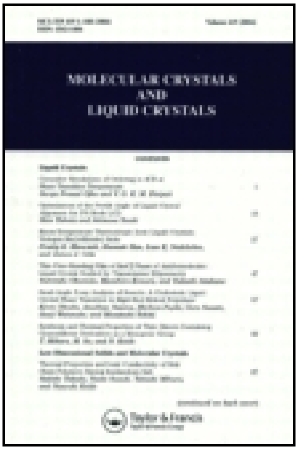

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High-Spin Heteronuclear Cyanometalates: g-Tensors and Magnetic Properties of $Cr^{III}Ni^{II}{}_{n}$ (n=2,3,4,5,6) and Heptanuclear $Cr^{III}Cu^{II}{}_{6}$ Compounds

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High-Spin Heteronuclear Cyanometalates: g-Tensors and Magnetic Properties of $Cr^{III}Ni^{II}{}_{n}$ (n=2,3,4,5,6) and Heptanuclear $Cr^{III}Cu^{II}{}_{6}$ Compounds

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Using the irreducible tensor operator technique we develop a computational approach to the problem of g-tensors for the heteronuclear polymetallic systems consisting of the arbitrary number of coupled paramagnetic ions. We deduce the effective g-values for the family of the heterometallic $Cr^{III}Ni^{II}{}_{n}$cyanometalates (n=2,3,4,5,6) possessing different topologies. For $Cr^{III}Ni^{II}{}_{6}$ complexes a good fit to experimental $\mu(T)$ is achieved. For $Cr^{III}Cu^{II}{}_{6}$ the local anisotropy of g for Cu^{II} ions is taken into account.

Keywords: high-spin molecules; cyanometalates; g-tensors

INTRODUCTION

One of the present interest in the EPR and magnetochemical study of clusters and particularly of the high-spin molecules[1-6] is the investigation of the correlation between the values peculiar for the monomeric constituent moieties and the cluster as a whole. Using the irreducible tensor operator (ITO) technique[7-11] the effective g- and D-tensors of heterobinuclear systems

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have been considered in detail in [12,13] and reviewed in [14]. A great impact on the use of the ITO technique for polynuclear compounds particularly in the problem of g- and D-tensors is given in [10].

In this article we report a general computational approach to the problem of g-tensors of polymetallic systems consisting of an arbitrary number of exchange coupled paramagnetic ions. We deduce the effective g-values for a family of heterometallic $Cr^{III}(CN\text{-}Ni^{II}\text{-}L_5)_n(CN)_{6-n}$ cyanometalates (n=2,3,4,5,6) possessing different topologies. Special attention is paid to the case of high spin heptanuclear heterometallic $Cr^{III}(CN\text{-}Mn^{II}\text{-}L_5)_6$ complexes [5]. The results are used for the study of the magnetic properties of these compounds. Assuming strong isotropic exchange between Cr^{III} and Cu^{II} ions we deduce molecular g-tensors for the $Cr^{III}(CN\text{-}Cu^{II}\text{-}L_5)_6$ cyanometalates. In this case the local anisotropy of Cu^{II} ions is significant and taken into account in the calculation of molecular g-tensor.

GENERAL CONSIDERATION

We assume that the heterometallic system under consideration consists of N ions with spins S_1, S_2, ... S_N coupled by isotropic exchange interaction:

$$H_{ex} = -\sum_{i,j=1}^{N} J_{ij}\vec{S}_i\vec{S}_j\,, \tag{1}$$

where J_{ij} are the exchange parameters. In the following, we use the successive spin coupling scheme:

$$S_1 + S_2 = \tilde{S}_2,\ \tilde{S}_2 + S_3 = \tilde{S}_3 \ldots\ \tilde{S}_{N-1} + S_N = \tilde{S}_N \equiv S\,, \tag{2}$$

In the coupling scheme (2) $\tilde{S}_2 = S_{12}$, $\tilde{S}_3 = S_{12} + S_3 = S_{123}$ etc. are the set of intermediate spins (shortly $(\tilde{S})$), $\tilde{S}_N \equiv S$ is the full spin of the system. The spin functions are represented as a superposition of $(\tilde{S})$ S states. In some cases the intermediate spins are the good quantum numbers and we consider these cases separately.

The Zeeman hamiltonian for a heterometallic polynuclear system can be expressed in terms of the first rank irreducible spin tensors $S_q^{(1)}(i)$:

$$H_Z = \beta\sum_{i=1}^{N} g_i \sum_q (-1)^q S_q^{(1)}(i)\, H_{-q}^{(1)} \tag{3}$$

where $H_0^{(1)} = H_Z$, $H_{\pm1}^{(1)} = \mp(H_x \pm iH_y)/\sqrt{2}$, g_i is the g-value of i-th ion. The initial hamiltonian (3) can be replaced by the effective one:

$$H_Z = \beta\, g_S(\tilde{S}'\tilde{S})\sum_q (-1)^q S_q^{(1)}\, H_{-q}^{(1)} \tag{4}$$

acting in the spin space $|(\tilde{S})SM\rangle$ belonging to a definite set $(\tilde{S})$ and full spin S and containing effective $g_S(\tilde{S}'\tilde{S})$ (molecular) values.

Following Chao[12] one can apply the Wigner-Eckart theorem to get:

$$g_S(\tilde{S}'\tilde{S}) = \left[\langle(\tilde{S}')S\|S^{(1)}\|(\tilde{S})S\rangle\right]^{-1} \sum_{i=1}^{N} g_i \langle(\tilde{S}')S\|S^{(1)}(i)\|(\tilde{S})S\rangle \tag{5}$$

where $\langle\ldots\|\ldots\|\ldots\rangle$ is the symbol of the reduced matrix element. Using the well-known expression for the reduced matrix element of $S^{(1)}$ [11,15] and the notation $C_i(\tilde{S}'\tilde{S}|S) = \langle(\tilde{S}')\, S\, \|\, S^{(1)}(i)\|(\tilde{S})\, S\rangle$ one can rewrite eq.(5) as:

$$g_S(\tilde{S}'\tilde{S}) = \left[S(S+1)(2S+1)\right]^{-1/2} \sum_{i=1}^{N} C_i(\tilde{S}'\tilde{S}|S)\, g_i \tag{6}$$

In the case of well isolated νS exchange multiplets (ν enumerates the eigenvalues of (1)) the g-value belonging to each multiplet can be presented as [11]:

$$g_S(\nu) = \sum_{\widetilde{S}'\widetilde{S}} a_\nu(\widetilde{S}) a_\nu(\widetilde{S}') g_S(\widetilde{S}'\widetilde{S}) \quad , \tag{7}$$

where the coefficients $a_\nu(\widetilde{S})$ are the eigenvectors of (1).

Let us introduce a complex ITO $\hat{T}_q^{(k)}$ of rank k (q enumerate the components) composed from the one-ion ITO $\hat{S}_{q_f}^{(k_f)}(f)$ in the following way:

$$\hat{T}_q^{(k)}(k_1 k_2 \widetilde{k}_2 \ldots \widetilde{k}_{N-1} k_N k) = \underbrace{\{\{\ldots\{}_{N-1} \hat{S}^{(k_1)} \otimes \hat{S}^{(k_2)}\}^{(\widetilde{k}_2)} \otimes \hat{S}^{(k_3)}\}^{(\widetilde{k}_3)} \ldots \otimes \hat{S}^{(k_N)}\}_q^{(k)} \tag{8}$$

where $\otimes$ is the sign of the ITO's product.

In order to evaluate the matrix element of the complex ITO $\hat{T}_q^{(k)}$ in the spin coupled representation we use the expression for the reduced matrix element of the double tensor operator in terms of the reduced matrix element of the constituent (one-ion) ITOs [9,11,15]. Applying the decoupling formula to the matrix element of $\hat{T}_q^{(k)}$ (N-1) times successively, one gets the following expression for the reduced matrix element of the complex ITO $\hat{T}_q^{(k)}$:

$$\begin{aligned} \left\langle \widetilde{S}'_2 \widetilde{S}'_3 \ldots \widetilde{S}'_{N-1} S \right\| \hat{T}_q^{(k)} \left\| \widetilde{S}_2 \widetilde{S}_3 \ldots \widetilde{S}_{N-1} S \right\rangle &= \left\langle S_1 \right\| S^{(k_1)} \left\| S_1 \right\rangle \prod_{m=1}^{N-1} \sqrt{(2\widetilde{k}_{m+1}+1)} \\ &\times \sqrt{(2\widetilde{S}'_{m+1}+1)(2\widetilde{S}_{m+1}+1)} \left\langle S_{m+1} \right\| S^{(k_{m+1})} \left\| S_{m+1} \right\rangle \begin{Bmatrix} \widetilde{k}_m & k_{m+1} & \widetilde{k}_{m+1} \\ \widetilde{S}'_m & S_{m+1} & \widetilde{S}'_{m+1} \\ \widetilde{S}_m & S_{m+1} & \widetilde{S}_{m+1} \end{Bmatrix} \end{aligned} \tag{9}$$

In eq.(9) $\widetilde{S}_1$ and $\widetilde{S}'_1$ should be defined as $\widetilde{S}_1 = \widetilde{S}'_1 = S_1$. Eq.(9) contains all matrix elements necessary for the calculation of $g_S(\widetilde{S}'\widetilde{S})$. In general the matrix element $\left\langle (\widetilde{S}')\, S \,\|\, S^{(1)}(i) \,\|\, (\widetilde{S})\, S \right\rangle$ can be found from eq.(9) by the substitution: $k_i=1$, $k_j=0$ ($j \neq i$), all $\widetilde{k}_j=0$ ($j<i$), $\widetilde{k}_j=1$ ($j \geq i$), $k=1$. The final

expression for all coefficients $C_i(\tilde{S}'\tilde{S}|S)$ contains 6j-symbols only [15]. For example, the first coefficient is found to be the following:

$$C_1(\tilde{S}'\tilde{S}|S) = \sqrt{S_1(S_1+1)(2S_1+1)} \times \sqrt{(2\tilde{S}'_2+1)(2\tilde{S}_2+1)}(-1)^{S_1+S_2+\tilde{S}_2+1}\begin{Bmatrix} \tilde{S}'_2 & \tilde{S}_2 & 1 \\ S_1 & S_1 & S_2 \end{Bmatrix} \times \prod_{m=2}^{N-1}\sqrt{(2\tilde{S}'_{m+1}+1)(2\tilde{S}_{m+1}+1)}(-1)^{\tilde{S}'_m+S_{m+1}+\tilde{S}_{m+1}+1}\begin{Bmatrix} \tilde{S}'_{m+1} & \tilde{S}_{m+1} & 1 \\ \tilde{S}_m & \tilde{S}'_m & S_{m+1} \end{Bmatrix} \tag{10}$$

The expression (6) with the coefficients $C_i(\tilde{S}'\tilde{S}|S)$ so far obtained can be considered as solution of the problem of the molecular g-values in heterometallic system with an arbitrary nuclearity.

g-FACTORS FOR THE HETEROMETALLIC $B^{III}A^{II}_n$ SPIN SYSTEMS

Hexacyanometalate $[B^{III}(CN)_6]$ behaves as Lewis base able to bind Lewis acid $A^{II}L_5$, where L is a pentadentate ligand to give heptanuclear complexes $[B^{III}(CN\text{-}A^{II}\text{-}L_5)_6]^{+9}$, abbreviated $B^{III}A^{II}_6$ in the following. The B^{III} ion is octahedrally surrounded by six ions A^{II} through the bridging cyanide (CN^-) ligand. The heptanuclear $Cr^{III}Cu^{II}_6$ and $Cr^{III}Ni^{II}_6$ display ferromagnetic interactions between Cr^{III} and Cu^{II} or Ni^{II} whereas $Cr^{III}Mn^{II}_6$ displays antiferromagnetic Cr^{III}-Mn^{II} interactions [4,5]. Syntheses are underway to get new compounds $Cr^{III}(CN\text{-}A^{II}\text{-}L_5)_n(CN)_{6-n}$ containing a smaller number (n=2,3,4,5) of $A^{II}L_5$ groups giving rise to systems of lower symmetry (Figs. 1b-1e) [16]. We denote $S_B \equiv S_0$, $S_{A_i} \equiv S_i$ (B=Cr, A_i=Ni,Mn) and take into account only BA_i interactions ($J \equiv J_{BA_i}$). $\tilde{S}_n$ is the full spin of the A^{II}_n moiety and $S \equiv \tilde{S}_{n+1}$ is the full spin of the $B^{III}A^{II}_n$ molecule. The energy levels are:

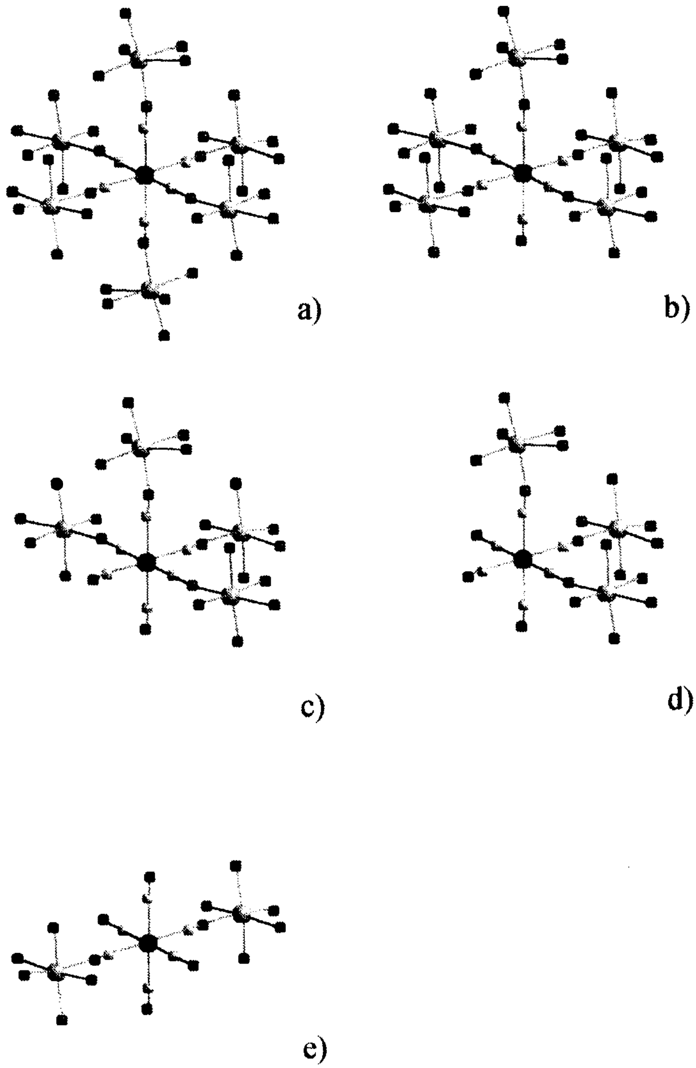

FIGURE 1. Structure of heterometallic $Cr^{III}Ni^{II}_n$ cyanometalates: a) n=6, O_h; b) n=5, C_{4v}; c) n=4, C_{2v}; d) n=3, fac isomer, C_{3v}; e) n=2, trans isomer, C_{2v}.

$$E(\tilde{S}_n S) = -\frac{J}{2}\left[S(S+1) - \tilde{S}_n(\tilde{S}_n+1) - S_0(S_0+1)\right] \tag{11}$$

are "accidentally" degenerate over all sets ($\tilde{S}_{n-1}$). All g-values are supposed to be isotropic, $g_0 \equiv g_B$ and $g_{A_1} \equiv g_1$.

In the case of "accidentally" degenerate spin levels the Zeeman interaction operates in the subspace of each $\tilde{S}_n S$ -level and can be represented by the matrix $\left\langle(\tilde{S}')SM\middle|H_Z\middle|(\tilde{S})SM\right\rangle$. The $g_S(\tilde{S}\tilde{S}')$ are the following:

$$g_S(\tilde{S}'\tilde{S}) = \left[S(S+1)(2S+1)\right]^{-1/2}\left[g_0 C_0(\tilde{S}'\tilde{S}|S) + g_1\sum_{i=1}^{n} C_i(\tilde{S}'\tilde{S}|S)\right] \tag{12}$$

If we consider the diagonal ($\tilde{S} = \tilde{S}'$) g_S values, we arrive to the final expression for the sum $\sum_{i=1}^{n} C_i(\tilde{S}|S)$ related to the A^{II}_n moiety of the $B^{III}A^{II}_n$ molecule:

$$\sum_{i=1}^{n} C_i(\tilde{S}|S) = \sqrt{\tilde{S}_n(\tilde{S}_n+1)(2\tilde{S}_n+1)}\,(2S+1)(-1)^{\tilde{S}_n+S_0+S+1}\begin{Bmatrix} S & S & 1 \\ \tilde{S}_n & \tilde{S}_n & S_0 \end{Bmatrix} \tag{13}$$

The coefficient $C_0(\tilde{S}|S) \equiv C_{n+1}(\tilde{S}|S)$ related to the central ion B^{III} is:

$$C_{n+1}(\tilde{S}|S) = \sqrt{\tilde{S}_0(\tilde{S}_0+1)(2\tilde{S}_0+1)}(2S+1)(-1)^{\tilde{S}_n+S_0+S+1}\begin{Bmatrix} S & S & 1 \\ S_0 & S_0 & \tilde{S}_n \end{Bmatrix} \tag{14}$$

Substituting eqs.(13) and (14) in eq.(6) and simplifying 6j-sumbols [15] one can find the following result for the diagonal part of the g-value for the $B^{III}A^{II}_n$:

$$g_S(\tilde{S}) = \frac{g_1 + g_0}{2} + (g_1 - g_0)\frac{\tilde{S}_n(\tilde{S}_n+1) - S_0(S_0+1)}{2S(S+1)} \tag{15}$$

As for the non-diagonal elements, one can prove that they are zero [15]. The expression for g's is therefore given by eq.(15). This expression looks like that for a binuclear system in which the first spin relates to the central ion B^{III}, meanwhile $\tilde{S}_n$ relates to A^{II}_n moiety.

In the fit to the experimental data on the magnetic moment we have used $g_0 = g_{Cr^{III}} = 1.99$ and $g_1 = g_{Ni^{II}} = 2.2$ which is a reasonable value for Ni^{II} in the nitrogen surrounding. The best fit parameter J_{NiCr}=15cm^{-1} (R= 3.06×10^{-4}).

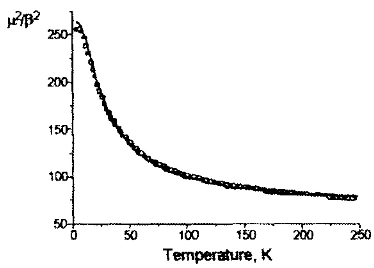

FIGURE 2. Temperature dependence of the magnetic moment of $Cr^{III}Ni^{II}_6$; (°) experimental data, (—) best fit

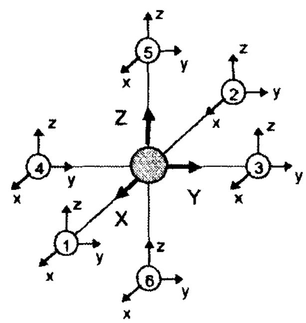

FIGURE 3. Metallic skeleton of $Cr^{III}Cu^{II}_6$ system, molecular (XYZ) and local ($x_iy_iz_i$) coordinates .

MOLECULAR g-TENSOR OF THE HEPTANUCLEAR $Cr^{III}Cu^{II}_6$ CYANOMETALATE

Here we take into account the axial symmetry of the local copper g-tensor, $g_{\parallel}$ and $g_{\perp}$ being the components relating to C_4 axes.

In the case of $Cr^{III}Cu^{II}_6$ system containing strongly anisotropic Cu^{II} ions the following spin coupling scheme closely related to the symmetry of the system seems to be more convenient that the general one (eq.(2)):

$$S_1+ S_2= S_{12}\ ,\ S_3+ S_4= S_{34}\ ,\ S_{12}+ S_{34}= \tilde{S}_4\ ,\ S_5+ S_6= S_{56}\ ,$$
$$\tilde{S}_4 + S_{56}= \tilde{S}_6\ ,\ \tilde{S}_6 + S_0= S \qquad (16)$$

In the coupling scheme (16) $\tilde{S}_4$ is the spin of Cu^{II}_4 square, $\tilde{S}_6$ is the full spin of the Cu^{II}_6 moiety. For Cu^{II} ions the local g-tensors are axial as implied by the tetragonal site symmetry. Applying the decoupling formula [11,15] 3 times successively one gets the expression for the reduced matrix element of $\hat{T}^{(k)}_q$ in terms of the matrix element of pair products (for Cu^{II}_6 subsystem) and matrix element of $S^{(k_0)}$ (Cr^{III} ion):

$$
\begin{aligned}
&\left\langle S'_{12}S'_{34}\tilde{S}'_4S'_{56}\tilde{S}_6S\left\|\hat{T}^{(k)}_q\right\|S_{12}S_{34}\tilde{S}_4S_{56}\tilde{S}_6S\right\rangle \\
&= (2S+1)\,(2\tilde{S}_6+1)\left[(2\tilde{k}_6+1)(2k+1)(2\tilde{S}'_4+1)(2\tilde{S}_4+1)(2\tilde{k}_4+1)\right]^{1/2} \\
&\times \quad \left\langle S_0\left\|S^{(k_0)}\right\|S_0\right\rangle \left\langle S_{12}\left\|\left\{S^{(k_1)}\otimes S^{(k_2)}\right\}^{(k_{12})}\right\|S'_{12}\right\rangle \\
&\times \quad \left\langle S_{34}\left\|\left\{S^{(k_3)}\otimes S^{(k_4)}\right\}^{(k_{34})}\right\|S'_{34}\right\rangle\left\langle S_{56}\left\|\left\{S^{(k_5)}\otimes S^{(k_6)}\right\}^{(k_{56})}\right\|S'_{56}\right\rangle \\
&\times \quad \begin{Bmatrix} k_{12} & k_{34} & \tilde{k}_4 \\ S'_{12} & S'_{34} & \tilde{S}'_4 \\ S_{12} & S_{34} & \tilde{S}_4 \end{Bmatrix}\begin{Bmatrix} \tilde{k}_4 & k_{56} & \tilde{k}_6 \\ \tilde{S}'_4 & S'_{56} & \tilde{S}_6 \\ \tilde{S}_4 & S_{56} & \tilde{S}_6 \end{Bmatrix}\begin{Bmatrix} \tilde{k}_6 & k_0 & k \\ \tilde{S}_6 & S_0 & S \\ \tilde{S}_6 & S_0 & S \end{Bmatrix}
\end{aligned} \tag{17}
$$

Omitting the details of the calculations we give only the final expressions for the coefficients $C_i(\tilde{S}|\tilde{S}_6S)$ in eq.(6) using X(abc)=a(a+1)+b(b+1)-c(c+1):

$$
\begin{aligned}
C_1(\tilde{S}|\tilde{S}_6S) = C_2(\tilde{S}|\tilde{S}_6S) &= \frac{X(S\tilde{S}_6S_0)X(\tilde{S}_4S_{12}S_{34})X(\tilde{S}_6\tilde{S}_4S_{56})}{16\tilde{S}_6(\tilde{S}_6+1)\tilde{S}_4(\tilde{S}_4+1)}\left[\frac{2S+1}{S(S+1)}\right]^{1/2} \\
C_3(\tilde{S}|\tilde{S}_6S) = C_4(\tilde{S}|\tilde{S}_6S) &= \frac{X(S\tilde{S}_6S_0)X(\tilde{S}_4S_{34}S_{12})X(\tilde{S}_6\tilde{S}_4S_{56})}{16\tilde{S}_6(\tilde{S}_6+1)\tilde{S}_4(\tilde{S}_4+1)}\left[\frac{2S+1}{S(S+1)}\right]^{1/2} \\
C_5(\tilde{S}|\tilde{S}_6S) = C_6(\tilde{S}|\tilde{S}_6S) &= \frac{X(S\tilde{S}_6S_0)X(\tilde{S}_6S_{56}\tilde{S}_4)}{8\tilde{S}_6(\tilde{S}_6+1)}\left[\frac{2S+1}{S(S+1)}\right]^{1/2}
\end{aligned} \tag{18}
$$

Combining eqs. (6) and (18) one can find the following expression for the diagonal ($\tilde{S}=\tilde{S}'$) part of the molecular g-value:

$$
\begin{aligned}
g(\tilde{S}|\tilde{S}_6S) = \frac{X(S\tilde{S}_6S_0)}{4S(S+1)\tilde{S}_6(\tilde{S}_6+1)}&\left[g_\perp X(\tilde{S}_6\tilde{S}_4S_{56})+g_\parallel X(\tilde{S}_6S_{56}\tilde{S}_4)\right] \\
&+\frac{g_0}{2}\left[1-\frac{\tilde{S}_6(\tilde{S}_6+1)-S_0(S_0+1)}{S(S+1)}\right]
\end{aligned} \tag{19}
$$

As before one can prove that all non-diagonal values $g(\tilde{S}'\tilde{S}|\tilde{S}_6S)$ are zero and therefore the accidentally degenerate spin states within the level $E(\tilde{S}_6S)$ are not mixed by the Zeeman interaction.

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