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## Structure of C<sub>36</sub>H<sub>52</sub>Cl<sub>6</sub>InN<sub>3</sub>O<sub>14</sub> Determined by Nonlinear Least Squares

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### Abstract

Tris(triethylammonium) tris[3,6-dichloro-4,5-dihydroxy-3,5-cyclohexadiene-1,2-dionato(2-)]indium dihydrate, [C<sub>6</sub>H<sub>16</sub>N]<sub>3</sub>[In(C<sub>6</sub>Cl<sub>2</sub>O<sub>4</sub>)<sub>3</sub>].2H<sub>2</sub>O, *M*<sub>r</sub> = 1078.36, orthorhombic, *Pbcn*, *a* = 26.639 (4), *b* = 16.667 (2), *c* = 10.538 (2) Å, *V* = 4678.6 (5) Å<sup>3</sup>, *Z* = 4, *D*<sub>x</sub> = 1.540 g cm<sup>-3</sup>, λ(Mo Kα) = 0.70926 Å, μ = 0.9087 mm<sup>-1</sup>, *F*(000) = 2208, room temperature, final *R*(*F*) = 0.061 for 2551 reflections. The structure could only be determined using least-squares with the Levenberg–Marquardt algorithm, including the second derivatives of the structure factors. A refinement with standard least-squares stopped at an *R*-value of 16%, but showed stability with the Levenberg–Marquardt result.

### Introduction

This investigation is the third in a series studying the behavior of different metals in anilates. The data showed problems in the refinement of the structure, caused by statistical distribution of one of the cations. Within the scope of a project working with structures showing pseudosymmetry, a recently developed least-squares program using the Levenberg–Marquardt algorithm improved the refinement procedure and led to the final solution of the structure.

### Synthesis of the compound

A suspension of the hydrated indium(III)hydroxide was digested in a water bath with a stoichiometric excess of solid chloranilic acid for *ca* 3 h, until the reaction was complete and the reagents thoroughly disappeared. The hydroxide was fully dissolved, while the excess acid remained as a solid.

Into this solution, the exact quantity of triethylamine free base was introduced stepwise in small portions, under continuous stirring. After full neutralization of the excess chloranilic acid, the final pH reached the range 7–8. The mixture was then slowly heated in a water bath, filtered and received in a mixture of acetone–ethanol with strong stirring. A lilac–violet crystalline complex salt was well separated with a yield of *ca* 70%.

The crystalline product was filtered, first washed with a mixture of ethanol–ether and finally with ether. The crystals were dried under an air stream and finally under vacuum in the presence of phosphorus pentoxide for 24 h. They were recrystallized from DMSO by the addition of absolute ethanol, giving long gray–violet crystals.

### Experimental

All measurements were performed on a rebuilt PW 1100 instrument (Gomm, 1993). Crystal dimensions

$0.22 \times 0.15 \times 0.11 \text{ mm}^3$ ;  $\omega$ - $2\theta$  scan; background-peak-background profile analysis; lattice parameters derived from 33 reflections with  $6.6 < \theta < 12.3^\circ$ ; absorption correction by Gaussian integration (Busing & Levy, 1957); transmission factors 0.900–0.925; intensities collected for  $-25 \leq h \leq 25$ ,  $-16 \leq k \leq 16$ ,  $0 \leq l \leq 11$ ;  $\theta_{\text{max}} = 22^\circ$ ; four standard reflections repeated after 100 reflections; diffraction standards decay of 4%, correction for decay applied; 12 242 reflections measured; 2872 unique reflections after merging; 321 reflections with negative intensities were omitted;  $R_{\text{int}}$  based on  $F$  is 0.061.

The structure was solved by direct methods and refined by full-matrix least squares based on  $F$  (for further refinement, see next section); weights derived from experimental standard deviations,  $w = 1/[\sigma^2(F)]$  and  $\sigma = \max(0.01F, \sigma_{\text{exp}})$ . In the latter stages of refinement, anisotropic temperature parameters were used for all non-H atoms. All H atoms could be located on a difference Fourier map. The resulting coordinates and  $U_{\text{eq}}$  values are given in Table 1. The final  $R$ -values are  $R = 0.053$ ,  $wR = 0.025$ ,  $\text{GoF} = 1.55$ , maximal shift-to-e.s.d. ratio 0.1. Maximal and minimal electron density residuals are  $\Delta\rho_{\text{max}} = 0.64$  and  $\Delta\rho_{\text{min}} = 0.55 \text{ e } \text{Å}^{-3}$ . No extinction correction was applied; form factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV). All computations were performed on a HP9000-700 computer using the last release of the program system *CRYSTAN88* (Burzlaff & Rothammel, 1988). The bond distances and angles are in very good agreement with the literature (Krogh Andersen, 1967; Krogh Andersen & Krogh Andersen, 1975).\*

#### Determination of the structure

The structure model of the title compound derived by direct methods was first refined with the usual least squares, containing all the features proposed by Cruickshank (1970). The refinement stopped with anisotropic displacement parameters at an  $R$ -value close to 16%. So far only the metal anilate and two of the three stoichiometric solvent molecules have been found. The difference Fourier map only showed some strange spider-like maxima on a twofold axis. The missing solvent molecule contained no twofold symmetry, and thus it was considered to have statistical occupancy. The refinement with an occupancy factor of 1/2 was unstable, even with damping factors down to 0.01.

Maximal subgroups of the space group were then tried, without success. Refinement with the recently developed nonlinear least squares program *LQFLEW* (Spengler & Zimmermann, 1994) using the Levenberg–

Table 1. Fractional atomic coordinates and equivalent (or  $U_{\text{iso}}$ ) isotropic thermal parameters ( $\text{Å}^2$ )

No.	Atom	Occupation	x	y	z	$U$
1	In(1)	1.0	1/2	0.218316 (6)	1/4	0.0363
2	Cl(1)	1.0	0.66146 (1)	0.19295 (2)	-0.01039 (3)	0.0712
3	Cl(2)	1.0	0.60830 (1)	0.03227 (2)	0.51629 (3)	0.0866
4	Cl(3)	1.0	0.573881 (9)	0.45717 (2)	0.48529 (3)	0.0503
5	O(1)	1.0	0.54431 (2)	0.13705 (4)	0.35762 (6)	0.0439
6	O(2)	1.0	0.56549 (2)	0.20264 (4)	0.13441 (6)	0.0403
7	O(3)	1.0	0.72561 (2)	0.08674 (5)	0.14732 (8)	0.0691
8	O(4)	1.0	0.70319 (2)	0.01741 (5)	0.36839 (8)	0.0786
9	O(5)	1.0	0.52868 (2)	0.31841 (4)	0.35313 (6)	0.0403
10	O(6)	1.0	0.53350 (2)	0.59967 (4)	0.34422 (7)	0.0520
11	O(7)	1.0	0.40411 (3)	0.36165 (5)	0.4330 (1)	0.1182
12	N(1)	1.0	0.28346 (3)	0.44411 (5)	0.25840 (9)	0.0514
13	N(2)	1.0	1/2	0.75937 (6)	1/4	0.0453
14	C(1)	1.0	0.58780 (3)	0.12213 (6)	0.3131 (1)	0.0384
15	C(2)	1.0	0.60057 (3)	0.16072 (6)	0.18523 (9)	0.0357
16	C(3)	1.0	0.64697 (3)	0.14908 (6)	0.1334 (1)	0.0419
17	C(4)	1.0	0.68377 (3)	0.09992 (6)	0.1904 (1)	0.0475
18	C(5)	1.0	0.67067 (3)	0.05996 (6)	0.3193 (1)	0.0504
19	C(6)	1.0	0.62293 (4)	0.07518 (6)	0.3700 (1)	0.0526
20	C(7)	1.0	0.51729 (3)	0.38693 (5)	0.30852 (9)	0.0333
21	C(8)	1.0	0.53387 (3)	0.45919 (6)	0.3551 (1)	0.0360
22	C(9)	1.0	0.51916 (3)	0.53368 (5)	0.30574 (9)	0.0380
23	C(10)	1.0	0.26705 (4)	0.39652 (7)	0.3728 (1)	0.0771
24	C(11)	1.0	0.22179 (5)	0.34508 (8)	0.3442 (2)	0.1200
25	C(12)	1.0	0.29146 (4)	0.39501 (7)	0.1419 (1)	0.0609
26	C(13)	1.0	0.32702 (5)	0.32434 (7)	0.1591 (1)	0.0851
27	C(14)	1.0	0.32844 (3)	0.49699 (8)	0.2911 (1)	0.0706
28	C(15)	1.0	0.33405 (4)	0.56635 (7)	0.2062 (1)	0.0851
29	C(16)	0.53 (3)	0.55731 (7)	0.7774 (1)	0.2718 (2)	0.0547
30	C(17)	1.0	0.41574 (4)	0.75350 (7)	0.3521 (1)	0.0893
31	C(18)	0.53 (3)	0.47309 (7)	0.7742 (1)	0.3716 (2)	0.0567
32	C(19)	0.50 (3)	0.47969 (7)	0.8009 (1)	0.1404 (2)	0.0633
33	C(20)	0.45 (3)	0.4762 (1)	0.8897 (2)	0.1582 (3)	0.1077
34	H(1)	1.0	0.2532 (2)	0.4827 (4)	0.2391 (7)	0.0695 (5)
35	H(2)	1.0	0.2576 (2)	0.4438 (4)	0.4374 (7)	0.0695 (5)
36	H(3)	1.0	0.2988 (2)	0.3650 (4)	0.3946 (6)	0.0695 (5)
37	H(4)	1.0	0.2029 (2)	0.3792 (4)	0.3350 (7)	0.0695 (5)
38	H(5)	1.0	0.2100 (2)	0.3258 (4)	0.4124 (7)	0.0695 (5)
39	H(6)	1.0	0.2351 (2)	0.2919 (4)	0.2917 (7)	0.0695 (5)
40	H(7)	1.0	0.3015 (2)	0.4287 (4)	0.0735 (7)	0.0695 (5)
41	H(8)	1.0	0.2574 (2)	0.3763 (4)	0.1133 (7)	0.0695 (5)
42	H(9)	1.0	0.3524 (2)	0.3492 (4)	0.1888 (7)	0.0695 (5)
43	H(10)	1.0	0.3277 (3)	0.3078 (4)	0.0669 (8)	0.0695 (5)
44	H(11)	1.0	0.3078 (2)	0.2823 (4)	0.2173 (7)	0.0695 (5)
45	H(12)	1.0	0.3538 (2)	0.4613 (4)	0.2903 (7)	0.0695 (5)
46	H(13)	1.0	0.3189 (2)	0.5007 (5)	0.3791 (7)	0.0695 (5)
47	H(14)	1.0	0.3417 (3)	0.5505 (4)	0.1131 (8)	0.0695 (5)
48	H(15)	1.0	0.3608 (2)	0.5987 (4)	0.2451 (8)	0.0695 (5)
49	H(16)	1.0	0.3028 (2)	0.6031 (4)	0.2070 (7)	0.0695 (5)
50	H(17)	1.0	1/2	0.6912 (6)	1/4	0.0695 (5)
51	H(18)	1.0	0.5594 (2)	0.7629 (4)	0.3572 (7)	0.0695 (5)
52	H(19)	1/2	0.5595 (4)	0.8339 (7)	0.277 (1)	0.0695 (5)
53	H(20)	1.0	0.4173 (2)	0.7042 (4)	0.3438 (7)	0.0695 (5)
54	H(21)	1.0	0.3954 (2)	0.7752 (4)	0.3214 (7)	0.0695 (5)
55	H(22)	1/2	0.4140 (4)	0.7874 (8)	0.426 (1)	0.0695 (5)
56	H(23)	1/2	0.4787 (4)	0.8172 (7)	0.400 (1)	0.0695 (5)
57	H(24)	1.0	0.4930 (3)	0.7492 (3)	0.4290 (7)	0.0695 (5)
58	H(25)	1/2	0.4607 (5)	0.9028 (8)	0.110 (1)	0.0695 (5)
59	H(26)	1/2	0.5006 (6)	0.9038 (7)	0.143 (1)	0.0695 (5)
60	H(27)	1/2	0.4812 (4)	0.9255 (6)	0.243 (2)	0.0695 (5)

\* Lists of structure factors, anisotropic displacement parameters, H-atom parameters and complete geometry have been deposited with the IUCr (Reference: SE0148). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Marquardt algorithm (Press, Teukolsky, Vetterling & Flannery, 1992), including the second derivatives of the structure factors, led to stability and showed an  $R$ -value close to 10%. The following difference Fourier map showed a maximum of  $5.17 \text{ e } \text{Å}^{-3}$ . This maximum had ideal hydrogen bridge distances to two oxygens and was identified as a crystal water molecule. After the introduction of this molecule, the refinement converged to an  $R$ -value of *ca* 6%.

The usual Levenberg–Marquardt computation as described in Press, Teukolsky, Vetterling & Flannery (1992) is an approximation and neglects the second derivatives; only the products of the first derivatives are used. Therefore, the cited approximation almost leads to the normally applied refinement procedure. In fact, the tangent is used instead of the parabola for the approximation.

Working correctly with a parabola, the second derivatives of the structure factors have to be used as *LQFLEV* is used (Spengler & Zimmermann, 1994). The results are very encouraging for solving this structure. Further investigations in this field are intended; a discussion of the program and other results will be presented in a separate paper.

With the knowledge of the crystal water molecule and the statistically occupied solvent molecule, the usual least-squares remained stable, refining to the same solution. The next difference Fourier map showed all H atoms which were taken into the refinement with a common isotropic displacement parameter. The standard

Table 2. Bond distances and angles

In(1)—O(1)	2.1246 (7)	In(1)—O(5')	2.1325 (6)
In(1)—O(1')	2.1246 (7)	In(1)—O(2)	2.1438 (6)
In(1)—O(5)	2.1325 (6)	In(1)—O(2')	2.1438 (6)
O(1)—In(1)—O(1')	100.79 (3)	O(2)—In(1)—O(1')	94.08 (3)
O(5')—In(1)—O(1)	165.88 (2)	O(2)—In(1)—O(5')	95.59 (2)
O(5')—In(1)—O(1')	91.58 (3)	O(2)—In(1)—O(5)	95.36 (2)
O(5)—In(1)—O(1)	91.58 (3)	O(2')—In(1)—O(1)	94.08 (3)
O(5)—In(1)—O(1')	165.88 (2)	O(2')—In(1)—O(1')	76.91 (3)
O(5)—In(1)—O(5')	77.06 (3)	O(2')—In(1)—O(5')	95.36 (2)
O(2)—In(1)—O(1)	76.91 (3)	O(2')—In(1)—O(5)	95.59 (2)
		O(2')—In(1)—O(2)	166.00 (2)

Symmetry code: (i)  $1 - x, y, \frac{1}{2} - z$ .

least-squares diverged, even with damping factors down to 0.005, while the nonlinear least-squares converged to the final solution with the *wR*-value 2.5%. The unweighted *R*-value was 5.3% for all reflections; using reflections with  $F > 1.4\sigma$ , *R* could be reduced to 4.2%.

The title compound contains an In atom with octahedral coordination distorted towards an antiprism (*cf.* Table 2), surrounded by three chloranilate cations [see Fig. 1(*a*)]. The indium complexes form a zero-shifted, *c*-centered orthorhombic cell, leading to a pseudocentering vector of  $\frac{1}{2}\frac{1}{2}0$ . Thus, the *oeo*-, *ooo*-, *oeo*- and *oeo*-reflections are weaker than the others. The positions of the In atoms differ from a hexagonal cell by 6° in  $\gamma$ . The indium chloranilate anion has threefold

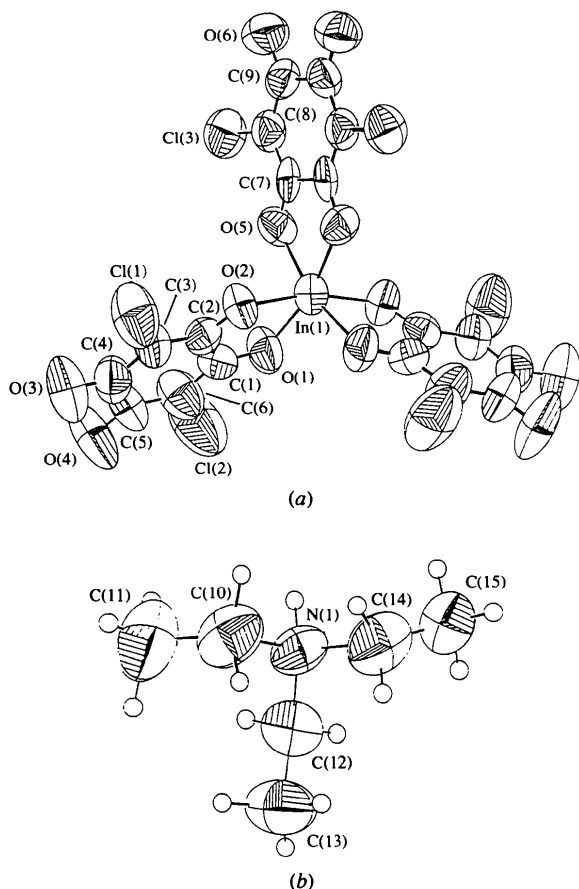


Fig. 1. Thermal ellipsoids of the molecules: (a) indium alinate (with 90% probability) and (b) solvent molecules (with 66.6% probability).

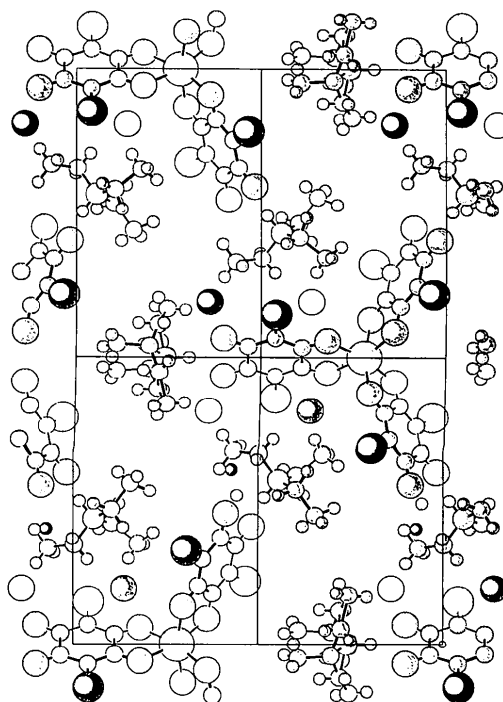


Fig. 2. Plot of the cell in the *ab*-plane (height from  $-6$  to  $1$  Å).

symmetry (see Fig. 2). There are three anions [see Fig. 1(b)], one on a twofold axis with statistical occupancy (see also Fig. 2).

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## Redetermination of the Crystal Structure of 3,5,7-Trimethyl-1-adamantyl Undecafluorodiantimonate(V)

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#### Abstract

The crystal structure of the 3,5,7-trimethyl-1-adamantyl cation (1) has been redetermined by X-ray diffraction at 103 K, since the structural data already published [Laube (1986a). *Angew. Chem.* **98**, 368–369; Laube (1986b). *Angew. Chem. Int. Ed. Engl.* **25**, 349–350] showed a poor *R*-value (0.070) and exhibited a rather large variety of lengths of chemically but not crystallographically equivalent bonds, which is no longer present in the newly determined structure with  $R_1 = 0.0452$ . A partial disorder model of the anion could be refined and the experimental data of (1) are compared with results of semi-empirical and *ab initio* calculations. The results are interpreted in terms of stabilization of (1) by C,C-hyperconjugation. The detailed experimental procedure for the synthesis and crystallization of (1).Sb<sub>2</sub>F<sub>11</sub> is described.

#### Introduction

The 3,5,7-trimethyl-1-adamantyl cation (1) is the only clear example yet known of C,C-hyperconjugation (Olah *et al.*, 1985) in a crystal structure where both C<sub>α</sub>–C<sub>β</sub> shortening and C<sub>β</sub>–C<sub>γ</sub> elongation could be proven experimentally [Fig. 1 (Laube, 1986a,b)]. In the recently determined structure of the *tert*-butyl cation (Hollenstein & Laube, 1993), only the C<sub>α</sub>–C<sub>β</sub> shortening could be observed, because the H atoms were partially disor-

dered and refined with constraints. The poor original refinement of (1).Sb<sub>2</sub>F<sub>11</sub> and the availability of high-quality *ab initio* data for comparison (Buzek, Schleyer & Sieber, 1992) made a more precise crystal structure determination necessary.

#### Experimental

##### Synthesis and crystallization of (1).Sb<sub>2</sub>F<sub>11</sub>

The reaction was carried out in a special apparatus (see Laube, 1994, Fig. 6 and *Experimental* section). In the reaction vessel, a solution of 413 mg of 1-

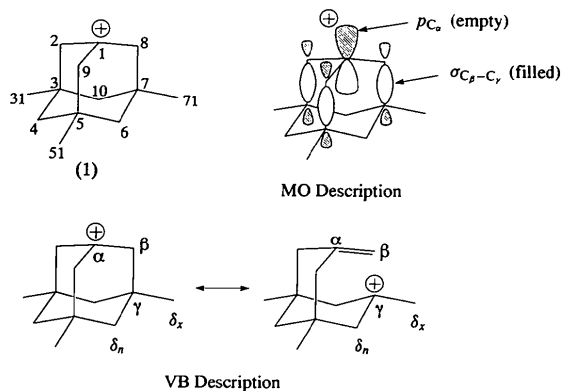


Fig. 1. Constitution and numbering of (1) and hyperconjugation in the MO and VB description ( $n$  = endocyclic,  $x$  = exocyclic).

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