ordinated base,[12] and the susceptibility toward hydrolysis which we observe for our reducing species is that expected for a $(H_2O)_2BH_2^+$ species. The ionic formulation for the reducing species is consistent with our inability to extract it into ether.

According to the above postulates, a cold acidic solution of $(H_2O)_2BH_2^+$, when neutralized with base, should evolve 1 mole of hydrogen/mole of $(H_2O)_2BH_2^+$, corresponding to hydrolysis to $H_2OBH(OH)_2$. This was proven to be the case in two experiments.

Unsolved Problems.—The extremely broad, featureless boron-11 nmr spectrum of the reducing species was very disappointing. McAchran and Shore[7] were unable to observe a well-defined spectrum of the $((CH_3)_2SO)_2BH_2^+$ ion, and Schaeffer, Tebbe, and Phillips[13] only observed a very broad $(\text{dioxane})_2BH_2^+$ signal. Apparently B^{11} quadrupole relaxation can be significant in ions of this type.[8] Boron-11 quadrupole relaxation also was probably responsible for our inability to see a proton nmr signal. Possibly B^{11} double-resonance experiments would be fruitful.

In our attempt to convert $(H_2O)_2BH_2^+$ to $[(CH_3)_3N]_2BH_2^+$, we necessarily neutralized the solution. According to our ideas regarding the relative stabilities of $(H_2O)_2BH_2^+$ and H_2OBH_2OH (expressed above), this neutralization caused deprotonation and hydrolysis of the reducing species. Our attempt to convert $(H_2O)_2BH_2^+$ to $[(CH_3)_3P]_2BH_2^+$ was unsuccessful probably because the trimethylphosphine was protonated in the acidic solution. It might be more worthwhile to attempt precipitation of insoluble salts of the $(H_2O)_2BH_2^+$ cation.

We were surprised to find that diborane reacts very slowly with cold aqueous acid. Under conditions such that diborane would react completely with an ethanol–water solution in about 20 min, diborane was only half-reacted with 8 *M* HCl in 3 hr. We can only surmise that the rate-determining step for the hydrolysis involves the attack of water and that the activity of water was so low in the acidic solutions as to reduce the rate significantly.

Acknowledgments.—We wish to thank Drs. Malcolm Judkins and Robert Marianelli for obtaining the B^{11} nmr spectra. This research was supported by the United States Atomic Energy Commission.

[12] N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964).

[13] R. Schaeffer, F. Tebbe, and C. Phillips, *Inorg. Chem.*, **3**, 1475 (1964).

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Neutron-Scattering Study of the Motions of Water Molecules in Hydrated Salts of Transition Metals[1]

BY J. J. RUSH,[2] J. R. FERRARO,[3] AND A. WALKER[3]

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The low-frequency motions of water molecules in a series of hydrated transition metal salts have been investigated by the energy-gain scattering of cold neutrons. The compounds studied include $CuSO_4 \cdot H_2O$, $CuSO_4 \cdot 5H_2O$, $Co(NO_3)_2 \cdot 2H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, and $UO_2(NO_3)_2 \cdot 6H_2O$. Broad bands observed in the spectra at neutron energy gains of 500–800 cm^{-1} are assigned to the wagging and rocking modes of the coordinated and hydrogen-bonded water molecules. Bands around 400–500 cm^{-1} are attributed both to $M–OH_2$ stretching modes and to the H_2O torsional vibrations around the bisectrix. Maxima are also observed at energy transfers below 300 cm^{-1}, which are tentatively assigned to hydrogen-bond stretching vibrations and possibly to $H_2O–M–OH_2$ deformation modes. Comparison of the various spectra appears to indicate that the average strength of binding of the water molecules does not change significantly in proceeding from the higher to the lower hydrates. The neutron results are compared in detail with previous infrared and structure results.

I. Introduction

Recent infrared spectra from 4000 to 70 cm^{-1} on a series of anhydrous and hydrated transition metal salts have provided considerable information concerning the coordination of anion groups and water molecules to the metal atoms.[4–6] In particular, the spectra indicate the existence of relatively strong metal–oxygen bonds to nitrate and sulfate anions in the anhydrous and lower hydrate salts. Low-frequency bands in the region 250–400 cm^{-1} have been assigned to the M–O stretching vibrations. These bands do not appear in the spectra for the penta- and hexahydrates, presumably because more water molecules enter the coordination sphere, and the anion groups move further away from the metal atoms. Other peaks in the infrared spectra of the hydrates in the region from 400 to 900 cm^{-1} have been attributed to $M–OH_2$ stretching modes of the coordinated water molecules, as well as to H_2O librations. The low-frequency motions of water molecules in these and other complex solids are many times difficult to observe or assign, however, owing to weak or

[1] Work supported by the U. S. Atomic Energy Commission.

[2] Argonne National Laboratory and National Bureau of Standards; address inquiries to this author at National Bureau of Standards.

[3] Argonne National Laboratory.

[4] J. R. Ferraro and A. Walker, *J. Chem. Phys.*, **42**, 1273, 1279 (1965).

[5] J. R. Ferraro and A. Walker, *ibid.*, **43**, 2689 (1965).

[6] J. R. Ferraro and A. Walker, *ibid.*, **45**, 550 (1966).

diffuse absorptions, or to the presence of a number of other normal or lattice modes in the same frequency region.

In the present experiments, we have investigated a number of the compounds for which infrared spectra have been measured,[4-6] including $CuSO_4 \cdot H_2O$, $CuSO_4 \cdot 5H_2O$, $Co(NO_3)_2 \cdot 2H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, and $UO_2(NO_3)_2 \cdot 6H_2O$, by the inelastic scattering of "cold" neutrons.[7] This type of scattering experiment involves the transfer of vibrational or rotational quanta from the sample to the incident neutrons, so that the scattered intensity from the various modes depends on the Boltzmann factor of populated states. Since the proton-scattering cross section is quite large and almost entirely incoherent,[8] the spectra of inelastically scattered neutrons from the crystal hydrates will primarily reflect the motions of the water molecules. In addition, the neutron technique[9] has no selection rules involving dipole moments or polarizabilities.

Previous neutron studies on hydrated salts[10-12] have yielded direct information on the librational and translational motions of the water molecules. These motions are influenced mainly by the coordination of the water oxygens to the metal ion and by hydrogen bonding with the outer ions. In the energy range covered by the cold-neutron technique ($\sim$40–1000 cm^{-1}), a number of different modes of the water molecules may result in spectral peaks. The librations around the A, B, and C axes of the H_2O molecules generally lie in the region 900–350 cm^{-1} and are designated as wagging, twisting, and rocking modes, respectively. If the water molecules are strongly coordinated to the metal atoms, M–OH_2 stretching modes (450–300 cm^{-1}) and O–M–O deformation modes ($\sim$150 cm^{-1}) may be observed.[4,13] In addition, if the H_2O molecules are hydrogen bonded to each other or to outer ions, hydrogen-bond (O–H$\cdots$O) stretching (250–150 cm^{-1}) or bending ($\sim$50 cm^{-1}) vibrations may contribute to the neutron spectra.

Our assignments for the peaks in the observed neutron spectra are primarily based on the above considerations. We further assume that the H_2O rocking and wagging modes in these compounds are at a higher frequency than the twisting (torsional) modes.[13] The analysis of the neutron spectra should provide information on the binding of the water molecules in the solid hydrates and on the changes that occur in proceeding from the higher to the lower hydrates.

II. Experimental Section

Samples.—The $CuSO_4 \cdot 5H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $UO_2(NO_3)_2 \cdot 6H_2O$ were reagent grade, polycrystalline chemicals. The lower hydrates were prepared as described previously.[4] A chemical analysis of the $UO_2(NO_3)_2 \cdot 6H_2O$ sample indicated a water content of 22 ± 1% by weight, compared to a theoretical value of 21.5%.

The thin, polycrystalline samples were backed with cadmium and contained in aluminum sample holders, which were milled out to the appropriate sample depth and covered by 0.35-mm aluminum windows. The neutron transmission of the samples, which were placed at an angle of 30° to the incident neutron beam, was 70% or higher in every case.

Neutron-Scattering Spectra.—The neutron spectra were measured using a cold-neutron facility at the CP-5 research reactor at Argonne National Laboratory. The ANL apparatus[14] utilized a beryllium filter, which removed neutrons with wavelengths less than 3.95 A ($E_n \geqq 5.2$ Mev) from the beam from the reactor and provided a neutron beam with an average energy of about 3.4 Mev (1 Mev = 8.07 cm^{-1}). A disk-type neutron chopper allowed periodic bursts of these neutrons to strike the scattering sample. The scattered neutrons were detected by a bank of $^{10}BF_3$ counters, placed at the end of a 3.1-m flight path at an angle of 60° to the incident beam. The velocity distribution of scattered neutrons was measured by conventional time-of-flight techniques, using a multichannel analyzer set at 25 μsec/channel. The scattered intensities were corrected for background, air scattering in the flight path, and counter efficiency.

It should be noted that the neutron method described here is a relatively course-resolution spectroscopic technique, owing to the width of the incident spectrum (full width at half-maximum $\approx$ 2 Mev), as well as to the finite burst time of the chopper. For example, a peak observed at an energy transfer of 25 Mev (202 cm^{-1}) will have an instrumental width at half-maximum of about 2.5 Mev. In addition, because of the dependence of neutron energy-gain scattering on the population of excited states, it is difficult at normal temperatures to observe vibrational transitions above about 1000 cm^{-1}.

III. Results and Discussion

The time-of-flight spectra of neutrons scattered by the various hydrate salts are shown in Figures 1–3. The elastic scattering of the incident cold neutrons is not included in the spectra but is indicated by a sharp increase in intensity at about channel 125. The energy-transfer scales included in the figures were obtained by subtracting the effective mean energy of the incident neutrons ($\bar{E}_n \cong 3.4$ Mev) from the scattered-neutron energies. Energy gains corresponding to the maxima on the time-of-flight spectra are indicated in cm^{-1}. The errors listed in the figures are the estimated uncertainties in the peak positions on the time-of-flight scale. They represent a combination of counting statistics (as indicated by the error bars) and uncertainties in the time-of-flight calibration.

$CuSO_4 \cdot H_2O$ and $CuSO_4 \cdot 5H_2O$.—The results for $CuSO_4 \cdot H_2O$ and $CuSO_4 \cdot 5H_2O$ are shown in Figure 1. The band peaked at 750 cm^{-1} in the monohydrate spectrum is assigned to the H_2O rocking and wagging librations.[13] The band centered at 450 cm^{-1} may be attributed to the Cu–OH_2 stretching vibrations of the coordinated water molecules, as well as to the tor-

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(7) A preliminary report of this work has already been presented (J. J. Rush, J. R. Ferraro, and A. Walker, paper presented at 16th Annual Mid-America Symposium on Spectroscopy, Chicago, Ill., June 1965).

(8) The scattering of neutrons from most hydrogenous compounds is 90% or more by the protons (see D. J. Hughes and R. B. Schwartz, "Neutron Cross Sections," BNL-325, 2nd ed, Brookhaven National Laboratory, 1958).

(9) For example, see P. A. Egelstaff, Ed., "Thermal Neutron Scattering," Academic Press Inc., New York, N. Y., 1965.

(10) H. Boutin, G. J. Safford, and H. R. Danner, *J. Chem. Phys.*, **40**, 2670 (1964).

(11) H. J. Prask and H. Boutin, *ibid.*, **45**, 699 (1966).

(12) J. J. Rush, P. S. Leung, and T. I. Taylor, *ibid.*, **45**, 1312 (1966).

(13) For a discussion of the various modes of coordinated water molecules in similar aquo complexes, as well as a theoretical and experimental study of a number of hydrates, see I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **20**, 429 (1964).

(14) See J. J. Rush and T. I. Taylor, "Inelastic Scattering of Neutrons," Vol. 2, International Atomic Energy Agency, Vienna, Austria, 1965, p 333. It should be pointed out that the apparatus described here was a temporary one. The present ANL facility utilizes a large volume of D_2O ice as a high-intensity source of cold neutrons, as well as a system of several phased neutron choppers and multiple detectors for time-of-flight analysis.

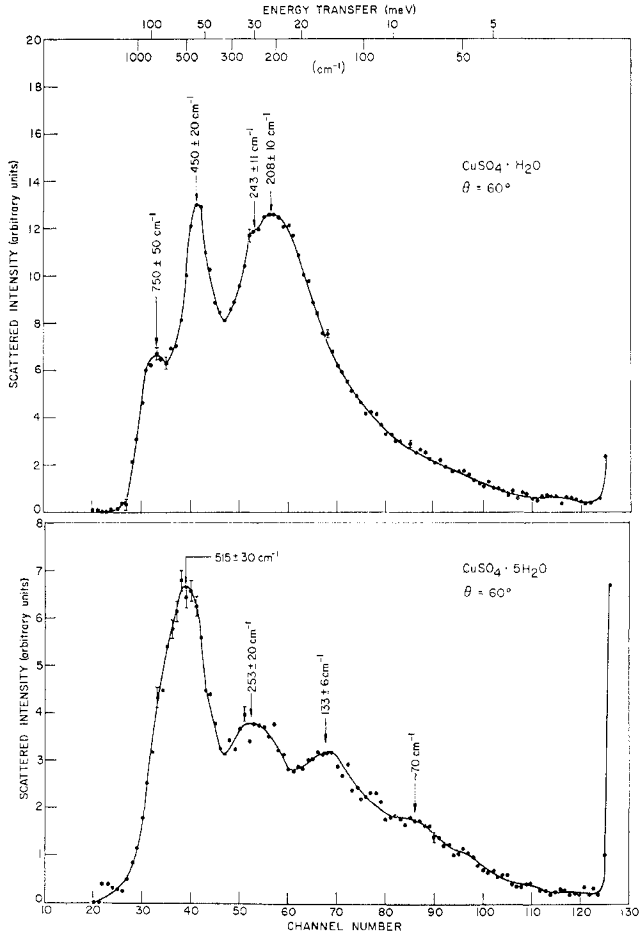

Figure 1.—Time-of-flight spectra of neutrons scattered at an angle $\theta = 60°$ by $CuSO_4 \cdot H_2O$ and $CuSO_4 \cdot 5H_2O$ at 293°K. The maxima are indicated in cm^{-1}, along with their estimated uncertainties.

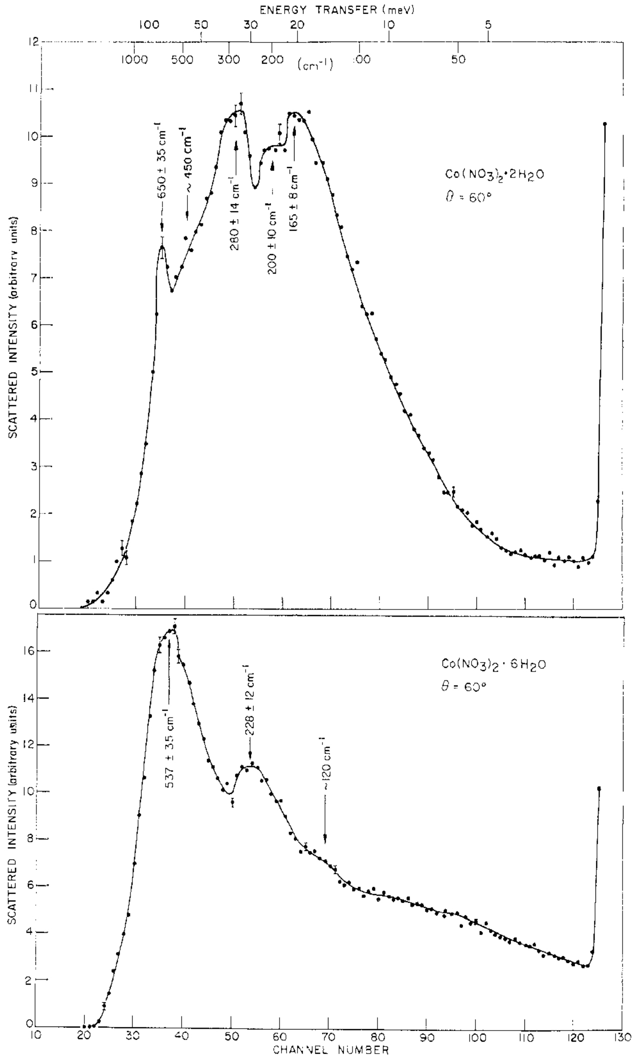

Figure 2.—Time-of-flight spectra of neutrons scattered by $Co(NO_3)_2 \cdot 2H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ at 293°K.

sional vibrations around the H_2O symmetry (B) axis, which are generally infrared inactive. Absorptions at 863 and 800 cm^{-1} and 410 cm^{-1} in the infrared spectra[4] were assigned to the $M-OH_2$ rocking and stretching modes, respectively, in reasonable agreement with the present results.

The structure of $CuSO_4 \cdot H_2O$ has been determined by X-ray diffraction to be monoclinic[15] and probably close to isostructural with $MgSO_4 \cdot H_2O$ and $CoSO_4 \cdot H_2O$.[16] In this arrangement, each copper atom would have six oxygen neighbors at distances around 2.0 A, four belonging to the sulfate ions and two to the water molecules. In addition, there would be two relatively close separations (~2.7–2.8 A) between the water and sulfate oxygens, which should represent hydrogen bonds. Such a structure is consistent with the neutron and infrared assignments. The relatively high librational and $Cu-OH_2$ stretching frequencies indicate strongly coordinated water molecules, which would agree with the short copper–water distance suggested above. The short metal–oxygen distances would also tend to confirm the assignment of a band in the infrared spectrum at 299 cm^{-1} to the Cu–O stretching modes of the coordinated sulfates.[4] Moreover, the presence of hydrogen bonds in the structure suggests that the maxima around 208 and 243 cm^{-1} in the neutron spectrum are due to hydrogen-bond stretching modes.

The spectrum in Figure 1 for $CuSO_4 \cdot 5H_2O$ is in reasonable agreement with a previous neutron result[10] and is quite different from the monohydrate spectrum. This can be qualitatively explained on the basis of structural differences between the two compounds. The structure of $CuSO_4 \cdot 5H_2O$ has been investigated by both X-ray[17] and neutron[18] diffraction and was determined to be triclinic, with two molecules per unit cell. Each copper atom is surrounded by an octahedron of oxygen atoms, four belonging to the water molecules and two to the sulfate ions. The $Cu-OH_2$ distances are short (1.94–1.99 A), while the $Cu-OSO_3$ distances (2.38 and 2.43 A) are considerably longer than those suggested above for the monohydrate. This indicates weak coordination of the sulfate ions and relatively strong coordination of the water molecules. The fifth

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(15) C. W. Pistorius, unpublished work. See "X-ray Powder Data File," Card No. 12-782, American Society for Testing Materials.

(16) R. W. G. Wyckoff, "Crystal Structures," Vol. 3, 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1965.

(17) C. A. Beevers and H. Lipson, *Proc. Roy. Soc.* (London), **A146**, 570 (1934).

(18) G. E. Bacon and N. A. Curry, *ibid.*, **A266**, 95 (1962).

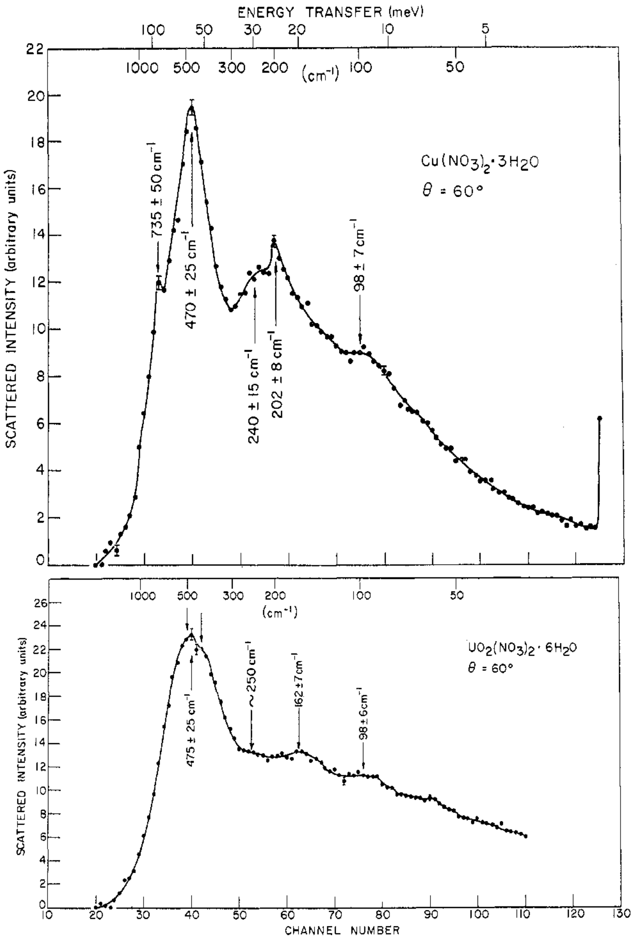

Figure 3.—Time-of-flight spectra of neutrons scattered by $Cu(NO_3)_2 \cdot 3H_2O$ and $UO_2(NO_3)_2 \cdot 6H_2O$ at 293°K.

water is not coordinated, but is hydrogen bonded in the lattice with one O–O distance of 2.99 A and three about 2.77 A. The four coordinated waters are also hydrogen bonded, with O–O distances in the range from 2.7 to 2.8 A.

The broad band peaked around 515 cm^{-1} in the pentahydrate spectrum in Figure 1 covers about the same range of energy transfers as the two higher energy bands in $CuSO_4 \cdot H_2O$. This band is again attributed to the H_2O librational modes and, possibly, on the low-energy side, to the $Cu–OH_2$ stretching vibrations. Such an unresolved band is consistent with the structure described above, since the presence of several different "types" of water molecules, some of which are coupled by hydrogen bonds, would be expected to produce a broad spectrum of overlapping librational modes. It is probable that a neutron measurement with improved resolution and statistics would reveal splitting in the observed peak. Absorptions in the infrared spectrum at 870 and 440 cm^{-1} have been assigned to the rocking and $Cu–OH_2$ stretching modes of the coordinated water molecules.[4,13]

The maxima around 253 and 133 cm^{-1} in the pentahydrate spectrum may be due to hydrogen-bond stretching vibrations and $H_2O–Cu–OH_2$ deformation modes,[13] respectively. In addition, it should be noted that the scattered intensity below 200 cm^{-1} in all of the hydrate spectra also includes contributions from a number of lattice-vibrational modes, including the oscillations of the sulfate (or nitrate) ions, as well as acoustic vibrations. Such modes contribute weakly to the spectra, owing to coupling with the H_2O molecules and because of the small but finite cross sections of the O, N, S, etc., nuclei in the crystal (~5–10% of the total scattering cross section).

$Co(NO_3)_2 \cdot 2H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$.—The spectra for the cobalt salts, shown in Figure 2, are analogous to the results for the hydrated copper sulfates. Neither of these compounds, however, has received a thorough structure analysis, although the unit cell parameters and space group for $Co(NO_3)_2 \cdot 6H_2O$ have been determined.[19]

The hexahydrate spectrum exhibits a broad, intense band peaked at 537 cm^{-1}, with an indication of a shoulder around 450 cm^{-1}, which can be assigned to overlapping H_2O librational peaks and $Co–OH_2$ stretching modes. This indicates strong coordination of a number of H_2O molecules to the cobalt atoms, as well as coupling through hydrogen bonds. The maxima around 228 and 120 cm^{-1} are also similar to those observed in $CuSO_4 \cdot 5H_2O$ and may again be due to hydrogen-bond vibrations and $H_2O–Co–OH_2$ deformation modes.

The cobalt atoms in $Co(NO_3)_2 \cdot 2H_2O$ are probably strongly coordinated to the nitrate ions (possibly through bidentate bonds), as well as to the two water molecules.[4] The results for the dihydrate show a relatively sharp band of water librations peaked at 650 cm^{-1}. An absorption at 650 cm^{-1} is also observed in the infrared spectrum and assigned to H_2O wagging modes and to the bending frequency (ν_5) of the coordinated nitrate ions.[4] A shoulder around 450 cm^{-1} in the neutron spectrum may be attributed to the Co–O stretch of the coordinated water molecules and possibly to torsional vibrations around the H_2O bisectrix. A weak absorption at 410 cm^{-1} in the infrared spectrum was assigned to the $Co–OH_2$ stretching vibrations. The maxima around 280 and 200 cm^{-1} could be assigned to hydrogen-bond modes, although the 280-cm^{-1} peak might also be due to metal–water stretching modes. The 165-cm^{-1} peak is again within the expected frequency range for $H_2O–Co–OH_2$ deformation modes.[13]

$Cu(NO_3)_2 \cdot 3H_2O$.—The structure of $Cu(NO_3)_2 \cdot 3H_2O$ is unknown, but the infrared results suggest strong coordination of both the nitrate ions and water molecules.[4] The spectrum for the trihydrate, shown in Figure 3, is similar to that for $CuSO_4 \cdot H_2O$. A shoulder peaked at 735 cm^{-1} is assigned to water librations. The broad band peaked at 470 cm^{-1} may again be assumed to include contributions from $Cu–OH_2$ stretching modes, as well as from the H_2O torsional and wagging vibrations. Absorptions at 895, 580, and 460 cm^{-1} in the infrared spectrum were attributed, respectively, to the rocking, wagging, and stretching modes of the coordinated water molecules. The maxima around 240,

(19) A. Jayaraman, *Proc. Indian Acad. Sci.*, **A47**, 147 (1958).

202, and 100 cm^{-1} are again in the region of hydrogen-bond modes and H_2O–Cu–OH_2 deformation frequencies, as previously discussed.

$UO_2(NO_3)_2 \cdot 6H_2O$.—Detailed structure studies on $UO_2(NO_3)_2 \cdot 6H_2O$ by X-ray[20] and neutron[21] diffraction have recently been completed. The unit cell is orthorhombic and contains four molecules. Each linear UO_2 group is surrounded equatorially by an irregular hexagon of oxygen atoms, four from two bidentate nitrate groups and two from symmetry-related water molecules. The two coordinated H_2O molecules (U–O distance = 2.4 A) are also strongly hydrogen bonded to uncoordinated waters, with O–H–O distances of 2.7 A. The uncoordinated H_2O molecules are tied into the structure by hydrogen bonds, including relatively strong bonds with other water oxygens (O–O distance = 2.70 and 2.76 A) and weaker bonds with nitrate oxygens (2.92 and 3.00 A).

The neutron spectrum for $UO_2(NO_3)_2 \cdot 6H_2O$ is shown in Figure 3. A broad band due to water librations is observed, with a maximum at 475 cm^{-1} and an indication of splitting. Such a spectrum is to be expected from the structure described above, with three "types" of water molecules (coupled by hydrogen bonds) providing a number of overlapping librational bands. Our result is also consistent with the assignment of absorptions at 570, 555, and 425 cm^{-1} in the infrared spectrum for this compound to H_2O modes,[6] although the width of the neutron band appears to infer additional librational modes at higher frequencies. The neutron diffraction results indicate that the coordinated H_2O molecules have a lower mean-square displacement than the other molecules.[21] Thus the coordinated waters probably contribute mainly to the high-frequency part of the librational band.

The diffuse distribution of scattered neutrons below 300 cm^{-1} also exhibits several maxima, including two around 250 and 162 cm^{-1}, which may be assigned the translational modes of the H_2O molecules. Moreover, transitions involving metal–H_2O deformation modes and other lattice modes should contribute to the distribution at lower energies.

A comparison of the spectra for the higher hydrates in Figures 1–3 shows that the librational and probably the translational modes of the water molecules in $UO_2(NO_3)_2 \cdot 6H_2O$ are generally at lower frequencies than those in $Co(NO_3)_2 \cdot 6H_2O$ and $CuSO_4 \cdot 5H_2O$. This would indicate that the H_2O molecules are more loosely bound in the uranyl salt than in the other higher hydrates. Such a conclusion is consistent with the fact that only one-third of the waters in the $UO_2(NO_3)_2 \cdot 6H_2O$ lattice are coordinated to the uranium atoms. In addition, the average hydrogen-bond length is somewhat longer in this hydrate than in $CuSO_4 \cdot 5H_2O$.

Corrected Librational Frequencies.—As mentioned in the Introduction, the spectra shown in Figures 1–3 are strongly influenced by the Boltzmann factor of populated states in the scattering system. Owing to this effect, as well as to the fact that the neutron intensity is plotted on a time-of-flight scale, the observed spectra provide only a distorted picture of the actual frequency distribution. At energy transitions considerably greater than kT, the time-of-flight peak positions may be considerably different from their "real" values. In view of this, we have transformed the high-energy part (>300 cm^{-1}) of all the time-of-flight spectra to a linear energy scale and then corrected the resulting distributions for the dependence of the scattering cross section on the Boltzmann factor and on the momentum transfer to the neutrons.[22] The resulting peak positions are listed in Table I, along with the uncorrected time-of-flight values and the infrared absorptions assigned to H_2O modes in the same frequency region. The approximate widths of some librational bands are also indicated.

TABLE I

COMPARISON OF CORRECTED NEUTRON PEAK ENERGIES WITH INFRARED RESULTS[a]

	Peak frequencies, cm^{-1}			
Compound	Neutron (TOF)	Neutron (cor)[b]	Band widths	Infrared
$CuSO_4 \cdot H_2O$	750 ± 50	860[c]	~500	863, 800, 550
	450 ± 20	450[d]		410
$CuSO_4 \cdot 5H_2O$	515 ± 30	600[c]	~560	870
		~400[d]		442
$Co(NO_3)_2 \cdot 2H_2O$	650 ± 35	650[c]		650
	~450	~475[d]		410
$Co(NO_3)_2 \cdot 6H_2O$	537 ± 35	630[c]	~500	No absorptions
	~450	~450[d]		
$Cu(NO_3)_2 \cdot 3H_2O$	735 ± 40	735, 620[c]		895, 580
	470 ± 25	470[d]		460
$UO(NO_3)_2 \cdot 6H_2O$	475 ± 25	535[c]	~560	570, 555
		420[d]		425

[a] Only water bands in the frequency range above 300 cm^{-1} are included. [b] Corrected peak positions. Estimated percentage errors are roughly the same as those listed for the time-of-flight peaks. [c] Assigned to H_2O rocking and wagging modes. [d] Tentatively attributed to M–OH_2 stretching modes and to H_2O torsional (B axis) vibrations.

Significant shifts in peak frequencies are observed for the very broad librational bands in the higher hydrates, since the Boltzmann-factor correction is sufficient to raise the intensity on the high-energy side of the bands above that at the time-of-flight peak position. This effect is less for the narrower bands, so that their peak positions show little or no shift. The "corrected" peaks are in somewhat better agreement with the infrared results than the time-of-flight peaks. It should be noted, however, that one-phonon infrared absorption bands in general only cover optical vibration modes at wave vectors ($q = 2\pi/\lambda$) very near $q = 0$,[23] whereas the neutron spectra represent energy transfers over a wide range of wave vectors for each optic (and acoustic) branch.[9] Thus for modes in which

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[20] D. Hall, A. D. Rae, and T. N. Waters, *Acta Cryst.*, **19**, 389 (1965).

[21] J. C. Taylor and M. H. Mueller, *ibid.*, **19**, 536 (1965).

[22] In performing these calculations, the differential neutron-scattering cross section of the hydrates was assumed to involve only one-phonon incoherent, scattering processes from a cubic crystal, with the Debye–Waller factor (e^{-2W}) equal to 1 (ref 9, p 30). For a more detailed discussion of such a calculation, see, for example, H. Boutin, *et al.*, *J. Chem. Phys.*, **40**, 1417 (1964), and J. J. Rush, *et al.*, *ibid.*, **45**, 3817 (1966). The psuedo-frequency distributions obtained under these assumptions might be seriously inaccurate with regard to the relative intensities and widths of the various peaks. The actual peak positions, however, should be reasonably well determined

[23] See, for example, S. S. Mitra and P. J. Gielisse, "Infrared Spectroscopy," Vol. 2, H. A. Szymanski, Ed., Plenum Press, New York, N. Y., 1964, p 47.

there is considerable dispersion in ω vs. q owing to intermolecular coupling in the crystal lattice, infrared measurements on solids are not necessarily expected to agree closely with neutron results.

IV. Conclusion

The H_2O librational and translational bands assigned from the present neutron study on a series of transition metal hydrates are generally consistent with previous infrared and structural results. The average strength of binding of the water molecules (as indicated by the H_2O bands) does not appear to change significantly in proceeding from the higher to the lower hydrates. A comparison between the librational bands in $UO_2(NO_3)_2\cdot 6H_2O$ and the other higher hydrates indicates somewhat weaker binding for the H_2O molecules in the uranyl salt. It is probable that neutron-scattering measurements with higher resolution would result in better separation of the broad, overlapping peaks in the neutron spectra.

Acknowledgments.—The authors are indebted to D. W. Connor and O. C. Simpson of the Solid State Science Division at Argonne for their encouragement of this work and to G. Ostrowski for his assistance in taking the data.

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The Reactions of N,N-Bis(trifluoromethyl)hydroxylamine with Perfluoroacyl and Carbonyl Halides

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N,N-Bis(trifluoromethyl)hydroxylamine reacts with either CsF or KF to form a solid adduct. This adduct reacts with COF_2 to form $[(CF_3)_2NO]_2CO$ and $(CF_3)_2NOC(O)F$ and with $COCl_2$ to form $(CF_3)_2NOC(O)Cl$. $(CF_3)_2NOC(O)CF_3$ and $(CF_3)_2NOC(O)C_3F_7$ are obtained with the perfluoroacyl chlorides, $CF_3C(O)Cl$ and $C_3F_7C(O)Cl$, respectively. These compounds have been characterized and the N,N-bis(trifluoromethyl)hydroxylamine–metal halide adduct is discussed.

Very few of the reactions of N,N-bis(trifluoromethyl)hydroxylamine,[1] $(CF_3)_2NOH$, have been investigated. It reacts with a variety of substances to give the bis(trifluoromethyl)nitroxide radical[2–4] and with PCl_5 to give bis(trifluoromethyl)amine.[1]

Fluorinated amidoximes of the type $R_fC(NH_2)=NOH$ react with fluorinated acid chlorides in ether solution to give solid compounds of the general formula $R_fC(NH_2)=NOC(O)R_f$.[5] Fawcett[6] has reported that carbonyl fluoride reacts with bis(trifluoromethyl)amine in the presence of CsF catalyst at 300° and with $\overline{\lfloor(CH_2)_5\overset{O}{C}NH\rfloor}$ to give $(CF_3)_2NC(O)F$ and $\overline{\lfloor(CH_2)_5\overset{O}{C}N\rfloor}$-C(O)F, respectively.

Our investigations have shown that N,N-bis(trifluoromethyl)hydroxylamine and either CsF or KF form an adduct which reacts with acid halides to give products of the general formula $(CF_3)_2NOC(O)X$. Compounds where X = F, Cl, CF_3, C_3F_7, and $ON(CF_3)_2$ have been prepared and characterized. The nature of the $(CF_3)_2NOH$–metal fluoride adduct has been examined.

Experimental Section

Reagents.—Cesium fluoride (99%), trifluoroacetyl chloride, and heptafluorobutyryl chloride were obtained from K & K Laboratories. Carbonyl fluoride was prepared by the room-temperature reaction of an equimolar mixture of carbon monoxide (Matheson Co.) and fluorine and was purified by fractional codistillation.[7] Carbonyl chloride was obtained from the Matheson Co. and anhydrous potassium fluoride (Allied Chemical) was used. N,N-Bis(trifluoromethyl)hydroxylamine was prepared by reaction of $(CF_3)_2NONO$[8] with aqueous HCl[1] in the presence of mercury and was purified by fractional codistillation.

General Methods.—All reactions were carried out in 100-ml Pyrex bulbs connected to a stopcock through a 19/38 ₮ Pyrex joint. Prior to reaction the finely divided metal fluoride was placed in the bulb and heated at 200° for 10 min under dynamic vacuum to remove any water. The metal fluoride–N,N-bis(trifluoromethyl)hydroxylamine adduct was formed simply by condensing the hydroxylamine onto the fluoride at −183°. When the contents had warmed to room temperature, the acid chloride or the carbonyl compound was added using standard vacuum techniques. The reaction occurred smoothly and usually within 0.5 hr. Infrared spectra were obtained using a Beckman IR5A infrared spectrophotometer. All spectra were recorded in the gas phase with a Pyrex cell of 25-mm path length and sodium chloride windows. A Varian Model 4311B high-resolution nuclear magnetic resonance spectrometer was used to determine the nmr spectra at 40 Mc. Trichlorofluoromethane was used as an internal standard. Mass spectra were recorded using a Consolidated Engineering Corp. Type 21-103 mass spectrometer. Molecular weights were determined by Regnault's method. Vapor pressure data were obtained by holding the com-

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[1] R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 1741 (1957).
[2] W. D. Blackley and R. R. Reinhard, *J. Am. Chem. Soc.*, **87**, 802 (1965).
[3] S. P. Makarov, A. Ya. Yakubovich, S. S. Dubov, and A. N. Medvedev, *Dokl. Akad. Nauk SSSR*, **160**, 1319 (1965).
[4] R. E. Banks, R. N. Haszeldine, and M. J. Stevenson, *J. Chem. Soc.*, 901 (1966).
[5] H. C. Brown and C. R. Wetzel, *J. Org. Chem.*, **30**, 3735 (1965).
[6] F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 4275 (1962).
[7] G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).
[8] J. Jander and R. N. Haszeldine, *J. Chem. Soc.*, 696 (1954).