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Chlorides with the Chrysoberyl Structure: Na_2CoCl_4 and Na_2ZnCl_4

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(*Received* 7 *May* 1976; *accepted* 15 *June* 1976)

Abstract. Na_2CoCl_4: *Pnma*, $a = 13{\cdot}713$ (2), $b = 8{\cdot}073$ (1), $c = 6{\cdot}4277$ (6) Å, $Z = 4$; and Na_2ZnCl_4: *Pnma*, $a = 13{\cdot}695$ (1), $b = 8{\cdot}0528$ (7), $c = 6{\cdot}4017$ (8) Å. Structure refinements based on neutron diffraction powder diagrams establish the chrysoberyl structure for both compounds.

Introduction. As part of a research programme on the structural relations of compounds in the systems NaCl–TCl_2 and LiCl–TCl_2 (where T represents a first-row transition or alkaline-earth metal) we investigated the crystal structure of Na_2CoCl_4 and Na_2ZnCl_4. Li_2ZnCl_4 was also prepared and its X-ray pattern indexed.

Detailed information about the background to the investigations can be obtained from some earlier papers (van Loon & Verschoor, 1973; van Loon, 1974; van Loon & IJdo, 1975; van Loon & de Jong, 1975).

The compounds Na_2ZnCl_4 and Li_2ZnCl_4 had been reported to have the chrysoberyl structure (Eysel, 1971) with the following structural data. Na_2ZnCl_4: space group *Pnam*; $a = 13{\cdot}72$, $b = 6{\cdot}42$, $c = 8{\cdot}09$ Å; Li_2ZnCl_4: space group $P2_12 2_1$; $a = 12{\cdot}78$, $b = 6{\cdot}12$, $c = 7{\cdot}43$ Å. The crystal structure of Na_2CoCl_4 has not previously been reported.

NaCl and LiCl were dried in vacuum at 200 and 400 °C respectively. $CoCl_2$ was obtained by dehydrating $CoCl_2.6H_2O$ in a vacuum in steps up to 400 °C, followed by melting in dry HCl gas. $ZnCl_2$ was melted in dry HCl gas after dehydration in a vacuum at 200 °C.

Stoichiometric amounts of the starting materials were evacuated up to 10^{-5} torr and fused together in a dry HCl atmosphere; the products were annealed for one week in a dry N_2 atmosphere just below the melting point. While Na_2ZnCl_4 could be cooled in the normal way, Na_2CoCl_4 had to be quenched in the liquid N_2. The latter compound has been investigated by DTA (by means of a Mettler Vacuum Thermal Analyzer TA1) and appears to be unstable below 367 °C.

The prepared samples were pulverized in a glove-box filled with dry N_2, again heated for a week just below their respective melting points (Na_2CoCl_4: 380; Na_2ZnCl_4: 400 °C) and cooled as before. Because of the extremely hygroscopic nature of the compounds, all handling was carried out in N_2- or Ar-filled glove-boxes.

An elemental analysis* was carried out for Na_2ZnCl_4 with the following results (wt %): Zn, obs. 25·38, calc. 25·82; Cl, obs. 56·83, calc. 56·02.

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* This analysis was carried out under the supervision of W. J. Buis at the Micro-Analytical Department of the Institute for Organic Chemistry, TNO, Utrecht, The Netherlands.

The X-ray powder diffraction patterns were obtained on a Philips PW 1050 diffractometer, modified for the investigation of hygroscopic samples. They could all be indexed in the orthorhombic system; systematic absences were of the type $k + l \neq 2n$ for $0kl$ reflexions and $h \neq 2n$ for $hk0$ reflexions. The consistency of the final results justified the choice of the space group *Pnma*, instead of the noncentrosymmetric $Pn2_1a$.

Neutron diffraction powder data were collected on the powder diffractometer at the HFR reactor in Petten. The neutron wavelength used was 2·57 Å. Soller slits with a horizontal divergence of 30′ were placed before the monochromator and in front of the BF_3 counter.

The neutron diffraction data showed that the Na_2CoCl_4 sample also contained $CoCl_2$ and NaCl, and that the Na_2ZnCl_4 sample contained NaCl. In the neutron diffraction diagrams used for the structure refinement, these regions have been excluded (Figs. 1 and 2).

With the neutron diffraction data in the range $5{\cdot}4 < 2\theta < 138°$, a structure refinement based on the Rietveld (1969) profile method has been carried out in space group *Pnma* by minimizing the residual function $\chi^2 = \Sigma_i w_i |y_i(\text{obs.}) - (1/c) y_i(\text{calc.})|^2$, where y(obs.) and y(calc.) represent the observed and calculated intensities per measuring point in a peak, w is the statistical weight and c the scale factor. The

Table 1. *Structural parameters for* Na_2ZnCl_4 *and* Na_2CoCl_4 *in space group Pnma with* $Z = 4$

		x	y	z
(a) Na_2ZnCl_4				
Na(1)	4(a)	0	0	0
Na(2)	4(c)	0·266 (1)	0·25	−0·002 (3)
Zn	4(c)	0·087 (1)	0·25	0·417 (2)
Cl(1)	4(c)	0·094 (1)	0·25	0·771 (1)
Cl(2)	4(c)	0·438 (1)	0·25	0·232 (2)
Cl(3)	8(d)	0·167 (1)	0·026 (1)	0·257 (1)
(b) Na_2CoCl_4		x	y	z
Na(1)	4(a)	0	0	0
Na(2)	4(c)	0·276 (2)	0·25	−0·026 (5)
Co	4(c)	0·079 (3)	0·25	0·421 (5)
Cl(1)	4(c)	0·094 (1)	0·25	0·707 (2)
Cl(2)	4(c)	0·437 (1)	0·25	0·236 (2)
Cl(3)	8(d)	0·168 (1)	0·025 (1)	0·256 (2)

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *in* Na_2ZnCl_4 *and* Na_2CoCl_4

	Na_2ZnCl_4	Na_2CoCl_4
Me—Cl(1)	2·27 (2)	2·23 (4)
Me—Cl(2)	2·26 (2)	2·20 (4)
Me—Cl(3) (2×)	2·34 (1)	2·42 (3)
Na(1)—Cl(1) (2×)	2·80 (1)	2·82 (1)
Na(1)—Cl(2) (2×)	2·78 (1)	2·77 (1)
Na(1)—Cl(3) (2×)	2·83 (1)	2·84 (1)
Na(2)—Cl(1) (2×)	2·77 (2)	2·93 (3)
Na(2)—Cl(2) (2×)	2·79 (2)	2·76 (4)
Na(2)—Cl(3) (2×)	2·79 (2)	2·85 (4)
Cl(1)—Cl(2)	3·87 (1)	3·88 (2)
Cl(1)—Cl(3) (2×)	3·88 (1)	3·89 (2)
Cl(2)—Cl(3) (2×)	3·62 (1)	3·64 (1)
Cl(3)—Cl(3)	3·61 (1)	3·63 (1)
Cl(1)—Me—Cl(2)	117·3 (7)	122 (2)
Cl(1)—Me—Cl(3)	114·7 (5)	113 (1)
Cl(2)—Me—Cl(3)	103·8 (5)	104 (1)
Cl(3)—Me—Cl(3)	100·6 (6)	97 (1)
Cl(1)—Na(1)—Cl(2)	86·6 (2)	86·8 (3)
Cl(1)—Na(1)—Cl(3)	81·8 (3)	83·5 (3)
Cl(2)—Na(1)—Cl(3)	81·5 (3)	81·0 (3)
Cl(1)—Na(2)—Cl(3)	42·1 (3)	40·0 (5)
Cl(2)—Na(2)—Cl(3)	51·6 (4)	48·8 (6)
Cl(3)—Na(2)—Cl(3)	48·5 (2)	47·0 (3)
Cl(3)—Na(2)—Cl(3)	80·4 (6)	76·6 (9)

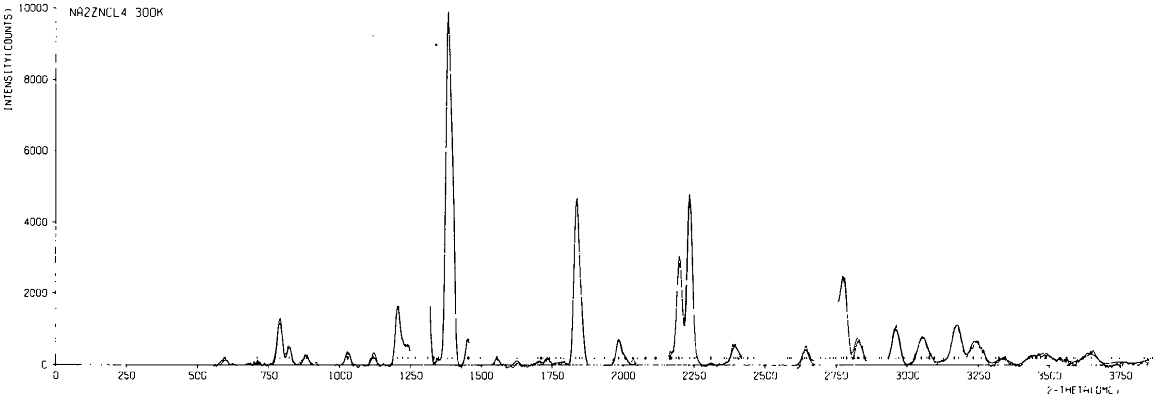

Fig. 1. Observed and calculated profile of Na_2ZnCl_4. The dotted line corresponds to the observed intensity and the full line to the calculated intensity. In this picture the background has been subtracted and the blank parts of the diagram are the excluded regions due to the contamination by NaCl and the peak intensities of the stainless steel sample holder.

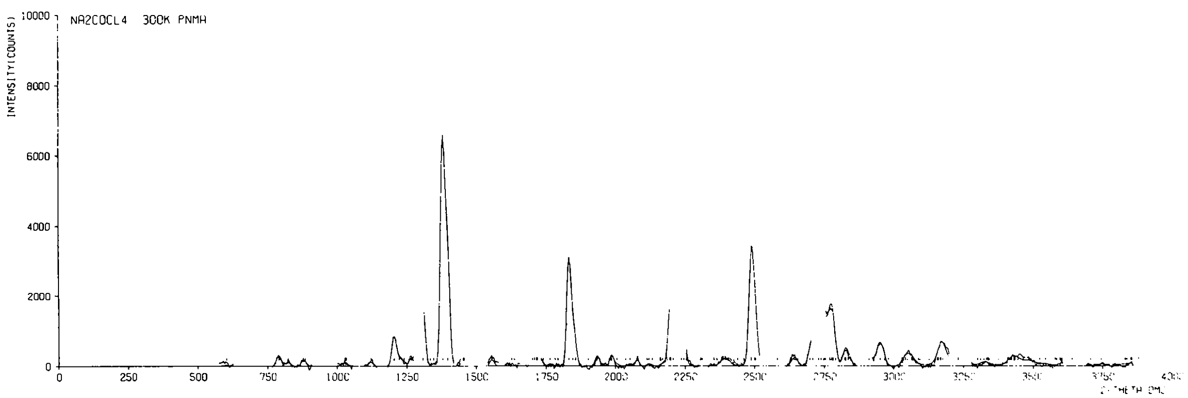

Fig. 2. Observed and calculated profile of Na_2CoCl_4. The dotted line corresponds to the observed intensity and the full line to the calculated intensity. In this picture the backgrounds have been subtracted and the blank parts of the diagram are the excluded regions due to the contamination by NaCl and $CoCl_2$.

coherent scattering lengths used were $0{\cdot}570 \times 10^{-12}$ for Zn, $0{\cdot}250 \times 10^{-12}$ for Co, $0{\cdot}351 \times 10^{-12}$ for Na and $0{\cdot}960 \times 10^{-12}$ cm for Cl (Neutron Diffraction Commission, 1969). The results are shown in Tables 1 and 2.

Discussion. In the A_2BCl_4 compounds a number of structures are realized, depending on the ionic radius ratios: the K_2NiF_4 structure type for K_2MgCl_4 (Witteveen, 1973), the β-K_2SO_4 structure type for Cs_2CoCl_4 (Poraï-Kochits, 1956), the deformed β-K_2SO_4 structure for K_2PbO_4 (Vermin, Verschoor & IJdo, 1976), the Sr_2PbO_4 structure type for Na_2MnCl_4 (Goodyear, Ali & Steigmann, 1971), the inverse spinel structure for Li_2MnCl_4 (van Loon & de Jong, 1975) and the chrysoberyl or olivine structure, characterized by octahedrally surrounded A ions and tetrahedrally surrounded B ions in a hexagonal close-packed arrangement of anions.

As mentioned previously, the compound Li_2ZnCl_4 was reported to have the space group $P2_122_1$. Since Li has a much smaller ionic radius than Na (Shannon & Prewitt, 1969) a deformation of the chrysoberyl structure (giving rise to a structure with lower symmetry) or a totally different crystal structure seemed possible, perhaps even likely (note the structural differences between Li_2MnCl_4 and Na_2MnCl_4). However, our X-ray experiments did not reveal reflexions allowed in $P2_122_1$ but forbidden for *Pnma*, thereby confirming *Pnma* for Li_2ZnCl_4. The following lattice parameters were determined: $a = 12{\cdot}76$ (1), $b = 7{\cdot}4111$ (6) and $c = 6{\cdot}122$ (6) Å.

In the system LiCl–$CoCl_2$ no chrysoberyl structure was found. This system is very complicated according to its phase diagram (Seifert, 1961). Its characteristics will not be discussed in this paper.

The authors wish to thank Mr J. F. Strang of Reactor Centrum Nederland, Petten, for collecting the neutron diffraction data. The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

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