Magnetic properties of a dinuclear complex $(2,3\text{-}Me_2C_5H_3N)_2Fe_2(\mu\text{-}OOCCMe_3)_4$ with "China lantern" structure

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Magnetic characteristics of the dinuclear complex $(2,3\text{-}Me_2C_5H_3N)_2Fe_2(\mu\text{-}OOCCMe_3)_4$ (**1**) were studied in the temperature interval 2—300 K. The magnetic behavior of complex **1** was interpreted in terms of the orbital-dependent exchange theory with allowance for the temperature dependence of the populations of the split $^5T_{2g}$ ground-state components of the Fe^{II} ions. The calculated values of the orbital-dependent exchange parameters are in good agreement with the results reported for dinuclear carboxylates of other 3d-transition metals and suggest the existence of strong ferromagnetism in some types of heterodinuclear carboxylates.

Key words: dinuclear carboxylate complexes, high-spin Fe^{II} atoms, studies of magnetic properties, orbital-dependent exchange theory.

Many carboxylates of 3d-elements have "China lantern" dinuclear structures. When studying these systems, the magnetic properties of the complexes with orbitally degenerate metal atoms (*e.g.*, Fe^{II}) are of particular interest because analysis of the temperature dependences of the populations of orbital levels allows information on the relative energies of these levels and on the exchange interactions between them to be extracted. Though the orbital-dependent exchange theory has been well developed,[1—4] there are only a few experimental studies of these systems.[5—9] The reasons are as follows. First, ground-state orbital degeneracy is possible for a few symmetry types and electron configurations, the corresponding ions often being in unstable oxidation states. Second, the relative energies of configurations and the corresponding exchange parameters of these systems are, as rule, unknown. Therefore, the total number of parameters that should be determined experimentally for degenerate systems much exceeds that necessary for nondegenerate systems. Unambiguous solution to this problem seems to be challengeable because experimental data usually fall on a smooth curve.

Recently,[10] we have reported the synthesis and molecular structure determination of the new dinuclear complex $(2,3\text{-}Me_2C_5H_3N)_2Fe_2(\mu\text{-}OOCCMe_3)_4$ (**1**) (Fig. 1) containing orbitally degenerate Fe^{II} atoms linked by four bridging carboxylate groups. In this work we studied, both experimentally and theoretically, the magnetic properties of complex **1**. Here, the problems mentioned above are not too complicated because Fe^{2+} ions are stable enough, the number of configurations with temperature-dependent populations is small, and the exchange parameters can be estimated using additional information provided by the model of exchange channels[2,11—13] and by the available experimental data for dinuclear carboxylates of other 3d-transition metals.[2,13—17]

Results and Discussion

Our study of the magnetic properties of complex **1** in the 2—300 K interval (Fig. 2) revealed a decrease in the effective magnetic moment, μ_{eff}, of the dinuclear iron(II) complex over the whole temperature range. High μ_{eff}(300 K) value, nearly 4.78 μ_B, is typical of high-spin Fe^{2+} ions (d^6, $S = 2$). As temperature decreases, μ_{eff} rapidly decreases owing to strong antiferromagnetic interactions characteristic of all homodinuclear carboxylates of 3d-transition metals.[2,13—17] At the same time, the experimental $\mu_{eff}(T)$ dependence is not described by the isotropic exchange model which holds for orbital-singlet sys-

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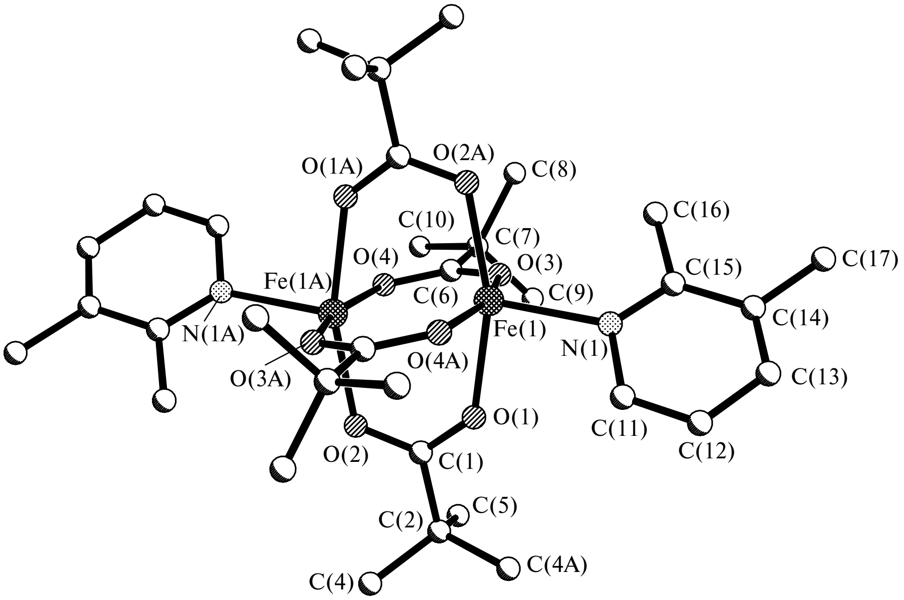

Fig. 1. Molecular structure of the dinuclear complex $(2,3\text{-Me}_2C_5H_3N)_2Fe_2(\mu\text{-OOCCMe}_3)_4$ (**1**).

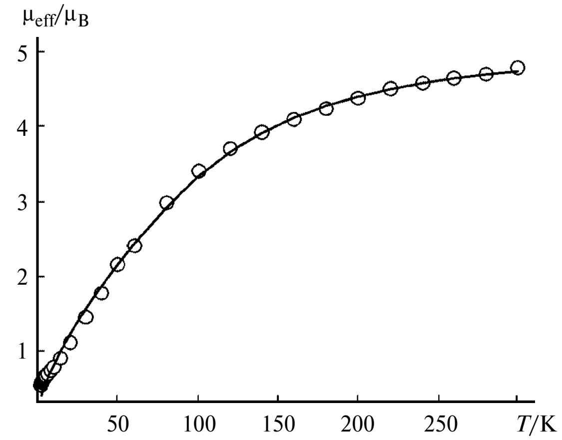

Fig. 2. Temperature dependence of the effective magnetic moment of the dinuclear carboxylate $(2,3\text{-Me}_2C_5H_3N)_2Fe_2(\mu\text{-OOCCMe}_3)_4$ (**1**) (open circles denote experimental values and the solid curve denotes the calculated data).

tems. Therefore, the experimental data were interpreted using the orbital-dependent exchange theory[2,3] adapted[1] to allow for peculiarities of the geometry and electronic structure of the complexes similar to complex **1** (see Fig. 1, the *z* axis is directed along the Fe...Fe line).

From the general theory of the electronic structure of transition-metal compounds it follows that the effective Hamiltonian for the complex under study can be written as[2]

$$\hat{H} = A + B + C + D, \qquad (1)$$

$$A = \Delta\cdot\hat{O}_a(C_{4v}) + \delta\cdot\hat{O}_a(C_{2v}) + $$

$$+ \Delta\cdot\hat{O}_b(C_{4v}) + \delta\cdot\hat{O}_b(C_{2v}), \qquad (1.1)$$

$$B = \lambda\hat{L}_a\hat{S}_a + \lambda\hat{L}_b\hat{S}_b, \qquad (1.2)$$

$$C = \sum{}_\alpha H_\alpha\cdot\hat{\mu}_\alpha, \qquad (1.3)$$

$$D = \sum \gamma_a,\gamma_b - 2J(\gamma_a,\gamma_b)(S_aS_b + \hat{S}_a\hat{S}_b), \qquad (1.4)$$

where the subscripts "a" and "b" enumerate the iron atoms.

Indeed, each Fe^{II} atom can be considered as being in an octahedral environment influenced by tetragonal and weaker orthorhombic distortions (see Fig. 1). In the octahedral field, the Fe^{2+} ions have a $^5T_{2g}$ ground state. The operators (1.1) describe a splitting of the $^5T_{2g}$ term affected by the tetragonal (C_{4v}) and orthorhombic (C_{2v}) components that are generally expressed *via* the effective orbital moment operators.[2] However, in our case the splittings generated by these operators can be determined with ease from simple qualitative considerations, *e.g.*, the point charge model. The resulting scheme of energy levels for the metal center "a" in the compact hole representation is shown in Fig. 3. The orbital components of the corresponding many-electron wave functions and their energies can be written as

$$|x\rangle = |x^2 - y^2\rangle|z^2\rangle|yz\rangle|xy\rangle \qquad E = \Delta + \delta/2,$$

$$|y\rangle = |x^2 - y^2\rangle|z^2\rangle|xz\rangle|xy\rangle \qquad E = \Delta - \delta/2, \qquad (2)$$

$$|z\rangle = |x^2 - y^2\rangle|z^2\rangle|yz\rangle|xz\rangle \qquad E = 0.$$

Fifteen full one-center wave functions can be obtained by multiplying the wave functions (2) by the components of the spin functions $|S = 2, M_S\rangle$.

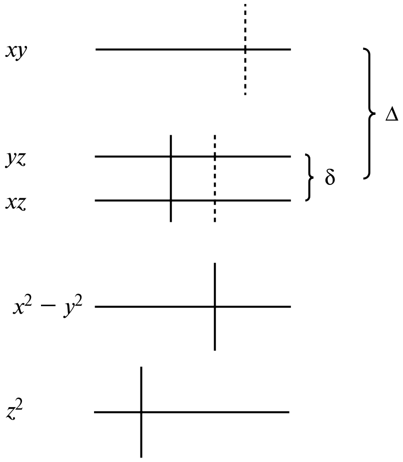

Fig. 3. Electronic structure of a mononuclear fragment of dinuclear carboxylate $(2,3\text{-}Me_2C_5H_3N)_2Fe_2(\mu\text{-}OOCCMe_3)_4$ (**1**) (d^6 configuration of Fe^{2+} ion) in the hole representation.

The energy level scheme for the second metal center, "b", differs only in permutation of the $|xz>$ and $|yz>$ orbitals because orthorhombic distortion is mainly due to the planar apical 2,3-lutidine ligands arranged in staggered conformation (see Fig. 1). Note that the splittings, δ, caused by these distortions are at most 100 cm^{-1}.[6] However, according to preliminary calculations, variation of δ values in the interval 0—100 cm^{-1} has no effect on the calculated $\mu_{eff}(T)$ values. Because of this, hereafter we set $\delta = 0$. A simple explanation for this effect is provided by similarity of the point symmetry group of the molecule under study to the S_4 group due to the staggered conformation of the apical ligands and by the degeneracy of the $|xz>$ and $|yz>$ orbitals in the S_4 group.

Expressions (1.2) describe the spin-orbit coupling. Here, the matrix elements of the spin operators $\hat{S}$ are calculated using conventional quantum mechanics rules while the matrix elements of the orbital moment operators are calculated by directly applying the operators $\hat{L} = \sum_{i=1}^{4} \hat{l}$ to the functions (2), among which only the following terms differ from zero:

$$<x|\hat{L}_z|y> = <y|\hat{L}_z|x>^* = -i,$$

$$<y|\hat{L}_x|z> = <z|\hat{L}_x|y>^* = -i,$$

$$<x|\hat{L}_y|z> = <z|\hat{L}_y|x>^* = -i.$$

The spin-orbit coupling constant, λ, is negative because we use the hole representation. The λ value calculated for Fe^{2+} configuration ions with allowance for covalency effects is nearly −90 cm^{-1}.[2]

The components of the magnetic moment operators of the two metal atoms

$$\mu_\alpha = \mu_B[k_\alpha(\hat{L}_{a\alpha} + \hat{L}_{b\alpha}) + g_e(\hat{S}_{a\alpha} + \hat{S}_{b\alpha})] \qquad (3)$$

($\alpha = x, y, z$) which, according to formula (1.3), interact with external magnetic field, are expressed *via* the same operators $\hat{S}$ and $\hat{L}$ as above. The expressions for the operators $\hat{\mu}_\alpha$ contain three orbital contraction factors k_α. Symmetry considerations allow the number of these parameters to be reduced to two, namely, $k_\| = k_z$ and $k_\perp = k_x = k_y$. Similarly to other 3d-transition metal complexes with a moderate degree of the metal—ligand bond covalency, complex **1** is characterized by $k_\|$ and $k_\perp$ values of nearly 0.8 and 0.9, respectively.[18]

The expression (1.4) is the effective Hamiltonian of the exchange interaction between the centers "a" and "b", which acts in the basis set of the product functions

$$|\gamma_a S_a M_{sa}>|\gamma_b S_b M_{sb}>, \qquad (4)$$

where the subscripts $\gamma = x, y, z$ enumerate the orbital functions (2). Consider expression (1.4) in more detail.

The exchange interaction operator for any configuration (γ_a, γ_b) has the form[2]

$$\hat{H}_{ex}(\gamma_a,\gamma_b) = \sum\nolimits_{ia,jb} - 2j(ia,ib)(1/4 + \hat{s}_{ia}\hat{s}_{jb}), \qquad (5)$$

where *i*a and *j*b enumerate the orbitals of the unpaired electrons of the "a" and "b" centers in this configuration. Since Fe^{2+} ions are in the high-spin states, the following equalities are valid

$$\hat{s}_{ia} = \hat{S}_a/2S_a, \qquad \hat{s}_{jb} = \hat{S}_b/2S_b,$$
$$\hat{s}_{ia}\hat{s}_{jb} = \hat{S}_a\hat{S}_b/4S_aS_b. \qquad (6)$$

Substitution of the last-mentioned equality into expression (5) gives

$$\hat{H}_{ex}(\gamma_a,\gamma_b) = -2J(\gamma_a,\gamma_b)(S_aS_b + \hat{S}_a\hat{S}_b), \qquad (7)$$

where

$$-2J(\gamma_a,\gamma_b) = [\Sigma_{ia,jb} - 2j(ia,jb)]/4S_aS_b. \qquad (8)$$

Systems with orbitally nondegenerate ions have only one (γ_a, γ_b) configuration and, hence, only one term of the type (7). This allows the exchange Hamiltonian to be used in the form $-2J\hat{S}_a\hat{S}_b$ and the S_aS_b contributions to be ignored because they only cause an insignificant shift of all levels. But in the case of orbitally degenerate systems the S_aS_b contributions cannot be ignored since they lead to relative shifts of nonequivalent configurations (γ_a, γ_b).

The case in point is a symmetrical dimer. Therefore, the number of nonequivalent configurations and, hence, exchange parameters $-2\mathrm{J}(\gamma_a, \gamma_b) = -2\mathrm{J}(\gamma_b, \gamma_a)$ ($\gamma = x, y, z$) is six. This is of course much less than a total of fifteen parameters $-2j(i\mathrm{a}, j\mathrm{b}) = -2j(j\mathrm{a}, i\mathrm{b})$ ($i, j = z^2, x^2 - y^2, xz, yz, xy$) in the general form of the exchange Hamiltonian (5) but still too many to unambiguously interpret the experimental data. However, the number of unknown parameters can be reduced by using the model of exchange channels[2,11,12] and the experimental data on related dinuclear carboxylate complexes of other transition metals.[2,13]

It is convenient to rewrite expression (8) in the form

$$-2\mathrm{J}_\Sigma(\gamma_a,\gamma_b) = -2\mathrm{J}(\gamma_a,\gamma_b)\cdot 4\mathrm{S_aS_b} = \Sigma_{i\mathrm{a},j\mathrm{b}} - 2j(i\mathrm{a},j\mathrm{b}), \qquad (9)$$

because, according to the model of exchange channels, it is the two-electron contributions $-2j(i\mathrm{a}, j\mathrm{b})$ rather than the exchange parameters $-2\mathrm{J}(\gamma_a, \gamma_b)$ that possess transferability in the series of related compounds.

Among dinuclear "lantern" carboxylates, $\mathrm{Cu^{II}}$ complexes with the unpaired electrons on the $|x^2 - y^2\rangle$ σ-orbitals have been studied in detail. For these systems, one has $-2\mathrm{J(Cu,Cu)} = 300$—$350\ \mathrm{cm^{-1}}$. The use of expression (9) gives $-2j(x^2 - y^2, x^2 - y^2) = -2\mathrm{J(Cu,Cu)}\cdot 1\cdot 1/2\cdot 1/2$, which leads to the same result (300—350 $\mathrm{cm^{-1}}$). "Lantern" $\mathrm{Ti^{III}}$ complexes, *e.g.*, $\mathrm{CpTi(OOCR)_4TiCp}$, are characterized by the exchange parameters, $-2\mathrm{J(Ti,Ti)}$, of nearly 1000 $\mathrm{cm^{-1}}$; here, the unpaired electrons are localized on the π-type $|xy\rangle$-orbitals. However, for all similar dinuclear carboxylates we also get $-2j(xy, xy) = -2\mathrm{J(Ti,Ti)}\cdot 1\cdot 1/2\cdot 1/2 \approx 1000\ \mathrm{cm^{-1}}$.

The available dinuclear $\mathrm{Mn^{II}}$ carboxylates have not been structurally characterized as yet. The assumption of a four-bridge structure of these complexes implies that the unpaired electrons must occupy all five d-orbitals. Seemingly, the parameter $-2\mathrm{J}\cdot 4\mathrm{S_aS_b}$ must at least be equal to $-2j(xy, xy) - 2j(x^2 - y^2, x^2 - y^2) \approx 1300\ \mathrm{cm^{-1}}$ because both these contributions are undoubtedly included in the sum (9). Nevertheless, estimation for the $\mathrm{Mn^{II}}$ complexes only gives $-2\mathrm{J}\cdot 4\mathrm{S_aS_b} \approx 30\cdot 4\cdot 5/2\cdot 5/2 = 750\ \mathrm{cm^{-1}}$. This divergence can be due to either another geometry of the complexes (*e.g.*, a two-bridge structure, as for some iron complexes[19]) or neglect of some ferromagnetic contributions. From the standpoint of maximum differential overlap in the latter case the greatest ferromagnetic contributions must come from the $-2j(x^2\text{-}y^2, xy)$ terms, so the approximate expression for the $\mathrm{Mn^{II}}$ carboxylates takes the form

$$-2\mathrm{J}_\Sigma(\mathrm{Mn,Mn}) = -2j(xy, xy) - 2j(x^2 - y^2, x^2 - y^2) - \\ - 4j(x^2\text{-}y^2, xy). \qquad (10)$$

The results of our analysis of the dominant contributions to the "lantern"-like carboxylate dimers containing orbitally nondegenerate divalent ions allow the orbital-dependent exchange parameters for dinuclear $\mathrm{Fe^{II}}$ carboxylate with the spins $\mathrm{S_a = S_b} = 2$ to be evaluated. Using the estimations obtained for the manganese complexes and relations (7) and (10), we get

$$-2\mathrm{J}(x,x) \approx 2\mathrm{J}(x,y) = -2\mathrm{J}(y,x) \approx -2\mathrm{J}(y,y) \approx \\ \approx [-2j(xy, xy) - 2j(x^2 - y^2, x^2 - y^2) - 4j(x^2 - y^2, xy)]/16 = \\ = -2\mathrm{J}_\Sigma(\mathrm{Mn,Mn})/16 \approx 50\ \mathrm{cm^{-1}}. \qquad (11)$$

Analogously, the inclusion of the parameters obtained for the copper complexes gives

$$-2\mathrm{J}(z,z) \approx -2j(x^2 - y^2, x^2 - y^2)/16 = \\ = -2\mathrm{J(Cu,Cu)}/16 \approx 20\ \mathrm{cm^{-1}}. \qquad (12)$$

Other parameters can be estimated as follows:

$$-2\mathrm{J}(x,z) = -2\mathrm{J}(z,x) \approx -2\mathrm{J}(y,z) = -2\mathrm{J}(z,y) \approx \\ \approx [-2j(x^2 - y^2, x^2 - y^2) - 2j(x^2 - y^2, xy)]/16. \qquad (13)$$

The result obtained is a small difference between two large numbers. Eventually, we only can state that the numerical value of the parameter $-2\mathrm{J}(x,z)$ is less than 20 $\mathrm{cm^{-1}}$ and, probably, positive. Nevertheless, this method permits a considerable reduction of the number of unknown parameters and analysis of experimental data.

The temperature dependence of the static magnetic susceptibility per mole of metal atoms was calculated using the formula[2]

$$\chi_{\alpha\beta} = \frac{N_\mathrm{A}}{n\cdot Z}\sum_i\left\{\sum_j{}' \langle i|\hat{\mu}_\alpha|j\rangle\langle j|\hat{\mu}_\beta|i\rangle/kT - \\ -\sum_j{}'' \frac{\mathrm{F}}{E_i^0 - E_j^0}\right\}\exp(-E_i^0/kT),$$

$$\mathrm{F} = \langle i|\hat{\mu}_\alpha|j\rangle\langle j|\hat{\mu}_\beta|i\rangle + \langle i|\hat{\mu}_\beta|j\rangle\langle j|\hat{\mu}_\alpha|i\rangle,$$

where N_A is the Avogadro constant, $Z = \Sigma_i\exp(-E_i^0/kT)$ is the statistical sum, and $n = 2$ is the number of metal atoms in the molecule. The subscripts $\alpha, \beta = x, y, z$ enumerate the components of the magnetic moment operators of the atoms and $|i\rangle$ and $|j\rangle$ are the zero-order functions corresponding to the states with the energies E_i^0 and E_j^0, respectively, which are obtained by numerical diagonalization of the matrix of the Hamiltonian (1.1) + (1.2) + (1.4) written in the basis set of the product functions (4). Summation in the primed sum, $\Sigma_j{}'$, is performed over all states with energies equal to the energy of the ith level. Summation in the double-primed sum, $\Sigma_j{}''$, is carried out over all states j with $E_j^0 \neq E_i^0$.

The magnetic susceptibility of the polycrystalline sample was calculated using the known formula[2]: $\chi = (\chi_{xx} + \chi_{yy} + \chi_{zz})/3$ and the effective magnetic moment was calculated as $\mu_\mathrm{eff}{}^2 = 3kT\chi/N_\mathrm{A}\mu_\mathrm{B} \approx 7.991\chi T$.

The theory parameters were determined by applying the best fit technique to the experimental and calculated χT values. The following parameters of the effective Hamiltonian (1) were considered constant: $\delta = 0$, $k_{\|} = 0.8$, $k_{\perp} = 0.9$, $-2J(x,x) = 50$ cm^{-1}, and $-2J(z,z) = 20$ cm^{-1} (see above). The best fit parameters obtained are $\Delta = -134(10)$ cm^{-1} and $-2J(x,z) = 6(1)$ cm^{-1}. To reproduce the low-temperature portion of the experimental curve, we had to apply a correction for the monomer impurity, which appeared to be small, $\alpha = 0.0025(5)$.

We believe that reasonable agreement between theory and experiment (see Fig. 2) substantiates the choice of the theoretical model and procedure for estimation of nearly ten constant parameters. The calculated value, $\Delta = -134(10)$ cm^{-1} $\approx \lambda$ is consistent with the concept of weakly split triplet $^5T_2$ as the ground state of Fe^{2+} ions. This is an unusual result because one should expect a greater splitting in the formally pentacoordinate mononuclear fragment. In addition, the estimate obtained ($-2J(x,z) = 6(1)$ cm^{-1} < 20 cm^{-1}) provides a convincing proof of the existence of a strong ferromagnetic exchange channel ($-2j(x^2 - y^2, xy) \approx -200$ cm^{-1}) in dinuclear Fe^{II} carboxylates. We believe that appropriate combinations of the electron configurations of the interacting magnetic metal centers can lead to the onset of ferromagnetism in "lantern" carboxylates provided that the ferromagnetic exchange channel predominates. Since almost all known "lantern" homonuclear carboxylates of 3d-metals (from titanium to copper) possess antiferromagnetic properties, such combinations are possible for either heteronuclear or homonuclear heterospin systems with nonequivalent electron configurations. However, this brings about a rather complicated problem concerned with the synthesis of these types of dimers, which is still hard to solve so far.

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