Studies on Metal Complexes of Pyrazine and Its Derivatives. Part IX. Unit Cell and Other Properties of Bis(pyzrine-2,3-dicarboxylato)cobalt(II) Dihydrate and Bis(pyr-
zine-2,3-dicarboxylato)zinc(II) Dihydrate

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Solid complexes formed by pyrazine-2,3-dicarboxylic acid with divalent cobalt and zinc were described in a previous paper. As far as is known, only a few structural investigations of solid metal complexes of pyrazine-2,3-dicarboxylic acid have been performed. Hartkamp studied the reaction between molybdenum and pyrazine-2,3-dicarboxylic acid and developed a new method for the spectrophotometric determination of small amounts of molybdenum. In the present paper, results for bis(pyr-
zine-2,3-dicarboxylato)cobalt(II) dihydrate and bis(pyr-
zine-2,3-dicarboxylato)zinc(II) dihydrate are given.

Preparation and analysis. Pyrazine-2,3-dicarboxylic acid was a puriss. grade product of Aldrich Chemical Co. The other chemicals used were of analytical reagent grade.

The complexes with a metal-to-ligand ratio of 1:2 were prepared by adding a hot solution of 0.04 mol of a metal salt (cobalt(II) sulphate heptahydrate or zinc(II) chloride) in 150 ml of water to a hot solution of 0.08 mol of pyrazine-
2,3-dicarboxylic acid in 150 ml of water. After recrystallization from hot water, the products were washed with water and ethanol and dried at room temperature. The orange crystals of the cobalt complex and the white crystals of the zinc complex were prismatic and soluble in water.

Cobalt and zinc contents were determined by EDTA titration and carbon, hydrogen, nitrogen, and oxygen by microanalyses. (Found: Co 13.4; C 33.9; H 2.5; N 13.5; O 37.3. Calc. for Co(C_6H_4NO_2)_2.2H_2O: Co 13.7; C 33.6; H 2.4; N 13.1; O 37.3. Found: Zn 14.9; C 33.3; H 2.3; N 12.8; O 36.4. Calc. for Zn(C_6H_4NO_2)_2.2H_2O: Zn 15.0; C 33.1; H 2.3; N 12.9; O 36.7.)

Measurements. The thermogravimetric analyses were carried out by heating the salts from room temperature to 800°C at a rate of 20°C/min in a Perkin-Elmer TGS-1 Thermobalance. The samples weighed about 2 mg.

The magnetic susceptibility of the cobalt(II) compound was measured on a Gouy balance system. Potassium hexacyanoferrate(III) was used for calibration. Diamagnetic corrections estimated from Pascal’s constants were applied. The temperature-independent paramagnetism was disregarded. The visible spectrum of the cobalt complex in a Nujol mull of filter paper was recorded with a Beckman DK-2A spectro-
photometer.

Infrared absorption spectra of the free acid and the metal complexes were measured on a Perkin-Elmer Model 125 grating infrared spectrophotometer using Nujol and hexachloro-
butadiene mulls and potassium bromide disks.

Approximate unit cell dimensions were obtained from rotation and equi-inclination Weissenberg photographs taken with a Nonius Weissenberg goniometer. Accurate values of the dimensions were calculated from powder reflections by the method of least squares. The photographs were taken employing CuKα radiation (λ=1.5418 Å) and the powder photographs with a Guinier camera employing calcium fluoride (α=5.4630 Å) as internal standard. The densities of the crystals were determined by the flotation method.

Results and discussion. The thermogravimetric curves show that bis(pyrazine-2,3-
dicarboxylato)cobalt(II) dehydrates in one step beginning at 195°C (weight loss found 8.5 %, theor. 8.4 %) and the dehydration of bis(pyrazine-2,3-
dicarboxylato)zinc(II) dihydrate begins at 205°C (weight loss found 8.4 %, theor. 8.3 %). The water molecules are thus not very easily removed and probably are structural water. The anhydrous complexes then decompose directly to the oxides. The residual cobalt compound at 495°C is Co_3O_4 (18.7 % found, 18.7 % theor.) and the residual zinc compound ZnO (18.9 % found, 18.7 % theor.) at 550°C.

The absorption maxima at 450 and 475 nm in the solid state visible spectrum and the effective magnetic moment (μ_eff = 4.76 B. M. at 23.7°C) of the cobalt compound are typical for high-spin octahedral coordination of cobalt. The metal ion is probably in a pseudo-octahedral environment. The zinc compound is diamagnetic.

The infrared spectrum of the free acid shows medium absorption bands between 2800 cm⁻¹ and 2300 cm⁻¹ that are typical of hydrogen-bonded carboxyl groups. No such absorption bands were evident in the IR spectra of the cobalt(II) and zinc(II)
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 \( \approx 1,700 \text{ cm}^{-1} \) 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 1,686–1,690 cm\(^{-1}\) and 1,615 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 I. The compounds are isosstructural and monoclinic with two formula units in the unit cell. The space group is \( P2_1/n \) in both cases.\(^9\)

The compounds are in all probability similar in structure to bis(pyridine-2,3-dicarboxylato)silver(II) dihydrate,\(^1\) the crystal and molecular structures of which have been confirmed by X-ray analyses.

1. Tenhunen, A. *Suomen Kemistilehti* 45 (1972) 76.


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

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<th>Bis(pyrazine-2,3-dicarboxylato) Cobalt(II) dihydrate</th>
<th>Bis(pyrazine-2,3-dicarboxylato) Zinc(II) dihydrate</th>
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<tr>
<td>( a )</td>
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<td>( b )</td>
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<td>11.82 Å</td>
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<tr>
<td>( c )</td>
<td>7.21 Å</td>
<td>7.30 Å</td>
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<td>( \beta )</td>
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<td>93.7°</td>
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<td>( V )</td>
<td>941 Å(^3)</td>
<td>959 Å(^3)</td>
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<tr>
<td>( Z )</td>
<td>2</td>
<td>2</td>
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<td>( D_{	ext{obs}} )</td>
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<td>1.49 g cm(^{-3})</td>
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</table>

Transformations of Hydrates into Instable Hydrates. The Crystallisation of CaCl\(_2\)-Hydrates in Quartz Flasks

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In a previous paper\(^1\) it was shown that a transformation of SrCl\(_2\)\(_6\)H\(_2\)O into the next lower hydrate (SrCl\(_2\)\(_2\)H\(_2\)O) can be avoided; SrCl\(_2\)\(_6\)H\(_2\)O transforms, if properly treated, into SrCl\(_2\)\(_2\)H\(_2\)O.

The transformation of CaCl\(_2\)\(_6\)H\(_4\)O into the next lower hydrate can also be avoided (CaCl\(_2\)\(_6\)H\(_2\)O and SrCl\(_2\)\(_6\)H\(_2\)O are isostructural). The next lower hydrate is \( \alpha \)-CaCl\(_2\)\(_4\)H\(_2\)O. Roozeboom\(^2\) found that CaCl\(_2\)\(_6\)H\(_2\)O can transform into the thermodynamically least stable tetrahydrate (\( \gamma \)-CaCl\(_2\)\(_4\)H\(_2\)O), and Lannung\(^3\) measured the equilibrium vapour pressures of the hydrate pair CaCl\(_2\)\(_6\)H\(_2\)O–\( \gamma \)-CaCl\(_2\)\(_4\)H\(_2\)O in the temperature interval 18–28°C; he found the temperature of transition to be 28.9°C.