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Published in:
Inorganic Chemistry

Link to article, DOI:
10.1021/ic00201a015

Publication date:
1985

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):

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Magnetic Dimer Excitations in Cs₃Cr₂Cl₉ Studied by Neutron Scattering

BRUNO LEUENBERGER,* HANS U. GÜDEL,** JORGEN K. KJEMS,* and DANIEL PETITGRAND†

Received June 26, 1984

The energy dispersion of the singlet–triplet dimer excitation in Cs₃Cr₂Cl₉ has been studied by inelastic neutron scattering (INS) at temperatures down to 1.3 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: Jₜ = −0.75 meV (intradimer), Jᵢ = −0.032 meV (interdimer, intrasublattice) and Jᵢ = −0.031 meV (interdimer, intersublattice). These values indicate that Cs₃Cr₂Cl₉ is far from ordering magnetically. The systematic variation of the exchange parameters on substitution of Cl by Br and I is discussed.

Introduction

Cs₃Cr₂Cl₉ exemplifies a family of compounds in which the magnetic ions occur as dimeric complexes, Cr₂Cl₉. The space group is hexagonal, P6₃/mmc and there are two dimers per unit cell forming two sublattices. A schematic structure is shown in Figure 1, indicating the two sublattices and the three exchange parameters. The Cr–Cr separation is 3.2 Å within the dimers and 7.2 Å (intrasublattice) and 7.1 Å (intersublattice) between nearest-neighbor dimers. There are Cr–Cl–Cl–Cr contacts between the dimers, providing pathways for weak interdimer interaction. The low-temperature magnetic and spectroscopic properties have so far been interpreted as resulting from isolated antiferromagnetically coupled dimers. EPR spectra at elevated temperatures, where the first excited dimer level becomes populated, showed some evidence for interdimer exchange. Previous inelastic neutron scattering (INS) experiments on Cs₃Cr₂Cl₉ indicated some interdimer interactions even at 1.8 K, where the dimer triplet population is negligible. But the data in ref 6 were ambiguous due to the bad quality of the crystal. Here we report INS results on a high-quality crystal.

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 under 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 Cs₃Cr₂Br₉ has recently been studied by 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 Jₜ and the interdimer exchange between nearest neighbors Jᵢ (intrasublattice) and Jᵢ.

Contributed by the Institut für anorganische Chemie, Universität Bern, CH-3000 Bern 9, Switzerland, and Laboratoire Léon Brillouin, CEN Saclay, F-91911 Gif-Sur-Yvette, France

0020-1669/85/1324-1035$01.50/0 © 1985 American Chemical Society
Figure 1. Schematic structure of Cs₃Cr₂Cl₉ indicating the three exchange parameters. The hexagonal lattice constants are \( a = 7.14 \text{ Å} \) and \( c = 17.72 \text{ Å} \) at 2 K. Only the Cr³⁺ ions are shown.

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 Orphée, CEN Saclay. A vertically focusing graphite (0, 0, 2) double monochromator was used, and a cooled beryllium filter was placed after the monochromator to eliminate higher order contaminations. The collimations were 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 analyzer 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 \( \Gamma \text{-A (001)} \) direction and the \( \Gamma \text{-K-M (110)} \) 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 5 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:

\[
\mathcal{H} = -J \sum_{i} \hat{S}_{i} \cdot \hat{S}_{i+1} - \frac{1}{2} \sum_{q} \left( \hat{S}_{i} \cdot \hat{S}_{i+1} + \hat{S}_{i} \cdot \hat{S}_{i+1} \right) - \frac{1}{2} \sum_{q} \left( \hat{S}_{i+1} \cdot \hat{S}_{i+2} + \hat{S}_{i} \cdot \hat{S}_{i} \right) \tag{1}
\]

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:

\[
\omega_{\text{acoustic}}(q) = |J| + M^2 J (n_0 - n_1) \langle J_0 | J_0 \rangle = J (n_1 \gamma_1(q)) \tag{2}
\]

\[M^2 = 5\] is the square of the singlet–triplet transition matrix element. The minus and plus signs correspond to the acoustic and optic modes, respectively. The singlet and triplet dimer states are populated according to the Boltzmann population factors \( n_0 \) and \( n_1 \). \( \gamma_1(q) \) and \( \gamma_1(q) \) are the Fourier sums over nearest-neighbor dimers within and between the sublattices. For the scattering law we obtain:

\[
\frac{d^2 \sigma}{d\Omega d\omega} = F^2(q) \left( 1 - e^{-\omega/kT} \right) \left( n_0 - n_1 \right) \langle -J \rangle \times \left( 1 - \cos (\vec{p} \cdot \vec{R}) \right) \left( 1 + \cos (\vec{p} \cdot \vec{R} + \phi) \right) \left( 1 - \cos (\vec{p} \cdot \vec{R} + \phi) \right) \right) \frac{1}{\omega^2(q)} \left( \delta \omega - \omega \right) + \left( 1 - \cos (\vec{p} \cdot \vec{R} + \phi) \right) \frac{1}{\omega^2(q)} \left( \delta \omega - \omega \right) \right) \tag{3}
\]
The excellent fit is shown in Figure 3. 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 k_p cot θ_0, where k_p is the final wave vector and θ_0 the analyzer angle. The agreement between calculated and observed intensities is good.

If we compare the parameters with those determined for Cs_2CrI_3, we obtain 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 intradimer exchange can be explained semiquantitatively within the framework of a simple model. The antiferromagnetic part of J is related to energy differences of molecular orbitals (MO) of the dimer built from atomic 3d orbitals:

\[ \frac{1}{2} J = -\frac{1}{9} U \left\{ (\epsilon_i - \epsilon_e)^2 + (\epsilon_e - \epsilon_{ex})^2 \right\} \]

\[ J = -1.75 \text{ (1 meV)} \quad J_p = -0.032 \text{ (1 meV)} \]

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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, MoV(TPP)X (X = F, Cl, Br, NCS; TPP = meso-tetraphenylporphinato), 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 MoV(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 [MoV(TPP)-Me2SO]X in Me2SO-CH2Cl2 via the solvated complex [MoV(TPP)X] as an intermediate. The values of the formation constants of [MoV(TPP)-Me2SO]X in the order X = F < NCS = Cl < Br.

Introduction

The reactions of molybdenum porphyrins in organic solvents are susceptible to influence from the impurities in solvents, air, and light. The complex MoV(TPP)CH3 is formed immediately from MoV(TPP)X (X = F, Cl, Br, NCS) in dichloromethane containing a trace amount of methanol and reduced photochemically to MoV(TPP). The oxidation of MoV(TPP) affords Mo(V) porphyrin complexes in the presence of anions or some impurities in organic solvents. In the γ-ray radiolytic reaction of MoV(TPP)X and the reaction of MoV(TPP)X with supersoxode,1 four solvents also play a very important role. Therefore, we necessitated the study of the behavior of MoV(TPP)X, in organic solvents.

There are many reports referring to the solvent effects on the behavior of metalloporphyrins in organic solvents. 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.

Acknowledgment. This work was supported, in part, by the Swiss National Science Foundation and a NATO Senior Scientist Exchange Program.

Registry No. Cs3Cr2Cl9, 21007-54-5.

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

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

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

Materials. Dichloromethane, distilled, passed twice through a column of basic alumina, and dried over 4A molecular sieves overnight, was redistilled under Ar immediately before use. The purity of dichloromethane was checked spectrophotometrically by dissolving MoV(TPP)HBr. When the dichloromethane contains a trace of impurities such as alcohols, Cl⁻, and some decomposed species as CHCl₃, the visible absorption spectra are changed by the formation of MoV(TPP)Cl or MoV(TPP)OR. Dimethyl sulfoxide was kept with calcium hydride and stored under an Ar atmosphere. Other solvents were also carefully purified by usual methods. The complex MoV(O(TPP)X) was synthesized by the method reported previously.15

Measurement. Visible absorption spectra were recorded with a Hitachi 808 spectrophotometer equipped with double-beam double monochromators 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-FEIX spectrometer at 25 ± 2 °C. The molecular weight of MoV(O(TPP)X) in dichloromethane was measured.