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[17] These minor peaks may be assigned to ^{6}LiC^{15}N and Bu^{6}Li, respectively, possibly in the form of a 1:1 complex. The "LiCN" was not detectable in the ^{15}N spectra of these samples, due to its low concentration and the broadness of its peak. One preparation contained about 20% of the presumed ^{6}LiC^{15}N $\cdot$ Bu^{6}Li (^{6}Li peaks at $\delta = 0.95$ and 1.83) and had a ^{15}N peak at $\delta = -67.5$ ($\Delta\nu_{1/2} = 95$ Hz). The peak at $\delta = 1.83$ was assigned to Bu^{6}Li by a standard addition experiment.

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Analysis of the Symmetry of Crystal Packing Forces by Methyl Proton Tunneling: A Strategy for the Unambiguous Assignment of the Magnetic Jahn – Teller Effect in Molecules[**]

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Christopher E. Anson, Elisha Karu, Ahmed K. Saad,
John P. Bourke, Gordon J. Kearley, and Ross P. White

Recent work on polynuclear complexes of magnetic metal ions is tending to confirm a hypothesis that was put forward some time ago in which it was stated that in such complexes there is an inherent tendency towards structural distortion with lowering of symmetry, due to spin-frustration or the magnetic Jahn – Teller effect.[1] For example, according to X-ray diffraction studies the complex [Cu$_4$OCl$_6$(OPPh$_3$)$_4$] crystallizes in a cubic lattice in which the molecules are located on sites of tetrahedral symmetry; however, recent FTIR measurements have revealed a lower symmetry, as shown by splittings of the vibrational frequency of the central oxygen atom.[2] Other systems have triangular clusters, and inelastic neutron scattering (INS) measurements have shown that these deviate from equilateral symmetry at low temperatures.[3] But before attempting to assign structural anomalies to intrinsic forces within the metal atom cluster as such, it is important to consider to what extent they may be driven by extrinsic forces, such as crystal packing or steric hindrance between peripheral groups in the ligands, unrelated to electronic forces at the center.

One classic approach to such problems is to compare structures of two materials that are chemically as similar as possible, apart from the asymmetry of the electron configuration. This has worked well in studies of Jahn – Teller effects in mononuclear systems, for example by comparing structures of copper(II) and zinc(II) complexes with identical ligands and counterions.[4] A similar approach to the phenomenon of spin-frustration or magnetic Jahn – Teller effect would need isostructural pairs of magnetic and nonmagnetic polynuclear

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complexes, but no suitable materials are known at present. Another approach to this problem is to embed the magnetic cluster at the center of a large "soft" ligand environment, and place this in turn at a crystal lattice point that is close to the idealized high symmetry. In such a strategy, what is needed is a technique that can sense structural anomalies at the periphery of the complex. If such anomalies are *not* found, but the central cluster is still found to be distorted, the case for saying that the distortion is intrinsic will be strong.

Herein we present the phenomenon of rotational tunneling of protons in units such as methyl groups as a sensitive tool for detecting extrinsic structural distortions. Using a test substance whose structure and spectra have been well studied, we show that six peripheral methyl groups can be distinguished into at least three structural types reflecting small differences in local environment.

A preliminary investigation of the proton tunneling in salts of the chromium complex ion $[Cr_3O(OOCCH_3)_6(OH_2)_3]^+$ by using INS showed at least two features for the chloride salt, a single broad overlapping peak for the perchlorate, and none for the nitrate.[5] We have now measured new tunneling spectra of the chloride salt at higher resolution, and we have compared the normal salt with a sample containing a statistical mixture of CH_3 and CD_3 groups. The purpose of the latter experiment is to detect any coupling between adjacent methyl rotors. Relatively large differences in the tunneling frequencies between the CH_3 and CD_3 groups will result in a decoupling of these rotors. The results show that at least three methyl group environments can be distinguished. A detailed introduction to the application of INS including rotational tunneling is given in a special issue of the journal *Spectrochimica Acta*.[6]

$[Cr_3O(OOCCH_3)_6(H_2O)_3]Cl \cdot 6H_2O$ was synthesized as previously,[7] and a sample containing a statistical mixture of CH_3 and CD_3 groups was prepared by starting with an equimolar mixture of acetic acid and perdeuterioacetic acid. INS spectra were recorded on finely powdered samples sealed in aluminum cans; the thickness was calculated to provide about 10% total scattering. The detectors were calibrated based on a spectrum of vanadium metal. Data reduction was carried out with the standard programs PRIME and CROSSX available at the Institut Laue-Langevin.

The INS spectra of the labeled and unlabeled samples are shown in Figure 1. X-ray powder diffraction patterns of the two samples were identical confirming that they have the same crystal and molecular structure. The differences between the two INS spectra are striking: two peaks, A and D, in the all-^1H sample, reappear almost unchanged in frequency as A and D in the $^1H/^2H$ sample, but at least two other peaks, B and C, in the all-^1H sample, collapse into one broad peak E in the $^1H/^2H$ sample. An empirical Gaussian fitting to the $^1H/^2H$ sample spectrum is consistent with the intensity ratios A:E:D = 1:4:1.

At room temperature $[Cr_3O(OOCCH_3)_6(H_2O)_3]Cl \cdot 6H_2O$ crystallizes in the space group $P2_12_12$; four molecules per unit cell occupy crystallographically general sites.[8] Below a phase transition at about 211 K it changes to $P2_12_12_1$, with the unit cell doubled in size to contain two inequivalent sets of four trinuclear complex cations;[9] that is, there are twelve structurally distinct methyl groups. The C–C distances between the methyl groups are such that intramolecular coupling can be discounted; the shortest intermolecular C–C distances in X-ray crystal structure at room temperature[10] are consistent with intermolecular coupling. Four of the methyl-C atoms per molecule have nearest neighbor methyl-C atoms within a distance of 3.37–3.66 Å and the other two have their nearest neighbors at distances of 3.7 and 3.8 Å. These values may be compared with distances of about 3.5 Å in other acetate materials in which coupling between rotors has been observed.[11]

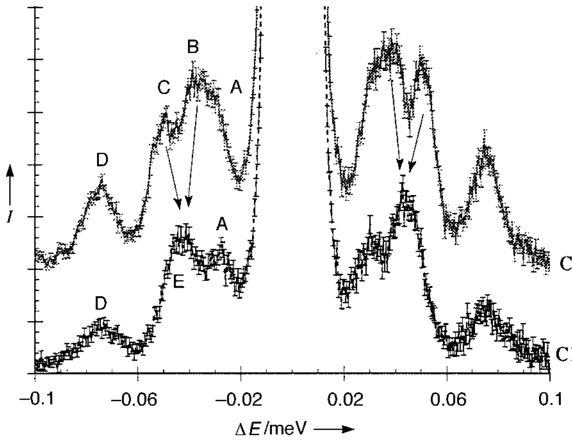

Figure 1. Methyl tunneling spectra of $[Cr_3O(OOCMe)_6(H_2O)_3]Cl \cdot 6H_2O$ recorded at $T = 2$ K (in the neutron down scattering mode) on the instrument IN5 at the Institut Laue-Langevin, Grenoble, France. Upper curve: Me = CH_3; lower curve: Me = 1:1 statistical distribution of CH_3 and CD_3 groups.

In the earlier work on the chloride salt, two possible reasons for the observed spectral profile were proposed, that is inequivalent environments of methyl groups, and coupling between pairs of very similar methyl groups, the two not being mutually exclusive. The observed intensity ratios suggest that both possibilities do in fact occur. That is, all twelve methyl groups are involved in tunneling, four of them rotating independently but grouped into two pairs with similar potentials to give the unshifted bands A and D, while the other eight are coupled intermolecularly in pairs, with similar interaction potentials, giving a set of overlapping peaks observed as bands B and C. On going over to the "scrambled" sample, which is a mixed crystal containing all possible molecules $[Cr_3O(OOCCH_3)_n(OOCCD_3)_{6-n}(H_2O)_3]^+$, the independent methyl groups remain unaffected, apart from a 50% reduction in numbers, but the coupled pairs become decoupled, and collapse to band E.[*]

From the widths and shapes of the observed spectral peaks in Figure 1, it is clear that these consist of many nearly coincident overlapping peaks. It may be possible to resolve them further by working at still lower temperatures, but with the present data we can still attempt an estimate of the methyl

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[*] Another factor that should be taken into consideration in isotopic substitution experiments is lattice compression, which can produce blue shifts, but the lack of significant shifts of bands A and D, and also the observation of a red shift of band C, both suggest that lattice compression is not a significant complication here.

group rotation potentials and the inter-rotor coupling potentials. Such two-rotor systems have been described in detail,[11] though these were usually for simpler crystal structures in which the rotating pairs are coaxial. According to Clough et. al.,[12] the Hamiltonian operator for a pair of coaxially coupled methyl rotors is given by Equation (1), where B is a

$$\mathscr{H} = B\left(\frac{\partial^2}{\partial\theta^2} + \frac{\partial^2}{\partial\phi^2}\right) + V(\theta) + V'(\phi) + W(\theta,\phi) \qquad (1)$$

constant, θ and ϕ are rotational coordinates of the two rotors, $V(\theta)$ and $V'(\phi)$ are the potentials for rotation of the methyl groups in their respective sites, and $W(\theta,\phi)$ is the coupling term which, considering only a threefold contribution, can be written according to Equation (2). For $V(\theta)$ and $V'(\phi)$ a Fourier series is used [Eq. (3)], where W and V_{3n} are constants and $N \leq 2$. $V'(\phi)$ is assumed to be equal to $V(\theta)$ in the simplified model used.

$$W(\theta,\phi) = \frac{W}{2}\{1 - \cos 3(\theta - \phi)\} \qquad (2)$$

$$V(\theta) = \sum_{n=0}^{N} V_{3n} \cos 3n\theta \qquad (3)$$

The resulting energy level diagram is shown in Figure 2, which also shows the allowed transitions and their theoretical relative intensities. A fit of this model to the spectrum of the all-H sample results in the band energies and assignments given in Table 1. The fit of calculated and observed spectra for the all H-sample is shown in Figure 3. The ($E_aE_a \leftarrow E_aE_b$) transition is calculated to be at about 3 μeV, and is thus hidden within the elastic peak. Although the model used here is oversimplified, it provides a quantitative measure of the potentials felt by these peripheral methyl groups, which are due mainly to packing forces in the solid state.

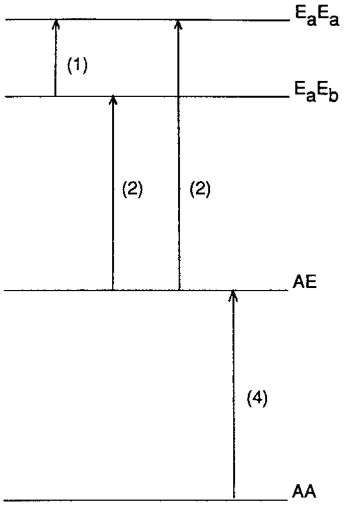

Figure 2. Energy level diagram showing the allowed transitions for two methyl groups coupled under a threefold potential. Energy levels are labeled with the symmetry species, according to reference [11]. Figures in parentheses are the relative intensities predicted for the INS spectrum.

Table 1. Summary of fitted tunneling energies ΔE [μeV] for [$Cr_3O(OOCMe)_6(H_2O)_3$]$Cl \cdot 6H_2O$ and its partially deuterated analogue.[a]

Me = CH_3				Me = CH_3/CD_3	
observed value[a]		calculated value[c]		observed value[a]	
ΔE[b]	I_{rel}[b]	ΔE	I_{rel}	ΔE[b]	I_{rel}[b]
	1[d]	3	1		
27 (A)	2.25			26 (A)	1
	2[d]	39	2		
38 (B)	2[d]	40	2	43 (E)	4
50 (C)	4[d]	50	4		
75 (D)	2.25			77 (D)	1

[a] Letters in parentheses refer to bands labeled in Figure 1. For details of the fitting procedure see reference [14]. [b] Empirical fit to the curves shown in Figure 1. [c] Best fit to the upper curve shown in Figure 3. [d] Constrained value.

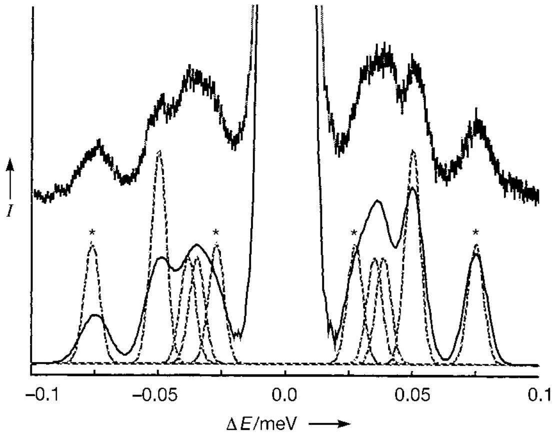

Figure 3. Methyl tunneling spectra of [$Cr_3O(OOCCH_3)_6(H_2O)_3$]$Cl \cdot 6H_2O$ recorded at $T = 2$ K (in neutron down scattering mode), showing the fit of the model described in the text. Upper curve: observed; lower curve: calculated. The bands labeled with an asterisk are tunneling transitions of the uncoupled methyl groups.

The vibrational spectrum of [$Cr_3O(OOCCH_3)_6(H_2O)_3$]$Cl \cdot 6H_2O$ in the region 100–150 cm^{-1} supports this interpretation. As measured by INS[5] it shows a strong peak at about 150 cm^{-1} and three others closely spaced at 100–130 cm^{-1}. A subsequent single-crystal Raman study has identified the 150 cm^{-1} band as the symmetric breathing mode of the oxo-centered metal triangle.[13] The other three peaks can therefore now be assigned to methyl torsions; the central peak is broader and stronger than the two side peaks, in agreement with the above conclusions on the methyl group environments.

The studies presented here clearly illustrate the sensitivity of the rotational tunneling of protons in methyl groups to the local environment. Polymetallic molecular systems with ligands such as carboxylic acids, provide useful systems for the investigation of the distortions that result from effects like the magnetic Jahn–Teller effect. As shown elsewhere,[3] the Cr_3 triangles in the present complex are "scalene" in the sense that all three Cr–Cr antiferromagnetic coupling constants are different. Inelastic magnetic neutron scattering and IR spectroscopy provide accurate information on the symmetry of the central metal core, while rotational tunneling of protons probes the symmetry of the external packing forces. Further work including a low-temperature structure determination will be needed to establish whether or not there is a correlation between central and external geometries for this molecule. Other systems containing probable proton tunneling groups such as NH_3 will also be suitable candidates for this purpose.

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Stereocontrolled Synthesis of (11*Z*)-Retinal and Its Analogues**

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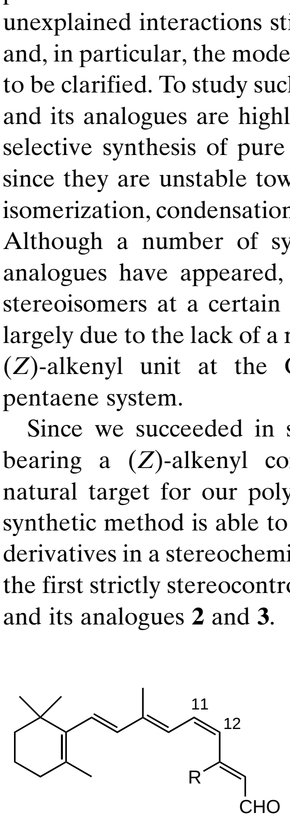
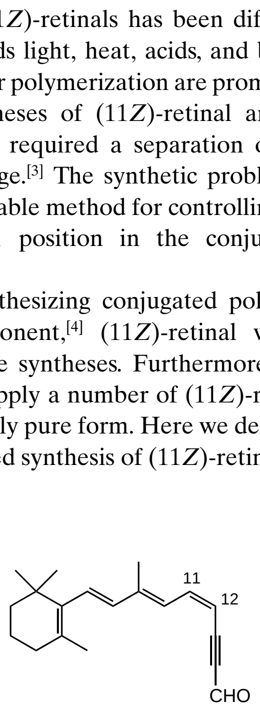
(11*Z*)-Retinal is a key chromophore in the visual system of the retina, which assembles with an apo-protein (opsin) to form rhodopsin.[1] When rhodopsin is exposed to photons, it is promoted to an excited state which induces a bleaching process by an enzymatic cascade. Thus, the signal is delivered to the brain through synaps, and vision is possible.[2] Although part of this mechanism was previously revealed, many unexplained interactions still remain for the visual pigments, and, in particular, the mode of action for sensing color has yet to be clarified. To study such a mechanism, pure (11*Z*)-retinal and its analogues are highly desired.[3] However, the stereoselective synthesis of pure (11*Z*)-retinals has been difficult, since they are unstable towards light, heat, acids, and bases; isomerization, condensation, or polymerization are promoted. Although a number of syntheses of (11*Z*)-retinal and its analogues have appeared, all required a separation of the stereoisomers at a certain stage.[3] The synthetic problem is largely due to the lack of a reliable method for controlling the (*Z*)-alkenyl unit at the C11 position in the conjugated pentaene system.

Since we succeeded in synthesizing conjugated polyenes bearing a (*Z*)-alkenyl component,[4] (11*Z*)-retinal was a natural target for our polyene syntheses. Furthermore, this synthetic method is able to supply a number of (11*Z*)-retinal derivatives in a stereochemically pure form. Here we describe the first strictly stereocontrolled synthesis of (11*Z*)-retinal (**1**) and its analogues **2** and **3**.



1 R = CH_3
2 R = H



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Scheme 1 summarizes the retrosynthesis of the (11*Z*)-retinals. Cleavage of the C12–C13 bond gives rise to the important and flexible intermediate **5**, which couples with an appropriate alkenylboronic acid or alkyne by Pd-catalyzed cross-coupling reactions to afford **1**, **2**, and **3** with retention of

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