# Crystal Structure of Tris(diethyldithiophosphato)indium(III)

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*Summary* *X*-Ray determination of the crystal structure of the title compound reveals it to have $C_3$ symmetry and unequal P–S bond lengths within each ligand.

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THE recent Communication[1] on the crystal structure of V dtp$_3$ [dtp = $S_2P(OEt)_2^-$], which was assigned to the space group *C*2/*c*, prompts us to report the results of our study on the corresponding indium compound (I).

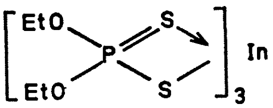
In dtp$_3$ crystallizes in the monoclinic system with cell dimensions $a = 8{\cdot}61$, $b = 18{\cdot}81$, $c = 17{\cdot}85$ Å, $\beta = 92{\cdot}2°$; $U = 2888$ Å$^3$, $M = 670{\cdot}5$, $D_m = 1{\cdot}51$ g.cm$^{-3}$, $Z = 4$, $D_c = 1{\cdot}54$ g.cm$^{-3}$. Systematically absent spectra, *hkl* when

TABLE

*Selected bond lengths and valency angles with standard deviations in parentheses*

| | | | |
|---|---|---|---|
| P(1)–S(1) | 2·037(15) Å | S(1)–In | 2·591(11) Å |
| P(1)–S(2) | 1·952(13) | S(2)–In | 2·633(9) |
| P(2)–S(3) | 2·137(11) | S(3)–In | 2·607(7) |
| P(2)–S(4) | 1·902(10) | S(4)–In | 2·578(7) |
| P(3)–S(5) | 2·066(9) | S(5)–In | 2·628(7) |
| P(3)–S(6) | 1·874(11) | S(6)–In | 2·609(6) |
| P(1)–S(1)–In | 85·2(0·5)° | S(1)–In–S(2) | 78·0(0·3)° |
| P(1)–S(2)–In | 85·8(0·4) | S(3)–In–S(4) | 79·1(0·2) |
| P(2)–S(3)–In | 83·0(0·3) | S(5)–In–S(6) | 77·1(0·2) |
| P(2)–S(4)–In | 88·5(0·3) | S(1)–P(1)–S(2) | 111·0(0·5) |
| P(3)–S(5)–In | 83·4(0·3) | S(3)–P(2)–S(4) | 109·5(0·4) |
| P(3)–S(6)–In | 87·7(0·3) | S(5)–P(3)–S(6) | 111·8(0·4) |

$h + k = 2n + 1$, and $h0l$ when $l = 2n + 1$, are consistent with two space groups, $C2/c$ and $Cc$. Intensity data were estimated visually from equi-inclination Weissenberg photographs of the 0—$7kl$ layers.



(I)

The structure was solved by the heavy-atom method. As a first model, a structure corresponding to that since reported for the vanadium compound was derived from the indium-phased three-dimensional electron-density distribution assuming the space group to be $C2/c$. With four molecules of In dtp$_3$ in the unit cell of space group $C2/c$ the indium atom is required to be at one of the four-fold special positions and the crystallographic two-fold axis must pass through the centres of the indium atom and one of the phosphorus atoms [P(1) in the Figure]. However, the peaks corresponding to O(1) and O(2), and to a lesser extent that corresponding to P(1), were significantly elongated in the $xz$-plane, approximately normal to the P–O bond directions. These observations were inconsistent with an ordered molecule conforming to the two-fold crystallographic symmetry requirements of $C2/c$. In the absence of similar elongation of the electron-density corresponding to other P, S, and O atoms, we were forced to conclude that the space group is $Cc$ with the In–P(1) vector tilted through some small angle from the pseudo two-fold axis imposed by the phasing calculations. This interpretation was consistent with the greatest elongation of the electron density being observed for O(1) and O(2). Carbon atoms bonded to O(1) and O(2) are excluded from this discussion as they were less well defined. Full-matrix least-squares refinement of the atomic positions and isotropic temperature factors of all non-hydrogen atoms was carried out initially in both space groups. At convergence, $R$ for $Cc$ was 0·122 while for $C2/c$ it was 0·146; moreover, when the former space group was employed the resulting temperature factors of most atoms were lower than when the latter was used, the largest differences being for O(1), O(2), and P(1). These results are in accord with the choice of space group $Cc$. Further full-matrix least-squares adjustment of the positional and thermal parameters (anisotropic for the In, P, and S atoms, isotropic for the C and O atoms) resulted in $R = 0·086$ over 1623 observed reflections.

The molecule as viewed in projection along the $b$ axis is shown in the Figure. The In–P vector makes an angle of 6° with the crystallographic $b$ axis. Listed in the Table are the more important bond lengths and valency angles. The molecule has essentially $C_3$ symmetry with the indium atom approximately equidistant from six sulphur atoms which are arranged in a distorted octahedron. There are two different P–S distances within each ligand. The difference of 0·17 Å between the average of the shorter P–S bonds, 1·91 Å, and the mean of the longer bonds, 2·08 Å, is highly significant. The P–O, C–O, and C–C bonds with average lengths of 1·60, 1·50, and 1·50 Å, respectively, do not differ significantly from accepted values.

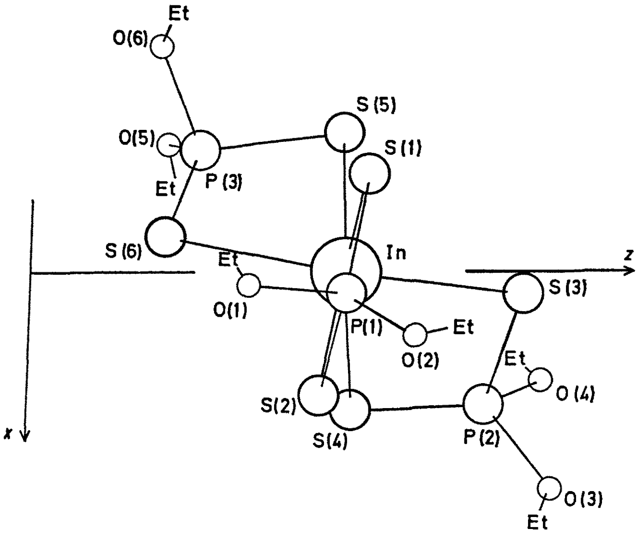


FIGURE. In dtp$_3$ *molecule viewed in projection along the* b *axis. The carbon atoms of the ethyl group have been omitted for clarity.*

The above results cast doubt on the assignment[1] of the space group $C2/c$ to the vanadium compound; the vanadium and indium compounds are probably isomorphous and both belong to the space group $Cc$.

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[1] C. Furlani, P. Porta, A. Sgamellotti, and A. A. G. Tomlinson, *Chem. Comm.*, 1969, 1046.