
Crystal-Field Splittings and Optical Spectra of Transition-Metal Mixed-Ligand Complexes by Effective Hamiltonian Method

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ABSTRACT

Many of the important properties of transition-metal complexes depend on the low-energy excitation spectrum formed by *d*-electrons of the central transition-metal atom. The spectra of this type are usually fit to the well-known crystal field theory or to the angular overlap model. The result of the fitting is a set of parameters which are considered as characteristics of the electronic structure of the complex such as strength of the ligand field or types and extent of metal–ligand bonding. We present here a short account of the effective Hamiltonian method recently developed to calculate the splitting of the *d*-levels by the ligands and the resulting *d–d* spectra of transition-metal complexes together with some results of its application to the mixed-ligand complexes with the general formula ML_4Z_2 , where $M = V, Co, Ni$; $L = H_2O, NH_3, Py$; and $Z = H_2O, NCS^-, Cl^-$. Particular attention is paid to the $V(H_2O)_4Cl_2$ and $Co(H_2O)_4Cl_2$ compounds. The former seems to have tetragonal structure, whereas for the latter, our method predicts a spatially degenerate ground state for the tetragonal arrangement of the ligands. That must lead to the Jahn–Teller distortion, which is actually observed. © 1996 John Wiley & Sons, Inc.

Introduction

Calculations on the electronic structure of transition-metal complexes (TMC) present a

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great interest for chemistry. For the direct quantum chemical calculation of the energies of the *d–d* excitations, both semiempirical [1–5] and ab initio [6–13] methods based upon the Hartree–Fock–Roothaan approximation have been applied. In the case of ab initio calculations with large CI expansions [6–10] or with a special selection of configurations in the MCSCF wave function [11, 12], a reasonable agreement of the calculated transition energies with experiment can be obtained. How-

ever, such calculations are very cumbersome and, for that reason, are restricted to relatively simple systems.

Recently, a semiempirical INDO/S-CI method for the calculation of the electronic transition energies was elaborated and extended to transition-metal atoms [2]. It successfully applies to rather complex systems like ferrocene [3] or porphyrin complexes of transition metals [4, 5]. However, despite reasonable numerical agreement between the observed and calculated $d-d$ transition energies obtained by this method, some fundamental problems remain unsolved. The main complication which arises when semiempirical quantum chemistry addresses TMC is the doubt in the validity of the fundamental quantum chemical approximation, the self-consistent field (SCF) approximation, for this class of molecules. The main problems that the SCF approximation encounters are the following (for more detailed discussion, see [14] and references therein):

- (i) The Koopmans' theorem is not valid for the states with large contributions from the atomic d -states;
- (ii) The *Aufbauprinzip* is frequently violated for the orbitals with significant contributions from the atomic d -states; and
- (iii) The iteration procedures implied by the SCF approximation converge very slowly or oscillate.

The violation of the Koopmans' theorem is the most spectacular among the problems listed above. This theorem appears as a consequence of the SCF approximation where each electron is treated as if it moved in a mean field induced by nuclei and other electrons. The ionization potentials are then equal to minus energies of electrons in such a potential (minus orbital energies). This picture is an approximation since the mean field itself changes when an electron is removed from the system or added to it. The difference between the minus orbital energy, which must be the ionization potential according to the Koopmans' theorem, and the real ionization potential is called the relaxation energy. For organic molecules, the relaxation energies are usually small and the whole picture remains consistent. In the case of TMC, the relaxation energies can reach values from 10 to 20 eV when the levels with some significant contribution

from d -orbitals are involved [15]. This suggests that the real behavior of d -electrons in TMC does not fit into the picture where independent electrons move in the mean field induced by the nuclei and other electrons but, by contrast, trace any motion of each other very carefully. In other words, d -electrons are strongly correlated. At the same time, namely, d -electrons are responsible for the ground-state total spin and for the low-energy excitations of TMC, whereas the description of electrons in the ligands seems to be less problematic.

Another problem, which is rarely recognized as a problem, is the violation of the *Aufbauprinzip* (the principle of the occupation of MOs by electrons by two from the bottom), which frequently happens in the semiempirical calculations on TMC [1-4]. In this case, as in the case of the Koopmans' theorem, the orbitals which turn out to be unoccupied or singly occupied but have lower orbital energy than some doubly occupied orbitals are the orbitals formed largely by the d atomic orbitals. One can check [16] that the Slater determinants breaking the *Aufbauprinzip* do not present a minimum of the Hartree-Fock energy functional but, rather, a saddle point. This, in turn, causes the well-known problems with the convergence of the SCF iterations. However, more important than the convergence problems is the doubtfulness of the very idea to parameterize a semiempirical Fock operator for transition metals using throughout the calculation a trial wave function which does not represent a stable solution of the SCF problem.

The instability of the Hartree-Fock solutions for TMC does not create any physical problem by itself. It simply means that the ground state cannot be presented by a single Slater determinant and some other configurations must be added. The problem which arises in this concern is that the CI series taking the Hartree-Fock orbitals as a one-electron basis set converge rather slowly and, thus, a large number of configurations must be taken.

From the above discussion, we see that there are some fundamental problems in the semiempirical description of the electronic structure of TMC. They are related to the highly correlated nature of d -electrons which are ultimately responsible for both the symmetry and the multiplicity of the ground state of TMC and for their low-energy excitation spectrum. To find a way out of all the problems outlined above, let us discuss first the basic properties related to the TMC electronic structure as they are known from experiment. It should

be mentioned first of all that the experimental data concerning the $d-d$ excitation spectra of TMC can be successfully fit to the models equivalent to the crystal field theory (CFT) [17]. That means that specific properties of TMC are determined by the d -electrons of the transition-metal ion. Their low-energy excitations are responsible for the absorption bands in the optical spectra and for the magnetic properties. The ground-state spin depends on the balance between the electron repulsion of d -electrons and their interaction with the ligands which provide some external field. The excitations of the ligands have much larger energies than those in the d -shell and, incidentally, the ligands have a closed electronic shell so that they cannot directly affect the spin multiplicity of the complex.

The features formulated above apparently correspond to the situation covered by the crystal field theory where all the interesting events take place in the d -shell of the transition-metal ions whose ligand environment remains inert [17]. The picture provided by the CFT is correct to a large extent. The majority of magnetic and optical experiments on TMC can be interpreted in the framework of the CFT operating with the multiplets of some fixed number of d -electrons in the external field of appropriate symmetry (see, e.g., [18]). The reason why the CFT is that successful is because of the correct form of the electronic wave function which is implicitly used in it. It obviously takes the wave function of the complex as an antisymmetrized product of the multiplet (full CI) state for some fixed number of d -electrons and of some closed-shell state of the remaining ligand electrons. However, the wave function of this remainder is not considered explicitly and that is the reason why the splitting parameters of the CFT cannot be satisfactorily calculated within its own framework.

In the effective Hamiltonian method [14], two of the most important features of the electronic structure of TMC, namely, the presence of an isolated group of strongly correlated d -electrons on the metal atom and the existence of the closed-shell ligands, are taken into account explicitly. The distinction between the ligands and the d -shell of TMC is used in order to describe d -electrons and electrons in the ligand orbitals employing different levels of accounting of the electron correlations. The following features were implemented in the method: (1) the multiplet structure of d -electrons in the central ion (to do so, the CI is completely taken into account in the d -shell); (2) the electronic

structure of the ligands must be treated realistically, but the single-determinant approximation is sufficient for them; and (3) the weak covalency resulting from the metal-ligand interactions must be included as well.

The method had been parameterized and then applied to the metal fluorine complexes, metal hexahydrate and hexamine complexes, metal hexachloro and tetrachloro complexes, and metallocenes [19–22]. In all the cases studied, we observed the perfect agreement between the experimental data concerning the spin and symmetry of the ground state of the complex and our calculation. The spectra of the $d-d$ excitations were reproduced within the accuracy of 1000 cm^{-1} .

The ML_4Z_2 complexes of tetragonal symmetry D_{4h} are of specific interest for our theory. The assignment of the absorption bands in the $d-d$ spectra of these complexes is normally made on the basis of some presumed picture of the d -levels split by the ligand field. This picture is frequently based upon some qualitative reasoning on the basis of the positions of the axial and equatorial ligands in the spectrochemical series [18]. Empirical approaches of that kind clearly are not capable to explain the splitting patterns obtained by such fits. As an example, we can mention a controversy lasting for more than a decade concerning the relative position of the $b_2(xy)$ and the $e_g(xz, yz)$ levels in the fields of tetragonal symmetry. Our method, by contrast, allows one to calculate directly the splitting parameters and the energies for the d -multiplets in the crystal fields for various ligand arrangements around the central ion. For that reason, it seems to be interesting to analyze the results of calculations on the tetragonal complexes ML_4Z_2 and to compare these results with existing experimental data on $d-d$ spectra of these complexes.

Method

The formal derivation of the effective Hamiltonian method proceeds as follows [14]: We separate the whole set of the valence atomic orbitals (AO) of the TMC (it includes the $4s$ -, $4p$ -, and $3d$ -AOs of the metal and the valence AOs of the ligand atoms) into two parts: The first part contains only $3d$ -orbitals of the transition-metal atom (d -subsystem). The second part contains $4s$ -, $4p$ -AOs of the transi-

tion metal and the valence orbitals of the ligand atoms (ligand subsystem or l -subsystem). Then, the total Hamiltonian for a TMC can be written as follows:

$$H = H_d + H_l + H_c + H_r, \quad (1)$$

where H_d is the Hamiltonian for the d -electrons in the field of the atomic cores of TMC, H_l is the Hamiltonian for the electrons of the l -subsystem, and H_c and H_r are, respectively, the Coulomb and the resonance interaction operators between the two subsystems.

For most of the TMC with closed-shell ligands, the excitations in the ligand subsystem are very high in energy as compared to the energies of the d - d excitations, and, thus, their contribution is negligible. The ground state of the ligand subsystem can be described by a Slater determinant $\Phi_l(^1A_1)$ with zero total spin. The wave function Φ_n for the n -th electronic state of a TMC then takes the form

$$\Phi_n = \left(\sum_k C_k^n |n_d k\rangle \right) \wedge \Phi_l = \Phi_d^n \wedge \Phi_l, \quad (2)$$

where $|n_d k\rangle$ are the spin and symmetry-adapted n_d -electron wave functions constructed on the metal d -orbitals and C_k^n are variation parameters. Both the spin multiplicity and the point symmetry of the functions of this type coincide with the multiplicity and the symmetry of the functions Φ_d^n of the d -subsystem.

The wave functions of the type Eq. (2) correspond to the fixed integer number (n_d) of electrons in the d -shell of the metal ion. It is not that bad from the point of view of the description of electron distribution itself, since for most of the complexes, the total charge transfer between the d -shell and the ligands usually does not exceed a few hundredths. A more serious problem is that all the matrix elements of the resonance operator H_r calculated with the functions of that type are vanishing. That prevents any correct description of the interaction between the ligands and the d -shell within the above class of the trial wave functions with the Hamiltonian Eq. (1). To include the effects of the resonance interaction between the subsystems, we consider the *effective* Hamiltonian H^{eff} [14] which operates in the subspace spanned by the functions Eq. (2). Its eigenvalues coincide with

those of the exact Hamiltonian Eq. (1):

$$\begin{aligned} H^{eff} &= PH_0P + H_{RR} \\ H_0 &= H_d + H_l + H_c \\ H_{RR} &= PH_rQ(EQ - QH_0Q)^{-1}QH_rP. \end{aligned} \quad (3)$$

Here, P is the projection operator on the subspace of functions with a fixed number of d -electrons; $Q = 1 - P$.

The variational problem for the effective Hamiltonian H^{eff} within the subspace spanned by the wave functions of the type Eq. (2) splits into a pair of interconnected equations for the functions Φ_d^n and Φ_l (see, e.g., [14, 23]):

$$\begin{aligned} H_d^{eff}\Phi_d^n &= E_d^n\Phi_d^n \\ H_l^{eff}\Phi_l &= E_l\Phi_l, \end{aligned} \quad (4)$$

with the effective Hamiltonians for the subsystems defined by

$$\begin{aligned} H_d^{eff} &= H_d + \langle \Phi_l | H_c + H_{RR} | \Phi_l \rangle \\ H_l^{eff} &= H_l + \langle \Phi_d^n | H_c + H_{RR} | \Phi_d^n \rangle. \end{aligned} \quad (5)$$

Since the l -subsystem is described by a single Slater determinant Φ_l , the latter must be found from the self-consistent-field procedure applied to the Fockian F_l^{eff} derived from the Hamiltonian H_l^{eff} by the standard method [23, 24]. Proceeding semiempirically, we apply the standard CNDO parameterization [24] for all ligand atoms. The core attraction parameters U_{ss} and U_{pp} of the metal $4s$ - and $4p$ -orbitals and the metal core charge Z_M are renormalized according to

$$\begin{aligned} U_{ss} &\rightarrow U_{ss} + n_d g_{sd} \\ U_{pp} &\rightarrow U_{pp} + n_d \bar{g}_{pd} \\ Z_M &\rightarrow Z_M - n_d. \end{aligned} \quad (6)$$

Here $g_{sd} = (ss | dd) - (sd | ds)/2$; \bar{g}_{pd} is the average of the integrals $g_{i\mu}$, where $i = 4p_x, 4p_y, 4p_z$ and $\mu = 3d_{z^2}, 3d_{x^2}, 3d_{yz}, 3d_{x^2-y^2}, 3d_{xy}$.

The solution of the Hartree-Fock problem for the l -subsystem with the above approximate CNDO Fockian gives the one-electron density matrix P_{kl} , the energies of the molecular orbitals (MO) ϵ_i , and MO LCAO coefficients c_{ik} [24]. These quantities completely describe the electronic structure of the l -subsystem within the accepted approximation. They are used to construct the effective Hamiltonian H_d^{eff} [Eq. (5)] in the following way: The operators H_c and H_{RR} are averaged over the ground state Φ_l of the l -subsystem which leads to

the effective Hamiltonian H_d^{eff} of the form [14]

$$H_d^{eff} = \sum_{\mu\nu\sigma} U_{\mu\nu}^{eff} d_{\mu\sigma}^+ d_{\nu\sigma} + \frac{1}{2} \sum_{\mu\nu\rho\eta} \sum_{\sigma\tau} (\mu\nu | \rho\eta) d_{\mu\sigma}^+ d_{\nu\sigma} d_{\rho\tau}^+ d_{\eta\tau}, \quad (7)$$

where the Coulomb interaction between d -electrons is taken as in the free ion and the effective core attraction parameters for metal d -electrons $U_{\mu\nu}^{eff}$ contain the corrections originating both from the Coulomb and the resonance interaction of d -electrons with the l -subsystem:

$$U_{\mu\nu}^{eff} = \delta_{\mu\nu} U_{dd} + W_{\mu\nu}^{ion} + W_{\mu\nu}^{cov}, \quad (8)$$

where

$$W_{\mu\nu}^{ion} = \delta_{\mu\nu} \left(\sum_{i \in s, p} g_{\mu i} P_{ii} \right) + \sum_L (P_{LL} - Z_L) V_{\mu\nu}^L \quad (9)$$

is an ionic term having the standard CFT form and

$$W_{\mu\nu}^{cov} = - \sum_i \beta_{\mu i} \beta_{\nu i} \left(\frac{(1 - n_i/2)}{\Delta E_{di}} - \frac{(n_i/2)}{\Delta E_{id}} \right) \quad (10)$$

comes from the resonance. Here, P_{ii} is the diagonal matrix element of the one-electron density matrix of the ligand subsystem; $P_{LL} = \sum_{i \in L} P_{ii}$ is the electronic population on the ligand atom L ; Z_L is the core charge of the ligand atom L ; $V_{\mu\nu}^L$ is the matrix element of the potential energy operator describing the interaction between a d -electron and an electron placed on the ligand atom L ; n_i is the occupation number of the i -th ligand MO ($n_i = 0$ or 2); ΔE_{di} (ΔE_{id}) is the energy which is necessary to transfer an electron from the d -shell (from the i -th MO) to the i -th MO (to the d -shell); $\beta_{\mu i}$ is the resonance integral between the μ -th d -orbital and the i -th ligand MO which is expressed through the resonance integrals $\beta_{\mu k}$ between the μ -th d -orbital and the k -th ligand AO:

$$\beta_{\mu k} = -(I_d + I_k) S_{\mu k} \beta^{ML},$$

where I_d and I_k are the valence-state ionization potentials; $S_{\mu k}$ is the overlap integral between the μ -th d -AO and the k -th ligand AO; and β^{ML} is the only fitting parameter specific for each ML pair, where M stands for a transition-metal atom and L stands for a donor atom in the ligand (like nitrogen, oxygen, etc.).

When deriving the expression Eq. (8) for the matrix element $U_{\mu\nu}^{eff}$ between the d -orbitals, we lifted some of the limitations of [14]. First, we do not need any more the high (not less than tetragonal) symmetry of the ligand environment and, second, we neglect the splitting of d -levels by the electric field of the charges residing in the ligand system when we calculate the energy denominators occurring in the above formula for the covalent contribution $W_{\mu\nu}^{cov}$.

The covalence term dominating the d -level splitting is apparently analogous by its origin to the ligand-field parameters of the angular overlap model (AOM) [25]. The important difference between them is that in the AOM all the ligand-field parameters are fit to the experimental spectra for each ligand and are not transferable from one ligand to another even if the donor atom is the same. In our approach, the electronic structure of the ligands is taken into account explicitly. That allowed us to parameterize (see [14, 19–22] and below) only the magnitude of the hopping between the orbitals of the given donor atom and d -orbitals of the given transition metal. The same value can be used for all the ligands containing the given donor atom, thus allowing us to reproduce the effects of the variations of the ligand structure on the crystal field induced by the ligands and thus on the d - d spectrum.

After the effective Hamiltonian for d -electrons is constructed, the states of n_d electrons in the d -shell are calculated by diagonalizing the matrix associated with H_d^{eff} in the n_d electron wavefunction basis set. The ground state of the whole complex is then obtained by taking the external product of the ligand Slater determinant and that n_d -electron wave function obtained by the diagonalization of H_d^{eff} which has the lowest eigenvalue. The d - d excited states (they are the low-lying excitations of the whole complex) are then obtained by multiplying other n_d -electron functions by the same Slater determinant. The d - d excitation energies can then be estimated as the differences between the eigenvalues of the corresponding eigenstates of the effective Hamiltonian H_d^{eff} .

Results and Discussion

We applied the method described in the previous section to calculate the electronic structure of the ligand sphere and d -shells of a series of the

ML_4Z_2 compounds where $M = V, Co, Ni$; $L = H_2O, NH_3, Py$; and $Z = H_2O, NCS^-, Cl^-$. The spin multiplicity and the spatial symmetry of the ground states of the considered mixed complexes are correctly reproduced by our method (the parameters β^{ML} were found from the calculations [20, 21] on the corresponding pure complexes [ML_6^{2+} and ML_6^{4-}]). For all three considered Ni(II) complexes $Ni(NH_3)_2(NCS)_2$, $Ni(Py)_4Cl_2$, and $Ni(Py)_4(H_2O)_2^{2+}$, the ${}^3B_{1g}$ state is the ground state in accord with the experiment [26, 27]. A detailed account of these results will be presented elsewhere. In this article, we concentrate mainly on two hydrochloro compounds: $V(H_2O)_4Cl_2$ and $Co(H_2O)_4Cl_2$.

$V(H_2O)_4Cl_2$

In this complex, water molecules occupy the equatorial positions whereas the axial positions are occupied by the chlorine atoms [28]. The following interatomic distances were used throughout the calculation: $R(V-O) = 2.15 \text{ \AA}$ [as in the $V(H_2O)_6^{2+}$ complex] and $R(V-Cl) = 2.50 \text{ \AA}$ (as in the VCl_6^{4-} complex).

The $3a_{2u}$ HOMO of the l -system of this complex is composed mainly of the p_σ -orbitals of the chlorine atoms, whereas its $5e_u$ LUMO is formed largely by the $p_{x(y)}$ -orbitals of the vanadium atom. This composition is analogous to that of the frontier orbitals of the l -system in the VCl_6^{4-} complex [20]. Comparing the atomic charges in the $V(H_2O)_4Cl_2$ complex with those in the $V(H_2O)_6^{2+}$ and VCl_6^{4-} complexes [20, 21], one can see that the substitution of the two water molecules in the axial positions by the Cl^- ions diminishes the total charge on the central ion as compared to the hexaqua complex due to the transfer of the electronic density from the Cl^- anions to the $4s$ - and $4p$ -metal orbitals. The atomic charges residing on the oxygen atoms do not change. The charges on the chlorine atoms are slightly smaller than those in the VCl_6^{4-} complex.

Now let us turn to the results of our calculation on the d -system of the $V(H_2O)_4Cl_2$ complex. The term ${}^4B_{1g}$ is the ground state in accord with the experiment [28]. The assignments of the $d-d$ -transitions in [28] were based on the following assumption concerning the splitting of the d -levels:

$$e_g(xz, yz) < b_{2g}(xy) < b_{1g}(x^2 - y^2) < a_{1g}(z^2). \quad (11)$$

Our calculation gives another picture of the d -level splitting:

$$b_{2g}(xy) < e_g(xz, yz) < b_{1g}(x^2 - y^2) < a_{1g}(z^2). \quad (12)$$

For the three electrons placed in the d -shell of the complex, they all give the same ground state, since, irrespective of its sign, the parameter $d\pi$ of the tetragonal splitting between the $b_{2g}(xy)$ and $e_g(xz, yz)$ orbitals is small. The spectral data of [28] do not allow one to distinguish between the pictures given by (11) and (12).

Let us turn to the analysis of the ionic and the covalent contributions to the d -level splitting in the $V(H_2O)_4Cl_2$ complex. According to our data, the splitting between the d_{z^2} - and $d_{x^2-y^2}$ -orbitals described by the $d\sigma$ parameter is equally contributed to by the ionic (large difference of the negative charges residing on the oxygen and chlorine atoms: -0.397 and -0.659 , respectively) and the covalent contributions. The greater destabilization of the d_{x^2} -orbital as compared to the $d_{x^2-y^2}$ -orbital appears to be from the virtual electron transfer from the $3s$ - and p_σ -orbitals of the Cl atoms to the d_{z^2} -orbital. The splitting between the d_{xy} and d_{xz}, d_{yz} is controlled largely by the ionic contribution. The positive sign of the $d\pi$ parameter [which means that $b_{2g}(xy) < e_g(xz, yz)$] is conditioned by the larger destabilization of the d -orbitals of the e_g symmetry due to the additional contribution from the virtual transfer of an electron to these orbitals from the high occupied $2e_g - MO$ formed by the p_π -orbitals of Cl.

$Co(H_2O)_4Cl_2$

Calculations on this complex present particular interest since it was an object of thorough experimental studies [29–31] which, however, have not brought definitive interpretation of its electronic structure. The results of the measurements were interpreted in [29, 30] in terms of the tetragonal crystal field. The measurements of the magnetic momenta [31] and of the polarized electronic absorption spectra performed on the monocrystals [29, 30] revealed that the ground state of the complex is a high-spin orbitally nondegenerate state. For the tetragonal geometry assumed in [29, 30], it is the ${}^4A_{2g}$ term appearing from the split octahedral ${}^4T_{1g}$ term. Irrespective of the details of the

assignments of the optical transitions, both works consistently place the $b_{2g}(xy)$ level above the degenerate $e_g(xz, yz)$ level [Eq. (11)]. The reason was that, within the tetragonal field, the ${}^4A_{2g}$ ground state for seven d -electrons (three holes) is possible only for this relative position of these levels. In terms of the splitting parameters, that means that $d\pi$ is negative.

We performed the calculations for the D_{4h} geometry with the following interatomic distances: $R(\text{Co}-\text{O}) = 2.12 \text{ \AA}$ and $R(\text{Co}-\text{Cl}) = 2.43 \text{ \AA}$ [29] and obtained a positive value of $d\pi$. That automatically led to the 4E ground state, in sharp contrast to the experimental data. However, what one would expect from a molecule with the spatially degenerate (E) ground state is the Jahn-Teller distortion. That is exactly what happens. The real geometry of the complex is not tetragonal, but can be described as an elongated octahedron with an additional distortion placing the equatorial water oxygens in the corners of a rectangle. For the real (distorted) geometry, the degenerate ground state is not possible regardless of the sign of the $d\pi$ parameter. For the experimental D_{2h} geometry where the water oxygens occupy the corners of a planar rectangle with the sides of 3.05 and 2.94 \AA , respectively [29], the water molecules in the real structure are only slightly shifted from their idealized positions, and for that reason, the results of the calculation on the ligand subsystem do not differ too much for the real and idealized structures. We performed the calculation and found that the sign of $d\pi$, of course, does not change because of the slight geometry variations accompanying the Jahn-Teller distortion. However, the ground state of the complex is not spatially degenerate any more though it is still spin degenerate.

The $d-d$ excitation spectrum is reasonably reproduced within the accuracy of 1000 cm^{-1} . For example, in our calculation on the spectrum, we do not have spurious low-energy $d-d$ -states with the energies of ca. $1000\text{--}1500 \text{ cm}^{-1}$, which were present in the fit of [30] without any explanation. We did not try to reproduce the spectral data in detail together with the assignments given in [29, 30] since they differ significantly and are both based on the wrong symmetry of the crystal field. However, it is worthwhile to note that we reproduced the general features of the spectra common for both experimental works (see Table I). In our calculation performed with the Racah parameters $B = 853 \text{ cm}^{-1}$ and $C = 3687 \text{ cm}^{-1}$ [30], we have

TABLE I
Spectrum of $d-d$ excitations in $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]$.

State	Calculated energies (cm^{-1})	Observed bands [29, 30]
${}^4B_{2g}$	0	
${}^4B_{3g}$	152	
${}^4B_{1g}$	465	
${}^4B_{2g}$	6,273	6000–9000
${}^4B_{3g}$	6,342	
${}^2B_{1g}$	8,626	Broad strong
4A_g	9,036	
2A_g	12,556	12,000–14,000
2A_g	14,447	Weak
${}^4B_{1g}$	15,487	15,000–17,000
${}^2B_{2g}$	16,356	
${}^2B_{3g}$	16,438	Broad shoulder
${}^2B_{1g}$	17,626	
${}^2B_{2g}$	18,102	
${}^2B_{3g}$	18,196	
${}^4B_{1g}$	18,382	18,600
${}^2B_{3g}$	20,634	
${}^2B_{2g}$	20,903	
${}^2B_{1g}$	21,866	
${}^4B_{3g}$	22,179	22,250
${}^4B_{2g}$	22,438	Broad
2A_g	22,480	
${}^2B_{2g}$	25,280	25,000–27,000
${}^2B_{3g}$	25,295	
2A_g	26,500	Weak broad
${}^2B_{3g}$	26,754	
${}^2B_{2g}$	26,836	
${}^2B_{1g}$	27,488	
${}^2B_{1g}$	27,992	

the spin-allowed bands in the region $6000\text{--}9000 \text{ cm}^{-1}$; relatively weak (spin-forbidden) transitions in the $12,000\text{--}14,000 \text{ cm}^{-1}$ region; a series of the bands of different intensity in the $18,000\text{--}19,000 \text{ cm}^{-1}$ and $20,000\text{--}22,000 \text{ cm}^{-1}$ regions; and weak bands about $25,000\text{--}27,000 \text{ cm}^{-1}$ —all in perfect agreement with the available experimental data.

As in the case of $\text{V}(\text{H}_2\text{O})_4\text{Cl}_2$, the transition from the hexahydrocobalt complex to the mixed complex diminishes the charge on the metal due to electron density transfer from the chlorine atoms to the $4s$ - and $4p_z$ -orbitals of the metal. The charges on the axial and equatorial donor atoms differ significantly (-0.575 and -0.378 , respectively).

The analysis of the contributions to the d -level splitting in the $\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2$ complex shows that the positive value of the $d\sigma$ parameter

$$[b_{1g}(d_{x^2-y^2}) < a_{1g}(d_{z^2})]$$

is mainly due to the presence of the high-energy-occupied $4a_{1g}$ - MO formed by the p_σ -orbitals of oxygens and chlorines. Since this MO is much higher in energy than is the occupied $2b_{1g}$ - MO formed by the $2s$ - and p_σ -oxygen orbitals and the energy of the corresponding virtual electron transfer from this MO to the corresponding d -orbital is smaller as compared to the analogous process for the $4a_{1g}$ - MO and the destabilization of the $a_{1g}(d_{z^2})$ orbital is larger than that of the $b_{1g}(d_{x^2-y^2})$ -orbital, the splitting of the $b_{2g}(d_{xy})$ - and $e_g(d_{xz}, d_{yz})$ -orbitals if it were controlled by the covalent contribution, would give a negative value of $d\pi$. The reason is, on the one hand, the larger resonance integral between the filled $1b_{2g}$ - MO of the ligand system and the d_{xy} -orbital as compared to the integral between the $2e_g$ -HOMO and the d_{xz} , d_{yz} -orbitals, leading to the larger destabilization of the d_{xy} -orbital and, on the other hand, the presence of the stabilizing contribution for the d_{xz} , d_{yz} -orbitals coming from the virtual electron transfer from these orbitals to the vacant $4e_g$ - MO of the ligand subsystem. Nevertheless, the ionic contribution to $d\pi$ coming from the difference between the charges on the equatorial and axial ligands overcomes the covalent one, and the total $d\pi$ is positive [as in (12)].

Conclusion

In the present article, we described the effective Hamiltonian method and analyzed the results of its application to the calculation of the d -level splitting and $d-d$ spectra in the similar tetrahydrochloro complexes of divalent vanadium and cobalt. A purely experimental approach to the problem of the relative positions of the d -levels led to contradictory results. The effective Hamiltonian method allows one to perform systematic calculations of the ligand field for various ligand environments. It predicts for both complexes the same order of the d -levels (12), which seems to be reasonable in view of the similarity of their composition.

The spatially degenerate ground state of seven d -electrons arises within our method in the case of

$\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2$ in a visible contradiction to the experimental data. It allows, however, one to rationalize the observed distortion of the equatorial square formed by the water molecules to the rectangular configuration. For $d\pi < 0$, as is adopted in [29, 30], the only possible ground state for seven d -electrons in the tetragonal environment is ${}^4A_{2g}$. It correlates with the experiment only in the respect that the ground state is not spatially degenerate. However, for such a ground state, it is difficult to explain the observed distorted geometry. On the other hand, for $d\pi > 0$, as it results from our calculation for the tetragonal ligand arrangement, the only possible high-spin ground state for seven d -electrons is 4E . In this case, the required distortion arises naturally due to the Jahn-Teller theorem. Incidentally, the distorted geometry is actually observed for the $\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2$ compound. This distortion would have no reason to appear should the ground state of the tetragonal d^7 -complex be spatially nondegenerate. We consider this as a rare case when X-ray measurements make it possible to visualize the order of d -levels in the crystal field. Since it is confirmed by the experiment, it may serve as an argument in favor of the positive sign of $d\pi$ and, thus, of the capability of our method to reproduce some fine balance of the different contributions to the crystal field. We can thus conclude that the calculations by the method [14] provide important supplementary information to the experimental probes of the electronic structure of TMC.

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References

1. M. C. Zerner and A. D. Bacon, *Theor. Chim. Acta* **53**, 21 (1979).

2. M. C. Zerner, G. H. Loew, R. F. Kirchner, and U. T. Mueller-Westerhoff, *J. Am. Chem. Soc.* **102**, 589 (1980).
3. W. D. Edwards, B. Weiner, and M. C. Zerner, *J. Phys. Chem.* **92**, 6188 (1988).
4. W. D. Edwards, B. Weiner, and M. C. Zerner, *J. Am. Chem. Soc.* **108**, 2196 (1986).
5. M. Kotzian, N. Rösch, H. Schröder, and M. C. Zerner, *J. Am. Chem. Soc.* **111**, 7687 (1989).
6. J. E. Newton and M. B. Hall, *Inorg. Chem.* **23**, 4627 (1984).
7. J. E. Newton and M. B. Hall, *Inorg. Chem.* **24**, 2573 (1985).
8. K. Pierloot and L. G. Vanquickenborne, *J. Chem. Phys.* **93**, 4154 (1990).
9. M. Rosi, C. W. Bauschlicher, S. R. Langhoff, and H. Partridge, *J. Phys. Chem.* **94**, 8656 (1990).
10. K. Morokuma, *Inorg. Chem.* **29**, 3110 (1990).
11. H. Johansen and N. K. Andersen, *Mol. Phys.* **58**, 965 (1986).
12. S. Y. Shashkin and W. A. Goddard III, *Phys. Rev. B* **33**, 153 (1986).
13. G. J. M. Janssen and W. C. Nieuwpoort, *Int. J. Quantum Chem. Symp.* **22**, 679 (1988).
14. A. V. Soudackov, A. L. Tchougreeff, and I. A. Misurkin, *Theor. Chim. Acta* **83**, 389 (1992).
15. M. C. Böhm, *Theor. Chim. Acta* **60**, 233 (1981).
16. J. P. Blaizot and G. Ripka, *Quantum Theory of Finite Systems* (MIT Press, Cambridge, MA, 1986); A. V. Soudackov, PhD Thesis (Karpov Institute of Physical Chemistry, Moscow, 1991) (in Russian).
17. C. K. Jorgensen, *Modern Aspects of Ligand Field Theory* (North-Holland, Amsterdam, 1971).
18. A. B. P. Lever, *Inorganic Electronic Spectroscopy* (Elsevier, Amsterdam, 1986).
19. A. V. Soudackov, A. L. Tchougreeff, and I. A. Misurkin, in *Electron-Electron Correlation Effects in Low-Dimensional Conductors and Superconductors*, A. A. Ovchinnikov and I. I. Ukrainskii, Eds. (Springer-Verlag, Berlin, 1991).
20. A. V. Soudackov, A. L. Tchougreeff, and I. A. Misurkin, *Zh. Fiz. Khim.* **68**, 1257 (1994) (in Russian); *Russ. J. Phys. Chem.* **68**, 1135 (1994) (in English).
21. A. V. Soudackov, A. L. Tchougreeff, and I. A. Misurkin, *Zh. Fiz. Khim.* **68**, 1265 (1994) (in Russian); *Russ. J. Phys. Chem.* **68**, 1142 (1994) (in English).
22. A. L. Tchougreeff, A. V. Soudackov, I. A. Misurkin, H. Bolvin, and O. Kahn, *Chem. Phys.* **193**, 19 (1995).
23. R. McWeeny and B. T. Sutcliffe, *Methods of Molecular Quantum Mechanics* (AP, London, 1969).
24. J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory* (McGraw-Hill, New York, 1970).
25. M. Gerloch and R. G. Wooley, *Progr. Inorg. Chem.* **31**, 371 (1984).
26. C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.* **40**, 792 (1964).
27. J. S. Merriam and J. R. Perrumareddi, *J. Phys. Chem.* **79**, 142 (1975).
28. L. F. Larkworthy, K. C. Patel, and D. J. Phillips, *J. Chem. Soc.* 1095 (1970).
29. J. Ferguson and T. E. Wood, *Inorg. Chem.* **14**, 184 (1975).
30. H. W. Joy and N. Fogel, *J. Phys. Chem.* **79**, 345 (1975).
31. M. Gerloch, P. N. Quedsted, and R. C. Slade, *J. Chem. Soc. A* 3741 (1971).