

## Theoretical approach to the magnetic properties of Mn(II), Cr(III), and Cu(II) complexes in the newly reported 12- and 15-membered macrocyclic ligands

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**Abstract.** The magnetic properties of Cu<sup>2+</sup>, Cr<sup>3+</sup>, and Mn<sup>2+</sup> ions in the newly reported 12- and 15-membered macrocyclic complexes are analysed by a theoretical approach. The calculated magnetic moment and magnetic anisotropy for various situations, especially for Cu(II) ion, suggest that the magnetic properties may lead to a better interpretation about the geometry. It is also suggested that the zero-field splitting Hamiltonian may be used for magnetic properties of some metal ions, which have orbital singlet ground term in these complexes.

**Keywords.** Magnetization; magnetic susceptibility; spin-orbit coupling; zero-field splitting; macrocyclic complexes; covalency factor.

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### 1. Introduction

Scientists were studying the magnetic properties of the first transition metal complexes in different surroundings for many years [1–8]. The magnetization and hence the magnetic susceptibility is one of the most important properties of matter, which is directly related to its electronic structure [9,10]. In other words, the information about the electronic structure of molecules is contained in its magnetic moment  $\mu$ . The magnetic properties of Mn(II), Cr(II), and Cu(II) ions in 12- and 15-membered macrocyclic ligands are the main part of this study. Metal complexes with macrocyclic ligands have gained an accelerated research interest in recent years [11–19]. Nature prefers macrocyclic derivatives for many fundamental biological functions such as photosynthesis and transport of oxygen in mammalian and other respiratory systems [20]. Metal ion complexes with macrocyclic ligands are significant for the development of new methodologies in separation science also. These ligands are also of theoretical interest as they are capable of furnishing an environment with controlled geometry and ligand field strength [21–24]. The magnetic

properties of these complexes show interesting behaviors depending on the central metal atoms. The observed room temperature magnetic moment of the Cu(II), Cr(III), and Mn(II) ions in 12-membered macrocyclic ligands are 1.98 BM, 3.72 BM, and 5.91 BM and in 15-membered macrocyclic ligands are 1.89 BM, 3.83 BM, and 5.94 BM respectively [7,8]. The common property of these ions from the magnetism point of view is that they do not have first-order orbital contribution to the magnetic moment in this environment. In an octahedral environment the ground term of Mn(II) and Cr(III) is orbital singlet, while of Cu(II) is orbital doublet. It is well-known that the expected magnetic moment of the term  $^{2S+1}\Gamma$  for orbitally singlet and doublet term is spin-only value and temperature independent and hence isotropic. Although there is no first-order orbital contribution to the susceptibility for these three ions, there is second-order contribution due to the coupling between this state and some excited states arising from the same free ion states through the spin-orbit coupling. This effect causes an anisotropy for the  $g$ -factor and zero-field splitting. The zero-field splitting is a property of the ground term  $^{2S+1}\Gamma$  when the spin multiplicity is greater than 2. If this multiplicity is 2 then we can only talk about the anisotropy of the  $g$ -factor. In the three above-mentioned ions, only the Cu(II) ion has spin multiplicity 2, the other two ions have spin multiplicity greater than 2. In this study three ions are considered separately. First, Cu(II) ion is considered in a tetragonally elongated octahedral surrounding since  $g_{\parallel} > g_{\perp}$  [7,8]. Secondly, Cr(III) ion and hence  $^4A_{2g}$  term wave function is analysed in a distorted octahedral environment. And finally Mn(II) ion, which has a ground term wave function  $^6A_{1g}$  in an octahedral surrounding, is analysed. All the calculated results are compared with experimental results.

## 2. The magnetic behavior of $^2E_g$ in axially symmetric crystal fields

Cu(II) is a  $d^9$  or one hole ion system. The ground term of Cu(II) ion in an octahedral environment is  $^2E_g$ . But it is well-known that a perfect octahedral complex is unlikely, except at very low temperatures. So it is almost certain that the octahedral symmetry does not exist at room temperature, and the symmetry would be lowered. As is well-known from the elementary level of quantum mechanics, one of the most important effects of lowering the symmetry from the cubic is to remove some of the degeneracy of triplet ground terms, which leads to a reduction of the orbital contribution to the magnetic susceptibility which therefore tends towards the spin-only value. However, there is no orbital contribution to the susceptibility directly from the  $E$  term [9,10,25,26]. The susceptibility to a first approximation must still be the spin-only value. On the other hand, the excited terms generally are mixed with the ground term, which not only makes the susceptibility different from the spin-only value but also makes it anisotropic. This anisotropy is related to the energy separation of the ground and excited energy levels. Before discussing the magnetic properties of  $^2E_g$  term in an axially symmetric crystal field, it should be useful to give some explanation about the reasons for the mixing between the ground and excited terms. This mixing is caused by two different mechanisms. One of them is that, if any of the excited terms transform in the same way as the ground term in the point group of the molecule, then the crystal field will cause mixing between the ground and excited term wave functions [9,10,25,26]. The second one

is that, spin-orbit coupling may cause mixing between excited and ground term wave functions. Both mixings are inversely proportional to the energy separation between the terms being mixed. The magnetic anisotropy is a true reflection of the magnitude of relative splitting of the ground and excited levels. We will not discuss all the possible distortions in this study. Using the results of EPR spectroscopy carried out by Chandra and Sharma [7] and Chandra and Gupta [8], it seems that the appropriate distortion is a tetragonal elongation for 12- and 15-membered Cu complex, since  $g_{\parallel} > g_{\perp}$ . The most likely energy diagram for this situation is given in figure 1 (please see <http://www.ias.ac.in/pramana/v69/p306a>).

For this situation it is not difficult to derive the ground state wave function as [10,25]

$$|x^2 - y^2, \pm \frac{1}{2}\rangle = |d_{x^2-y^2}, \pm \frac{1}{2}\rangle \mp \frac{\lambda}{2\Delta_3} |d_{xz}, \mp \frac{1}{2}\rangle + \frac{i\lambda}{2\Delta_3} |d_{yz}, \mp \frac{1}{2}\rangle + \frac{i\lambda}{2\Delta_2} |d_{xy}, \pm \frac{1}{2}\rangle.$$

Once finding corrected wave functions for each of the ground state components, it is not difficult to calculate first- and second-order Zeeman perturbation coefficients. Ignoring the terms in  $(\lambda/\Delta)^2$ , one can find the spectroscopic splitting factors for parallel and perpendicular directions as [10]

$$g_z = 2 \left( 1 - \frac{4\lambda\kappa_z}{\Delta_2} \right), \quad g_x = 2 \left( 1 - \frac{\kappa_x\lambda}{\Delta_3} \right) \quad \text{and for the susceptibilities}$$

$$\chi_z = \frac{N\beta^2}{3kT} 3 \left( 1 - \frac{4\lambda\kappa_z}{\Delta_2} \right)^2 + \frac{8N\beta^2\kappa_z^2}{\Delta_2} \quad \text{and} \quad \chi_x = \frac{N\beta^2}{3kT} 3 \left( 1 - \frac{\kappa_x\lambda}{\Delta_3} \right)^2 + \frac{2N\beta^2\kappa_x^2}{\Delta_3}.$$

Here the last terms in both equations are the temperature-independent terms. It is easily seen from the above equations that the magnetic properties are anisotropic. The electronic spectrum of the 12-membered complex shows a band at  $14085 \text{ cm}^{-1}$  and a well-defined shoulder at  $16000 \text{ cm}^{-1}$  and the electronic spectrum of the 15-membered complex shows a band at  $9671, 16077, \text{ and } 31446 \text{ cm}^{-1}$  respectively [7,8]. These transitions were assigned for 12-membered complex to the  ${}^2B_{1g}$  to  ${}^2A_{1g}$  and  ${}^2B_{1g}$  to  ${}^2E_g$  transitions and for 15-membered complex to the  ${}^2B_{1g}$  to  ${}^2A_{1g}$ ,  ${}^2B_{1g}$  to  ${}^2B_{2g}$ , and  ${}^2B_{1g}$  to  ${}^2E_g$  respectively [7,8]. Using these spectroscopic evidences and the results of the EPR spectroscopy, one can easily calculate the amount of covalency for perpendicular direction which is around 0.77 for 12-membered complex. Using the same amount of covalency for the parallel direction one can easily note that there should be another transition around  $14222 \text{ cm}^{-1}$ . So it seems the band at  $14085 \text{ cm}^{-1}$  should be assigned to the  ${}^2B_{1g}$  to  ${}^2B_{2g}$ , not to  ${}^2A_{1g}$ . Using the same argument for 15-membered complex one can easily note that using free ion spin-orbit coupling constant the amount of covalency should be greater than 1 for the band at  $31446 \text{ cm}^{-1}$ , which indicates that this band should be a charge transfer band. So we use the band at  $16077$  for  ${}^2B_{1g}$  to  ${}^2E_g$ . In this case we found that the covalency of perpendicular direction is around 0.61. Using the same amount of covalency for parallel direction we realize that the above assignment for 15-membered complex is not relevant for anisotropic splitting factors. From this particular calculation it is obvious that the magnetic properties may lead to a better interpretation about the geometry.

### 3. The magnetic behavior of ${}^4A_{2g}$ in axially symmetric crystal fields

As mentioned above, when the ground state has a spin multiplicity greater than 2, its coupling with the excited states through spin-orbit coupling may provoke a splitting of its Zeeman components in a zero applied magnetic field which may also lead to an anisotropy of the magnetic properties. The ground term of a Cr(II) ion in an octahedral surrounding is  ${}^4A_{2g}$ . In other words it is an orbital singlet. For the magnetic properties with an orbital singlet, the standard procedure is to use a non-degenerate perturbation theory in which the  $\mathbf{S}$  operators are simply non-commuting operators [26]. In such a case the second-order corrections take the form [26]

$$\sum_n \frac{|\langle 0 | \lambda \vec{L} \cdot \vec{S} + \beta \vec{H} \cdot (\vec{L} + 2\vec{S}) | n \rangle|^2}{E_0 - E_n},$$

where  $|0\rangle$  is the ground orbital state with energy  $E_0$  and  $|n\rangle$  ranges over the excited orbital states, which have energies  $E_n$ . Using the idea of spin Hamiltonian method which is firstly introduced by Pryce [27] and developed by Abragam and Pryce [28], one can arrive at a phenomenological zero-field splitting Hamiltonian as [10,26]  $H_{ZFS} = \vec{S} \cdot \vec{D} \cdot \vec{S}$ , where  $\vec{D}$  is a symmetric and traceless tensor. In matrix notation the total spin Hamiltonian taking into account the Zeeman perturbation is then [10,26],  $H = \beta \vec{S} \cdot \vec{g} \cdot \vec{H} + \vec{S} \cdot \vec{D} \cdot \vec{S}$ . Assuming that the  $\vec{D}$  and  $\vec{g}$  tensors have the same principle axis, this equation may be rewritten as [10,26]

$$H = g_u \beta S_u H_u + D \left[ S_z^2 - \frac{S(S+1)}{3} \right] + E(S_x^2 - S_y^2),$$

where the index  $u$  denotes the direction of the applied field.  $D$  and  $E$  are the axial and rhombic zero-field splitting parameters, which are related to the principle values  $D_{uu}$  ( $u = x, y, z$ ) of the  $\vec{D}$  tensor through [10,26]  $D = 3D_{zz}/2$  and  $E = |D_{xx} - D_{yy}|/2$ .

In axially distorted surroundings obviously the rhombic parameter  $E$  is zero. For the Cr(III) ion in tetragonally distorted surroundings, in zero applied field, the  ${}^4A_2$  ground state is split into two Kramer's doublets. Using this zero-field splitting Hamiltonian, one can easily find the parallel and perpendicular susceptibilities, which is given as [10]

$$\chi_z = \left( \frac{N g_z^2 \beta^2}{4kT} \right) \frac{1 + 9 \exp(-2D/kT)}{1 + \exp(-2D/kT)}$$

and

$$\chi_x = \left( \frac{N g_x^2 \beta^2}{kT} \right) \frac{1 + (3kT/4D)[1 - \exp(-2D/kT)]}{1 + \exp(-2D/kT)}.$$

Using these susceptibilities one can define the average susceptibility as  $\chi = (\chi_z + 2\chi_x)/3$  which can be used for average magnetic moment as  $\mu = 2.828 \times \sqrt{\chi \cdot T}$ . The variation of this quantity with temperature for either sign of  $D$  value is shown in figure 2 (please see <http://www.ias.ac.in/pramana/v69/p306a>).

Experimentally reported room temperature magnetic moments of Cr(III) in 12- and 15-membered ligands are 3.72 BM and 3.83 BM respectively [7,8]. It seems that

by this theoretical approach these values can be obtained around  $D = \pm 150 \text{ cm}^{-1}$  for 12-membered complex and around  $D = \pm 22 \text{ cm}^{-1}$ . The value for 12-membered complex is quite far from reality, since the reported value varies from  $10^{-2}$  to a few tens of  $\text{cm}^{-1}$ , but the value for 15-membered complex is well-expected. So one can suggest that the zero-field splitting Hamiltonian, especially for 15-membered complex may be used for magnetic properties of Cr(III) ion in such an environment. But it has to be noted that zero-field splitting works quite well in the low temperature regions. Unfortunately we do not have low temperature data. If we had low temperature data we would be able to be certain about the validity of the analysis and the predicted  $D$  value.

#### 4. The magnetic behavior of ${}^6A_{1g}$ in axially symmetric crystal fields

The same zero-field splitting Hamiltonian may be used in order to analyse the magnetic properties of  ${}^6A_{1g}$  term in a tetragonally distorted octahedral environment. For the Mn(II) ion in tetragonally distorted surroundings, in zero applied field, the  ${}^6A_{1g}$  ground state is split into three Kramer's doublets. Using the zero-field splitting Hamiltonian, the parallel and perpendicular susceptibilities of Mn(II) ion in a tetragonally distorted octahedral surrounding are given somewhere else [10]. Following the same steps as in Cr(III) one can define an average magnetic moment from the average susceptibility. The variation of average magnetic moment with temperature for both signs of  $D$  is shown in figure 3 (please see <http://www.ias.ac.in/pramana/v69/p306a>).

Experimentally reported room temperature magnetic moments of Mn(II) for 12- and 15-membered ligands are 5.92 BM and 5.94 BM respectively [7,8]. It seems that by this theoretical approach these values can be obtained around  $D = \pm 11 \text{ cm}^{-1}$  for 12-membered complex, but we have realized that there is no possible way to get 5.94 BM for 15-membered complex. The value, especially for 12-membered complex is likely to be the relevant value for such a complex. But as we mentioned for the Cr(III) case the zero-field splitting works quite well at the low temperature regions. Same conclusion can be derived for Mn(II) case for the predicted  $D$  value and the validity of the analysis.

#### 5. Conclusions

In this study the magnetic properties of  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Mn}^{2+}$  ions in newly reported 12- and 15-membered macrocyclic complexes are analyzed by a theoretical approach. The calculated magnetic moment and magnetic anisotropy for various situations, especially for Cu(II) ion, suggest that the magnetic properties may lead to a better interpretation about the geometry. It is also realized that zero-field splitting Hamiltonian may be used for magnetic properties of some metal ions, which have orbital singlet ground term in such environments at low enough temperature. From the analysis it is also found that the covalency should be quite different for different complexes. In this particular study one can easily note that a detailed analysis of magnetic moments and magnetic anisotropy may also be used in order to get a deeper understanding of the geometry of some metal complexes. So it is suggested that the magnetic properties together with spectroscopic evidences may

lead not only to a better understanding about the structure of complexes but also a better interpretation about the energy levels splitting.

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