Synthesis and Structural Characterisation of a Soluble, Metastable Indium(I) Halide Complex, [InBr(tmeda)]

Shaun P. Green, Cameron Jones* and Andreas Stasch

SUPPLEMENTARY MATERIAL

Experimental Section

General considerations. All manipulations were carried out using standard Schlenk and glove box techniques under atmospheres of high purity argon or dinitrogen. Toluene was distilled over molten potassium metal and was freeze thaw degassed prior to use. Melting points were determined in sealed glass capillaries under argon and are uncorrected. Mass spectra were recorded at the EPSRC National Mass Spectrometric Service at Swansea University. Microanalyses were obtained from Campbell Microanalytical, Ottago. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates. The insolubility of the compounds in non-coordinating deuterated solvents precluded the acquisition of meaningful solution state NMR data. All reagents were purchased commercially and used as received.

Synthesis of [InBr(tmeda)] 3. Powdered InBr (0.30 g, 1.5 mmol) was added to a mixture of toluene (5 cm^3) and tmeda (0.5 cm^3) kept at -85°C. The suspension was allowed to warm to -30°C over 2 hours yielding a yellow-orange solution containing a suspended blue-violet solid. This was filtered at -30 ^oC and the filtrate placed at -80°C for seven days to yield yellow crystals of **3** (0.14 g, 28%). When warmed above -30 ^oC, the compound changes colour to blue-violet. M.p. decomposes at 20 ^oC over several hours; IR (Nujol) ν(cm^{-1}): 1579 (m), 1537 (s), 1261 (m), 1028 (m), 948 (m), 789 (m), 723 (s); MS/EI *m/z* (%): 115.0 ($tmeda^+$, 100), 193.9 ($InBr^+$, 74). Reproducible microanalyses could not be obtained for **3** because of its thermal instability at 25°C.

N.B. The yield of **3** from the reaction described above suggests that InBr has a higher concentration in 10% v/v tmeda/toluene than originally reported by Tuck *et al* (i.e. limiting solubility: 15.7 x 10^{-3}M).[1] Saying this, the reaction mixture apparently consists of a solution of **3** being in equilibrium with solid **3** (blue-violet), prior to its filtration. When the reaction was repeated using 0.1g InBr and 10 cm^3 of a 10% v/v tmeda/toluene mixture, the indium salt completely dissolved at -30 ^{o}C to yield a clear yellow-orange solution with no evidence of precipitated **3**, or indium metal. Therefore, we suggest that the limiting solubility of InBr in a 10% v/v tmeda/toluene mixture is at least 51 x 10^{-3} M at -30 ^{o}C.

Synthesis of [(quin)$_2$H][In$_5$Cl$_8$(quin)$_5$]. To a suspension of InCl (0.10 g, 0.67 mmol) in toluene (10 cm^3) at -85 ^{o}C was added quinuclidine (0.15g, 1.34 mmol) over 5 mins. The mixture was allowed to warm to room temperature over 1 h and then stirred for 10 min to yield a dark red solution with accompanying indium metal deposition. Filtration of the solution and storage of the filtrate at 0 °C over 3 d yielded yellow crystals of the title compound (0.074g, 54% based on Cl). M.p. 94°C (rapid decomp.), N.B. the compound slowly decomposes at 20 ^{o}C; IR (Nujol) ν(cm^{-1}): 2594 (s. br, N-H str.), 1318 (m), 1047 (s), 981 (s), 826 (m), 774 (m); MS/EI *m/z* (%): 296.0 [InCl$_2$(quin)$^+$, 6], 184.9 [InCl$_2^+$, 6], 150.0 [InCl$^+$, 84], 115.0 [In$^+$, 100], 111.2 [(quin)$^+$, 75]; anal. calc. for $C_{49}H_{92}Cl_8In_5N_7$: C 35.95, H 5.66, N 5.99; found: C 37.55, H 5.66, N 5.30. The results of the analysis are affected by the slow decomposition of the compound at ambient temperature.

X-Ray Crystallography

Crystals of all compounds suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97[2]) using all unique data. Hydrogen atoms have been included in calculated positions (riding model) for all structures. The methylene groups of the tmeda ligand of **3** were found to be disordered over two sites. This disorder was successfully modelled. The crystal of [(quin)$_2$H][In$_5$Cl$_8$(quin)$_5$] chosen for the diffraction experiment was a non-merohedral twin. All attempts to find a more suitable crystal for the experiment failed. In addition, all attempts to deconvolute the diffraction patterns of the twin components failed. This led to a number of large residual electron density peaks in the final difference map (highest 5.152 e$^-$/Å^3, near In5). This led to poor r-factors for the structure. Despite this, the molecular connectivity of the compound is unambiguous.

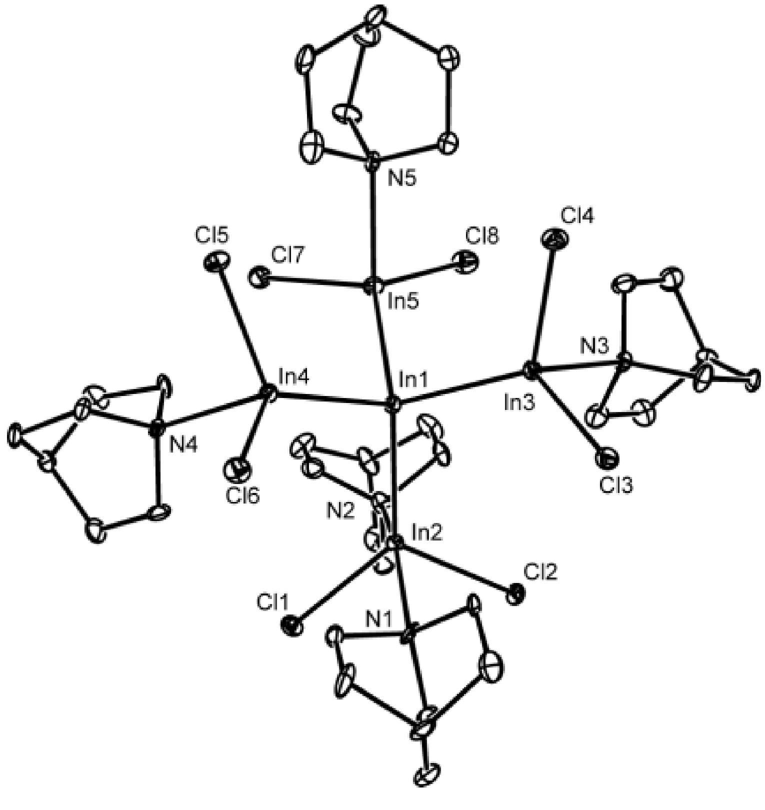

Fig. S1. Structure of the anionic component of [(quin)$_2$H][In$_5$Cl$_8$(quin)$_5$] (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): In(1)-In(4) 2.749(2), In(1)-In(3) 2.752(2), In(1)-In(5) 2.763(2), In(1)-In(2) 2.776(2), In(2)-Cl(1) 2.461(6), In(2)-N(1) 2.461(19), In(2)-Cl(2) 2.463(5), In(2)-N(2) 2.54(2), In(3)-N(3) 2.325(17), In(3)-Cl(4) 2.424(6), In(3)-Cl(3) 2.431(6), In(4)-N(4) 2.330(17), In(4)-Cl(6) 2.421(6), In(4)-Cl(5) 2.449(5), In(5)-N(5) 2.284(18), In(5)-Cl(7) 2.455(6), In(5)-Cl(8) 2.465(6), In(4)-In(1)-In(3) 110.93(7), In(4)-In(1)-In(5) 104.77(7), In(3)-In(1)-In(5) 103.21(7), In(4)-In(1)-In(2) 111.45(7), In(3)-In(1)-In(2) 112.61(7), In(5)-In(1)-In(2) 113.33(7).

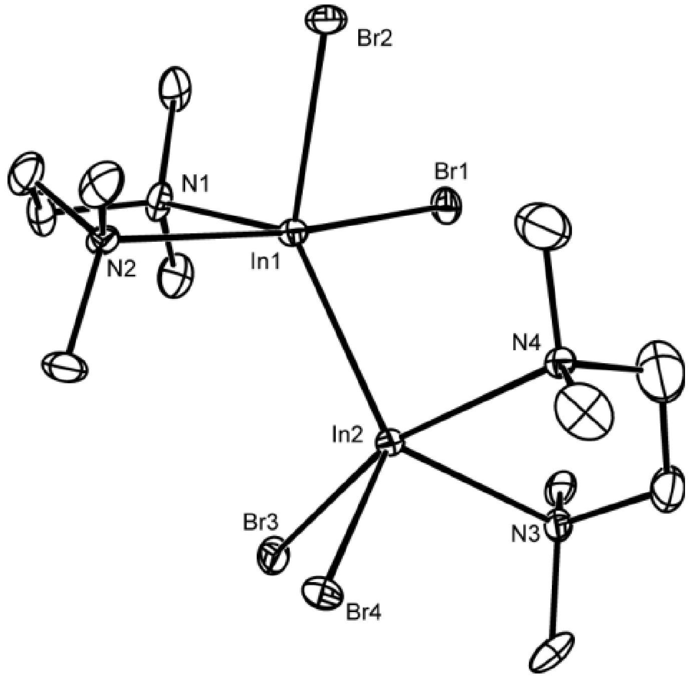

Fig. S2. Molecular structure of [$In_2Br_4(tmeda)_2$] (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): In(1)-N(1) 2.326(9), In(1)-N(2) 2.440(8), In(1)-Br(2) 2.5752(14), In(1)-Br(1) 2.7190(14), In(1)-In(2) 2.7608(11), In(2)-N(3) 2.341(8), In(2)-N(4) 2.478(8), In(2)-Br(4) 2.5639(14), In(2)-Br(3) 2.7070(14), N(1)-In(1)-N(2) 75.7(3), Br(2)-In(1)-Br(1) 91.97(5), N(3)-In(2)-N(4) 75.4(3), Br(4)-In(2)-Br(3) 93.32(5).

Theoretical Studies.

Method: *Ab initio* calculations were carried out on the full complex [InBr(tmeda)]. The geometry of the complex was optimised (starting from the crystal structure atomic coordinates), using the Gaussian 98 package[3], at the MP2 level of theory,[4] with a 6-31G* basis sets[5] for C, N and H, and SDD ECP/basis sets[6] for In and Br. Atomic charges and orbital populations were obtained from the NBO scheme[7] of the optimised structure. The representations of the Kohn-Sham orbitals were generated using the MOLEKEL package.[8]

Cartesian coordinates of the optimised structure of [InBr(tmeda)]

In	-0.61427	-0.99575	-0.08262
Br	-0.22109	0.66631	2.13080
N	1.82421	-0.46179	-0.91618
N	-0.64906	1.15556	-1.50536
C	2.72104	-0.09512	0.19544
H	2.70632	-0.88696	0.94702
H	2.37135	0.81679	0.67684
H	3.75138	0.04275	-0.16670
C	2.33197	-1.68571	-1.55697
H	3.32837	-1.52853	-1.99628
H	1.64014	-2.00613	-2.34044
H	2.39903	-2.48057	-0.81039
C	-1.55726	2.18159	-0.95857
H	-1.24275	2.43656	0.05349
H	-2.57118	1.77604	-0.91559
H	-1.56097	3.08207	-1.59081
C	-1.10655	0.78110	-2.85196
H	-2.15232	0.47086	-2.79367
H	-0.53167	-0.06210	-3.23955
H	-1.02454	1.62589	-3.55283
C	0.72592	1.68759	-1.52605
H	0.79879	2.53251	-2.23367
H	0.93548	2.07424	-0.52428
C	1.75746	0.63455	-1.90213
H	1.51791	0.20400	-2.87864
H	2.74368	1.11615	-2.00796

References

1. C. Peppe, D.G. Tuck and L. Victoriano, *J. Chem. Soc., Dalton Trans.*, 1982, 2165.

2. G.M. Sheldrick, *SHELX-97*, University of Göttingen, 1997.

3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J.

Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 98, Revision A.10*, Gaussian, Inc., Pittsburgh PA, Pittsburgh PA, 2001.

4. (a) M. Head-Gordon, J. A. Pople and M. J. Frisch, *Chem. Phys. Lett.*, 1988**, 153**, 503; (b) M. J. Frisch, M. Head-Gordon and J. A. Pople, *Chem. Phys. Lett.*, 1990*,* **166**, 275; (c) M. J. Frisch, M. Head-Gordon and J. A. Pople, *Chem. Phys. Lett.*, 1990, **166**, 281; (d) M. Head-Gordon and T. Head-Gordon, *Chem. Phys. Lett.*, 1994, **220**, 122; (e) S. Saebo and J. Almlof, *Chem. Phys. Lett.*, 1989, **154**, 83.
5. (a) R. Ditchfield, W.J. Hehre and J.A. Pople, *J. Chem. Phys.*, 1971, **54**, 724; (b) W.J. Hehre, R. Ditchfield and J.A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257; (c) M.S. Gordon, *Chem. Phys. Lett.*, 1980, **76**, 163; (d) P.C. Hariharan and J.A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.
6. (a) M. Dolg, U. Wedig, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1987, **86**, 866; (b) A. Bergner, M. Dolg, W. Kuehle, H. Stoll and H. Preuss, *Mol. Phys.*, 1993, **80**, 1431.
7. (a) A.E. Reed, L.A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899; (b) E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold, NBO Version 3.1.
8. P. Flükiger, H.P. Lüthi, S. Portmann and J. Weber, *MOLEKEL 4.0*, Swiss National Supercomputing Centre CSCS, Manno, Switzerland, 2000.