

complexes of pyrazine-2,3-dicarboxylic acid.

The IR spectra of bis(pyrazine-2,3-dicarboxylato)cobalt(II) dihydrate and bis(pyrazine-2,3-dicarboxylato)zinc(II) dihydrate are very similar. The bands centered at $\approx 1700 \text{ cm}^{-1}$ in the mull spectrum of the free acid can be assigned to stretching vibrations of the carbonyl bond of the carboxyl group. The related vibrations in the cobalt(II) and zinc(II) complexes are centered at $1686-1690 \text{ cm}^{-1}$ and 1615 cm^{-1} , respectively. The spectra reveal the presence of covalently bonded carboxylate and free carboxyl groups so that each ligand molecule coordinates to the metal ion through the nitrogen atom and an oxygen atom of the 2-carboxylate group. The spectra and thermograms of both salts confirm that the water is structural water.

The crystal data for bis(pyrazine-2,3-dicarboxylato)cobalt(II) dihydrate and bis(pyrazine-2,3-dicarboxylato)zinc(II) dihydrate are shown in Table 1. The com-

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Table 1. Crystal data for bis(pyrazine-2,3-dicarboxylato)cobalt(II) dihydrate and bis(pyrazine-2,3-dicarboxylato)zinc(II) dihydrate.

	Bis(pyrazine-2,3-dicarboxylato) Co(II) dihydrate	Bis(pyrazine-2,3-dicarboxylato) Zn(II) dihydrate
<i>a</i>	11.06 Å	11.14 Å
<i>b</i>	11.83 Å	11.82 Å
<i>c</i>	7.21 Å	7.30 Å
β	94.0°	93.7°
<i>V</i>	941 Å ³	959 Å ³
<i>Z</i>	2	2
<i>D</i> _{obs}	1.50 g cm ⁻³	1.49 g cm ⁻³
<i>D</i> _{calc}	1.51 g cm ⁻³	1.51 g cm ⁻³
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
F.W.	429.19	435.62

pounds are isostructural and monoclinic with two formula units in the unit cell. The space group is *P*2₁/*n* in both cases.¹⁰

The compounds are in all probability similar in structure to bis(pyridine-2,3-dicarboxylato)silver(II) dihydrate,¹¹ the crystal and molecular structures of which have been confirmed by X-ray analyses.

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Transformations of Hydrates into Instable Hydrates. The Crystallization of CaCl₂-Hydrates in Quartz Flasks

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In a previous paper¹ it was shown that a transformation of SrCl₂·6H₂O into the next lower hydrate (SrCl₂·2H₂O) can be avoided; SrCl₂·6H₂O transforms, if properly treated, into SrCl₂·H₂O.

The transformation of CaCl₂·6H₂O into the next lower hydrate can also be avoided (CaCl₂·6H₂O and SrCl₂·6H₂O are isostructural). The next lower hydrate is α -CaCl₂·4H₂O. Roozeboom² found that CaCl₂·6H₂O can transform into the thermodynamically least stable tetrahydrate (γ -CaCl₂·4H₂O), and Lannung³ measured the equilibrium vapour pressures of the hydrate pair CaCl₂·6H₂O - γ -CaCl₂·4H₂O in the temperature interval 18 - 28°C; he found the temperature of transition to be 28.9°C.

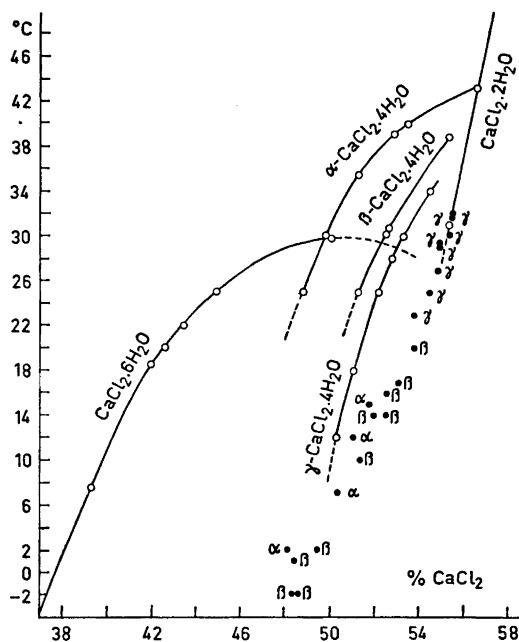


Fig. 1. Solubility curves of the hydrates of CaCl_2 in comparison with CaCl_2 -conc. and temperatures at which the hydrates were formed in supercooled solutions in quartz flasks. The solubility of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ at 31°C and the solubility of $\gamma\text{-CaCl}_2 \cdot 4\text{H}_2\text{O}$ at 18°C and 12°C were found by extrapolations, using Lannung's³ and Stokes's⁴ results.

The formation of thermodynamically instable hydrates from supersaturated solutions has been known for a long time. Wilhelm Ostwald used the formation of thermodynamically instable phases from supersaturated solutions and supercooled melts as the basis for his law of stages (Stufenregel).

The transformation of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ into $\text{SrCl}_2 \cdot \text{H}_2\text{O}$ and the transformation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ into $\gamma\text{-CaCl}_2 \cdot 4\text{H}_2\text{O}$ show that thermodynamically instable phases can also be obtained from (higher) hydrates. These hydrates do not have one transition point. $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ has at least three; the hydrate can transform into the three known tetrahydrates.

The purpose of the following experiments was to find out whether or not $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ could transform into the dihydrate, or to study whether defects or foreign seeds may be necessary to start a formation of a tetrahydrate. The expected temperature of transition for the system $\text{CaCl}_2 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{CaCl}_2 \cdot 2\text{H}_2\text{O} + 4\text{H}_2\text{O}_{\text{sat. sol.}}$ lies

between 27 and 28°C (Fig. 1). The experimental results show that $\gamma\text{-CaCl}_2 \cdot 4\text{H}_2\text{O}$ is formed before the transition point can be reached.

Can $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ transform into $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$? The experiments indicate that before being able to answer this question we have to solve the problem of supercooling a solution saturated with respect to $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ a good deal below the expected temperature of transition without a disturbing influence from the container or from other foreign seeds.

Experimental details and results. Sample $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, analyzed reagent from Merck, Germany.

Vapour pressure measurements were used to identify a hydrate in a saturated solution and to identify a hydrate pair as described in a previous paper.¹ The measured vapour pressures were compared with the vapour pressures found by Lannung,³ who appears to have performed the most reliable measurements for CaCl_2 -hydrate

pairs and for solutions saturated with CaCl_2 -hydrates.

Vapour pressure measurements were also used to determine the CaCl_2 -conc. in a solution, making use of results found by Stokes.⁴ His results are in good agreement with results found by others.⁵ Stokes's measurements show that $\ln p$ (p being the vapour pressure of a CaCl_2 -solution at 25°C) is nearly a linear function of the CaCl_2 -conc. At concentrations higher than 54.5% calcium chloride, γ - $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ was generated before 25°C was reached (cf. Fig. 1). In this case vapour pressures had to be measured at higher temperatures and the CaCl_2 -contents were found by extrapolations. For further details the reader is referred to the previous paper.¹

Table 1 and Fig. 1 show the results obtained (the hydrate which was generated) when a CaCl_2 -solution was supercooled in a quartz flask. Either α - $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ or β - $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ was generated between -2°

Table 1. The CaCl_2 -concentration and the temperature at which a hydrate was generated in a supercooled solution in three quartz flasks. α , β , and γ stand for α -, β -, or γ - $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, and 2 stands for $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. Values marked with * are obtained by extrapolations.

% CaCl_2	t °C	Hydrate generated
48.2	2	α
48.4	-2	β
48.5	1	β
48.6	-2	β
49.5	2	β
50.4	7	α
51.1	12	α
51.4	10	β
51.8	15	α
52.0	14	β
52.5	14	β
52.6	16	β
53.1	17	β
53.8	20	β
53.8	23	γ
54.5	25	γ
54.9*	27	γ
54.9*	29.2	γ
54.9*	29.5	γ
55.4*	30.2	γ
55.5*	31.8	γ
55.5*	32.0	γ
>63*	35.0	2

and 16°C if a solution was rapidly (4-6°C/h) supercooled. A slow (1°C/h) and a continuous cooling always resulted in β - $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$.

The temperatures, at which the hydrates were formed in the CaCl_2 -solutions (in three different quartz flasks), are roughly a linear function of the CaCl_2 -conc. (cf. Fig. 1). The results show that a solution saturated with respect to (and in contact with) $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ cannot be supercooled in quartz flasks below approx. 31.5°C, and a solution saturated with respect to (and in contact with) γ - $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ cannot be supercooled below approx. 1°C. This was also confirmed experimentally by supercooling the system $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + sat. solution and the system γ - $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ + sat. solution, respectively. γ -Tetrahydrate was always generated at approx. 31°C when the first system was supercooled and β -tetrahydrate was created at approx. 1°C when the second system was supercooled. The system $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + sat. solution in a definite quartz flask gave γ -tetrahydrate at a temperature, which could be reproduced within $\pm 0.2^\circ\text{C}$. The same solution (but without $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) in the same quartz flask gave γ -tetrahydrate within the same temperature interval. Therefore, it is concluded that the thermodynamically unstable hydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) does not influence the limit of supercooling, but that foreign seeds (e.g. quartz) do. It is probably difficult (but necessary) to control the influence of foreign seeds in experiments, the purpose of which is to answer whether or not $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ can be transformed into $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.

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