Dynamics of Ligated Water Molecules in Oxo-Centered Trinuclear Carboxylates: An Incoherent Inelastic Neutron Scattering Study**

John A. Stride, Upali A. Jayasooriya,* and Jürgen Eckert

Oxo-centered trinuclear transition metal complexes of the general formula $[M_3O(L)_6(L_t)_3]$, where L a bidentate bridging ligand and L_t a terminal ligand, have provided an important template to study a range of fundamental chemical and physical phenomena.[1] Of particular interest is the mechanism of electron transfer for the mixed-valent members of this family of complexes. Much effort has therefore been spent on obtaining a detailed understanding of the potential energy surfaces of these materials by measuring the low-lying magnetic and vibrational transitions. The most difficult part of assigning the vibrations of these compounds up to now has been for those vibrations of water molecules, when present as terminal ligands L_t and as water of crystallization. Here we illustrate a technique which consists of inelastic neutron scattering spectroscopy of isotopically diluted species which substantially simplifies the assignments of vibrations of such strongly hydrogen bonded systems.

The first compound of this family of compounds to be discovered was the chromium acetate complex $[Cr_3O(CH_3CO_2)_6(H_2O)_3]Cl \cdot 5H_2O$ (CRAC), and it is the most studied member.[2–7] A fairly detailed crystal structure of CRAC was reported by Chang and Jeffreys,[8] where CRAC was shown to crystallize in the orthorhombic space group $P2_12_12$ with four molecules per unit cell in sites of C_1 symmetry. This determination was of low accuracy and was unable to discriminate effectively between the noncoordinated water molecules and the counterions, and therefore arrived at the conclusion that these units were extensively and mutually disordered. A recent accurate redetermination of this crystal structure[9] clearly shows the chloride ions to be well-defined with no disorder between the chloride ions and the water molecules. Phase transitions were also reported at temperatures of 211.4 to 215.5 K, and established by anomalies in specific heat[10] and by NMR data. X-ray diffraction showed the low-temperature space group to be $P2_12_12_1$, with the unit cell doubled in size along the c axis. Although the low-temperature structure has still not been determined completely, it is known to contain equal numbers of two crystallographically nonequivalent sets of trimer complex ions. Sorai et al.[10] found that the low-temperature specific heat could best be interpreted by assuming that one of the two sets of compounds is significantly more distorted than the other. Ferguson and Güdel[11] came to the same conclusion from electronic spectroscopy, and Jayasooriya et al.[12] from neutron magnetic scattering.

Mixed-valent and mixed-metal compounds of this class have the general formula of $A_2^{III}B^{II}O$ for the central triangular unit; the unique ion B may be of the same or of a different metallic element to A. The vibrational and magnetic studies of these compounds highlight the marked distortion of the central oxygen bonding geometry.[13, 14] No structural data on the aquo complexes are available, possibly because they are normally difficult to crystallize.

The vibrational spectra of the trinuclear carboxylate complexes have been the subject of a number of studies.[13, 15, 16] The complexity of the molecules results in a large number of normal modes, and the detailed assignment by the semi-empirical force-field approach is nontrivial.[17] However isotopic substitution studies have resulted in many useful assignments. Of particular interest is the recognition of the vibrations of the central oxygen atom and the use of these vibrations to probe the electron transfer properties of the mixed-valent compounds.

Despite these compounds being extensively characterized by a host of techniques, attempts at determining the strength of the bonding interaction between a metal ion and a terminal water ligand have never been successful. Previous efforts to assign the metal–water stretching modes in the vibrational spectra of these compounds have been thwarted by the interference of strong overlapping carboxylate bands, both in the IR and Raman spectra.[15]

This problem can be overcome by the use of incoherent inelastic neutron scattering spectroscopy (IINS). The intensities of energy transfers in this technique are determined by the neutron scattering cross-section of the atoms and their amplitudes of motion in the normal mode of relevance to the transition. Hydrogen, being the lightest element and also possessing the largest incoherent scattering cross-section (almost one order of magnitude larger than that for any other element), therefore dominates IIN spectra of hydrogen-containing molecules. Further, deuterium-substitution studies are of particular interest. In addition to the frequency shifts to lower energies as observable with IR and Raman spectroscopies, one would also notice an almost complete disappearance of the mode of interest, due to the very low incoherent scattering cross-section of deuterium, thus potentially leading to reliable assignments. Previous attempts at measuring the metal–water vibrational modes by IINS were unsuccessful due to the presence of a strong hydrogen-bonding network of both coordinated and uncoordinated water molecules in the solid.[15] A broad envelope of features between about 400 and 800 cm^{-1}, due to the hydrogen-bonding network, was observed, and no detailed assignments of the ligated water vibrations were possible. Here we report an experiment where an isotope dilution technique was used to decouple the O–H

---

[*] Dr. U. A. Jayasooriya, Dr. J. A. Stride[+]
School of Chemical Sciences
University of East Anglia
Norwich NR4 7TJ (UK)
Fax: (+44) 1603-259-396
E-mail: u.jayasooriya@uea.ac.uk

Dr. J. Eckert
LANSCE, Los Alamos National Laboratory, New Mexico (USA)

[+] Present address:
BENSC, Hahn-Meitner-Institut, D-14109 Berlin (Germany)

[**] Funding of this research by the SERC, UK, and a studentship to J.A.S. are gratefully acknowledged. This work has benefited from the use of facilities at the Los Alamos neutron scattering center, and neutron user facility funded as such by the DOE/Office of Basic Energy Science. We also thank Dr Roderick Cannon for useful discussions.

vibrations from the broad features of the network of hydrogen bonds, which includes the water of crystallization. By using an almost fully deuterated sample (ca. 5% H) the broad envelopes of bands found in the fully protonated compounds were almost totally removed from the IIN spectra, thus giving better access to $\nu(M{-}OH_2)$ vibrations.

The IIN spectra were collected at about 20 K on the Filter Difference Spectrometer (FDS)[18] at LANSCE (Los Alamos, New Mexico, USA) with a usable spectral window of approximately about 75–3500 cm^{-1}. The spectra were gathered using the Be filter detector, and a numerical method of Mezei and Vorderwisch[19, 20] was applied to filter out the long time of flight tails in the spectra and thus increase the spectral resolution. However, the reliable spectral range in the reported spectra is only that below about 1500 cm^{-1} due to insufficient counting statistics.

Samples were prepared by literature methods[15] and characterized by elemental analysis and IR spectroscopy. The synthetic methods used for the mixed-metal compounds studied here have been shown to produce stoichiometric compounds.[15, 21]

An important complication to be expected with IINS in comparison to IR and Raman spectroscopies is the possible observation of overtone and combination bands and the accompaniment of external modes with each internal mode, which is dependent on the strength of such a coupling. Therefore, we provide an assignment based on a comparison of the spectra of all the isotopomers, which is facilitated by a spectral deconvolution.

The IIN spectrum of $[Cr_3O(CH_3CO_2)_6(H_2O)_3]Cl \cdot 5H_2O$ (CRACHH) is shown in Figure 1a. The spectrum is dominated by a broad feature stretching from about 400 to 800 cm^{-1}, which is due to the water molecules of crystallization. Standing out above this broad envelop are at least four features. Other strong features are found around 1000 cm^{-1}, and there are a number of peaks below 400 cm^{-1}. The partially deuterated sample $[Cr_3O(CD_3CO_2)_6(H_2O)_3]Cl \cdot 5H_2O$ (CRACDH) gave a spectrum in which the latter features were of much lower intensity (Figure 2), indicating the acetate group motion in these normal modes. What are left behind are the very intense broad features due to the vibrations involving the water molecules. By using D_2O and CH_3COOH in the synthesis, the compound $[Cr_3O(CH_3CO_2)_6(D_2O)_3]Cl \cdot 5D_2O$ (CRACHD) was produced, whose IIN spectrum (Figure 1b) shows the absence of the broad peaks due to H_2O vibrations which dominated the other spectra. This spectrum clearly shows the acetate modes as relatively sharp features at about 272, 342, 395, 550, 595, 710, 800, and 1010 cm^{-1}, which correspond well to some of the peaks in the fine structure observed on top of the broad water feature in the spectrum of CRACHH (Figure 1a).

The IIN spectrum of the fully deuterated compound, $[Cr_3O(CD_3CO_2)_6(D_2O)_3]Cl \cdot 5D_2O$ (CRACDD) is shown in Figure 1d. The most intense peak is a relatively sharp feature around 500 cm^{-1}. Other peaks are observed at about 380, 621, 700, 860, and 970 cm^{-1}, and are clearly due to the vibrations of the residual protons (see below). The present investigation will be confined mainly to the modes of ligated water, as these were the least understood prior to this study. The IIN spectroscopy is applied here to a sample containing a few HOD molecules in a D_2O host matrix. Therefore, the vibrational interactions across the hydrogen-bonded water network are sufficiently disrupted to justify treatment of the H vibrations of the HOD molecules as localized modes. The spectra obtained from such isotopically dilute samples can be understood by considering the evolution of the normal modes

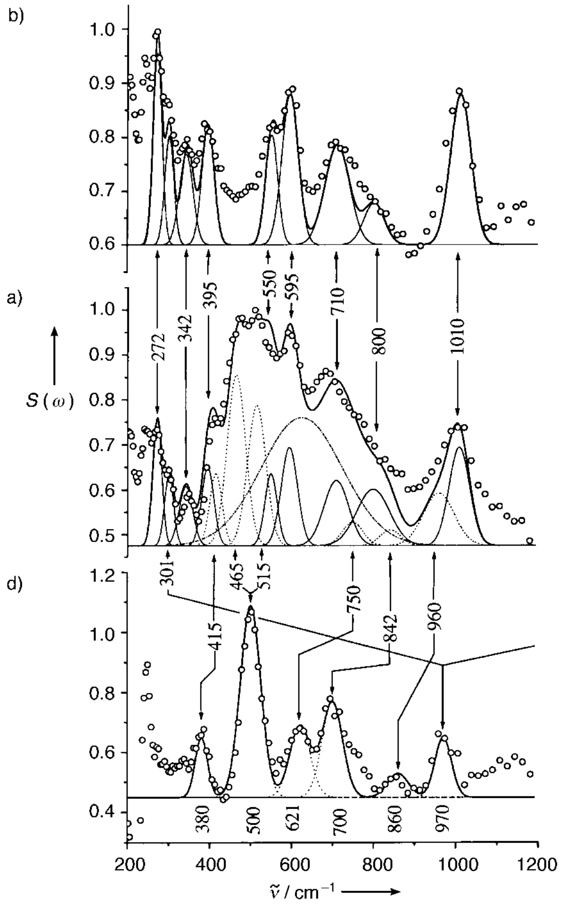


Figure 1. IIN spectra of b) CRACHD, a) CRACHH, and d) CRACDD taken at 20 K showing the shift in peak positions with isotopic substitution. The spectra are numbered in this unconventional manner to correspond with the spectra in Figures 4 and 5; that is, the degree of deuteration for the isotopic variants is similar in each series a, b, and d. Spectral deconvolutions are provided to clarify the assignments proposed. $S(\omega)$ = inelastic scattering intensity (in arbitrary units), $\tilde{\nu}$ = neutron energy loss.

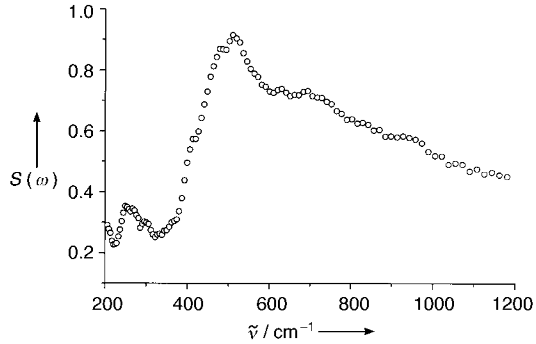


Figure 2. IIN spectrum of CRACDH taken at 20 K. As far as the degree of deuteration of the complex is concerned, the spectrum corresponds to Figures 4c and 5c. $S(\omega)$ = inelastic scattering intensity (in arbitrary units), $\tilde{\nu}$ = neutron energy loss.

of vibration (Figure 3) from their respective internal modes. Let us consider the ligated water first. The normal modes ν_s(HOH) and ν_{as}(HOH) are in-phase and out-of-phase combinations of the OH stretching internal modes. In HOD, this mixing will mainly disappear, leaving an OH stretching mode with a frequency almost half-way between those of ν_s(HOH) and ν_{as}(HOH), and an O–D stretching mode at almost $1/\sqrt{2}$ times the isolated O–H frequency. These modes appear at higher frequencies and will not be discussed further. A similar line of argument could be used to predict the outcome for the pair of in-plane OH deformations, the scissoring mode δ(HOH) and the rocking mode ρ(HOH), as well as the pair of out-of-plane deformations, the wag ω(HOH) and the twist τ(HOH). In summary, the effect of going from HOH to HOD will broadly bring about the replacement of each of these pairs of frequencies for HOH by a band approximately half-way between them, due to the now isolated O–H bond normal mode, and another band shifted by approximately $1/\sqrt{2}$ in frequency from it due to the O–D bond vibration. However, the latter mode will be of very reduced intensity in the IIN spectrum due to the very low incoherent neutron scattering cross-section of deuterium when compared to hydrogen. The remaining internal mode of ligated water, the Cr–OH_2 stretching mode, will be expected to show behavior different to the above, with a relatively small shift corresponding to the change in relative ligand mass in going from 18 (H_2O) to 19 (HOD). Similarly, the librational modes of the water molecules of crystallization will show small shifts due to the change in moment of inertia with this isotopic modification.[22, 23]

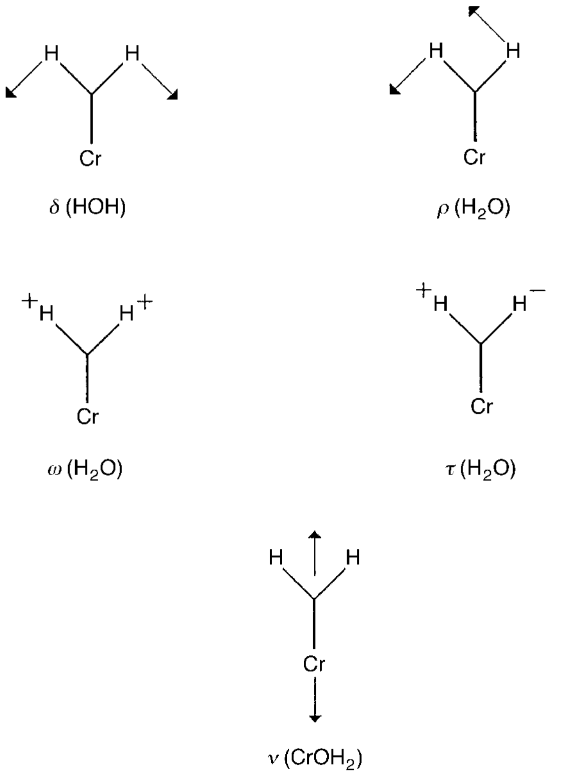


Figure 3. Vibrational normal modes of coordinated water in CRAC expected to appear above about 250 cm^{-1}.

The ^{1}H contamination of the D_2O molecules of the CRACDD and CRACHD samples was around 5%. Considering the respective neutron scattering cross-sections for H and D, a vibrational mode of the H–O bonds in these compounds will be expected to be about four to eight times the intensity of the corresponding mode of the D–O bonds. The statistical probability of finding any H_2O units in this matrix is negligible, and so the vibrations of the HOD features are expected to dominate the IIN spectrum of this material, in spite of the high isotopic dilution of ^{1}H. The deuterium content of the acetate methyl groups is better than 99.9% for CRACDH and CRACDD.

The spectra of CRACHH, CRACHD, and CRACDD are collected together in Figure 1, in order to highlight the relative changes in intensity associated with the isotopic substitutions and thus to clarify the assignment proposed. Let us consider the spectrum of CRACHH first (Figure 1 a). The acetate vibrations are assigned by comparison with the spectrum of CRACHD (Figure 1 b), that is, to bands at about 1010, 800, 710, 595, 550, 395, 342, and 272 cm^{-1}. The assignment of the vibrations of the water molecules is best started using the spectrum of CRACDD (Figure 1 d). The dominant features in this spectrum are expected to be due to the hydrogenic modes in residual HOD species. The vibrational modes of HOD expected to appear in the region of 300–1200 cm^{-1} in this spectrum are the following: The in-plane and out-of-plane motions of the O–H bond in HOD molecules ligated to the Cr atoms, the Cr–OHD stretching mode, and the three librations R, W, and T of the HOD molecules of crystallization. The X-ray diffraction study of Anson et al.[9] does not provide accurate information on the detailed structure of the water molecules. However, it is unlikely that the different molecules of water of crystallization are distinguishable within the resolution of this inelastic neutron scattering experiment. Therefore six vibrational modes are expected in this frequency range, as was experimentally observed (Figure 1 d).

The in-plane deformation of the O–H bond in ligated HOD, which is predicted to be half-way in frequency between the modes δ_{sym}(HOH) (ca. 1650 cm^{-1}) and ρ(HOH) of the ligated water molecule, is assignable to the highest wavenumber band in this region at about 970 cm^{-1}. This in turn provides the assignment of a wavenumber of approximately 290 cm^{-1} in the spectrum of CRACHH to the rocking mode of the HOH ligand. Band overlap makes this assignment difficult, and a wavenumber of 301 cm^{-1} is therefore tentatively assigned to this mode. Of the bands left to be assigned in the spectrum of Figure 1 d, that at about 500 cm^{-1} is clearly of greatest intensity. An inelastic neutron scattering study of a single crystal of barium chlorate hydrate by Thaper et al.[23] shows the intensities of the R, W, and T modes of a water molecule of crystallization to be of similar intensity, suggesting similar amplitudes of proton motion for all of these modes. Further, the Cr–OHD stretching mode is expected to show a band of low intensity because the hydrogen motion in this mode is determined by the motion of the oxygen atom on which the hydrogen rides. This therefore provides the assignment of the relatively strong band at about 500 cm^{-1} to the out-of-plane deformation of the O–H bond in the Cr–OHD unit. It is very reasonable to expect a large amplitude of hydrogen motion for such a mode, and hence the large IINS intensity. Following our previous reasoning, the bands at around 465 and 515 cm^{-1} in the spectrum of CRACHH (Figure 1 a) are assigned to the twist and wag of the HOH ligand. Of the remaining four bands, the lowest frequency band at approximately 380 cm^{-1} is most reasonably assigned to the Cr–OHD stretching mode. The possible mixing of this mode with the OH out-of-plane deformation mode, which gives the strongest peak in this spectral region, provides a mechanism for intensity enhancement. The effect of such mixing is more evident in the case of the mixed-valent compounds to be discussed later. The corresponding assignment in the spectrum of CRACHH (Figure 1 a) is to the shoulder at about 415 cm^{-1}. The remaining three bands around 621, 700, and 860 cm^{-1} in the spectrum of CRACDD (Figure 1 d) are assigned to the librations of water molecules of crystallization. With the present data it is not possible to make a more detailed assignment of these librations. The isotopic shifts expected for these modes are reported by Tayal et al.[22] Assuming an HOH angle of 116° and an assignment of the HOD vibrations R, T, and W to the peaks at about 621, 700, and 860 cm^{-1}, respectively, in the spectrum of CRACDD leads to the prediction of peaks at about 750, 842, and 960 cm^{-1} for the corresponding librations of the HOH molecules of crystallization in CRACHH. There is substantial neutron scattering intensity corresponding to the latter frequencies in the spectrum of CRACHH. The IINS intensity envelope due to hydrogen-bonding effects and the translational modes of the water molecules of crystallization are empirically modeled by an intense broad band at approximately 625 cm^{-1} in the spectrum of CRACHH. The final assignments are summarized in Tables 1 and 2.

Spectra of the isotopic variants of two mixed-metal complexes $[Fe^{III}_2Mn^{II}O(CH_3CO_2)_6(H_2O)_3]\cdot 3H_2O$ (FeMn) and $[Fe^{III}_2Co^{II}O(CH_3CO_2)_6(H_2O)_3]\cdot 3H_2O$ (FeCo) are shown in Figures 4 and 5. These sets of spectra are similar to each other, as would be expected from their molecular formulae. A comparison of these spectra with those of CRAC (Figures 1 and 2) shows the largest differences to be between the spectral regions showing vibrations of the water of crystallization. This

Table 1. Vibrational assignments in the region between 240 and 1100 cm^{-1} in the spectra of CRAC, FeMn, and FeCo containing either H_2O (a; Figures 1 a, 4 a, and 5 a) or D_2O (b; Figures 1 b, 4 b, and 5 b) as ligands and molecules of crystallization. The estimated relative intensities are given in parenthesis.

CRAC		FeMn		FeCo		Assignment
(a)	(b)	(a)	(b)	(a)	(b)	
1010 (25)	1010 (25)	1007 (24)	1007 (24)	1005 (25)	1005 (25)	acetate
960 (20)						W (H_2O of cryst.)
842 (4)						T (H_2O of cryst.)
800 (23)	800 (7)	790 (10)		790 (10)		acetate
750 (6)						R (H_2O of cryst.)
710 (20)	710 (12)	715 (30)	715 (30)	715 (28)	715 (28)	acetate
625 (130)		650 (55)		660 (60)		H-bonded water background
595 (20)	595 (15)	590 (27)	590 (26)	595 (27)	595 (27)	acetate
550 (11)	550 (7)	507 (18)	507 (23)	510 (22)	510 (22)	acetate
515 (32)		515 (12)		515 (12)		$\tau/\omega(H_2O\text{–}Cr)$
465 (39)		465 (9)		465 (9)		$\omega/\tau(H_2O\text{–}Cr)$
415 (11)		420 (5)		420 (5)		$\nu(Cr\text{-}OH_2)$
395 (12)	395 (7)	390 (10)	390 (11)	390 (12)	400 (12)	acetate
342 (10)	345 (6)	335 (7)	335 (8)	320 (9)	330 (9)	acetate
301 (8)	298 (6)	297 (5)	297 (6)	295 (5)	295 (5)	overlapping $\rho(H_2O\text{–}Cr)$ and acetate
272 (14)	272 (8)	272 (8)	272 (10)	272 (10)	272 (10)	acetate

Table 2. Vibrational assignments in the region between 240 and 1100 cm^{-1} in the spectra of fully deuterated CRAC (CRACDD, Figure 1 d), FeMn (Figure 4 d), and FeCo (Figure 5 d). The estimated relative intensities are given in parenthesis.

CRACDD	FeMn	FeCo	Assignment
970 (10)	970 (10)	990 (9)	ligand O–H in-plane deformation
860 (5)	815 (5)	805 (28)	W (HDO of cryst.)
700 (20)	700 (20)	690 (16)	T (HDO of cryst.)
621 (15)	615 (12)	628 (18)	R (HDO of cryst.)
500 (40)	500 (45)	500 (65)	ligand O–H out-of-plane-deformation
380 (7.5)			$\nu(Cr\text{–}OHD)$
	325 (4)	328 (11)	$\nu(Fe\text{–}OHD)$
	385 (7.5)		$\nu(Mn\text{–}OHD)$
		395 (11)	$\nu(Co\text{–}OHD)$

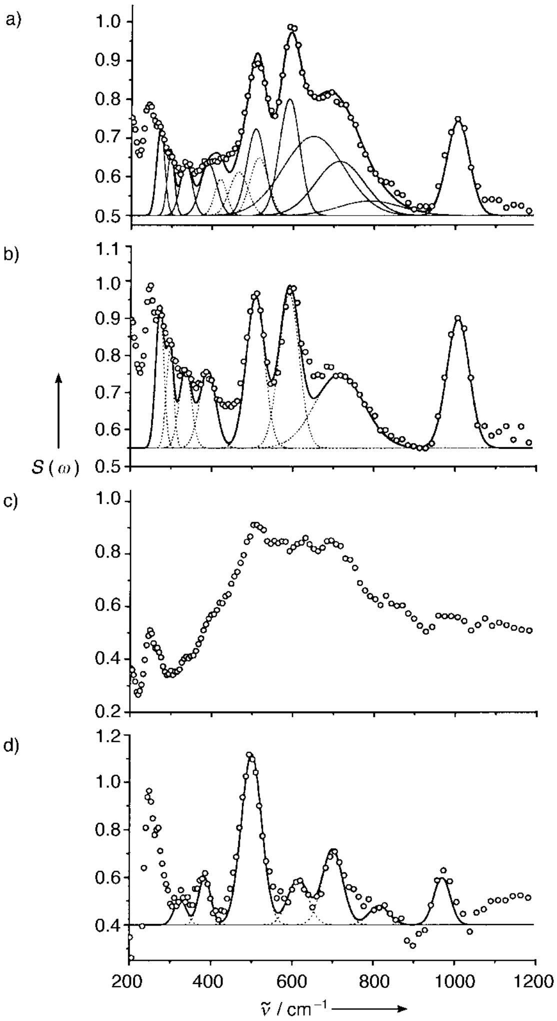


Figure 4. IIN spectra of a) $[Fe_2MnO(CH_3CO_2)_6(H_2O)_3]\cdot 3H_2O$, b) $[Fe_2MnO(CH_3CO_2)_6(D_2O)_3]\cdot 3D_2O$, c) $[Fe_2MnO(CD_3CO_2)_6(H_2O)_3]\cdot 3H_2O$, and d) $[Fe_2MnO(CD_3CO_2)_6(D_2O)_3]\cdot 3D_2O$ taken at 20 K. $S(\omega)$ = inelastic scattering intensity (in arbitrary units), $\tilde{\nu}$ = neutron energy loss.

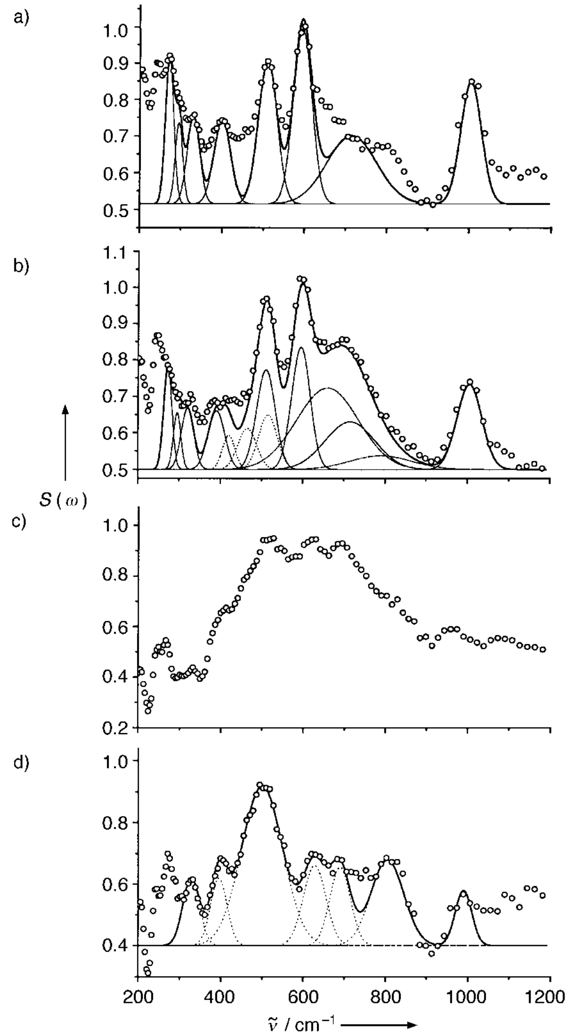


Figure 5. IIN spectra of a) $[Fe_2CoO(CH_3CO_2)_6(H_2O)_3]\cdot 3H_2O$, b) $[Fe_2CoO(CH_3CO_2)_6(D_2O)_3]\cdot 3D_2O$, c) $[Fe_2CoO(CD_3CO_2)_6(H_2O)_3]\cdot 3H_2O$, and d) $[Fe_2CoO(CD_3CO_2)_6(D_2O)_3]\cdot 3D_2O$ taken at 20 K. $S(\omega)$ = inelastic scattering intensity (in arbitrary units), $\tilde{\nu}$ = neutron energy loss.

observation is compatible with the different numbers of molecules of water of crystallization found in these compounds, five per formula unit in CRAC compared to three in the mixed-metal compounds.

In Figures 4 and 5, a comparison between spectra a and b provides assignments of bands to acetate modes. These bands are at similar frequencies for both FeMn and FeCo (Table 1). The most significant difference between these bands and those assigned to acetate modes in CRAC is the shift of the band at about 550 cm^{-1} for CRAC to approximately 507 and 510 cm^{-1} for FeMn and FeCo, respectively. This is the spectral region where $M{-}O_{acetate}$ stretching modes are expected to appear, and is therefore likely to be due to the two types of metal–acetate bonds present in these compounds.

Just as was found with the CRAC spectra, the vibrations of the water molecules are best assigned using the fully deuterated compounds. The IIN spectra of the fully deuterated variants of FeMn and FeCo are shown in Figures 4d and 5d, where the prominent features are those due to the approximately 5% residual protons in the samples. The spectrum of fully deuterated FeMn (Figure 4d) is directly assigned by comparison with that of CRACDD (Figure 1d). The only significant difference between these spectra is the metal–water stretch, which for the former appears to be split into two peaks of unequal intensity at about 385 and 325 cm^{-1}. The band at 385 cm^{-1}, which is more intense, suggests an assignment to the stretching modes of the two $Fe{-}OH_2$ bonds, while the weaker band at 325 cm^{-1} corresponds to the stretching of the single $Mn{-}OH_2$ bond. However, the possibility exists that the cause of increased intensity of the former band may not be the multiplicity of bonds, but intensity stealing from the strong out-of-plane deformation at about 500 cm^{-1} through mode mixing.

In spite of poor statistics, the spectrum of fully deuterated FeCo (Figure 5d) could also be assigned by comparison with the spectrum of CRACDD (Figure 1d), the difference being the possible assignment of the $Fe{-}OH_2$ stretch to that band at 395 cm^{-1} and the $Co{-}OH_2$ stretching mode to 328 cm^{-1}. Here again a mixing of internal modes with the out-of-plane deformation may be the cause of the stronger intensity of the former band.

The above assignments for the metal–water stretching modes in FeMn and FeCo give the same frequency of about 325 cm^{-1} for the $Mn{-}OH_2$ and $Co{-}OH_2$ vibrations (that is, involving two different metals), while two different frequencies are assigned to the $Fe{-}OH_2$ vibration in the two compounds. If intensity stealing through mode mixing is assumed, the more reasonable assignment of a single frequency for the $Fe{-}OH_2$ bond stretching modes for the two compounds become acceptable. Further, the latter assignment is consistent with the studies reported for the metal–water stretching modes of a number of hexaaquo complexes.[24] The value for $\nu(Co^{II}{-}OH_2)$ is greater than that for $\nu(Mn^{II}{-}OH_2)$ and $\nu(Fe^{II}{-}OH_2)$; this reflects the relative bond strengths for the transition metals in octahedral environments and may be a consequence of the ligand field stabilization energy, analogous to that found by Jenkins and Lewis[25] in their study of Ni^{II}, Fe^{II}, and Zn^{II} hexaaquo ions in simple salts. It is interesting to note the substantially larger widths of the peaks in the spectra of FeCo, for example the out-of-plane OH deformation at about 500 cm^{-1} in the spectrum in Figure 5d, compared to the spectra of the other two compounds. This may be another indication of a larger difference in bond strengths between $Fe{-}OH_2$ and $Co{-}OH_2$ than between $Fe{-}OH_2$ and $Mn{-}OH_2$. Poor spectral statistics prevent any firm conclusions.

Here we have illustrated the use of an isotopic dilution technique in inelastic neutron scattering spectroscopy to simplify assignment of a complicated hydrogen-bonded molecular system. The trimeric complexes studied were found to have lower metal–water stretching frequencies and bond strengths (even after taking the involvement of the metal ions in the vibrational modes into consideration) than their respective monomeric complexes. This parallels the observations of longer bond lengths for $Mn{-}OH_2$ bonds in the trimeric complexes compared to the monomeric analogues, thus confirming the *trans* effect of the central oxygen atom. The method of assignment reported here should be of general applicablility to vibrational assignments of systems where there is extensive hydrogen bonding.

Received: April 14, 1998
Revised version: September 17, 1998 [Z11717IE]
German version: *Angew. Chem.* **1999**, *111*, 172–177

Keywords: aquo complexes · hydrogen bonds · isotope effects · neutron scattering · vibrational spectroscopy

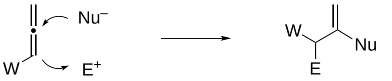
---

[1] R. D. Cannon, R. P. White, *Prog. Inorg. Chem.* **1988**, *36*, 195.
[2] A. Werner, *Ber. Dtsch. Chem. Ges.* **1908**, *41*, 3447.
[3] R. F. Weinland, *Chem. Ztg.* **1908**, *32*, 812.
[4] R. F. Weinland, *Ber. Dtsch. Chem. Ges.* **1908**, *41*, 3236.
[5] L. A. Welo, *Phys. Rev.* **1928**, *32*, 320.
[6] L. A. Welo, *Philos. Mag.* **1928**, *6*, 481.
[7] B. N. Figgis, G. B. Robertson, *Nature* **1965**, *205*, 694.
[8] S. C. Chang, G. A. Jeffreys, *Acta Crystallogr. Sect. B* **1970**, *26*, 673.
[9] C. E. Anson, J. P. Bourke, R. D. Cannon, U. A. Jayasooriya, M. Molinier, A. K. Powell, *Inorg. Chem.* **1997**, *36*, 1265.
[10] M. Sorai, M. Tachiki, H. Suga, S. Seki, *J. Phys. Soc. Jpn.* **1971**, *30*, 750.
[11] J. Ferguson, H. U. Güdel, *Chem. Phys. Lett.* **1972**, *17*, 547.
[12] U. A. Jayasooriya, R. D. Cannon, R. P. White, J. A. Stride, R. Grinter, G. J. Kearley, *J. Chem. Phys.* **1993**, *98*, 9303.
[13] L. Meesuk, U. A. Jayasooriya, R. D. Cannon, *J. Am. Chem. Soc.* **1987**, *109*, 2009; R. P. White, J. A. Stride, S. K. Bollen, N. C. Sa-Ard, G. J. Kearley, U. A. Jayasooriya, R. D. Cannon, *J. Am. Chem. Soc.* **1993**, *115*, 7778.
[14] A. B. Blake, A. Yavari, W. E. Hatfield, C. N. Sethulekshmi, *J. Chem. Soc. Dalton Trans.* **1985**, 2509.
[15] R. P. White, N. C. Sa-Ard, S. K. Bollen, R. D. Cannon, U. A. Jayasooriya, S. T. Robertson, U. Steigenberger, J. Tomkinson, *Spectrochim. Acta A* **1990**, *46*, 673.
[16] M. K. Johnson, D. B. Powell, R. D. Cannon, *Spectrochim. Acta A* **1981**, *37*, 995.
[17] A. Triantafillou, Ph.D. Thesis, University of East Anglia, **1993**.
[18] A. D. Taylor, E. J. Wood, J. A. Goldstone, J. Eckert, *J. Nucl. Instr. Meth.* **1984**, *221*, 408.
[19] F. Mezei, P. Vorderwisch, *Physica B* **1989**, *156*, 678.
[20] D. S. Sivia, P. Vorderwisch, R. N. Silver, *J. Nucl. Instr. Meth. A* **1990**, *290*, 492.
[21] J. B. Vincent, *Inorg. Chem.* **1994**, *33*, 5604.
[22] V. P. Tayal, B. K. Srivastava, P. Khandelwal, *Appl. Spec. Rev.* **1980**, *16*, 43.
[23] C. L. Thaper, B. A. Dasannacharya, A. Sequeira, P. K. Iyengar, *Solid State Commun.* **1970**, *8*, 497.
[24] S. P. Best, J. K. Beattie, R. S. Armstrong, *J. Chem. Soc. Dalton Trans.* **1992**, 299.
[25] T. E. Jenkins, J. Lewis, *Spectrochim. Acta A* **1981**, *37*, 47.

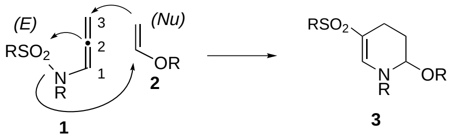
Efficient Entry to Tetrahydropyridines: Addition of Enol Ethers to Allenesulfonamides Involving a Novel 1,3-Sulfonyl Shift[**]

Yoshikazu Horino, Masanari Kimura, Yoshinori Wakamiya, Toshiya Okajima, and Yoshinao Tamaru[*]

Owing to the ground-state strain and the allylic stabilization of the resultant carbanion, allenes bearing electron-withdrawing substituents (W) are highly reactive toward nucleophilic addition at the central sp carbon atom [Eq. (a)].[1] Nucleophilic addition to the terminal sp^2 carbon atom of allenes, on the other hand, takes place with difficulty[2] owing to the lack of a substituent to stabilize the developing anionic charge on the central carbon atom.[3] Here we report that enol ethers **2** assist *N*-allenesulfonamides **1** to undergo a novel 1,3-shift of the sulfonyl group and eventually furnish tetrahydropyridines **3** in good to excellent yields [Eq. (b)]. The reaction is triggered most likely by nucleophilic attack of **2** at the terminal carbon atom of the allenic C2–C3 double bond, activated through space by the nearby sulfonyl group ($\pi^*_{C-C3} - \sigma^*_{N-S}$ interaction).



(a)



(b)

As reported recently from our laboratories,[4] 4-vinylidene-1,3-oxazolidin-2-one **1a**, when heated with electron-deficient or conjugated alkenes (e.g., styrene, 1,3-butadienes) at 70–100 °C, undergoes a facile [2+2] cycloaddition reaction via a concerted [$\pi_{2s}+\pi_{2s}+\pi_{2s}$] Hückel transition state to provide cyclobutane derivatives **4** in excellent yields. For example, **1a** reacts with methyl acrylate (**2a**) to provide **4a**, which can be isolated in 73% yield (Scheme 1). We were pleasantly surprised to find that methyl *β*-methoxyacrylate ((*E*)-**2b**) reacted in a completely different manner than **2a** (Scheme 1): When a mixture of **1a** (0.5 mmol) and (*E*)-**2b** (20 mmol) was

---

[*] Prof. Dr. Y. Tamaru, Y. Horino, Dr. M. Kimura, Y. Wakamiya
Department of Applied Chemistry, Faculty of Engineering
Nagasaki University
1-14 Bunkyo-machi, Nagasaki 852–8521 (Japan)
Fax: (+81) 958-47-9008
E-mail: tamaru@net.nagasaki.u-ac.jp
Dr. T. Okajima
Department of Chemistry, Faculty of Culture and Education
Saga University
1 Honjo, Saga 840–8502 (Japan)

[**] We thank Mr. Y. Ohhama (NMR facility) and Mrs. J. Nagaoka (X-ray facility) for their splendid technical assistance. Financial support by the Ministry of Education, Science, Sports and Culture, Japanese Government, is gratefully acknowledged.