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# Indium Trichloride Trihydrate Trisdioxane, $InCl_3.3H_2O.3(C_4H_8O_2)$

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**Abstract.** $InCl_3.3H_2O.3(C_4H_8O_2)$, $P2_1/c$, $Z=4$, $D_x=1{\cdot}637$ g cm$^{-3}$, $a=9{\cdot}243$ (4), $b=18{\cdot}259$ (10), $c=13{\cdot}189$ (6) Å, $\beta=100{\cdot}51$ (4)°. The indium atom is in the centre of a distorted octahedron of three Cl atoms and three $H_2O$ molecules. These octahedra form layers at $y=\frac{1}{4}$ and $\frac{3}{4}$, which interleave with layers of dioxane molecules at $y=0$ and $\frac{1}{2}$. A simple hydrogen-bonding scheme between the water molecules and the oxygen atoms of the dioxane rings holds the layers together. In–Cl distances are 2·399, 2·420 and 2·447 (Å) and In–$OH_2$ distances are 2·199, 2·250 and 2·283 Å.

**Introduction.** The milky-white parallelepipedal crystals are extremely hygroscopic and were mounted in Lindemann capillaries in a dry nitrogen atmosphere. In spite of this precaution all but one of the crystals mounted decomposed to a white powder. The remaining crystal, which measures $0{\cdot}3\times0{\cdot}3\times0{\cdot}4$ mm was used for all X-ray work. Precession photographs showed that the space group is $P2_1/c$ and intensity data were collected on an automatic Picker diffractometer (Grant & Gabe, 1974) with monochromated Mo $K\alpha$ radiation ($\alpha_1=0{\cdot}70926$ Å). 2057 reflexions with $2\theta\leq40°$, were measured with the $\theta/2\theta$ scan technique, at 2° min$^{-1}$, and the scan range was corrected for dispersion so that the total scan width $\Delta2\theta=0{\cdot}5+0{\cdot}69\tan\theta+0{\cdot}5°$. Background measurements were taken at each end of the scan range for half the scan time. Of the reflexions measured, 1916 considered significant at the 10 % probability level were used in subsequent analysis. Cell dimensions were determined by a least-squares procedure on the angular measurements of 24 reflexions with $2\theta$ between 30 and 40°.

The structure was solved with considerable difficulty from the Patterson synthesis and repeated Fourier calculations. The difficulty arises from the fact that the $y$ coordinates of the In and one Cl atom are close to $\frac{1}{4}$ and the other two Cl atoms are equally spaced above and below the $y=\frac{1}{4}$ plane. From this point, however, refinement proceeded smoothly to a final $R$ of 0·064 with anisotropic thermal parameters for the four heavier atoms and 24 of the 30 hydrogen atoms included at their calculated positions. The six hydrogen atoms of the water molecules could not be found on the final difference Fourier synthesis. Final positional and thermal parameters are presented in Table 1.* All calculations were performed by the X-RAY System (1972).

* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31162 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

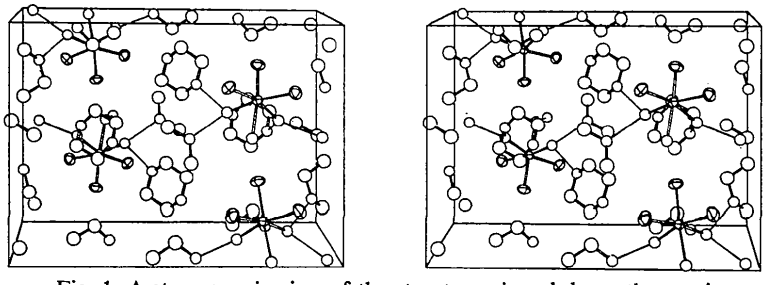

Fig. 1. A stereoscopic view of the structure viewed down the *a* axis.

Table 1. *Final positional* ($\times10^4$) *and thermal parameters* (Å$^2\times10^3$) *with standard deviations in parentheses*

The anisotropic temperature factor is of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2}+\ldots+2U_{23}klb^*c^*+2U_{13}hla^*c^*\cos\beta^*+\ldots)]$.

| | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| In | 343 (1) | 2599 (1) | 3208 (1) | 41 (1) | 36 (1) | 28 (1) | −3 (1) | 10 (1) | 1 (1) |
| Cl(1) | 1797 (3) | 2496 (2) | 1838 (2) | 58 (2) | 67 (3) | 36 (2) | −9 (2) | 21 (2) | −11 (2) |
| Cl(2) | −1274 (3) | 1566 (2) | 2713 (2) | 50 (2) | 45 (2) | 56 (2) | −10 (2) | 5 (2) | −5 (2) |
| Cl(3) | −1353 (3) | 3546 (2) | 2517 (2) | 52 (3) | 55 (2) | 57 (2) | 6 (2) | 8 (2) | 15 (2) |

Table 1 (*cont.*)

| | *x* | *y* | *z* | $U_{iso}$ |
|---|---|---|---|---|
| O(1) | 444 (8) | 2793 (4) | 4728 (5) | 41 (2) |
| O(2) | 1993 (8) | 3449 (4) | 3900 (5) | 40 (2) |
| O(3) | 1825 (7) | 1865 (4) | 4236 (5) | 43 (2) |
| O(4) | 1296 (8) | 390 (5) | −29 (6) | 60 (3) |
| C(1) | 516 (13) | 406 (7) | 895 (9) | 53 (4) |
| C(2) | −1040 (15) | 303 (8) | 558 (10) | 65 (4) |
| O(5) | 924 (9) | 589 (4) | 4835 (6) | 56 (2) |
| C(3) | 695 (4) | −32 (8) | 4134 (10) | 71 (5) |
| C(4) | 344 (14) | −733 (7) | 4702 (10) | 63 (4) |
| O(6) | 5641 (10) | −189 (6) | 6939 (8) | 91 (3) |
| C(5) | 5278 (21) | −421 (11) | 7905 (15) | 138 (8) |
| C(6) | 4784 (16) | 246 (9) | 8460 (11) | 84 (5) |
| O(7) | 3774 (9) | 675 (5) | 7904 (6) | 61 (3) |
| C(7) | 4056 (18) | 902 (11) | 6920 (14) | 127 (7) |
| C(8) | 4538 (19) | 209 (10) | 6334 (13) | 111 (6) |
| O(8) | 6669 (8) | 1959 (4) | 9578 (6) | 56 (2) |
| C(9) | 5830 (13) | 1801 (7) | 10380 (9) | 55 (4) |
| C(10) | 5443 (14) | 2488 (7) | 10853 (9) | 60 (4) |
| O(9) | 4761 (9) | 2963 (5) | 10059 (6) | 67 (3) |
| C(11) | 5506 (14) | 3128 (8) | 9720 (11) | 71 (4) |
| C(12) | 5825 (15) | 2402 (7) | 8718 (11) | 71 (4) |

Calculated hydrogen atom positions ($\times 10^3$); $U_{iso}=0{\cdot}051$ Å$^2$

| C atom | H atom | | | H atom | | |
|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | *x* | *y* | *z* |
| C(1) | 91 | 1 | 138 | 70 | 89 | 125 |
| C(2) | −154 | 31 | 117 | −144 | 71 | 8 |
| C(3) | −15 | 8 | 356 | 161 | −11 | 384 |
| C(4) | 13 | −115 | 420 | 120 | −86 | 52 |
| C(5) | 446 | −79 | 78 | 616 | −65 | 83 |
| C(6) | 437 | 6 | 906 | 567 | 55 | 871 |
| C(7) | 314 | 112 | 651 | 486 | 127 | 702 |
| C(8) | 366 | −12 | 613 | 490 | 38 | 570 |
| C(9) | 491 | 153 | 1007 | 643 | 149 | 1092 |
| C(10) | 480 | 238 | 1136 | 636 | 274 | 1121 |
| C(11) | 493 | 347 | 876 | 646 | 336 | 959 |
| C(12) | 489 | 215 | 840 | 643 | 240 | 817 |

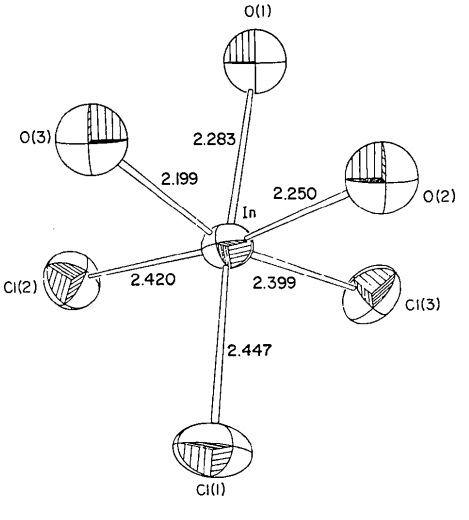


Fig. 2. The In octahedron, showing In–Cl and In–O distances. E.s.d.'s for In–Cl and In–O distances are 0·003 and 0·007 Å.

**Discussion.** A stereoscopic view of the structure viewed down the *a* axis is shown in Fig. 1. It can be seen that there are layers of distorted In octahedra at approximately $y=\frac{1}{4}$ and $\frac{3}{4}$, which interleave with dioxane layers at $y=0$ and $\frac{1}{2}$. The In octahedron is shown in Fig. 2 with the appropriate distances. The geometry of this octahedron is not unusual; the Cl atoms are all on one side of the In atom and the water molecules are all on the other. The three angles O–In–O are close to 80°, while the three angles Cl–In–Cl are near 100°, presumably to accommodate the larger Cl ions (Table 2). The six angles O–In–Cl vary from 86 to 95°. Distances are comparable with those found in other structures (Brown, Einstein & Tuck, 1969; Veidis & Palenik, 1969; Prewitt, Shannon, Rogers & Sleight, 1969).

Table 2. *Selected bond distances* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| Cl(1)–In–Cl(2) | 97·9 (1) | C(1)—C(2) | 1·44 (2) |
| –Cl(3) | 100·6 (1) | C(2)—O(4$^{i}$) | 1·44 (2) |
| –O(1) | 165·1 (2) | O(4)—C(1) | 1·53 (2) |
| –O(2) | 86·0 (2) | C(3)—C(4) | 1·55 (2) |
| –O(3) | 92·6 (2) | C(4)—O(5$^{ii}$) | 1·44 (2) |
| | | O(5)—C(3) | 1·45 (2) |
| Cl(2)–In–Cl(3) | 97·5 (1) | C(5)—C(6) | 1·53 (3) |
| –O(1) | 94·5 (2) | C(6)—O(7) | 1·33 (2) |
| –O(2) | 170·6 (2) | O(7)—C(7) | 1·43 (2) |
| –O(3) | 88·6 (2) | C(7)—C(8) | 1·58 (3) |
| | | C(8)—O(6) | 1·38 (2) |
| Cl(3)–In–O(1) | 86·0 (2) | O(6)—C(5) | 1·44 (2) |
| –O(2) | 90·2 (2) | C(9)—C(10) | 1·47 (2) |
| –O(3) | 164·5 (2) | C(10)–O(9) | 1·44 (1) |
| | | O(9)—C(11) | 1·44 (2) |
| O(1)–In–O(2) | 80·6 (3) | C(11)–C(12) | 1·57 (2) |
| –O(3) | 79·3 (3) | C(12)–O(8) | 1·49 (2) |
| O(2)–In–O(3) | 82·6 (3) | O(8)—C(9) | 1·45 (2) |

| Hydrogen bonding | | Symmetry code | | | |
|---|---|---|---|---|---|
| O(1)···O(8$^{iii}$) | 2·68 (1) | (i) | $-x$ | $-y$ | $-z$ |
| O(2)···O(4$^{iv}$) | 2·69 (1) | (ii) | $-x$ | $-y$ | $-z+1$ |
| O(2)···O(7$^{v}$) | 2·79 (1) | (iii) | $x-1$ | $-y+\frac{1}{2}$ | $z-\frac{1}{2}$ |
| O(3)···O(5) | 2·64 (1) | (iv) | $x$ | $-y+\frac{1}{2}$ | $z+\frac{1}{2}$ |
| O(3)···O(9$^{v}$) | 2·67 (1) | (v) | $x$ | $-y+\frac{1}{2}$ | $z-\frac{1}{2}$ |

Two of the dioxane rings have crystallographic centres of symmetry and all have the chair conformation with O atoms displaced on opposite sides of the plane formed by the four C atoms of the ring. The mean O atom displacements are 0·69, 0·65, 0·54 and 0·67 Å for the four rings. Variations in bond lengths within the dioxane rings have no apparent chemical explanation; the mean C–C and C–O bonds are 1·52 (6) and 1·44 (2) Å respectively. Valence angles within the rings vary from 103 to 116° with e.s.d.'s of 1°. Again no particular significance can be attached to the variation. Three of the dioxane rings are hydrogen-bonded at both ends to water molecules, but O(6) is too distant from the nearest $H_2O$ and that ring is held by a single H bond. O···O distances for the assumed hydrogen bonds are in the range 2·64 to 2·79 Å.

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# Dimethyl Sulfone Diimine, a Neutron Study

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**Abstract.** $(CH_3)_2S(NH)_2$, orthorhombic, *F*2*dd* (No. 43), $a=5{\cdot}44$, $b=10{\cdot}59$, $c=16{\cdot}13$ Å, $Z=8$. The structure was refined from neutron diffraction data. The molecules lie on twofold axes, and are linked together by a three-dimensional network of N–H···N hydrogen bonds. The methyl groups are in an eclipsed conformation.

**Introduction.** A single crystal about 2 mm in diameter, kindly provided by Dr A. J. Mabis, was mounted on a four-circle neutron diffractometer at the National Bureau of Standards reactor. Of 262 reflections measured ($\lambda=1{\cdot}00$ Å) 206 had intensities significantly above background. Unit-cell dimensions and a trial set of phases were obtained from the X-ray structure deter-

Table 1. *Final refined atomic parameters for dimethyl sulfone diimine*

Temperature factors are given as the coefficients of the expression $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$. Values are $\times 10^4$.

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| S | 0 | 0 | 0 | 193 (39) | 58 (7) | 20 (3) | 0 | 0 | −5 (4) |
| C | −2058 (22) | 1266 (5) | 211 (3) | 422 (23) | 82 (5) | 34 (2) | 78 (8) | 37 (6) | −2 (3) |
| N | 1339 (22) | −456 (3) | 783 (2) | 309 (12) | 88 (3) | 24 (1) | 5 (6) | −25 (3) | 6 (2) |
| H(1) | 2414 (27) | 246 (12) | 998 (6) | 458 (42) | 144 (12) | 40 (4) | 2 (22) | −33 (10) | 4 (6) |
| H(2) | −3112 (40) | 1450 (18) | −324 (7) | 1056 (108) | 302 (26) | 51 (6) | 435 (27) | −33 (17) | 5 (8) |
| H(3) | −3297 (39) | 1001 (11) | 696 (8) | 567 (50) | 157 (10) | 66 (6) | 64 (23) | 74 (16) | 0 (7) |
| H(4) | −1074 (48) | 2037 (12) | 390 (8) | 886 (77) | 86 (9) | 126 (10) | −31 (28) | 87 (28) | −41 (7) |

Table 2. *Interatomic distances and angles in dimethyl sulfone diimine*

Distances marked with an asterisk are involved in hydrogen bonds.

| $i$ | $j$ | $k$ | $D_{ij}$ | $D_{jk}$ | $D_{ik}$ | $\angle ijk$ |
|---|---|---|---|---|---|---|
| C | S | C′ | 1·780 (8) | 1·780 (8) | 2·767 (10) | 102·0 (7) |
| C | S | N | 1·780 (8) | 1·536 (6) | 2·593 (6) | 102·6 (3) |
| C | S | N′ | 1·780 (8) | 1·536 (6) | 2·756 (6) | 112·2 (2) |
| N | S | N′ | 1·536 (6) | 1·536 (6) | 2·706 (6) | 123·4 (8) |
| S | N | H(1) | 1·536 (6) | 1·008 (17)* | 2·094 (13) | 109·0 (5) |
| N | H(1) | N″ | 1·008 (17)* | 2·359 (16)* | 3·335 (3)* | 162·8 (9) |
| S | C | H(2) | 1·780 (8) | 1·056 (15) | 2·345 (14) | 108·9 (8) |
| S | C | H(3) | 1·780 (8) | 1·070 (16) | 2·366 (16) | 109·8 (8) |
| S | C | H(4) | 1·780 (8) | 1·018 (18) | 2·322 (13) | 109·1 (1·1) |
| H(2) | C | H(3) | 1·056 (15) | 1·070 (16) | 1·717 (16) | 107·8 (1·6) |
| H(2) | C | H(4) | 1·056 (15) | 1·018 (18) | 1·715 (25) | 111·7 (1·6) |
| H(3) | C | H(4) | 1·070 (16) | 1·018 (18) | 1·705 (22) | 109·6 (1·1) |