Magnetic Dimer Excitations in Cs3Cr2Cl9 Studied by Neutron Scattering

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The energy dispersion of the singlet-triplet dimer excitation in Cs$_3$Cr$_2$Cl$_9$ has been studied by inelastic neutron scattering (INS) experiments on Cs$_3$Cr$_2$Cl$_9$. The singlet-triplet excitation was found far from ordering magnetically. The systematic variation of the exchange parameters on substitution of Cl by Br and I is discussed.

The antiferromagnetic intradimer exchange leads to a Landé splitting pattern with the singlet dimer state as ground state and the triplet as first excited state. Much effort has been devoted to the question of what conditions a singlet ground-state system can order magnetically. The present study was motivated by the interest in magnetic dimers and in singlet ground-state magnets. The closely related Cs$_3$Cr$_2$Br$_9$ has been studied using INS. The singlet–triplet excitation was found to exhibit pronounced dispersion. It could be accounted for by using three exchange parameters corresponding to the interactions shown in Figure 1, the intradimer exchange $J$ and the interdimer exchange between nearest neighbors $J_p$ (intrasublattice) and $J_I$.

Magnetic Dimer Excitations in Cs$_3$Cr$_2$Cl$_9$ Studied by Neutron Scattering

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The energy dispersion of the singlet–triplet dimer excitation in Cs$_3$Cr$_2$Cl$_9$ has been studied by inelastic neutron scattering (INS) at temperatures down to $1.3 \, \text{K}$. The results can be accounted for by using a completely isotropic Heisenberg Hamiltonian in the random phase approximation (RPA). Only nearest-neighbor interactions need to be considered. From the excellent fit, three exchange parameters were obtained: $J = -1.75 \, \text{meV}$ (intradimer), $J_p = -0.032 \, \text{meV}$ (interdimer, intrasublattice) and $J_I = -0.031 \, \text{meV}$ (interdimer, intersublattice). These values indicate that Cs$_3$Cr$_2$Cl$_9$ is far from ordering magnetically. The systematic variation of the exchange parameters on substitution of Cl by Br and I is discussed.

The antiferromagnetic intradimer exchange leads to a Landé splitting pattern with the singlet dimer state as ground state and the triplet as first excited state. Much effort has been devoted to the question of what conditions a singlet ground-state system can order magnetically. The present study was motivated by the interest in magnetic dimers and in singlet ground-state magnets. The closely related Cs$_3$Cr$_2$Br$_9$ has been studied using INS. The singlet–triplet excitation was found to exhibit pronounced dispersion. It could be accounted for by using three exchange parameters corresponding to the interactions shown in Figure 1, the intradimer exchange $J$ and the interdimer exchange between nearest neighbors $J_p$ (intrasublattice) and $J_I$.

References


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Figure 1. Schematic structure of Cs3Cr2Cl9 indicating the three exchange parameters. The hexagonal lattice constants are $a = 7.14$ Å and $c = 17.72$ Å at 2 K. Only the Cr3+ ions are shown.

(intersublattice). The bromide is slightly undercritical; i.e., the interdimer exchange is almost strong enough to induce magnetic order. The substitution of Br by Cl is expected to increase the intradimer exchange, while the interdimer exchange is likely to decrease and thus reduce the tendency for magnetic order.

Experimental Section

Single crystals of Cs3Cr2Cl9 were grown from stoichiometric mixtures of CsCl and CrCl3 in quartz tubes at 900 °C by using the Bridgman technique. The crystals are fragile, soft, and air sensitive. For the neutron scattering experiments a single crystal of 2 cm³ volume was mounted in an aluminum can under helium gas. All manipulations were performed in a glovebox under dry nitrogen or helium. The mosaic of the crystal was 0.8°.

INS experiments were carried out on the triple-axis spectrometer 4F1, which is located at the cold source of the reactor Orphé, CEN Saclay. A vertically focusing graphite (002) double monochromator was used, and a cooled beryllium filter was placed after the monochromator to eliminate higher order contaminations. The collimations were 60'-open-60/-40'-60' along the path of the neutrons. The wave vector of the incident beam was fixed to 1.55 Å⁻¹, and scans were performed by varying the analyzing energy. The crystal was mounted in a pumped He cryostat with (0, 0, 1) and (1, 1, 0) lying in the scattering plane.

INS scans were obtained in the Γ-A (001) direction and the Γ-K-M (110) direction of the hexagonal lattice. The temperature was 1.3 K for the former and 2.6 K for the latter, but no influence of this temperature change was observed.

Results and Discussion

Transitions between the exchange-split levels of dimers of paramagnetic transition-metal ions can be observed by inelastic neutron scattering. In molecular systems with no or negligible interdimer exchange the excitations show no energy dispersion. This is not true in Cs3Cr2Cl9. Weak interdimer interactions lead to a dispersion of the singlet-triplet dimer excitation. Some selected INS scans of Cs3Cr2Cl9 are shown in Figure 2. Well-defined peaks were observed, and the peak widths are due to the instrumental resolution. The peak positions evidently depend on the scattering vector, a quantity in reciprocal space. Figure 3 show the results of all the measurements.

We can interpret these results by applying a theory developed for Cs3Cr2Br9, which was outlined in detail in ref 8. It will be summarized here. The following isotropic Hamiltonian can be written for Cs3Cr2Cl9:

$$H = -J \sum \mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{2} \sum \eta_q (\mathbf{S}_{i_1} \cdot \mathbf{S}_{j_1} + \mathbf{S}_{i_2} \cdot \mathbf{S}_{j_2})$$

(1)

The double sums are restricted to nearest neighbors. By using the Green function method in the random phase approximation, we obtain two triply degenerate excitations:

$$\omega_{\alpha \beta}(q) = [J^2 + M^2(J_n - n_t)(J_\alpha \gamma_\beta(q) = J_\beta \gamma_\alpha(q))]^{1/2}$$

(2)

$M^2 = 5$ is the square of the singlet–triplet transition matrix ele-

Magnetic Dimer Excitations in Cs₃Cr₂Cl₉

![Image](https://example.com/image.png)

**Figure 4.** MO diagram of Cr₂X₄⁺ obtained from an extended Hückel calculation. Only the relevant 3d part is shown. The point symmetry of the dimer is D₄h.

The relevant part of the MO diagram for the chloride, bromide, and iodide is shown in Figure 4. Included in the figure is a comparison of the observed and calculated intensities. Since analyzer scans were done, the observed integrated intensities were approximately corrected for the instrumental resolution by the factor k₀² cot (θ_a), where k₀ is the final wave vector and θ_a the analyzer angle. The agreement between calculated and observed intensities is good.

If we compare the parameters with those determined for Cs₃Cr₂Br₄, we can compare ratios (chloride/bromide) of 1.706, 0.602, and 0.797 for J_p, J_c, and J_e, respectively. The reduction of the interdimer exchange compared to that for the bromide is related to the decrease of covalency when Br is substituted by Cl. This indicates that the interdimer exchange is due to superexchange pathways of the type Cr-X-X-Cr.

The increase of the interdimer exchange can be explained semiquantitatively within the framework of a simple mode. The antiferromagnetic part of J is related to energy differences of molecular orbitals (MO) of the dimer built from atomic 3d orbitals:

\[ \frac{1}{2} J = \frac{1}{9} \left( \varepsilon_e - \varepsilon_e \right)^2 + \left( \varepsilon_e - \varepsilon_e \right)^2 \]  

(5)

\( \varepsilon_e \) is the MO energy of the orbital of symmetry e, and U is the electron-transfer energy, which is considered to be independent of halogen type. The MO energies were obtained from an extended Hückel calculation. The relevant part of the MO diagram for the chloride, bromide, and iodide is shown in Figure 4. It should be mentioned that this diagram has only semi-quantitative character especially due to the small energy differences involved and the neglect of relativistic effects. Nevertheless, the diagram nicely explains the observed trend. Using the above formula, we obtain the ratio \( J^C(J^B) = 1.8 \), which, somewhat fortuitously, is in excellent agreement with the observed ratio of 1.71. From Figure 4 it is evident that the interdimer exchange for the iodide is expected to be smaller than for the bromide, indicating that the ferromagnetic part of J, neglected in this discussion, could become important.

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The ratio \( J_p/J_c \), which is 1.3, for the bromide, is reduced to 1.05 for the chloride. As a consequence the minimum of the acoustic mode becomes more flat and less pronounced compared with that of the bromide and the M point is nearly a minimum point for the chloride, as can be seen from Figure 5. The change of this ratio must be related to small changes of the superexchange pathways. Neglecting the influence of the Cs⁺ ions, we have to consider two exchange pathways for each of the interdimer interactions \( J_p^e \) and \( J_c^e \). Relevant Cr-X-X angles as well as Cr-X-X distances as well as Cr-X-X angles are listed in Table I. The low-temperature structural information of the chloride and the bromide were determined by neutron diffraction. For the iodide the lattice constants were obtained from a powder X-ray pattern and the scaled atomic positions of the bromide were used. No detailed structural information on the iodide is available at present. Therefore, this discussion contains some uncertainty as far as the iodide is concerned. It is interesting to note that all Cr-X-X angles in Table I are similar. In order to relate the X-X distances to exchange interactions, we subtract twice the x ionic radii and thus obtain the "covalent part" of the X-X distance. This can then be used to predict the trend of the \( J_p/J_c \) ratio. Using ionic radii (Goldschmidt) of 1.81, 1.96, and 2.20 Å for Cl⁻, Br⁻, and I⁻, respectively, and taking, for simplicity, the average X-X distance for a given interaction, we obtain the values listed in Table I. It is evident from these numbers that an increase of the \( J_p/J_c \) ratio is expected in the series chlorides, bromide, iodide. This is in good agreement with the experimental values of 1.05 for the chloride and 1.39 for the bromide.

As a measure of the tendency for magnetic order in singlet ground-state systems, one often uses the ratio:

\[ \frac{M^2 J^*}{J} \]

where \( J^* = J_p \delta_p(\delta_0) - J_c \delta_c(\delta_0) \) at the minimum point \( \delta_0 \) of the

(16) Fischer, P., unpublished results.
Visible Absorption Spectral Studies of Molybdenum(V) Tetraphenylporphyrins in Organic Solvents

TAIRA IMAMURA,* TETSUYA TANAKA, and MASATOSHI FUJIMOTO*

Received April 18, 1984

Visible absorption spectra of molybdenum(V) tetraphenylporphyrin complexes, MoO(TPP)X (X = F, Cl, Br, NCS; TPP = meso-tetraphenylporphinoato), in organic solvents and the substitution reactions of these complexes with dimethyl sulfoxide (Me2SO) are discussed. The measurements of molecular weight revealed that these complexes exist as monomers in dichloromethane. Organic solvents used are classified as noncoordinating and coordinating solvents for these complexes. The shift of the main absorption bands, Soret, α, and β bands, of MoO(TPP)X in the noncoordinating solvents correlates with the function of refractive index, (n² - 1)/(2n² + 1). The axial ligand X of these complexes is substituted by Me2SO to form [MoO(TPP)Me2SO]⁺X⁻ as an intermediate. The values of the formation constants of [MoO(TPP)+Me2SO]⁺X⁻ are in the order X = F < Cl < Br < NCS. The oxidation of MoO(TPP) with Me2SO gives a red complex MoO(TPP)Me2SO via the solvated complex [MoO(TPP)X]⁺Me2SO⁻ as an intermediate. The accuracy and reproducibility of the measurements of molecular weight revealed that these complexes exist as monomers in dichloromethane. The present paper reports the studies of the visible absorption spectra of six-coordinated complexes MoO(TPP)X in various organic solvents and the substitution reactions of MoO(TPP)X with Me2SO.

Introduction

The reactions of molybdenum porphyrins in organic solvents are susceptible to influence from the impurities in solvents, air, and light. The complex MoO(TPP)Cl2 is formed immediately from MoO(TPP)X (X = F, Cl, Br, NCS) in dichloromethane containing a trace amount of methanol and reduced photochemically to MoO(TPP). The oxidation of MoO(TPP) affords Mo(V) porphyrin complexes in the presence of anions or some impurities in organic solvents. In the γ-radiolytic reaction of MoO(TPP)X and the reaction of MoO(TPP)X with superoxide,1,4 solvents also play a very important role. Therefore, we necessitated the study of the behavior of MoO(TPP)X, in organic solvents.

There are many reports referring to the solvent effects on the behavior of metalloporphyrins in organic solvents.1–5 However, the subjects of these studies are almost four-coordinated and compared to the bromide. We are currently investigating chemical and physical properties of the iodide.

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Registry No. Cs2Cr3Cl6, 21007-54-5.

Visible absorption spectra were recorded with a Hitachi 808 spectrophotometer equipped with double-beam double mono-andrometer at 25 ± 0.5 °C. The accuracy and reproducibility of the spectrophotometer are ±0.5 and ±0.2 nm, respectively. ESR spectra were recorded with a JEOL JES-FEXI spectrometer at 25 ± 2 °C. The molecular weight of MoO(TPP)X in dichloromethane was measured

Table I. Molecular Weight of MoO(TPP)X in Dichloromethane at 31 °C

<table>
<thead>
<tr>
<th>complex</th>
<th>mol wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO(TPP)F</td>
<td>743.73</td>
</tr>
<tr>
<td>MoO(TPP)Cl</td>
<td>760.18</td>
</tr>
<tr>
<td>MoO(TPP)Br</td>
<td>804.63</td>
</tr>
<tr>
<td>MoO(TPP)NCS</td>
<td>782.73</td>
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</tbody>
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