

(1966) with the configuration of camphor as a reference (Fredga & Miettinen, 1947; Wunderlich, 1967).

The hydantoin ring is planar as in DPH (Camerman & Camerman, 1970). The angles between the phenyl groups and the hydantoin ring are given in Table 4 with the corresponding values in DPH.

Table 4. *Angles between the planes of the rings in HPPH and DPH*

HPPH	DPH
phenyl-hydantoin: 104°	phenyl-hydantoin: 114°
phenol-hydantoin: 104	phenyl-hydantoin: 113
phenol-phenyl: 105	phenyl-phenyl: 90

The molecules are hydrogen bonded to two neighbouring molecules as shown in Fig. 2.

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SHORT COMMUNICATIONS

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Acta Cryst. (1975). **B31**, 2549

Some chlorides with the inverse spinel structure: Li_2TCl_4 (T = Mg, Mn, Fe, Cd). By C. J. J. VAN LOON and J. DE JONG, *Gorlaeus Laboratories, Section of Solid State Chemistry, University of Leiden, P.O. Box 75, Leiden, The Netherlands*

(Received 8 April 1975; accepted 27 May 1975)

X-ray diffraction patterns suggest that the compounds Li_2TCl_4 (T = Mg, Mn, Fe, Cd) have the inverse spinel structure. A structure refinement, based on neutron diffraction powder data, has been carried out for Li_2MnCl_4 .

Introduction

An investigation of the systems NaCl-TCl_2 and LiCl-TCl_2 (T = Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd, Ca, Sr, Ba, Pb) has been started in order to enlarge the number of structural data available for comparison with theoretically derived structure models. A systematic derivation of $^{\text{VI}}\text{A}^{\text{VI}}\text{BX}_3$ structures (van Loon, 1974) has been carried out, but the number of ABX_3 compounds found within the investigated range is only very small. Three compounds, *viz.* NaMnCl_3 , NaMgCl_3 and NaCdCl_3 , have been prepared. Single crystals of one of these isostructural compounds, NaMnCl_3 , have been used in a structure refinement (van Loon & Verschoor, 1973). Several compounds with different stoichiometries (Na_2TCl_4 , Na_6TCl_8 , $\text{Na}_2\text{T}_3\text{Cl}_8$; T = Mg, Mn, Fe, Cd) have been established and their structures determined (van Loon & IJdo, 1975). The compounds Na_2CoCl_4 , Na_2ZnCl_4 and Li_2ZnCl_4 apparently have the chrysoberyl (Wyckoff, 1964) structure; their structure refinement will be the subject of a subsequent paper.

Experimental

LiCl was dried *in vacuo* at 400°C. MnCl_2 was obtained by dehydrating $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in HCl atmosphere in steps up

to 350°C, followed by melting in dry nitrogen. Molten MgCl_2 was obtained by heating Mg metal at 900°C in a stream of dry HCl gas. FeCl_2 and CdCl_2 were obtained from the hydrates $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{CdCl}_2 \cdot x\text{H}_2\text{O}$ by

Table 1. *Structural data of Li_2TCl_4 compounds*

Space group: $Fd\bar{3}m$, $Z=8$ (origin at centre, $\bar{3}m$)				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>n</i>
Li(1) 16(<i>d</i>)	0.5	0.5	0.5	0.25
Li(2) 8(<i>a</i>)	0.125	0.125	0.125	0.25
Mn 16(<i>d</i>)	0.5	0.5	0.5	0.25
Cl 32(<i>e</i>)	0.2564 (1)	0.2564 (1)	0.2564 (1)	1.0
<i>a</i>				
Li_2MnCl_4	10.5031 (3) Å			
Li_2MgCl_4	10.413 (1)			
Li_2CdCl_4	10.637 (5)			
Li_2FeCl_4	10.405 (3)			

Refinement of site occupation number
 $n[\text{Li}(1) \text{ at } 16(d)] = 0.284 (8)$
 $n[\text{Li}(2) \text{ at } 8(a)] = 0.216 (8)$
 $n[\text{Mn}(1) \text{ at } 8(a)] = 0.034 (8)$
 $n[\text{Mn}(2) \text{ at } 16(d)] = 0.216 (8)$
 $c = 0.0410 (4)$ $B = -1.94 (6)$
 $x_{\text{Cl}} = 0.2564 (1)$

Table 2. *Interionic distances (Å) and bond angles (°) in Li₂MnCl₄*

Li(2)—Cl	4 ×	2.391 (1)	Cl—Li(1), Mn—Cl	180.00 (0)
Li(1), Mn—Cl	6 ×	2.560 (1)	Cl—Li(1), Mn—Cl	86.94 (4)
Cl—Cl	3 ×	3.523 (3)	Cl—Li(1), Mn—Cl	93.06 (4)
Cl—Cl	6 ×	3.7159 (1)	Cl—Li(2)—Cl	109.47 (6)
Cl—Cl	3 ×	3.904 (3)	Li(1), Mn—Cl—Li(1), Mn	92.98 (4)
Li(1), Mn—Li(1), Mn	6 ×	3.7134 (0)	Li(1), Mn—Cl—Li(2)	123.13 (5)
Li(1), Mn—Li(2)	6 ×	4.3544 (0)		

dehydration in a stream of dry HCl gas in steps up to 500°C and 350°C respectively.

Stoichiometric amounts of the starting materials were fused together in dry nitrogen atmosphere after an evacuation up to 10⁻⁵ torr; thereupon they were annealed during one week just below the melting point.

The X-ray powder diffraction patterns were obtained by means of a Philips PW 1050 diffractometer, modified for the investigation of hygroscopic samples. The compounds in question appeared to have cubic symmetry; systematic absences indicated a face-centred structure. Intensity calculations, carried out for both the inverse and the normal spinel structure, suggested that the compounds Li₂TCl₄ (T = Mg, Mn, Fe, Cd) have the inverse spinel structure. This means that half of the lithium ions are tetrahedrally surrounded by chlorine ions whereas the other half, together with the T ions, are distributed statistically over the occupied octahedral sites (Wyckoff, 1964).

A structure refinement of Li₂MnCl₄, based on neutron diffraction powder data, confirmed our conclusions. The neutron diffraction diagram was collected at 300 K on the powder diffractometer at the Petten High Flux Reactor. The complete range of data (5.4° < 2θ < 138.7°) obtained with a wavelength of 2.5718 Å was used in the refinement. Absorption and extinction effects were small and no corrections were made. The sample, about 20 g, was contained in a thin-walled vanadium tube. The scattering lengths (10⁻¹²) were -0.194 for Li, -0.360 for Mn and 0.960 for Cl (Neutron Diffraction Commission, 1969). The function minimized during the least-squares analysis of the powder diffraction profile (Rietveld, 1967) was $\sum w[y(\text{obs}) - (1/c)y(\text{calc})]^2$; $y(\text{obs})$ and $y(\text{calc})$ represent the observed and calculated intensities per measuring point in a peak, w is the statistical weight and c the scale factor. A few cycles of full matrix refinement led to convergence at $R_1 = 100 \sum |I(\text{obs}) - (1/c)I(\text{calc})| / \sum I(\text{obs}) = 2.59$, $R_2 = 100 \sum [y(\text{obs}) - (1/c)y(\text{calc})] / \sum y(\text{obs}) = 6.36$, $R_3 = 100 / \{ \sum w [y(\text{obs}) - (1/c)y(\text{calc})]^2 / \sum w [y(\text{obs})]^2 \} = 6.70$.

Acta Cryst. (1975). B31, 2550

The crystal and molecular structure of bis[diethyl bis-(1-pyrazolyl)borato]nickel(II): a correction. By H. M. ECHOLS and D. DENNIS, *Department of Chemistry, University of Delaware, Newark, Delaware 19711, U.S.A.*

(Received 21 April 1975; accepted 21 April 1975)

In Fig. 2 of Echols & Dennis [*Acta Cryst.* (1974). B30, 2173–2176], the bond distance N(1)–C(3) should read 1.34 instead of 1.39.

The correction of a typographical error: In the paper on bis[diethyl bis-(1-pyrazolyl)borato]nickel(II) by Echols & Dennis (1974), Fig. 2, the bond distance N(1)–C(3) should read 1.34 instead of 1.39. All other bond lengths and angles are printed correctly.

The final scale factor and overall temperature factor were 0.0411(4) and -1.92(6). Inclusion of a site occupation number resulted in reliability indices $R_1 = 1.90$, $R_2 = 6.38$ and $R_3 = 6.53$.

All structural data of interest are gathered in Table 1. Standard deviations, given in parentheses, are based on counting statistics. Interionic distances and bond angles are presented in Table 2.*

The computations were carried out partly at the Computing Division of the Reactor Centre in Petten and partly at the Computing Institute of Leiden University. We wish to thank the staff of the R. C. N. in Petten. One of us (J. de J.) is especially grateful for an allowance provided during a six-month stay. The investigations were supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z. W. O.).

* A list of intensities has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31174 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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