

This article was downloaded by:

On: 23 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

Synthesis and X-Ray Structure of $\text{Me}_2\text{InI}(\text{NH}_2(t\text{-Bu}))$: The First Structurally Characterized Amine Adduct of a Dialkyl Indium Iodide

David A. Atwood^a; Alan H. Cowley^a; Richard A. Jones^a; Jerry L. Atwood^b; Simon G. Bott^b

^a Department of Chemistry, The University of Texas, Austin, Texas, USA ^b Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama, USA

To cite this Article Atwood, David A. , Cowley, Alan H. , Jones, Richard A. , Atwood, Jerry L. and Bott, Simon G.(1992) 'Synthesis and X-Ray Structure of $\text{Me}_2\text{InI}(\text{NH}_2(t\text{-Bu}))$: The First Structurally Characterized Amine Adduct of a Dialkyl Indium Iodide', *Journal of Coordination Chemistry*, 26: 4, 293 – 297

To link to this Article: DOI: 10.1080/00958979209407931

URL: <http://dx.doi.org/10.1080/00958979209407931>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

NOTE

SYNTHESIS AND X-RAY STRUCTURE OF $\text{Me}_2\text{InI}(\text{NH}_2(t\text{-Bu}))$: THE FIRST STRUCTURALLY CHARACTERIZED AMINE ADDUCT OF A DIALKYL INDIUM IODIDE

DAVID A. ATWOOD, ALAN H. COWLEY,* RICHARD A. JONES*

Department of Chemistry, The University of Texas, Austin, Texas 78712, U.S.A.

JERRY L. ATWOOD* and SIMON G. BOTT

Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35487, U.S.A.

(Received 30 January 1992)

Keywords: Indium(III), iodide, adduct, X-ray structure, *t*-butylamine

INTRODUCTION

Our research involving the alkyl derivatives of gallium and indium with nitrogen-based ligands has focussed mainly on trialkyl metal amine adducts ($\text{R}_3\text{M}^{\text{P}}\cdot\text{NRH}_2$), and alkyl metal amides, $(\text{R}_2\text{MNRH})_n$.¹ Recent work has included the structural characterization of dialkyl metal halide complexes, as $[\text{Cy}_2\text{GaCl}]_2$,² which are generally used *in situ*, and are used as starting materials for the amido species.³ To expand this work we have now isolated primary amine adducts of the dialkyl metal halide species.⁴ The complex $\text{Me}_2\text{InI}(\text{NH}_2(t\text{-Bu}))$ (**1**) is one such example and represents the first structurally characterized bisalkyl indium halide amine adduct. Interestingly, **1** crystallizes with one molecule of the ammonium iodide salt, $[\text{NH}_3(t\text{-Bu})]$ in the crystal lattice.

EXPERIMENTAL

Standard Schlenk-line techniques were employed in conjunction with an inert atmosphere glove box. Diethylether and toluene were distilled from sodium metal under purified N_2 prior to use. InI_3 was used as received from Aldrich. ^1H NMR spectra were recorded on a General Electric QE-300 spectrometer. X-ray diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer.

* Authors for correspondence.

Synthesis of $\text{Me}_2\text{InI}(\text{NH}_2(t\text{-Bu}))(I)$

A solution of MeLi in Et_2O (10.39 cm^3 of a 0.77 M solution, 8.00 mmol) was added dropwise to a stirring solution of InI_3 (1.98 g , 4.00 mmol) in diethylether (50 cm^3) at -78°C . The reaction mixture was allowed to warm to room temperature and then stirred (6 h) before *tert*-butyl amine (0.84 cm^3 , 8.00 mmol) was added to the reaction mixture. The solution was then stirred (12 h) before volatile materials were removed *in vacuo*. The residue was extracted with toluene (100 cm^3) and filtered. The filtrate was concentrated (30 cm^3) and then cooled (-20°C) for 1 month to yield colourless, X-ray quality needles of $\text{Me}_2\text{InI}(\text{NH}_2(t\text{-Bu}))(I)$; Mp $62\text{--}64^\circ\text{C}(\text{dec.})$, yield 30% based on InI_3 . ^1H NMR(300.15 MHz , C_6D_6): δ 0.22 (s, $\text{CH}_3\text{-In}$), 0.59, 0.85 (m, m, $t\text{-Bu-NH}_3^+$), 1.2 (m, $t\text{-Bu-NH}_2$).

Structural solution and refinement

Crystals of **1** were sealed in Lindemann capillaries under an atmosphere of dry argon. Intensities were collected on an Enraf-Nonius CAD-4 diffractometer at 25°C using the $\theta/2\theta$ scan technique. reflections were measured in the range $2 < 2\theta < 50^\circ$. Of 3818 independent reflections collected, 2379 having $I > 3\sigma(I)$ were used for the structure analysis. The intensities were collected for Lorentz and polarization effects. No absorption correction was applied. Details of the data collection are given in Table I. Positional and equivalent isotropic thermal parameters are listed in Table II and selected bond lengths and angles are given in Table III.

All calculations were performed on a MICROVAX 3100 computer, using the SHELX software package.⁵ The structure was solved by Patterson and Fourier methods. The hydrogen atoms were placed in their geometrically calculated positions and included in the final structure factor calculations with fixed isotropic thermal

TABLE I
Data collection and processing parameters for (1).

Formula	$\text{C}_{10}\text{H}_{29}\text{N}_2\text{I}_2\text{In}$
MW	546.03
Space group	$P2_1/c$
<i>a</i>	14.903(2)
<i>b</i>	6.5340(7)
<i>c</i> (Å)	20.133(2)
β (°)	94.623(8)
<i>V</i> (Å ³)	1952(4)
<i>Z</i>	4
<i>D_c</i> (g cm ³)	1.865
<i>F</i> (000)	1032
μ (cm ⁻¹)	43.25
Radiation	MoK α
2θ range (°)	2–50
Unique reflections	3818
Reflections with $I > 3\sigma(I)$	2379
Refined parameters	136
<i>R</i>	0.031
<i>R_w</i>	0.040

TABLE II
Positional and equivalent isotropic thermal parameters for (1).

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (<i>eqv</i>), Å ²
In	0.30123(3)	0.93224(8)	0.97486(2)	0.054(1)
I(1)	0.40398(3)	0.7755(1)	1.08770(2)	0.073(24)
I(2)	0.8171(3)	0.22416(7)	0.84555(2)	0.056(6)
Me(1)	0.3329(6)	1.252(1)	0.9762(5)	0.080(28)
Me(2)	0.1794(5)	0.759(1)	0.9666(4)	0.072(15)
N(1)	0.4009(4)	0.7951(9)	0.9060(2)	0.057(16)
C(1)	0.3827(6)	0.788(1)	0.8311(3)	0.060(19)
C(2)	0.3591(5)	0.999(1)	0.8075(4)	0.071(10)
C(3)	0.3062(9)	0.647(2)	0.8134(4)	0.141(73)
C(4)	0.4684(7)	0.717(2)	0.8014(4)	0.104(43)
N(2)	0.0310(4)	0.2241(8)	0.6690(3)	0.050(5)
C(11)	0.1146(5)	0.224(1)	0.6318(3)	0.053(3)
C(12)	0.1705(6)	0.407(1)	0.6563(5)	0.087(13)
C(13)	0.1633(5)	0.025(1)	0.6507(5)	0.083(17)
C(14)	0.0837(6)	0.232(1)	0.5589(4)	0.082(24)

TABLE III
Selected bond lengths and angles for (1).

Atoms	Distance (Å)	Atoms	Distance
In -I(1)	2.8247(7)	In -N(1)	2.292(5)
In -Me(1)	2.145(7)	In -Me(2)	2.135(7)
N(1) -C(1)	1.511(8)	N(2) -C(11)	1.503(8)
C(1) -C(2)	1.49(1)	C(1) -C(3)	1.49(1)
C(1) -C(4)	1.52(1)	C(11) -C(12)	1.51(1)
C(11) -C(13)	1.52(1)	C(11) -C(14)	1.50(1)

Atoms	Angle (°)	Atoms	Angle
I(1) -In -N(1)	90.4(1)	I(1) -In -Me(1)	103.9(3)
N(1) -In -Me(1)	103.7(3)	I(1) -In -Me(2)	105.7(2)
Me(1) -In -Me(2)	134.8(3)	N(1) -I -Me(2)	109.4(3)
In -N(1) -C(1)	122.7(4)	N(1) -C(1) -C(2)	107.9(6)
N(1) -C(1) -C(3)	109.2(6)	C(2) -C(1) -C(3)	110.2(8)
N(1) -C(1) -C(4)	108.1(6)	C(2) -C(1) -C(4)	109.9(7)
C(3) -C(1) -C(4)	111.4(8)	N(2) -C(11) -C(12)	107.0(6)
N(2) -C(11) -C(13)	105.8(6)	C(12) -C(11) -C(13)	110.9(6)
N(2) -C(11) -C(14)	106.5(6)	C(12) -C(11) -C(14)	113.9(7)
C(13) -C(11) -C(14)	112.1(7)		

parameters. The final R value was 0.03 ($R_w=0.040$). Full supplementary structural data are available from the authors on request.

RESULTS AND DISCUSSION

The molecular structure of **1** is shown in Figure 1. The coordination geometry about the gallium atom is approximately tetrahedral. However, the most notable deviation from T_d geometry can be seen in the Me(1)–In–Me(2) bond angle of $134.8(3)^\circ$. Large C–M–C bond angles are not unusual in dialkyl metal halide species such as $Cy_2GaBr(NH_2Ph)^4$ ($124.9(4)$), and the bis solvated cationic complex $[Me_2Ga(NH_2(t-Bu))_2]Br^6$ ($121.2(5)$). Indeed, the unsolvated $[Me_2In]Br^7$ and $[Me_2Tl]Cl^8$ species exist as separate ions wherein the Me–M–Me bond angles are perfectly linear. This trend is also seen in other main group complexes such as $Me_2Cd(bipyridyl)_2$, which has a Me(1)–Cd–Me(2) angle of $148.4(8)^\circ$.⁹ One result from the widening of the Me(1)–In–Me(2) bond in **1** is a concurrent narrowing of the I–In–N(1) angle to $90.4(1)^\circ$. There is the possibility that internal hydrogen bonding between the N–H(2) group and indium may be the distorting factor in **1**. Intramolecular hydrogen bonding has been seen in $Cy_2GaBr(NH_2Ph)$ (N–H...Br 2.84 Å). However, the wide C–M–C bond angle was not attributed to this interaction. In **1** the greater length of the In–N bond (2.292(5) Å) and In–I (2.8247(7) Å) bond places the nitrogen hydrogen and iodide beyond bonding range (> 3.6 Å).

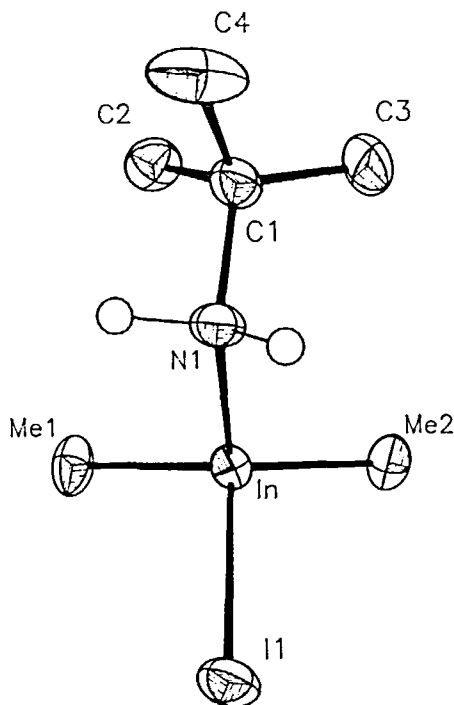


FIGURE 1 ORTEP view of $Me_2InI(NH_2(t-Bu))$ (**1**) showing the atom numbering scheme. All carbon hydrogen atoms are omitted for clarity.

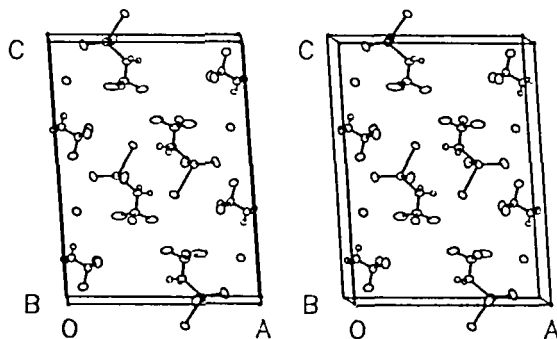


FIGURE 2 Unit cell view of compound (I) showing the location of co-crystallized $[\text{NH}_3(t\text{-Bu})]\text{I}$.

ACKNOWLEDGEMENTS

The authors are grateful to the National Science foundation, the Robert A. Welch foundation, the Army Research office, the Petroleum Research fund, administered by the American Chemical Society, and the National Science and technology Center Program of the National Science Foundation, NSF grant CHE-8920120 for generous support.

REFERENCES

1. D.A. Atwood, A.H. Cowley, R.A. Jones, S.G. Bott and J.L. Atwood, *Polyhedron*, **10**, 1897 (1991).
2. D.A. Atwood, A.H. Cowley, R.A. Jones, S.G. Bott and J.L. Atwood, *J. Coord. Chem.*, **25**, 233 (1992).
3. D.A. Atwood, A.H. Cowley, R.A. Jones, J.L. Atwood and S.G. Bott, *J. Coord. Chem.*, in press.
4. D.A. Atwood, A.H. Cowley and R.A. Jones, *J. Organomet. Chem.*, in press.
5. G.M. Sheldrick, "SHELX—A System of Computer Programs for X-ray Structure Determination" (Cambridge, U.K., 1976).
6. D.A. Atwood, R.A. Jones, A.H. Cowley, S.G. Bott and J.L. Atwood, *J. Organomet. Chem.*, **425**, C1 (1992).
7. H.D. Hausen, K. Mertz, J. Weidlein and W. Schwarz, *J. Organomet. Chem.*, **93**, 291 (1975).
8. H.D. Hausen, E. Veigel and H.J. Guder, *Z. Naturforsch.*, **B29**, 269 (1974).
9. M.J. Almond, M.P. Beer, M.G.B. Drew and D.A. Rice, *Organometallics*, **10**, 2072 (1991).