Studies on Crystal Hydrates. V. Zeolitic Dehydration of* DL-*Tris-ethylenediamine-cobalt(III) Chloride Hydrate,* DL-$[Co\,en_3]Cl_3\cdot nH_2O$. *Sorption and Desorption of Water Vapor. A Preliminary Study of the Dielectric Properties*

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Crystal hydrates may be classified into two extremes from the standpoint of the dehydration isotherm[1]:

i) crystals which are dehydrated in a stepwise manner (Fig. 1a); $CuSO_4\cdot 5H_2O$ belongs to this class of hydrates,

ii) crystals which are dehydrated continuously (Fig. 1b); zeolite minerals belong to this class.

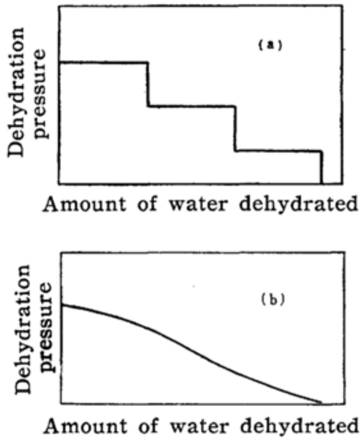

Fig. 1. Two extreme types of dehydration isotherm. (a) the stepwise dehydration, (b) the continuous dehydration.

Zeolites, chabazite, for instance, generally possess two or more kinds of channels of different diameter and each channel crosses with others at cage-like rooms[2]. Analcite has spiral channels which are relatively independent of each other but their diameter is not uniform throughout a channel[3]. We have long been looking for a type of crystal which belongs to the class ii and has only one kind of channel in which positions of water molecules can be located exactly by the method of X-ray analysis. If we can obtain such a crystal, it will provide us with an ideal model substance for examining the role of water in the stabilization of crystal lattice, the capillary condensation theory generally adopted in the adsorption research and the state of aggregation of water molecules in the channels.

The crystal structure of DL-$[Co\,en_3]Cl_3\cdot nH_2O$ ($n=3$) has recently been determined[4] and this was found to be a substance that nearly meets our requirements.

The present paper deals with the experiments aiming at establishing the zeolitic nature of the dehydration of this crystal and with some results obtained in regard to the thermodynamic quantities of dehydration. A preliminary measurement of the dielectric absorption will also be briefly reported.

Experimental

Material.—The preparation of DL-tris-ethyleneamine-cobalt(III) chloride has already been described[4]. Crystals were purified by repeating recrystallization from aqueous solution (Found: C, 20.77; H, 7.01; N, 24.73; Cl, 29.83% on the basis of the anhydrous crystal. From the residue the Co purity was found to be 99.601% by the α-nitroso-β-naphthol method**). The measurements of the dehydration pressure were conducted with powdered crystals unless otherwise stated. Dielectric measurements were made with single crystals grown from the aqueous solutions.

Differential Thermal Analysis.—The differential thermal analysis (Fig. 2) shows that the dehydration takes place over the temperature region between 70 and 170°C. Such gradual

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* Report IV may be found in This Bulletin, **32**, 897 (1959).

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** The analysis of Co was kindly carried out by Dr. T. Fujino of the Institute of Science and Industry, Osaka University, Sakai, Osaka, to whom the authors are very grateful.

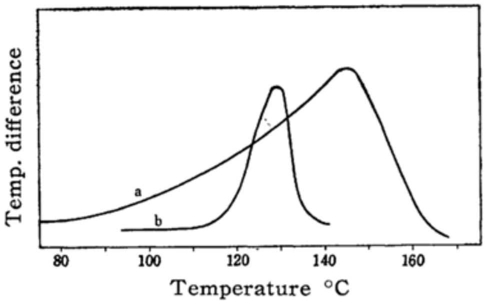

Fig. 2. The differential thermal analysis of (a) DL-[Co en$_3$]Cl$_3$ hydrate and (b) NiSO$_4$·6H$_2$O.

dehydration stands in contrast with the case of nickel sulfate hydrate, for example, and suggests the zeolitic nature of dehydration.

Dehydration Pressures. — The dehydration pressures of the hydrate were measured between 19 and 45°C at various water contents by using the apparatus already described in the preceding paper. The results are summarized in Table I and Fig. 3. The approach to the equilibrium was very rapid, not later than ten minutes after the water bath was thermostated. The pressure values were read by use of a traveling microscope to 0.01 mm. Corrections in the value of the water content for the amount of water present in the vapor phase were not made, since a rough estimate based on the dimensions of the manometer and the sample container showed that it was well within the experimental error. No hysteresis effect was observed: the pressures in the heating and in the cooling directions coincided with each other.

TABLE I. DEHYDRATION PRESSURES. n IS THE NUMBER OF MOLES OF WATER PER FORMULA WEIGHT OF [Co en$_3$]Cl$_3$

n	Pressure equation (in mmHg)
3.35	$\log P = 9.0406 - (2334.0/T)$
3.11	$\log P = 10.003 - (2693.1/T)$
2.96	$\log P = 10.577 - (2910.0/T)$
2.63	$\log P = 10.734 - (3035.9/T)$
2.47	$\log P = 10.699 - (3045.6/T)$
2.02	$\log P = 9.7583 - (2773.2/T)$
1.18	$\log P = 9.7791 - (2782.0/T)$
0.82	$\log P = 9.3500 - (2649.8/T)$
0.39	$\log P = 9.7320 - (2770.1/T)$
0.23	$\log P = 10.119 - (2889.5/T)$
0.02$_5$	$\log P = 7.5790 - (2206.9/T)$

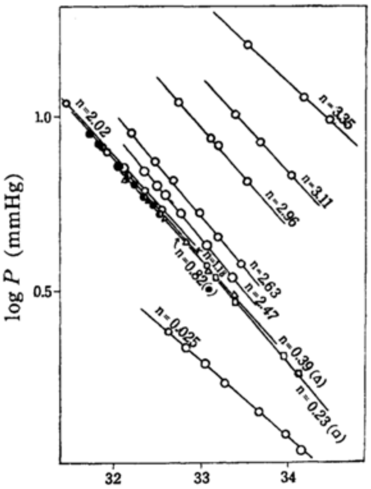

Fig. 3. Dehydration pressure of DL-[Co en$_3$]Cl$_3$·nH$_2$O at different water contents n.

The experiments of dehydration and rehydration (desorption and sorption) of a single crystal was undertaken in order to compare it with the powder data. A single crystal (about 325.6 mg.) placed in a glass vessel (144.9 mg.) was hung under a quartz helical balance, the sensitivity of which was 0.2711 mm./mg. The water vapor pressure in the apparatus was kept constant by use of 72% sulfuric acid solution covering the water vapor pressures up to 13 mmHg. The results are plotted in Fig. 7. No hysteresis was observed between the dehydration and rehydrotion branches.

The differential molar heats and entropies of dehydration were computed from the pressure equations given in Table I. Table II lists these results and Fig. 6 indicates that there is a maximum both in the heat and in the entropy at a certain water content (approximately at n=2.7 mol. of water per formula weight of the hydrate).

TABLE II. DIFFERENTIAL MOLAR HEAT AND ENTROPY OF DEHYDRATION AS A FUNCTION OF WATER CONTENT

n	ΔH (kcal./mol.)	ΔS (e.u.)	n	ΔH (kcal./mol.)	ΔS (e.u.)
3.35	10.7	28.2	1.18	12.7	31.6
3.11	12.3	32.6	0.82	12.1	29.6
2.96	13.3	35.2	0.39	12.7	31.2
2.63	13.9	35.9	0.23	13.2	33.1
2.47	13.9	35.8	0.02$_5$	10.1	21.5
2.02	12.7	31.5			

Description of Crystal Structure

The crystal structure may be briefly outlined here with particular attention to the arrangement of the water molecules. The structure projected on the (0001) plane is represented in Fig. 4. A channel of hexagon cross-section filled with water molecules runs through the origin in the direction of the c-axis. The way in which the water molecules are arranged is schematically shown in Fig. 5 and the crystal data together with the atomic coordinates are reproduced in Table III.

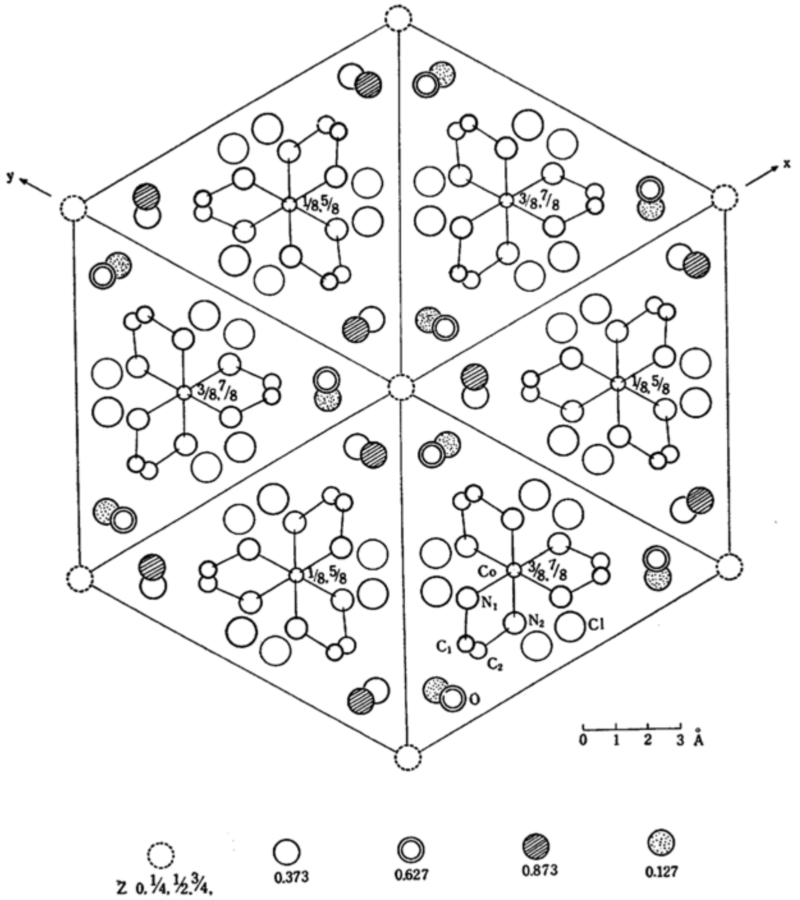

Fig. 4.

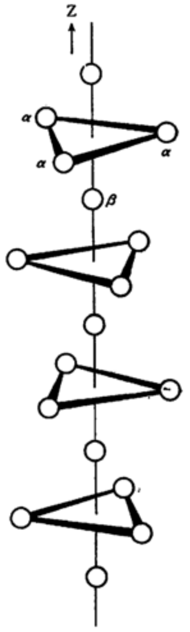

Fig. 5.

TABLE III. CRYSTALLOGRAPHIC DATA

$a = 11.50 \pm 0.02$ Å, $c = 15.52 \pm 0.04$ Å,

Density 1.504 (17°C), $Z = 4$,

Space Group P$\bar{3}$c1-D_{3d}^{4}

Fractional atomic coordinate

Atom	No. of positions & Wyckoff notation	x	y	z
C_0	4d	1/3	2/3	0.125
Cl	12g	0.097	0.493	0.372
O_1	12g	0.087	0.225	0.873
O_2	2a	0	0	1/4
O_3	2b	0	0	0
C_1	12g	0.180	0.397	0.077
C_2	12g	0.215	0.397	0.173
N_1	12g	0.192	0.525	0.050
N_2	12g	0.333	0.535	0.200

TABLE IV. SOME INTERATOMIC DISTANCES

$O_\alpha \cdots Cl$	3.34 Å
$O_\alpha \cdots C_1$	3.36, 3.61 Å
$O_\alpha \cdots C_2$	3.12, 3.55 Å
$O_\alpha \cdots O_\alpha$	3.90, 4.19, 4.54 Å

Water molecules which occupy the 12g positions amount to three moles per formula weight of the hydrate (n=3). These positions will be referred to as the α-sites. In view of the long O···O distances listed in Table IV, if water molecules are to occupy only α-sites, and of the improvement of the reliability index by about 2%, it was concluded that water molecules are distributed also on the 2a and 2b special positions (referred to as the β-sites). The fact that the peak at the origin in the electron-density projection on the (0001) plane was not eliminated even at the final stage of the refinement of the structure analysis also led to this conclusion. This addition of water is also consistent with the chemical analysis that the water content of a freshly prepared crystal is n=3.6. The $O_\alpha \cdots O_\beta$ distances will then be 2.96 and 3.00 Å corresponding to weak hydrogen bonding.

A single-crystal oscillation photograph was obtained after the crystal was almost dehydrated and its unit cell dimensions were the same as those of the hydrate crystal.

Results and Discussion

The dehydration isotherm derived from the data of Table I by inter- or extrapolating them to 25°C is shown in Fig. 7 by solid circles. The pressure at 25°C remains almost constant (2.85 mmHg) between the water contents n=0.2 and 2.5. Another independent direct measurement of the isotherm at 25°C for a single crystal (denoted by open circles in Fig. 7) gave nearly the same result as that derived from the powder data***. Important conclusions may be drawn from these experimental data.

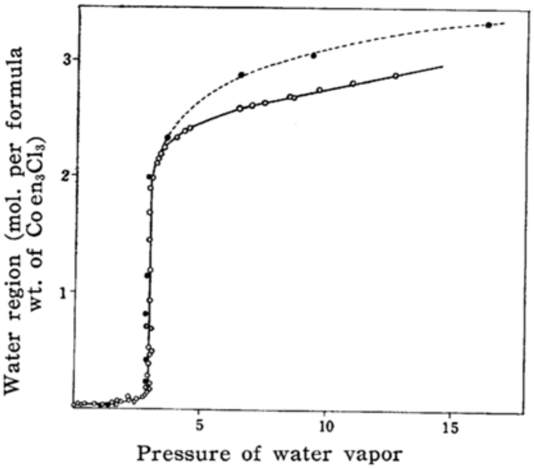

Fig. 7. Dehydration isotherm at 25°C derived from the powder data (solid circle) and determined directly for a single crystal (open circle).

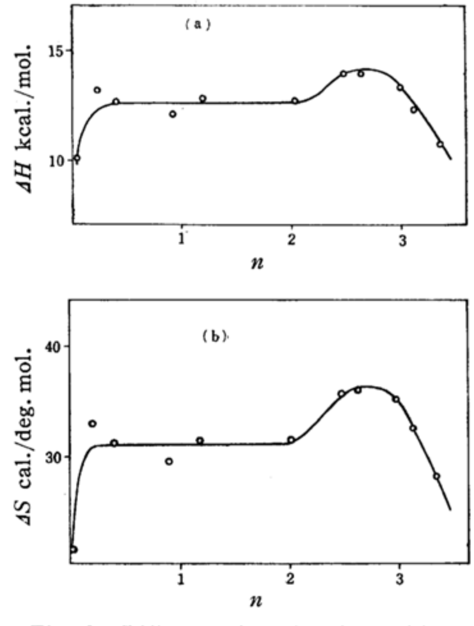

Fig. 6. Differential molar heat (a) and entropy (b) of dehydration as functions of water content n.

(a) The fact that the powder and the single-crystal data give the same results clearly shows that the isotherm obtained for the single crystal is not due to adsorption of water vapor on the outer surface of the solid but to the sorption and desorption into and from the interior of the crystal lattice.

(b) That the pressure is constant over a wide range of n reminds us of the character of the destructive dehydration (class i). A close examination, however, shows that the boundary values of n (0.2 and 2.5) do not correspond to any single crystalline phases. In fact there is no set of equivalent positions in the space group P$\bar{3}$cl that can accommodate the states n= 0.2 or n=2.5. Therefore, it must be emphasized that an appearance of the stepwise dehydration does not always correspond to the destructive dehydration. This conclusion argues against the widely accepted criterion for zeolitic dehydration[1,5-7]. X-ray examination would be necessary for the decision as to whether

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*** The small discrepancy at higher pressures is probably due to the larger adsorption of water on the outer surface of powdered crystals.

or not the dehydration is zeolitic.

(c) From the standpoint of the sorption-desorption system, the isotherm of Fig. 7 corresponds to the type V isotherm of the Brunauer-Emmett-Teller classification[8]. It is evident that the horizontal portion of the isotherm corresponds to the capillary condensation into pores of uniform size. Analogous transitions in adsorbed monolayer have been reported and interpreted by many investigators since Harkins and his collaborators observed the first-order phase transition of *n*-heptane on the surface of silver[9], although its reality was open to some discussion[10]. Recent investigations[11] show that such transitions are due to a kind of cooperative phenomena occurring in the assembly of adsorbed vapors. The transitions are sharp on a homogenous surface but they are diffuse on a heterogeneous surface. Capillary condensation phenomena that have been observed at any time are diffuse, because the experiments were carried out on gels which are inevitably inhomogeneous. The transition phenomenon observed in the present study is unique because it occurs in the true equilibrium system (the water regain of the solid did not change during 24 hr. after dosage of vapor; cf. E. V. Ballou, Ref. 10) and also because it is the capillary condensation entirely equivalent, in principle, to the transition on a uniform outer surface of a single crystal.

(d) The maxima in the differential molar heat and entropy in Fig. 6 will be accounted for by the theory of cooperative phenomena. Analogous results were reported by Rhodin[12] for nitrogen adsorbed on single crystals of copper, by Young[13] for argon absorbed on octahedral potassium chloride and by Hayakawa[14]. In all the adsorption systems ever examined, the maximum of the differential heat of adsorption appears when the amount of the gas adsorbed nearly suffices to cover the surface with a monolayer. This is also to be expected theoretically[15]. In the present case the maximum is also near the monolayer coverage of the inner surface of pores ($n=2.7$). The number of pairs of water molecules in a channel interacting with each other increases more rapidly than linearly as the coverage increases, even after the monolayer has been completed. The differential heat thus increases with the coverage on the assumption that the pair interaction energy is constant. On the other hand, the water molecules in the second layer (β-sites) interact with the lattice much more weakly than do the molecules in the first layer (α-sites). Those two counteracting effects give rise to the maximum of the heat of sorption branch.

(e) The differential heat and entropy are very small at very low n values. This is an extraordinary fact as many sorption systems exhibit a great increase in ΔH towards the lower surface coverage. On the surface of a single crystal, the differential heat is constant down to very low pressures[12]. The experimental error involved in the present determination of ΔH does not exceed 0.7 kcal./mol. and, therefore, the small value of ΔH and ΔS may possibly be due to a slight rearrangement of atoms in the completely dehydrated crystal lattice.

The Preliminary Results of Dielectric Measurements.—The dielectric power loss was measured of single crystals ($n=3.6$) between $-180°$C and room temperature in the frequency range of 300 c/sec. to 10 Mc/sec. The dielectric absorption was found with the electric field in the *c*-axis direction and perpendicular to the *a*-plane of the hexagonal crystal. The activation energies for the relaxation process were 7.7 and 6.3 kcal./mol., respectively. By extrapolation to room temperature, the relaxation times ($\log \tau = (1379/T) - 14.72$ for the *c*-plane) nearly agree with the relaxation time in liquid water and it was inferred that the absorption is due to the hindered rotation of water molecules. In the experiment with the electric field parallel to the *c*-axis, an additional absorption increasing progressively towards lower frequencies was observed. Further precise study of the dielectric properties and the d. c. conduction is going on and will be reported later.

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Summary

The dehydration pressures of DL-[Co en$_3$] Cl$_3$·nH$_2$O ($n \leqq 4$), were measured between 19 and 45°C at various water contents. The dehydration isotherm derived from the data is of type V of the BET classification with a constant pressure (2.85 mmHg at 25°C) region between $n=2.5$ and $n=0.2$, corresponding to the case of capillary condensation into pores of uniform size. The crystal lattice is stable after dehydration, showing the zeolitic nature of dehydration. The usual criterion of stepwise dehydration for the lattice-destructive dehydration does not apply to this type of crystal. The differential molar heat and entropy of dehydration have maximum values around $n=2.7$; this can be accounted for by the theory of co-operative phenomena. At very low water content, there is a possibility of rearrangement of atoms in the crystal as inferred by the entropy consideration. A preliminary study of the dielectric properties showed that the relaxation absorption occurs between -180°C and room temperature in the megacycle region with the activation energy for the relaxation about 7 kcal./mol. The dielectric loss due probably to the d. c. conduction was observed in the c-axis direction.

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