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Concealed Asymmetry in an Exchange-Coupled Trichromium(III) Cluster: Structure and Magnetic Spectrum of $[Cr_3O(OOCPh)_6(py)_3](py)_{0.5}ClO_4$

**Roderick D. Cannon,[*,†] Upali A. Jayasooriya,[†]
Frank E. Sowrey,[†] Claire Tilford,[†] Alastair Little,[†]
John P. Bourke,[†] Robin D. Rogers,[‡]
John B. Vincent,[*,‡] and Gordon J. Kearley[§]**

School of Chemical Sciences, University of East Anglia,
Norwich NR4 7TJ, UK, Department of Chemistry, The
University of Alabama, Tuscaloosa, Alabama 35487-0336,
and Institut Laue-Langevin, BP 156, 38042, Grenoble,
France

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Introduction

Trinuclear oxo-centered metal complexes of the general type $[M_3O(OOCR)_6L_3]$ have been of great interest as systems to test current theories of magnetic and electronic coupling between metal atoms. A feature that has attracted attention is that when the three metal atoms are identical, and of the same oxidation state, the complex nearly always fails to adopt the 3-fold symmetry that might be expected. The most studied case is that of the acetate-bridged trichromium(III) complex, in the chloride salt $[Cr_3O(OOCMe)_6(aq)_3]Cl \cdot 5aq$ (Me = CH_3, aq = H_2O and/or deuterated analogues). Thermodynamic properties (specific heat and bulk magnetization)[1] and spectra (optical emission[2] and inelastic neutron scattering[3]) all agree in showing that the triangular metal cluster is nonequilateral. This is consistent with X-ray diffraction studies which confirm that the complexes lie on sites with no crystallographic symmetry.[4] It has been suggested that any homonuclear triangular complex with net antiferromagnetic coupling should distort spontaneously to a non-3-fold symmetry as a result of spin frustration (the so-called "magnetic Jahn−Teller effect"),[5] but it has also been emphasized that distortion could be imposed on the molecule by external packing forces.[6]

It was therefore of great interest to find a group of oxo-centered triangular chromium(III) cluster complexes, benzoate-bridged (R = C_6H_5) with properties consistent with equivalent chromium atoms: crystals in a hexagonal space group with the molecules stacked on 3-fold rotation axes and EPR and NMR spectra consistent with 3-fold symmetry.[7,8] These results do not conflict with the proposed Jahn−Teller symmetry lowering, provided that the distortions are small enough to be concealed in the crystal structure by rotational disorder and in the glassy and solution states[8] by pseudorotation at rates faster than the relevant time scales,[9] but they did suggest that this molecule should be examined more closely.

The ground state of the $(Cr^{3+})_3$ cluster has net total spin $S = {}^1/_2$, and in the Heisenberg scheme of spin-only interaction in equivalent sites, it is 4-fold degenerate.[1] Distortion to isosceles or scalene geometry splits the ground state into two Kramers doublets. The transition between the two components is optically forbidden but is allowed in inelastic incoherent neutron scattering (IINS). We therefore searched for the splitting by direct measurement of the IINS spectrum. At $T = 1.5$ K, two low-energy IINS transitions were found, implying at least two sets of inequivalent molecules, both distorted as predicted, though with less distortion than in any case reported previously.

Experimental Section

Synthesis. Warning. *Perchlorate salts were assumed to be explosive and were handled with great care, avoiding heat, friction, or percussion.* However, careful tests on this material showed no hazards. Small amounts charred when heated strongly in test tubes or in open air and burned quietly when flamed.

$[Cr_3O(OOCPh)_6(py)_3](py)ClO_4$. Benzoic acid (6.1 g, 0.050 mol) was dissolved in pyridine (50 mL). Hydrated chromium(III) perchlorate, $[Cr(OH_2)_6](ClO_4)_3 \cdot 3H_2O$ (9.35 g, 0.023 mol) was added quickly with stirring, whereupon the mixture became hot and the color of solution, which was initially green, quickly became dark purple. After stirring 10 minutes, the mixture was refluxed for 4 h, still with stirring, then allowed to cool slowly with the oil bath still in place; the solid product was filtered off and washed with dry ether. In powder form all samples appeared sage-green, but individual crystals were purple by transmitted light. Anal. Found: C, 56.4; H, 3.71; N, 4.29; Cl, 2.85. Calcd for $C_{62}H_{50}N_4O_{17}ClCr_3$: C, 56.6; H, 3.84; N, 4.27; Cl, 2.70. Yields were typically 65% based on Cr. The perdeuterio analogue was synthesized in the same way using perdeuteriobenzoic acid and perdeuteriopyridine (99.5% D; Aldrich). Anal. Found: C, 54.6; N, 4.02; Cl, 2.71. Calcd for $C_{62}D_{50}N_4O_{17}ClCr_3$, assuming 99% deuteration: C, 54.6; N, 4.11; Cl, 2.61. The compounds were stored in dry air.[10]

Structure Determination and Refinement. A purple, parallepiped-shaped block, 0.20 × 0.35 × 0.40 mm, was mounted in a glass capillary, and intensity data were collected at −100 °C on a Siemens SMART diffractometer with CCD area detector with graphite-monochromated Mo Kα radiation in the range $\theta = 1.74-27.86°$. The space group $P6_3/m$ was assigned on the basis of extinctions. A total of 18 958 reflections were collected, of which 2456 were considered independent. The structure was solved by direct methods using the computing package SHELXTL, version 5,[11] and refined with 2161 observed

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[†] University of East Anglia.

[‡] The University of Alabama.

[§] Institut Laue-Langevin.

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(10) Washing with pyridine effectively removed excess $[pyH]ClO_4$, and after dry nitrogen was passed through the products on the filter tube, the strong odor of pyridine was removed. Most products treated in this way analysed well for one pyridine molecule per trimer complex ($N = 4.25 \pm 0.045\%$, seven determinations), and they lost only a little pyridine when heated in air at ca. 120° for several hours (4.29 down to 4.22%; 4.33 down to 4.23%). But a few were significantly low, e.g. one well-crystallized sample, $N = 3.83\%$, and it seems possible that pyridine content varied from one crystal to another.

(11) *SHELXTL*, Version 5; Siemens Industrial Automation, Inc., Analytical Instrumentation Business Unit: Madison, WI, 1995.

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Table 1. Crystallographic Data for $[Cr_3O(OOCPh)_6(py)_3]ClO_4(py)_{0.5}$

empirical formula	$C_{59.5}H_{47.5}ClCr_3N_{3.5}O_{17}$
fw	1275
space group	$P6_3/m$
a (Å)	13.4821(1)
c (Å)	19.0317(2)
V (Å^3)	2995.87
Z	2
λ(Mo Kα) (Å)	0.710 73
ρ_{calcd} (g cm^{-3})	1.413
μ (mm^{-1})	0.651
T, K	173(2)
R1	0.0316[a]
wR2	0.0819[b]

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma F_o$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

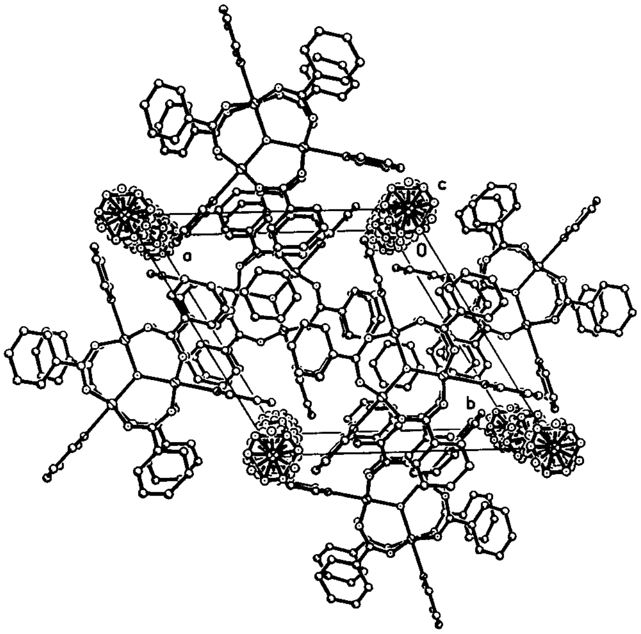

Figure 1. Crystal structure of $[Cr_3O(OOCPh)_6(py)_3](py)_{0.5}ClO_4$, viewed along the c axis.

reflections having $I > 2\sigma(I)$, by full-matrix least-squares minimization of $\Sigma\, w(|F_o| - F_c)^2$ with anisotropic thermal parameters for all the non-hydrogen atoms. Final R factors were 0.0316 and 0.0819 for R1 and wR2, respectively. Crystal data and further numerical details are listed in Table 1.

IINS spectra of the fully deuterated material were measured on MARI at the Rutherford Appleton Laboratory, using incident neutrons of energy 15 meV (neutron wavelength $\lambda = 2.35$ Å) and chopper speed 200 Hz, and on IN5 at the ILL using energies of 6.76 and 1.96 meV ($\lambda = 3.5$ and 6.5 Å). Data reduction was carried out using standard in-house programs at the two laboratories. All the reported spectral features were confirmed to be magnetic on the basis of the momentum-transfer dependence of the intensity.

Results

At the temperature T = 173K, the unit cell contains two symmetry-related molecules on parallel 3-fold axes. The complex molecules appear to be stacked alternately with free pyridines which are perpendicular to the axis (Figure 1). Although the bulk samples analyzed well for one pyridine molecule per trimeric complex, the crystal was found to refine at an occupancy of approximately 1 py for per 2 complexes.[10] The free pyridines are rotationally disordered. The disorder is presumed to be 3-fold, but the occupancy factors of the C and N sites could not be distinguished.[12] The perchlorate ions also occupy 3-fold sites, with disorder as shown.

On both of the neutron scattering instruments, a clear feature was observed at energy transfer 4.07 meV (32.6 cm^{-1}), without the well-resolved sidebands which characterize the lower-symmetry complexes of this type which have been measured previously.[3] The line shape however does suggest unresolved peaks at energies of up to 0.3 meV (2.5 cm^{-1}) on either side of the main band (Figure 2). In further measurements with neutrons of lower energy (1.96 meV) and therefore higher resolution, a low-energy feature was found as shown in Figure 3. Fitting to a single Lorentzian gave a peak energy of 0.21 meV, but the fitted bandwidth is more than twice the value predicted from the instrument resolution at this incident energy (measured, full width at half-height, 0.11 meV; calculated, 0.047 meV). By convoluting two Lorentizians of equal height and width with the resolution function a good fit was obtained as shown in Figure 3, with down-scattering energy transfers of 0.28 and 0.14 meV; and assuming two independent sets of molecules with first excited states at these energies, the up-scattering intensity was also calculated in good agreement with observation.

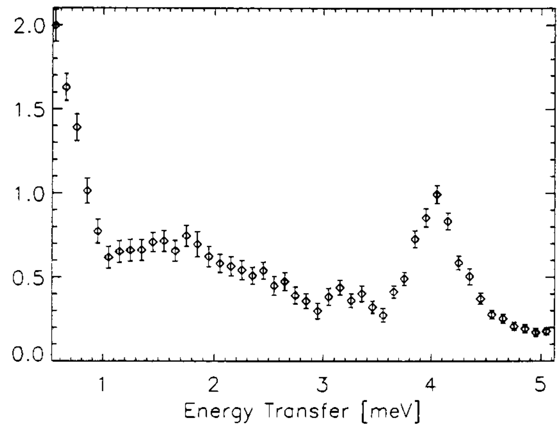

Figure 2. Inelastic neutron scattering spectrum of $[Cr_3O(OOCC_5D_5)_6(C_5D_5N)_3](C_5D_5N)ClO_4$; $T = 1.5$ K; incident neutron wavelength, 2.35 Å. Measured on MARI at Rutherford Appleton Laboratory, Chilton, UK.

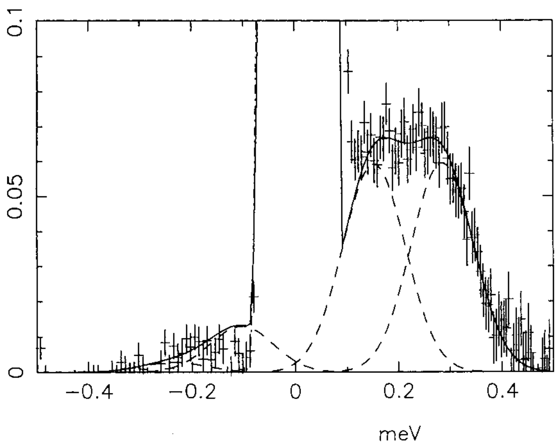

Figure 3. Inelastic neutron scattering spectrum of $[Cr_3O(OOCC_5D_5)_6(C_5D_5N)_3](C_5D_5N)ClO_4$; $T = 1.5$ K; incident neutron wavelength, 6.5 Å. The fitted curve corresponds to energy transfers of 0.14 and 0.28 meV. Measured on IN5 at ILL, Grenoble, France.

Conclusions

It seems clear that this material, at least at low temperature, contains molecules slightly distorted from 3-fold symmetry and is therefore not an exception to the rule which has been found

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(12) The original structure determination at room temperature was of low accuracy and did not detect the uncoordinated pyridine. In the present work a different crystal was used, from the same batch.

in all other cases so far. The low-energy excitations are assigned to the splitting ΔE of the electronic ground state. Using the Heisenberg spin-only formalism, and assuming isosceles models for simplicity, the transition energies are identified as $4|\Delta J|$, where $|\Delta J|$ is the difference between the larger and smaller values of the intramolecular Cr−Cr coupling constant, i.e., $|\Delta J| = 0.56$ and 0.28 cm^{-1}, whereas the higher energy excitation at 32.6 cm^{-1} is assigned as $3\langle J\rangle$, the mean of the three exchange constants. The residual disorders in the structure associated with the anions and the noncoordinated solvent molecules presumably account for the concealment of the molecular asymmetry in the X-ray crystal structure at 173 K.

The smaller of the two ratios $|\Delta J|/\langle J\rangle$, i.e., 8.6×10^{-3}, is the smallest yet found for an exchange-coupled trinuclear system of this class. If we assume that the crystal lattice in this case would tend to reinforce rather than oppose the ideal 3-fold symmetry of the complex, this ratio sets an upper limit on the magnitude of the predicted magnetic Jahn−Teller effect.

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Supporting Information Available: Tables of crystal structure data and refinement; atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for non-H atoms; H coordinates and isotropic displacement parameters are available (7 pages). Ordering information is given on any current masthead page.

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