The shortest intramolecular nonbonded distances are 2·863 (3) and 2·903 (4) Å for the F(2)···F(6)($y\bar{x}\bar{z}$) and F(2)···C(6)($y\bar{x}\bar{z}$) contacts, respectively.

References

AHMED, N. A., KITAIGORODSKY, A. I. & MIRSKAYA, K. V. (1971). Acta Cryst. B27, 867–870.

CROMER, D. T. & LIBERMAN, D. (1970). J. Chem. Phys. 53, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). Acta Cryst. A24, 321–324.

DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975a). Acta Cryst. B31, 221–234.

DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975b). Acta Cryst. B31, 1630–1641.

GLIDEWELL, C. & SHELDRICK, G. M. (1971). J. Chem. Soc. A, pp. 3127–3129.

HUTCHINGS, M. G., ANDOSE, J. D. & MISLOW, K. (1975). J. Am. Chem. Soc. 97, 4553–4561.

HUTCHINGS, M. G., NOURSE, J. G. & MISLOW, K. (1974). Tetrahedron, 30, 1535–1549.

KARIPIDES, A., FORMAN, C., THOMAS, R. H. P. & REED, A. T. (1974). Inorg. Chem. 13, 811–815.

KARIPIDES, A. & OERTEL, M. (1977). Acta Cryst. B33, 683–687.

ROBBINS, A., JEFFREY, G. A., CHESICK, J. P., DONOHUE, J., COTTON, F. A., FRENZ, B. A. & MURILLO, C. A. (1975). Acta Cryst. B31, 2395–2399.

TAMBORSKI, C., SOLOSKI, E. J. & DEC, S. M. (1965). J. Organomet. Chem. 4, 446–454.

Comments on *A study of the crystal structure of* $(CH_3NH_3)_2MnCl_4$ *by neutron diffraction at* 188 ± 1 K and *A study of the crystal structure of* $(CH_3NH_3)_2MnCl_4$ *by neutron diffraction at* 404 K by I. Mikhail.

By G. HEGER, Kernforschungszentrum Karlsruhe GmbH, Institut für Angewandte Kernphysik 1, Postfach 3640, D-7500 Karlsruhe, Federal Republic of Germany, G. CHAPUIS and D. SCHWARZENBACH, Université de Lausanne, Institut de Cristallographie, BSP Dorigny, CH-1015 Lausanne, Switzerland and D. MULLEN, Fachbereich Geowissenschaften der Universität Marburg, D-3550 Marburg, Federal Republic of Germany

The new refinements reported by Mikhail [Acta Cryst. (1977), B33, 1317–1321, 1321–1325] of the tetragonal low-temperature and tetragonal high-temperature phases of $(CH_3NH_3)_2MnCl_4$ and the arguments leading to the assignment of space groups different from those proposed earlier seem to be doubtful.

The two papers by Mikhail (1977a,b) show a variety of discrepancies with respect to our previous results on $(CH_3NH_3)_2MnCl_4$ and $(CH_3NH_3)_2CdCl_4$. In this comment we would like to discuss some specific points which lead us to doubt the conclusions given by Mikhail (1977a,b).

(1) It should first be mentioned that the same neutron diffraction data have already been used for complete structure determinations (Heger, Mullen & Knorr, 1975, 1976).

(2) In his papers, Mikhail has not mentioned the dominant role of the incoherent neutron scattering by hydrogen and the necessity for correcting the measured intensity data for absorption. With an effective linear absorption coefficient of $\mu = 2\cdot46$ cm^{-1} for $(CH_3NH_3)_2MnCl_4$ and crystal dimensions of approximately 4·60 × 4·95 × 1·35 mm a correction for absorption is necessary (Heger et al., 1975). Mikhail based his argument and calculations on absorption-corrected and averaged data, which were handed to him.

(3) Mikhail describes a desymmetrization of the published structures, assuming subgroups of the space groups used earlier: for $(CH_3NH_3)_2MnCl_4$ at 404 K: $I4/m$ instead of $I4/mmm$ (HTT phase), and at 188 K: $Pccn$ instead of $P4_2/ncm$ (LTT phase). The author supports this by noting 'marked inconsistencies' with the diffraction symmetry 4/mmm. However, the maximum differences between the absorption-corrected intensities of symmetry-related reflections were within 10%, but the corresponding value for the un-corrected measured intensities was 150% (Heger et al., 1975). Moreover, Mikhail used for his refinements independent intensities with respect to the higher symmetry averaged according to 4/mmm (the same data as Heger et al., 1975, 1976).

(4) In the re-refinement of the LTT phase in space group $Pccn$, which is a subgroup of the previously assumed symmetry $P4_2/ncm$, the ratio of the number of observations to the number of refined parameters is only 2·5. 183 independent reflections with respect to tetragonal symmetry were taken from Heger et al. (1976). This represents only half of the data required for orthorhombic symmetry. A refinement as described by Mikhail is admissible only if the crystal is, in fact, an orthorhombic single crystal and if the intensities used are not averaged over equivalent reflections with respect to tetragonal symmetry. In this case, a loss of information due to the incompleteness of the data is still to be taken into account. In all other cases, the least-squares program must be modified since the intensity of a reflection is given by $I = q|F_{hkl}|^2 + (1 - q)|F_{khl}|^2$, q and $(1 - q)$ being the relative amounts of the two twin components contributing to the measured or averaged value. Derivatives of I with respect to the structural parameters and q are easily calculated. In the absence of any such modification, the new parameters cannot describe the real orthorhombic structure, even if it should exist.

(5) The re-refinement of the HTT phase in space group $I4/m$ may be questioned on the basis of group-theoretical

considerations. From DTA (Arend, Hoffmann & Waldner, 1973; Depmeier, Felsche & Wildermuth, 1977), birefringence, X-ray and neutron diffraction (Knorr, Jahn & Heger, 1974) measurements of $(CH_3NH_3)_2MnCl_4$, the phase transition $I4/mmm \rightleftharpoons Abma$ at 393 K was shown to be of second order. Under such conditions, the orthorhombic room-temperature space group must be a subgroup of the HTT space group. Among the symmetry groups which satisfy the diffracting conditions of the HTT phase, only $I4/mmm$ (and not $I4/m$) has $Abma$ as a subgroup (Neubüser & Wondratschek, 1969).

(6) The refinement of a structure can always be attempted assuming a subgroup of the actual space-group symmetry, thus increasing the number of variables. With a ratio of number of observations to number of variables of 2·9 for the HTT phase, conclusions from such a refinement should be judged carefully. This ratio would even reduce to 2·6 taking into account the six variables (two positional and four thermal parameters) listed in Table 2 of the HTT phase given without any e.s.d. (Mikhail, 1977b). For this refinement also, the same remark concerning the loss of information as mentioned under (4) can be made. Although $I4/m$ requires double the amount of data compared with $I4/mmm$, the new refinement with space-group symmetry $I4/m$ has been performed with the 133 reflections taken from Heger et al. (1975).

(7) Mikhail's papers give unusual interatomic distances and angles; e.g. in the HTT phase an octahedral angle of 86·08° for the $MnCl_6$ group and C—H bond lengths between 0·779 and 1·06 Å are given without interpretation. The corresponding values from Heger et al. (1975) are 89·9° and 1·03–1·09 Å. Furthermore, hydrogen bonds of the type C—H$\cdots$Cl are unusual.

In conclusion, we assert that we have no indication that the space groups $P4_2/ncm$ of the low-temperature and $I4/mmm$ of the high-temperature phases as reported by Heger, Mullen & Knorr (1975, 1976) from neutron diffraction are incorrect. This conclusion is supported by the refinement of the low- and high-temperature phases of the related compound $(CH_3NH_3)_2CdCl_4$ where the same tetragonal space groups had to be adopted (Chapuis, Arend & Kind, 1975; Chapuis, Kind & Arend, 1976). In addition, a recent theoretical study by Blinč, Zeks & Kind (1978) shows that the LTT phase follows logically from a phase-transition model based on the order–disorder of the CH_3NH_3 groups.

References

AREND, H., HOFFMANN, R. & WALDNER, F. (1973). Solid State Commun. 13, 1629–1632.
BLINČ, R., ZEKS, B. & KIND, R. (1978). Phys. Rev. Sect. B. Submitted.
CHAPUIS, G., AREND, H. & KIND, R. (1975). Phys. Status Solidi A, 31, 449–454.
CHAPUIS, G., KIND, R. & AREND, H. (1976). Phys. Status Solidi A, 36, 285–292.
DEPMEIER, W., FELSCHE, J. & WILDERMUTH, G. (1977). J. Solid State Chem. 21, 57–65.
HEGER, G., MULLEN, D. & KNORR, K. (1975). Phys. Status Solidi A, 31, 455–462.
HEGER, G., MULLEN, D. & KNORR, K. (1976). Phys. Status Solidi A, 35, 627–637.
KNORR, K., JAHN, I. R. & HEGER, G. (1974). Solid State Commun. 15, 231–238.
MIKHAIL, I. (1977a). Acta Cryst. B33, 1317–1321.
MIKHAIL, I. (1977b). Acta Cryst. B33, 1321–1325.
NEUBÜSER, J. & WONDRATSCHEK, H. (1969). Maximal Subgroups of the Space Groups, 2nd version. Univ. Karlsruhe.

Book Reviews

Works intended for notice in this column should be sent direct to the Book-Review Editor (J. H. Robertson, School of Chemistry, University of Leeds, Leeds LS2 9JT, England). As far as practicable books will be reviewed in a country different from that of publication.

Reactivity of solids. Edited by J. WOOD, O. LINDQVIST, C. HELGESSON and N. G. VANNERBERG. Pp. xx + 810. New York: Plenum, 1977. Price $71.40.

For three decades, the rapid progress of solid state chemistry had led to many congresses. This book contains the 116 papers presented at the 8th International Symposium on the Reactivity of Solids which was held in Göteborg (Sweden) in June 1976.

It is divided into six topics, each of which is headed by a general introduction to the subject: reaction at surfaces and interfaces, especially at elevated temperatures (33 papers), influence of structural defects on the reactivity of solids (34 papers), solid state reactions in organic materials (6 papers), reactions in vitreous solids (8 papers), new developments in experimental techniques for the study of reactivity of bulk solids and of surfaces (15 papers), solid state reactions in technology (20 papers).

This book is specially intended for solid state chemists who will find a wide coverage of the work in progress in this field of chemistry. The main aims of research, often connected with basic present day problems, are faithfully reflected: catalysis, corrosion, ionic superconductors, reaction selectivity and new materials are the more frequent subjects of papers.

Most of these results, often very different from each other through their aim and through the experimental methods used, underline the prominent part played by all sorts of defects in the common solid. It has been possible to undertake this kind of research into real solids often because of the always increasing efficiency and flexibility of the physical methods which may be used in solid state chemistry (X-ray, electron, neutron diffraction, LEED, IR, Raman, Auger, mass and Mössbauer spectroscopies, ESR, NMR etc.). The simultaneous use of diffraction and spectroscopy seems to be more and more frequent and leads to quite interesting results.