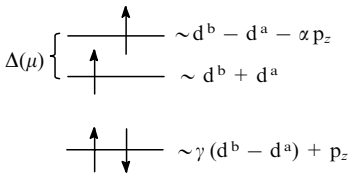


Figure 6. Molecular orbital scheme of the triatomic four-electron fragment.

In the case of a heterobinuclear system, the $-2J^{af}$ values somewhat increase, but the corresponding corrections for the metals of the same row are small.[85]

As shown above, the sign and trends of the changes in the parameter $-2J$ are mainly determined by the antiferromagnetic contribution, which, according to the HTH model, depends on the energy difference between the MOs $d_\mu^a \pm d_\mu^b$ (plus the ligand orbitals). This allows the powerful formalism of the MO method to be employed. For instance, it is convenient to calculate the $\Delta(\mu)$ values using the generalised angular overlap model [21, 86–88] based on the variational perturbation theory.[89]

In the approximation of weak metal–ligand bond covalency, the matrix elements of the effective Hamiltonian for the metal orbitals can be represented as the sum over all *k* ligands [21, 86–88]

$$h_{ij} = \sum_k \sum_{mn} H_m H_n U_{mn}^k \langle i|m\rangle_k \langle j|n\rangle_k, \qquad (35)$$

where the subscripts *i* and *j* label the orbitals of the metal atoms, the subscripts *m* and *n* label the ligand orbitals and $H_{m,n}$ are the ligand orbital energies. The matrices, *U*, of the intraligand interactions can be most conveniently expressed through the inverted matrices

$$U_{mn}^{-1} = \begin{cases} (H_d - H_m - H_n)\langle m|n\rangle, & m \neq n, \\ H_d - H_n, & m = n. \end{cases} \qquad (36)$$

Here H_d are the energies of the atomic d-orbitals. No restrictions are imposed on the number of the metal atoms and on the energy of intraligand interactions. Because of this, expression (35) can be applied to mono- and polynuclear complexes with both monatomic and polyatomic ligands that can be either monodentate or polydentate.

a. Polynuclear compounds with OR (XX′) bridges

An example of efficient use of the HTH model and the generalised model of angular overlap is provided by the theory of exchange interactions for binuclear copper(II) complexes with OR bridges (Fig. 7).

Often, the O – R bonds in complexes with such a geometry are ignored.[19] In this case, one should expect that the angular dependence of superexchange in such complexes is described by relationship (32). However, this is not the case, as shown by the experimental dependence $2J(\theta)$ presented in Fig. 8. As can be seen, this plot is a broken rather than smooth line and obeys the same pattern as the plot $\varphi(\theta)$, where φ is the angle OOC. Such a shape of the $2J(\theta)$ plot can be explained based on the generalised model of angular overlap.

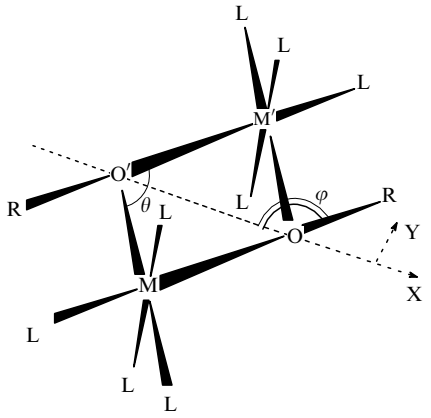


Figure 7. Structure of the central fragment of binuclear complexes with OR bridges (L is any ligand; OR is a carboxylate or alcoholate group).

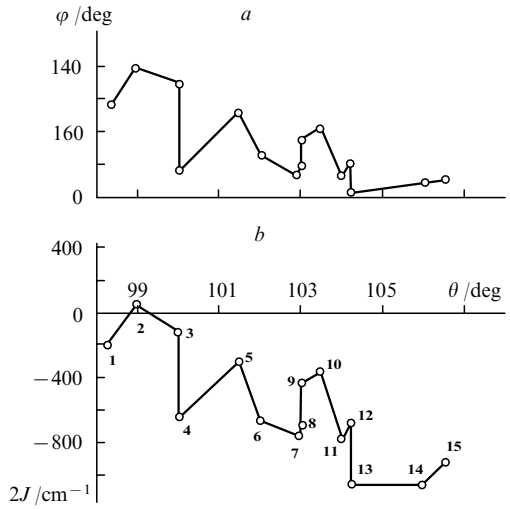


Figure 8. Experimental dependences $\varphi(\theta)$ (*a*) and $2J(\theta)$ (*b*) for binuclear Cu(II) complexes with OR bridges.

Compounds: bis[*N*-picolinoyl-3-aminopropoxidoaqua cuprate(II)] (**1**, see Ref. 90); bis(piperidinium)[di{μ-methoxobis(2,4-dinitrophenolato)-cuprate(II)}] (**2**, see Ref. 91); tetraisothiocyanocuprate(I)-bis{μ-[2-(3-aminopropyl)aminoethanolato]-*N*,*N*′,μ-O}dicopper(II) thiocyanate (**3**, see Ref. 92); $Cu_2(fsa)_2en \cdot CH_3OH$ (**4**, see Ref. 93); (2-diethylaminoethanolato)copper(II) thiocyanate (**5**, see Ref. 94); di-μ-(benzyloxo)-bis[(2,2,6,6-tetramethylheptane-3,5-dionato)copper(II)] (**6**, see Ref. 95); di-μ-methoxo-bis[(2,4,6-trichlorophenolato)(quinoline)copper(II)] (**7**, see Ref. 96); bis[heptanetrionato(2)]bispyridinedicopper(II) (**8**, see Ref. 97); bis[*N*,*N*-bis(2-diethylaminoethyl)-2-hydroxyethylamino-O]dicopper(II) diperchlorate (**9**, see Ref. 98); bis[3-(*N*,*N*-dimethylamino)propyl-2-hydroxyethylamino-O]dimethanoldicopper(II) diperchlorate (**10**, see Ref. 99); bis[*N*-(3-hydroxypropyl)(pyrrol-2-yl)methylideneiminato]dicopper(II) (**11**, see Ref. 100); (2-dipropylaminoethanolato)copper(II) isocyanate (**12**, see Ref. 101); [2-hydroxy-*N*-(3-hydroxypropyl)-α-methylbenzylideneiminato]copper(II) (**13**, see Ref. 102); [2-hydroxy-*N*-(3-hydroxypropyl)-5-nitrobenzylideneiminato]copper(II) (**14**, see Ref. 102) and (5-methyl-7-oxo-4-azaoct-4-enolato)copper(II) (**15**, see Ref. 103).

The complexes in question are comprised of two nearly square mononuclear fragments with the unpaired electrons in the $|x^2 - y^2\rangle$ orbitals. Possible schemes of arrangement of the orbitals of the metal ions, the bridging atom and the substituent are shown in Fig. 9. For simplicity, we will restrict ourselves to analysis of the strongest σ-interactions between these orbitals and the p-orbitals of the bridging O atoms and the σ-bonds O – R.

Figure 9 *c* presents the projection of the geometry of exchange through one bridging ligand on the *XY* plane. The letters a and b denote the lobes of the $|x^2 - y^2\rangle$ orbitals, directed at the bridging ligand; p_1 and p_2 are the in-plane p-orbitals of the bridging O atom, p_3 (not shown) is the orbital p_z; and σ is the σ-orbital of the carbon atom. From symmetry considerations, for the matrix elements of the effective Hamiltonian (35) constructed in the basis set of the orbitals of copper atoms, $|a\rangle$ and $|b\rangle$, one gets $h_{aa} = h_{bb}$ and $\Delta = 2h_{ab}$. To include the second oxygen bridge, this value should be doubled. Finally, according to expression (34),

$$-2J^{af} = \frac{\Delta^2}{2K_{ab}}.$$

Thus, revealing trends of changes in the $-2J^{af}$ values requires only the parameter h_{ab} to be analysed.

Using relationships (35) and (36) and Figs 7, 9 *c*, one can easily show that

$$h_{ab} = A\cos\theta + A\frac{x}{1-x}\cos^2\varphi\cos^2\frac{\theta}{2}. \quad (37)$$

Here

$$A = \frac{H_p^2(\langle d|p\rangle^*)^2}{H_d - H_p},$$

$$x = \frac{(H_d - H_p - H_\sigma)^2(\langle p|\sigma\rangle^*)^2}{(H_d - H_p)(H_d - H_\sigma)};$$

$\langle d|p\rangle^*$ and $\langle p|\sigma\rangle^*$ are the radial components of the overlap integrals for the Cu – O and O – C bonds.

Since $|x| \gg 1$ in the case of interest (strong O – C interaction), one gets

$$h_{ab} \approx A(\cos\theta - \cos^2\varphi\cos^2\frac{\theta}{2}). \quad (38)$$

In addition, $\theta \approx 90^\circ$. Then

$$h_{ab} \approx A\cos^2\varphi\cos^2\frac{\theta}{2}$$

and

$$-2J^{af} \approx \cos^4\varphi\cos^4\frac{\theta}{2}. \quad (39)$$

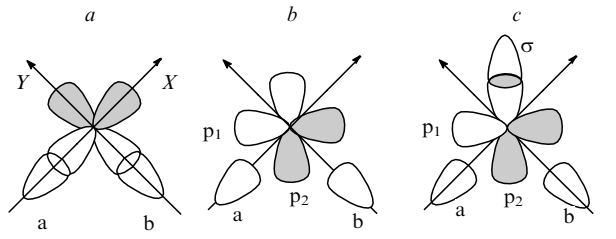


Figure 9. Possible schemes of arrangement of the orbitals of the metal ions (*a*), bridging atom (*b*) and the substituent linked to the bridging atom (projection on the *XY* plane) (*c*).

These relationships point to strong dependence of exchange on the angles M–O–M and O–O–C. In real complexes, variations of the angles θ are small (see Fig. 7) because of steric hindrances. Therefore, the $2J^{af}$ values and, hence, the values

$$-2J = -2J^{f} - 2J^{af},$$

must be primarily determined by the angles O–O–C, which can vary over a wide range (from 180° to 90°). A decrease in the angle between the O–C and the Cu_2O_2 plane favours manifestation of the properties of a strong antiferromagnetic, because $\varphi \approx 180°$ corresponds to the maximum $-J^{af}$ value. On the contrary, deviation of the O–C bond from the Cu_2O_2 plane leads to a dramatic decrease in $-2J^{af}$ and, finally, to ferromagnetic properties. Correlations of the experimental dependences shown in Fig. 8 are in good agreement with these conclusions. The fact that $-2J < 0$ already at $\varphi \approx 140°$ can be explained by a very strong dependence of $-2J^{af}$ on φ.

The results obtained have a clear physical meaning. Figure 9 *a* illustrates a 90° exchange through the monatomic bridge while Fig. 9 *b* differs from it only in that the orbitals p_x and p_y are transformed into the equivalent orbitals p_1 and p_2, respectively (*i.e.*, Fig. 9 *b* corresponds to the same 90° ferromagnetic exchange). This can be understood with ease if one takes into account the fact that the orbital $d_a - d_b$ interacts with the orbital p_1 in exactly the same manner as the orbital $d_a + d_b$ interacts with the orbital p_2. Because of this, $\Delta = 0$ and the system is ferromagnetic. Consider now Fig. 9 *c* drawn with inclusion of the O–C bond. Here, the orbitals $|p_2\rangle$ and $|\sigma\rangle$ form two combinations (a strongly bonding and a strongly antibonding one), which virtually do not interact with the orbitals of the metal atom. Thus, only the overlap between the $d_a - d_b$ and p_1 orbitals remains, which is strong in the whole range of changes in the angle θ, except for the non-physical range $\theta \approx 0°$. As a consequence, $\Delta \neq 0$, thus providing conditions for antiferromagnetism of all complexes with $\varphi \approx 180°$. At $\varphi \approx 90°$, the in-plane p-orbitals of the O atom are no longer overlapped with the carbon σ-orbital. In this case, the exchange geometry corresponds to the interaction through a monatomic bridge (at $\theta \sim 90°$, this interaction is ferromagnetic; see Fig. 9 *a*, *b*). Quantitative description of experimental data for some alcoholates and related compounds (cubanes) was also reported.[86]

According to Eqn (34), the antiferromagnetic contribution (39) is typical of not only Cu(II) complexes but also any other compounds which contain the unpaired electrons in the $|x^2 - y^2\rangle$ orbitals and have appropriate structures (see Fig. 7). In addition, not only the OR bridges but also other $\mu_{1,1}$-coordinated ligands XX′ with strong X–X′ bonds can be involved. Therefore, in the case of similar Ni(II), Mn(II), Mn(III), Fe(II), Fe(III) and Co(II) complexes one should expect manifestation of antiferromagnetic properties at $\varphi \approx 180°$ and ferromagnetic properties at $\varphi \approx 90°$. Numerous examples substantiating the correctness of this conclusion have been reported.[16, 20]

General relationships (37) and (38) allow the limiting cases, *viz.*, transition to monatomic ligands ($x = 0$) and to $\theta = 180°$, to be reproduced correctly. In the latter case, the parameter $-2J$ is independent of the position and even the presence of a substituent. If X–X′ interactions are weak ($|x| \ll 1$), relations (37) and (38) predict a shift of the minimum $-2J^{af}$ value (strongest ferromagnetic properties) from that corresponding to $\theta \approx 90°$. This can be qualitatively explained with ease using Figs. 9 *b*, *c*. Indeed, the lobes of the orbitals p_1 and p_2 (Fig. 9 *b*) have the same amplitudes, thus being responsible for $\Delta = 0$. Hence, $-J^{af} = 0$ at $\theta = 90°$. The interaction $|p_2\rangle - |s\rangle$ (Fig. 9 *c*) changes the amplitude and energy of the orbital p_2. Therefore, to obtain $-2J^{af} = 0$ again, one should change the angle θ. Of course, this can be done if the orbital p_2 is not completely suppressed in the case of strong $|p_2\rangle - |s\rangle$ interaction. This is also in agreement with the experimental data.[104]

Relations (37) and (38) also describe more subtle effects, *e.g.*, a linear dependence $-2J(\theta)$ in dimeric hydroxo-bridged complexes of Cu(II).[105] This required the inclusion of correlation between the angles θ and φ, which was observed experimentally. The reasons for qualitatively different character of the dependences $-2J(\theta)$ in dimeric fragments of oxo- and hydroxo-bridged chromium(III) complexes were established and corresponding quantitative description was obtained using a more complicated theory.[106] Finally, the simple physical nature of the phenomena in question favoured a better insight into the magnetic properties of complexes with more complex ligands.

b. Complexes with bridging ligands N_3^-

Similarly to, *e.g.*, ligands of the OCH_3 type, the bonds in the linear ligands N_3^- are strong. However, high symmetry of the N_3^- ligand leads to quite different structure of energy levels.

The p_y orbitals of this anion are shown in Fig. 10 *a*. As can be seen, the MO $\phi_y(s) \approx p_{y1} + p_{y3}$ is involved in strong π-interaction with the orbital p_{y2}, while the orbital $\phi_y(as) \sim p_{y1} - p_{y3}$ retains its nonbonding character and, hence, can be involved in the interaction with metal atoms. This orbital is schematically shown in Fig. 10 *b*. Clearly, the orbital $\phi_z(as)$ has the same shape. The orbitals p_x are involved in interactions with one another and also with s-orbitals. Therefore, symmetry analysis is insufficient to obtain correct MOs. However, the results of simple calculations using extended Hückel theory [84] showed that, among all orbitals of this type, only the MO $\phi_x(s)$ shown in Fig. 10 *c* has an energy similar to that of the $\phi_{y,z}(as)$ MO. In addition, the amplitudes of the outer lobes of all the three orbitals $\phi_x(as)$, $\phi_z(as)$ and $\phi_y(s)$ are similar.

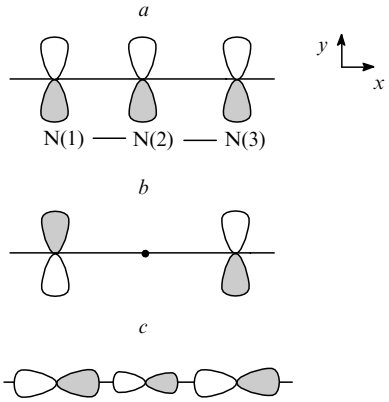


Figure 10. Orbitals of the linear ligand N_3^-;
p_y-orbitals (*a*), nonbonding orbital $\phi_y(as)$ (*b*) and nearly nonbonding orbital $\phi_x(s)$ (*c*).

Let us proceed to interpretation of experimental data. The bridging ligands N_3^- can be coordinated in two fashions. One type of coordination, $\mu_{1,3}$-N_3, is shown in Fig. 11 *a*. The overlap of the orbitals of the $\mu_{1,3}$-N_3 ligand with the lobes of the $|x^2 - y^2\rangle$ orbitals of two Cu(II) atoms, a and b, is schematically presented in Fig. 11 *b*. As can be seen, the combination $d^a - d^b$ is involved in effective interaction with both the $\phi_y(as)$ and $\phi_x(s)$ orbitals, while the orbital $d^a + d^b$ remains nonbonding. This must result in large splitting, $\Delta(x^2 - y^2)$, between them and in strong antiferromagnetism [see Eqn (34)].

Indeed, all the known Cu(II) complexes with the structure in question possess nearly diamagnetic (or weakly paramagnetic) properties.[19, 107] Similar complexes of nickel(II) and manganese(II) also contain unpaired electrons in the orbitals $|x^2 - y^2\rangle$; as a consequence, they also exhibit strong antiferromagnetic properties.[108]

The structure of complexes with $\mu_{1,1}$-N_3 bridges is shown in Fig. 12 *a*. The overlap of the orbitals of the $\mu_{1,1}$-N_3 ligand with the

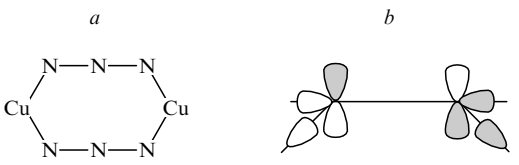


Figure 11. Structure (*a*) and orbital overlap scheme (*b*) for binuclear Cu(II) complexes with $\mu_{1,3}$-bridging ligands N_3^-.

lobes of the orbitals $|x^2 - y^2\rangle$ of two Cu(II) atoms (a and b) is illustrated in Fig 12 *b*. Visually, this scheme is similar to that of the overlap with orbitals of the monatomic ligand (see Fig. 9 *b*). They are also similar in essence, because we have shown that the energies and amplitudes of the orbitals ϕ_x(as) and ϕ_y(s) are also similar (see above). Hence, one should expect that at Cu—N—Cu angles $\approx 90^\circ$ copper(II) complexes with $\mu_{1,1}$-N_3 bridges manifest strong ferromagnetic properties similarly to the complexes with monatomic ligands.

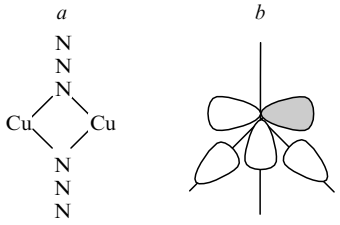


Figure 12. Structure (*a*) and orbital overlap scheme (*b*) for binuclear Cu(II) complexes with $\mu_{1,1}$-bridging ligands N_3^-.

Indeed, all Cu(II) complexes of this type are ferromagnetic (provided there are no significant structural distortions) and the $-2J$ value can be as high as ~ -200 cm^{-1} (see Refs 74 and 109).

Similar nickel(II) complexes also possess ferromagnetic properties,[108] because they also contain the unpaired electrons in the $|x^2 - y^2\rangle$ orbitals. Besides, nickel(II) complexes also contain the unpaired electrons in the $|z^2\rangle$ orbitals, for which the conditions for the overlap with the in-plane orbitals of bridging ligands at $\approx 90^\circ$ are much like those for the $|x^2 - y^2\rangle$ orbitals. It should be emphasised that, in addition to the high ground-state spin, these nickel(II) complexes are characterised by large (in absolute value) parameters D (-10 to -20 cm^{-1}, see Refs 110–112). Therefore, such complexes are of particular interest for design of molecular magnets.

Potentially, the N_3^- ligand is a bisbidentate one (see Figs 11 and 12). Therefore, it is convenient for the synthesis of polynuclear complexes and even multidimensional structures. To date, some advances have been achieved in this field.[26]

It is an easy matter to find out that a symmetric system with an odd number of ligand orbitals always contains a nonbonding orbital which can be involved in efficient interaction with the orbitals of the metal atoms. Because of this, such ligands are rather promising for creating a strong exchange at long metal–metal distances. Indeed, a Cu(II) complex characterised by an exchange parameter, $-2J$, of 26 cm^{-1} at a metal–metal separation of about 7.6 Å was synthesised.[113] This is four to five orders of magnitude greater than the value predicted by expression (29). At the same time, it is not surprising because the shortest way of metal–metal exchange is a pentaatomic symmetric chain.[113]

c. 'Parallel' and 'antiparallel' coordination

According to Eqn (35), an increase in the number of identical, symmetrically coordinated bridging ligands must cause the splitting Δ to increase. In the case of heteroligand complexes, the situation can change. Consider a model system without writing expressions for particular cases.

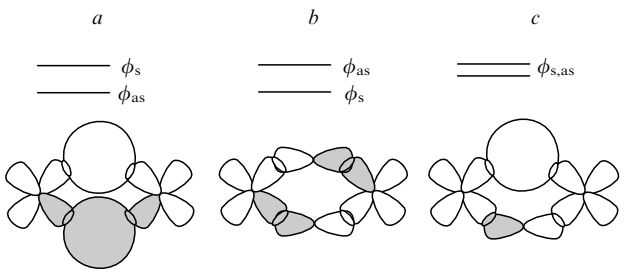


Figure 13. Parallel (*a*, *b*) and antiparallel (*c*) coordination of the bridging ligands.

Figure 13 *a*,*b* presents the schemes of the interaction between the bridging ligands through the s- and p-orbitals. In both cases, the ligands contribute to $\Delta(x^2-y^2)$ in an identical manner (*i.e.*, their action is mutually strengthened):

$$\Delta_s \approx \Delta_{s1} + \Delta_{s2};$$

$$\Delta_p \approx \Delta_{p1} + \Delta_{p2}.$$

Due to different symmetry of the s- and p-orbitals, the high-lying combinations are symmetric (Fig. 13 *a*) and antisymmetric ones (Fig. 13 *b*). Both cases must lead to manifestation of strong antiferromagnetic properties, because Eqn (34) contains a term proportional to Δ^2. However, for a heteroligand complex (Fig. 13 *c*) the different signs of Δ_s and Δ_p lead to

$$|\Delta_{sp}| \approx |\Delta_{s1}| - |\Delta_{p2}|.$$

Therefore, 'antiparallelism' of these contributions should lead to a decrease in Δ even with respect to Δ_{s1} and Δ_{p2}. It is 'antiparallelism' of the contributions that provides an explanation for unexpectedly weak antiferromagnetic properties of a large number of heteroligand complexes (see, *e.g.*, Ref. 114).

In principle, Δ_{sp} can be nearly equal to zero. This is the only reason for ferromagnetic properties of Ni(II) complexes of low symmetry, in which the metal atoms are linked through monatomic, triatomic (OH_2) and polyatomic (*e.g.*, OOCMe)[115,116] ligands with different node structure of the σ-orbitals.

d. Heterocyclic and other complex bridging ligands

Until now, we have considered complexes with relatively simple ligands that have a clear orbital structure. In complex ligands, the orbital lobes can be oriented in different ways and simple formulae for the angular dependence of superexchange are no longer valid.

Using EHT,[84] it was shown that in binuclear complexes of Cu(II) with imidazole (Fig. 14 *a*) the largest contribution to exchange comes from the symmetric and antisymmetric ligand orbitals (Fig. 14 *b*).[117] The strongest ferromagnetic properties should be observed at a Cu—N—N angle of about 158° (see Ref. 117), which nearly corresponds to the bisectrix of the angles between the lobes of the symmetric and antisymmetric ligand orbitals. This is not surprising because of the similar amplitudes and energies of these orbitals.

Expression (35) permits the contributions of these and even more complex ligands to be included by simply inverting the matrices $||\boldsymbol{U}^{-1}||$ [see relation (36)]. This allows one to obtain results in the analytical form, which is convenient for revealing various trends. However, in the case of polyatomic ligands of low symmetry, such an inversion will result in complicated multiparameter expressions, which can hardly be analysed. Therefore, it is more appropriate to analyse complexes with such ligands using a compromise approach, which involves calculations of the electronic structures of the ligands using quantum chemistry methods followed by substitution of the results obtained into expression (35).

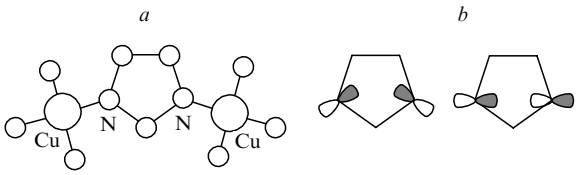


Figure 14. Structure of imidazole-bridged binuclear Cu(II) complexes (*a*) and the imidazole orbitals involved in effective interaction with the orbitals of unpaired electrons (*b*).

3. The model of exchange channels

In the case of multielectron metal atoms, the parameter $-2J$ is determined by the sum of the contributions over all pairs of half-filled orbitals [see Eqn (34)]. This strongly complicates analysis and/or the trends in manifestation of exchange interactions, especially if there is no predominant contribution. The model of exchange channels [118] allows one to eliminate these problems.

Expression (34) can be re-written in more compact form:

$$-2J = \sum_{ij} \frac{-2J_{ij}}{4S_a S_b} = \frac{-2J_\Sigma}{4S_a S_b}. \qquad (40)$$

From relation (34) it can be seen that the parameters $-2J_{ij}$ are independent of the degrees of orbital filling if the orbitals differ from $|i\rangle$ and $|j\rangle$. Therefore, pairs of one-electron orbitals of the sites a and b form specific channels of exchange interaction. The denominator, $4S_aS_b$, is the number of such interaction channels. Among the series of isostructural compounds containing paramagnetic ions of metals of the same row in similar oxidation states, variations of the number of electrons should not cause significant changes in the electronic structure parameters that appear in relationship (34). This suggests transferability of the contributions of the corresponding exchange channels in the series of isostructural systems. Transferability permits the parameters $-2J_{ij}$ to be 'calibrated' against the known experimental data and then used for predicting the magnetic properties of other systems belonging to the given isostructural series.

Let us re-write expression (40) as follows

$$-2J_\Sigma = \sum_{ij}(-2J_{ij}) = -2J4S_aS_b. \qquad (41)$$

The parameter $-2J_\Sigma$ is spin independent. It is determined only by the contributions of the exchange channels. Because of this, physically, this is the exchange energy, which is a convenient parameter for analysing the changes in the mechanisms of exchange interactions upon replacement of paramagnetic ions.[119]

Consider some binuclear carboxylates $[LM(COOR)_2]_2$, where M = Ti^{3+}, V^{3+}, Mn^{2+}, Ni^{2+} and Cu^{2+} (for M = Ti^{3+} and V^{3+}, L = Cp^- only).[120–123] These complexes have a rigid structure similar to that of copper acetate monohydrate (Fig. 15) and possess the properties of strong antiferromagnetics due to indirect exchange through OC(O) bridges.

Table 1 lists the half-filled orbitals, the $-2J$ values averaged over a large number of compounds with different R and L as well as the $-2J_\Sigma$ values.

Taking into account the maximum overlap, it is clear that the most effective interaction channels are due to superexchange between the σ-orbitals ($d_{x^2-y^2}$, $-2J_{vv}$) and π-orbitals (d_{xy}, $-2J_{\xi\xi}$) through the OC(O) bridges.

It is an easy matter to find out that pronounced variations of the parameter $-2J$ on going from one metal to another can be explained using the model of exchange channels.

Indeed, among four channels ($d_{xy}-d_{xy}$, $d_{xy}-d_{z^2}$, $d_{z^2}-d_{xy}$ and $d_{z^2}-d_{z^2}$) in the V^{3+} complexes, only the $d_{xy}-d_{xy}$ channel is effective. According to Eqn (41), in this case we get

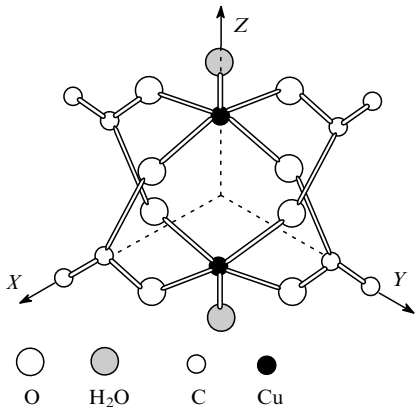


Figure 15. Structure of Cu(II) acetate monohydrate.

Table 1. Magnetic parameters of binuclear carboxylates.

Ion	Half-filled orbitals	$-2J$/cm^{-1}	$-2J_\Sigma$/cm^{-1}
Ti^{3+}	d_{xy}	1000±200	1000±200
V^{3+}	d_{xy}, d_{z^2}	280±40	1120±150
Mn^{2+}	d_{xy}, d_{z^2}, $d_{x^2-y^2}$, d_{xz}, d_{yz}	30±4	750±100
Ni^{2+}	d_{xy}, $d_{x^2-y^2}$	300±20	1200±80
Cu^{2+}	$d_{x^2-y^2}$	340±50	340±50

$$-2J_\Sigma = -2J(V^{3+}) \times 4 \times 1 \times 1 \approx -2J_{\xi\xi} \approx -2J(Ti^{3+}) = 1000\ \text{cm}^{-1},$$

which is in good agreement with the experimental data. Similarly, for Ni^{2+} dimers one gets

$$-2J_\Sigma \approx -2J_{\xi\xi} - 2J_{vv} \approx -2J(Ti^{3+}) - 2J(Cu^{2+}) \approx 1300\ \text{cm}^{-1},$$

which coincides with the experimental value within the limits of experimental error. In the case of Mn(II) complexes, agreement is somewhat worse due to ignoring a total of twenty small ferromagnetic cross-contributions $-2J_{ij}^f$.

Many other examples are also available.[124–127] Based on the model of interaction channels, the $-2J$ values for ten systems were estimated to a high accuracy using only a set of three calibration parameters.[125–127]

4. Antiferromagnetics with metal – metal bonds

Until recently, it was accepted that compounds with metal – metal bonds can possess only trivial magnetic properties, *viz*., be diamagnetic or paramagnetic at an even or odd number of electrons, respectively (see Ref. 128 and references cited therein). However, chromium(III) cyclopentadienylchalcogenates (Fig. 16) have strained structures [129–131] indicating the presence of metal – metal bonds but possess antiferromagnetic properties ($-2J \sim 400$ cm^{-1}, which is typical of the systems with 'through-ligand' exchange).

Using the model of exchange channels, one can also determine the conditions for this class of magnetic materials to exist. Indeed, for the magnetic moment of an antiferromagnetic complex to be temperature dependent at not too high temperatures, at least the first excited state should be populated. This leads to the requirement

$$-2J = \frac{-2J_\Sigma}{4S_aS_b} < 1000\ \text{cm}^{-1}, \qquad (42)$$

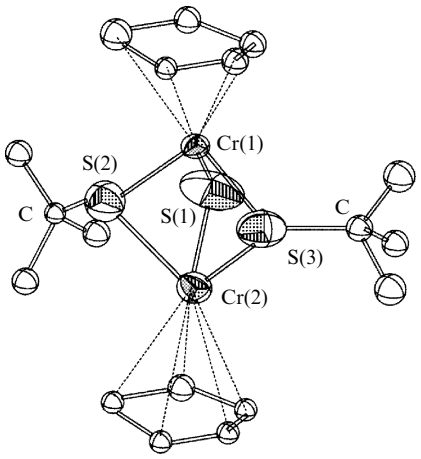


Figure 16. Structure of $(\pi\text{-}C_5H_5)_2Cr_2(\mu\text{-}S)(\mu\text{-}SCMe_3)_2$.[129]

i.e., $-2J < 1000 \times 4S_aS_b$. From this it follows that the large value of the parameter $-2J_\Sigma$, which is due to the presence of the metal–metal bond, does not necessarily cause diamagnetic properties to be possessed at rather large values of the product $4S_aS_b$. The chromium(III) complexes under consideration ($S_i = 3/2$) meet this condition.

This approach allowed compounds with metal–metal bonds to be found among double chlorides of composition $AMCl_3$.[132]

At the same time, there are strong grounds to believe that if the major contribution to the exchange is due to the formation of the metal–metal bond $d_\eta^a - d_\eta^b$, the largest contribution in expression (34) comes from the second term. Therefore, the energy difference, $\Delta(\eta)$, between the antibonding and bonding MOs is given by [133]

$$\Delta(\eta) \approx \sqrt{-2J \cdot 4S_aS_b \cdot 2K_{ab}}. \quad (43)$$

This value is a natural measure of the binding energy, which can be estimated with ease, because relationship (43) contains some known or readily measurable parameters. It should be emphasised that attempts to reveal weak metal–metal bonds using other experimental or theoretical methods face great difficulties.

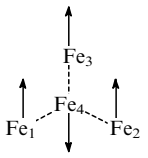
IV. Design of molecular magnets

The term 'design of molecular magnets' was introduced to denote targeted synthesis and studies of compounds built of molecular blocks and containing unpaired electrons involved in some interactions. This is a very broad field of research. In this review, molecular magnets mean polynuclear complexes which have high spins of the low levels and, hence, high magnetic moments. This bridges the gap between molecular magnets and conventional magnetic materials.

As mentioned above, high magnetic moments due to ferromagnetism can be expected in the case of specific geometry of the bridging groups, different symmetry of the magnetic orbitals and mixed valence of the complex-forming metal. However, the first two cases can hardly be implemented in practice in a predictable manner, while the mixed-valence systems (in addition) tend to be transformed into heterovalent weak ferromagnetic complexes. At the same time, the conditions for occurrence of strong antiferromagnetism are much simpler. This is often employed in various methods of attaining high magnetic moments.

1. Tetranuclear complexes

A typical example of tetranuclear complexes is provided by a trivalent iron complex (Fe_4^{III}), which was synthesised and studied recently.[64, 134] The structure of this complex is shown in Fig. 1 *b*. The interactions between the central and peripheral iron atoms occur through pairs of methoxo bridges and have an antiferromagnetic character ($-2J_{1234} = 21.1$ cm^{-1}). However, this causes no diamagnetism and the ground-state spin, S, equals five. At first glance, this is a quite unexpected result, but this is not the case [it is sufficient to simply substitute $S_i = 5/2$ and $-2J_{1234} > 0$ ($-2J_{123} \sim 0$) into relation (21)]. However, there is also a simple qualitative substantiation of this result. Indeed, antiferromagnetic interaction between the central and peripheral Fe atoms leads to antiparallel orientation of the spins of the latter with respect to the spin of the former atom and, hence, their alignment.



Thus, we get $S = 3 \times 5/2 - 5/2 = 5$. The cluster under study is characterised by a rather large D value (-0.2 cm^{-1}) and therefore exhibits a magnetic memory effect (see Section II.4.b), which, however, is observed only at $T \leqslant 1$ K due to the relatively small S and $|D|$ values.[134]

The magnetic properties of a series of complexes with the $[Mn_4(\mu_3\text{-}O)(\mu_3\text{-}X)]^{6+}$ core and a structure similar to that of a distorted cubane, which resembles the structure shown in Fig. 1 *b*, were studied.[135–137] Since the atoms of the magnetic core, $Mn^{IV}Mn_3^{III}$, are in different oxidation states, antiferromagnetic exchange Mn(IV)–Mn(III) results in $S = 9/2$ and a spin alignment similarly to the case of complex Fe_4^{III}. For all complexes of this type the parameter D is negative (more exactly, -0.3 to -0.5 cm^{-1}); therefore, they exhibit a magnetic memory effect at $T \leqslant 1$ K similarly to Fe_4^{III}.

In a 'butterfly'-like $Mn_2^{II}Mn_2^{III}$ complex the central Mn(III) ions are linked through two O atoms of methanolic groups while their interaction with the terminal Mn(II) atoms occurs through the same oxygen and bidentate acetate bridges. All the Mn–Mn exchange interactions have a ferromagnetic character;[138] as a consequence, $S = 9$. In combination with the value of the parameter D (-0.32 cm^{-1}) this leads to a relatively high activation energy for relaxation of the magnetisation (~ 12 cm^{-1}). In the dehydrated form of the complex $Mn_2^{II}Mn_2^{III}$, antiferromagnetic exchange through the solvent molecules leads to a decrease in S down to 8, the anisotropic exchange also weakens ($D \approx -0.25$ cm^{-1}) and the activation barrier decreases.

A similar complex V_4^{III} is characterised by the $-2J_{12}$ and $-2J_{13}$ values of -31.2 and 27.5 cm^{-1}, respectively (see Ref. 139). The competition between ferromagnetic and antiferromagnetic exchange causes the total spin ($S = 3$) to become smaller than the sum of the spins $S_{max} = 4$. Because of this, the activation barrier is at most 1.5 cm^{-1}. Complexes of Cr_4^{III}, Mn_4^{III} and Fe_4^{III} (analogues of the vanadium complex in question) also have low ground-state spins.[139]

2. Complex Fe_8

A Fe(III) complex with the central fragment $[Fe_8(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_{12}]^{8+}$ (see Ref. 140) is usually denoted as Fe_8. It has a D_2 symmetry (Fig. 17), which allows the full matrix of the secular determinant of dimension 1 679 616 to be divided into blocks of dimension $\leqslant 4170$ (see Section II.3.b). Exact numerical calculations of the magnetic susceptibility were carried out and the exchange parameters were estimated.[40] All interactions in the Fe_8 complex have antiferromagnetic character; nevertheless, the ground state has a spin S of 9. The anisotropic exchange parameter D equals -0.19 cm^{-1} (see Refs 141 and 142); therefore, at $T \leqslant 1$ K the complex exhibits a marked hysteresis of the magnetisation and the activation barrier to relaxation of the magnetisation is rather high (~ 17 cm^{-1}, see Ref. 40).

3. Complexes Mn_{12}

A typical representative of Mn_{12} complexes is $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4] \cdot 2\,MeCOOH \cdot 4\,H_2O$ (R = Me) [143]

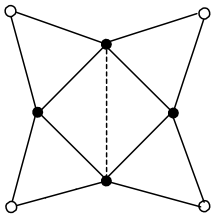


Figure 17. Structure of complex Fe_8.

with a tetragonal structure (Fig. 18). Even full inclusion of symmetry considerations provides no possibility of division of a total of 10^8 basic states into blocks of admissible size for computer calculations. However, the exchange parameters were estimated by comparing the calculated positions of several low levels with experimental data (see the caption to Fig. 18).[144] This complex is characterised by $S = 10$ and $D = -0.4\ cm^{-1}$; therefore, the activation barrier to relaxation of the magnetisation reaches a value of 49 cm^{-1} (see Refs 145 and 146). Complex Mn_{12} has a higher symmetry (C_4) than complex Fe_8 so the anisotropic exchange parameters of the type $C(S_+^4 + S_-^4)$ make a much smaller contribution. It is these operators that make the $|S, M\rangle \rightarrow |S', M'\rangle$ transitions allowed; therefore, it is not surprising that at 2 K the Mn_{12} complexes retain their magnetisation for a period of several months.[147]

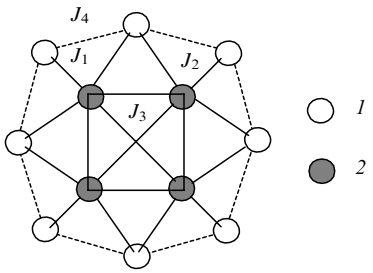


Figure 18. Structure of Mn_{12} complexes.
Mn(III) atoms with a spin of 2 (*1*) and Mn(IV) atoms with a spin of 3/2 (*2*). The exchange parameters are as follows: $-2J_1 = 150\ cm^{-1}$, $-2J_2 \simeq -2J_3 = 60\ cm^{-1}$ and $-2J_4 = -45\ cm^{-1}$.

Generally, the outer-sphere ligands have little effect on the magnetic properties of Mn_{12} complexes. However, replacement of bidentate bridging ligands O_2CMe by O_2CEt results in a decrease in S down to 9, while the one-electron reduction of acetate is accompanied by the transformation of $Mn_8^{III}Mn_4^{IV}$ into $Mn^{II}Mn_7^{III}Mn_4^{IV}$ and by an increase in S to 19/2.[148] These and a number of other substituted complexes are also characterised by slow relaxation of the magnetisation.[149]

4. Complex Fe_{13}

The first thirteen-nuclear complex of trivalent iron is $(C_5H_6N^+)_5[Fe_{13}(\mu_4\text{-}O)_4(\mu_2\text{-}OMe)_{12}F_{24}]MeOH \cdot 4\,H_2O$.[150] Its structure comprises four triangular $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}OMe)_3]$ subunits linked to the central tetrahedral FeO_4 moiety *via* monatomic oxygen bridges. The structure of this complex is schematically shown in Fig. 19. Ignoring weak exchange through fluorine bridges, the four triangular subunits can be considered non-interacting. In this case, the theorem (see Section II.3.a) can be applied to this complex. This permits analytical calculations of the energies of all $\sim 1.3 \times 10^{10}$ spin levels of the system and plotting of the theoretical curves of the temperature dependence of the magnetic susceptibility. Interpretation of experimental data (obtained in the temperature range 2–300 K) in the framework

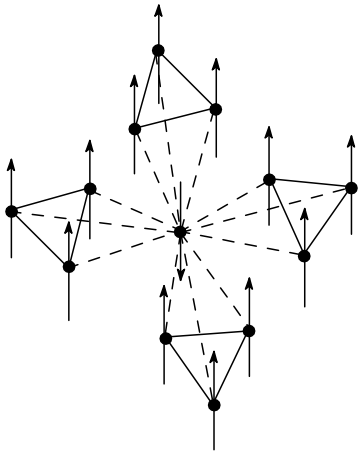


Figure 19. Structure of complex Fe_{13}.

of this theory showed that interactions within the triangular subunits and with the central iron atom are characterised by the exchange parameters $-2J_{12} = 30\ cm^{-1}$ and $-2J_{13} = 43\ cm^{-1}$, respectively.[151] In spite of the antiferromagnetic character of all interactions, the ground state has a nonzero spin. The high ground-state spin is due to the interaction between the central and peripheral atoms, which tends to align the spins of the latter (see Fig. 19). Unlike the Fe_4 complex, in the compound Fe_{13} due to the competing interactions within the triangular subunits the highest possible spin $S_{max} = 12 \times 5/2 - 5/2 = 55/2$ is not reached. However, calculations showed that the ground-state spin can increase up to 31/2 and even more with an increase in the J_{13}/J_{12} ratio from ~ 0.7 to ~ 1. In practice, this can be attained by, *e.g.*, replacing the μ_4-O bridging ligands by some ligands with enhanced electron-donor ability.

5. *n*-Nuclear complexes with $n > 13$

Currently, the problem of synthesis of polynuclear complexes containing a prescribed number of magnetic metal atoms is still far from being solved. However, methods of synthesis of such complexes are rapidly developing. In particular, crystals containing alternating complexes of trivalent iron $[Fe_{19}(\mu_3\text{-}O)_6(\mu_3\text{-}OH)_6.(\mu_2\text{-}OH)_8L_{10}(H_2O)_{12}]^+$ (Fe_{19}) and $[Fe_{17}(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_6.(\mu_2\text{-}OH)_{10}L_8(H_2O)_{12}]^{3+}$ (Fe_{17}), where $H_3L = N(CHRCOOH)_2.(CH_2CH_2OH)$, R = H, were synthesised and studied.[152] Both complexes have flattened compact structures (Fig. 20) and can be considered as a result of further complication of the structures of complexes Fe_8 and Mn_{12}. Experimental data showed that at least one of the two complexes has a ground-state spin, S, of 33/2. Complexes of Fe_{19} with R = Et and Me characterised by $S = 31/1 - 33/2$ and $S = 33/2$, respectively, were synthesised.[153] Currently, they have the highest ground-state spins. However, the magnetic memory effects in these complexes are weak because the parameter D of the complex with R = Me equals only $-0.035\ cm^{-1}$.

Attainment of large negative D values is likely a common problem to studies of the systems comprising only metal atoms in the S-states. Indeed, in this case the single-ion contribution to D is small [68] while the exchange is nearly isotropic. Only the dipole–dipole contribution can be large, provided that all the metal–metal bond axes are nearly parallel. Clearly, this is not probable for compact polynuclear molecules. For the same reason, strong magnetic memory effects are also not probable in the high-spin systems containing organic radicals.[154]

Experimental data for a large number of other polynuclear complexes and their theoretical interpretation can be found in the literature.[22–25, 154]

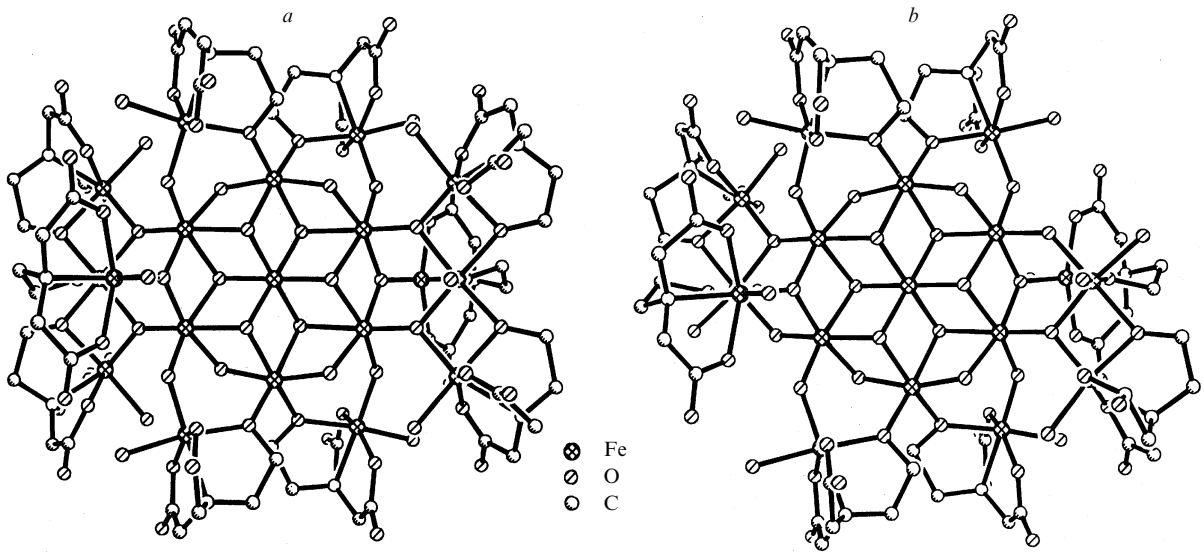


Figure 20. Structures of complexes $[Fe_{19}(\mu_3\text{-}O)_6(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_8(L)_{10}(H_2O)_{12}]^+$ (*a*) and $[Fe_{17}(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{10}(L)_8(H_2O)_{12}]^{3+}$ (*b*).

V. Conclusion

The last five decades have been characterised by rapid development of the chemistry, crystal chemistry and magnetic chemistry of exchange clusters. Analysis of experimental data for several thousands of relatively simple complexes allowed researchers to reveal and theoretically substantiate a variety of correlations between the exchange parameters and the characteristics of the electronic structure and the geometry of both molecular fragments and entire molecules. Taken together with the progress of preparative methods, this serves as a reliable basis for the development of a new research avenue in the field of coordination chemistry, namely, design of molecular magnets. In contrast to colloid chemistry,[155] coordination chemistry concerns polynuclear systems ($N \sim 10-20$) in the form of crystalline substances composed of 'building blocks' (molecules of a particular shape, size and orientation). Hence, such systems possess definite physical properties. At the same time, if magnetic inorganic crystals are usually grown from high-temperature melts, polynuclear complexes can be obtained from solutions at room temperature. This opens up considerable promise for the synthesis of magnets of various composition, structure and properties.[156–158] In particular, the magnetic sites in crystals of polynuclear complexes can comprise molecular and submolecular units possessing nontrivial magnetic properties rather than simple metal ions.

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