Jahn—Teller effect in trigonal μ-oxoclusters

Yu. V. Rakitin,[a]★ V. T. Kalinnikov,[a] and V. M. Novotortsev[b]

[a]*I. V. Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials,*
Kola Research Center of the Russian Academy of Sciences,
14 ul. Fersmana, 184200 Apatity, Murmansk Region, Russian Federation.
Fax: +7 (815 55) 7 9414. E-mail: apa7tit@mail.ru
[b]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 954 1279. E-mail: vmnov@igic.ras.ru

A theory of the Jahn—Teller effect in trinuclear Cr^{III} and Fe^{III} μ-oxocomplexes based on the generalized angular overlap model is developed. The central bridging O atom is not localized at the center of the triangle formed by the metal atoms. Rather, it executes a free or hindered motion along a circular groove of radius 0.05—0.1 Å. The theory provides a qualitative explanation for apparent discrepancy between the X-ray structural data and the results of the heat capacity, magnetic susceptibility, and inelastic neutron scattering measurements. Namely, X-ray structural data correspond to a regular triangle symmetry while other data correspond to an equilateral or even irregular triangle symmetry.

Key words: carboxylates, Cr^{III} complexes, Fe^{III} complexes, Jahn—Teller effect.

Trigonal transition metal μ_3-oxoclusters have long been attractive as metal enzyme models[1] and building blocks for complexes with more intricate structures[2,3] that can potentially exhibit magnetic memory effects.

Trinuclear complexes of general formula $[M_3O(OOCR)_6L_3]^+ \cdot nL'$, where $M = Fe^{III}$ or Cr^{III}, L is a monodentate neutral ligand, and L´ are outer-sphere ligands (including an anion, usually Cl^-) (Fig. 1) have been studied in most detail. According to the results of numerous X-ray studies (see, *e.g.*, Refs 4—12), the atoms M are separated by nearly 3.3 Å and occupy vertices of a regular or nearly regular triangle with a bridging atom $O(\mu_3)$ at the center. Pairs of carboxyl groups $OOCR^-$ form additional bridges connecting the atoms M and the terminal O atoms of these groups form the equatorial planes of the MLO_5 distorted octahedra. In all complexes the atoms M deviate from the plane passing through four oxygen atoms of the carboxyl groups toward the central oxygen atom. The $M—O(\mu_3)$ distance is nearly 1.9 Å, being much shorter than the length of the "normal" bond between the atom M and the atom O of the OOCR group (~2.0 Å) but appreciably longer than the length of the multiple M—O bond (~1.7 Å) in dinuclear μ_2-oxocomplexes.[13] As result, trinuclear carboxylate complexes have strained structures because the $M—O(\mu_3)$ distance exceeds an optimum value. The axial ligands L complete
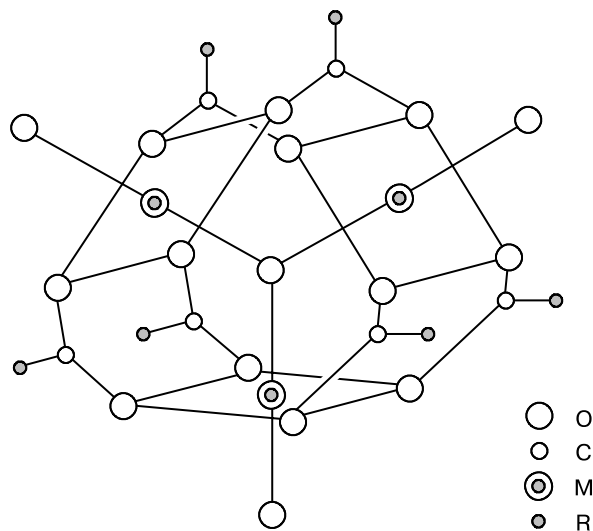

Fig. 1. Structure of $[M_3O(OOCR)_6L_3]^+$ cation.

the coordination sphere of the M atoms to a pseudo-octahedral one.

In this ligand environment, Cr^{III} and Fe^{III} ions have orbitally nondegenerate ground states $^4A_2$ and $^6A_1$ with the spins $s_i = 3/2$ and $5/2$, respectively (the subscript "*i*" enumerates the metal atoms). Therefore, the spin level

schemes of polynuclear Cr^{III} and Fe^{III} complexes must be correctly described by bilinear isotropic spin Hamiltonian,[14] which for trinuclear complexes with a regular triangle symmetry has the form

$$\hat{H}_0 = -2J_0(\hat{s}_1\hat{s}_2 + \hat{s}_2\hat{s}_3 + \hat{s}_3\hat{s}_1), \qquad (1)$$

where $-2J_0$ is the exchange parameter, and $\hat{s}_i$ are the particle spin operators ($i = 1, 2, 3$).

A solution of the spin Hamiltonian (1) is well known:

$$E = -J_0[S(S + 1) - 3s_1(s_1 + 1)], \qquad \varphi = |s_1, s_{23}, S\rangle, \qquad (2)$$

where

$$s_{23} = s_2 + s_3, s_2 + s_3 - 1, ..., |s_2 - s_3|,$$
$$S = s_1 + s_{23}, s_1 + s_{23} - 1, ..., |s_1 - s_{23}|. \qquad (3)$$

According to the results of magnetic measurements, the complexes under study are characterized by $-2J_0 \approx 18-22$ cm^{-1} (M = Cr^{III})[15-17] and $-2J_0 \approx 50-60$ cm^{-1} (M = Fe^{III}).[16-20] Thus, both types of complexes are antiferromagnetic with the ground state $\varphi = |s_1, s_{23}, 1/2\rangle$ degenerate with respect to s_{23}, namely, $s_{23} = 1, 2$ for $s_i = 3/2$ and $s_{23} = 2, 3$ for $s_i = 5/2$.

Studies[15,18] showed that agreement between the theoretical curves $\chi(T)$ and experimental data can be significantly improved by considering a distorted rather than regular geometry of the M_3O triangles. In particular, for a bilateral M_3O triangle the spin Hamiltonian (1) takes the form

$$\hat{H}_1 = -2J_0(\hat{s}_1\hat{s}_2 + \hat{s}_3\hat{s}_2 + \hat{s}_3\hat{s}_1) - 2J_{23}\hat{s}_2\hat{s}_3. \qquad (4a)$$

For clarity, here we assume that the atom M_1 is nonequivalent. It should be noted that our interest is with the distortion induced deviations of the exchange parameters from some average values rather than the exchange parameters themselves. Because of this, it is convenient to rewrite the spin Hamiltonian $\hat{H}_1$ in the form

$$\hat{H}_1 = -2J_0(\hat{s}_1\hat{s}_2 + \hat{s}_2\hat{s}_3 + \hat{s}_3\hat{s}_1) - 2(J_{23} - J_0)\hat{s}_2\hat{s}_3 =$$
$$= -2J_0(\hat{s}_1\hat{s}_2 + \hat{s}_2\hat{s}_3 + \hat{s}_3\hat{s}_1) - 2j'\hat{s}_2\hat{s}_3. \qquad (4b)$$

The corresponding solution is given by

$$E = -J_0[S(S + 1) - 3s_1(s_1 + 1)] -$$
$$- j'[s_{23}(s_{23} + 1) - 2s_1(2s_1 + 1)]. \qquad (5)$$

Here, spin degeneration with respect to s_{23} is removed. In particular, the ground-state levels (S = 1/2) become split with a splitting value of Δ. Since for complexes of both metals one has $|j'/J_0| = 0.15-0.20$, the Δ value is rather large, namely, ~10 cm^{-1} for Cr and ~25 cm^{-1} for Fe.[15-20]

Splitting of the ground-state levels of complex $[Cr_3O(AcO)_6(H_2O)_3]Cl \cdot 6H_2O$ corresponding to $|j'/J_0| \approx 0.1$ was confirmed by the results of low-temperature heat capacity measurements[21,22] and by high-resolution optical spectroscopy.[23] Spin level splitting measurements in related iron complexes by inelastic neutron scattering at helium temperatures were also reported.[10,24] The results obtained suggest that to describe splittings between the spin levels for S = 1/2 and S = 3/2, one should use the spin Hamiltonian given by expressions (4)[24] or even the spin Hamiltonian of irregular triangle model[10]

$$\hat{H}_2 = -2J_{12}\hat{s}_1\hat{s}_2 - 2J_{23}\hat{s}_2\hat{s}_3 - 2J_{31}\hat{s}_3\hat{s}_1. \qquad (6a)$$

Similarly to the spin Hamiltonian (4), here it is convenient to group the terms describing structural distortion, *i.e.*, to rewrite $\hat{H}_2$ in the form

$$\hat{H}_2 = -2J_0(\hat{s}_1\hat{s}_2 + \hat{s}_2\hat{s}_3 + \hat{s}_3\hat{s}_1) - 2j_{12}\hat{s}_1\hat{s}_2 -$$
$$- 2j_{23}\hat{s}_2\hat{s}_3 - 2j_{31}\hat{s}_3\hat{s}_1, \qquad (6b)$$

where

$$-2J_0 = (-2J_{12} - 2J_{23} - 2J_{31})/3,$$
$$-j_{12} = 2J_0 - 2J_{12} \text{ etc.}$$

The spin Hamiltonian (6) has no analytical solution; a corresponding numerical solution can be obtained by straightforward diagonalization of the spin Hamiltonian matrix. Convenient relations for calculating the matrix elements of the spin Hamiltonian (6) are available in the literature.[25] They can also be derived using the irreducible tensor operator method.[26]

Since X-ray diffraction studies revealed no strong distortions of the M_3O triangles, a possible alternative to the spin Hamiltonians (4) and (6) is to consider other types of interactions in addition to the spin Hamiltonian (1) .

For instance, the results of low-temperature heat capacity[21] and magnetic susceptibility[27] measurements for complex $[Cr_3O(AcO)_6(H_2O)_3]Cl \cdot 6H_2O$ were explained[28] taking into account antisymmetrical exchange:

$$\hat{H}_{as} = D_z \sum_{i,j} [\hat{s}_i \times \hat{s}_j]_z, \qquad (7)$$

i, j = 1, 2; 2, 3; 3, 1,

which leads to splitting of the ground-state levels. The accuracy of theoretical description of the magnetic properties of this complex significantly increases assuming that structural distortion rather than antisymmetrical exchange makes the major contribution to Δ value.[29] This model also permits a correct description of the EPR spectra of chromium complexes,[29] being consistent with the Moria estimate, namely, $|D_z| \approx |(g - 2) \cdot J_0/2|$.[14,30] Indeed, because for high-spin Cr^{III} complexes the g-factor anisotropy, $|g - 2|$, is at most 0.03,[31] one gets $|D_z| \leq 0.25$ cm^{-1}.

The estimate of the ground-state level splitting, $\Delta = 4\sqrt{3}\,D_z \approx 2$ cm^{-1}, is much less than the observed value ($\Delta \approx 10$ cm^{-1}). For the iron complexes, $|g - 2| < 0.01$ [31] and the relative contribution of antisymmetrical exchange to the Δ value is even smaller.

Agreement between the regular triangle model and experimental data on low-temperature heat capacity of complex $[Cr_3O(AcO)_6(H_2O)_3]Cl \cdot 6H_2O$ can be improved[32] with allowance for intermolecular exchange. However, the necessary intermolecular exchange parameter value is an order of magnitude greater than the upper bounds of the estimates obtained from magnetochemical[28] and spectroscopic[33] data.

Finally, agreement with the bilateral triangle model can be somewhat improved by taking into account biquadratic exchange[28,32]:

$$\hat{H}_{bq} = -2j_1 \sum_{i,j} (\hat{s}_i \hat{s}_j)^2 - 2j_2 \left(\sum_{i,j} \hat{s}_i \hat{s}_j \right)^2, \tag{8}$$

$i < j = 1, 2, 3,$

where $-2j_1 - 2j_2$ and $-2j_2$ are parameters corresponding to two types of biquadratic exchange described by the operators of the types $(\hat{s}_1\hat{s}_2)^2$ and $(\hat{s}_1\hat{s}_2)(\hat{s}_2\hat{s}_3) + (\hat{s}_2\hat{s}_3)(\hat{s}_1\hat{s}_2)$, respectively. However, this improvement is insignificant compared to that achieved using the unsymmetrical cluster model.[17] In addition, trinuclear Cr^{III} and Fe^{III} clusters with a regular triangle symmetry have a doublet orbitally degenerate ground state ^2E.[34] This degeneracy cannot be removed by any Coulomb interaction including biquadratic exchange.

Thus, the nature of the discrepancy between the X-ray structural data and the results of magnetic, thermodynamic, and spectroscopic measurements remains unclear as yet. In this work we will consider a mechanism providing an explanation for these facts.

Consider trinuclear Fe^{III} complexes which have been studied in most detail. Variation of radical R in the cation $[Fe_3O(OOCR)_6L_3]^+$ has a little effect on the magnetic properties of the complexes.[16−20] Moreover, replacement of the bridging ligands OOCR by SO$_4$ groups also insignificantly affects the parameter $-2J_0$ [35] (*cf.* a decrease in $-2J_0$ by nearly two orders of magnitude in other types of compounds[36]). This unambiguously proves that exchange interactions *via* the bridging atom O(μ_3) are predominant in the complexes under study. We can also state that exchange due to the overlap between the z^2-orbitals and the bridging atom orbitals is the strongest. Indeed, d-orbitals of the metal atom in pseudooctahedral environment are arranged in the order $x^2 - y^2 \approx z^2 > xy \approx xz \approx yz$. Therefore, on going from Cr^{III} d^3-complexes to Fe^{III} d^5-complexes the unpaired electrons appear in the $x^2 - y^2$-orbitals, which are not involved in the interaction with orbitals of the O(μ_3) atom, and in the z^2-orbitals. This is accompanied by a dramatic increase in the ex-
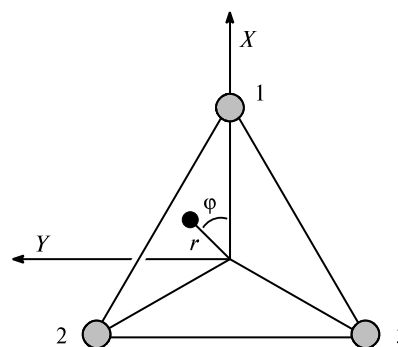

Fig. 2. Systems of coordinates in M$_3$O fragments. Local axes *z* of the metal atoms M are directed toward the center of the triangle.

change parameter $-2J_0$. Even stronger is the increase in the exchange energy $-2J_\Sigma = -2J_0 \cdot 4S_iS_j$, namely, from ~200 cm^{-1} to ~1500 cm^{-1}.[14]

The structure of the Fe$_3$O fragment is schematically shown in Fig. 2. The undistorted unit has a D_{3h} symmetry. X-Ray diffraction studies revealed no strong static distortions of the Fe$_3$O structure. This gives grounds to consider the dynamics of the Fe$_3$O fragment, *i.e.*, atomic vibrations. To a first approximation, we can allow for the motion of the O atom only because it is much lighter than the Fe atoms and its vibration amplitude is larger. We will not dwell on out-of-plane vibrations of the O atom because they do not violate the trigonal symmetry. To describe the in-plane motion of the atom O, we will introduce cylindrical coordinates *r* and φ (see Fig. 2) and use them along with Cartesian coordinates $x = r\cos\varphi$ and $y = r\sin\varphi$.

Since the thermal vibration amplitude is small,[12] we can consider $r \ll R_0$, where R_0 is the distance from the Fe atom to the center of the triangle. In this approximation the changes in the Fe—O distances due to the motion of the O atom are

$$\rho_i = R_0 - |R_0\cos\theta_i - x, \ R_0\sin\theta_i - y| =$$
$$= R_0 - |R_0\cos\theta_i - r\cos\varphi, \ R_0\sin\theta_i - r\sin\varphi| \approx$$
$$\approx -r\cos(\varphi - \theta_i), \tag{9}$$

where $\theta_i = 0°, \pm120°$ are the angular coordinates of the Fe atoms.

Since the Fe—O bonds are strained, the elastic force, $k_e \cdot \Delta x$, decreases as these bonds are shortened and increases as they are elongated. Therefore, the additional force exerted by each Fe atom on the O atom displaced from the equilibrium position is $F_i = -k_e \cdot r\cos(\varphi - \theta_i)$ and the direction of this force is given by the vectors $\vec{n}_i = (\cos\theta, \sin\theta)_i$. Summing the contributions of all the three interactions, we get

$$\vec{F} = -(3/2)k_e r(\cos\varphi, \sin\varphi), \qquad |\vec{F}| = (3/2)k_e r. \tag{10}$$

Thus, the central atom O moves in a cylindrical potential with no preferential directions. The equilibrium position corresponds to $r = 0$ and the cluster has a trigonal effective symmetry in this approximation.

As mentioned above, both Cr^{III} and Fe^{III} complexes have an orbitally degenerate ground state ^2E. As a consequence, they must exhibit first-order Jahn—Teller effect.[37] Indeed, from the symmetry theory[37] it follows that z^2-orbitals of the three Fe atoms are involved in the in-plane antibonding orbitals in the form of the following combinations:

$$A_1 \approx \left(1/\sqrt{3}\right)\left(z_1^2 + z_2^2 + z_3^2\right), \tag{11a}$$

$$E_1 \approx \left(1/\sqrt{6}\right)\left(2z_1^2 - z_2^2 - z_3^2\right), \tag{11b}$$

$$E_2 \approx \left(1/\sqrt{2}\right)\left(z_2^2 - z_3^2\right). \tag{11c}$$

The orbital A_1 weakly interacts with the s-orbital of the central atom O. The corresponding antibonding orbital is a nearly nonbonding orbital occupied by two electrons. The degenerate orbitals E_1 and E_2 strongly interact with the x- and y-orbitals of the atom O. The corresponding antibonding orbitals have higher energies and are occupied by one unpaired electron, which leads to the ground state ^2E.

To obtain a correct ground-state energy with allowance for the motion of the central atom O, one should construct a matrix for the operator of electron-vibrational interaction in the basis set of the functions E_1 and E_2[37]:

$$V = V'_x x + V'_y y. \tag{12}$$

From the generalized angular overlap model[38,39] it follows that the matrix elements of the effective Hamiltonian of the interaction between i-orbitals of metal atoms through a monatomic bridge can be written in the form

$$h_{ij} = \Sigma_m e_\sigma \langle i|m\rangle\langle m|j\rangle, \tag{13}$$

where e_σ is the energy parameter; $\langle i|m\rangle = t_i \cdot G(i,m)$ is the term appearing in the overlap integral of the type "metal i-orbital—ligand m-orbital", where t_i describes the radial dependence of the term and $G(i,m)$ describes the angular dependence of the term. By definition, the function $G(i,m)$ is equal to unity at maximum angular overlap. The parameter e_σ contains the absolute value of the overlap integral at $G(i,m) = 1$ and a "standard" metal—ligand distance R_0. Summation is performed over all ligand orbitals $(m = x, y)$. If the metal—ligand distance varies only slightly, one has[38]

$$t_i \approx (1 + \rho_i/R_0)^{-\beta} \equiv (1 + q_i)^{-\beta} \approx (1 - \beta q_i), \tag{14}$$

and expression (13) takes the form

$$h_{ij} = \Sigma_m e_\sigma (1 - \beta q_i)(1 - \beta q_j) G(i,m) G(j,m). \tag{15}$$

From the definition of ρ_i (9) it follows that at $r \ll R_0$

$$\partial\rho_i/\partial x = -R_0 \cos\theta_i, \qquad \partial\rho_i/\partial y = -R_0 \sin\theta_i.$$

From here and from Eqn (15) one gets for expression (12)

$$V'_x = \beta e_\sigma(\cos\theta_i + \cos\theta_j)\Sigma_m G(i,m) G(j,m),$$

$$V'_y = \beta e_\sigma(\sin\theta_i + \sin\theta_j)\Sigma_m G(i,m) G(j,m), \tag{16}$$

and the expressions for the matrix elements of the electron-vibrational interaction (12) take the form

$$\langle E_1|V|E_1\rangle = 3/2\beta e_\sigma r \cos\varphi,$$

$$\langle E_2|V|E_2\rangle = -3/2\beta e_\sigma r \cos\varphi,$$

$$\langle E_1|V|E_2\rangle = \langle E_2|V|E_1\rangle = -3/2\beta e_\sigma r \sin\varphi. \tag{17}$$

The eigenvalues of the 2×2 matrix thus obtained are as follows

$$\varepsilon_{1,2} = \pm 3/2\beta e_\sigma\sqrt{x^2 + y^2} = \pm 3/2\beta e_\sigma r. \tag{18}$$

Thus, the energy of the lowest sheet of adiabatic potential with allowance for the elastic interaction considered above is given by

$$W = 3/4 k_e r^2 - 3/2\beta e_\sigma r. \tag{19}$$

In the coordinates r,φ the potential W has a "Mexican hat" shape.[38] Potential minima corresponding to $W' = 0$ are arranged in a circumference of radius

$$r_0 = \beta e_\sigma/k_e, \tag{20}$$

and the corresponding Jahn—Teller stabilization energy is

$$\Delta W = 3/4\beta^2 e_\sigma^2/k_e. \tag{21}$$

Let us evaluate r_0 and ΔW. For the Fe—O bonds, $e_\sigma \approx 10^4$ cm^{-1}.[38] At normal bond lengths, one has $\beta \approx 3$, while at shortened bonds, $\beta \approx 1$—2. Since the energy of in-plane vibrations of the O atom is of the order of 600 cm^{-1} [40] and the reduced mass is 16 a.u., for the force constant we get $\sim 2 \cdot 10^5$ cm^{-1} A^2.[41] Substitution of these values into Eqn (20) gives $r_0 \approx 0.05$—0.1 Å. Similarly, for the Jahn—Teller stabilization energy (21) we get $\Delta W \approx 10^3$ cm^{-1}.

Thus, the central atom O is on the average located within a circular groove of radius $r_0 \approx 0.07$ Å whose depth ($\sim 10^3$ cm^{-1}) is sufficient to hold the atom O at all reasonable temperatures. As applied to X-ray diffraction data, this leads to apparent isotropy of the thermal ellipsoid of the atom O in the *XY* plane. However, at every instant of time the triangle is distorted. Consider how this manifests itself in magnetic interactions.

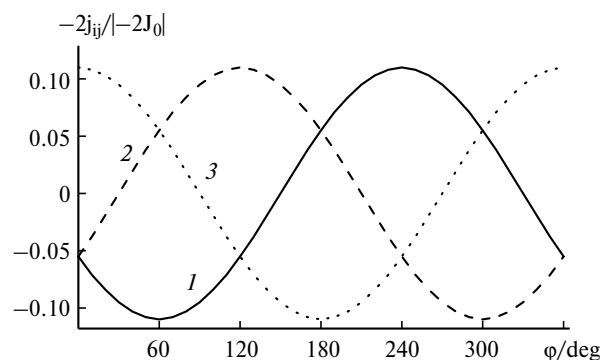From general considerations[14,38] it follows that the exchange parameter is proportional to the product of the

Fig. 3. Angular dependences of exchange parameters $-2j_{12}$ (*1*), $-2j_{31}$ (*2*), and $-2j_{23}$ (*3*) plotted using relationship (22) at $-2j = -6$ cm^{-1}.

metal—ligand overlap integrals squared. In our notations (see Ref. 14) this means that

$$-2j_{ij} \approx -2J_0(1 - 2\beta q_i)(1 - 2\beta q_j) + 2J_0 \approx$$

$$\approx -2J_0(-2\beta r_0/R_0)[\cos(\varphi - \theta_i) + \cos(\varphi - \theta_j)]. \quad (22)$$

Taking into account the estimates given above, we have $-2\beta r/R_0 \approx -0.11$. Therefore, for the Fe^{III} complexes with the exchange parameter $-2J_0 \approx 50$ cm^{-1} we get $-2J_0(-2\beta r_0/R_0) = -2j \approx -6$ cm^{-1}.

Figure 3 presents the calculated dependences of the parameters $-2j_{ij}$ on the angle φ plotted with $-2j = -6$ cm^{-1}. In accord with Fig. 2, the plots $-2j_{ij}(\varphi)$ are periodic functions with a period of 360° shifted by 120° relative to one another. All three parameters $-2j_{ij}$ differ from one another at any φ value. However, two out of the three parameters $-2j_{ij}$ become equal in 60° intervals, which corresponds to position of the bridging atom O in one of three bisectrixes. At least at these points we have $|j'/J_0| \approx 0.2$, which is consistent with experimental data (see above).

Let us analyze the energy spectrum. Fig. 4 presents the angular dependences of the energies of all levels with the total spins S = 1/2 and 3/2 corresponding to the angular dependences of the exchange parameters $-2j_{ij}$ at $-2J_0 = 50$ cm^{-1} and $-2j = -6$ cm^{-1} plotted using relationship (22). The necessary solutions to the spin Hamiltonian (6) were obtained by numerical diagonalization of the spin Hamiltonian matrices constructed using relations similar to those reported in Ref. 25.

The energy levels for S = 1/2 are independent of the angle φ (see Fig. 4). It is easy to understand taking into account that at any half-integer s_i

$$\langle E(S = 1/2)\rangle \approx j_{12} + j_{23} + j_{31}, \quad (23)$$

$$\Delta E(S = 1/2) = (j_{12}^2 + j_{31}^2 + j_{23}^2 - j_{12}j_{23} - j_{23}j_{31} - j_{31}j_{12})^{1/2}, \quad (24)$$

and substituting expressions (22) into these relationships. Therefore, information on the dynamics or possible lo-
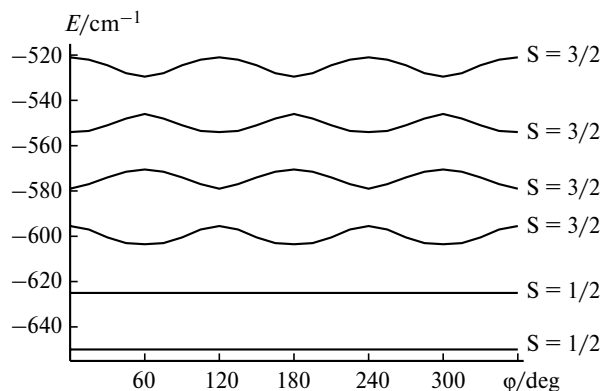

Fig. 4. Angular dependences of energy levels with the total spins S = 1/2 and 3/2 plotted at $-2J_0 = 50$ cm^{-1} and $-2j = -6$ cm^{-1}. The number of levels with the same total spins is determined by the rule of quantum composition of moments s$_i$.

calization of the atom O can only be extracted by probing upper-lying levels. Note that the results of heat capacity measurements are inappropriate in this case because at high temperatures the magnetic contributions are masked by lattice contributions while at low temperatures only two low-lying levels are populated. The magnetic susceptibility χ is also mainly "responsive" to the splitting Δ rather than the angular coordinate φ of the atom O. Indeed, determination of all three parameters $-2J_0$, $-2j$, and φ appeared in expression (22) requires that three exchange parameters $-2J_{ij} = -2J_0 - 2j_{ij}$ be extracted from experimental data. However, test calculations showed that the $\chi(T)$ curves plotted at $-2J_0 = 50$ cm^{-1}, $-2j = -6$ cm^{-1}, and any φ in the temperature range 5—300 K can be reproduced using the equilateral triangle model employing the spin Hamiltonian (4) with an accuracy that exceeds the experimental error (~1%) by an order of magnitude. For this reason the results obtained in studies where the experimental curves $\chi(T)$ were interpreted using the irregular triangle model (see, *e.g,*, Ref. 42) cast some doubt.

Now we will dwell on the results of neutron diffraction studies that allow positions of all energy levels for S = 1/2 and 3/2 to be determined with spectroscopic accuracy. It was found[10] that complex [Fe$_3$O(O$_2$CPh)$_6$(py)$_3$]ClO$_4$·py exists in two forms, one of them having an equilateral triangle symmetry and the other being characterized by three different equidistant values of the parameters $-2j_{ij}$ (or $-2J_{ij}$). This means (see Eqn (22) and Fig. 3) that $\varphi \approx 0° \pm n$ 60° for the first form and $\varphi \approx 30° \pm n$ 60° for the second form. To a first approximation, the geometry and electronic structure of the cations do not reveal the presence of preferential directions (see above). However, it is these preferential directions characteristic of the stacks of triangular molecules packed with a sequential shift of 60° that correspond to the point group $P6_3/m$. Electrostatic fields induced along these directions can partially or even

completely retard the motion of the atom O in the circular groove.

A neutron diffraction study of two complexes, $[Fe_3O(O_2CCD_3)_6(C_5D_5N)_3]NO_3$ and $[Fe_3O(O_2CC(CD_3)_3)_6(DOCD_3)_3]Cl$, was reported.[24] It was concluded that the complexes are best described using the equilateral triangle model ($\varphi \approx 0° \pm n\ 60°$) and the irregular triangle model ($\varphi \approx 30°$), respectively. The authors[24] also revised the results obtained[35] for a related trinuclear complex $K_5[Fe_3O(SO_4)_6(D_2O)_3] \cdot 6D_2O$ and showed that it is also best described using the model with $\varphi \approx 30°$. Unfortunately, the linewidths in the inelastic neutron scattering spectra[24,35] were as large as 10 cm^{-1}, which is comparable with energy variations of the S = 3/2 levels on change in the angle φ (see Fig. 4). Therefore, the localization problem of the bridging atom O in the last three complexes is still to be solved.

In conclusion, consider trinuclear Cr^{III} μ-oxocomplexes. Information on this type of complexes is scarce. However, the available data also point to displacement of the bridging atoms O from the center of the triangle. Of course, Cr^{III} complexes have no unpaired electrons in z^2-orbitals to form the ground state ^2E. However, this role can be played by the in-plane π-type xz- or yz-orbitals, which are also involved in the interaction with the x- and y-orbitals of the central atom O. Naturally, in this case the interaction energy is 2—3 times lower[38] but the parameter β appearing in relationships (20) and (22) is much larger.[38] Therefore, it is no wonder that trinuclear Cr^{III} carboxylates are characterized by a $|j'/J_0|$ ratio of nearly 0.1—0.15, which is somewhat smaller but of the same order of magnitude as that typical of related Fe^{III} complexes.

References

1. E. M. Holt, S. L. Holt, W. F. Tucker, R. O. Asplund, and K. J. Watson, *J. Am. Chem. Soc.*, 1974, **96**, 2621.
2. A. Bino, M. Ardon, D. Lee, B. Spingler, and S. J. Lippard, *J. Am. Chem. Soc.*, 2002, **124**, 4578.
3. Yu. V. Rakitin and J. van Slageren, *Koord. Khim.*, 2004, **30**, 859 [*Russ. J. Coord. Chem.*, 2004, **30** (Engl. Transl.)].
4. B. N. Figgis and G. B. Robertson, *Nature*, 1965, **205**, 694.
5. S. C. Chang and G. A. Jeffrey, *Acta Crystallogr., Sect. B*, 1970, **26**, 672.
6. A. B. Blake and L. R. Fraser, *J. Chem. Soc., Dalton Trans.*, 1975, 193.
7. C. E. Anso, J. P. Bourke, R. D. Cannon, U. A. Jayasooriay, M. Molinier, and A. K. Powel, *Inorg. Chem.*, 1997, **36**, 1265.
8. R. V. Thundathil, E. M. Holt, S. L. Holt, and K. J. Watson, *J. Am. Chem. Soc.*, 1977, **99**, 1818.
9. K. I. Turte, S. G. Shova, and F. A. Spatar´, *Zh. Strukt. Khim.*, 1994, **35**, 112 [*Russ. J. Struct. Chem.*, 1994, **35** (Engl. Transl.)].
10. F. E. Sowrey, C. Tilford, S. Wocadlo, Ch. E. Anson, A. K. Powel, S. M. Bennington, W. Montfrooij, U. A. Jayasooriya, and R. D. Cannon, *J. Chem. Soc., Dalton Trans.*, 2001, 862.
11. M. R. Silva, A. M. Beja, J. A. Paxão, L. A. da Veiga, and J. Martin-Gil, *Acta Crystallog., Sect. C*, 2001, **57**, 542.
12. K. I. Turte, A. G. Lazaresku, Yu. A. Simonov, Ya. Lipkovskii, A. A. Dvorkin, and L. Patron, *Koord. Khim.*, 1996, **22**, 45 [*Russ. J. Coord. Chem.*, 1996, **22** (Engl. Transl.)].
13. P. Gomez-Romero, N. Casan-Pastor, Ah. Ben-Hussein, and G. B. Jameson, *J. Am. Chem. Soc.*, 1988, **110**, 1989.
14. Yu. V. Rakitin and V. T. Kalinnikov, *Sovremennaya magnetokhimiya* [*Modern Magnetochemistry*], Nauka, St.-Petersburg, 1994, 272 (in Russian).
15. J. Wucher and H. M. Gijsman, *Physica*, 1954, **20**, 361.
16. V. V. Zelentsov, T. A. Zhemchuzhnikova, Yu. V. Yablokov, and Kh. M. Yakubov, *Koord. Khim.*, 1975, **1**, 194 [*Sov. J. Coord. Chem.*, 1975, **1** (Engl. Transl.)].
17. Yu. V. Rakitin, T. A. Zhemchuzhnikova, and V. V. Zelentsov, *Inorg. Chim. Acta*, 1977, **23**, 145.
18. A. Earnshaw, B. N. Figgis, and J. Lewis, *J. Chem. Soc., A*, 1966, 1656.
19. J. F. Duncan, C. R. Kanekar, and K. F. Mok, *J. Chem. Soc., A*, 1969, 480.
20. G. J. Long, W. T. Robinson, W. P. Tappmeyer, and D. L. Bridges, *J. Chem. Soc., Dalton Trans.*, 1973, 573.
21. J. Wucher and J. D. Wasscher, *Physica*, 1954, **20**, 721.
22. M. Sorai, M. Tachiki, H. Suga, and S. Seki, *J. Phys. Soc. Jpn*, 1971, **30**, 750.
23. J. Ferguson and H. U. Güdel, *Chem. Phys. Lett.*, 1972, **17**, 547.
24. R. D. Cannon, U. A. Jayasooriya, R. Wu, S. K. arapKoske, J. A. Stride, O. F. Nielsen, R. P. White, G. J. Kearley, and D. Summerfield, *J. Am. Chem. Soc.*, 1994, **116**, 11869.
25. V. A. Gaponenko, M. V. Eremin, and Yu. V. Yablokov, *Fizika Tverdogo Tela*, 1973, **15**, 1336 [*Sov. Phys. Sol. State*, 1973, **15** (Engl. Transl.)].
26. D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, *Kvantovaya teoriya uglovogo momenta* [*Quantum Theory of Angular Momentum*], Nauka, Leningrad, 1975, 439 pp. (in Russian); D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, *Quantum Theory of Angular Momentum*, World Scientific, Singapore, 1988, 449 p.
27. J. T. Schriempf and S. A. Friedberg, *J. Chem. Phys.*, 1964, **40**, 296.
28. M. I. Belinskii, B. Ya. Kuyavskaya, B. S. Tsukerblat, A. V. Ablov, and L. M. Kushkulei, *Koord. Khim.*, 1976, **2**, 1099 [*Sov. J. Coord. Chem.*, 1976, **2** (Engl. Transl.)].
29. Yu. V. Rakitin and Yu. V. Yablokov, *Zh. neorg. khim.*, 1982, **27**, 104 [*J. Inorg. Chem. USSR*, 1982, **27** (Engl. Transl.)].
30. T. Moriya, *Phys. Rev.*, 1960, **120**, 91.
31. S. A. Al´tshuler and B. M. Kozyrev, *Elektronnyi paramagnitnyi rezonans* [*Electron Paramagnetic Resonance*], Nauka, Moscow, 1972, 672 pp. (in Russian).
32. J. T. Wrobleski, Ch. T. Dziobkowski, and D. B. Brown, *Inorg. Chem.*, 1981, **20**, 684.

33. K. Schenk and H. U. Güdel, *Inorg. Chem.*, 1982, **21**, 2253.
34. B. S. Tsukerblat, M. I. Belinskii, and A. V. Ablov, *Dokl. Akad. Nauk SSSR*, 1971, **201**, 1410 [*Dokl. Chem.*, 1971 (Engl. Transl.)].
35. A. Furrer and H. U. Güdel, *Helv. Phys. Acta*, 1977, **50**, 439.
36. Yu. V. Rakitin, V. T. Kalinnikov, and M. V. Eremin, *Theor. Chim. Acta*, 1977, **45**, 167.
37. I. B. Bersuker, *Elektronnoe stroenie i svoistva koordinatsionnykh soedinenii* [*Electronic Structure and Properties of Coordination Compounds*], Khimiya, Leningrad, 1976, 349 pp. (in Russian).
38. Yu. V. Rakitin and V. T. Kalinnikov, *Model´ uglovogo perekryvaniya v teorii stroeniya soedinenii perekhodnykh metallov* [*Angular Overlap Model in Molecular Structure Theory of Transition Metal Compounds*], Izd-vo Kol´skogo Nauchnogo Tsentra RAN, Apatity, 2000, 306 pp. (in Russian).
39. Yu. V. Rakitin, S. G. Khodasevich, and V. T. Kalinnikov, *Koord. Khim.*, 1997, **23**, 3 [*Russ. J. Coord. Chem.*, 1997, **23** (Engl. Transl.)].
40. L. Montri and R. D. Cannon, *Spectrochim. Acta, Part A*, 1985, **41**, 643.
41. A. A. Radtsig and B. M. Smirnov, *Spravochnik po atomnoi i molekulyarnoi fizike* [*Handbook of Atomic and Molecular Physics*], Atomizdat, Moscow, 1980, 240 pp. (in Russian).
42. J. Darriet, J. Mur, and J.-P. Sanchez, *New J. Chem.*, 1987, **11**, 21.