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Indium(I) trifluoromethanesulfonate and other soluble salts for univalent indium chemistry

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Herein we report the synthesis, structure and preliminary reactivity studies of a series of unusually soluble indium(I) salts that are improved alternatives to indium(I) halide reagents.

The chemistry of group 13 elements in the +1 oxidation state has been an area of extensive investigation over the last decade.[1,2] Such compounds are of interest both for the fundamental insights they provide and because of their utility as reagents or as precursors for the formation of clusters and materials.[3,4] While Tl(I) salts are commonplace and are useful metathesis reagents, many of the lighter homologues are either unknown or have properties that preclude their use in synthesis. For example, there are no stable monomeric boron(I) halides and the well-characterised aluminium(I) and gallium(I) halides are metastable species that are made in the gas-phase and stabilised with donor solvents.[5] The only commonly-used gallium(I) halide is the ill-defined material known as “GaI” obtained from the sonocation of Ga metal and one half equivalent of I_2.[6] While indium(I) halides do exist, the salts are virtually insoluble in most organic solvents. Some +2 oxidation state group 13 halides disproportionate to +1 and +3 species in aromatic solvents, however these revert to the +2 species in the presence of electron donors.[7] Herein we report the synthesis of $[In][SO_3CF_3]$ **1** which is a stable In(I) salt that is soluble in many organic solvents and may be used as an alternative to In(I) halides. In addition, we detail some of our initial results regarding the coordination chemistry of this unique source of univalent indium.

Protonolysis of cyclopentadienide substituents has proven useful for the synthesis of main group cations from groups 13 and 14 cyclopentadienyl compounds.[8,9] In this context, the reaction of Cp*In (Cp* = C_5Me_5)[10] with trifluoromethane sulfonic acid (HO_3SCF_3, HOTf) in toluene solution results in the elimination of Cp*H and the formation of the colourless salt [In][OTf] upon concentration, as shown in Scheme 1. The hygroscopic, air-sensitive salt is isolated in more than 83% yield after washing with pentane (this yield is relatively low only because of mechanical losses) and melts without decomposition at 162–165 °C under an N_2 atmosphere. The ^{19}F NMR spectrum in C_6D_6 consists of a single resonance at −79.5 ppm and the ^{13}C NMR spectrum exhibits a quartet at 119.9 ppm ($^1J_{C-F}$ 318 Hz). Analytical data are consistent with the proposed composition.†

Needle-shaped crystals of [In][OTf] that are suitable for X-ray diffraction are readily obtained through the concentration of toluene solutions of the salt.‡ The asymmetric unit of **1**, shown in Fig. 1, consists of two independent ion pairs each having one particularly short In–O contact of 2.579(6) Å or 2.589(6) Å. Overall, the coordination environment about each In ion is complex, including: four close (less than 3 Å) contacts to oxygen atoms on different triflate anions arranged in a roughly see-saw geometry, and a total of 12 contacts to O and F atoms within a 4 Å radius. The metrical parameters of the triflate anions are consistent with a partially localized SO_3 fragment, in that there are two shorter S–O distances (1.428(6) and 1.434(6) Å [1.436(6) and 1.437(7) Å]) and a longer distance to the O atom that is closest to an In atom (1.462(6) Å [1.450(6) Å]).

$$\mathrm{InCp^* + HX \longrightarrow InX + Cp^*H}$$

Scheme 1 (X = OTf or BF_4).

A packing diagram of **1**, depicted in Fig. 2, shows that the structure consists of columns of In cations that are aligned along the crystallographic *a* axis, and thus possess an In–In distance of 4.9834(4) Å. These In cation columns are separated from each other by columns of triflate anions. Perhaps the most surprising aspect of the crystal structure is the lack of solvent of crystallisation. It is well-known that In(II) halides of the form In_2X_4 typically disproportionate in aromatic solvents to give $[In][InX_4]$ salts, which crystallise with arenes that are η^6-coordinated to the univalent In ion. It is likely that the numerous contacts between the In ions and the O and F atoms obviate the need for arene solvation in **1**.

A more economical synthesis of **1** is provided by the reaction of a suspension of InCl in toluene and HOTf in toluene, followed by the removal of volatiles and washing with pentane. This procedure also provides **1** in greater than 80% yield with physical and spectroscopic features that are indistinguishable from those of the material produced using the protonolysis method described above.

The most important property of [In][OTf] is its incredible solubility in organic solvents. For example, **1** is readily soluble (more than 100 mg mL^{-1}) in toluene and THF and is somewhat less soluble in diethyl ether and dichloromethane. It appears that **1** is only virtually insoluble in alkanes such as pentane or hexanes. This remarkable solubility of **1** makes it a uniquely useful reagent for

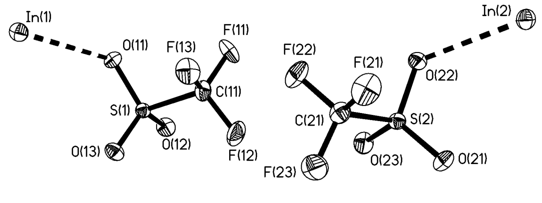

Fig. 1 Thermal ellipsoid (30%) plot of the asymmetric unit of [In][OTf] **1**. Selected metrical parameters, distances in angstroms and angles in degrees: In(1)–O(11), 2.579(6); In(2)–O(22), 2.589(6); S(1)–O(11), 1.462(6); S(1)–O(12), 1.434(6); S(1)–O(13), 1.428(6); O(11)–S(1)–O(12), 113.2(4); O(11)–S(1)–O(13), 113.4(4); O(12)–S(1)–O(13), 116.8(4).

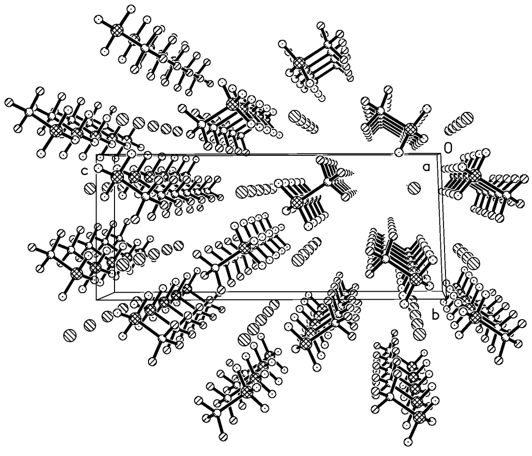

Fig. 2 Depiction of the crystal structure of **1** showing the columnar nature of the [In] and [OTf] ion packing.

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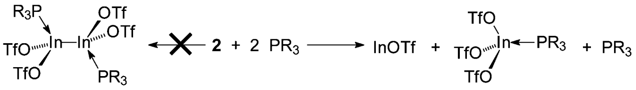
low-oxidation state In chemistry and In cluster chemistry in that it eliminates the need for the use of heterogeneous mixtures of reagents.

Products obtained from investigations of the acceptor chemistry of univalent group 13 compounds often result from the disproportionation of the group 13 metal.[11] As an initial study of the acceptor chemistry of the In(I) salt, **1** was mixed with triisopropylphosphite in toluene solution. Although the ^{31}P NMR spectra of the reaction mixtures indicate the presence of a coordination complex in solution (δ^{31}P: broad singlet at 6.6), we have only been able to isolate crystals of **1** and free donor upon concentration of the solution. The absence of observable disproportionation products in this reaction suggests that the triflate salt may be more resistant to redox reactions than are the analogous halide salts, however experiments with other donors are currently underway to prove this hypothesis.

[In][OTf] was mixed with an equimolar amount of $InOTf_3$ to ascertain whether such a reaction would yield the comproportionation In(II) product $(TfO)_2In–In(OTf)_2$ **2a** or the mixed valence salt $[In][In(OTf)_4]$ **2b**. The white powder obtained upon concentration of the reaction mixture decomposes at 325 °C and has an infrared spectrum that is not consistent with the superposition of the spectra of **1** and $In(OTf)_3$. Furthermore, the ^{19}F NMR spectrum in C_6D_6 consists of a single resonance at −78.2 ppm and the ^{13}C NMR spectrum displays a quartet at 120.6 ppm ($^1J_{C–F}$ 317 Hz). Analytical data are consistent with the proposed composition.† While we have not yet been able to obtain crystalline material suitable for crystallographic examination to date, the reaction of **2** with two equivalents of triisopropylphosphite results in the regeneration of crystalline **1** in high yield and the concomitant formation of $(^iPrO)_3P–InOTf_3$ (δ^{31}P: 8.4) upon concentration. This result, outlined in Scheme 2, suggests that **2** exists in the mixed valence form rather than as an In(II) species, which would be expected to provide a simple donor–acceptor adduct.

Another important aspect of the work presented herein is the generality of the Cp* protonolysis reaction; many strong, non-oxidizing protic acids are suited to this synthetic method. For example, the reaction of an ethereal solution of $[H][BF_4]$ with Cp*In in toluene produces the new salt $[In][BF_4]$ **3** in high yield (quantitative formation of Cp*H by ^{1}H NMR in C_6D_6, 83% isolated product). The tetrafluoroborate salt melts without decomposition at 135–137 °C and exhibits analytical and spectroscopic data consistent with the proposed formulation.† In particular the ^{11}B and ^{19}F NMR spectra and the IR spectrum suggest the presence of an intact tetrafluoroborate anion in both solution and the solid state. While we have not yet been able to obtain crystals suitable for analysis by single-crystal X-ray diffraction, preliminary powder X-ray diffraction experiments show that **3** produces an XRD spectrum similar to that of $[Tl][BF_4]$.[12] Although **3** dissolves in polar solvents, its solubility is generally less than that of **1** in the solvents we have investigated.

In addition to allowing variation in the nature of the anion, the protonolysis approach may also be applicable to the synthesis of the lighter group 13 analogues. In this context, we are presently investigating analogous Cp* protonolysis reactions using Cp*Al[13] and Cp*Ga[14] to determine if this relatively gentle synthetic method can be applied to the synthesis of lighter, and typically less stable, univalent group 13 reagents.



Scheme 2

In conclusion, we have prepared a new series of In(I) salts, some of which are remarkably soluble in organic solvents and may be used as alternatives to In(I) halides. The donor, acceptor and metathesis chemistry of these and related salts is currently under investigation.

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Notes and references

† Selected characterisation data for **1**, **2** and **3**.

1: Colourless crystals, yield 83%, mp 162–165 °C. ^{19}F NMR δ: −79.5(s). ^{13}C NMR δ: 119.9(q, $^1J_{C–F}$, 318 Hz). IR (Nujol mull on KBr plates, cm^{-1}): 1299s, 1198s, 1025s, 800m, 750w, 638s, 583w, 526m, 510m. Elemental Analysis (CF_3InO_3S, 263.88), Calcd: C 4.55; O 18.19; F 21.60; S 12.15. Found: C 4.55; O 17.75; F 22.24; S 12.14%.

2: Colourless microcrystalline powder, yield 53%, dp 325 °C. ^{19}F NMR δ: −78.2(s). ^{13}C NMR δ: 120.6(q, $^1J_{C–F}$, 317 Hz). IR (Nujol mull on KBr plates, cm^{-1}): 1318s, 1204s, 1164m, 1138m, 1029s, 992w, 663m, 519w. Elemental Analysis ($C_4F_{12}In_2O_{12}S_4$, 825.92), Calcd: C 5.82; O 22.25; F 27.60; S 15.53. Found: C 5.73; O 23.50; F 28.20; S 16.10%.

3: Cream-coloured microcrystalline solid, yield 83%, mp 135–137 °C. ^{11}B NMR δ: −1.36 (sharp s). ^{19}F NMR δ: −153.2(s). IR (Nujol mull on KBr plates, cm^{-1}): 1278w, 1019s(br), 795w, 761w, 514w. Elemental Analysis (BF_4In, 201.62), Calcd: F 37.69. Found: F 37.36%.

‡ Suitable single crystals of **1** were covered with mineral oil and mounted in the 174 K N_2 stream of a Bruker Apex CCD diffractometer equipped with a Mo Kα radiation (λ = 0.71073 Å) source. The structure was solved by direct methods and refined using full matrix, least squares on F^2. Crystal data for **1**: CF_3InO_3S, triclinic, $P1$, a = 4.8934(4), b = 7.2298(6), c = 16.950(2) Å, α = 91.011(2)° β = 93.835(2)°, γ = 107.711(2)°,V = 585.56(9) Å^3, Z = 4, D_{calcd} = 2.993 g cm^{-3}, μ (Mo Kα) = 4.389 mm^{-1}. A total of 5,324 reflections was collected in the range 2.40 < 2θ < 55.02. Of these, 2,619 were considered observed ($I > 2.0\sigma(I)$); $wR2$ = 0.1213, R = 0.0479. CCDC 222071. See http://www.rsc.org/suppdata/cc/b3/b312983g/ for crystallographic data in .cif or other electronic format.

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