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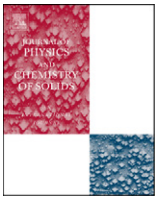

Crystal field and exchange interactions in rare earth transition metal salen compounds containing bipyridine, pyrazole complexes

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ABSTRACT

Crystal field parameters for Pr^{3+} in {[Ni(salen)Pr–$(hfac)_3$](H_2O)} (noted as NiPr) and {[Ni(salen)Pr$(hfac)_3$(pyr)]–($CHCl_3$)} (noted as NiPrpyr) have been found from a fit to the thermal variation in the magnetic susceptibility of NiPr and NiPrpyr. The nature of exchange interaction in [Cu(salen)Pr(hfac)3(pyr)] (noted as CuPrpyr), {[{Cu(salen)Pr$(hfac)_3$}$_2$(pyz)](H_2O)$_3$} (noted as Cu_2Pr_2pyz) and {[{Cu(salen)Pr$(hfac)_3$}$_2$(bpy)]–($CHCl_3$)$_2$} (noted as Cu_2Pr_2bpy, bpy=4,4_-bipyridine) have been found using the derived results for NiPr and NiPrpyr. All the exchange interactions give significant contribution to the thermal variation in magnetic susceptibility below 50 K. The contribution due to Pr–Cu interaction is positive while that of the Cu–Cu and Pr–Pr interactions are negative. The behaviors below 10 K for Pr–Cu and Pr–Pr are difficult to explain, and point to a possible change in structure of CuPrpyr, Cu_2Pr_2pyz and Cu_2Pr_2bpy below 10 K. The theoretical thermal variations in the magnetic specific heat of NiPr and NiPrpyr are computed and discussed.

1. Introduction

During the last two decades, research and development activities in molecular magnetism have received considerable attention [1]. Single molecule magnets (SMM) are a class of molecules exhibiting magnetic properties similar to those observed in conventional bulk magnets, but of molecular origin. When these molecules are magnetized in a magnetic field they show slow relaxation when the magnetic field is removed. These materials possess very high spin state and large magnetic anisotropy. These materials are now known for their potential technological applications [2]. These include information processing, data storage, quantum computing, spintronics, biomedical applications (like MRI contrast agents), magnetic refrigeration, etc. Therefore molecular magnets are often predicted to be the smart magnets of the future. Some of the compounds synthesized with rare earth and transition metals, in which two transition metal ions are present in the terminal positions and are bridged to the central lanthanide ion by oxygen ligands, show SMM behavior at low temperatures. However, it may be pointed out that compounds having similar molecular disposition [3,4], which do not exhibit slow relaxation and very high spin state, are not SMM materials.

Very recently [5], some organo-metallic compounds, {[T(salenR)PrX_3]$_2$(L)}(H_2O)$_n$ (where L=4,4'-bipyridine, pyrazine; n=0,1, T=Ni and Cu; salenR is the Schiff base derived from salicylaldehyde or 2-hydroxy-3-methoxybenzaldehyde and X=NO^{3-}, 1,1,1,5,5,5-hexafluoroacetylacetonate (hfac–) or tetramethylheptanedionate (thd–)), exhibiting SMM behavior at low temperatures have been prepared. Five such compounds, {[Ni(salen)Pr−$(hfac)_3$](H_2O)} (noted as NiPr), {[Ni(salen)Pr$(hfac)_3$(pyr)]−($CHCl_3$)} (noted as NiPrpyr), [Cu(salen)Pr(hfac)3(pyr)] (noted as CuPrpyr), {[{Cu(salen)Pr$(hfac)_3$}$_2$(pyz)](H_2O)$_3$} (noted as Cu_2Pr_2pyz) and {[{Cu(salen)Pr$(hfac)_3$}$_2$(bpy)]–($CHCl_3$)$_2$} (noted as Cu_2Pr_2bpy, bpy=4,4_-bipyridine), were studied for their crystal structures. The average magnetic susceptibilities of these systems have been studied in the temperature range 300–2 K, to find the Cu−Cu and Cu−Pr exchange interactions empirically using a comparative method. No other information regarding the electrical resistivity, magnetic specific heat, nuclear electric quadrupole splitting, etc. are available for the systems till date. Some of the SMM materials are insulators, some are semiconducting and some are conductors. The electrical conductivity measurement for the present systems has not been reported till date. Hence the electrical nature of the samples is not known. In NiPr and NiPrpyr, Ni has been found to be diamagnetic and the magnetic moment is solely due to the Pr^{3+} ion, while in CuPrpyr, Cu_2Pr_2pyz and Cu_2Pr_2bpy, both the crystal field and the exchange interactions are effective. It has been assumed [5] that the presence of Cu in place of Ni does not modify the crystal field around Pr^{3+} and in these Cu based compounds, the rare earth magnetic moment due to the crystal field effect, the magnetic moment of Cu^{2+} and the Pr–Cu exchange interaction together account for the observed magnetic properties. The assumption is not in conformity with earlier studies [6,7], where the crystal fields of rare earth intermetallic compounds with different transition metal ions (Fe, Co, Ni, Cu, etc.) differ considerably. No crystal field analyses have been carried out.

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A systematic study of the crystal-field effect around the Pr^{3+} ions with such ligands could yield the Stark energies and their eigenfunctions in such systems, which besides being helpful in finding the magnetic properties and the specific heat of the systems would provide a better understanding of the exchange interactions between Pr–Pr, Cu–Cu and Pr–Cu can be obtained [5] from such studies. In this context, it is important to study the nature of the crystal field in these systems.

In the present work, the crystal field parameters of NiPr and NiPrpyr have been found from a fit to the observed thermal variation in magnetic properties from 300 to 2 K. The nearly constant value of average magnetic susceptibility of divalent Cu (assumed to be temperature independent [5]) is added to the values calculated for the magnetic susceptibility of NiPrpyr (χ_{NiPrpyr}) at different temperatures. The results are then subtracted from the reported values [5] of the magnetic susceptibility of CuPrpyr (χ_{CuPrpyr}) at different temperatures to find the Pr–Cu exchange contribution to magnetic susceptibility. A comparison with the reported values [5] has been done to test the assumption that the crystal field is not altered due to the substitution of Ni with Cu. Similarly the reported values of the magnetic susceptibility of Cu_2Pr_2pyz ($\chi_{\mathrm{Cu_2Pr_2pyz}}$) and Cu_2Pr_2bpy ($\chi_{\mathrm{Cu_2Pr_2bpy}}$) have been used to find the exchange contribution to the magnetic susceptibility of Cu_2Pr_2pyz and Cu_2Pr_2bpy, respectively. The Stark energy levels, wave functions of the different states of the ground manifold and magnetic heat capacity are evaluated for the NiPr and NiPrpyr compounds. Since the single crystals of these compounds are not stable due to the presence of $CHCl_3$, the measurement of anisotropic magnetic susceptibilities are not possible. The verification of the energy levels and magnetic heat capacity from inelastic neutron scattering and heat capacity measurements, respectively, can be employed to check the proposed crystal fields for all the systems.

2. Crystal structure

The crystal structures of NiPr, CuPrpyr and Cu_2Pr_2bpy are monoclinic and that of NiPrpyr and Cu_2Pr_2pyz are triclinic. So far as the crystal field environment of the Pr^{3+} ion is concerned, the crystal field site symmetry is much higher (D_{3h}) [5]. In NiPr, the Pr^{3+} ion is nine coordinated by oxygen atoms (coming from three bidentate hfac ligands and one water molecule). Hence in NiPr, the Pr^{3+} ion is in a PrO_9 environment. But for the rest of the compounds, the Pr^{3+} ion is in a PrO_8N environment. PrO_9 or PrO_8N has the following structure: the Pr^{3+} ion is surrounded by nine oxygen atoms, six at the corners of a trigonal prism at distances of approximately 0.255 nm and three out of the prism faces at distances close to 0.244 nm. The distorted four capped square antiprism has fourteen triangular faces [8]. All of the Pr–O distances are not equal but range from 0.2437(4) to 0.2624(4) nm. For the PrO_8N structure, the Pr–O salen (0.2585(4) nm) bonds are longer than the Pr–O hfac bonds (0.2479(4) nm). The ninth coordination position is occupied by a nitrogen atom from the pyrazole ligand. The ligand environment around the Pr^{3+}ion is quite similar to $Pr(BrO_3)_3 \cdot 9H_2O$ (PrBr) [9,10], where the far Pr – O distances are 0.252 nm and the near Pr – O distances are 0.249 nm. A comparison of the Pr – O distances is depicted in Table 1. The distances, angles, symmetries (D_{3h}) and geometries (4,4,4-tricapped trigonal prism) of all the compounds involving the metallic ions (Ni^{2+}, Cu^{2+} and Pr^{3+}) are similar [5].

Table 1
Bond lengths in PrBr, NiPr and NiPrpyr.

Compounds	Approximate longer bond distances (nm)	Approximate shorter bond distances (nm)	Approximate Pr–N bond length (nm)	Surrounding complex
PrBr	0.252	0.249	–	$Pr(H_2O)_9^{3+}$
NiPr	0.2545	0.2434	–	$Pr(hfac)_3$
NiPrpyr	0.2585	0.2479	0.2655	$PrNO_8$

3. Methodology

3.1. Crystal field interactions

The nearest neighbor site symmetry for Pr^{3+} in NiPr and NiPrpyr is D_{3h}. The CF Hamiltonian appropriate to the D_{3h} symmetry can be expressed as

$$H_{\mathrm{CF}} = B_{20}C_{20} + B_{40}C_{40} + B_{60}C_{60} + B_{66}(C_{66} + C_{6-6}) \tag{1}$$

where C_{kq} are the tensor operators and B_{kq} are the so-called crystal field parameters (CFP) in the Wybourne convention. The matrix elements of the tensor operators C_{kq} appearing in Eq. (1) are computed using a standard procedure [11] using the relation

$$\langle f^n \alpha SLJJz | C_{kq} | f^n \alpha' S'L'J'Jz' \rangle = (-1)^{J-Jz} \begin{pmatrix} J & k & J' \\ -Jz & q & J'z \end{pmatrix}$$

$$\delta(SS')(-1)^{S'+L'+J+k} \begin{Bmatrix} J & J' & k \\ L' & L & S \end{Bmatrix} \langle f^n \alpha SL | C_{kq} | f^n \alpha' S'L' \rangle ([J,J])^{0.5} \tag{2}$$

The Hamiltonian matrix, set up with the matrix elements and the CF parameters, is diagonalized to obtain the energy eigenvalues and the corresponding eigenfunctions. The first and second order Zeeman energies of the Stark states, W_{njm} (1) and W_{njm} (2), were obtained using the interaction $\beta\mathbf{H}.(\mathbf{L}+2\mathbf{S})$ with the magnetic field parallel and perpendicular to the symmetry axis (*c*-axis). The values of the magnetic susceptibilities along c- and a-axis (χ_c and χ_a, respectively) were finally computed using the well-known susceptibility expression of Van Vleck following the usual procedure [11]. The average magnetic susceptibility is then found out using the relation $\chi_{\mathbf{average}}=(\chi_c+2\chi_a)/3$. The crystal field strength parameter (S) can be calculated using the following relation [12]:

$$S = [(1/3)\Sigma(1/(2k+1)\{B_{ko}^2 + 2\Sigma \mathrm{Re}(B_{km}^2) + \mathrm{Im}(B_{km}^2)\}]^{0.5} \tag{3}$$

3.2. Electronic specific heat

Magnetic contributions to the specific heat (C_s; also called the Schottky specific heat) can be obtained by subtracting the lattice contribution (C_{latt}) from the total specific heat (C_p). At very low temperatures, however, a large variety of contributions such as the phonon contribution to specific heat (C_{ph}), the magnon contribution to specific heat (C_m), conduction electron contribution to the specific heat (C_{el}) and the nuclear contribution (C_N) might be there. So C_s can be evaluated as $C_s = C_p - C_{\mathrm{latt}} - C_{\mathrm{el}} - C_{\mathrm{ph}}) - C_m$. Nuclear contribution ($C_N$) is dominant below 0.5 K and conduction electron contribution within the $0.5\ K < T < 4\ K$ range. C_{el} being very small, C_s, C_{ph} and C_m mainly contributes to the specific heat. In the present work, the thermal variation of magnetic specific heat has been calculated for NiPr and NiPrpyr. Due to the variation in electron population in various low lying Stark levels, electronic specific heat C_s shows its characteristic thermal variation. The variation of C_s with temperature has been computed using the relation

$$C_s = (R/z^2)[z\{\Sigma E_i^2 \exp(-E_i/kT)/k^2T^2\} - \Sigma\{E_i^2 \exp(-E_i/kT)\}^2] \tag{3}$$

where E_i are the energies of different Stark states and $z = \sum \exp(-E_i/kT)$ is the partition function. The anomaly in the specific heat at low temperatures arising out of the phonon, magnon or nuclear effects [13] have not been considered here.