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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

Citation (APA):

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Magnetic Dimer Excitations in Cs₃Cr₂Cl₈ Studied by Neutron Scattering

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Received June 26, 1984

The energy dispersion of the singlet–triplet dimer excitation in Cs₃Cr₂Cl₈ 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 second-order rate constants (25 °C) for the reaction of OH⁻ with \( \text{NH}_4^+ \) (pKₐ 12.4) have been reported as 3.4 \times 10^{10} \text{ M}^{-1} \text{s}^{-1} \) and \( \text{Ru(NH}_3)_6^{3+} \) (pKₜ = 12.4) have been reported as 3.4 \times 10^{10} \text{ M}^{-1} \text{s}^{-1} \), respectively. The hexammineruthenium(III) ion offers as especially interesting comparison, given the analogy between this ion’s \( (t_2g)^3 (e_g)^1 \) configuration and the \( (t_2g)^3 (e_g)^1 \) configuration of the LF state of the hexaammineruthenium(III) ion.

In summary, measurement of the excited-state emission lifetimes of \( \text{Rh(NH}_3)_6^{3+} \) and \( \text{Rh(ND}_3)_6^{3+} \) in solution supports the conclusion that deuterium effects on photoreaction quantum yields can be attributed to perturbations of the nonradiative deactivation rates. Dynamic quenching of both photoaquation and photoemission by hydroxide further supports the view that both processes originate from the same state or an ensemble of equilibrated states. Lastly, the kinetic isotope effect of 1.5 seen in the \( k_q \) values supports the suggestion of reactive quenching by excited-state proton transfer from coordinated ammine.

Acknowledgement. This research was supported by a grant from the National Science Foundation to P.C.F. The rhodium used in these studies was provided on loan from Johnson Matthey, Inc.

Registry No. Rh(NH₃)₆³⁺, 16786-63-3; D₂, 7782-39-0.

Introduction

Cs₃Cr₂Cl₈ exemplifies a family of compounds in which the magnetic ions occur as dimeric complexes, \( \text{Cr}_2\text{Cl}_8 \). The space group is hexagonal, \( P6_3/mmc \), 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 interactions. 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 Cs₃Cr₂Cl₈ 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 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 a similar one reported for the quenching of \( \text{Rh(NH}_3)_6^{3+} \) and \( \text{Rh(ND}_3)_6^{3+} \) in solution supports the conformation of \( \text{Rh(NH}_3)_6^2+ \) and \( \text{Rh(ND}_3)_6^2+ \) ion with \( \text{OH}^- \) by using 4.4 Å as the distance of closest approach implies that the ammines of the excited-state complex are significantly more acidic than those of the ground-state complex (pKₛ > 14). For comparison, the agreement was completely quenched.

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 Cr$^{3+}$ 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 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 60'-open-60/-40'-60' along the path of the neutrons. The wave vector of the incident beam was fixed to $1.55 \text{ Å}^{-1}$, 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 $\Gamma$-A (001) direction and the $\Gamma$-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 CsJCr₂Br₉, which was outlined in detail in ref 8. It will be summarized here. The following isotropic Hamiltonian can be written for Cs₃Cr₂Cl₉:

$$\mathcal{H} = -J \sum_{i} \mathbf{S}_{i} \cdot \mathbf{S}_{i+1} - \frac{1}{2} J' \sum_{\langle ij \rangle} \left( \mathbf{S}_{i} \cdot \mathbf{S}_{j} + \mathbf{S}_{i+1} \cdot \mathbf{S}_{j+1} \right) - \frac{1}{2} J'' \sum_{\langle ij \rangle} \left( \mathbf{S}_{i} \cdot \mathbf{S}_{j+1} + \mathbf{S}_{i+1} \cdot \mathbf{S}_{j} \right)$$

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:

$$\omega_{\sigma}(\mathbf{q}) = \sqrt{J^2 + M^2 J(n_0 - n_i)(J \gamma_{\sigma}(\mathbf{q}) = J \gamma_{\sigma}(\mathbf{q}))^{1/2}}$$

$$M^2 = 5$$

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 $n_i$. $\gamma_{\sigma}(\mathbf{q})$ and $\gamma_{\sigma}(\mathbf{q})$ are the Fourier sums over nearest-neighbor dimers within and between the sublattices. For the scattering law we obtain

$$d^2 \sigma(\tilde{q}, \omega) = F^2(\tilde{q}) \left( 1 - e^{i \omega/\hbar} \right)^{-1} (n_0 - n_i) (-J) \times$$

$$\int d\Omega d\omega \left\{ (1 + \cos (\tilde{q} \cdot \tilde{R})) \left( 1 + \cos (\tilde{q} \cdot \tilde{R} + \phi) \right) \delta(\omega - \omega^p(\mathbf{q})) + \right.$$

$$\left. (1 - \cos (\tilde{q} \cdot \tilde{R} + \phi)) \delta(\omega - \omega^{ap}(\mathbf{q})) \right\}$$

(3)
The antiferromagnetic part of $J$ is related to energy differences
that the diagram nicely explains the observed trend. Using the above
ences involved and the neglect of relativistic effects. Nevertheless,
tended Hückel calculation.~\(^{(15)}\) The relevant part of the MO
pathways of the type Cr-X-X-Cr.

The increase of the intradimer exchange can be explained
semiquantitatively within the framework of a simple mode.~\(^{(11,12)}\)
The antiferromagnetic part of $J$ is related to energy differences
of molecular orbitals (MO) of the dimer built from atomic 3d
orbitals:~\(^{(13)}\)

$$\frac{1}{2}J = \frac{1}{9}U \left\{ (\epsilon_a^e - \epsilon_b^e)^2 + (\epsilon_a^o - \epsilon_b^o)^2 \right\}$$

(5)

$\epsilon_i$ is the MO energy of the orbital of symmetry $i$, and $U$ is
the electron-transfer energy, which is considered to be independent
of halogen type. The MO energies were obtained from an exten-
sed Hückel calculation.~\(^{(14,15)}\) 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-
quantiative 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 $J_{Cl}/J_{Br} = 1.8$, which, somewhat fortuitously,
is in excellent agreement with the observed ratio of 1.71. From Figure 4 it is evident that the intradimer exchange

$$J = -1.75 \text{ meV} \quad J_p = -0.032 \text{ meV} \quad J_c = -0.031 \text{ meV}$$

(4)

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
analyzer angle. The agreement between calculated and observed
intensities is good.

If we compare the parameters~\(^{4}\) with those determined for
Cs$_2$Cr$_2$Br$_4$~\(^{(4)}\) we obtain ratios (chloride/bromide) of 1.706, 0.602,
and 0.797 for $J$, $J_p$, and $J_c$, respectively. The reduction of the
intradimer 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 change of the intradimer exchange can be explained
semiquantitatively within the framework of a simple mode.~\(^{(11,12)}\)

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 in-
teractions $J_p$ and $J_c$. Relevant Cr-X-X distances as well as
Cr-X--X angles are listed in Table I. The low-temperature
structure parameters for the chloride and the bromide were
determined by neutron diffraction.~\(^{(16)}\) 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 chloride, 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~\(^{(9)}\)

$$\frac{M^2J^*}{J}$$

where $J^* = J_p \delta_p(\bar{q}_0) - J_c \delta_c(\bar{q}_0)$ at the minimum point $\bar{q}_0$ of the

\(^{(14)}\) Howell, J.; Rossi, A.; Wallace, D.; Haraki, K.; Hoffmann, R. QCPE
1977, 5, 344.

F($\vec{q}$) is the square of the form factor of Cr$^{3+}$, $\vec{r}$ is the
scattering vector, $\vec{q}$ a reciprocal lattice vector, $\vec{p}$ a vector
connecting the two sublattices, and $R$ connects the two Cr$^{3+}$ ions in
a dimer. The Fourier sum $\gamma_3(\vec{q})$ is complex, and its phase is
denoted by $\phi$. On the basis of the factors ($1 \pm \cos(2\vec{r} + \delta)$)
we are able to distinguish acoustic and optic modes in our neutron
spectra. From a least-squares fit to the observed energy dispersion
we obtain the three exchange parameters

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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\(^{(16)}\) 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-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 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 < Me2SO. Five-coordinated metalloporphyrins with vacant sites at axial position. 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)CH3 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)2. 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)X3 and the reaction of MoO(TPP)X with superoxide,4,5 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.5,15 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.

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

<table>
<thead>
<tr>
<th>complex</th>
<th>calc</th>
<th>obsd</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO(TPP)F</td>
<td>743.73</td>
<td>759 ± 17</td>
</tr>
<tr>
<td>MoO(TPPCl)</td>
<td>760.18</td>
<td>771 ± 12</td>
</tr>
<tr>
<td>MoO(TPPIbr)</td>
<td>804.63</td>
<td>793 ± 14</td>
</tr>
<tr>
<td>MoO(TPP)NCs</td>
<td>782.73</td>
<td>770 ± 14</td>
</tr>
</tbody>
</table>

Five-coordinated metalloporphyrins with vacant sites at axial position. 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.

Experimental Section

Materials. Dichloromethane, distilled, passed twice through a column of basic alumina, and dried over 4A molecular sieves overnight, was distilled under Ar immediately before use. The purity of dichloromethane was checked spectrophotometrically by dissolving MoO(TPP)Br. 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 MoO(TPP)Cl or MoO(TPP)OR.6 Dimethyl sulfoxide was kept with calcium hydride under reduced pressure, and stored under an Ar atmosphere. Other solvents were also carefully purified by usual methods. The complex MoO(TPP)X was synthesized by the method reported previously.16

Measurements. 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 MoO(TPP)X in dichloromethane was measured.

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

Registry No. Cs2Cr2Br9, 21007-54-5.

Contribution from the Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan
