

- MONTGOMERY, H. & LINGAFELTER, E. C. (1964). *Acta Cryst.* **17**, 1478–1479.
- MORIMOTO, C. (1970). PhD thesis, Univ. of Washington, Seattle, Washington.
- PENFOLD, B. R. (1969). Univ. of Canterbury crystallographic programs, Christchurch, New Zealand (versions of *ORFLS* and *ORFFE*).
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, p. 456. New York: Macmillan.
- VICAT, J., TRANQUI, D., FILHOL, A., ROUDAUT, E., THOMAS, M. & ALÉONARD, S. (1975). *Acta Cryst.* **B31**, 1895–1903.

*Acta Cryst.* (1980). **B36**, 2123–2126

## New Indium Molybdenum Selenides: $\text{InMo}_6\text{Se}_8$ and $\text{In}_2\text{Mo}_{15}\text{Se}_{19}$

BY A. LIPKA\* AND K. YVON

*Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 quai Ernest Ansermet, CH-1211 Genève, Switzerland*

(Received 15 March 1980; accepted 8 April 1980)

**Abstract.**  $\text{InMo}_6\text{Se}_8$ : rhombohedral,  $R\bar{3}$ ,  $a_{\text{hex}} = 9.55$  (1),  $c_{\text{hex}} = 11.85$  (1) Å;  $a_{\text{rh}} = 6.78$  (1) Å,  $\alpha = 89.5$  (3)°,  $Z = 1$ . It crystallizes with the  $\text{PbMo}_6\text{S}_8$  structure type.  $\text{In}_2\text{Mo}_{15}\text{Se}_{19}$ : rhombohedral,  $R\bar{3}c$ ,  $a_{\text{hex}} = 9.84$  (1),  $c_{\text{hex}} = 57.47$  (8) Å;  $a_{\text{rh}} = 19.98$  (3) Å,  $\alpha = 28.5$  (1)°,  $Z = 6$ . It contains  $\text{Mo}_6\text{Se}_8$  and  $\text{Mo}_9\text{Se}_{11}$  building blocks and may be considered as a stacking variant of the hexagonal  $\text{In}_{\sim 3}\text{Mo}_{15}\text{Se}_{19}$  phase. The Mo–Mo distances in the  $\text{Mo}_6$  and  $\text{Mo}_9$  clusters are examined and the bonding is discussed. (The final  $R$  values are 0.10 and 0.08 respectively.)

**Introduction.** Indium is one of the few metals for which a rhombohedral molybdenum selenide of formula  $M\text{Mo}_6\text{Se}_8$  ( $M = \text{metal}$ ) has not yet been found (Fischer, 1978; Yvon, 1979). There are, however, related compounds of similar composition such as hexagonal  $\text{In}_x\text{Mo}_{15}\text{Se}_{19}$  ( $2.9 < x < 3.4$ ) containing  $\text{Mo}_6\text{Se}_8$  and  $\text{Mo}_9\text{Se}_{11}$  building blocks (Grüttner, Yvon, Chevrel, Potel, Sergent & Seeber, 1979; Seeber, Decroux, Fischer, Chevrel, Sergent & Grüttner, 1979; Chevrel, Sergent, Seeber, Fischer, Grüttner & Yvon, 1979), and hexagonal  $\text{InMo}_3\text{Se}_3$  containing one-dimensional  $\frac{1}{3}(\text{Mo}_3\text{Se}_3)$  fibres (Hönle, von Schnering, Lipka & Yvon, 1980). The apparent absence of a rhombohedral phase in this system was curious because a rhombohedral  $\text{InMo}_6\text{S}_8$  phase in the corresponding sulphur system exists (Yvon, 1979; Yvon & Paoli, 1977).

In this article we report on the synthesis and structural analysis of the rhombohedral selenide  $\text{InMo}_6\text{Se}_8$  which contains  $\text{Mo}_6\text{Se}_8$  building blocks. It

forms simultaneously with another rhombohedral phase of composition  $\text{In}_2\text{Mo}_{15}\text{Se}_{19}$  containing  $\text{Mo}_6\text{Se}_8$  and  $\text{Mo}_9\text{Se}_{11}$  building blocks similar to those found in the more In-rich hexagonal  $\text{In}_{\sim 3}\text{Mo}_{15}\text{Se}_{19}$  phase. The existence of a rhombohedral  $\text{In}_2\text{Mo}_{15}\text{Se}_{19}$  phase has been reported recently (Potel, Chevrel, Sergent, Decroux & Fischer, 1979) but no atomic coordinates and no details of its formation were given.

The two crystals investigated in this work were isolated from a sample of approximate composition  $\text{In}:\text{Mo}:\text{Se} = 1:6:8$  whose preparation has been described (Grüttner *et al.*, 1979). The heat treatment was carried out at about 1450 K in an evacuated quartz tube for a few days. A Guinier photograph showed that the powder pattern was different from those of the hexagonal  $\text{In}_{\sim 3}\text{Mo}_{15}\text{Se}_{19}$  and  $\text{InMo}_3\text{Se}_3$  phases. The diffraction lines were relatively diffuse, indicating that the compounds were not well crystallized. This was later confirmed by the structural analysis which showed that the quality of the single crystals was rather poor. Both substances have a rhombohedral structure. For  $\text{InMo}_6\text{Se}_8$  the cell parameters and space group ( $R\bar{3}$ ) suggested isotypy with  $\text{PbMo}_6\text{S}_8$  (Marezio, Dernier, Remeika, Corenzwit & Matthias, 1973). For  $\text{In}_2\text{Mo}_{15}\text{Se}_{19}$  the Laue group ( $3m$ ) and the systematically absent reflexions ( $hh0l$  with  $l = 2n + 1$ ) indicated the possible space groups  $R\bar{3}c$  and  $R3c$  (*International Tables for X-ray Crystallography*, 1969). A comparison of the hexagonal cell parameters  $a_{\text{hex}}$  and  $c_{\text{hex}}$  with those of  $\text{In}_{\sim 3}\text{Mo}_{15}\text{Se}_{19}$  ( $a \sim a_{\text{hex}}$ ,  $c \sim c_{\text{hex}}/3$ ) suggested that the two compounds were structurally related.

Integrated intensities of 480 ( $\text{InMo}_6\text{Se}_8$ ) and 236 ( $\text{In}_2\text{Mo}_{15}\text{Se}_{19}$ ) reflexions with  $I > 3\sigma(I)$  were recorded on an automated diffractometer to a limit of  $\sin \theta/\lambda = 0.5 \text{ \AA}^{-1}$ . For  $\text{In}_2\text{Mo}_{15}\text{Se}_{19}$  the data were collected at

\* On leave from : Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf, Federal Republic of Germany.

233 K. The structure of  $\text{InMo}_6\text{Se}_8$  was refined from the known atomic coordinates of  $\text{PbMo}_6\text{S}_8$  (Marezio *et al.*, 1973). The final  $R$  ( $= \sum | \Delta F | / \sum F_o$ ) was 0.10.\* The structure of  $\text{In}_2\text{Mo}_{15}\text{Se}_{19}$  was solved by testing the different possibilities of stacking the  $\text{Mo}_6\text{Se}_8$  and  $\text{Mo}_9\text{Se}_{11}$  units in space group  $R\bar{3}c$ . The final  $R$  was 0.08.\* The atomic coordinates of both compounds are listed in Table 1.

**Discussion.** In the In–Mo–Se system four different ternary compounds of similar stoichiometry are currently known: the hexagonal compounds  $\text{In}_{n-3}\text{Mo}_{15}\text{Se}_{19}$  (Grüttner *et al.*, 1979; Seeber *et al.*, 1979; Chevrel *et al.*, 1979) and  $\text{InMo}_6\text{Se}_8$  (Hönle *et al.*, 1980), and the title rhombohedral compounds  $\text{InMo}_6\text{Se}_8$  and  $\text{In}_2\text{Mo}_{15}\text{Se}_{19}$ . They are closely related from both a topological and a bonding point of view. Their cell dimensions parallel to the hexagonal base are almost identical whereas their  $c$  parameter varies mainly as a function of the size and the stacking sequence of the  $\text{Mo}_{3n}\text{X}_{3n+2}$  building blocks ( $n = 2, 3, \infty$ ). Projections of the  $\text{InMo}_6\text{Se}_8$ ,  $\text{In}_2\text{Mo}_{15}\text{Se}_{19}$  and  $\text{In}_{n-3}\text{Mo}_{15}\text{Se}_{19}$  structures on the (1120) plane are shown in Fig. 1. One can see that the latter two can be derived from the former by a periodic unit-cell twinning operation parallel to (0001) (Andersson & Hyde, 1974). While the hexagonal  $\text{In}_{n-3}\text{Mo}_{15}\text{Se}_{19}$  ( $c = 19.45 \text{ \AA}$ ) has the stacking sequence  $AB_m B' A' C'_m$

$CAB_m B' \dots$ , the rhombohedral  $\text{In}_2\text{Mo}_{15}\text{Se}_{19}$  ( $c = 57.47 \text{ \AA}$ ) has

$AB \frac{1}{2} B' C' A' \frac{1}{2} ABC \frac{1}{2} C' A' B' \frac{1}{2} BCA \frac{1}{2} A' B' C' \frac{1}{2} CAB \frac{1}{2} B' \dots$

where the twinning operations  $\frac{1}{m}$  and  $\frac{1}{2}$  refer to the fusion of two  $\text{Mo}_6\text{Se}_8$  units into one  $\text{Mo}_9\text{Se}_{11}$  unit, and the letters  $A, B, C$  and  $A', B', C'$  refer to the three positions and two orientations of the  $\text{Mo}_6\text{Se}_8$  units.

$\text{InMo}_6\text{Se}_8$ . The structural feature of main interest with respect to its bonding is the size and the elongation of the  $\text{Mo}_6$  octahedron. For the  $M\text{Mo}_6\text{X}_8$  compounds ( $X = \text{chalcogen}$ ) it has been shown (Yvon, 1979; Yvon & Paoli, 1977) that this cluster contracts and becomes more regular if the number of bonding electrons on the Mo atoms is increased. In the selenides having, for instance, 23 electrons per  $\text{Mo}_6$  cluster, such as  $\text{LaMo}_6\text{Se}_8$ , the Mo–Mo distances parallel to the hexagonal base are 2.69 Å whereas those away from it are 2.73 Å. Since the corresponding distances in the present  $\text{InMo}_6\text{Se}_8$  are almost the same, 2.69 and 2.74 Å respectively, the In atoms are here probably in a trivalent state. This is also supported by the short In–Se bonds along the ternary axis [ $\text{In–Se}(2) = 2.83 \text{ \AA}$ ;  $r(\text{Se}^{2-}) + r(\text{In}^{3+}) = 2.79 \text{ \AA}$ ]. Surprisingly, the distribution of the In atoms in the chalcogen-atom network differs from that in the corresponding sulphide  $\text{InMo}_6\text{S}_8$ . While the In atoms are localized at the cell origin in the selenide, they are delocalized from the origin by about 0.7 Å (Yvon, 1979) in the sulphide. These features correlate well with previous

\* Lists of structure factors for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35269 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic parameters ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{InMo}_6\text{Se}_8$  (space group  $R\bar{3}$ ,  $T = 298 \text{ K}$ ) and  $\text{In}_2\text{Mo}_{15}\text{Se}_{19}$  (space group  $R\bar{3}c$ ,  $T = 233 \text{ K}$ )

The e.s.d.'s are in parentheses and the temperature factor is defined as  $\exp[-2\pi^2 U(2 \sin \theta / \lambda)^2]$ .

Equi-point	$x$	$y$	$z$	$U$	
<b><math>\text{InMo}_6\text{Se}_8</math></b>					
Mo	18( $f$ )	146 (3)	1695 (3)	4052 (3)	7 (1)
Se(1)	18( $f$ )	3295 (4)	2962 (4)	4163 (3)	10 (1)
Se(2)	6( $e$ )	0 (–)	0 (–)	2389 (6)	15 (1)
In	3( $a$ )	0 (–)	0 (–)	0 (–)	42 (2)
<b><math>\text{In}_2\text{Mo}_{15}\text{Se}_{19}</math></b>					
Mo(1)	18( $e$ )	8429 (15)	0 (–)	$\frac{1}{2}$ (–)	17 (3)
Mo(2)	36( $f$ )	–156 (8)	1506 (12)	191 (2)	11 (2)
Mo(3)	36( $f$ )	5036 (8)	3201 (8)	443 (3)	14 (2)
Se(1)	12( $c$ )	0 (–)	0 (–)	562 (7)	32 (5)
Se(2)	12( $c$ )	0 (–)	0 (–)	1760 (5)	15 (4)
Se(3)	18( $e$ )	3050 (12)	0 (–)	$\frac{1}{2}$ (–)	16 (3)
Se(4)	36( $f$ )	6777 (11)	–383 (10)	173 (3)	18 (2)
Se(5)	36( $f$ )	–133 (9)	3632 (9)	461 (3)	14 (2)
In	12( $c$ )	$\frac{1}{3}$ (–)	$\frac{2}{3}$ (–)	456 (7)	85 (7)

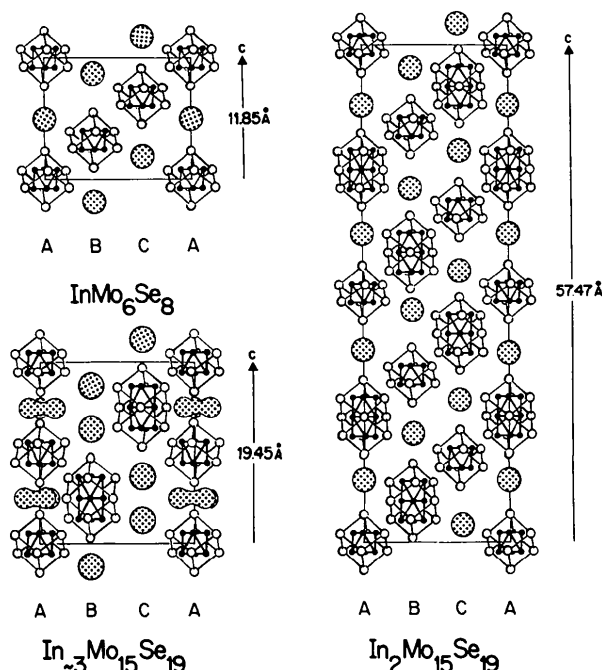


Fig. 1. Projections of  $\text{InMo}_6\text{Se}_8$ ,  $\text{In}_{n-3}\text{Mo}_{15}\text{Se}_{19}$  and  $\text{In}_2\text{Mo}_{15}\text{Se}_{19}$  on the hexagonal (1120) plane. Filled circles: Mo atoms; dotted circles: In atoms. The Mo–Se bonds within and between the  $\text{Mo}_6\text{Se}_8$  and  $\text{Mo}_9\text{Se}_{11}$  units have been omitted for clarity.

observations (Yvon, 1978), according to which delocalized  $M$  atoms lead to relatively large rhombohedral angles and localized  $M$  atoms to relatively small ones ( $\text{InMo}_6\text{Se}_8$ :  $\alpha = 93.2^\circ$ ;  $\text{InMo}_6\text{Se}_8$ :  $\alpha = 89.5^\circ$ ).

$\text{In}_2\text{Mo}_{15}\text{Se}_{19}$ . Apart from the stacking of the  $\text{Mo}_6\text{Se}_8$  and  $\text{Mo}_9\text{Se}_{11}$  units, this compound shows two major structural differences with respect to the more In-rich hexagonal  $\text{In}_{\sim 3}\text{Mo}_{15}\text{Se}_{19}$  phase. Firstly, it contains only one In site whereas the hexagonal compound contains two, of which one is fully occupied by a monovalent In atom and the other is partially occupied ( $\sim 0.4$ ) by trivalent In atoms (Fig. 1). The In–Se distances and the configuration of the seven nearest Se atoms surrounding the In site in the title compound indicate that the In atoms are monovalent.

Secondly, the point symmetry of the  $\text{Mo}_9\text{Se}_{11}$  unit in the rhombohedral compound is  $\bar{3}2$  and not  $3/m$  as found in the hexagonal phase. Consequently the orientation of these units with respect to the hexagonal base vectors is slightly different in these two compounds (Fig. 1). The symmetry of the  $\text{Mo}_6\text{Se}_8$  units, on the other hand, is the same ( $\bar{3}$ ) in  $\text{In}_2\text{Mo}_{15}\text{Se}_{19}$  and  $\text{In}_{\sim 3}\text{Mo}_{15}\text{Se}_{19}$ .

Comparing the Mo–Mo distances of the  $\text{In}_x\text{Mo}_{15}\text{Se}_{19}$  compounds as a function of the In concentration ( $x = 2, 2.9, 3.3$ ) one observes an interesting trend. As the In concentration is increased, the  $\text{Mo}_6$  octahedron contracts whereas the  $\text{Mo}_9$  bioctahedron expands around its centre (Fig. 2). Calculating the Mo–Mo bond order,  $\sum n$  (Hönle *et al.*,

1980), one obtains with increasing In concentrations  $\sum n = 2.7, 2.8$  and  $2.9$ , respectively, for the  $\text{Mo}(2)$  atoms forming the  $\text{Mo}_6$  cluster, and  $\sum n = 4.0, 3.6$  and  $3.3$ , respectively, for the  $\text{Mo}(1)$  atoms forming the centre triangle of the  $\text{Mo}_9$  cluster. The bond order around the  $\text{Mo}(3)$  atoms forming the top and bottom triangle of the  $\text{Mo}_9$  biocatahedron remains approximately unchanged.

The observations above are relevant for the description of the bonding. According to the model of Hönle *et al.* (1980) there are  $12n$  orbitals per  $\text{Mo}_{3n}\text{X}_{3n+2}$  unit available for the formation of metal-to-metal bonds. Out of these,  $6n$  orbitals have more or less bonding character. In compounds having less than  $12n$  electrons per  $\text{Mo}_{3n}$  cluster, such as  $M_x\text{Mo}_6\text{X}_8$  ( $M_x = \text{Cu}_{1.8}, \text{Cu}_{2.4}, \text{Cu}_{3.6}, \text{Pb}, \text{In}, \text{rare earth}, \text{etc.}$ ), the bonding orbitals are not all occupied which explains why the  $\text{Mo}_6$  octahedron contracts as the valency and the concentration of  $M$  is increased. In compounds having more than  $6n$  electrons per  $\text{Mo}_{3n}$  cluster, such as  $\text{TiMo}_3\text{Te}_3$ , some antibonding orbitals are also occupied which explains why the metal atom fibres tend to expand as the Mo atoms are replaced by Fe atoms such as in  $\text{TlFe}_3\text{Te}_3$  (Klepp & Boller, 1979).

If this model is applied to the  $\text{In}_x\text{Mo}_{15}\text{Se}_{19}$  series of compounds it follows that the apparent contraction of the  $\text{Mo}_6$  octahedron is due to a filling of Mo orbitals which are bonding with respect to the other metal atoms of this cluster. The apparent expansion of the  $\text{Mo}_9$  biocatahedron around its centre, however, indicates that some Mo orbitals are filled which are antibonding with respect to the other metal atoms of this cluster. These findings therefore suggest that the fusion of the  $\text{Mo}_6\text{X}_8$  units into larger  $\text{Mo}_{3n}\text{X}_{3n+2}$  aggregates ( $n > 2$ ) leads to the population of antibonding metal orbitals, regardless of the size of the aggregates actually formed. With respect to the stability of these aggregates it is interesting to notice that all condensed  $\text{Mo}_{3n}\text{X}_{3n+2}$  units known so far ( $n = 3, 4, \infty$ ) (Grüttner *et al.*, 1979; Seeber *et al.*, 1979; Chevrel *et al.*, 1979; Potel *et al.*, 1979; Hönle *et al.*, 1980) form in the presence of cations  $M$  which are rather large, such as  $\text{In}^+, \text{Tl}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$  and  $\text{Ba}^{2+}$  [ $r(M) > 1.3 \text{ \AA}$ ]. Smaller cations [ $r(M) < 1.3 \text{ \AA}$ ] usually lead to the formation of the rhombohedral  $M\text{Mo}_6\text{X}_8$  compounds which are built up by  $\text{Mo}_6\text{X}_8$  units only. This indicates that the condensation of these units into larger  $\text{Mo}_{3n}\text{X}_{3n+2}$  aggregates is favoured both by electronic factors, such as a high number of valence electrons on the  $\text{Mo}_{3n}$  clusters, and geometrical factors, such as the presence of large cations  $M$ . On the other hand the orientation and stacking of these aggregates in the different chalcogenides suggest that they form by epitaxial intergrowth from the basic  $M\text{Mo}_6\text{X}_8$  species along the  $c$  direction. Such a growth mechanism favours the creation of stacking faults and could explain why these substances are often poorly crystallized.

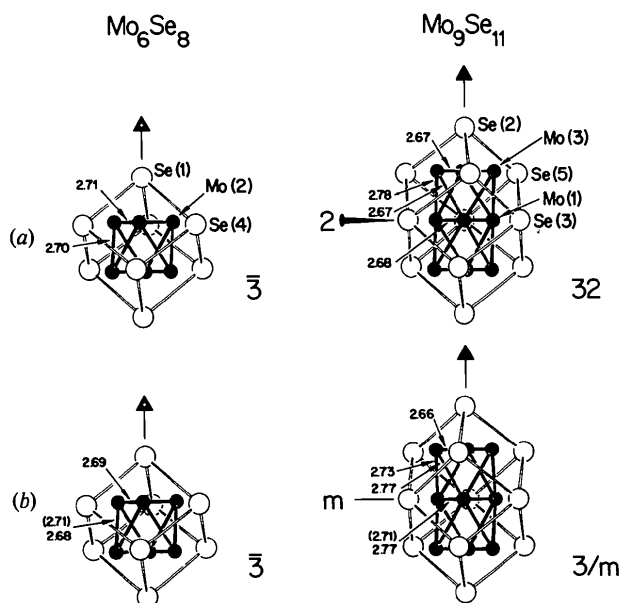


Fig. 2. A comparison of the Mo–Mo bond lengths ( $\text{\AA}$ ) in the  $\text{Mo}_6\text{Se}_8$  and  $\text{Mo}_9\text{Se}_{11}$  building blocks of (a) rhombohedral  $\text{In}_2\text{Mo}_{15}\text{Se}_{19}$  and (b) hexagonal  $\text{In}_{3.3}\text{Mo}_{15}\text{Se}_{19}$  and  $\text{In}_{2.9}\text{Mo}_{15}\text{Se}_{19}$ . The bond lengths of  $\text{In}_{2.9}\text{Mo}_{15}\text{Se}_{19}$ , which differ significantly from those of  $\text{In}_{3.3}\text{Mo}_{15}\text{Se}_{19}$  are given in parentheses. The e.s.d.'s for  $\text{In}_2\text{Mo}_{15}\text{Se}_{19}$  are  $0.02 \text{ \AA}$  and for  $\text{In}_{\sim 3}\text{Mo}_{15}\text{Se}_{19}$ ,  $0.01 \text{ \AA}$ .

One of us (AL) acknowledges the financial support of the Max-Planck-Institut, Stuttgart. The authors thank Professors H. G. von Schnering and E. Parthé for their constructive comments and criticisms.

### References

- ANDERSSON, S. & HYDE, B. G. (1974). *J. Solid State Chem.* **9**, 92–101.  
 CHEVREL, R., SERGENT, M., SEEBER, B., FISCHER, Ø., GRÜTTNER, A. & YVON, K. (1979). *Mater. Res. Bull.* **14**, 567–577.  
 FISCHER, Ø. (1978). *Appl. Phys.* **16**, 1–28.  
 GRÜTTNER, A., YVON, K., CHEVREL, M., POTEI, M., SERGENT, M. & SEEBER, B. (1979). *Acta Cryst.* **B35**, 285–292.  
 HÖNLE, W., VON SCHNERING, H. G., LIPKA, A. & YVON, K. (1980). *J. Less-Common Met.* In the press.

- International Tables for X-ray Crystallography* (1969). Vol. I, 3rd ed. Birmingham: Kynoch Press.  
 KLEPP, K. & BOLLER, H. (1979). *Monatsh. Chem.* **110**, 677–684.  
 MAREZIO, M., DERNIER, P. D., REMEIK, J. P., CORENZWIT, E. & MATTHIAS, B. T. (1973). *Mater. Res. Bull.* **8**, 657–668.  
 POTEI, M., CHEVREL, R., SERGENT, M., DECROUX, M. & FISCHER, Ø. (1979). *C. R. Acad. Sci. Sér. C*, **288**, 429–432.  
 SEEBER, B., DECROUX, M., FISCHER, Ø., CHEVREL, R., SERGENT, M. & GRÜTTNER, A. (1979). *Solid State Commun.* **29**, 419–423.  
 YVON, K. (1978). *Solid State Commun.* **25**, 327–331.  
 YVON, K. (1979). *Current Topics in Materials Science*, Vol. 3, ch. 2, edited by E. KALDIS. Amsterdam: North-Holland.  
 YVON, K. & PAOLI, A. (1977). *Solid State Commun.* **24**, 41–45.

*Acta Cryst.* (1980). **B36**, 2126–2128

## Structure of Ammonium Tetrachlorozincate(II)

BY I. MIKHAIL

*Institut für Kristallographie, Freie Universität Berlin, Takustrasse 6, D-1000 Berlin 33, Federal Republic of Germany*

(Received 25 September 1979; accepted 10 April 1980)

**Abstract.**  $(\text{NH}_4)_2[\text{ZnCl}_4]$ , orthorhombic,  $Pna2_1$ ,  $Z = 16$ ,  $a = 37.172$  (3),  $b = 7.221$  (3),  $c = 12.643$  (4) Å,  $\rho(\text{calc}) = 1.904$  Mg m<sup>-3</sup>. The structure was solved by direct methods and refined by least squares ( $R = 0.057$ ) with 1452 reflections measured on an automatic four-circle diffractometer (Mo  $K\alpha$  radiation). It consists of isolated  $\text{ZnCl}_4$  tetrahedra connected by  $\text{NH}_4$  groups which exhibit a wide range of coordination numbers and geometries.

**Introduction.** Since X-ray diffraction patterns taken for  $A_2[\text{ZnCl}_4]$ , where  $A = \text{Cs}, \text{Rb}, \text{K}$  and  $\text{NH}_4$ , exhibit pronounced differences (Jacobi, 1970), the information available on the isostructural Co compound (Vermin, Verschoor & IJdo, 1976) and  $\text{K}_2[\text{ZnCl}_4]$  is insufficient to allow a detailed comparison between the members of the series. We felt it appropriate to undertake a complete crystal structure analysis of  $(\text{NH}_4)_2[\text{ZnCl}_4]$ , in order to confirm the characterization of the anion and to study further the physical properties of these compounds.

Clear, colourless crystals were obtained by slow evaporation of an aqueous solution of  $\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2$  in the ratio 2:1. Since they are deliquescent, the freshly prepared crystals were enclosed in thin-walled

capillaries. Preliminary X-ray photographs showed additional reflexions corresponding to a cell with a quadruple  $a$  axis, while those at  $h = \pm 0.5$  are completely absent. This investigation differs from that of  $\text{K}_2[\text{ZnCl}_4]$  (Mikhail & Peters, 1979) in which satellite reflections at  $a = \pm \frac{1}{2}$  occur.

A crystal of dimensions  $0.16 \times 0.20 \times 0.18$  mm was optically centred on a Syntex P1 four-circle diffractometer. The orientation matrix and the cell parameters were determined on the basis of 15 reflections.

The linear absorption coefficient  $\mu$  for Mo  $K\alpha$  radiation was calculated to be  $4.12 \mu\text{m}^{-1}$ .

The intensities of 1736  $hkl$  reflections were measured according to the  $\omega$ -scan technique (Mo  $K\alpha$ , graphite monochromator) using a scan range of  $1^\circ$  and a scan speed between  $0.5$  and  $24.0^\circ \text{min}^{-1}$  depending on the intensity of the measured reflections. In the range  $3.0^\circ < 2\theta < 55.0^\circ$ , 1452  $hkl$  reflections with  $I > 1.96(I)$  were obtained for the structure refinement. For the evaluation, the XTL system (Syntex, Nova 1200) was employed. An absorption correction was applied to all intensities, based on  $\Psi$ -scan measurement.

The structure was solved by the direct method with the MULTAN program system (Germain, Main & © 1980 International Union of Crystallography