Infrared Absorption Spectra of Water of Crystallization in Cobaltous Chloride Hexa- and Dihydrate Crystals

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The infrared absorption spectra of cobaltous chloride hexahydrate and dihydrate have been separately subject to two investigations[1,2]. However, there has been no comparative study of the two crystals in relation to their structural difference.

In the present paper, observed spectra were examined in relation to the difference of the binding states of the water molecules in them. The two crystals have an advantage over the hydrated salts of oxy-acids such as hydrated sulfates, because all the observed bands can be attributed to the vibrations of water molecules without ambiguity except for those due to the skeletal vibrations of the metal atom and ligands. Furthermore their structures are well determined by X-ray diffraction[3] and by electron diffraction[4] respectively.

Experimental

Preparation. — Commercial cobaltous chloride hexahydrate of guaranteed grade was recrystallized from water. Cobaltous chloride dihydrate was obtained by keeping the purified hexahydrate over calcium chloride at ordinary temperature for 24 hr.[5]

Measurement.—Spectra were recorded by means of a Kôken DS 301 infrared spectrophotometer using a sodium chloride or potassium bromide prism. The potassium bromide disk technique was employed.

Results

The spectra are given in Fig. 1. In the 3 μ region one peak is observed for the hexahydrate at 3430 cm^{-1}, and one shoulder and two peaks for the dihydrate at 3564, 3444 and 3226 cm^{-1}. These are comparable to the peaks of various inorganic hydrated salts[6] in this region, and can be assigned to the O–H stretching vibrations of water molecules affected by coördination on a cobalt atom and by the hydrogen bonding with a chlorine atom or an oxygen atom of an outer water molecule. Overlapping of several stretching bands is probably responsible for the broadness of the band for the hexahydrate. In the 6 μ region, two bands of medium intensity are observed at 1625 and 1599 cm^{-1} for the hexahydrate. The latter is fairly sharp. Both can be assigned to the bending mode of water molecules, the former being presumably due to a ligand water

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[1] J. Lecomte, *J. chim. phys.*, **50**, C 53 (1953).

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[3] J. Mizuno, K. Ukei and T. Sugawara, *J. Phys. Soc. Japan*, **14**, 383 (1959).

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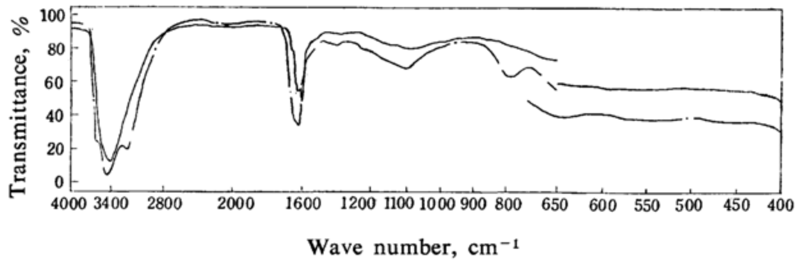

Fig. 1. Observed bands of $CoCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 2H_2O$.

――――― $CoCl_2 \cdot 6H_2O$ —·—· $CoCl_2 \cdot 2H_2O$

molecule and the latter to a water molecule free from coördination. For the dihydrate, one band of medium intensity is observed at 1610 cm⁻¹. It can be assigned to the bending mode of a ligand water molecule. In the 9 μ region, the spectrum of the hexahydrate shows a very broad weak band at 1090 cm⁻¹, and that of the dihydrate shows a similar one at 1100 cm⁻¹. The origins of these bands cannot be decided at present. Probably they are the combinations or overtones of some restricted rotation modes of water molecules. The band observed at 790 cm⁻¹ for the dihydrate can be attributed to the wagging vibration of a ligand water molecule affected by hydrogen bonding, because of its position, intensity and shape. The bands so far reported were observed in the sodium chloride region.

In the potassium bromide region, no band was observed for the hexahydrate. For the dihydrate only one very broad band was observed at 642 cm⁻¹. It is tentatively attributed to the rocking mode of the water molecule which is responsible for the wagging band at 790 cm⁻¹, because the twisting band of a water molecule is usually too weak to be observed. It cannot be assigned to any skeletal vibration of the metal atom and ligands since the skeletal vibration bands should appear in a lower frequency region.

Tables I and II summarize these results.

TABLE I. OBSERVED FREQUENCIES OF $CoCl_2 \cdot 6H_2O$

Wave number, cm⁻¹	Assignment
3430 s	O–H stretch.
1625 m	H–O–H bend.
1599 m, sh	H–O–H bend.
1090 w, v.b	

TABLE II. OBSERVED FREQUENCIES OF $CoCl_2 \cdot 2H_2O$

Wave number, cm⁻¹	Assignment
3564 s, shoulder	
3444 s	O–H stretch.
3226 s	O–H stretch.
1610 m	H–O–H bend.
1100 w, v.b	
790 w, b	H_2O wag.
642 m, v.b	H_2O rock.

Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, sharp.

Discussion

According to X-ray analysis³⁾, four water molecules and two chlorine atoms in cobaltous chloride hexahydrate are coördinated on the cobalt atom, making an octahedron with the cobalt atom at the center. Two other water molecules are far distant from the cobalt atom, and each of their oxygen atoms forms a hydrogen bond with one of the two O–H bonds of a ligand water molecule. The other O–H bond of this water molecule forms another hydrogen bond with a chlorine atom of a neighboring octahedron (for details, see Fig. 2).

An electron diffraction study⁴⁾ shows that two water molecules and two chlorine atoms in

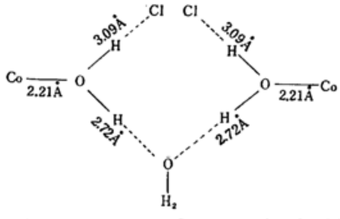

Fig. 2. Arrangement of atoms in $CoCl_2 \cdot 6H_2O$.

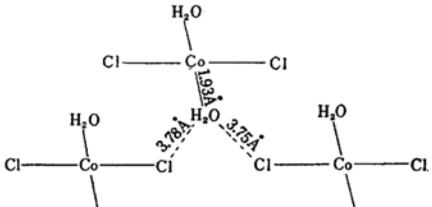

Fig. 3. Arrangement of atoms in $CoCl_2 \cdot 2H_2O$*.

* The three parallelograms are respectively in different planes. The values 3.75 and 3.78 Å were calculated from the data in Ref. 4.

cobaltous chloride dihydrate are coördinated on the cobalt atom, making a parallelogram with the cobalt atom at the center (Fig. 3).

As in the previous studies(6,7), it shall be assumed that the water frequencies are influenced by coördination and hydrogen bonding.

As is seen from Fig. 2, at least four O–H stretching frequencies are expected theoretically for the hexahydrate: one for the O–H bond of the ligand water molecule which forms the hydrogen bond O–H···Cl, one for the bond O–H···O, and two (symmetric and antisymmetric) for the almost free water molecule. The peak observed at 3430 cm^{-1} probably corresponds to either one of the first two, because the frequency shift from the value of the vapor state is of the same order as in many cases(6) where the water molecule is affected by coördination and hydrogen bonding. The last two frequencies should appear in a higher region since they correspond to an almost free water molecule. Probably they are weak and hidden in the above-mentioned band.

In the dihydrate, the nearest distance between a ligand water molecule and a chlorine atom of a neighboring parallelogram is 3.75 Å, and the next to the nearest distance is 3.78 Å. The two observed bands, at 3444 and 3226 cm^{-1} can be explained in relation to the crystal structure by the following assumption: one of the O–H bonds of the ligand water molecule forms a hydrogen bond with one of these two chlorine atoms, and the other is free from hydrogen bonding. We can correlate the 3226 cm^{-1} band with the fomer O–H bond and the 3444 cm^{-1} band with the latter since hydrogen bonding lowers the stretching frequency and the coördination effects are equal in the two cases. It is unlikely that one of the O–H bonds forms a hydrogen bond of distance 3.75 Å and the other forms a hydrogen bond of distance 3.78 Å respectively with each of the two chlorine atoms, because the frequency difference of 218 cm^{-1} is far too great to be explained by the difference of the hydrogen bond distances 0.03 Å since the stretching frequency is relativery insensitive to the hydrogen bonding effect. The shoulder at 3564 cm^{-1} cannot be interpreted for the present.

For the bending vibration in the hexahydrate two frequencies are observed. They can be explained readily from the crystal structure. The higher frequency (1625 cm^{-1}) can be attributed to the mode of the coördinated and hydrogen bonded water molecule, and the lower frequency (1599 cm^{-1}), the value of which is almost equal to that of the vapor state frequency (1595 cm^{-1}), can be assigned to the almost free water molecule since in general the two effects are likely to increase the bending frequency(8). For the dihydrate there is observed only one bending frequency (1610 cm^{-1}), corresponding to the fact that there is only one kind of water molecule in the unit cell of the crystal. It is 15 cm^{-1} lower than that for the ligand water molecule in the hexahydrate. This indicates that the additive effect of coördination and hydrogen bonding is greater in the hexahydrate than in the dihydrate although the coördination distance between the cobalt atom and the water molecule is somewhat shorter, and so the coördination effect is greater in the dihydrate.

The position and the shape of the wagging band at 790 cm^{-1} for the dihydrate are reasonable as compared with those in the usual cases. For the hexahydrate no band was observed in this region. (These results suggest that the band at 781 cm^{-1} reported for the hexahydrate in a previous paper(6) may be in fact due to the dihydrate which may have happened to be produced by partial dehydration of part of the hexahydrate during the vacuum process in the preparation of the KBr disk.)

The position and the shape of the rocking band at 642 cm^{-1} for the dihydrate seem also to be reasonable. The frequencies of the wagging and the rocking band are somewhat lower than the corresponding frequencies for aluminum sulfate octodecahydrate(8) respectively.

Summary

The observed spectra of the water of crystallization were interpreted by the effects of coördination and hydrogen bonding. The total difference in the spectra of the two crystals was explained in relation to the difference in their atomic arrangements.

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7) I. Gamo, ibid., 34, 764 (1961).

8) I. Gamo, ibid., to be published.