Scientific Research

Electronic States in Trans-CoCl$_2$(H$_2$O)$_4$ Complex

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ABSTRACT

The polarized absorption spectra of cobalt(II) *in trans-CoCl$_2$(H$_2$O)$_4$.2H$_2$O provides important information about the electronic structure. Semi-empirical calculation of the crystal-field levels of the cobalt*(II) *with D$_{4h}$ point group symmetry in CoCl$_2$(H$_2$O)$_4$·2H$_2$O are carried out, leading to a good agreement between the theoretical and experimental energy levels.*

Keywords: *Crystal And Ligand Fields*, *Transition-Metal Compounds*, *Cocl$_2$(H$_2$O)$_4$ Chromophore*

1. Introduction

Several spectroscopic investigations of the transition metal complexes with the trans-dichlorotetraaquo ligand environment MCl$_2$(H$_2$O)$_4^{n+}$ (M: transition metal, M = V^{3+}, Ni^{2+}, Co^{2+}, Cr^{3+}) are reported in literature [1-8]. For these complexes, the bands of the absorption and luminescence spectra are related to the transition metal ions M with 3d^n (n = 2, 3, 7, 8) configuration and originate from electronic transition in the unfilled 3d electronic shell. A detailed crystal-field studies of the electronic energy levels of trans-NiCl$_2$(H$_2$O)$_4$, trans-VCl$_2$(H$_2$O)$_4^+$ and trans-CrCl$_2$(H$_2$O)$_4^+$ complexes were presented in a recent work [9-11]. These theoretical studies emphasized the importance of coupling between electronic states in the case of the NiCl$_2$(H$_2$O)$_4$ chromophore and of the Jahn-Teller effect in the case of CrCl$_2$(H$_2$O)$_4^+$. Crystals of trans-CoCl$_2$-(H$_2$O)$_4$.2H$_2$O crystallize as regular monoclinic mauve prisms [8,12]. Crystallographic studies confirm that crystal of CoCl$_2$(H$_2$O)$_4$.2H$_2$O contain the trans-CoCl$_2$(H$_2$O)$_4$ chromophore where the Co^{2+}(3d^7) ions occupy a site with D$_{4h}$ symmetry [8]. A spectroscopic studies of the optical characteristics of trans-CoCl$_2$(H$_2$O)$_4$ complex were presented by Bussière *et al*. [8]. In their publications, the crystal field calculations based on the angular overlap model (AOM) were performed for this complex.

In this actual work, we present a detailed crystal-field analysis of the electronic energy levels of trans-CoCl$_2$ (H$_2$O)$_4$ complex. This analysis based on the Racah theory was carried out for the Co^{2+} centre with a D$_{4h}$ site symmetry. The objective of this theoretical analysis is to determine the Racah and the crystal-field parameters for the CoCl$_2$(H$_2$O)$_4$ chromophore, and, therefore, to deduce the Stark levels which are not observed experimentally.

2. Experimental Support

The bases of our theoretical analysis will be the experimental energy data obtained from the optical spectra of trans-CoCl$_2$(H$_2$O)$_4$ complex. For this reason, we present briefly in this section the results of the spectroscopic studies carried out by Bussière *et al*. at low temperature [8,12]. The polarized absorption spectra of trans-CoCl$_2$(H$_2$O)$_4$ is measured at low temperature 5 K (**Figure1**) [8]. Three quartet bands are expected for Cobalt(II) in octahedral symmetry : the first one is seen in the near-infrared region of the spectrum around 8000 cm^{-1}, involving the ^{4}T$_{2g}$(^{4}F) state. This band will be split into ^{4}E$_g$ and ^{4}B$_{2g}$ in the D$_{4h}$ point group. The assignment of the other two quartet bands is problematic and there are substantial differences between the assignments given by different authors [8]. For this reason Bussière *et al*. l declare that this assignment is uncertain [8]. For a mixed water and chloride ligand spheres, the ^{4}A$_{2g}$(^{4}F) and ^{4}T$_{1g}$ (^{4}P) states should be near a crossing point [8]. Bussière et al.l have reported the ^{4}A$_{2g}$ (^{4}F) state to be at 16450 cm^{-1} (^{4}B$_{1g}$ in D$_{4h}$ symmetry) and the ^{4}T$_{1g}$ (^{4}P) state, to be split into ^{4}E$_g$ and ^{4}A$_{2g}$(in D$_{4h}$ symmetry) at 18600 and 22250 cm^{-1} corresponding to the strong bands in **Figure 1**. The experimental energy levels are listed in **Table 1**. The angular overlap model (AOM) [13] was used by Bussière *et al*. in order to obtain the energetic order of quartet and doublet excited states in this tetragonal chromophore.

Table 1. Experimental and calculated energies (cm⁻¹), and AOM parameters (cm⁻¹) of trans-CoCl₂(H₂O)₄ [8].

Absorption 5 K [{D_{4h}} Oh (ion)] <polarization>	Calculated ligand-field energies [D_{4h}]
	167 [(Γ_7) $^4A_{2g}$][a]
	919 [^4E_g][b]
8060 [{^4E_g} $^4T_{2g}$(^4F)]	8054 [$^4B_{2g}$][b]
8330 [{$^4B_{2g}$} $^4T_{2g}$(^4F)]	8297 [^4E_g][b]
16450 [{$^4B_{1g}$} $^4A_{2g}$(^4F)]	16954 [$^4B_{1g}$][b]
18600 [{^4E_g} $^4T_{1g}$(^4P)]	18805 [^4E_g][b]
20268 [{^2E_g} $^2T_{1g}$(^2P)]	20273 [Γ_7][a]
22250 [{$^4A_{2g}$} $^4T_{1g}$(^4P)]	21167 [$^4A_{2g}$][b]

[a]Calculated with $\zeta \neq 0$; [b]Calculated with $\zeta = 0$.
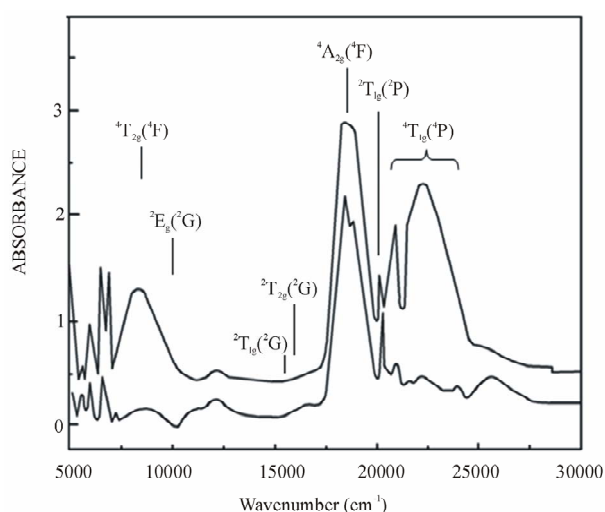
Figure 1. Polarized absorption spectra of trans-CoCl₂(H₂O)₄ at 5 K [8].

The parameters e_σ(H₂O), $e_{\pi S}$(H₂O) and $e_{\pi C}$(H₂O) are set to 4300, 1000 and 700 cm⁻¹, respectively, while e_σ(Cl) and e_π(Cl) are set to 3300 and 1000 cm⁻¹, respectively, for the trans-CoCl₂(H₂O)₄ complex. The Racah parameter B was set to 824 cm⁻¹ and the ratio C/B to 4.40. The calculated energy levels by Bussière *et al.* of the CoCl₂(H₂O)₄ chromophore are also listed in **Table 1** [8].

3. Theoretical Background

3.1. Hamiltonian

The total Hamiltonian of 3d^N ion in an arbitrary symmetry site is written as [9-11]:

$$H = H_0 + H_{CF} + H_{SO} \quad (1)$$

H_0 is the Coulomb interaction including electron-electron repulsions, this Hamiltonian gives the ^{2S+1}L terms: two quartet terms (^4F ground state and ^4P excited state) and six doublet excited terms (^2H, ^2G, ^2F, ^2D, $^2D'$ and ^2P). The eigenvalues of the Hamiltonian H_0 are ex-

pressed as a function of the Racah parameters B and C [14-15]. H_{SO} is the spin-orbit coupling (ξ is the SO parameter).

H_{CF} is the crystal field Hamiltonian which can be represented quite simply as follows [14-15].

$$H_{CF} = \sum_{k=0}^{\infty} \sum_{q=-k}^{k} B_{kq} C_q^{(k)} \quad (2)$$

where B_{kq} are the crystal-field parameters and $C_q^{(k)}$ are the Racah tensor operators defined as follows :

$$C_q^{(k)} = \sqrt{\frac{4\pi}{(2l+1)}} Y_k^q \quad (3)$$

Y_k^q are the spherical harmonics.

For tetragonal symmetry site (D_{4h}), the crystal-field Hamiltonian H_{CF} is invariant under this symmetry group. The values of k and q permitted in the summations over k and q in **Equation (2)**, depend both on the D_{4h} site symmetry and on the selection rules imposed to the matrix elements of H_{CF} [14-15]. So, the CF Hamiltonian H_{CF} for tetragonal symmetry D_{4h} is given by:

$$H_{CF}(D_{4h}) = B_{20}C_0^{(2)} + B_{40}C_0^{(4)} + B_{44}\left(C_4^{(4)} + C_{-4}^{(4)}\right) \quad (4)$$

For the CoCl₂(H₂O)₄ complex a distorted octahedral coordination geometry is observed leading to a lower symmetry D_{4h} [8]. Hence, the crystal field Hamiltonian $H_{CF}(D_{4h})$ of Co²⁺(3d⁷) ions can be considered as the sum of a dominant octahedral Hamiltonian $H_{CF}(O_h)$ and a perturbation Hamiltonian $\Delta H_{CF}(D_{4h})$ translating the light distortion. So in a D_{4h} site symmetry, the Hamiltonian $H_{CF}(D_{4h})$ takes the following form:

$$H_{CF}(D_{4h}) = H_{CF}(O_h) + \Delta H_{CF}(D_{4h}) \quad (5)$$

with:

$$H_{CF}(O_h) = B_4^{cub}[C_0^{(4)} + \sqrt{\frac{5}{14}}\left(C_4^{(4)} + C_4^{(-4)}\right) \quad (6\text{-a})$$

$$\Delta H_{CF}(D_{4h}) = B_{20}C_0^{(2)} + B_4^0 C_0^{(4)} \quad (6\text{-b})$$

with the z-axis taken along the C_4 symmetry axis of the octahedral and :

$$B_4^{cub} = \sqrt{\frac{14}{5}}B_{44} \quad , \quad B_4^0 = B_{40} - \sqrt{\frac{14}{5}}B_{44} \quad (7)$$

3.2. The Matrix Elements of the Crystal-Field Hamiltonian

The effect of the CF Hamiltonian H_{CF} on the energy levels of the 3d^N ion is studied by the degenerate perturbation theory method. In first order perturbation theory, the matrix associated to H_{CF} can be diagonalized to find the energy levels of the ion in the crystalline field. For this

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reason, we give the method of calculation of the matrix elements of the Hamiltonian H_{CF}. Since for 3d^N ions of the first series in crystals the crystal-field is of the intermediate strength [14-15], the basis functions

$$\left\{ \left| d^N L S M_L M_S \right\rangle \right\}$$

in the LS-coupling scheme have been adopted in our computer package. The CF Hamiltonian is developed as a function of the Racah tensor $C_q^{(k)}$. The matrix elements of $C_q^{(k)}$ operators are calculated numerically by using the Racah tensor algebraic methods [14,15]:

$$\left\langle L S M_L M_S \left| C_q^{(k)} \right| L' S M_{L'} M_S \right\rangle =$$

$$(-1)^{L-M_L} \begin{pmatrix} L & k & L' \\ -M_L & q & M_{L'} \end{pmatrix} \left\langle L S \| C^k \| L'S \right\rangle$$

The 3j-symbols

$$\begin{pmatrix} L & k & L' \\ -M_L & q & M_{L'} \end{pmatrix}$$

carry all the dependence on the labels M_L, q and $M_{L'}$ while the reduced matrix elements $\left\langle L S \| C^k \| L'S \right\rangle$ is independent of these labels, but depends on the normalization of the tensor operators.

3.3. A Crystal-Field Analysis Computer Package for 3d^N (N = 2, 3, 7, 8) Ions

As a part of a larger project we have set to develop a computer package based on Maple software to calculate the energy levels and state vectors for any transition metal ions with the 3d^N configuration (N = 2, 3, 7, 8) located at sites with symmetry given by any of the 32 crystallographic point groups. This computer package comprises the following extensions: (1) the calculation of the matrix elements of the crystal-field H_{CF} by considering the 3j-symbols and the reduced matrix elements. (2) diagonalization of the full Hamiltonian matrices (taking into account H_0, H_{CF} and H_{SO}), this diagonalization yields the energy levels as functions of the Racah parameters B and C, crystal-field parameters B_{kq} and spin-orbit coupling constant ξ. These parameters are regarded as empirical parameters to be determined from the optical spectra. (3) the determination of the Racah, crystal-field and spin-orbit coupling parameters by minimising the gap between the experimental and the theoretical energies. These parameters allow us to deduce the calculated energy levels.

4. Results and Discussion

In this work, we are interested in the crystalline-field splitting of the energy levels of Co^{2+}(3d^7) ions in CoCl$_2$(H$_2$O)$_4$ chromophore. The energetic contribution of the Hamiltonian $H_0 + H_{CF}(O_h)$ is dominant compared to

that of $\Delta H_{CF}(D_{4h})$ translating the light distortion. So, we firstly determine the Racah parameter B and the octahedral crystal-field parameter B_4^{cub} from the mean values of the observed spin-allowed bands in O_h symmetry ($<^4T_{2g}(^4F)> = 8195$ cm^{-1}, $<^4A_{2g}(^4F)> = 18600$ cm^{-1} and $<^4T_{1g}(^4P)> = 22250$ cm^{-1}). These parameters are deduced from the eigenvalues obtained by diagonalising the matrix 10 × 10 associated to the Hamiltonian $H_0 + H_{CF}(O_h)$ in the free-ion eigenstates $\left| L, M_L \right\rangle$ within ^4F and ^4P terms. According to Sugano et al. [16], the (10-N)-electron system can be regarded as the N-hole system. So, one can obtain the d^7 matrix by changing the signs of only the crystal-field matrix elements within the complete energy matrix for the d^3 configuration. The Racah parameter C is deduced from the observed spin-forbidden bands in O_h symmetry and the eigenvalues obtained by diagonalising the matrix 40 × 40 associated to $H_0 + H_{CF}(O_h)$ in the free-ion eigenstates $\left| L, M_L \right\rangle$ within ^2H, ^2G, ^2F, ^2D, $^2D'$ and ^2P terms. The values of the Racah and crystal-field parameters B, C and B_4^{cub} obtained are listed in **Table 2**.

The calculated O_h energies for CoCl$_2$(H$_2$O)$_4$ chromophore are listed in **Table 3**. Then, the matrix elements of the Hamiltonian perturbation $\Delta H_{CF}(D_{4h})$ are calculated within the basis formed by the octahedral eigenstates. The remaining crystal-field parameters B_{20} and B_4^0 were calculated from the eigenvalues of the matrix associated to $\Delta H_{CF}(D_{4h})$ and the observed bands at 8060 and 8330 cm^{-1} corresponding respectively to transitions from ^4E_g ($^4T_{1g}(^4F)$) ground state to $^4E_g(^4T_{2g}(^4F))$ and $^4B_{2g}(^4T_{2g}(^4F))$ excited states. The crystal-field parameters B_{20} and B_4^0 obtained are respectively -540 cm^{-1} and -405 cm^{-1}. From **equation 7**, we deduce the values of the crystal-field parameters B_{44} and B_{40}. The spin-orbit coupling constant λ ($\lambda = \xi/3$) considered in this work is similar to that of reference [8]. The values of the crystal-field parameters B_{20}, B_{40} and B_{44} and the spin-orbit coupling constant λ are listed in **Table 2**. By using these parameters, the diagonalization of the 120 × 120 matrix within the quartet and doublet states associated to the Hamiltonien $H_{CF}(D_{4h})$ of **equation 4** lead to the calculated energies for CoCl$_2$(H$_2$O)$_4$ chromophore listed in **Table 4**.

Table 2. Racah and Crystal-field parameter values (cm^{-1}) for CoCl$_2$(H$_2$O)$_4$ chromophore.

B	948
C	3460
B$_4^{cub}$	-19710
B$_{20}$	-540
B$_{40}$	-20115
B$_{44}$	-11778
λ	-171

Table 3. Computed energies (cm⁻¹) in O_h symmetry for CoCl₂(H₂O)₄ chromophore.

$^4T_{1g}(^4F)$	0
$^4T_{2g}(^4F)$	8195
$^2E_g(^2G)$	9788
$^2T_{1g}(^2G)$	15786
$^2T_{2g}(^2G)$	16135
$^4A_{2g}(^4F)$	17580
$^2T_{1g}(^2P)$	20006
$^4T_{1g}(^4P)$	21223
$^2A_{1g}(^2G)$	21308
$^2A_{2g}(^2F)$	40268

Table 4. Calculated energies for Co²⁺ centres with D_4h symmetry in CoCl₂(H₂O)₄ chromophore.

O_h	D_{4h}	$E_{calculated}$ (cm⁻¹)	Spin-orbit coupling
			0
$^4T_{1g}(^4F)$	^4E_g	0	320
			369
			904
	$^4A_{2g}$	90	946
			978
			8766
$^4T_{2g}(^4F)$	^4E_g	8270	8810
			8846
			8951
			9057
			9169
	$^4B_{2g}$	8441	9170
$^2E_g(^2G)$	$^2A_{1g}$	8880	9170
	$^2A_{2g}$	9187	9476
$^2T_{1g}(^2G)$	^2E_g	15094	15639
			15692
	$^2A_{2g}$	15232	15806
$^2T_{2g}(^2G)$	$^2B_{2g}$	15801	16310
	^2E_g	15931	16418
			16756
$^4A_{2g}(^4F)$	$^4B_{1g}$	17826	18463
			18464
$^2T_{1g}(^2P)$	^2E_g	20103	20588
			20618
	$^2A_{2g}$	20174	20932
$^4T_{1g}(^4P)$	$^4A_{2g}$	21086	21549
			21587
			21837
	^4E_g	21486	22084
			22207
			22385
$^2A_{1g}(^2G)$	$^2A_{1g}$	22228	22817
$^2A_{2g}(^2F)$	$^2A_{2g}$	41196	41764

Our calculated energies are in agreement with the observed ones.

The discrepancy between the theoretical energies of this work and the experimental energies is explained by the existence of a recovery between the d orbitals of the central metallic ion and the orbitals of the ligands.

The crystal field theory provides a way of determining, by simple electrostatic considerations, how the energies of the d central metal ion orbitals will be affected by the set of the surrounding ligands. So, the electrostatic crystal field theory deals only with the d orbitals. The molecular orbitals d are not pure metal d orbitals, these orbitals are influenced by the interactions with the σ and π orbitals of the ligands. The theoretical results give values of B = 948 cm⁻¹, C = 3460 cm⁻¹, Dq = 938.57 cm⁻¹ (B_4^{cub} = −19710 cm⁻¹), Dq/B = 0.99 and C/B = 3.65. The Racah parameters B and C are reduced compared to the free ion values ($B_{free\,ion}$ = 1038 cm⁻¹ and $C_{free\,ion}$ = 4366 cm⁻¹ [14,16]) due to covalency effects. With $\beta_B = B_{complex\,ion}/B_{free\,ion}$ and $\beta_C = C_{complex\,ion}/C_{free\,ion}$ it follows: β_B = 0.91 and β_C = 0.80. The Dq/B ratio for CoCl₂(H₂O)₄ is lower than the ratio of 1.2 reported for Co(H₂O)₆²⁺ [7]. This comparison shows that the crystal field strength for CoCl₂(H₂O)₄ is slightly lower than in [Co(H₂O)₆]²⁺. This can be explained by the dependence of crystal field strength parameter Dq on the distance between Co²⁺ ion and ligands. Effectively, the bond length Co-Cl (2.488 Å [17]) is higher than the bond length Co-O (1.896 to 1.916 Å [17]). So, the crystal-field strength Dq is reduced by increasing the number of cobalt ligator atoms. Co²⁺ occupy an O_h site symmetry in [Co(H₂O)₆]²⁺ [7]. The Racah parameters B and C were set respectively to 829 cm⁻¹ and 3316 cm⁻¹ for Co(H₂O)₆²⁺ [7]. As the values of B and C are higher for the case of CoCl₂(H₂O)₄, the nephelauxetic effect is more important in our complex. The comparison with Cr³⁺ ion in CrCl₂(H₂O)₄ (β = 0.63) fits well into the sequence $\beta(Cr^{3+}) < \beta(Co^{2+})$. Also, the crystal field parameter Dq fits into the expected sequence $Dq(Cr^{3+})$ = 1638 cm⁻¹ [11] > $Dq(Co^{2+})$ = 938.57 cm⁻¹.

In **Figure 2**, the Tanabe-Sugano diagram for d⁷ ions in octahedral coordination is shown with the crystal field strength of the Co²⁺ ion in CoCl₂(H₂O)₄ indicated by a vertical line.

The set of calculated parameters given in **Table 2** reproduce well the energies of the observed spin-allowed absorption band of **Figure 1**. Moreover, we have deduced the energy levels which are not observed experimentally in D_4h symmetry taking into account the spin-orbit coupling. From Tanabe-Sugano diagram, we remark that the $^4T_{2g}(^4F)$ quartet state and the $^2E_g(^2G)$ doublet state are nearly for the calculated parameters Dq, B and C. This shows a strong coupling between the electronic states of different multiplicities. Tetragonal D_{4h} symmetry offers two doublet states $^2A_{1g}(^2E_g(^2G))$ and $^2A_{2g}(^2E_g(^2G))$ interacting with tow quartet states $^4E_g(^4T_{2g}(^4F))$ and $^4B_{2g}(^4T_{2g}(^4F))$ (**Figure 3**). All these ex-

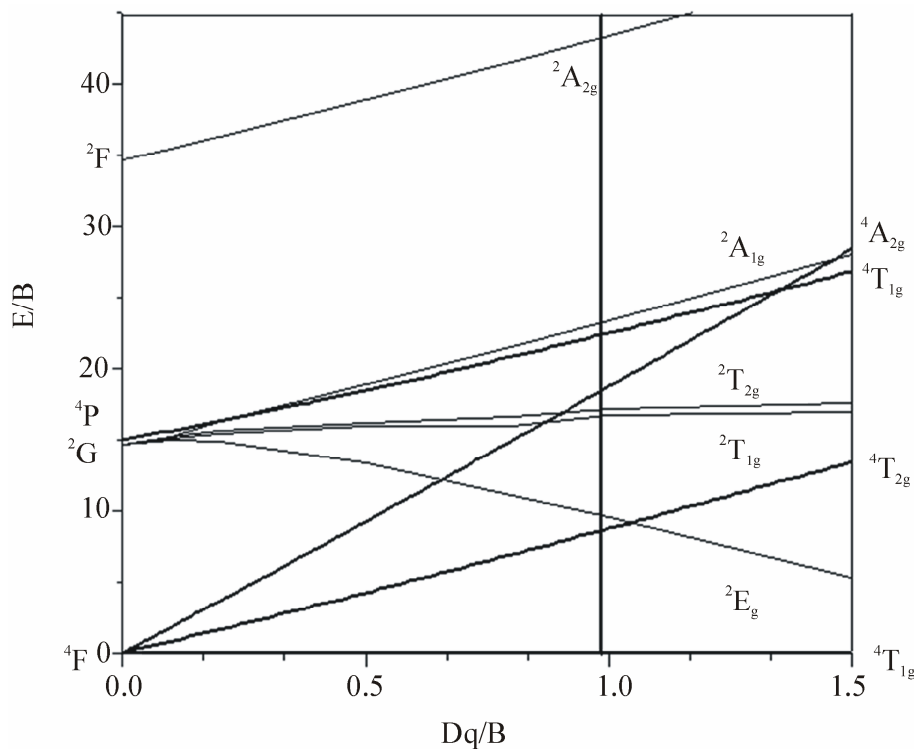**Figure 2. Tanabe-Sugano diagram for octahedrally coordinated Co^{2+} ion with C/B=3.64. The vertical line represents the case of CoCl$_2$(H$_2$O)$_4$ chromophore.**
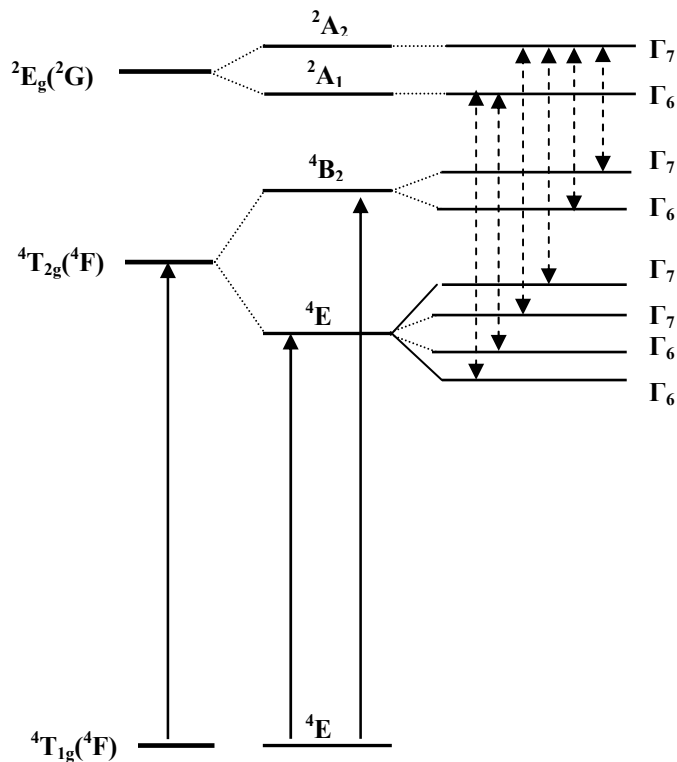

Figure 3. Tetragonal D$_{4h}$ symmetry offers two doublet states ^{2}A$_{1g}$(^{2}E$_g$(^{2}G)) and ^{2}A$_{2g}$(^{2}E$_g$(^{2}G)) interacting with tow quartet states ^{4}E$_g$(^{4}T$_{2g}$(^{4}F)) and ^{4}B$_{2g}$(^{4}T$_{2g}$(^{4}F)).

cited states are subdivided into doublet Kramer's states Γ_6 and Γ_7 by spin-orbit coupling. The interaction between the same symmetry levels Γ_6 and Γ_7 deriving from electronic states of different multiplicities leads to the observed spin-forbidden transition $^4T_{1g}(^4F) \rightarrow {}^2E_g(^2G)$ (O_h symmetry) with lower intensity compared to a spin-allowed transition (**Figure 3**). The same explanation is also applied for the $^4A_{2g}(^4F)$ quartet state and the $^2T_{1g}(^2G)$ and $^2T_{2g}(^2G)$ doublet states.

5. Conclusions

A theoretical crystal-field analysis, based on the Racah theory, was carried out for the electronic energy levels of CoCl$_2$(H$_2$O)$_4$. The observed crystalline-field splittings of the Co^{2+} levels were accounted by using a D_{4h} symmetric Hamiltonian. As a result, Racah and crystal field parameters have been reliably obtained. Calculated crystalline field levels are in agreement with the observed ones. The theoretical study confirms the charge state Co^{2+} of cobalt and the site occupied D_{4h}. The assignment of the first quartet band $^4T_{2g}(^4F)$ seen in the near-infrared region is in agreement with the literature. Whereas, we find that the assignment of the two other quartet bands are respectively $^4A_{2g}(^4F)$ and $^4T_{1g}(^4P)$. This assignment is uncertain in the literature.

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