Studies of Crystal Hydrates. VII.[1] *The Dielectric Properties of Capillary Water in Single Crystals of* DL-$[Co(en)_3]Cl_3 \cdot nH_2O$*

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The molecules of water of crystallization in DL-$[Co(en)_3]Cl_3$ hydrate are packed in linear, four-lane array in cylindrical channels which extend in the direction of the crystallographic c axis of this hexagonal crystal.[2] The partial dehydration of the hydrate crystal does not produce any substantial change in its X-ray diffraction patterns; this suggests a zeolitic nature of the dehydration. The thermodynamic properties of the dehydration[3] are also consistent with the structural studies and, further, suggest that the water is in a state similar to capillary-condensed water, such as is found in zeolite minerals. Water molecules in zeolites are usually so mobile that they are detected by means of high-resolution nuclear magnetic resonance at room temperatures.[4] However, the structural studies of zeolites have not been successful in locating the water molecules in the crystal lattice, and even had this been done, the arrangement of water molecules would still be quite complex.

The water molecules in DL-$[Co(en)_3]Cl_3 \cdot nH_2O$, where n runs from 0 to 4, were located by the X-ray diffraction technique; a brief account of the structure and the arrangement of the water molecules has already been given in a previous paper.[3] An investigation into the extent to which these molecules are mobile in the crystalline channels was considered to be of interest; it was also thought that the dielectric absorption study would give us some clue to the mode of motion of the water molecules. A preliminary experiment on the dielectric absorption[3] has shown that a relaxation absorption occurs below room temperature in the radio frequency region; this merits more detailed systematic study.

Experimental

Material. — The powdered DL-$[Co(en)_3]Cl_3$ used was from the same source as has been described previously.[3] Single crystals were grown by slowly cooling the nearly-saturated solution from 40°C. at the rate of about 1°C/day. Hexagonal prism crystals about 1″ long and 3/4″ across were readily obtained; these were shaped with Emery powder and kerosene into disks about 1 mm. thick. Kerosene was washed with benzene, and the crystals were finally polished with a drop of water. The crystals were then stored over powdered DL-$[Co(en)_3]Cl_3 \cdot 3.6H_2O$ for at least a month prior to the measurements in order to secure a uniform water content throughout. In obtaining disks with (0001) faces, drops of water had to be used instead of Emery powder and kerosene because the crystal was readily cleaved parallel to the c axis.

Apparatus and Equipment. — Measurements of the dielectric constant and loss between 40 c./s. and 5 Mc./s. were made with a mutual-inductance bridge of the Cole type[5] (Ando Elec. Co., Model TR-1B), which works between 30 c./s. and 5 Mc./s. Oscillators were of the low-distortion type, General Radio 1301A and Ando Elec. GET-2. A Q-meter of the Yokogawa Elec. Works, Model QM-101, was used to determine rough estimates at higher frequencies in order to check the consistency.

The measuring electrodes were designed so as to chill the specimen close to 90°K and to secure good electrical contacts between the electrodes and the specimen at all temperatures by making allowance for the thermal expansion and contraction of the crystal. Several pieces of measuring apparatus of slightly different designs were constructed; the one which is illustrated in Fig. 1 is typical of them. Here, A is a bakelite base for an electron tube (type Z), C is the glass stem with six Ni lead wires fused in, D are mica-disk spacers, E is a brass electrode (high-impedance side) 5 mm. in diameter and 1 mm. thick, and H is the other electrode (low-impedance side) with a spring of music wire, G, underneath, one end of which is soft-soldered to the electrode, H, and the other end of which is soldered to the supporting brass plate, F. The lead wires J are brass rods 2 mm. thick and are connected to Ni wires at the upper ends with soft solder. The temperature of the crystal was measured with a copper-constantan thermocouple junction, I, which was attached to the lower electrode, H (electrically insulated).

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[1] Part VI: This Bulletin, 32, 908 (1959).

[2] K. Nakatsu, Y. Saito and H. Kuroya, ibid., 29, 428 (1956).

[3] H. Chihara and K. Nakatsu, ibid., 32, 903 (1959).

[4] R. Kiriyama, H. Kiriyama and T. Wada, 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959. Abstract of Paper No. 4048.

[5] R. H. Cole and P. M. Gross, Jr., *Rev. Sci. Instr.*, 20, 252 (1949).

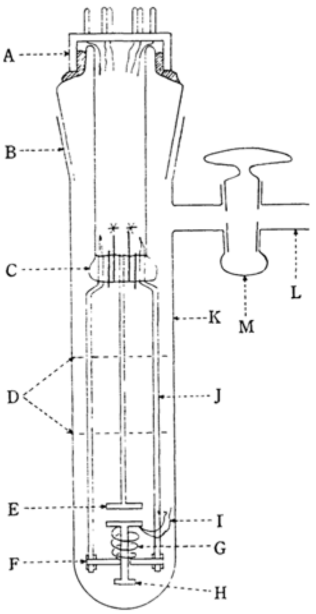

Fig. 1. Sample cell and electrodes for dielectric measurements.

The glass jacket, K, had a side tubing, L, which permitted control of the ambient pressure. The whole jacket was cemented to the six-legged base, A, with an Epoxy resin above the ground-glass joint, B. The apparatus was inserted in a Dewar vessel below the level of L and further placed in a shielded enclosure. To minimize the external disturbances, two of the fused lead wires (* marks in Fig. 1) and one of the thermocouple lead wires were electrically grounded.

Such construction of the apparatus, particularly the use of the base, A, proved to make the calibration procedure easy if a needle-and-mercury switch was employed to reduce the variation of the stray capacitance when the measuring cell was switched on and off.

Determination of the Cell Constants.—As there are no guard electrodes in the apparatus, the edge corrections had to be estimated experimentally. This was done in conjunction with the determination of the stray capacity by referring to the dielectric constant (5.30) of the (001) face of sodium chloride. The apparent total capacity of the cell was determined with single crystals of sodium chloride (aluminum foils of $1\times1\,\mathrm{cm}^2$ on either side) of different thicknesses (between 0.99 and 1.37 mm.) inserted between the measuring electrodes. The apparent capacity, plotted against the reciprocal of the crystal thickness, gave a good straight line; the slope gave the cell constant, including the edge corrections, and the intercept gave the stray capacity. This was further checked favorably with a single crystal of potassium chloride ($\varepsilon'_{100}=4.41$).

Procedure and Determination of the Water Content of the Crystal in situ. — The specimen crystals were sandwiched, for the measurements, between aluminum foils $1\times1\,\mathrm{cm}^2$ which were glued on the crystal with a very thin film of silicone grease. The thickness of the crystal was measured to within 0.01 mm. and was found to be uniform all over within these limits. The initial water content of the crystal was determined gravimetrically. The practical limit of the hydration of DL-$[\mathrm{Co(en)_3}]\mathrm{Cl_3}\cdot n\mathrm{H_2O}$ is $n=3.6$ at room temperature, as may be seen from the sorption-desorption isotherm.[3] Crystals of a smaller degree of hydration were prepared in the dielectric apparatus. The side tubing (L in Fig. 1) was connected to a vacuum line through a trap with an appendix glass tube with narrow walls. The specimen having been placed, the glass jacket, K, was chilled with liquid nitrogen and evacuated. After the crystal had been warmed to room temperature, some water of crystallization was distilled into the trap cooled with liquid nitrogen for a variable length of time. The distilled water was then recollected in the appendix tube, which was then fused off and weighed. The same procedure was repeated in situ after dielectric measurements had

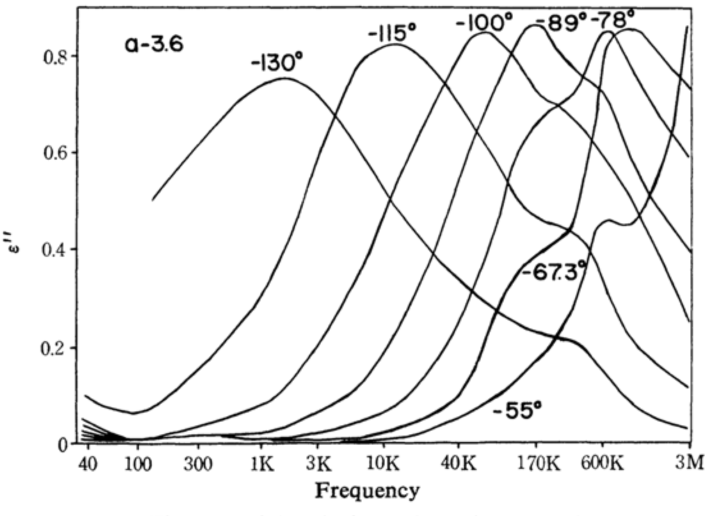

Fig. 2. Dielectric loss of specimen a-3.6.

been made at particular water contents, the final weight of the crystal being used to monitor the accuracy of the amounts of the water distilled between the successive series of dielectric measurements. Usually the total weight of the trapped water and the weight loss of the crystal agreed to within several parts per cent. Where the rate of dehydration is high (for a large n value) it was necessary to cool the crystal during the distillation. For crystals with (0001) flat faces, the distillation was slower than for those with $(10\bar{1}0)$ faces. After a certain amount of dehydration, the stopcock, M, was closed and the crystal was allowed to regain its transparency (quick dehydration often made the surface of the crystal opaque). It took about a week for a new equilibrium to be achieved. Dielectric measurements were made in most cases with a rising temperature at about 1 deg./min. from $-170°C$ at a prefixed frequency. In one case, at $-78°C$, the apparatus was immersed in a dry ice-petroleum benzine mixture and the frequency was scanned from 40 c./s. to 3 Mc./s. in order to compare it with the other measurements.

Experimental Results and Discussion

The experimental results were converted to plots of ε' or ε'' as a function of the frequency at several selected temperatures; some of them are shown in Figs. 2 through 5, where a-3.6, for example, denotes that the external electric field was perpendicular to the $(10\bar{1}0)$ or a plane (i. e., perpendicular to the axis of the channel) and that the water content of the crystal was 3.6 mol. per formula unit of the salt.

The anomalous dispersion and absorption were found to depend on the water content of the crystal and are apparently associated with some motion of the water molecules in the channels. The wavelengths and the temperatures where the absorption is seen are low for the water of crystallization. This suggests considerable mobility in the water molecules. Thus, the frequency of the maximum absorption, when extrapolated to room temperature, comes very close to the critical frequency for liquid water.[3]

There are two absorptions in the frequency range examined; one is larger than the other and is markedly displaced to higher frequencies at higher temperatures. The smaller peak (300 to 600 kc.) does not seem to move with the change in temperature, although it seems to change with the water content. This temperature-independent absorption is rather difficult to interpret.* Therefore, we will here consider only the temperature-dependent part of the dielectric absorption.

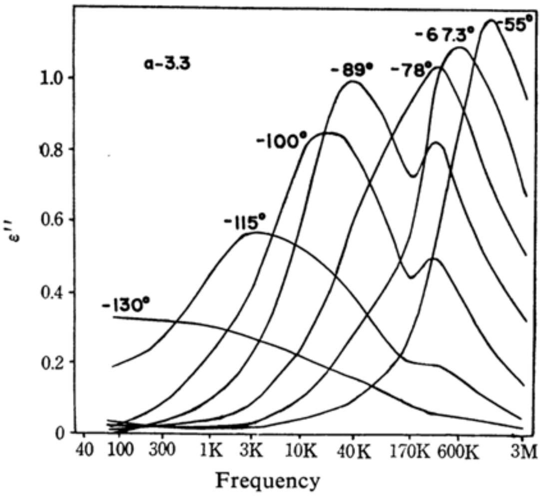

Fig. 3. Dielectric loss of specimen a-3.3.

The anisotropy of the absorption is rather small. The only difference is in the additional large dielectric loss, which increases towards lower frequencies when the electric field is parallel to the crystallographic c axis (see Fig. 5 for the results with c-3.6). This additional loss is most probably due to d. c. conductivity; it is also seen in a-2.7 and to a much smaller extent in a-3.6. The appearance of d. c. conductivity in the "a" specimens indicates that the crystal starts to fissure as the water of crystallization is successively removed. The d. c. conductivity would thus be due to the grain-boundary diffusion of water in the "a" specimens. The "c" specimens, on the other hand, shows a large d. c. conductivity, even with a good crystal; this may be reasonably accounted for by the ionic conduction due to proton jumps through the hydrogen bond between α and β sites in cooperation with the rotation of water molecules at both types of sites.

The shape of the absorption curve changes with the temperature, as Fig. 3 shows. It generally becomes sharper at higher temperatures; this tendency is more pronounced as the water content is decreased.

The main dielectric loss peak is the relaxation absorption due to the hindered rotation of the water molecules. The relaxation is

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* On the basis of the crystal structure described previously,[3] two possibilities which would give rise to the almost temperature-independent absorption were considered. One is the rotational isomerism between the two gauche configurations of ethylenediamine units that coordinate a Co^{3+} ion. However, such isomerism has to take place in synchronism at least among the three ethylenediamine molecules belonging to the same Co^{3+} ion. The other possibility is the rotation of the water molecules at the α sites about the axis of the hydrogen bond, $O\text{-}H \cdots\cdots Cl^-$. Because the other hydrogen atom of this water is only very weakly engaged in the $O\text{-}H \cdots\cdots O$ hydrogen bond to a water molecule at a β site, such axial rotation would require a very small activation energy, which in turn might cause the absorption to be almost independent of the temperature. While this seems to be a plausible explanation, the frequencies at which the absorption is observed are too low for such a mechanism.

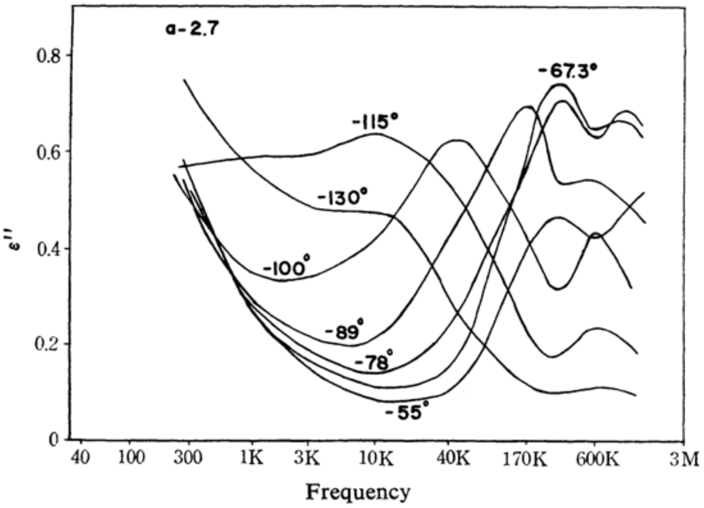

Fig. 4. Dielectric loss of specimen a-2.7.

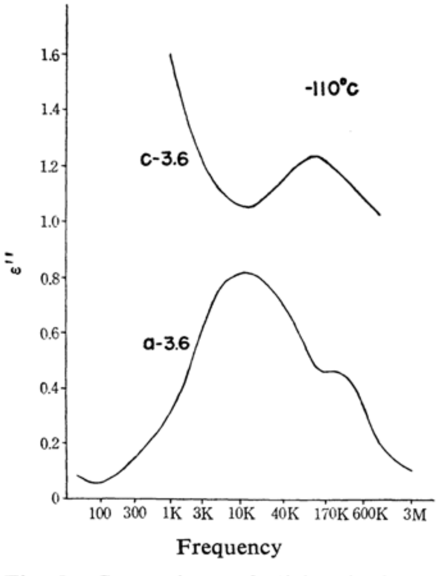

Fig. 5. Comparison of dielectric loss of specimens a and c.

not, however, that of a simple mechanism, as the shapes of the semi-circular Cole-Cole plots show in Figs. 6 and 7. Their asymmetric shape is, of course, partly due to the inclusion of the temperature-independent loss in the plots, but it also suggests a distribution of the relaxation times. The so-called activation plots of the log of the frequency that gives maximum ε'' versus $1/T$ are linear and the activation energies were obtained therefrom (Table I). The location fo the absorption maxima for a-2.7 was determined with difficulty; therefore, its activation energy may be in error by as much as 1 kcal./mol. It would be interesting to note a correlation between the activation energies and the differential heat of hydration or dehydration; either quantity shows a minimum or maximum between $n=2$ and 3. Generally these activation energy values are consistent with a mechanism of the molecular rotation of water accompanying the dissociation of several weak hydrogen bonds.

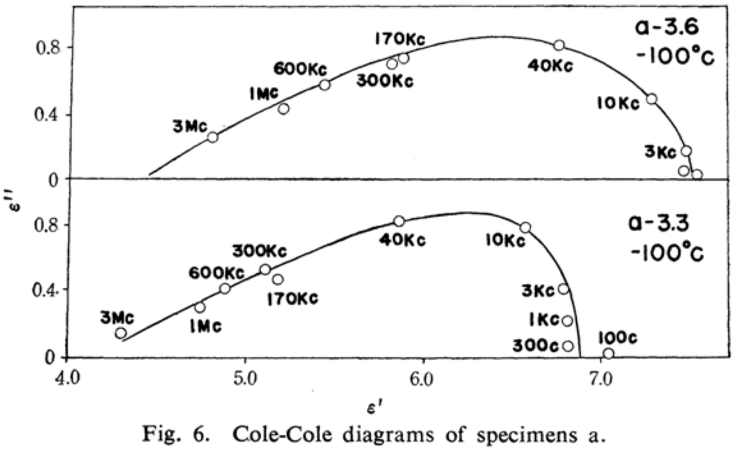

Fig. 6. Cole-Cole diagrams of specimens a.

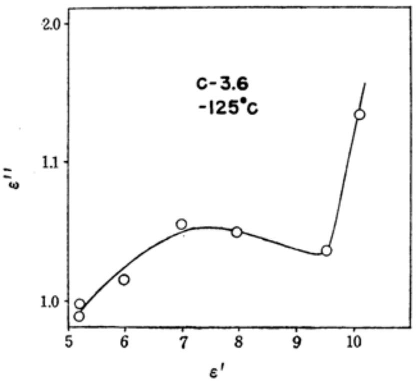

Fig. 7. Cole-Cole diagram of specimen c.

TABLE I. ACTIVATION ENERGIES (kcal./mol.)

a-3.6	7.3	c-3.6	5.6
a-3.3	7.9	c-2.9	4.9
a-2.7	4.7	c-0.43	5.5
a-0.9	6.8	c-0.27	8.3

There is one feature of interest in the temperature dependence of the maximum of ε'', as is most evident in Fig. 3. The maximum of ε'' increases with the temperature as the absorption becomes sharper; its rates of increase are different above and below about −90°C. Such differentce in behavior is also seen in the static dielectric constant, ε'_0 and these are compared in Fig. 8. There is a sharp break in ε'_0 at −90°C as well as in $\varepsilon''_{\max}$ for the specimen a-3.3. In contrast, ε'_0 for the specimen a-3.6 decreases linearly as the temperature is raised with the same slope as does ε'_0 for a-3.3 above −90°C. Such a decrease is due to thermal agitation opposing the static polarization. We shall now examine the structural mechanism in which a break point in ε'_0 appears with a-3.3. The two possible sites, α and β, for water molecules should have different potential energies; the β sites become stable only after the surrounding α sites have been occupied by water molecules. There must thus be an equilibrium partition of water molecules for a fixed total number of water molecules between the two types of sites, a partition governed by the Boltzmann distribution. The potential energy at a β site depends on the configuration of the environment and, therefore, has a certain distribution. At the lowest temperatures, the α sites will be almost filled if n is larger than 3, while a fraction of the β sites will remain vacant. Thus, the molecules are more or less fixed rigid, giving a small static polarization. As the temperature is raised, some molecules at the α sites would be vaporized into the β sites, leaving 'defects' behind at the α sites. When this occurs, an average β site molecule will see a potential field which is relaxed to some extent because of the defect formation. Thus the static dielectric constant will tend to increase until a critical temperature (−90°C for $n=3.3$) is reached, at which the maximum possible number of O–H groups can be oriented in the direction of the applied electric field either through the dissociation of O–H⋯O hydrogen bonds or through the rotation of water molecules and the reformation of the hydrogen bonds, the number being consistent with the equilibrium partition of molecules between the α and β sites.

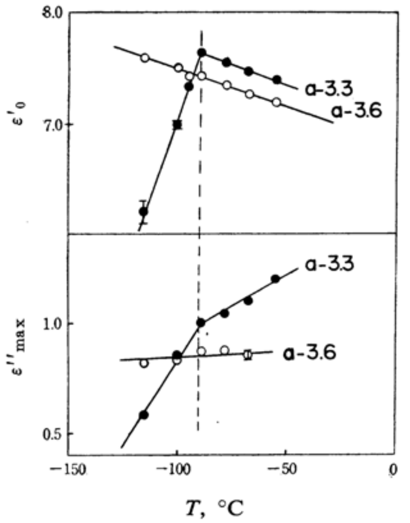

Fig. 8. Static dielectric constants and the loss maxima as a function of temperature.

Assuming that there are two different states of minimum potential energies, corresponding to different hydrogen bond schemes, we may estimate the difference in the potential energies by a formal application of a plot of $\log \varepsilon'' T$ against $1/T$.[6] Figure 9 shows the results thus obtained; this, however, should not be considered as representing the potential curve of a molecule but be regarded as the total potential energy of the assembly of water molecules. The potential energy difference of a-3.3 drops by about 0.7 kcal./mol. from 1.6 to 0.9 kcal./mol. at −90°C, at which kT_c amounts to about 0.4 kcal./mol.

When the water content is larger, say, when $n=3.6$, this critical temperature would be lowered because the number of vacant β sites is much smaller. This may be a reason for the failure to observe a break in ε'_0 for a-3.6. Such a mechanism of defect formation and the aquisition of molecular mobility is also

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[6] J. S. Dryden and R. J. Meakins, *Rev. Pure Appl. Chem.*, 7, 15 (1957).

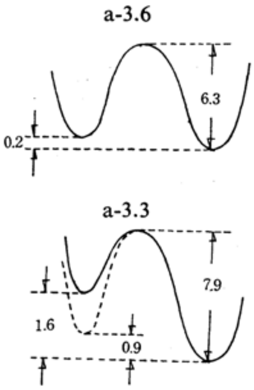

Fig. 9. Schematic potential energy curves for the assembly of water molecules.
—— Below −90°C, - - - Above −90°C

related to the results of thermodynamic investigation, in which an isothermal order-disorder phenomenon was observed in the differential heat and entropy of sorption of water by the anhydrous crystal.[3] It is possible that the transition phenomenon found here by the dielectric measurements may have some consequences on such other properties as the heat capacity of the partly hydrated crystal of this salt.

Summary

The dielectric constant and loss of single crystals of DL-$[Co(en)_3]Cl_3 \cdot nH_2O$ have been measured between −150°C and room temperature in the frequency range 40 c./s. and 3 Mc./s. The water content, n, was varied from 0.27 to 3.6. The anomalous dispersion and relaxation absorption due to the hindered rotation of water have been observed and they are strongly dependent on n. The activation energies for the relaxation absorption have been determined for different n values and for different orientations of the crystals. A molecular mechanism for the absorption has been presented on the basis of the zeolitic nature of the water molecules in the crystal as determined previously from structural[2] and thermodynamic[3] investigation.

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