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Short Communications

Single crystal structure refinement of $MnCl_2$

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***Crystal structure* / *C-19 structural type* / $MnCl_2$**

Introduction

During the crystallization process of NH_4MnCl_3, a different material appeared in the closed crucible. It consisted of very exfoliable rose crystals, which curved easily. Suggesting them to be a new ternary phase of a NH_4^+ intercalated compound, they were analyzed by X-ray diffraction.

Experimental

As the crystals were very hygroscopic, some fragments were put, under argon atmosphere, into closed capillary tubes. The XRD pictures showed somewhat broad spots, specially for those reflexions which correspond to the exfoliable and curved layers. The crystal lattice found was the same as that assigned to $MnCl_2$ by Ferrari, Braibanti and Bigliari (1963) using powder X-ray diffraction. This is a C-19 structure type consisting of layers of grouped $MnCl_{6/3}$ octahedra (Krebs, 1968). Nevertheless, we still suggested that some NH_4 could be embedded between layers as observed with Na in $NaCrS_2$ or $NaCrSe_2$ compounds (Krebs, 1968). And, in any case, as it seemed desirable to refine the crystal structure of $MnCl_2$ with single crystal X-ray data, we decided to solve the structure of this material.

The best single crystal fragment of $0.7 \times 0.4 \times 0.08$ mm^3 was mounted in a single crystal X-ray diffractomer with graphite-monochromated Mo$K\alpha$ radiation. The hexagonal cell dimensions were refined using 21 selected

Table 1. Atomic parameters of $MnCl_2$. The thermal parameters are in the form $10^2 \times \exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots - 2U_{12}hka^*b^* + \ldots)]$. The l.s.s.d. are given in parentheses.

	x	y	z	$U_{11} = U_{22}$	U_{33}	U_{12}	$U_{13} = U_{23}$
Mn	0	0	0	$2U_{12}$	4.3(1)	0.58(1)	0
Cl	0	0	0.2545(1)	$2U_{12}$	3.22(8)	0.70(2)	0

reflexions with $\theta > 14°$, they are $a = 3.711(2)$ and $c = 17.59(7)$ Å and the space group was confirmed to be $R\bar{3}m$. The 597 independent intensities measured for $\theta < 75°$, which were not corrected for absorption, were reduced to structure factors by Lorentz and polarization correction. To refine the crystal structure of $MnCl_2$, the 15 (00l) reflexions and 12 more around the [001] direction, were ignored for their spread. Then, 435 reflexions with $I > 3\sigma(I)$, were used for the anisotropic least-squares refinement, which converged to $R = 0.105$ (Stewart, Kundell and Baldwin, 1980). The atomic form factors were corrected for anomalous dispersion. The refined structure confirms the C-19 structural type with the atomic parameters shown in Table 1.[1]

Discussion

The $MnCl_6$ octahedra are somewhat flattened along the 3-fold axis. Representative bond distances and bond angles are: Mn–Cl = 2.548(2) Å, Cl–Cl = 3.708(3) and 3.497(2) Å, Cl–Mn–Cl = 93.36(7) and 86.64(6)°. The shortest distance between Cl atoms of neighboured layers is 3.754(2) Å, the thickness of one layer and one interlayer being 2.765(3) and 3.084(3) Å, respectively.

While a Fourier map showed peaks of 120 and 90 e/A^3 for the Mn and Cl positions, a difference map showed neither peaks nor holes with an absolute density greater than 4 e/A^3. The electron density in the interlayer keeps lower than 1 e/A^3. Hence no NH_4 is embedded in the crystal lattice.

References

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Krebs, H.: *Fundamentals of Inorganic Crystal Chemistry*, p. 224, London, McGraw-Hill, 1968.

Stewart, J. M., Kundell, F. A., Baldwin, J. C.: The X-Ray 80 System. Computer Science Centre. Univ. of Maryland, College Park 1980.

[1] A F_o/F_c table can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 53531, the names of the authors and the title of the paper.