$Br_2$–$ZnBr_2$–$H_2O$ system at 298 K (Duhlev & Balarew, 1986), the corresponding chloride, $CaZnCl_4.5H_2O$, is the only double salt reported in the $CaCl_2$–$ZnCl_2$–$H_2O$ system at 298 K (Hudgins, 1964). We expect the chloride compound to be built of the same structural motifs, packed in a similar if not the same way. Another compound with the same formula type, $MgZnCl_4.5H_2O$, has been reported (Balarew & Spassov, 1980) but because of the large difference in size between $Mg^{2+}$ and $Ca^{2+}$, the environment around $Mg^{2+}$ is expected to be different from that of $Ca^{2+}$ in the present structure.

We wish to thank the Natural Science and Engineering Research Council of Canada for an operating grant to one of us (IDB).

### References

Balarew, Chr. & Duhlev, R. (1984). *J. Solid State Chem.* **55**, 1–6.
Balarew, Chr. & Spassov, D. (1980). *Russ. J. Inorg. Chem.* **25**, 1551–1556.
Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.
Duhlev, R. & Balarew, Chr. (1986). *Rev. Chim. Miner.* **23**, 116–124.
Hall, S. R. (1981). *Acta Cryst.* A**37**, 517–525.
Hudgins, C. M. (1964). *J. Chem. Eng. Data.* **9**, 434–435.
*International Tables for X-ray Crystallography* (1974). Vol. IV, Tables 2.2B and 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Larson, A. C. (1967). *Acta Cryst.* **23**, 664–665.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
Sheldrick, G. M. (1986). *SHELXS86*. Program for crystal structure solution. Univ. of Göttingen, Federal Republic of Germany.

---

*Acta Cryst.* (1988). C**44**, 965–967

# Structures of $Rb_2[InCl_5(H_2O)]$ and $Cs_2[InCl_5(H_2O)]$

By Xavier Solans

*Depto de Cristalografía, Universidad de Barcelona, Gran Via 585, 08007 Barcelona, Spain*

and Mary C. Moron and Fernando Palacio

*Instituto de Ciencia de Materiales de Aragón, CSIC y Univ. de Zaragoza, 50009 Zaragoza, Spain*

(*Received* 22 *July* 1987; *accepted* 1 *February* 1988)

**Abstract.** (I) Rubidium aquapentachloroindate, $Rb_2[InCl_5(H_2O)]$, $M_r$ = 481·04, orthorhombic, *Pnma*, $a$ = 14·050 (3), $b$ = 10·087 (2), $c$ = 7·215 (2) Å, $D_x$ = 3·124 g cm$^{-3}$, $Z$ = 4, $V$ = 1022·5 (7) Å$^3$, $F(000)$ = 872, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu$(Mo $K\alpha$) = 135·01 cm$^{-1}$, $T$ = 288 K. Final $R$ = 0·021 for 764 reflections. (II) Caesium aquapentachloroindate, $Cs_2[InCl_5(H_2O)]$, $M_r$ = 575·91, orthorhombic, *Pnma*, $a$ = 14·410 (3), $b$ = 10·382 (2), $c$ = 7·416 (1) Å, $D_x$ = 3·447 g cm$^{-3}$, $Z$ = 4, $V$ = 1109·5 (3) Å$^{-3}$, $F(000)$ = 1016, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu$(Mo $K\alpha$) = 98·06 cm$^{-1}$, $T$ = 288 K. Final $R$ = 0·020 for 765 reflections. In both compounds the anions are distorted octahedra, with In, O and three Cl atoms on the mirror plane. Cl···O ($-x$, $-y$, $2-z$) distances of 3·148 (9) (I) and 3·09 Å (II) indicate hydrogen bonding between O and Cl atoms of neighbouring octahedra. All other bond lengths are normal. Comparison of both structures with related $A_2[MX_5(H_2O)]$ structures is also made.

**Introduction.** The series of compounds $A_2[InCl_5(H_2O)]$, where $A$ = $NH_4$, K, Rb, Cs, are of interest because they are the diamagnetic analogues of the intensively studied series of antiferromagnets $A_2[FeCl_5(H_2O)]$ (Carlin & Palacio, 1985). In fact, all the compounds in both series whose structures are known are orthorhombic, although they are not all isomorphic. The Cs/Fe compound belongs to the space group *Cmcm* (O'Connor, Deaver & Sinn, 1979; Greedan, Hewitt, Faggiani & Brown, 1980) and is isomorphic to the analogous ruthenium(III) material (Hopkins, Zalkin, Templeton & Adamson, 1966). The remaining compounds belong to space group *Pnma* (Carlin, Bhatia & O'Connor, 1977) and therefore the K and $NH_4$ derivatives of the Fe and In compounds are isomorphic (Lindqvist, 1947; Bellanca, 1948; Klug, Kummer & Alexander, 1948; Wignacourt, Mairesse & Barbier, 1976; Figgis, Raston, Sharma & White, 1978).

We report here on the crystal structures of both the Cs and Rb derivatives of the In series. Our aim was to elucidate whether $Cs_2[InCl_5(H_2O)]$ would follow the tendency of its Fe and Ru analogues or would belong to the much wider family of isomorphic compounds with space group *Pnma*. In addition, since $Rb_2[FeCl_5(H_2O)]$ is very interesting from a magnetic point of view

0108-2701/88/060965-03$03.00

Table 1. *Final atomic coordinates* (× $10^5$) *of* $A_2[InCl_5(H_2O)]$, $A$ = Rb *and* Cs

$$B_{eq} = 8\pi/3 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| In | 11455 (2) | 25000 | 80901 (4) | 0·64 (2) |
| Rb | 35547 (3) | −10 (3) | 84459 (4) | 1·96 (2) |
| Cl(1) | 22249 (9) | 25000 | 107884 (15) | 1·97 (5) |
| Cl(2) | 25254 (7) | 25000 | 59682 (14) | 1·40 (4) |
| Cl(3) | 322 (8) | 25000 | 54228 (17) | 1·76 (5) |
| Cl(4) | 10431 (7) | 470 (7) | 81926 (13) | 1·84 (4) |
| O | −1102 (22) | 25000 | 100574 (47) | 2·11 (15) |
| | | | | |
| In | 11560 (2) | 25000 | 69073 (4) | 1·27 (2) |
| Cs | 35727 (2) | −183 (2) | 83830 (3) | 2·00 (2) |
| Cl(1) | 2242 (1) | 2500 | 10673 (2) | 2·32 (5) |
| Cl(2) | 2485 (1) | 2500 | 5963 (2) | 1·87 (5) |
| Cl(3) | 53 (1) | 2500 | 5517 (2) | 2·12 (4) |
| Cl(4) | 1023 (1) | −95 (1) | 8289 (1) | 2·02 (4) |
| O | −68 (2) | 2500 | 10091 (4) | 2·91 (17) |

Table 2. *Selected bond lengths* (Å) *and angles* (°) *for* $A_2[InCl_5(H_2O)]$, $A$ = Rb *and* Cs

| $Rb_2[InCl_5(H_2O)]$ | | $Cs_2[InCl_5(H_2O)]$ | |
|---|---|---|---|
| Cl(1)–In | 2·468 (1) | Cl(1)–In | 2·472 (1) |
| Cl(2)–In | 2·470 (1) | Cl(2)–In | 2·483 (1) |
| Cl(3)–In | 2·480 (1) | Cl(3)–In | 2·484 (1) |
| Cl(4)–In | 2·480 (1) | Cl(4)–In | 2·508 (1) |
| O–In | 2·264 (3) | O–In | 2·304 (4) |
| Rb···In | 4·2291 (5) | Cs···In | 4·358 (1) |
| Rb$^{i}$···In | 4·2142 (5) | Cs$^{i}$···In | 4·360 (1) |
| Cl(1)···Rb | 3·565 (1) | Cl(1)···Cs | 4·279 (1) |
| Cl(2)···Rb | 3·413 (1) | Cl(2)···Cs | 3·128 (1) |
| Cl(4)···Rb | 3·534 (1) | Cl(4)···Cs | 3·815 (1) |
| Cl(1$^{ii}$)···Rb | 3·351 (1) | Cl(1$^{ii}$)···Cs | 2·976 (1) |
| Cl(2$^{iii}$)···Rb | 3·460 (1) | Cl(2$^{iii}$)···Cs | 4·244 (1) |
| Cl(3$^{iii}$)···Rb | 3·512 (1) | Cl(3$^{iii}$)···Cs | 4·210 (1) |
| Cl(3$^{iv}$)···Rb | 3·367 (1) | Cl(3$^{iv}$)···Cs | 3·877 (1) |
| Cl(1$^{v}$)···Rb | 3·565 (1) | Cl(1$^{v}$)···Cs | 4·279 (1) |
| Cl(2$^{v}$)···Rb | 3·413 (1) | Cl(2$^{v}$)···Cs | 3·128 (1) |
| Cl(3$^{vi}$)···Rb | 3·367 (1) | Cl(3$^{vi}$)···Cs | 3·877 (1) |
| Cl(4$^{vi}$)···Rb | 3·691 (1) | Cl(4$^{vi}$)···Cs | 3·535 (1) |
| Cl(1$^{vii}$)···Rb | 3·351 (1) | Cl(1$^{vii}$)···Cs | 2·976 (1) |
| Cl(2$^{viii}$)···Rb | 3·460 (1) | Cl(2$^{viii}$)···Cs | 4·244 (1) |
| Cl(3$^{viii}$)···Rb | 3·511 (1) | Cl(3$^{viii}$)···Cs | 4·210 (1) |
| Cl(4$^{vii}$)···Rb | 3·471 (1) | Cl(4$^{vii}$)···Cs | 2·748 (1) |
| O···Cl(4) | 3·249 (9) | O···Cl(4) | 3·39 (1) |
| O($^{ix}$)···Cl(4) | 3·148 (9) | O($^{ix}$)···Cl(4) | 3·09 (1) |
| | | | |
| Cl(2)–In–Cl(1) | 90·4 (1) | Cl(2)–In–Cl(1) | 90·2 (1) |
| Cl(3)–In–Cl(I) | 178·8 (1) | Cl(3)–In–Cl(1) | 179·5 (1) |
| Cl(3)–In–Cl(2) | 90·8 (1) | Cl(3)–In–Cl(2) | 90·2 (1) |
| Cl(4)–In–C(1) | 90·7 (1) | Cl(4)–In–Cl(1) | 90·2 (1) |
| Cl(4)–In–Cl(2) | 93·7 (1) | Cl(4)–In–Cl(2) | 95·5 (1) |
| Cl(4)–In–Cl(3) | 89·2 (1) | Cl(4)–In–Cl(3) | 89·8 (1) |
| O–In–Cl(1) | 89·1 (1) | O–In–Cl(1) | 89·2 (2) |
| O–In–Cl(2) | 179·5 (1) | O–In–Cl(2) | 179·5 (2) |
| O–In–Cl(3) | 89·7 (1) | O–In–Cl(3) | 90·3 (2) |
| O–In–Cl(4) | 86·3 (1) | O–In–Cl(4) | 84·5 (2) |

Symmetry code: (i) $\frac{1}{2}-x, y-\frac{1}{2}, z+\frac{1}{2}$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, z+\frac{1}{2}$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}$; (iv) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{3}{2}-z$; (v) $x, \frac{1}{2}-y, z$; (vi) $x-\frac{1}{2}, y, \frac{3}{2}-z$; (vii) $\frac{1}{2}-x, -y, z+\frac{1}{2}$; (viii) $\frac{1}{2}-x, -y, z-\frac{1}{2}$; (ix) $-x, -y, 2-z$.

(Puértolas, Navarro, Palacio, Bartolomé, González & Carlin, 1985), it is relevant to characterize crystallographically a diamagnetic isomorph.

**Experimental.** Prismatic crystals (0·1 × 0·1 × 0·2 mm) (I) and (0·1 × 0·1 × 0·15 mm) (II) were selected and mounted on a Philips PW 1100 four-circle diffractometer. Unit-cell parameters were determined from 25 reflections (4° ≤ $\theta$ ≤ 12°) and refined by least squares. Intensities were collected with graphite-monochromatized Mo $K\alpha$ radiation, using the $\omega$-scan technique, with scan width 0·8° and scan speed 0·03° $s^{-1}$. 1032 reflections for (I) and 1034 for (II) were measured in the range 2° ≤ $\theta$ ≤ 25°, of which 764 and 765, respectively, were taken as observed with $I \geq 2{\cdot}5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity controls, no significant intensity decay was observed. Lorentz–polarization and absorption corrections were made [transmission factors 0·84–0·73 (I) and 0·93–0·86 (II)]. Both structures were solved by direct methods, using the *MULTAN*84 system of computer programs (Main, Fiske, Hull, Lessinger,

Table 3. *Unit-cell parameters of isomorphic compounds of the series* $A_2[MX_5(H_2O)]$, *with space group Pnma*

| $A$ | $M$ | $X$ | $a$(Å) | $b$(Å) | $c$(Å) | $Z$ | Reference |
|---|---|---|---|---|---|---|---|
| $NH_4$ | In | Cl | 14·10 | 10·17 | 7·16 | 4 | (*a*) |
| K | In | Cl | 13·905 | 9·952 | 7·185 | 4 | (*b*) |
| Rb | In | Cl | 14·050 | 10·087 | 7·215 | 4 | This work |
| Cs | In | Cl | 14·410 | 10·382 | 7·416 | 4 | This work |
| $H_3O$ | Fe | Cl | 13·720 | 9·926 | 7·038 | 4 | (*c*) |
| $NH_4$ | Fe | Cl | 13·706 | 9·924 | 7·024 | 4 | (*d*) |
| K | Fe | Cl | 13·75 | 9·92 | 6·93 | 4 | (*e*) |
| Rb | Fe | Cl | 13·825 | 9·918 | 7·100 | 4 | (*f*) |
| Rb | Fe | Br | 14·2 | 10·4 | 7·4 | 4 | (*g*) |
| Cs | Fe | Br | 14·7 | 10·7 | 7·6 | 4 | (*g*) |
| $NH_4$ | Mo | Cl | 13·860 | 9·944 | 7·133 | 4 | (*h*) |
| $NH_4$ | Mo | Br | 14·423 | 10·373 | 7·516 | 4 | (*h*) |
| K | Ru | Cl | 13·53 | 9·55 | 6·96 | 4 | (*i*) |

References: (*a*) Klug, Kummer & Alexander (1948); (*b*) Wignacourt, Mairesse & Barbier (1976); (*c*) Søtofte & Nielsen (1981); (*d*) Figgis, Raston, Sharma & White (1978); (*e*) Bellanca (1948); (*f*) O'Connor, Deaver & Sinn (1979); (*g*) Carlin, Bhatia & O'Connor (1977); (*h*) Cavell & Quail (1983); (*i*) Khodashova (1960).

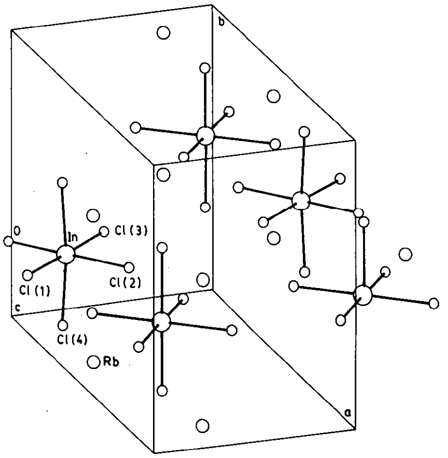

Fig. 1. Unit cell of $Rb_2[InCl_5(H_2O)]$.

Germain, Declercq & Woolfson, 1984) and refined by full-matrix least squares, using the *SHELX*76 program (Sheldrick, 1976). The function minimized was $\sum w||F_o| - |F_c||^2$, where $w = \{\sigma^2(F_o) + \kappa(F_o)^2\}^{-1}$, $\kappa = 0.045$ for (I) and 0·0 for (II). $f, f'$ and $f''$ were taken from *International Tables for X-ray Crystallography* (1974). H atoms were not located.

The final $R$ values were 0·021 ($wR = 0.020$) in (I) and 0·020 ($wR = 0.020$) in (II) for all observed reflections. Max. and min. peaks in final difference maps were $\pm 0.3$ e Å$^{-3}$ at 1·81 Å from Rb for (I) and +0·3, −0·4 e Å$^{-3}$ at 1·69 Å from Cs for (II). Max. shift/e.s.d. = −0·07, $U_{22}$ of O in (I), and −0·08, $U_{33}$ of O in (II).

**Discussion.** The crystals are isomorphous and contain discrete $[InCl_5(H_2O)]^{2-}$ distorted octahedra, the In, O and three Cl atoms being positioned on the mirror plane (Fig. 1). Final positional coordinates for $A_2[InCl_5(H_2O)]$, $A$ = Cs and Rb, are given in Table 1.* Table 2 contains a selection of bond lengths and angles. From the magnitude of the O···Cl distance, it can be stated that in each octahedral unit the O atom is within hydrogen-bonding distance of Cl atoms of neighbouring $[InCl_5(H_2O)]^{2-}$ octahedra, a fact which is common to the rest of the members in the isomorphic series. Available crystallographic results of isomorphic related compounds are summarized in Table 3.

We thank the American–Spain Joint Committee for Grant No. CCB-8504/001.

### References

Bellanca, A. (1948). *Period. Mineral.* **17**, 59–72.

Carlin, R. L., Bhatia, S. N. & O'Connor, C. J. (1977). *J. Am. Chem. Soc.* **99**, 7728–7729.

Carlin, R. L. & Palacio, F. (1985). *Coord. Chem. Rev.* **65**, 141–165.

Cavell, R. G. & Quail, J. W. (1983). *Inorg. Chem.* **22**, 2597–2599.

Figgis, B. N., Raston, C. L., Sharma, R. P. & White, A. H. (1978). *Aust. J. Chem.* **31**, 2717–2720.

Greedan, J. E., Hewitt, D. C., Faggiani, R. & Brown, I. D. (1980). *Acta Cryst.* B**36**, 1927–1929.

Hopkins, T. E., Zalkin, A., Templeton, D. H. & Adamson, M. G. (1966). *Inorg. Chem.* **5**, 1431–1433.

*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Khodashova, T. S. (1960). *Zh. Strukt. Khim.* **1**, 333–336. (Engl. transl. *J. Struct. Chem.* **1**, 308–311.)

Klug, H. P., Kummer, D. & Alexander, L. (1948). *J. Am. Chem. Soc.* **70**, 3064–3068.

Lindqvist, I. (1947). *Ark. Kemi Mineral. Geol.* **24**A, No. 1.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1984). *MULTAN84. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

O'Connor, C. J., Deaver, B. S. Jr & Sinn, E. (1979). *J. Chem. Phys.* **70**, 5161–5167.

Puértolas, J. A., Navarro, R., Palacio, F., Bartolomé, J., González, D. & Carlin, R. L. (1985). *Phys. Rev. B*, **31**, 516–526.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Søtofte, I. & Nielsen, K. (1981). *Acta Chem. Scand. Ser. A*, **35**, 821–822.

Wignacourt, J. P., Mairesse, G. & Barbier, P. (1976). *Cryst. Struct. Commun.* **5**, 293–296.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44741 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

---

*Acta Cryst.* (1988). C**44**, 967–970

# *trans*-Hexakis(pyrazole)manganese(II) Bisperchlorate (1) and *trans*-Dichlorotetrakis(pyrazole)manganese(II) (2)

By Paavo O. Lumme,* Eva Lindell and Ilpo Mutikainen

*Department of Inorganic Chemistry, University of Helsinki, Vuorik.* 20, *SF*-00100 *Helsinki, Finland*

(*Received* 6 *July* 1987; *accepted* 25 *January* 1988)

**Abstract.** (1): $[Mn(C_3H_4N_2)_6](ClO_4)_2$, $M_r = 662.31$, trigonal, $P\bar{3}$, $a = 10.129$ (4), $c = 8.039$ (5) Å, $V = 714.3$ (6) Å$^3$, $Z = 1$, $D_m = 1.55$ (2), $D_x = 1.54$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 0.73$ mm$^{-1}$, $F(000) = 339$, $T = 295$ (1) K, $R = 0.050$ for 577 unique reflections with $I > 3\sigma(I)$. (2): $[MnCl_2(C_3H_4N_2)_4]$, $M_r = 398.16$, monoclinic, $C2/c$, $a = 13.695$ (3), $b = 9.426$ (2), $c = 15.239$ (2) Å, $\beta = 118.03$ (1)°, $V = 1736.4$ (5) Å$^3$, $Z = 4$, $D_m = 1.57$ (1), $D_x = 1.52$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 1.11$ mm$^{-1}$, $F(000) = 812$, $T = 295$ (1) K, $R = 0.032$ for 1633 unique reflections with $I > 3\sigma(I)$. The coordination

---

* To whom all correspondence should be addressed.

0108-2701/88/060967-04$03.00