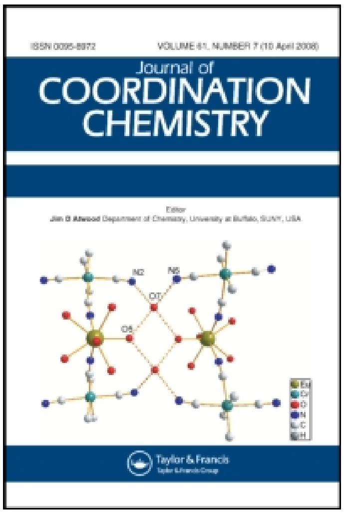

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Sun, Hong-Sui , Wang, Xi-Meng , Liu, Yong-Jiang , Huang, Xiao-Ying and You, Xiao-Zeng(1996) 'SYNTHESIS AND CHARACTERIZATION OF AN ADDUCT OF Me_3In WITH 5, 6-BENZOQUINOLINE X-RAY CRYSTAL STRUCTURE OF $Me_3In \cdot (BQ)_2$ (BQ = 5, 6 BENZOQUINOLINE)', Journal of Coordination Chemistry, 39: 3, 265 — 271

To link to this Article: DOI: 10.1080/00958979608024334
URL: http://dx.doi.org/10.1080/00958979608024334

J. Coord. Chem., 1996, Vol. 39, pp. 265–271
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SYNTHESIS AND CHARACTERIZATION OF AN ADDUCT OF ME$_3$In WITH 5, 6-BENZOQUINOLINE X-RAY CRYSTAL STRUCTURE OF ME$_3$In · (BQ)$_2$ (BQ=5,6-BENZOQUINOLINE)

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(Received 20 October 1995; In final form 12 April 1996)

Reaction of Me$_3$In with 5, 6 - benzoquinoline (1:1 molar ratio) resulted in the formation of the Lewis acid-base adduct Me$_3$In(BQ)$_2$. This adduct is much less air and moisture sensitive than the trialkyl indium. It was found to be a discrete 1:2 molecular adduct of trimethylindium. The stereochemistry about 5-coordinated indium is trigonal bipyramidal. ^{1}H NMR spectra of the adduct revealed a downfield shift of the metal alkyl protons. The complex crystallizes in the orthorhombic space group *Pbcn* with $a = 16.672(4)$, $b = 7.537(4)$, $c = 18.969(3)$Å and $Z = 4$. The structure was refined to $R = 0.040$ for 1732 observed reflections. The In—N bond length is 2.709(2)Å. C—In—N bond angles are in the range of 85.56(6)–92.6(1)°. This compound has a structure different to corresponding BQ adducts with Me$_3$Al and Me$_3$Ga.

Keywords: crystal structure; trimethylindium; 5,6-benzoquinoline; adduct

INTRODUCTION

The growth of epitaxial layers of semiconductors comprising compounds of Groups III–V and II–VI by metal-organic chemical vapour deposition (MOCVD) has become of major importance to the electronics industry. Extensive studies have shown that the electric properties of these layers depend critically upon the purity of the metal alkyl sources employed in their growth.[1–3] Me$_3$In(BQ)$_2$ is a

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comparatively air stable adduct of trimethylindium. The stability was attributed to the fact that the indium atom is 5-coordinate and is very effectively shielded by the two nitrogen atoms of two separate BQ ligands and the three methyl groups. The high stability imparted to trimethylindium by BQ was in marked contrast to the reactivity of the 1:1 adduct formed by trimethylgallium[4] and trimethylaluminum.[5] We now report the synthesis, characterization and X-ray crystal structure of the indium complex, which is a source of indium providing in particular a means of forming contacts on Si-based devices.[6–7]

RESULTS AND DISCUSSION

Preparation and Structure of $Me_3In(BQ)_2$

Reaction of BQ with trimethylindium gave the Lewis acid-base adduct compound $Me_3In(BQ)_2$. The product was recrystallized from Et_2O to give transparent, colourless crystals. This compound is much less air-sensitive than the parent metal trimethyl.

The structure of the adduct is shown in Figure 1. Crystal data and geometrical parameters are given in Tables I to IV. The structure is of a discrete 1:2 molecular adduct of trimethylindium bonded to BQ; the compound contains 5-coordinated indium about which the stereochemistry can be described as being a trigonal bipyramid. The dihedral angle between the two BQ planes is 142.2° and this may be the result of steric repulsion between three methyl groups and two BQ rings. The C—In—N bond angles (85.56–92.6°) are smaller than the C—Al—N (103.9–105.5°) [5] and C—Ga—N (101.0–103.4°)[4] cases this is due to the fact that indium complex is 5-coordinate and has more bulky steric repulsion than the 4-coordinate distorted tetrahedral cases of Me_3Al and Me_3Ga with BQ.

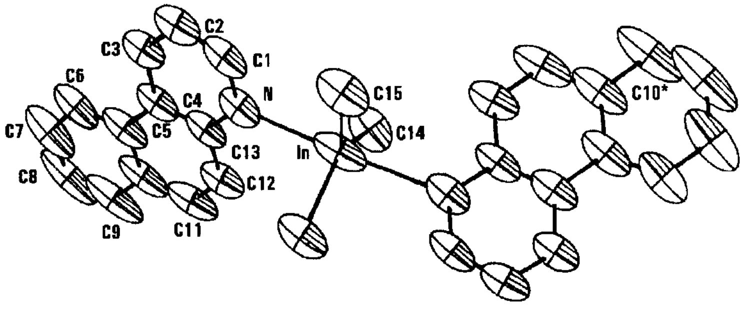

FIGURE 1 Hong-sui Sun *et al.*

TABLE I Summary of crystal data, intensity collection and structure refinement for the complex

Formula	$InN_2C_{29}H_{27}$
Mol. wt. /g mol^{-1}	518.37
Crystal system	Orthorhombic
space group	*Pbcn*
a/Å	16.672(4)
b/Å	7.537(4)
c/Å	18.969(3)
V/Å^3	2384(2)
Z	4
dcalc/*g* cm^{-3}	1.44
Radiation	MoK$_a$(λ = 0.71069 Å)
μ(MoK$_a$)/ mm^{-1}	99.3
Crystal size/mm^3	1.0 × 0.45 × 0.40
Crystal description	columnar
$2\theta_{max}$/°	49.9
θ range/°	9.48–16.39
Crystal colour	colourless
Diffractometer	Enraf-nonius CAD 4
F(000)	1056
cell measurement	25
T/K	296
Data Collection	ω-Scan
Scan Speed /° min^{-1}	5.49
Scan Width /°	0.45 + 0.35 tan θ
No. of observations with $I > 3.00\sigma(I)$	1732
No. Variables	147
Absorption correction	Empirical
Weighting Scheme	$\omega = 1/\sigma^2(F_o)$
R	0.040
R_w	0.057
S	1.84
h,k,l ranges	0–8, 0–19, –22–0
$\Delta\rho_{max}$, $\Delta\rho_{min}$/eÅ^{-3}	0.59, –0.76
T_{min}/T_{max}	0.6870/1.000
No. of reflections measured	2423

TABLE II Positional parameter for the complex

atom	*x/a*	*y/b*	*z/c*	*B/(eq)*
In	1/2	0.50399(3)	1/4	4.48(3)
N	0.6542(1)	0.4825(3)	0.2058(1)	4.0(1)
C(1)	0.7077(3)	0.5243(4)	0.2532(1)	4.1(2)
C(2)	0.7904(3)	0.5108(4)	0.2426(1)	4.4(2)
C(3)	0.8179(2)	0.4588(4)	0.1789(1)	4.0(1)
C(4)	0.7638(1)	0.4160(3)	0.1225(1)	3.5(1)
C(5)	0.7883(1)	0.3604(3)	0.0553(1)	3.8(1)
C(6)	0.8685(2)	0.3580(4)	0.0335(2)	4.9(1)
C(7)	0.8887(2)	0.3038(5)	–0.0339(2)	6.3(2)
C(8)	0.8307(2)	0.2507(4)	–0.0808(2)	6.3(2)
C(9)	0.7524(2)	0.2517(3)	–0.0614(2)	5.4(2)
C(10)	0.7291(2)	0.3085(4)	0.0062(1)	4.2(1)
C(11)	0.6465(2)	0.3154(4)	0.0261(4)	4.8(1)
C(12)	0.6234(1)	0.3746(4)	0.0901(1)	4.5(1)
C(13)	0.6812(1)	0.4267(3)	0.1471(1)	3.5(1)
C(14)	1/2	0.2172(6)	1/4	5.3(2)

TABLE II *(Continued)*

atom	*x/a*	*y/b*	*z/c*	*B/(eq)*
C(15)	0.5353(2)	0.6605(4)	0.3403(2)	5.7(2)

TABLE III Selected bondlenghts for the complex (Å)

In—C(15)*	2.159	(3)C(4)—C(5)	1.455(3)
In—C(14)	2.161(5)	C(5)—C(6)	1.399(4)
In—C(15)	2.163(3)	C(5)—C(10)	1.412(4)
In—N	2.709(2)	C(6)—C(7)	1.384(5)
In—N*	2.709(2)	C(7)—C(8)	1.374(5)
N—C(1)	1.305(4)	C(8)—C(9)	1.357(4)
N—C(13)	1.365(3)	C(9)—C(10)	1.407(4)
C(1)—C(2)	1.396(6)	C(10)—C(11)	1.429(5)
C(2)—C(3)	1.351(4)	C(11)—C(12)	1.351(4)
C(3)—C(4)	1.396(3)	C(12)—C(13)	1.429(3)
C(4)—C(13)	1.412(3)		

TABLE IV Intramolecular bond angles(°) for non-hydrogen atoms of the complex

C(15)—In—C(14)*	123.0(1)	C(3)—C(4)—C(5)	123.4(2)
C(15)—In—C(15)*	113.8(2)	C(13)—C(4)—C(5)	119.3(2)
C(15)—In—N*	92.6(1)	C(6)—C(5)—C(10)	118.0(2)
C(15)—In—N	91.1(1)	C(6)—C(5)—C(4)	122.9(2)
C(14)—In—C(15)	123.2(1)	C(10)—C(5)—C(4)	119.1(2)
C(14)—In—N*	86.56(6)	C(7)—C(6)—C(5)	120.6(3)
C(14)—In—N	86.59(6)	C(8)—C(7)—C(6)	120.9(3)
C(15)*—In—N*	91.1(1)	C(9)—C(8)—C(7)	120.0(3)
C(15)*—In—N	92.6(1)	C(8)—C(9)—C(10)	120.9(3)
N—In—N*	173.14(8)	C(9)—C(10)—C(5)	119.6(3)
C(1)—N—C(13)	117.6(3)	C(9)—C(10)—C(11)	121.(3)
C(1)—N—In	114.9(2)	C(5)—C(10)—C(11)	119.3(2)
C(13)—N—In	127.4(2)	C(12)—C(11)—C(10)	121.6(3)
N—C(1)—C(2)	123.9(3)	C(11)—C(12)—C(13)	121.0(2)
C(3)—C(2)—C(1)	119.0(3)	N—C(13)—C(4)	122.2(2)
C(2)—C(3)—C(4)	119.9(3)	N—C(13)—C12)	118.3(2)
C(3)—C(4)—C(13)	117.3(2)	C(4)—C(13)—C(12)	119.5(2)

It is noteworthy that the Al—C (1.965–1.987Å), Ga—C (1.972–1.984Å) and In—C (2.159–2.163Å bond lenghts are close in value, but the In—N bonds (2.709Å) are significantly longer than the Ga—N (2.15Å) and the Al—N (2.057Å) bonds, implying weaker bonding of BQ to Me$_3$In than to GaMe$_3$ and AlMe$_3$. This too may due to repulsion between methyl groups and BQ rings. It may also be due to electronics effects. The 1:1 adducts of Me$_3$AlBQ and Me$_3$GaBQ thought of as causing donation of electron density by the base donor atom into an sp^3 hybrid orbital of the metal, whereas the 5-coordinate indium adduct can be considered in terms of contribution from the 5p$_z$ and 4d$_z{}^2$ orbital of indium and donation from the nitrogen lone pair. It is understandable that donation of electron density from nitrogen atoms to sp^3 hybrid Al and Ga atoms might be stronger than with In. Metal atoms are nearly always 4-coordinated in trialkylaluminum and triakygalium adducts, but 5-coordinated in trialkylindum adducts. This can be explained in terms of covalent radii. The covalent radius of indium (1.497Å) is considerably larger than the covalent radii of Al (1.248Å) and Ga (1.245Å)[9]. Hence the indium atom is large enough to accomodate three methyl groups and two BQ ligands.

Previous work has revealed that M—N (Al—N 2.065(8)Å, Ga—N 2.154(9)Å, In—N 2.62(2)Å bondlengths in $Me_3M)_n$-dabco are very close to values for the respective M—N bonds in the $(Me_3M)_n$-BQ. This is the result of similar steric properties of dabco and BQ. However, Ga—N (2.203(3)Å) in Me_3Ga-acridine[8] is longer than Ga—N in Me_3GaBQ, since the acridine ligand is more bulky than BQ. Unfortunately there are no acridine complexes of trimethylaluminum and trimethylindium to compare with the Me_3AlBQ and $Me_3In(BQ)_2$.

NMR Spectra

The ^1H NMR spectra of these compounds are characterized by two groups of resonances, one group attributable to the protons of BQ and the other sharp single peak to the methyl protons. Methyl signals are shifted downfield, resulting from the deshielding and anisotropic effect of the aromatic BQ rings. This is opposite to results reported for dabco adducts of trimethylaluminum, timethylgallium and trimethylindium (see Table V). Usually, coordination of a Lewis base would increase the electron density on the metal, and the metal methyl protons would thus become more shielded and shift upfield.

TABLE V ^1H NMR data for the group III trimethyls and their adducts with BQ and dabco[a]

Compound	*δ(Me$_3$M) ppm*	*δ(N—CH$_2$) ppm*	*δAr—H ppm*
Me_3Al[b]	–0.35		
Me_3Ga[b]	–0.10		
Me_3In[b]	–0.18		
$N(C_2H_4)_3N$		2.47	
$Me_3Al \bullet N(C_2H_4)_3N \bullet AlMe_3$[c]	–0.62	2.03	
$Me_3Ga \bullet N(C_2H_4)_3N \bullet GaMe_3$[c]	–0.35	1.98	
$[Me_3In \bullet N(C_2H_4)_3N]_n$[c]	–0.15	2.03	
BQ			9.63–8.85
$Me_3Al \bullet BQ$[d]	0.09		6.56–8.84
$Me_3Ga \bullet BQ$[e]	0.37		6.69–8.82
$Me_3In \bullet (BQ)_2$	0.32		6.61–8.67

[a] Values relative to TMS; solvent C_6D_6; [b] Reference 10; [c] Reference 2; [d] Reference 5; [e] Reference 4.

EXPERIMENTAL

^1H NMR spectra (C_6D_6) were recorded on a Bruker AM500 spectrometer instrument with $SiMe_4$ as internal standard. BQ was obtained from Aldrich. All operations were performed under an atmosphere of purified nitrogen using Schlenk apparatus and a glove box. Solvents were distilled from sodium benzophenone under nitrogen.

A solution of TMIn (1.79g, 11.2 mmol) in Et_2O was added to a stirred solution of 5, 6-benzoquinoline (2g, 11.2 mmol) in Et_2O ($40cm^3$), immediately giving a white precipitate. The clear colourless solution was stirred at room temperature for 5h. Ether was removed *in vacuo* and the white solid residue was recrystallized from Et_2O/cyclohexane; colourless needle crystals suitable for X-ray crystallography were obtained, yield *ca* 2.8g, 78%, based 5,6-benzoquinoline. The compound could be sublimed at 68°C/10^{-1}Torr.

X-ray Crystallography[11]

X-ray measurements were made on a crystal sealed in Lindemann capillaries under nitrogen. Data collection was performed using an Enraf-Nonius CAD 4 diffractometer[12] operating in the $\omega/2\theta$ scan mode with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$Å). The structure was solved by direct methods and difference Fourier syntheses and refined by full-matrix least-squares methods with anisotropic displacement factors for all non-H atoms. All calculations were carried out on a MICRO VAX 3100 computer using *TEXSAN* crystallographic system.[13] Crystal data, details of the intensity measurements and refinement data are given in Table I. Positional parameters and geometrical parameters are given in Tables II to IV. Full lists of anisotropic temperature factors, bond distances and angles, and calculated and observed structure factors are available on request from the authors.

Acknowledgments

This work was supported by the National Natural Science Foundation, the Major Project of State Science and Technology Commission of China, and the Analytical Centre of Nanjing University.

References

[1] D.C. Bradley, H. Dawes and D.M. Frigo, *J. Organomet. Chem.*, **325**, 55 (1987).
[2] A.M. Bradford, D.C. Bradley, M.G. Hursthouse and M. Motevalli, *Organometallics*, **11**, 111 (1992).

[3] D.F. Foster, S.A. Rushworth and D.J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.* **7** (1988).

[4] Hong-sui Sun, Xi-Meng Wang, Xiao-Ying Huang and Xiao-Zeng You, *Polyhedron*, **14**, 2159 (1995).

[5] Xi-Meng Wang, Hong-sui Sun, Xiao-Ying Huang and Xiao-zeng You, *Acta Crystallogr.*, C**52**, 35 (1996).

[6] L.M. Green, R.A. Levy, R.G. Nuzzo and E. Coleman, *Thin Solid Films*, **114**, 367 (1984).

[7] M.J. Cooke, R.A. Weinecks, R.C. Stern and J.W.C. Maes, *Solid State Technol.*, **25**, 62 (1982).

[8] Hong-sui Sun, Xi-Meng Wang, Xiang-Zhen Sun, Xiao-Ying Huang and Xiao-zeng You, *Acta Crystallogr.*, C**52**, 1184 (1996).

[9] T. Moeller, *Inorganic Chemistry*, p 135, (Wiley, New York, 1952).

[10] D.C. Bradley, H. Chudzynska, M.M. Faktor, D.M. Frigo, M.B. Hursthouse, B. Hussain and L.M. Smith, *Polyhedron*, **7**, 1289 (1988).

[11] Xi-meng Wang, Hong-sui Sun, Xiang-zhen Sun, Xiao-zeng You and Xiao-ying Huang, *Acta Crystallogr.*, C**51**, 1754 (1995).

[12] Enraf-Nonius, CAD-4 Software, Version 5, (Enraf-Nonius, Delft, The Netherlands, 1989).

[13] Molecular Structure Corporation, TEXSAN, Single Crystal Structure Analysis Software, Version 5.0, (MSC, 3200 Research Forest Dtive, The Woodlands, TX. 77381, USA, 1989).