2

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

AD-A257 404

REPORT DOCUMENTATI

m Approved
IB No. 0704-0188

DTIC
ELECTE
OCT 27 1992
S B D

1a. REPORT SECURITY CLASSIFICATION Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT
Approved for Public Release
Distribution Unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
Technical Report No. DU/DC/TR-31

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
Department of Chemistry
Duke University

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c. ADDRESS *(City, State, and ZIP Code)*
Durham, NC 27708-0346

7b. ADDRESS *(City, State, and ZIP Code)*
300 North Quincy Street
Arlington, VA 22217-5000

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
N00014-89-J1545 R&T Code 4135008

8c. ADDRESS *(City, State, and ZIP Code)*
800 North Quincy Street
Arlington, VA 22217-5000

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO.
NR	053	841	

11. TITLE *(Include Security Classification)*
X-Ray Crystal Structure of an Organoindium Alkoxide Dimer, $(Ph_2InOSiMe_3)_2$.

12. PERSONAL AUTHOR(S)
Mark F. Self, Andrew T. McPhail, and Richard L. Wells*

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT *(Year, Month, Day)*	15. PAGE COUNT
Technical	FROM ______ TO ______	1992-10-20	12

16. SUPPLEMENTARY NOTATION
Accepted for Publication in *J. Coord. Chem.*

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
indium-oxygen, alkoxide, ring compound,
synthesis, crystal structure

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

The solid-state structure of $(Ph_2InOSiMe_3)_2$ **1** has been established by single-crystal X-ray analysis. Monoclinic crystals of **1** belong to space group $P2_1/c$, with $a = 9.136(1)$, $b = 15.503(2)$, $c = 11.836(1)$ Å, $\beta = 102.46(1)°$, $Z = 2$. Refinement of atomic parameters converged at $R = 0.050$ ($R_w = 0.063$) over 1718 observed reflections with $I > 3.0\sigma(I)$. The dimeric molecule lies on a crystallographic centre of symmetry with In-O distance of 2.15(7) and 2.149(8) Å, O-In-O = 78.9(3)°, and In-O-In = 101.1(3)°. Compound **1** is only the second example of a simple dimeric organoindium alkoxide to be structurally characterized in this manner.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL
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22b. TELEPHONE *(Include Area Code)*
(919) 660-1541

22c. OFFICE SYMBOL

DD Form 1473, JUN 86

Previous editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

OFFICE OF NAVAL RESEARCH

Grant NOOO14-89-J-1545

R&T Code 4135008

Technical Report No. DU/DC/TR-31

X-RAY CRYSTAL STRUCTURE OF AN ORGANOINDIUM ALKOXIDE DIMER, $(Ph_2InOSiMe_3)_2$

by

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October 20, 1992

(Submitted to *J. Coord. Chem.* 26 June 1992)
(Revised submitted 6 October 1992)

NOTE

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(Recieved ...., 1992)

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Keywords: indium, alkoxide, siloxide, X-ray structure

INTRODUCTION

Chemical investigations involving alkoxides of indium have recently undergone a resurgence[1,2] due in part to their potential as precursors to III-VI materials some of which have found utility in applications such as conducting and transparent oxide films for displays and solar cell windows.[3] Although a variety of organoindium alkoxides have been fabricated for use in relation to these

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material science studies, determinations of their detailed structures have thus far been lacking.

During the period 1956 to 1974, there appeared numerous literature reports of simple organoindium alkoxides (*e.g.*, R_2InOR': R = Me; R' = $SiMe_3$,[4] $SiPh_3$,[5] CMe_3,[6] CPh_3,[7] Me,[8] CD_3,[9] *t*-Bu[10]: R = CD_3; R' = Me, CD_3:[9] R = Et; R' = Me, Et [9] R = Bu; R' = Bu, Ph[11]). The nature of these compounds was established by a combination of NMR spectroscopy, cryoscopic molecular weight determination, and infrared techniques. It is surprising that no X-ray crystallographic analyses of these compounds have appeared to date. In fact, the first and only report of the determination of the crystal structure of a simple dimeric organoindium alkoxide, $(t\text{-}Bu_2InOEt)_2$, was published only recently.[12] The solid-state structure of $(Ph_2InOSiMe_3)_2$ described herein represents only the second complete characterization of a member of this class.

EXPERIMENTAL

Materials and Measurements

All manipulations were performed using general Schlenk techniques in a Vacuum/Atmospheres HE-493 Dri-Lab containing an argon atmosphere. Toluene and benzene-d_6 were distilled from sodium/benzophenone ketyl under dry dinitrogen. $P(SiMe_3)_3$ [13] and Ph_2InCl [14] were prepared by literature procedures. The ^1H NMR spectrum was recorded on a Varian XL-300 spectrometer using a flame sealed 5 mm tube and referenced to TMS by use of the residual protons of deuterated benzene at δ 7.15 ppm. The melting point (Thomas-Hoover Uni-melt, sealed capillary) is uncorrected. Elemental analysis was performed by E+R Microanalytical Laboratory, Inc., Corona, New York.

Preparation of $(Ph_2InOSiMe_3)_2$ **1**

The title compound was prepared *via* the adventitious hydrolysis of a reaction mixture containing $P(SiMe_3)_3$ and Ph_2InCl in 100 mL of toluene. This hydrolysis occurred through the probable contamination of the solvent by a trace amount of water. The procedure which was employed follows. In the dry box, Ph_2InCl (0.250 g, 0.82 mmol) in 25 mL of toluene and $P(SiMe_3)_3$ (0.103 g, 0.41 mmol) in 75 mL of toluene were combined in a 150-mL one-necked round-bottomed flask equipped with a Teflon valve and a micro-stirbar. The resulting *milky* suspension was taken out of the box and stirred at room temperature for 24 h. Removal of the volatiles *in vacuo* yielded an oily off-white residue that was dissolved in approximately 15 mL of hot toluene and cooled to -15 °C for 1 day. Compound **1** was isolated in 71% yield (0.416g, based on Ph_2InCl) from an intractable yellow oil as clear colourless platelets. Mp = 230 °C (dec), Anal. Calcd (Found) for $C_{30}H_{38}In_2O_2Si_2$: C, 50.30 (49.93); H, 5.35 (5.46). ^1H NMR: δ 0.02 (s, 18 H, $OSiMe_3$), 7.02 (m, 20 H, Ph).

X-Ray Crystal Structure Analysis of Compound 1

All measurements were made on a sample mounted inside a flame-sealed 0.6 mm thin-walled glass capillary under an inert argon atmosphere. Oscillation and Weissenberg photographs provided preliminary unit cell parameters and space group information. Crystallographic data are summarized in Table I. The monoclinic space group $P2_1/c$ was established unequivocally from the Laue symmetry and systematic absences ($0k0$ when $k \neq 2n$, $h0l$ when $l \neq 2n$). Intensity data ($+h, +k, \pm l$, 3590 reflections, $\theta_{max} = 75°$), recorded on an Enraf-Nonius CAD-4 diffractometer using Cu-Kα radiation ($\lambda = 1.5418$ Å, graphite monochromator), were corrected for the usual Lorentz and polarization effects. An empirical absorption correction, based on the ϕ-dependency of the intensities of two reflections with ψ ca. 90°, was applied, and equivalent reflections were averaged

[R_{merge} = 0.038 on (I)] to yield 3378 reflections out of which those 1718 with $I >$ 3.0$\sigma(I)$ were retained for the analysis.

The crystal structure was solved by the heavy-atom approach. Approximate indium atom coordinates were derived from a Patterson map. The remaining non-hydrogen atoms were located in a weighted F_o Fourier synthesis phased by the indium atom. Several rounds of full-matrix least-squares adjustment of non-hydrogen atom positional and thermal parameters (at first isotropic, then anisotropic) followed. Hydrogen atoms were incorporated at their calculated positions in the later iterations which converged (max. shift:esd = 0.02) at R = 0.050 (R_w = 0.063). A final difference Fourier synthesis revealed no unusual features (max. 0.91, min. -0.84 e/Å^3; both in the vicinity of the In atom). Crystallographic calculations were performed using the Enraf-Nonius Structure Determination Package.[15] For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref. 16. In the least-squares iterations, $\Sigma w\Delta^2$ [$w = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$] was minimized. Fractional atomic coordinates are listed in Table II; selected distances and angles are provided in Table III. A view of the solid-state structure of **1**, with the atom numbering scheme, is presented in the Figure.

RESULTS AND DISCUSSION

From solution studies, the complexes R_2InOR' where R = Me; R' = $SiMe_3$,[4] $SiPh_3$,[5] CMe_3,[6] CPh_3,[7] or t-Bu:[10] R = Bu; R' = Bu or Ph[11] are postulated to exist primarily as dimers whereas when R = Me; R' = Me:[8] R = CD_3; R' = Me or CD_3:[9] R = Et; R' = Me or Et[9] the complexes are said to be trimeric. It is unfortunate that the limited solubility of **1** in organic solvents precludes the use of solution cryoscopic molecular weight determination. As is evident from the Figure, **1** exists in the solid state as a siloxy-bridged dimer. This degree of oligomerization is undoubtedly due to size effects of the ligands bonded to the indium and oxygen atoms as the aforementioned trimeric alkoxides all involve relatively small substituents.

Though the formation of **1** was accomplished by a rather serendipitous event, this does not diminish the fundamental value that the elucidation of its structure and bonding geometry contributes to the general knowledge of alkoxide chemistry. As was stated earlier, the only previously reported structure of a simple organoindium alkoxide involved the dimer $(t\text{-Bu}_2\text{InOEt})_2$ **2**.[12] Interestingly, **2** was also prepared by a non-conventional method involving the reaction of *n*-BuLi, $\overline{\mathrm{NHCMe_2(CH_2)_3C}}\mathrm{Me_2}$, and $t\text{-Bu}_2\text{InCl}$ in Et_2O solvent. The shortest intermolecular separations between the discrete dimeric units in crystals of **1** and **2** correspond to normal van der Waals distances. Compounds **1** and **2** both lie on crystallographic centres of symmetry and thus involve planar four-membered In_2O_2 cores. The mean In-O bond distances [2.154 Å **1**; 2.156 Å **2**] are essentially identical in both compounds, and the Si-O distance of 1.654(8) Å in **1** is in accord with the expected value of 1.63(2) Å.[17] One of the oxygen atoms in **1** lies close to one of the phenyl ring planes [O-In-C(11)-C(12) torsion angle = 3(1)°] whereas both are nearly equidistant from the other phenyl ring plane [torsion angles: O-In-C(21)-C(26) = 46(1)°, O'-In-C(21)-C(26) = -39(1)°] which, accordingly, approximately bisects the O-In-O' angle. Ring aryl substituents are similarly oriented in crystals of $[\text{In(2,4,6-trimethylphenyl)}_2\text{I}]_2$ **3**[18] where the mean In-C distance of 2.169 Å asociated with the bulkier ligands is slightly longer than that of 2.149 Å in **2**. In both **1** and **2**, the geometry about the oxygen atoms is distorted trigonal planar while that at the indium atoms is distorted tetrahedral. The O-In-O' and In-O-In' angles in **1** at 78.9 (3)° and 101.1 (3)°, respectively, are similar to corresponding values in **2** [75.2(3)° and 104.8 (2)°]. The considerable enlargement of the C-In-C angles [133.3(4)° in **1**, 127.2(4)° in **2**, 127.7(1)° in **3**] over the ideal tetrahedral value is probably due principally to electronic factors with intramolecular non-bonded steric interactions between ring substituents also making some contribution.

SUPPLEMENTARY DATA

Additional material consisting of H-atom coordinates, thermal parameters, and a complete list of bond distances and angles are available from R.L.W.

ACKNOWLEDGEMENTS

We thank the Office of Naval Research for financial support.

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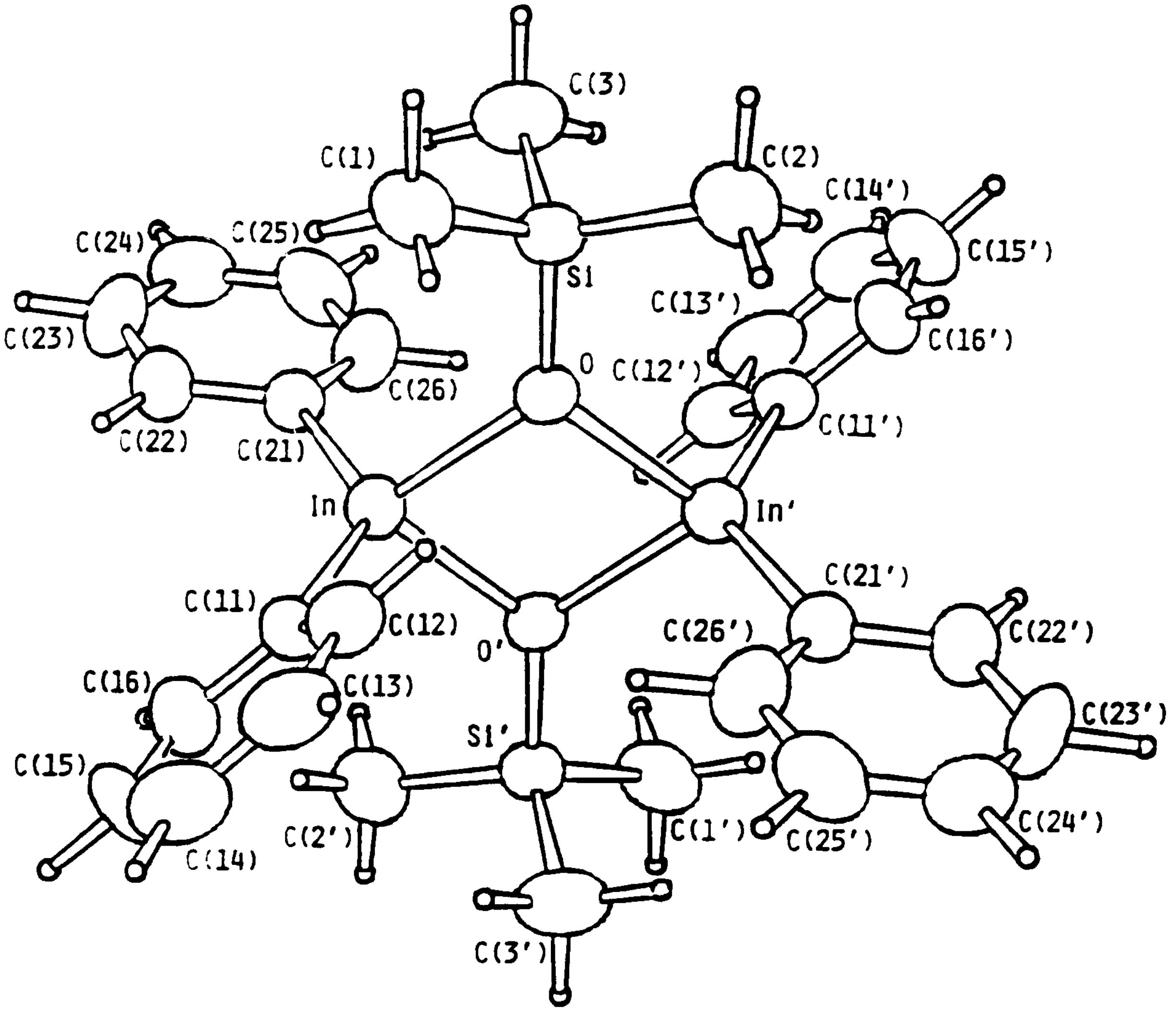
Caption to Figure

Figure. ORTEP diagram (40% probability ellipsoids) showing the atom numbering scheme and solid-state conformation of $(Ph_2InOSiMe_3)_2$ **1**; primed atoms are related to the unprimed atoms by a crystallographic centre of symmetry. Small circles represent hydrogen atoms.


C(3)
C(1)
C(2)
C(14')
C(24)
C(25)
Si
C(15')
C(13')
C(23)
O
C(12')
C(16')
C(26)
C(22)
C(21)
C(11')
In
In'
C(21')
C(11)
C(12)
C(26')
C(22')
O'
C(16)
C(13)
Si'
C(23')
C(15)
C(2')
C(1')
C(25')
C(24')
C(14)
C(3')

Figure

Table I

Crystallographic data for $(Ph_2InOSiMe_3)_2$ **1**.

Molecular formula	$C_{30}H_{38}In_2O_2Si_2$
Formula weight	716.45
Crystal system	monoclinic
Space group	$P2_1/c(C_{2h}^5)$ - No.14
a/Å	9.136(1)
b/Å	15.503(2)
c/Å	11.826(1)
β(°)	102.46(1)
No. of orientation refls.; ϑ(°) range	25; 36-40
U/Å^3	1635.5(6)
Z	2
D_c/g cm^{-3}	1.455
μ/cm^{-1}(Cu-$K\alpha$ radiation, λ 1.5418 Å)	124
T/K	298
Crystal size/mm	0.14 x 0.18 x 0.22
T_{max}:T_{min}	1.00:0.37
Scan type	ω-2θ
Scanwidth/°	1.00 + 0.14tanθ
θ_{max}/°	75
Intensity control refls.	1 3 2, 1 1 3, 1 2 3, 2 3 1;
Overall variation in standards (%);	<2
Repeat time /hr	2
Total no. of refls. ($+h,+k,\pm l$) recorded	3590
No. of non-equiv. refls. recorded	3378
R_{merge} (on I)	0.038
No. of refls. retained [$I > 3.0\sigma(I)$]	1718
No. of parameters refined	163
$R = \Sigma \lvert\, \lvert F_o \rvert - \lvert F_c \rvert \,\rvert / \Sigma \lvert F_o \rvert$	0.050
$R_w = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w \lvert F_o \rvert^2]^{1/2}$	0.063
$S = [\Sigma w \Delta^2 / (N_{obs.} - N_{para.})]^{1/2}$	1.39
Max. shift:esd in final least-squares cycle	0.02
Final $\Delta\rho$(e/Å^3) max.;min.	0.91 ; -0.84

Table II

Non-Hydrogen Atom Fractional Coordinates and equivalent isotropic thermal parameters (x 10^2) for $(Ph_2InOMe_3)_2$ **1**,with Estimated Standard Deviations in Parentheses.

Atom	*x*	*y*	*z*	B_{eq}(Å^2)
In	0.03169(8)	0.08616(5)	-0.07494(6)	3.77(1)
Si	-0.2315(3)	0.0991(2)	0.0930(2)	4.26(6)
O	-0.1169(7)	0.0416(5)	0.0320(5)	3.7(1)
C(1)	-0.3412(13)	0.1719(9)	-0.0152(10)	6.6(3)
C(2)	-0.3531(13)	0.0203(10)	0.1476(10)	6.3(4)
C(3)	-0.1190(16)	0.1622(10)	0.2162(11)	7.1(4)
C(11)	-0.0888(12)	0.0809(7)	-0.2525(6)	4.2(2)
C(12)	-0.2364(12)	0.0555(8)	-0.2769(9)	4.7(3)
C(13)	-0.3160(15)	0.0498(9)	-0.3938(11)	6.3(3)
C(14)	-0.2451(16)	0.0688(9)	-0.4801(11)	7.2(4)
C(15)	-0.0961(19)	0.0954(11)	-0.4547(9)	9.1(4)
C(16)	-0.0218(13)	0.1017(8)	-0.3413(10)	5.4(3)
C(21)	0.1857(10)	0.1767(7)	0.0214(9)	3.9(2)
C(22)	0.2155(14)	0.2539(8)	-0.0280(9)	5.5(3)
C(23)	0.3158(15)	0.3139(8)	0.0392(13)	6.9(4)
C(24)	0.3860(13)	0.2958(9)	0.1477(11)	6.3(3)
C(25)	0.3569(14)	0.2201(11)	0.1967(11)	6.8(4)
C(26)	0.2568(14)	0.1612(8)	0.1327(10)	5.7(3)

Table III

Interatomic Distances (Å) and Angles (deg.) for $(Ph_2InOMe_3)_2$ **1**, with Estimated Standard Deviations in Parentheses.

In-O	2.159(7)	Si-O	1.654(8)
In-O'	2.149(8)	Si-C(1)	1.834(12)
In-C(11)	2.152(7)	Si-C(2)	1.858(14)
In-C(21)	2.135(10)	Si-C(3)	1.868(13)

O-In-O'	78.9(3)	C(1)-Si-C(3)	110.4(6)
O-In-C(11)	107.8(3)	C(2)-Si-C(3)	110.1(6)
O-In-C(21)	108.9(3)	In-O-In'	101.1(3)
O'-In-C(11)	106.2(3)	In-O-Si	128.3(4)
O'-In-C(21)	108.5(3)	In'-O-Si	128.7(4)
C(11)-In-C(21)	133.3(4)	In-C(11)-C(12)	119.2(7)
O-Si-C(1)	109.2(5)	In-C(11)-C(16)	121.5(8)
O-Si-C(2)	106.2(5)	In-C(21)-C(22)	120.7(7)
O-Si-C(3)	109.2(5)	In-C(21)-C(26)	121.6(9)
C(1)-Si-C(2)	111.7(6)		

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