Theor Chem Acc (2005) 114: 97–109
DOI 10.1007/s00214-005-0649-9

REGULAR ARTICLE

M. B. Darkhovskii · A. V. Soudackov
A. L. Tchougréeff

Transition metal complexes with open *d*-shell in semiempirical context. Application to analysis of Mössbauer data on spin–active iron(II) compounds

Received: 27 September 2004 / Accepted: 28 February 2005 / Published online: 18 July 2005

Abstract With use of cumulants of two-electron density matrices semiempirical methods are analyzed from a point of view of their suitability to describe qualitative features of electronic correlation important for calculation of electronic structure of the transition metal complexes (TMC). It is shown that traditional semiempirical methods relying upon the Hartree–Fock–Roothaan form of the trial wave function suffer from a structural deficiency not allowing them to distinguish the energies of the atomic multiplets of the TMCs' d-shells. On the other hand, the effective Hamiltonian of the crystal field (EHCF) previously proposed by the authors is shown to be suitable for further parameterization and has been successfully applied for calculations on polyatomic TMCs. Here we describe in details its recent modifications performed in relation to the SINDO/1 parameterization scheme and present the results of the calculations on spin-active Fe(II) complexes with nitrogen-containing polydentate ligands in relation with interpretation of the Mössbauer measurements performed on these complexes.

1 Introduction

The molecular modeling of the transition metal complexes (TMC), reproducing characteristic features of their stereochemistry and electronic structure, is one of the important goals in the modern computational chemistry. The need for such modeling arises while studying and developing various processes involving TMCs.

The tools generally available for performing a required modeling are inconsistent with the problem. Quantum chemistry (QC) in general seems to be indispensable for performing the required modeling since the number of bonds (or coordinated ligands) may become variable. Also the presence of the open d-shell of the metal ion requires quantum mechanical modeling tools since a number of the electronic (spin) states of the complex closely lying on the energy scale arises, and thus the PESs belonging to different electronic terms closely approach each other, or even cross, which manifests itself in experimentally observed spin transitions [1] or Jahn-Teller distortions [2]. However, employing ab initio QC methods for the purpose of TMC modeling faces serious problems since the molecules under consideration are generally rather large whereas the computational costs of the methods to be used in order to reach at least an acceptable result scale up to N^7 with the system size (N is the number of AOs in the molecule) due to the importance of electron correlation.

When a similar problem, the necessity of modeling of large molecular systems like polypeptides or simply polyatomic organic molecules, is faced by "organic" QC, semiempirical methods are usually applied. With clearly identifiable exceptions like the long polyene chains or systems with breaking σ-bonds these methods in general perform quite reasonably giving relative heats of formation within series of related molecules and corresponding molecular geometries with "chemical" precision. The progressive route of improvements in the semiempirical methods as applied to "organic" molecules consisted of (1) increasing the number of the Coulomb interaction integrals taken into account, (2) the sophistication of the core-core repulsion terms added to the semiempirical electronic energy. However, the numerous readjustments of the parameterization of the traditional semiempirical protocols were not too much profitable for their usage for modeling of TMCs which previously faced and still faces severe problems. These problems are widely known in the literature as reviewed in Refs. [3,4]. Briefly they can be formulated as follows:

Dedicated to Prof. Dr. Karl Jug on the occasion of his 65th birthday

M. B. Darkhovskii · A. L. Tchougréeff (✉)
Karpov Institute of Physical Chemistry
10 Vorontsovo Pole
Moscow 105064, Russia
E-mail: andrei@cc.nifhi.ac.ru

A. V. Soudackov
Department of Chemistry
The Pennsylvania State University
104 Chemistry Research Building
University Park, PA 16802, USA

1. the Koopmans' theorem is not valid for the states with large contributions from the atomic d-states;
2. the *Aufbauprinzip* frequently breaks for the orbitals with significant contributions from the atomic d-states;
3. the iteration procedures implied by the Hartree–Fock–Roothaan (HFR) approximation converge very slowly or oscillate.

In a more general aspect one can state based on the analysis even of the recent attempts of semiempirical treatment of TMCs [5–8] that the errors can be generally characterized as unexpected and nonsystematic deviations in the calculated ground state spins and symmetries from the corresponding experimental data. The long persistence of these problems (in fact, for several decades) indicates their fundamental rather than technical character. Something is wrong with the very idea to parameterize the traditional HFR-based semiempirical description for the electronic structure of TMC.

The paper is organized as follows. In the next section, a formal point of view on the problem of constructing a semiempirical description of TMCs is presented and applied to analysis of the corresponding difficulties. Further sections are devoted to description of a semiempirical procedure of effective Hamiltonian of crystal field (EHCF) satisfying the validity conditions to be used for TMCs' modeling and of its application to analysis of spin-active complexes of iron (II). Finally, discussion and conclusions are given.

2 Theory

2.1 Electron correlations and density matrix cumulant

The relevant formal treatment starts from the notion that all the quantities related to the electronic structure of molecules can be calculated with use of only one- and two-electron density matrices for the relevant electronic state of the system under study [9]. Taking the energy for the sake of definiteness we get:

$$
\begin{aligned}
&E(C\mathbf{Q}\Gamma S \mid \omega)\\
&\quad = \min_{\xi}\Big[\iint \rho^{(1)}_{C\mathbf{Q}\Gamma \mathbf{S}}(\xi\omega \mid x, x')h^{(1)}(C\mathbf{Q}\omega \mid x', x)\mathrm{d}x\ \mathrm{d}x'\\
&\qquad + \int \rho^{(2)}_{C\mathbf{Q}\Gamma S}(\xi\omega \mid x_1x_2, x_1'x_2')h^{(2)}\\
&\qquad \times\ (C\mathbf{Q}\omega \mid x_1'x_2', x_1x_2)\mathrm{d}x_1\ \mathrm{d}x_2\ \mathrm{d}x_1'\ \mathrm{d}x_2'\Big] \qquad (1)
\end{aligned}
$$

The meaning of the notations introduced is the following. We assume that the electronic energy of the chemical species with the composition C is calculated at the nuclear configuration $\mathbf{Q}$ for its ground electronic state having the spatial symmetry Γ and the total spin S. Considering ground states of different spins and symmetry allows for description of the electronic spectra of the species to some extent. Variable ω of which the result is dependent refers to the set of *parameters* of the electronic problem: Slater or gaussian exponents, contraction coefficients, semiempirical parameters of the Hamiltonians (Fockians) etc. Set of variables ξ refers to true *variables* (something which varies) of the electronic problem: MO LCAO expansion coefficients, CI configurations' or coupled clusters' amplitudes, etc. The matrix elements of the one- and two-electron parts of the Hamiltonian: $h^{(1)}(C\mathbf{Q}\omega \mid x', x)$ and $h^{(2)}(C\mathbf{Q}\omega \mid x_1'x_2', x_1x_2)$, respectively, depend on the system composition, nuclear configuration (those defining the "external" Coulomb field acting upon electrons) and also on the parameters ω adopted in the method. The one-electron state indices $x = (\mathbf{r}, \sigma)$, $\mathbf{x}'$, $\mathbf{x_1}$, $\mathbf{x_2}$, $\mathbf{x_1'}$, $\mathbf{x_2'}$ can be understood either as continuous spatial coordinates of electrons or as discrete set of quantum numbers characterizing the states in the adopted restricted basis set. In the latter case the integration can be understood as summation over discrete values of x's giving the necessary traces of the matrix products.

In practice the density matrices are constructed as partial integrals of the corresponding trial wave functions $\Psi_{C\mathbf{Q}\Gamma S}(\xi\omega \mid x_1, x_2, \ldots, x_N)$ for the given composition, nuclear configuration, and the specified total spin and spatial symmetry:

$$
\begin{aligned}
&\rho^{(1)}_{C\mathbf{Q}\Gamma S}(\xi\omega \mid x, x')\\
&\quad = N\int \Psi^{*}_{C\mathbf{Q}\Gamma S}(\xi\omega \mid x, x_2, \ldots, x_N)\\
&\qquad \times\Psi_{C\mathbf{Q}\Gamma S}(\xi\omega \mid x', x_2, \ldots, x_N)\mathrm{d}x_2\cdots\mathrm{d}x_N \qquad (2)\\
&\rho^{(2)}_{C\mathbf{Q}\Gamma S}(\xi\omega \mid x_1x_2, x_1'x_2')\\
&\quad = \frac{N(N-1)}{2}\int \Psi^{*}_{C\mathbf{Q}\Gamma S}(\xi\omega \mid x_1, x_2, x_3, \ldots, x_N)\\
&\qquad \times\Psi_{C\mathbf{Q}\Gamma S}(\xi\omega \mid x_1', x_2', x_3, \cdots, x_N)\mathrm{d}x_3\ldots dx_N \qquad (3)
\end{aligned}
$$

The necessity of using much more complex objects as are the N-electronic wave functions $\Psi_{C\mathbf{Q}\Gamma S}$ (antisymmetric functions of N points in the direct space and N discrete spin projections) instead of by far more simple density matrices which are functions of only two or four points and spin projections, respectively, is that in the many-electron systems not any function $\rho^{(1)}$ and $\rho^{(2)}$ (even satisfying the hermicity, normalization, and symmetry conditions) can be a density matrix. The density matrix functions must result from the partial integration as stipulated by Eqs. (2, 3), which ensures the property of N-representability reflecting the extremely complex structure of the wave functions Ψ. The N-representability problem is not solved so far at least for the $\rho^{(2)}$ density matrices [10], so that the only available method to parameterize the two-electron density matrices is one with mediation of the trial wave functions, as formally presented by Eqs. (2, 3).

The expressions Eqs. (1 – 3) are completely general. In order to adjust these technique for using in relation to the TMCs' modeling, we have to consider a circle of *concepts* known as electron correlation [11]. Indeed, the statement that the motion of electrons is correlated can be given an exact meaning only with use of the two-electron density matrix Eqs. (2, 3). Generally, it looks like (with the normalization of paper [12])

$$
\begin{aligned}
\rho^{(2)}(x_1, x_2; x_1', x_2') = &\begin{vmatrix} \rho^{(1)}(x_1, x_1') & \rho^{(1)}(x_2, x_1') \\ \rho^{(1)}(x_1, x_2') & \rho^{(1)}(x_2, x_2') \end{vmatrix}\\
&-\chi(x_1, x_2; x_1', x_2') \qquad (4)
\end{aligned}
$$

Table 1 Spin-crossover iron(II) complexes with nitrogen-containing polydentate ligands selected for calculations

Complex	Ligand	Spin transition characteristics	Structural data	Ref.
$[Fe(mtz)_6]^{2+}$	1-methyl-tetrazole-N^4	Hysteresis in magnetism with $T \downarrow = 167$ and $T \uparrow = 179$ K	X-ray for HS form of the isomorphic Ni(II) complex	[43]
$[Fe(ptz)_6]^{2+}$	1-propyl-tetrazole	Steep transition at $T = 178$ K	X-ray for HS form	[44]
$[Fe(teec)_6]^{2+}$	1-(2-chloroethyl)-tetrazole	Two iron(II) sites with different spin-crossover behavior; both gradual and hysteresis transitions observed	X-ray for HS form	[45]
$[Fe(Hpt)_3]^{2+}$	3-(2-pyridyl)-1,2,4-triazole	Gradual transition with $T_{1/2} = 135$ K	X-ray for HS and LS forms	[41]

The first term in this expression expands as

$$\begin{vmatrix} \rho^{(1)}(x_1, x_1') & \rho^{(1)}(x_1', x_2) \\ \rho^{(1)}(x_1, x_2') & \rho^{(1)}(x_2, x_2') \end{vmatrix} = \rho^{(1)}(x_1, x_1')\rho^{(1)}(x_2, x_2') - \rho^{(1)}(x_1, x_2')\rho^{(1)}(x_1', x_2) \quad (5)$$

and corresponds to the model where electrons are independent i.e., non-correlated. Strictly speaking, correlations are present also in this term: omitting them by dropping the term with the "minus" sign in Eq. (5) would result in the two-electron density which would be a simple product of one-electron densities: $\rho^{(1)}(x_1, x_1)\rho^{(1)}(x_2, x_2)$. (The two-electron density is the density of the conditional probability to observe two electrons at points x_1 and x_2, simultaneously. This probability density is the diagonal element of the corresponding two-electron density matrix: $\rho^{(2)}(x_1, x_2; x_1, x_2)$.) However, the Fermi correlations, represented by the second term in Eq. (5) have too fundamental character and neglecting them would be equivalent to breaking the Pauli's exclusion principle, which is certainly too crude approximation (the Hartree approximation) to be followed further in the context of molecular modeling. Therefore, these correlations are included in the definition of independent *fermions*. The χ-term on the other hand is responsible for reducing the above product of densities when it is too large. The correspondence of the above picture with the standard language of quantum chemistry based on the many-electron wave functions rather than on the density matrices can be reestablished by noticing that the trial wave function Ψ taken in the form of a single Slater determinant formed by molecular orbitals (MO), where the variation parameters ξ are the expansion coefficients of MOs taken as linear combinations of atomic orbitals (LCAO) (HFR approach) automatically results in the two-electron density matrix of the form of Eq. (5) [10]. Thus in this framework the two-electron density matrix is not an independent quantity any more and the properties of the system are ultimately expressed through its one-electron density matrix.

All the technical tricks invented to go beyond the HFR calculation scheme in terms of different forms of the trial wave function or various perturbative procedures reduce in fact to attempts to estimate somehow the second term χ in Eq. (4) which is the cumulant of the two-particle density matrix [12] responsible for deviation of electrons' behavior from the model of independent fermions. It comprises the qualitative features of electron correlations.

2.2 Semiempirical parameterizations of the HFR approximations for TMC

The above considerations may seem to be too much theoretical and to lay too far from the practical needs of modeling electronic structure of TMC's. It is not true, however. It is easy to understand that the nature of failure of the long lasting attempts to construct an acceptable semiempirical parameterization for the transition metal compounds within the framework of the HFR MO LCAO paradigm lays precisely in the inadequate treatment of the cumulant of the two-electron density matrix.

The procedure of developing a semiempirical parameterization can be formalized in terms of Eq. (1). From this point of view a set of experimental energies $\mathcal{E}(C\mathbf{Q}\Gamma S)$ corresponding to different chemical compositions C, molecular geometries $\mathbf{Q}$, and electronic states with specific values of S and Γ is given. Developing a parameterization means to find a certain (sub)set of parameters ω which minimizes the norm of the deviation vector $\delta\mathbf{E}_\omega$ with the components $\mathcal{E}(C\mathbf{Q}\Gamma S) - E(C\mathbf{Q}\Gamma S \mid \omega)$ numbered by the tuples $C\mathbf{Q}\Gamma S$:

$$\min_{\omega} \left(\delta\mathbf{E}_\omega \left| M \right| \delta\mathbf{E}_\omega\right) , \quad (6)$$

where the norm is calculated with some positively (semi) definite metric matrix M. On one hand we know that quite a number of enterprizes of this sort were very successful leading to the whole family of semiempirical procedures useful largely for describing the ground state of "organic" molecules [13]. At the same time in case of TMCs the success is much more modest (as briefly mentioned above) and even the ground state multiplicities and spatial symmetries escape from being correctly reproduced. One can easily realize that the reason is the SCF approximation built in the computation scheme of semiempirical methods. Indeed, from a very general point of view the energies $E(C\mathbf{Q}\Gamma S \mid \omega)$ are the *linear* functionals of the density matrices Eqs. (2, 3) as well as the components of the deviation vectors $\delta\mathbf{E}_\omega$. When the cumulant of the two-electron density comes into play the energies $E(C\mathbf{Q}\Gamma S|\omega)$ and the deviations become quadratic functionals of the one-electron density matrix and remain the linear functionals of the cumulant (just the same as previous linear function of the two-electron density matrix). The HFR approximation is nothing but restricting the corresponding functionals to their respective quadratic parts with respect to the one-electron density matrix and dropping the cumulant dependent contribution completely. By this two states having the wave functions yielding the same one-electron density matrices, but different two-electron density matrices are deemed to have the same energy. (It is obvious that two such states differ namely by the cumulant of the two-electron density matrices, since the determinantal parts produced by the same one-electron density matrices apparently coincide). If such a situation (a pair of states having the above property) happens, the optimization procedure Eq. (6) would try to drive the one-electron densities in these states to be different. However, it may be impossible for the symmetry reasons if the latter is high enough at least effectively. Let us consider e.g., a two-orbital two-electron model system. Let the orbitals be a and b which can be understood as notation of one-dimensional irreducible representations. In this case, it is easy to see that the corresponding singlet and triplet states ^1B and ^3B ($\Gamma = B$, $S = 0, 1$) are given correspondingly by:

$$\begin{aligned}\Psi_{B0}(x_1, x_2) &= \frac{1}{2}\,[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)]\\ &\quad\times [a(\mathbf{r}_1)b(\mathbf{r}_2) + b(\mathbf{r}_1)a(\mathbf{r}_2)]\\ \Psi_{B1}(x_1, x_2) &= \frac{1}{2}\,[\alpha(s_1)\beta(s_2) + \beta(s_1)\alpha(s_2)]\\ &\quad\times [a(\mathbf{r}_1)b(\mathbf{r}_2) - b(\mathbf{r}_1)a(\mathbf{r}_2)]\ ,\end{aligned} \tag{7}$$

irrespective of the values of subscripts $C\mathbf{Q}$ introduced after Eq. (1) and the actual values of either parameters $\xi\omega$. Performing the integration according to Eqs. (2, 3) we immediately get that irrespective of the total spin of these states the *exact* one-electron density matrices become:

$$\begin{aligned}\rho^{(1)}_{BS}(x, x') &= \frac{1}{2}\left[\alpha^*(s)\alpha(s') + \beta^*(s)\beta(s')\right]\\ &\quad\times \left[a^*(\mathbf{r})a(\mathbf{r}') + b^*(\mathbf{r})b(\mathbf{r}')\right]\end{aligned} \tag{8}$$

and do not depend on total spin [14]. Obviously, the Hartree–Fock approximation for the two-electron density matrices coming from the one-electron densities Eq. (8) gives a wrong result since the *exact* two electron density matrices calculated according to their definition Eqs. (2, 3) from the wave functions Eq. (7) *are* different:

$$\begin{aligned}\rho^{(2)}_{B\binom{0}{1}}(x_1x_2, x_1'x_2') &= \frac{1}{4}\left[\alpha^*(s_1)\beta^*(s_2) \mp \beta^*(s_1)\alpha^*(s_2)\right]\\ &\quad\times \left[\alpha(s_1')\beta(s_2') \mp \beta(s_1')\alpha(s_2')\right]\\ &\quad\times \left[a^*(\mathbf{r}_1)b^*(\mathbf{r}_2) \pm b^*(\mathbf{r}_1)a^*(\mathbf{r}_2)\right]\\ &\quad\times \left[a(\mathbf{r}_1')b(\mathbf{r}_2') \pm b(\mathbf{r}_1')a(\mathbf{r}_2')\right]\end{aligned} \tag{9}$$

with the upper sign corresponding to $S = 0$ and the lower one to $S = 1$, irrespective of the values of the subscripts $C\mathbf{Q}$ and parameters $\xi\omega$. Opening the brackets in the above expression gives rather long formula which contains the part depending on the total spin i.e., which is different for the singlet and triplet states of the same spatial symmetry B. The physical consequences of this difference are well known: it is what immediately leads to the first Hunds rule stating that in an atom the term of a higher spin (under other equal conditions) has lower energy. The energy difference between these terms is nothing but the exchange integral. By this we clearly see that the situation we face in TMCs is intimately related to the (*grammatically*) correct treatment of the cumulant of the two-electron density matrix. Two states of say d-shell differing by the total spin only must have different energy whereas the HFR theory does not provide any quantity to which this difference can be anyhow ascribed. Notice, that the problem is not in the type of the Coulomb exchange integrals whether appearing or not in the parameterization scheme, but in its density cumulant counterpart the integral must be multiplied by. Even in the case when the Hartree–Fock part of the two-electron density matrix provides a multiplier to be combined with that or another type of exchange integrals which are responsible for the energy difference between the states of the different total spin, in the absence of the necessary component of the two-electron cumulant this difference remains zero anyway. In more complex situation than that of two electrons occupying each its orbital one can expect much more sophisticated interconnections between the total spin and two-electron densities than those demonstrated above. In any case they are concentrated in the cumulant. This explains to some extent the failure of almost 40 years of attempts to squeeze the TMCs into the semiempirical HFR theory by extending the variety of the two-electron integrals included in the parameterization.

We do not intend to further elaborate on characteristics of the widespread semiempirical methods. It is enough to say, that all of them which are restricted to the HFR approximation suffer from the shortcoming described above and, hence, one has not to have too much hope to reach a consistent description of TMCs within their framework. The recent semiempirical attempt to develop a parameterization for the transition metal compounds is the PM3 (tm) method [15, 16]. It is intensively applied to calculations of various TMCs. The calculations carried out [6,7] show that the method is not capable to reproduce even very simple characteristics in a series of TMCs having similar structure, though other authors [8,17] state that in some cases reasonable estimates of geometrical characteristics may be received, nevertheless. This situation can be understood by thorough analysis of the sets of complexes used by different groups of authors. In papers [6,7] authors study the uniform set of about 30 complexes of Ni^{2+} with the ligands bound by the nitrogen donor atoms. The analysis of this series performed there clearly shows that PM3 (tm) fails for Ni^{2+} for the now understandable reason. In the papers [8,17] the authors by contrast try to explore a comparable number of complexes but much more dispersed over the range of molecule classes which includes both the first and second row transition metal complexes, high- and low-spin ones, those having "ionic" and "covalent" bonds etc. In this test set the problematic *classes* of compounds are presented by a couple of examples each and look out to be completely isolated exceptions. This can serve as an example of how trying to test the method on a wide and apparently "random" selection of objects may lead to a smeared picture due to absence of clear criteria designed to introduce an adequate classification within the chosen set. On the other hand, we have to mention that the semiempirical method ZINDO/1 [18] which allows for some true correlation by taking into account the configuration interaction may be considered as a setting prospective for further parameterization.

3 Consistent description of TMCs' electronic structure

The grim prospects to obtain the semiempirical HFR-based picture of electronic structure of TMCs which follow from the above analysis are in a sharp contrast with the situation with the empirical understanding of detailed features of the latter. The description of TMCs used to interpret and analyze their UV–VIS spectra, magnetic and partially structural properties is based on the crystal field theory (CFT) [19,20] allowing qualitatively correct description of these characteristics of TMCs.

3.1 The crystal field theory

The CFT was introduced in the classical work by Bethe [19] devoted to the description of splittings of atomic terms in crystal fields of various symmetry. The qualitative pattern of this splitting is established by considering the change of symmetry properties of atomic wave functions while lowering the spatial symmetry from the spherical one (in case of an atom) down to the symmetry of a point group of the crystal environment. To calculate the energies of the d-d-excitations in this model, it is necessary to diagonalize the matrix of the Hamiltonian constructed in the basis of n_d-electronic wave functions (n_d is the number of d -electrons). Matrix elements of the Hamiltonian are expressed through the parameters of splitting ($10Dq$–in case of an octahedral field) and those of the Coulomb repulsion of d-electrons, that are the Slater-Condon parameters $F^k(dd)$, $k = 0, 2, 4$, or the Racah parameters A, B, C related to the former. In a simplest version of the CFT these quantities are taken as empirical parameters and determined from comparison of the excitation energies, calculated within this ionic model, to the experimental ones. Such an approach allows to describe with high accuracy the spectra of lower excitations of the impurity ions in crystals and of the TMCs, and in many cases to assign successfully the absorption bands observed experimentally.

Although the predictive force of the described approach is lost due to presence of empirical parameters in the theory, which makes it dependent on completeness of experimental data, the CFT correctly reproduces the basic qualitative features of the electronic structure of transition metal ions in crystals and TMCs well known to chemists. These features are the presence of specific group of electrons in the d-shell and symmetry of the external field which both determine the form of the spectrum of lower excitations. Analysis of the basic assumptions and constructs of the CFT shows its striking difference from those of the semiempirical HFR-based methods. Indeed, the CFT restricts itself with the electrons in the d-shell only, whereas the HFR-based semiempirical methods extend their description to all valence electrons. On the other hand the CFT uses possibly the most precise form of the electronic wave function: the full configuration interaction (FCI) one in the space of the considered one-electron states, which allows to reproduce all the components of the cumulant on the two-electron density matrix "block" which relates to the corresponding subset of the one-electron states. Incidentally, the problem of simultaneous description of several many-electron terms of similar occupancy of the one-electron states but of different total spin arises in the context of molecular modeling, namely, when it goes about TMCs and more precisely about the states of their open d-shells. The latter preserve largely their characteristics inherited from the free atoms or ions and thus the corresponding system of multiplets. The latter to be reproduced requires as it is shown above a proper description of electron correlations or equivalently correct form of the two-electron density matrix cumulant. The HFR wave function on the other hand neglects all the nontrivial parts of electron correlation. Our belief is that the above difference reflects the distinction between the details of electronic structures of the compounds described by them. The HFR form of the wave function springs from the Hückel method. In early years of development of quantum chemistry this type of the wave function had been applied to "organic" molecules like benzene and other aromatic compounds whereas the constructs specific for the CFT were used to describe "inorganic" molecules and materials reproducing by this the separation of chemistry itself into organic and inorganic and thus taking into account specificity of compounds related to these two classical subtopics of chemistry. The essential differences in the corresponding electronic structures are reflected in the form of the trial wave function accepted as zero approximations. Further development, dominated largely by numerical methods stemmed from the Hückel form of the wave function rather than qualitative reasoning, faces problems when addressing open d-shells. The general theorems (the Löwdin theorem, for example) are not of much help here since they are *existence* theorems which only state the *possibility* of obtaining the exact many-electron wave function as an expansion over Slater determinants composed of orthogonal one-electron states, for example, coming from the HFR–MO–LCAO procedure, but says nothing about *how long* an expansion giving an acceptable accuracy is going to be.

The CFT by contrast gets directly to business when it goes to TMCs' description. All key features of the electronic structure of TMC are fixed in the structure of this theory and the only problem is a consistent and independent estimation (calculation) of parameters of the crystal field induced by the metal ion's environment. All the development of CFT was concentrated on this problem. It is the basic difficulty, that has no solution in the framework of the CFT itself. The reason of this failure is transparent enough and consists in oversimplified description of the transition metal ion environment with the purely ionic model. It neglects all electrons outside the d-shell and takes into account only the symmetry of the external field and electron-electron interaction inside the d-shell. This deficiency can be lifted by considering the CFT as a special case of the effective Hamiltonian theory for one group of electrons being part of an N-electron system where other groups of electrons also present. This allows a sequential deduction of the effective Hamiltonian for the d-shell as performed in Ref. [3]. By this the matrix elements of the said Hamiltonian are expressed through characteristics of the electronic structure of the metal ion's environment. A brief description of the corresponding moves is given in the next Section.

3.2 Effective Hamiltonian of the crystal field (EHCF) method

The deduction [3] of the EHCF is based on representation of the wave function of TMC in a form of the antisymmetrized product of the group function for d-electrons and of that for other (valence) electrons of a complex which separates the electronic variables. The detailed analysis of the formal elements of the electronic structure theory together with that of the electronic structure of TMCs, distinguishing these from molecules not containing transition metal atoms reveals the basic features which must be taken into account when developing an adequate semiempirical description of their electronic structure:

1. A TMC molecule contains strongly localized electrons in its partially filled valence d-shell of the transition metal atom;
2. The electrons inside the d-shell of transition metal atom are strongly correlated;
3. Total charge transfer between the d-shell of transition metal atom and the ligand environment is small;
4. The spectrum of low-energy excited states of partially filled d -shell of transition metal atom (d-d-spectrum) is dense and well separated on the energy scale from other excitations of the system (e.g., those with electron transfer from or to the d-shell).

These features on one hand constitute the physical reasons why the HFR based approaches do not apply for the description of electronic spectra of TMCs, and on the other hand prove the necessity of the localized description of d-electrons of transition metal atom in TMC with explicit account for effects of electron correlations inside the d-shell. This can be done if one explicitly takes into account correlations of electrons in the d-shell of the transition metal atom (mentioned further as the d-shell). In a zero approximation for the TMCs' wave function one may use the function formalizing the CFT ionic model, i.e., one with a fixed number of electrons in the d-shell. The interactions responsible for electron transfer between the d-shell and the ligands can be considered as perturbations. Following the standards of semiempirical theory, we restrict the AO basis for all atoms of TMC by the valence ones. For the metal ion the vacant $4s$-and $4p$-orbitals are included. All the AOs are separated into two subsets from which one (the d-system) contains $3d$-orbitals of the transition metal atom, and another (the "ligand subsystem", or the l -system) contains $4s$-and $4p$-orbitals of the transition metal atom and the valence AOs of all the ligand atoms. Furthermore, we consider only such complexes, where excitation energies in the l-system are by far larger than the excitation energies in the d-shell of the metal atom. This singles out a subset of the Werner TMCs which can be alternatively characterized as ones with the close electronic shells ligands, such as F^-, Cl^-, Br^-, I^-, saturated organic molecules with donor atoms. This comprises the set of objects we are going to cover in this theory.

Formally the theory evolves as following. The electronic wave function for the n-th state of the complex is written as the antisymmetrized product of wave functions of the electron groups introduced above:

$$\Psi_n = \Phi_d^{(n)} \wedge \Phi_l \tag{10}$$

This reflects the main feature of the electronic structure of the TMC, that is the presence of the strongly correlated d-shell and of relatively inert ligands. The low-energy d-d-spectrum of the whole TMC described by the Hamiltonian

$$H = H_d + H_l + H_c + H_r \tag{11}$$

where H_d is the Hamiltonian of d-electrons, H_l is the Hamiltonian of the ligand system, H_c is the Coulomb interaction, and H_r is the resonance interaction, is that of the effective Hamiltonian for the d-system:

$$\begin{aligned} H_d^{\text{eff}} = &\sum_{\mu\nu\sigma} U_{\mu\nu}^{\text{eff}} d_{\mu\sigma}^{\dagger} d_{\nu\sigma} \\ &+\frac{1}{2} \sum_{\mu\nu\rho\eta} \sum_{\sigma\tau} (\mu\nu \mid \rho\eta) d_{\mu\sigma}^{\dagger} d_{\rho\tau}^{\dagger} d_{\eta\tau} d_{\nu\sigma} \end{aligned} \tag{12}$$

where the d-electron Coulomb interaction term is inherited from the free ion and the effective core parameters $U_{\mu\nu}^{\text{eff}}$ contain contributions from the Coulomb and the resonance interaction between the d- and l-systems:

$$U_{\mu\nu}^{\text{eff}} = \delta_{\mu\nu} U_{dd} + W_{\mu\nu}^{\text{atom}} + W_{\mu\nu}^{\text{field}} + W_{\mu\nu}^{\text{cov}}, \tag{13}$$

where

$$W_{\mu\nu}^{\text{atom}} = \delta_{\mu\nu} \left(\sum_{\alpha\in s,p} g_{\mu\alpha} P_{\alpha\alpha} \right), \tag{14}$$

is the repulsion of electrons in the d-shell from those in the $4s$- and $4p$-AO's of the metal,

$$W_{\mu\nu}^{\text{field}} = \sum_L Q_L V_{\mu\nu}^L, \tag{15}$$

is the Coulomb interaction of d-electrons with the net charges on the ligand atoms, having the standard CFT form [21]; and the covalent part:

$$W_{\mu\nu}^{\text{cov}} = -\sum_i \beta_{\mu i}\beta_{\nu i} \left(\frac{1-n_i}{\Delta E_{di}} - \frac{n_i}{\Delta E_{id}} \right) \tag{16}$$

ultimately comes from the resonance interaction between the d- and l-systems. According to the EHCF method [3] the l-system is described by a single Slater determinant Φ_l which has to be obtained from an HFR procedure using the effective renormalized Hamiltonian of the ligand subsystem. Solving the HFR problem for the l-system allows to determine one-electron density matrix $P_{\alpha\beta}$, orbital energies ϵ_i, and the MO–LCAO coefficients $c_{i\alpha}$. These quantities completely define the electronic structure of the l-system and are used to calculate the effective Hamiltonian (12) by Eqs. (14)–(16), where $Q_L = \sum_{\alpha\in L} P_{\alpha\alpha} - Z_L$ is the effective charge of the ligand atom L; Z_L is the core charge of the ligand atom L; $V^L_{\mu\nu}$ is the matrix element of the potential energy operator describing the interaction between a d-electron and a unit charge placed on the ligand atom L; n_i is the occupation number of the ith l-MO ($n_i = 0$ or 1); ΔE_{di} (ΔE_{id}) is the energy necessary to transfer an electron from the d-shell (from the ith l-MO) to the ith l-MO (to the d-shell):

$$\begin{aligned}\Delta E_{di} &= -A_i + I_d - \bar{\gamma}_{di}\\ \Delta E_{id} &= I_i - A_d - \bar{\gamma}_{di},\end{aligned} \tag{17}$$

where I_i and A_i are the ionization potential and the electron affinity of the ith l-MO within the HFR scheme equal to $-\epsilon_i$–the corresponding orbital energy with the opposite sign, I_d and A_d are, respectively, the effective ionization potential and the electron affinity of the d-shell, and $\bar{\gamma}_{di}$ is the Coulomb integral averaged over the d orbitals of a transition metal atom. The resonance integrals $\beta_{\mu i}$ in Eq. (16) are given by

$$\beta_{\mu i} = \sum_{\alpha} \beta_{\mu\alpha} c_{i\alpha} \tag{18}$$

where $c_{i\alpha}$ is the MO-LCAO coefficient, and $\beta_{\mu\alpha}$ is the resonance integral between the α-th l-AO and the μ-th d-AO.

3.3 Semiempirical implementations of the EHCF paradigm

In the context of the EHCF construct described in the previous Section the problem of semiempirical modeling of TMCs' electronic structure is seen in a somewhat different perspective. The EHCF implicitly contains the crucial element of the theory: the block of the two-electron density matrix cumulant which relates to the d-shell. Instead of hardly justifiable attempts to extend a parameterization to the transition metals it is now possible to check in a systematic way the value of different parameterization schemes already developed in the "organic" context for the purpose of estimating the quantities necessary to calculate the crystal field according to prescriptions of the EHCF theory Eqs. (14)–(16). Solving the wave equation for the effective Hamiltonian for the d-system H^{eff}_d with the matrix elements which are estimated with use of any "organic" semiempirical scheme with the CI wave function constructed in the basis of the d-system, we obtain the complete description of the many-electron states of the d-shell of the metal ion in the complex. In such a formulation the EHCF method was parameterized for calculations of various complexes of metals of the first transition row, with mono- and polyatomic ligands. In the works [3,4,22–24], parameters for compounds with donor atoms N, C, O, F, Cl and doubly and triply charged ions V, Cr, Mn, Fe, Co, Ni are fitted. These parameters do not depend on details of chemical structure of the whole ligand, but are characteristic only for each pair metal-donor atom. The dependence of the excerted effective field on details of geometry and chemical composition of the ligands are believed to be reproduced in a frame of a standard HFR-based semiempirical procedure used to describe "organic" l-system within the proposed hybrid approach. The further evaluations [23–25] have shown applicability of the fitted system of parameters for calculations of the electronic structure and spectra of numerous complexes of divalent cations with use of the CNDO parameterization for the l-system. In Refs. [26,27] the EHCF method is also extended for calculations of ligands by the INDO and MINDO/3 parameterizations. In all calculations the experimental multiplicity (spin) and spatial symmetry of the corresponding ground states were reproduced correctly. The summit of this approach was reached [25] in the calculations on the complex *cis*-[Fe(NCS)$_2$(bipy)$_2$]. The molecular geometry is known for both the high- and low-spin isomers of the said compound. The calculations reproduce the respective ground state spins and the spectra of low lying d-d-excitations in remarkable agreement with the experimental data.

Another semiempirical implementation of the EHCF method is based on the well-known SINDO1 scheme developed by Jug et al. [28–30]. The SINDO1 scheme has some specific features which seem to be very important in the light of the EHCF formulation. First of all, the explicit account of the nonorthogonality of the atomic orbitals by using a Löwdin orthogonalized basis set provides a validity of the strong orthogonality condition between the group functions Φ^n_d and Φ_l and justifies the derivation of the system of the effective Schrödinger-like equations for the electronic subsystems of a TMC. The second quite important point is that the SINDO1 method uses a theoretically justified and well parameterized expression for the semiempirical resonance integrals. This expression makes it possible to reproduce the features of the distance dependence of the resonance integrals in the relatively wide range of bond distances.

The details of the EHCF/SINDO1 implementation are described in details in [31]. Here, we will briefly outline the specific features arising from using the orthogonalized atomic basis sets in the parameterization scheme.

The single-determinant wavefunction Φ_l for the ligand subsystem is calculated with slightly modified SINDO1 method using the effective Fockian for the l-subsystem. First, the matrix elements of the core Hamiltonian of the l-system are renormalized to reflect the interaction of the ligand electrons with the electron density in the d-system. At the next stage, the effective core Hamiltonian matrix is transformed to a symmetrically orthogonalized atomic orbital (OAO) basis set. This transformation takes into account the d-orbitals of the metal atom as well, so that the resulting OAO basis set in the l-system and the transformed d-orbitals of the metal are orthogonal to each other. The resulting effective core Hamiltonian matrix elements in the OAO basis for the l-system include two types of the first-order orthogonalization corrections originating from ligand atomic orbitals and metal d-orbitals, respectively. The two-center off-diagonal matrix elements of the core Hamiltonian in the OAO basis (resonance integrals) have additional empirical correction terms with adjustable pair parameters fit to reproduce the geometries, heats of formation, and ionization potentials for a representative set of transition metal compounds [31].

Compared to the Eq. (13) the effective one-electron parameters for the d-system $U^{\text{eff}}_{\mu\nu}$ in EHCF/SINDO1 scheme contain two additional contributions

$$U^{\text{eff}}_{\mu\nu} = \delta_{\mu\nu} U_{dd} + W^{\text{atom}}_{\mu\nu} + W^{\text{field}}_{\mu\nu} + W^{\text{cov}}_{\mu\nu} + W^{\text{exch}}_{\mu\nu} + W^{\text{orth}}_{\mu\nu} \,. \tag{19}$$

The exchange correction terms $W^{\text{exch}}_{\mu\nu}$ originate from the exchange interactions between d-electrons and electrons on the MOs of the ligand subsystem. They have the following form:

$$W^{\text{exch}}_{\mu\nu} = -\frac{1}{2} \sum_{k,l}^{\{L\}} P_{kl} (\mu k \mid \nu l). \tag{20}$$

The exchange integrals $(\mu k \mid \nu l)$ are calculated using the Mulliken approximation (M is a metal atom; A and B are ligand atoms):

$$(\mu^M k^A \mid \nu^M l^B) = \frac{1}{4} S_{\mu k} S_{\nu l} \left(\bar{\gamma}_{dd} + \gamma_{MA} + \gamma_{MB} + \gamma_{AB}\right), \tag{21}$$

where S_{ij} are the overlap integrals; $\bar{\gamma}_{dd}$ is an average one-center Coulomb integral of the type $(dd \mid dd)$ and the γ_{MA}, γ_{MB}, γ_{AB} are average two-center Coulomb integrals. The average values for the Coulomb integrals have been used in order to secure the invariance with respect to orthogonal transformations of the atomic basis set.

The term $W^{\text{orth}}_{\mu\nu}$ is a first order correction originating from the Löwdin orthogonalization of the d orbitals with respect to the ligand orbitals:

$$W^{\text{orth}}_{\mu\nu} = -\frac{1}{2} \sum_{l}^{\{L\}} \left(S_{\mu l} L_{\nu l} + L_{\nu l} S_{\mu l} \right), \tag{22}$$

where $S_{\mu l}$ are the overlap integrals between metal d-orbitals and ligand AO's, and $L_{\nu l}$ are the empirical terms used in the SINDO1 parameterization of the resonance integrals [32]:

$$L_{\nu l} = -\frac{1}{2} (\zeta_\nu^2 + \zeta_l^2) \frac{S_{\nu l} \left(1 - |S_{\nu l}|\right)}{1 + \frac{1}{2}(\zeta_\nu + \zeta_l) R_{ML}} \,. \tag{23}$$

Here ζ_i are basis set exponents and R_{ML} is the distance between the metal atom and the ligand atom on which the atomic orbital l is centered.

The EHCF/SINDO1 method has proved to be useful for calculations of spectra of low-energy excitations in some iron(II) complexes and ionic crystals [31]. In all cases the method reproduces not only the experimentally observed spin and symmetry of the electronic ground state but also provides the excitation energies with a good accuracy. The calculation of the splittings of the d-levels of the metal complex with partitioning of the total splittings into various contributions according to Eq. (19) gives a unique possibility to analyze the details of the electronic structure of the complex in simple terms analogous to the crystal field theory, so widely used by inorganic chemists for the interpretation of the electronic spectra of these compounds.

3.4 Calculation of quadrupole splittings in Mössbauer spectra

The quadrupole splitting measured in the Mössbauer spectra of iron compounds is due to the interaction of the quadrupole moment Q of the ^{57}Fe nucleus in its excited state and the electric field gradient (EFG) at the position of this nucleus. The EFG at $\mathbf{r} = \mathbf{R}^{(Fe)}$ in the presence of the external charge density $\rho(\mathbf{r})$ (electrons and other nuclei) is represented by the traceless tensor with the components

$$V_{\alpha\beta} = \int v_{\alpha\beta}(\mathbf{r}) \rho(\mathbf{r}) \, \mathrm{d}^3\mathbf{r} \,, \tag{24}$$

$$v_{\alpha\beta}(\mathbf{r}) = \frac{3(r_\alpha - R^{(Fe)}_\alpha)(r_\beta - R^{(Fe)}_\beta) - \delta_{\alpha\beta} \left|\mathbf{r} - \mathbf{R}^{(Fe)}\right|^2}{\left|\mathbf{r} - \mathbf{R}^{(Fe)}\right|^5}, \tag{25}$$

where r_α, r_β are the cartesian components of the position vector $\mathbf{r}$.

In a line with the EHCF representation of the total wavefunction as an antisymmetrized product Eq. (10) of the group functions for the d-system and l-system the total EFG tensor for the TMC in its n-th electronic state can be expressed as a sum of two contributions

$$V^{(n)}_{\alpha\beta} = V^{(n)}_{\alpha\beta}(n_d) + V_{\alpha\beta}(n_l) \tag{26}$$

The first contribution $V^{(n)}_{\alpha\beta}(n_d)$ is due to the d-electrons of the metal atom

$$V^{(n)}_{\alpha\beta}(n_d) = \sum_{\mu\nu} \left\langle \mu \left| v_{\alpha\beta} \right| \nu \right\rangle \sum_{I,J} C^{(n)}_I C^{(n)}_J \left\langle I \left| \hat{E}_{\mu\nu} \right| J \right\rangle, \tag{27}$$

where μ, ν represent the one-electron atomic d-orbitals; I, J are the n_d-electron basis states (belonging to the irreducible representations of the unitary group $U(n_d)$); $\hat{E}_{\mu\nu} = \sum_\sigma d^\dagger_{\mu\sigma} d_{\nu\sigma}$ are the generators of the unitary group; and $C^{(n)}_I$, $C^{(n)}_J$ are the eigenvector amplitudes at the basis configurations I and J, respectively.

The second contribution $V_{\alpha\beta}(n_l)$ is due to the electrons and nuclei of the l-subsystem. It can be further partitioned into the contribution of the valence $4p$-electrons of the metal atom $V^{4p}_{\alpha\beta}$ and the contribution of the effective charges on the ligand atoms $V^L_{\alpha\beta}$ (the contribution of the valence $4s$ electrons vanishes due to the spherical symmetry)

$$V_{\alpha\beta}(n_l) = V^{4p}_{\alpha\beta} + V^L_{\alpha\beta} \tag{28}$$

$$V^{4p}_{\alpha\beta} = \sum_{p,q \in 4p} P_{pq} \left\langle p \left| v_{\alpha\beta} \right| q \right\rangle \tag{29}$$

$$V^L_{\alpha\beta} = \sum_{A \in L} Q_A v_{\alpha\beta}(\mathbf{r}_A) \tag{30}$$

Here, P_{pq} are the elements of the one-electron SCF density matrix for the l-system and $Q_A = Z_A - \sum_{q \in A} P_{qq}$ is the effective charge on the atom A.

Table 2 *d-d* Excitation energies (cm^{-1}) for spin crossover Fe(II) complexes

[Fe(mtz)$_6$]$^{2+}$					
HS (X-ray [43])			LS (EHCF/MM)		
Transition	Calculated	Exp.[43]	Transition	Calculated	Exp.[43]
^{5}T$_2$ → ^{5}E(1)	10211		^{1}A$_1$ → ^{1}T$_1$(1)	14929	
→ ^{5}E(2)	10284	11750	→ ^{1}T$_1$(2)	14980	18200
			→ ^{1}T$_1$(3)	15083	
			→ ^{1}T$_2$(1)	22963	
			→ ^{1}T$_2$(2)	23075	26600
			→ ^{1}T$_2$(3)	23130	
[Fe(ptz)$_6$]$^{2+}$					
HS (EHCF/MM)			LS (EHCF/MM)		
Transition	Calculated	Exp.[44]	Transition	Calculated	Exp.[44]
^{5}T$_2$ → ^{5}E(1)	8774		^{1}A$_1$ → ^{1}T$_1$(1)	14478	
→ ^{5}E(2)	8855	12590	→ ^{1}T$_1$(2)	14577	19231
			→ ^{1}T$_1$(3)	14666	
			→ ^{1}T$_2$(1)	22512	
			→ ^{1}T$_2$(2)	22533	27778
			→ ^{1}T$_2$(3)	22650	
[Fe(teec)$_6$]$^{2+}$					
HS (X-ray [45])					
Transition	Calculated	Exp.[45]	Transition	Calculated	Exp.
^{5}T$_2$ → ^{5}E(1)	6550				
→ ^{5}E(2)	6972	11800			
[Fe(Hpt)$_3$]$^{2+}$					
HS (X-ray [41])			LS (X-ray [41])		
Transition	Calculated^b	Exp.[41]	Transition	Calculated^b	Exp.[41]
^{5}T$_2$ → ^{5}E(1)	6625 (8896)		^{1}A$_1$ → ^{1}T$_1$(1)	10995 (13564)	
→ ^{5}E(2)	8169 (10412)	11765	→ ^{1}T$_1$(2)	11426 (13893)	18868
			→ ^{1}T$_1$(3)	11668 (14613)	
			→ ^{1}T$_2$(1)	17993 (20892)	
			→ ^{1}T$_2$(2)	18778 (21999)	
			→ ^{1}T$_2$(3)	19448 (23148)	

Calculated excitation energies correspond to the actual symmetry of the complexes which is lower than O_h, hence the splittings between the components of the degenerated E and T states

^{b} numbers in brackets are the results of calculation with the geometry of the complex optimized with hybrid EHCF/MM method

The one-electron matrix elements $\langle \mu \left| v_{\alpha\beta} \right| \nu \rangle$ and $\langle p \left| v_{\alpha\beta} \right| q \rangle$ have the following structure

$$\langle \mu \left| v_{\alpha\beta} \right| \nu \rangle = \langle r^{-3} \rangle_{3d} \, f_{\mu\nu}^{\alpha\beta} \tag{31}$$

$$\langle p \left| v_{\alpha\beta} \right| q \rangle = \langle r^{-3} \rangle_{4p} \, g_{pq}^{\alpha\beta}, \tag{32}$$

where the radial factors $\langle r^{-3} \rangle$ are calculated with the corresponding radial atomic wavefunctions and the analytical expressions for the angular factors $f_{\mu\nu}^{\alpha\beta}$ and $g_{pq}^{\alpha\beta}$ for $3d$ and $4p$ atomic orbitals are presented in Appendix A.

Due to the presence of electrons in the inner shells of the iron atom the contributions to the total EFG tensor have to be corrected to reflect the shielding and antishielding effects of inner electrons. The shielding effects for the valence $3d$ and $4p$ electrons and antishielding effects for the charges on ligand atoms are described by the Sternheimer factors $1 - R$ and $1 - \gamma_\infty$, respectively [33] (in this work we adopted the values $R = 0.32$ and $\gamma_\infty = -9.1$ used previously for Fe(II) complexes [34,35]). With this taken into account the total EFG tensor is represented as

$$\begin{aligned} V_{\alpha\beta}^{(n)} &= (1 - R) V_{\alpha\beta}^{(n)}(n_d) + (1 - R) V_{\alpha\beta}^{4p} \\ &\quad + (1 - \gamma_\infty) V_{\alpha\beta}^{L} \end{aligned} \tag{33}$$

The total temperature dependent EFG tensor $V_{\alpha\beta}(T)$ can be calculated by averaging all the components over all the excited electronic states acording to Boltzmann statistics

$$V_{\alpha\beta}(T) = \frac{\sum_n V_{\alpha\beta}^{(n)} \exp\left(-E_n / k_{\mathrm{B}} T\right)}{\sum_n \exp\left(-E_n / k_{\mathrm{B}} T\right)} \tag{34}$$

Finally, the quadrupole splitting ΔE_Q in ^{57}Fe Mössbauer spectra is given by the expression

$$\Delta E_Q = \frac{1}{2} e Q V_{ZZ} \left(1 + \frac{\eta^2}{3} \right)^{\frac{1}{2}}, \tag{35}$$

where e is the (positive) unit charge, Q is the nuclear quadrupole moment of the Mössbauer nucleus, V_{ZZ} is the main

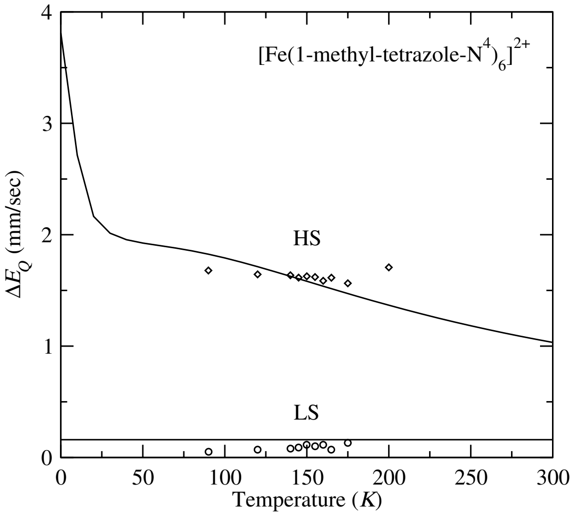

Fig. 1 Temperature dependence of the quadrupole splitting ΔE_Q in Mössbauer spectra of high spin (HS) and low spin (LS) forms of [Fe(mtz)$_6$]$^{2+}$ complex. The calculated data are shown with *solid lines* and experimental data [43] are shown with diamonds (HS) and circles (LS)

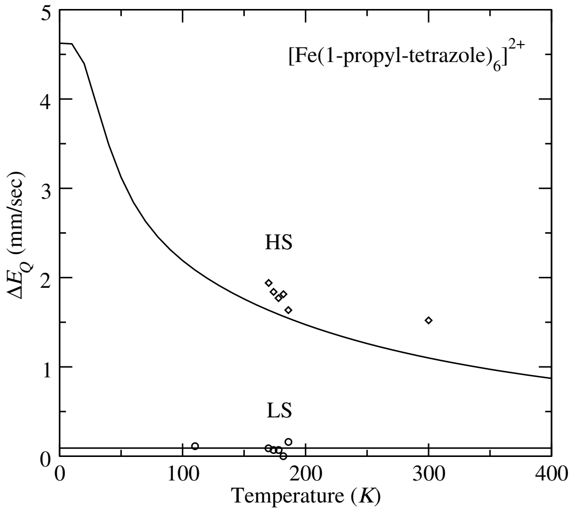

Fig. 2 Temperature dependence of the quadrupole splitting ΔE_Q in Mössbauer spectra of high spin (HS) and low spin (LS) forms of [Fe(ptz)$_6$]$^{2+}$ complex. The calculated data are shown with *solid lines* and experimental data [44] are shown with diamonds (HS) and circles (LS)

component of the EFG tensor defined by $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$, and η is the asymmetry parameter

$$\eta = \frac{|V_{XX}| - |V_{YY}|}{|V_{ZZ}|} . \tag{36}$$

3.5 Hybrid method EHCF/MM

In its simple version the EHCF/X method treats the electronic structure of the ligands within a semiempirical approximation X. These methods are not, however, designed to conduct the systematic studies of potential energy surfaces (PESs) of TMCs. Further application of the EHCF methodology would be to develop a method for the calculation of PESs of TMCs. The CNDO or INDO parameterizations for the ligands are probably of high enough accuracy when it goes about the charge distribution in the ligands and the orbital energies at fixed experimental geometries. However, these methods do not suit for geometry optimizations (or more generally for searching PESs) of TMCs. Applying the electron partitioning into groups [9] allows to effectively formulate hybrid schemes of the QM/MM type. In the original implementation [3] EHCF method does not allow to follow the PESs of TMCs. Nevertheless, the EHCF method can be adapted for this application in a framework of the hybrid scheme QM/MM. Indeed, according to [12] complete electronic energy of the wave function (14) in its nth state is:

$$E_n = E_d^{\mathrm{eff}}(n) + E_l , \tag{37}$$

where $E_d^{\mathrm{eff}}(n)$ is the energy of the n-th state of the effective Hamiltonian for d-electrons in the crystal field. An alternative to the step by step improvement of semiempirical descriptions of the ligand's electronic structure X for the computation of the PES of TMCs would be to use the molecular mechanics (MM) model to calculate the ligand's energy E_l. In such a setting the EHCF/X (X = CNDO, INDO) method is only retained for the d-shell electrons [36,37]. This simply replaces the ligand's energy E_l by E_{MM}, estimated by an MM calculation. The total energy of the state n becomes:

$$E_n = E_d^{\mathrm{eff}}(n) + E_{\mathrm{MM}} . \tag{38}$$

This represents a natural way of combining MM and EHCF [38–40]. Thus calculating energy of multielectronic states of the d-shell $E_d^{\mathrm{eff}}(n)$ for different nuclear configurations of TMC and ligand energy E_{MM} it is possible to obtain approximate PES for various states of the d-shell of TMC.

The general scheme of the energy evaluation Eq. (38) is based on the implementation of the EHCF method in which the wave function Φ_l for the l-system is calculated within a semiempirical version of the HFR approach (for example, CNDO) and then used to construct H_d^{eff}. This scheme appears rather expensive to be used for searches of PES, since it requires the HFR calculations on the l-system for each geometry of the complex. To clear this, we have developed the local version of the EHCF method which allows to calculate the crystal field much more economically.

Not going into too much details we can say that the local EHCF method developed for this purpose allows to calculate the covalent contribution to the effective crystal field through the characteristics of ligands' lone pairs. The local EHCF method was implemented and used for the analysis of the molecular geometries of complexes of iron (II) in works [38,39]. In our work [40] we describe the effect of electrostatic field of the metal ion on the ligands within the electrostatic polarization model. The appropriate objects allowing to test the described approach are spin isomers of TMCs. Satisfactory precision of the estimates of geometry dependence of the effective crystal field in a series of complexes of iron (II) and cobalt (II) (both low- and high-spin

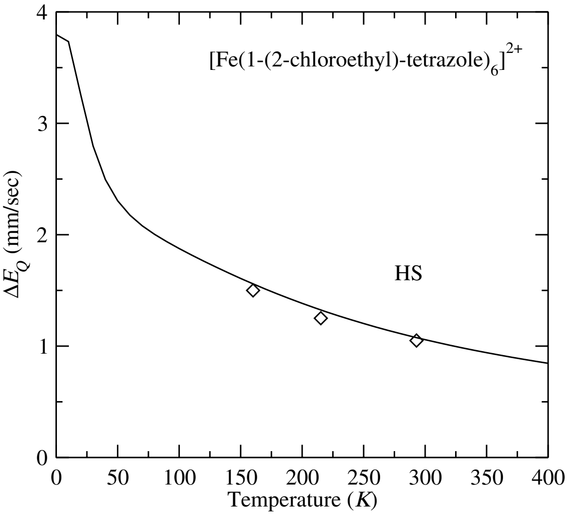

Fig. 3 Temperature dependence of the quadrupole splitting ΔE_Q in Mössbauer spectra of the high spin form of [Fe(teec)$_6$]$^{2+}$ complex. The calculated data are shown with a *solid line* and experimental data (roughly estimated from the Mössbauer spectra presented in Ref. [45]) are shown with *diamonds*

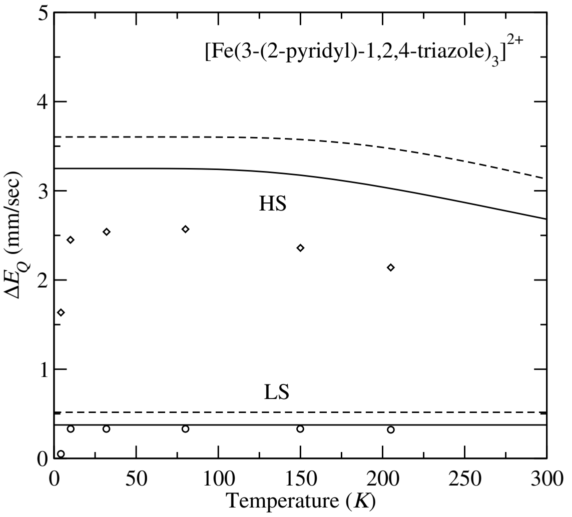

Fig. 4 Temperature dependence of the quadrupole splitting ΔE_Q in Mössbauer spectra of high spin (HS) and low spin (LS) forms of [Fe(Hpt)$_3$]$^{2+}$ complex. The calculated data for the experimental and optimized with EHCF/MM method geometries are shown with *solid* and *dashed lines*, respectively, and experimental data [41] are shown with *diamonds* (HS) and *circles* (LS)

ground states) is achieved [40]. We considered totally 26 six-coordinated iron complexes with mono- and polydentate ligands, containing both aliphatic and aromatic donor nitrogen atoms (mixed complexes with different types of donor nitrogen atoms and different spin isomers of one complex are included in this number) and ten cobalt complexes also with different types of donor nitrogen atoms and coordination numbers ranging from four up to six. Deviations of calculated bond lengths Fe–N and Co–N from the experimental ones are randomly distributed according to the normal (Gauss) law with almost zero mean value, thus, indicating to the evanescence of the systematic error and with the dispersions of 0.004 and 0.001 Å^2, respectively. These data are obtained from the set of 180 Fe–N and 46 Co–N internuclear separations.

4 Electronic spectra and Mössbauer quadrupole splittings in spin-crossover Fe(II) complexes

Using the EHCF/SINDO1 method we performed the calculations of the electronic spectra and quadrupole splittings in Mössbauer spectra of four spin-crossover Fe(II) complexes with nitrogen-containing polydentate ligands. A short description of these complexes is presented in Table 1. The geometries of the high-spin (HS) forms of the complexes have been determined from X-ray experiments (see references in Table 1) and we used these geometries in our calculations. The structural data for the low-spin (LS) forms of the first three complexes listed in Table 1) are not available due to the experimental difficulties with the isolation of syngle crystals. In such cases the geometries were obtained by optimization of the structures for the corresponding LS forms using the hybrid EHCF/MM method [40]. In all calculations of Mössbauer and spectral parameters we used the standard set of EHCF/SINDO1 parameters [31], the Racah parameters B and C were set to 650 cm^{-1} and 2400 cm^{-1}, respectively, as in our previous calculations of the Fe(II) spin-crossover complexes [25].

The calculated *d-d* excitation energies for all four selected complexes are presented in Table 2. In all cases the EHCF/SINDO1 method correctly reproduces the spin multiplicity of the ground state in accordance with experimental observations. The calculated excitation energies for the first three complexes are also in satisfactory agreement with the experimental measurements, especially taking into account that the interpretation of the experimental spectral data and assignment of the spectral bands in the visible region is usually done using the simple crystal field model for the octahedral environment and the presented measured excitation energies actually correspond to the average over the convolution of several overlapping spectral lines which are sometimes very difficult to resolve. The calculated excitation energies for the [Fe(Hpt)$_3$] complex seem to be underestimated compared to the available experimental data, especially for the LS form of the complex. However, the observed transition at 18868 cm^{-1} interpreted in Ref. [41] as the $^1A_1 \rightarrow ^1T_1$ *d-d* transition might be interpreted based on our calculations as the transition from the ground $^1A_1$ state to one of the Jahn-Teller components of the excited $^1T_2$ state. Unfortunately, the details of the interpretation of the measured ligand-field spectrum are not discussed in Ref. [41].

The Mössbauer spectra of the spin-crossover iron complexes are with no doubt a very powerful source of information about electronic structure and nature of spin transitions in these complexes. The measured parameters of the spectra, isomer shift and quadrupole splitting, differ significantly for two spin isomers which allows to monitor the composition of the sample by decomposing the measured spectrum into HS and LS components and evaluating their relative contributions. From the theoretical point of view the calculations of the Mössbauer spectral parameters and comparing the results to the experimental data presents a unique and very sensitive way of probing the local electronic structure of the metal ion in the complex due to the extreme sensitivity of the isomer shift and quadrupole splitting to the details of the electron density in the vicinity of the iron atom and to the symmetry of the electrostatic field created by the environment (ligands). We performed the calculations of the temperature dependent quadrupole splittings for the HS and LS forms of the complexes listed in Table 1 using the wavefunctions obtained in our EHCF/SINDO1 calculations. For the quadrupole moment of the ^{57}Fe nucleus we used the value of $Q = 0.187$ barn, for the radial factors $\langle r^{-3} \rangle_{4p}$ and $\langle r^{-3} \rangle_{3d}$ we used the values of 1.697 and 4.979, respectively, obtained in HFR atomic calculations [42]. No other empirical parameters were introduced in Eq. (35). The calculation results are presented in Figs. 1–4 along with the available experimental data. The agreement between the calculated and experimental data for the first three complexes (Figs. 1–3) is quite remarkable. That indicates that the EHCF/SINDO1 method describes the electronic structure of the d-system as well as the details of the electrostatic field in the vicinity of the metal atom quite accurately. As in the case with the electronic excitation spectra, the calculated quadrupole splittings for the [Fe(Hpt)$_3$] complex (especially for the HS form) are in a relatively poor numerical agreement with the experimental data, although qualitatively the results are still satisfactory. The true reason for this exceptional behavior remains unclear, but one of the possible explanations can be related to the uncertainties in the structural data. Among the complexes considered the [Fe(Hpt)$_3$] complex is the only one which undergoes a gradual spin transition, so that both the LS and HS forms are present in the sample over all range of temperatures. To demonstrate the sensitivity of the calculated values of Mössbauer parameters to the geometry of the complex we performed additional calculations of the quadrupole splittings for the geometries optimized with the hybrid EHCF/MM method instead of experimental ones. As one can see from Fig. 4, very slight changes in the geometry produced by the EHCF/MM optimization on the HS form result in significant variation of the calculated quadrupole splitting. In any case further studies are necessary to elucidate the correspondence between experimental and theoretical spectra and molecular geometries of the present compound.

Despite of the mentioned difficulties, the overall results of calculations strongly support the applicability of the EHCF methodology for studying the electronic structure of polyatomic TMC's for which high-level ab initio calculations are not feasible. Moreover, the results of calculations also support the whole EHCF paradigm and its ability to describe the most important features of the electronic structure of the systems with strongly localized correlated groups of electrons on the quantitative level.

5 Concluding remarks

In the present paper, we tried to demonstarte the feasibility of a semiempirical description of the electronic structure and properties of the Werner TMCs on a series of rather sophisticated examples. Spin active complexes (those undergoing spin transitions) of iron(II) with nitrogen containing ligands have been considered. It turned out that using a semiempirical description with the electron correlation adequately “biult in” to the structure of the method allows to reproduce the entire collection of the relevant experimental data ranging from the molecular geometry for the both observed spin isomers to the optical and Mössbauer spectra.

Acknowledgements AVS thanks Professor Dr. Karl Jug for many stimulating discussions during the initial stages of the development of the EHCF/SINDO1 method and for the encourangement and strong support throughout his whole career. This paper is dedicated to Professor Dr. Karl Jug in recognition of his significant contribution to modern quantum chemistry and on occasion of his 65-th birthday. The work is supported by the RFBR grants Nos 04-03-32146, 04-03-32206. Authors also thank Prof. Dr. Paul Ziesche for sending (p)reprints of his work on density matrix cumulants.

Appendix A

Angular parts of the EFG matrix elements

Here, we present the analytical expressions for the angular factors $f^{\alpha\beta}_{\mu\nu}$ and $g^{\alpha\beta}_{pq}$ (Eqs. 31, 32). The expressions are given in the basis of the eigenfunctions of the angular momentum operator $|l, m\rangle$, $m = -l, -l+1, \ldots, l$ with $l = 1$ for the $4p$-functions and $l = 2$ for the $3d$-functions.

$$\begin{aligned}
g^{xx}_{pq} &= (-1)^{m_p} G^{(0)} \left[3G^{(1)}_{pq} - \frac{3\sqrt{3}}{\sqrt{2}} \left(G^{(2)}_{pq} + G^{(3)}_{pq} \right) \right] \\
g^{yy}_{pq} &= (-1)^{m_p} G^{(0)} \left[3G^{(1)}_{pq} + \frac{3\sqrt{3}}{\sqrt{2}} \left(G^{(2)}_{pq} + G^{(3)}_{pq} \right) \right] \\
g^{zz}_{pq} &= 6(-1)^{m_p+1} G^{(0)} G^{(1)}_{pq} \\
g^{xy}_{pq} &= i(-1)^{m_p} \frac{3\sqrt{3}}{\sqrt{2}} G^{(0)} \left(G^{(3)}_{pq} - G^{(2)}_{pq} \right) \\
g^{xy}_{pq} &= (-1)^{m_p} \frac{3\sqrt{3}}{\sqrt{2}} G^{(0)} \left(G^{(5)}_{pq} - G^{(4)}_{pq} \right) \\
g^{yz}_{pq} &= i(-1)^{m_p+1} \frac{3\sqrt{3}}{\sqrt{2}} G^{(0)} \left(G^{(4)}_{pq} + G^{(5)}_{pq} \right) ,
\end{aligned} \tag{39}$$

where

$$G^{(0)} = \begin{pmatrix} 1 & 2 & 1 \\ 0 & 0 & 0 \end{pmatrix} = \frac{\sqrt{2}}{\sqrt{15}}; \quad G^{(1)}_{pq} = \begin{pmatrix} 1 & 2 & 1 \\ -m_p & 0 & m_q \end{pmatrix};$$
$$G^{(2)}_{pq} = \begin{pmatrix} 1 & 2 & 1 \\ -m_p & 1 & m_q \end{pmatrix}; \quad G^{(3)}_{pq} = \begin{pmatrix} 1 & 2 & 1 \\ -m_p & -1 & m_q \end{pmatrix}; \tag{40}$$
$$G^{(4)}_{pq} = \begin{pmatrix} 1 & 2 & 1 \\ -m_p & 2 & m_q \end{pmatrix}; \quad G^{(5)}_{pq} = \begin{pmatrix} 1 & 2 & 1 \\ -m_p & -2 & m_q \end{pmatrix},$$

are the Wigner $3j$-symbols.

$$\begin{aligned}
f^{xx}_{\mu\nu} &= (-1)^{m_\mu} \frac{5}{\sqrt{70}} \left[\frac{3\sqrt{2}}{\sqrt{3}} \left(F^{(1)}_{\mu\nu} + F^{(2)}_{\mu\nu} \right) - 2F^{(3)}_{\mu\nu} \right] \\
f^{xy}_{\mu\nu} &= i(-1)^{m_\mu} \frac{15}{\sqrt{35}} \left(F^{(2)}_{\mu\nu} - F^{(1)}_{\mu\nu} \right) \\
f^{xz}_{\mu\nu} &= (-1)^{m_\mu} \frac{5\sqrt{6}}{\sqrt{70}} \left(F^{(5)}_{\mu\nu} - F^{(4)}_{\mu\nu} \right) \\
f^{yy}_{\mu\nu} &= (-1)^{m_\mu + 1} \frac{5}{\sqrt{70}} \left[\sqrt{6} \left(F^{(1)}_{\mu\nu} + F^{(2)}_{\mu\nu} \right) + 2F^{(3)}_{\mu\nu} \right] \\
f^{yz}_{\mu\nu} &= i(-1)^{m_\mu} \frac{5\sqrt{6}}{\sqrt{70}} \left(F^{(4)}_{\mu\nu} + F^{(5)}_{\mu\nu} \right) \\
f^{zz}_{\mu\nu} &= (-1)^{m_\mu} \frac{20}{\sqrt{70}} F^{(3)}_{\mu\nu},
\end{aligned} \tag{41}$$

where

$$F^{(1)}_{\mu\nu} = \begin{pmatrix} 2 & 2 & 2 \\ -m_\mu & 2 & m_\nu \end{pmatrix}; \quad F^{(2)}_{\mu\nu} = \begin{pmatrix} 2 & 2 & 2 \\ -m_\mu & -2 & m_\nu \end{pmatrix};$$
$$F^{(3)}_{\mu\nu} = \begin{pmatrix} 2 & 2 & 2 \\ -m_\mu & 0 & m_\nu \end{pmatrix}; \quad F^{(4)}_{\mu\nu} = \begin{pmatrix} 2 & 2 & 2 \\ -m_\mu & 1 & m_\nu \end{pmatrix}; \tag{42}$$
$$F^{(5)}_{\mu\nu} = \begin{pmatrix} 2 & 2 & 2 \\ -m_\mu & -1 & m_\nu \end{pmatrix}.$$

References

1. König E, Ritter G, Kulshreshtha SK (1985) Chem Rev 85:219
2. Bersuker IB (1987) Jahn Teller effect and vibronic interactions in modern chemistry [in Russian]. Nauka, Moscow.
3. Soudackov AV, Tchougréeff AL, Misurkin IA (1992) Theor Chim Acta 83:389
4. Soudackov AV, Tchougréeff AL, Misurkin IA (1996) Int J Quantum Chem 58:161
5. Cundari TR, Deng J, Fu W (2000) Int J Quantum Chem 77:421
6. Adam KR, Atkinson IM, Lindoy LF (1996) J Mol Struct 384:183
7. Bosque R, Maseras F (2000) J Comp Chem 21:562
8. Cundari TR, Deng J (1999) J Chem Inf Comp Sci 39:376
9. McWeeny R (1992) Methods of molecular quantum mechanics 2nd edn. Academic, New York
10. Mestechkin MM (1977) Density matrix method in theory of molecules [in Russian]. Naukova Dumka, Kiev
11. Löwdin PO (1959) Adv Chem Phys 2:207
12. Ziesche P (1994) Physics Lett A 195:213
13. Clarck T (1987) Jahn Teller effect and vibronic interactions in modern chemistry [in Russian]. Nauka, Moscow
14. Zülicke L (1973) Quantenchemie. Band 1. Deutscher Verlag der Wissenschaften, Berlin
15. Cundari TR, Deng J, Fu W (2000) Int J Quantum Chem 77:421
16. Spartan 5.0, wavefunction inc., irvine, ca
17. Gomez-Lara J, Basiuk VA, Basiuk EV (2001) J Mol Struct (THEOCHEM) 536:17
18. Zerner MC (1996) In: Russo N, Salahub D (eds) NATO ASI Workshop. Kluwer, Dordrecht, pp 493–531
19. Bethe H (1929) Ann Physik 3:133
20. Jörgensen CK (1962) Absorption spectra and chemical bonding in complexes. Pergamon Press, Oxford
21. Lever ABP (1984) Inorganic electronic spectroscopy 2nd edn. Elsevier Oxford, Amsterdam New York
22. Soudackov AV, Tchougréeff AL, Misurkin IA (1996) Int J Quantum Chem 57:663
23. Soudackov AV, Tchougréeff AL, Misurkin IA (1994) Russ J Phys Chem 68:1256
24. Soudackov AV, Tchougréeff AL, Misurkin IA (1994) Russ J Phys Chem 68:1264
25. Tchougréeff AL, Soudackov AV, Misurkin IA, Bolvin H, Kahn O (1995) Chem Phys 193:19
26. Tokmachev AM, Tchougréeff AL (1999) Khim Fiz 18:80
27. Tokmachev AM (2003) PhD Thesis, Karpov Institute of Physical Chemistry, Moscow
28. Jug K, Iffert R, Schulz J (1987) Int J Quantum Chem 32:265
29. Li J, de Mello PC, Jug K (1992) J Comput Chem 13:85
30. Li J, Jug K (1992) J Comput Chem 13:93
31. Soudackov AV, Jug K (1996) Int J Quantum Chem 62:403
32. Nanda D, Jug K (1980) Theoret Chim Acta 57:95
33. Sternheimer RM (1963) Phys Rev 130:1423
34. Trautwein A, Harris FE (1973) Theoret Chim Acta 30:45
35. Trautwein A, Zimmermann R, Harris FE (1975) Theoret Chim Acta 37:89
36. Darkhovskii MB, Tchougréeff AL (1999) Chem Phys Reports 18:149
37. Tchougréeff AL (1997) In: Banci L, Comba P (eds) Molecular modeling and dynamics of bioinorganic systems, Kluwer, Dordrecht, p 217
38. Darkhovskii MB, Razumov MG, Pletnev IV, Tchougréeff AL (2002) Int J Quant Chem 88:588
39. Darkhovskii MB, Pletnev IV, Tchougréeff AL (2003) J Comp Chem 24:1703
40. Darkhovskii MB, Tchougréeff AL (2004) J Phys Chem A 108:6351
41. Stassen AF, Matthijs de Vos PJvK, Renz F, Ensling J, Kooijman H, Spek AL, Haasnoot JG, Gütlich P, Reedijk J (2000) Eur J Inorg Chem 2000:2231
42. Bunge CF, Barrientos JA, Bunge AV (1993) Atomic data and nuclear data tables. 53:113
43. Stassen AF, Roubeau O, Gramage IF, Linarés J, Varret F, Mutikainen I, Turpeinen U, Haasnoot JG, Reedijk J (2001) Polyhedron 20:1699
44. Roubeau O, Stassen AF, Gramage IF, Codjovi E, Linarés J, Varret F, Haasnoot JG, Reedijk J (2001) Polyhedron 20:1709
45. Stassen AF, Dova E, Ensling J, Schenk H, Gütlich P, Haasnoot JG, Reedijk J (2002) Inorganica Chimica Acta 335:61