Chemistry

1963

SovietRxiv

Abstract

Full Text

Chemistry

S. N. Andreev, T. G. Balicheva

On the State of Water Molecules in Crystal Hydrates of Salts of Certain Elements

(Presented by Academician I. I. Chernyaev, 16 V 1962)

The solution of the problem of ion hydration is inseparably connected with the study of the properties of water molecules that constitute the immediate environment of ions in aqueous solutions. The works of P. Pfeiffer ([1]), A. Werner ([2]), and A. A. Grinberg ([3]) showed that water molecules entering the inner sphere of a complex are capable of protolytic dissociation. Studies of the interaction of metal powders with salt crystal hydrates established that water molecules in crystal hydrates in a number of cases behave as strong acids ([4]).

In the chemical literature, the ability of coordinated molecules to undergo protolytic dissociation is assessed mainly from the standpoint of the polarizing action of the cation—the complex former—on the coordinated molecules ([3,5]). The role of the particles forming the outer coordination sphere of cations in solutions, as a rule, is not considered in this connection.

The extremely low polarity of the O–H bond in isolated water molecules, found recently in the quantum-mechanical calculation of L. Bernell and C. Coulson ([6]), required the assumption, made by I. V. Aleksandrov and N. D. Sokolov ([7]), that significant polarization of the O–H bond occurs in the process of formation of a hydrogen bond. Data on the magnetic shielding of the proton upon formation of a hydrogen bond confirmed this hypothesis.

Infrared spectra are very sensitive to the formation of a hydrogen bond. A quantum-mechanical calculation by N. D. Sokolov shows that the formation of a hydrogen bond of the type R_1—O—H ... R_2 and the loosening of the O–H bond are accompanied by a shift of the frequency of the valence O–H vibrations into the long-wavelength region. The magnitude of this shift is proportional to the energy of the hydrogen bond being formed ([8]):

$$\frac{\Delta\tilde{\nu}}{\tilde{\nu}_0} \simeq \rho\frac{\varepsilon}{D},$$

where $\tilde{\nu}_0$ is the frequency of the valence O–H vibrations in the isolated molecule, in reciprocal centimeters; $\Delta\tilde{\nu}_0$ is the shift of this frequency under the action of a hydrogen bond; ρ is a proportionality coefficient equal to 0.016 kcal^{-1}; ε is the

energy of the hydrogen bond in kilocalories; D is the dissociation energy of the O–H bond in the isolated H_2O molecule, equal to 110 kcal. These data indicate that, in assessing the state of the O–H bond in water molecules forming the immediate environment of cations in aqueous solutions, along with the polarizing action of the cation on the O–H bond, one should also take into account the influence on this bond of those hydrogen bridges that may be formed between coordinated water molecules and particles (anions, water molecules) entering the outer coordination sphere of the cation.

Thus, when discussing the polarity of the O–H bond in H_2O molecules forming the immediate hydrate environment of cations in aqueous solutions, one should consider not the groupings $Me^{n+} \dots H_2O$, but the groups $Me^{n+} \dots H_2O \dots A$, where A is the salt anion or water molecules of the more distant hydrate environment of the cation.

In the present work we attempt to estimate the influence of the nature of the cation and of the anion located in the outer coordination sphere on the force constant of the O–H bond of water molecules forming the immediate environment of the cation. We solved this problem by measuring the shift of the frequency of the valence O–H vibration of coordinated water molecules in their IR spectra. In the spectra of aqueous salt solutions the absorption band of coordinated water molecules and the absorption band of water molecules not included in complexes overlap so strongly that it would be very difficult to make any assumptions about the state of the O–H bond from these spectra. Therefore we undertook a study of the vibrational frequencies of coordinated water molecules in the following crystalline hydrates:
$Mn(ClO_4)_2 \cdot 6H_2O$, $Co(ClO_4)_2 \cdot 6H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, $Fe(ClO_4)_2 \cdot 6H_2O$, $Zn(ClO_4)_2 \cdot 6H_2O$, $Ca(ClO_4)_2 \cdot 6H_2O$. The first five crystals are isostructural; the dimensions of their unit cells differ very little, and the ions Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+} have almost the same radius.

In a first approximation it may be assumed that the Madelung potential, whose magnitude should not be neglected when discussing the state of the O–H bond in coordinated water molecules, has one and the same value in these crystals. The interatomic distances in the compounds listed permit the formation of two types of hydrogen bond: $H_2O \dots H_2O$ and $H_2O \dots OClO_3^-$. This gives grounds to expect the appearance in the IR spectra of these crystals of two frequencies corresponding to the valence O–H vibrations of water molecules interacting with the cation and with particles of the outer coordination sphere according to two schemes:

$$Me^{2+} \dots H_2O \dots OClO_3^- \quad \text{and} \quad Me^{2+} \dots H_2O \dots H_2O.$$

Fig. 1. Dependence of the optical density of crystals on the wave number $\tilde{\nu}$: **1**–absorption in a crystal of $Ni(ClO_4)_2 \cdot 6H_2O$, layer thickness $d \simeq 15\,\mu$; **2**–absorption in a crystal of $NiSO_4 \cdot 6H_2O$, $d \simeq 10\,\mu$.

Information on the vibrational spectra of these crystalline hydrates is very scanty and relates mainly to the region 500-2100 cm^{-1} ([9,10]). Large single-crystal specimens of the compounds listed were grown by us by the planetary-rotation method with a gradual lowering of the solution temperature from 30 to 15°. From the single crystals, plates of dimensions $10 \times 10 \times 3$ mm^3 were cut parallel to one of the faces of the hexagonal prism. By grinding and then polishing with a mixture of crocus and vaseline oil, the thickness of the plate was brought to 10-20 μ. The thickness of the plates was measured with an accuracy of 1-2 μ on an IKB-1 vertical optimeter.

The absorption spectra of the crystalline plates were recorded in natural radiation, point by point, on an IKS-6 IR spectrometer with a Hilger galvanometer-type projection system and on an IKS-14 recording spectrometer with LiF prisms. The absorption curves obtained by us are given in Figs. 1 and 2.

The IR spectra of the hexahydrates of the perchlorates of Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+} are identical, and in Fig. 1 they are represented by a single absorption curve. The maxima of the curve are at 3530 and 3440 cm^{-1}. We assign the first of these to O–H vibrations in the groups $Me^{2+} \ldots H_2O \ldots OClO_3^-$, the second to O–H vibrations in $Me^{2+} \ldots H_2O \ldots H_2O$.

We indicated above the possibility of formation of such groups: the data of X-ray structural analysis of these crystalline hydrates, given in the work of West ([11]), make it possible to calculate the distances $H_2O \ldots H_2O$ and $H_2O \ldots OClO_3$. The latter are equal to 2.92 and 2.98 Å.

The frequency of the valence O–H vibrations of the crystal $Ca(ClO_4)_2 \cdot 6H_2O$ is shifted into the high-frequency region by almost 130 cm^{-1} in comparison with the frequency of the same vibrations in crystals of the perchlorate hexahydrates of Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+}. The data given show that the dif–

the loosening action of the ions Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+} on the $O—H$ bond in coordinated water molecules is practically the same. Consequently, it is not the chemical nature of these cations, but their charge and radius, that are responsible for the polarization of the $O—H$ bond of water molecules forming the nearest hydrate environment.

In water molecules coordinated by the Ca^{2+} ion, which has a considerably larger radius, the $O—H$ bond is loosened to a much smaller extent.

To clarify the question of the influence on the $O—H$ bond of water molecules constituting the hydrate shell of the cation, of the hydrogen bonds of these molecules with anions of the outer sphere, we compare the frequencies of the $O—H$ vibrations of the crystals $Ni(ClO_4)_2 \cdot 6H_2O$ and $NiSO_4 \cdot 6H_2O$. The frequency of the $O—H$ vibrations in the groups $Ni^{2+}—H_2O \ldots OSO_3^{2-}$ is shifted into the low-frequency region by almost 300 cm^{-1} in comparison with the frequency of the same vibrations in the groups $Ni^{2+}—H_2O \ldots OClO_3^-$, which indicates a greater loosening of the $O—H$ bond of the water molecules in the former case. We suppose that the reason for this is, first, the difference in the

Fig. 2. Absorption in a crystal of $Ca(ClO_4)_2 \cdot 6H_2O$; layer thickness was not measured

Figure 1: Fig. 2. Absorption in a crystal of $Ca(ClO_4)_2 \cdot 6H_2O$; layer thickness was not measured

distances $H_2O \ldots OSO_3^{2-}$ and $H_2O \ldots OClO_3^-$, which are equal to 2.71 and 2.98 Å, respectively ([12]); second, the difference in the chemical nature of the oxygen of the anion: the oxygen of the SO_4^{2-} anion bears an excess of negative charge in comparison with the oxygen atoms of the ClO_4^- anion. Consequently, the hydrogen bond $H_2O \ldots OSO_3^{2-}$ must be stronger than the bond $H_2O \ldots OClO_3^-$, and the O—H bond in the former case must be loosened more than in the latter.

Fig. 2. Absorption in a crystal of $Ca(ClO_4)_2 \cdot 6H_2O$; layer thickness was not measured.

The data presented indicate that, when considering the state of the O—H bond in water molecules coordinated by a cation, one should evaluate not only the polarizing action of the cation on this bond, but also the action on it of particles entering the outer sphere of the aquo complex. Replacement of the ClO_4^- ions, which form the more distant environment of the Me^{2+} cations in aquo complexes $[Me(H_2O)_6](ClO_4)_2$, by SO_4^{2-} anions exerts no smaller an influence on the O—H bond of the coordinated water molecules than does a change in the chemical nature of the cation.

Leningrad State University
named after A. A. Zhdanov

Received
17 II 1962

REFERENCES CITED

1. P. Pfeiffer, Ber., **39**, 1864 (1906).
2. A. Werner, *New Views in the Field of Inorganic Chemistry*, L., 1936.
3. A. A. Grinberg, ZhFKh, **4**, 204 (1933).
4. V. I. Semishin, ZhNKh, **10**, 319, 328, 339 (1940).
5. A. A. Grinberg, *Introduction to the Chemistry of Complex Compounds*, 1951.
6. L. Burnell, C. A. Coulson, Trans. Farad. Soc., **53**, 403 (1957).
7. I. V. Aleksandrov, N. D. Sokolov, DAN, **124**, 115 (1959).

8. N. D. Sokolov, Usp. fiz. nauk, **57**, 244 (1955).

9. J. Miller, C. Wilkins, Anal. Chem., **24**, 1253 (1952).

10. B. J. Hathaway, A. E. Underhill, J. Chem. Soc., **1961**, No. 7, 3091.

11. C. D. West, Zs. Kristallogr., **91**, 480 (1935).

12. C. A. Beevers, H. Lipson, Zs. Kristallogr., **83**, 123 (1932).

Note: Figure translations are in progress. See original paper for figures.