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Theoretical approach to the magnetic behaviors of newly reported Cobalt(II) complex of Schiff base: distortion and covalency at room temperature

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The magnetic behavior of Co(II) complex in newly reported Schiff base complex derived from benzyl-2,4-dinitrophenylhydrazone with aniline, is investigated by a theoretical approach for various geometrical situations. It is found that in order to obtain the observed room temperature magnetic moments, some of the parameters, which are related to the geometry of the complexes, should be varied in the magnetic Hamiltonian. From the calculations and experiments published in the literature, it is suggested that the environments of complex seem to be a low field distorted octahedral surrounding. It is also suggested that, allowing a bit of covalency the reported complex seems to be a good candidate to one of the low field octahedral Co(II) complexes.

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1. Introduction

Magnetic properties of high-spin octahedral Co(II) complex in different surroundings have been studying for many years[1-9]. The magnetization and hence the magnetic susceptibility is one of the most important properties of matter, which is directly related to its electronic structure[10,11]. In other words the information about the electronic structure of molecules is contained in its magnetic moment μ. The ground term of bivalent cobalt complex in an octahedral environment is $^4T_{1g}$. The orbital contribution to the magnetic moment is non-zero when the T term is split by low symmetry crystal fields and spin-orbit interaction, but the splitting magnitude is not very large compared with kT. As is well known the magnetic moments for complexes with T ground terms are obtained by performing the sums for the first and second order Zeeman effects among the states which arise from the splitting of the terms by both spin-orbit coupling and low symmetry crystal field [10-15]. The effect of spin-orbit coupling and low symmetry crystal fields in T terms is found by operating with an appropriate Hamiltonian on the appropriate wave functions. The wave function of this term generally varies depending on the field strength, since it has some mixing in terms from the exited states. In this particular study the magnetic properties of Co(II) ion in Schiff base have been analyzed by a theoretical approach. The coordination chemistry of metal complexes of Schiff base are studied extensively due to synthetic flexibility of these compounds and their selectivity as well as sensitivity towards the central metal atom [4]. Metal complexes of Schiff bases have played a central role in the development of coordination chemistry. From the survey of existing literature, it appears that benzil monophenylhyrazone and its related compounds have been extensively used as biologically active complexing agents and analytical reagents [16-21]. The observed room temperature magnetic moment of the cobalt(II) complex of Schiff base derived from benzyl-2,4-dinitrophenylhydrazone with aniline [which was synthesized by the condensation of benzyl-2,4-dinitrophenylhydrazone with aniline in 1:1 molar ratio dissolved in ethanol. The resulting reaction mixture was refluxed for *ca.* 1 h. The yellow solid precipitate of Schiff base obtained was filtered, washed with distilled water dried and recrystallised from ethanol, m.p. 138 ^oC, Molecular formula: $C_{26}H_{19}N_5O_4$. The cobalt(II) complex was obtained by mixing an ethanolic solution of the above Schiff base (10 mM) with cobalt(II) chloride(5 mM) in ethanol keeping ligand-metal ratio 2:1 followed by few drops of acetic acid (pH=6). The mixture was then refluxed for *ca.* 1 h on a water bath till the complex precipitated out. The solid product obtained was filtered, washed with distilled water and dried *in vacuum.* Molecular formula: $CoC_{52}H_{42}N_{10}O_{10}$. The structures of the Schiff base(ligand) and its cobalt(II) complex are given in Chart 1] is 4.81 B.M. [9] From a detailed analysis of the spectra done by Raman *et al.* [9], this Co(II) complex possesses an octahedral geometry. In general, the cobalt(II) Schiff base complexes exist tetrahedral, octahedral and square-planar geometry which can be easily identified by determining their magnetic moments. Hence, the magnetic properties of these complexes are the main part of this study. Co(II) is a d^7 or three hole ion. The ground term of free Co(II) ion is ^4F, which is sevenfold degenerate. In a field of cubic symmetry, the ^4F-state breaks up into states which form irreducible representations of the cubic group. If the symmetry was purely octahedral, then the ground state

would be $^4T_{1g}$ which is orbitally triplet. The magnetic moment of above mentioned Co(II) complex is calculated by simply summing the first and second order Zeeman terms in the presence of spin-orbit coupling and low symmetry crystal field. Using the results of the calculations the amount of distortions and the covalancy effects are also analyzed in order to obtain the measured room temperature magnetic moment for the complex. Since experimentally there is no published result except that room temperature, the calculations are restricted to this particular temperature.

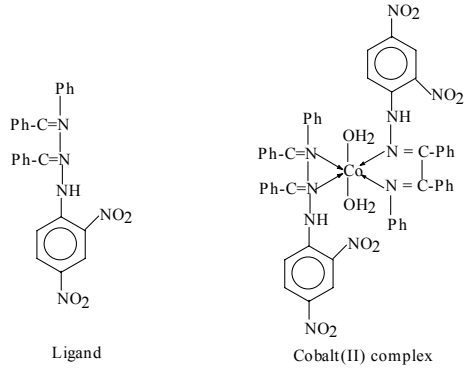

Chart 1

2. The Magnetic Behavior of the $^4T_1$ term in a perfect octahedral surroundings

2.1 Low Field Case

In a perfect octahedral environments the ground state of Co(II) ion would be the $^4T_1$ term [11-14]. The magnetic susceptibility of this term can conventionally be calculated by considering the effects of spin-orbit coupling and a magnetic field as sequential perturbations to the wave functions for the weak field $^4T_1$ term [11-14]. The average magnetic moment of this term is given somewhere else [11,12,15]. The variation of μ with temperature for λ=-170 is illustrated in Fig. (1).

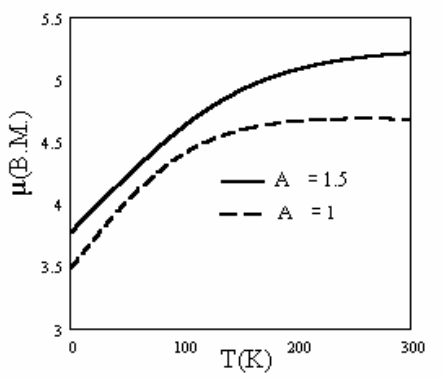

Fig. 1. Temperature variation of magnetic moment for various field strength.

At room temperature μ is expected to be about 5.2 B.M. and it will fall steadily until a value of 3.76 is reached at 0 K. It is clear that 4.81 B.M. value is obtained only if the covalancy factor is around 0.75 in this field strength limit. But it is quite obvious that this amount of covalancy is unlikely for any octahedral Co(II) complex.

2.2 High Field Case

Since the behavior of Co(II) complex in the considered example has three unpaired electron, the field strength should have a value such that it would not cause any spin pairing. Keeping this point in mind, the magnetic properties for medium and strong field case can be analyzed in a similar fashion. In this case the strength of the ligand field will not change the spin multiplicity of the ground term. In such a case the wave-functions for the ground term can be expressed as a linear combinations of those for the $^4T_1(4F)$ and $^4T_1(4P)$ terms as [11-15].

$$\psi(T_1) = \left(1 + c_i^2\right)^{\frac{-1}{2}} \left[\psi(T_1^0(F)) + c_i \psi(T_1^0(P))\right]$$

The mixing coefficient can be found from the equation $c_i = \dfrac{6Dq + E}{4Dq}$ [14,15]. The coefficient c_i varies from 0 for a weak ligand field to -1/2 for a strong ligand field. The magnetic properties of $^4T_1$ terms are generally discussed by neglecting any contributions which may arise from any other excited terms, except of course the P term. This is conventionally done by defining a parameter,

$$A = \frac{1.5 - c_i^2}{1 + c_i^2}$$

And expressing the orbital parts of wave-function of the $^4T_1$ terms as combinations of |L,ML> basis as

$$|\pm A\rangle = \left(1 + c_i^2\right)^{\frac{-1}{2}} \left[\sqrt{\frac{9}{24}}\,|3,\pm 3\rangle - \sqrt{\frac{9}{24}}\,|3,\mp 1\rangle + c_i\,|1,\mp 1\rangle\right]$$

and

$$|0\rangle = \left(1 + c_i^2\right)^{\frac{-1}{2}} \left[|3,0\rangle + c_i\,|1,0\rangle\right]$$

The spin-orbit coupling splits this term into three components at energies –(3λA/2), Aλ, and (5Aλ/2). When A=1.5 this splitting pattern corresponds to that of the weak field case. The behavior of magnetization against temperature for both high and low field strength is shown in Fig(1). It is obvious that μ decreases as the crystal field strength is increased. The observed room temperature magnetic moment (4.81 B.M.) is obtained when the field strength is 1.124. This value for a field strength is a bit higher than the reported value for Co(II) complex. On the other hand if we include some covalency (for example κ=0.85) this value would be around 1.32. Still the field

strength is higher than the reported values. The reported field strength for octahedral Co(II) complexes is generally around 1.4[15]. Since the covalency factor for octahedral Co(II) complexes is generally around 1-0.9 we had to investigate the distorted octahedral case too.

3. Magnetic Behavior of the $^4T_1$ term in an axially symmetric surroundings

It is well known that for real compounds the symmetry is at best axial, and the ground term generally splits into an orbital singlet ground term and an orbital doublet excited state. If the distortion is tetragonal (D_{4h}) these states may be labeled as $^4A_{2g}$ and ^4E_g. They are split by the spin-orbit coupling such that the spectrum is as shown in fig(2), where the levels are labeled with the irreducible representations of the double group D_4'.

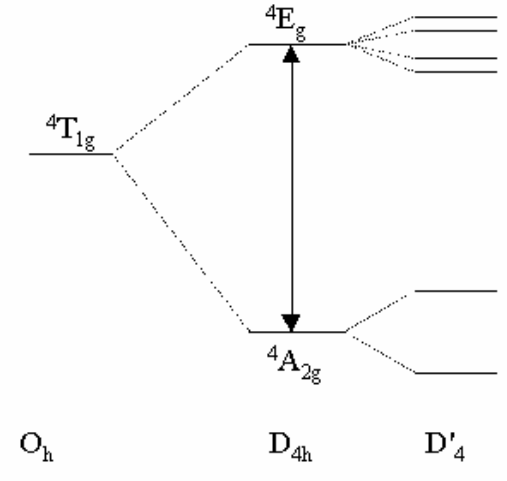

Fig. 2. Energy spectrum for a Co(II) ion in an axially distorted environment.

In order to find the magnetic properties of such a system we need to describe the right Hamiltonian, which acts to the 12 basis sets of the $^4T_{1g}$ term. The correct Hamiltonian involving the tetragonal distortion, spin-orbit coupling, and Zeeman perturbation term is given as [10-13,22].

$$H = V_{dis} + \kappa\lambda\vec{L}\cdot\vec{S} + \beta\left(\kappa\vec{L} + g_e\vec{S}\right)\cdot\vec{H}$$

where κ is the orbital reduction factor, λ is the spin-orbit coupling constant, β is the Bohr magneton, and g_e is the free electron g value. It is obvious that the $^4T_{1g}$ term arises from the $t_{2g}^5e_g^2$ configuration and the wave function is of the form [11-14]

$$\psi = \frac{2\sqrt{5}}{5}\psi\left[{}^4T_{1g}({}^4F)\right] + \frac{\sqrt{5}}{5}\psi\left[{}^4T_{1g}({}^4P)\right].$$

In order to solve the problem one must diagonilise spin-orbit coupling and distortion together then calculate the Zeeman coefficients for the two directions parallel and perpendicular to the applied magnetic field. For this type of calculations the appropriate Hamiltonian is

$$H = \Delta\left(L_z^2 - \frac{2}{3}\right) - (3/2)\kappa\lambda\vec{L}\cdot\vec{S} + \beta\left[(3/2)\kappa\vec{L}_u + g_e\vec{S}\right]\cdot\vec{H}$$

In this Hamiltonian the factor (-3/2) indicates that the real angular momentum of $^4T_{1g}$ state is equal to the angular momentum of the ^4P free-ion state multiplied by (-3/2). In order to perform these calculations the suitable form of the wave functions would be |ML,MS> basis and these are[9,17]

$$\psi_1 = |1,\frac{3}{2}>,\quad \psi_2 = |1,\frac{1}{2}>,\quad \psi_3 = |1,\frac{-1}{2}>,$$
$$\psi_4 = |1,\frac{-3}{2}>,\quad \psi_5 = |0,\frac{3}{2}>,\quad \psi_6 = |0,\frac{1}{2}>,$$
$$\psi_7 = |0,\frac{-1}{2}>,\quad \psi_8 = |0,\frac{-3}{2}>,\quad \psi_9 = |-1,\frac{3}{2}>,$$
$$\psi_{10} = |-1,\frac{1}{2}>,\ \psi_{11} = |-1,\frac{-1}{2}>,\ \psi_{12} = |-1,\frac{-3}{2}>,$$

such that the wave-functions are specified in terms of $|M_L,M_S>$. Defining the suitable wave functions, the derivation of the principle susceptibilities is not difficult, which can be easily performed with a microcomputer. The size of matrices to diagonalise to get the zero field energies and the Zeeman coefficients is 12×12. Once obtaining the energies and zero-order wave-functions resulting from the perturbation by the low symmetry crystal field and by spin-orbit coupling, one can calculate magnetic field perturbation. Since the system is anisotropic the perturbation in parallel and perpendicular directions will be different from each other. For this reason we calculated two susceptibilities**:** for parallel and perpendicular directions. The average susceptibility may be calculated using the relationship

$$\chi = \frac{\chi_{\parallel} + 2\chi_{\perp}}{3}$$

For our study, it is more convenient to calculate the average magnetic moment which is driven from the average susceptibility as

$$\mu = 2.828\cdot\sqrt{\chi\cdot T}$$

The variation of this quantity at room temperature with the distortion and covalency factor are given from Fig. (3) and Fig. (4).

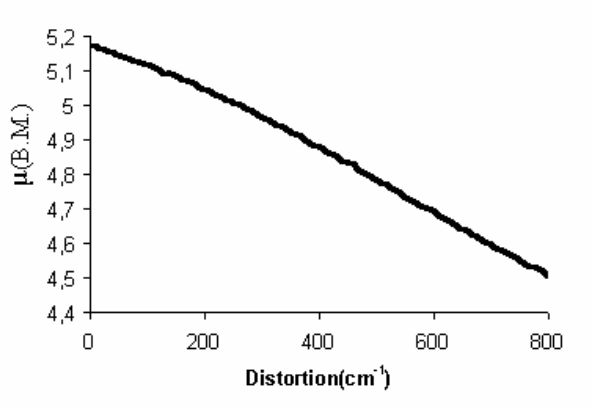

Fig. 3. The room temperature magnetization as a function of distortion.

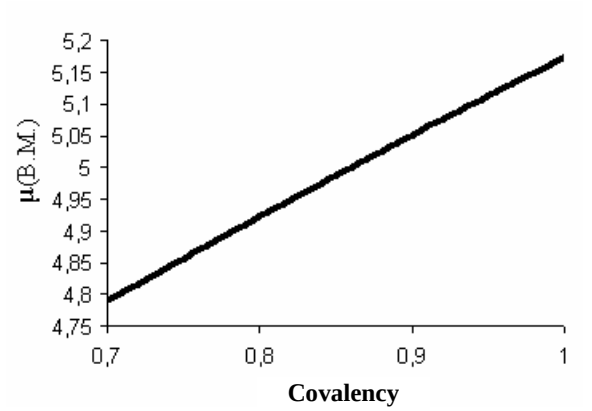

Fig. 4. The room temperature magnetization as a function of orbital reduction factor.

4. Results and discussions

The problem is analyzed in three different approaches. In the first case, it is assumed that the environment is nearly a perfect octahedral and the covalancy is 1. In this approximation it is found that the value 4.81 B.M. is obtained at the field strength 1.124. The reported crystal field strength for octahedral Co(II) complexes generally lie between 1.4-1.5. This value for field strength seems to be too high. We also analyzed the covalancy effect in the low field case (A=1.5). For this case the room temperature value is obtained when the covalency (probably the orbital reduction factor should be used instead of covalency here because in such complex κ takes into account both the covalence of Co-Ligand bonds and the admixture of $^4T_{1g}(P)$ excited state into $^4T_{1g}$ ground term) factor is 0.75. Since the reported values are around 1-0.9, this value seems to be inappropriate for a bivalent cobalt complex. As it is expected, when the field strength is changed, the orbital reduction factor may be changed as well, so one should consider both orbital reduction and field strength effects together. In the final approach it is assumed that the systems are a bit tetragonally distorted. In this approach, it is found that the observed magnetic moments are obtained when the distortion is 420 cm^{-1} as shown in Fig(3). All these results indicate that this complex is an octahedral and the distortion is around 420 cm^{-1}. The experimentally analyzed geometry done by Raman et al. [9] is well supported with this theoretical approach. May be one point should be cleared out here that the possibility of internuclear exchange interactions are not included in the calculations. The reason for this is that we do not have any experimentally published data for different temperatures. That is why this possibility is not considered and the calculations are restricted to a particular temperature.

Comparison with other studies. As mentioned above, our results indicate that the effect of distortion is not very big as expected for many octahedral Co (II) complexes. It is quite obvious that when the effect of the distortion is not very large for a low field octahedral Co (II) complex, the magnetic moment involves some orbital contribution. Of course there are some Co (II) complexes where the effect of distortion is very large such that the magnetic moment involves only spin contribution[23, 24]. But it should be noted here that these complexes are very rare. The derived distortion effect in this study is well inside for the expectations [25,26].

5. Conclusions

In this study the magnetic properties of Co(II) ion in Schiff base ligand **derived from benzyl-2,4-dinitrophenylhydrazone with aniline** are analyzed for various situations. The calculated magnetic moment for various situations suggest that the surrounding of Co(II) ion should be just a bit distorted octahedral and also it seems that the distortion should be around 400 cm^{-1}, if there is no covalency. In this particular study one can easily note that a detailed analysis of magnetic moments may also be used in order to get a deeper understanding of geometry of some metal complexes. But it should be pointed out here that the calculations are performed at room temperature which was the only result we got from the literature for this complex. Of course this point is quite open to the further investigations especially whether or not there are some intermolecular exchange interactions. We wish to see some temperature dependent experimental magnetic data such that we would be able to predict the magnetic behavior a little bit more precisely.

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