**Mono- and Di-Phosphine Oxide Complexes of Aluminium, Gallium and Indium with Weakly Coordinating Triflate Anions – Synthesis, Structures and Properties**

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**Abstract**

Reaction of the Group 13 triflates, M(OTf)3 (M = Al, Ga, In; OTf = CF3SO3-), with 3 mol. eq. of R3PO (R = Ph or Me) gives the six-coordinate complexes, [M(OTf)3(R3PO)3], with coordinated triflate, as white powdered solids. Similarly, using 3 mol. eq. of PyNO (pyridine-N-oxide) readily forms [In(OTf)3(PyNO)3], whose crystal structure confirms a mer octahedral arrangement. In contrast, reaction of the harder Lewis acids Al(III) and Ga(III) with PyNO produce mixtures, mostly likely of the 3:1 and 4:1 species, [M(OTf)3(PyNO)3] and [M(OTf)2(PyNO)4][OTf] (M = Al, Ga). Both of the tetrakis species have been confirmed via single crystal X-ray studies and shown to exist as *trans* isomers. Higher ratios (4:1, 5:1 and 6:1) of Me3PO coordinated to In(OTf)3 can also be achieved by varying the reaction stoichiometry appropriately, with the coordinated OTf groups readily displaced by the Me3­PO.

Crystal structures of two polymorphs of the salt, [In(OTf)2(Me3PO)4][In{(OH2)2(OTf)4}(Me3PO)4], in which the [In{(OH2)2(OTf)4}(Me3PO)4]− anion is (unusually) comprised of a ‘InIII(OH2)2(Me3PO)4’ unit with four OTf anions H-bonded to the aquo ligands, giving the overall monoanionic charge. A similar arrangement is present in [In(OTf)2(Ph3PO)4][In{(OH2)4(OTf)4}(Ph3PO)2], the structure of which shows that all of the H atoms associated with the four aquo ligands in the [In{(OH2)4(OTf)4}(Ph3PO)2]− form significant H-bonds to the OTf groups; specifically, the four OTf− anions each show two O⋅⋅⋅H interactions, forming bridges that link the equatorial aquo ligands into a 24-membered ‘pseudo-macrocyclic’ ring. The crystal structure of the mononuclear 5:1 complex, [Ga(Me3PO)5(MeCN)][OTf]3, is also described.

Using the diphosphine dioxide, dppmO2 (Ph2P(O)CH2­P(O)Ph2), with M(OTf)3 in a 3:1 ratio readily affords the tris-chelate species, [M(dppmO2)3][OTf]3 for all three metals, while a 2:1 ratio also gives [Ga(OTf)2(dppmO2)2][OTf]. Crystal structures of both [Al(dppmO2)3][OTf]3⋅MeCN and [Ga(dppmO2)3][OTf]3⋅2CHCl3 are reported.

Multinuclear (1H, 13C{1H}, 19F{1H}, 31P{1H}, 27Al, 71Ga and 115In, where appropriate) NMR data show that in CD3CN the complexes are labile and the different R3PO coordination environments are not distinguished (although exchange between coordinate and ‘free’ Me3PO is slow on the 31P NMR timescale), while the MeCN solvent also replaces the OTf in the metal coordination sphere.

**Keywords:**aluminium; gallium; indium; phosphine oxide; diphosphine dioxide; crystal structures

**1. Introduction**

Although much less extensive than that of the d-block elements, the coordination chemistry of the p-block metals and metalloids has developed steadily over the last 50 years, with a major increase in interest post 1990, in part driven by applications in catalysis, as precursors to semi-conducting electronic materials and as carriers for medicinal radio-isotopes [1,2,3,4,5,6]. The great improvements in instrumentation, especially in X-ray crystallography and multinuclear NMR spectroscopy have also helped to accelerate the development of this field. Complexes of trivalent aluminium, gallium and indium have figured strongly in these studies, with the heavier halides (Cl, Br, I) being the most common anions present, except in the semi-conductor precursor work where metal alkyls are the key reagents. A limited range of complexes of the metal fluorides has been obtained recently [7], and examples with non- or very weakly coordinating anions like ClO4–, BF4–, [MX4] – (M = Al, Ga, In) [1,4] are also known.

Here we report the synthesis and characterisation of three series of phosphine oxide complexes containing Me3PO, Ph3PO and Ph2P(O)CH2P(O)Ph2 (dppmO2), along with PyNO (PyNO = pyridine-N-oxide) with the metal triflates, M(OTf)3 (OTf− = CF3SO3–), with the aim of identifying how the weakly coordinating triflate anion competes with the neutral O-donor ligands to influence the stoichiometries, structures and properties or the resulting complexes.

Phosphine oxide complexes with the heavier three halides are known for all three metals [8,9,10,11,12,13], but unexpectedly, attempts to make complexes of the corresponding trifluorides either directly from MF3⋅3H2O or by Cl/F exchange from the corresponding chloride complexes were unsuccessful, with no coordination observed [14]. However, complexes of aluminium and gallium trifluorides with a single pyridine N-oxide ligand, [M’(OH2)2(pyNO)F3] (M’= Al, Ga), have been reported [14].

**2. Experimental**

Infrared spectra were recorded as Nujol mulls between CsI plates using a PerkinElmer Spectrum 100 spectrometer over the range 4000−200 cm-1. 1H, 13C{1H},19F{1H},31P{1H}, 27Al, 71Ga, and 115In NMR spectra were recorded from CD3CN solutions using a Bruker AV400 spectrometer and referenced to SiMe4 via the residual solvent resonance (1H and 13C), external CFCl3 (19F), 85% H3PO4 (31P), [Al(H2O)6]3+ (27Al), [Ga(H2O)6]3+ (71Ga) and [In(H2O)6]3+ (115In) in H2O/D2O at pH 1, respectively. Microanalyses were undertaken at London Metropolitan University or Medac Ltd. n-Hexane was dried by distillation from sodium and CH2Cl2 and MeCN from CaH2, and all preparations were carried out under anhydrous conditions via a dry dinitrogen atmosphere and standard Schlenk and glovebox techniques. Aluminium, gallium and indium triflates, Ph3PO, Me3PO and PyNO were obtained from Sigma-Aldrich. DppmO2 was prepared from dppm by oxidation in dry air using SnI4 as the catalyst [15]. Although formulated as “anhydrous”, the IR spectra of the M(OTf)3 typically showed varying amounts of water, which was not removed completely by prolonged drying *in vacuo.* These triflates were used satisfactorily in the syntheses, but the varying water content means the metal:ligand ratios deviate slightly from those calculated, with a small excess of ligand in each case.

**X-ray experimental**. Crystals of the complexes were grown from CH2Cl2 solutions by slow evaporation, by vapour diffusion or layering CH2Cl2 or CHCl3 solutions with hexane, while solutions in MeCN were allowed to evaporate slowly in the glovebox or were layered with diethyl ether. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum (λ = 0.71073 Å) rotating anode generator with VHF Varimax optics (70 μm focus) with the crystal held at 100 K, or an Agilent Xcalibur Gemini S diffractometer with a CCD plate detector using Mo Kα (λ = 0.71073 Å) radiation with the crystal held at 100 K. Structure solution and refinement were performed using SHELX(S/L)97, SHELX2013, or SHELX-2014/7 [16,17,18]. Details of the crystallographic parameters are given in Table 1. Note that the [Al(dppmO2)3][OTf]3⋅2MeCN structure exhibits significant disorder within the OTf anions and MeCN solvent molecules, which could not be fully modelled, hence while the cation is well-defined, detailed comparisons of the geometric parameters require caution.

***2.1 [Al(OTf)3(Ph3PO)3]***

Al(OTf)3 (95 mg, 0.2 mmol) was dissolved in CH2Cl2 (10 mL) before addition of triphenylphosphine oxide (167 mg, 0.6 mmol) and the mixture stirred for 2 h. The solution was concentrated to ca. 50% volume in vacuo before addition of n-hexane (10 mL), which caused precipitation of a white solid. This was isolated by filtration before drying *in vacuo.* Yield: 112 mg, 67%. Required for C57H45AlF9O12P3S3⋅0.5CH2Cl2 (1351.57): C, 51.10; H, 3.43. Found: C, 50.82; H, 3.58%. 1H NMR (295 K, CD3CN): δ = 7.67 (t, [3H], 7.40 (br m, [12H]), 5.45 (s, CH2Cl2). 19F{1H} NMR (295 K, CD3CN): δ = −78.6 (s, OTf−). 31P{1H} NMR (295 K, CD3CN): δ = 42.5 (s, Ph3PO), 27Al NMR (295 K, CD3CN): not observed. IR spectrum (ν/cm-1): 1156 (P=O).

***2.2 [Ga(OTf)3(Ph3PO)3]***

Ga(OTf)3 (103 mg, 0.2 mmol) was dissolved in CH2Cl2 (10 mL) before addition of triphenylphosphine oxide (167 mg, 0.6 mmol) and the mixture stirred for 2 h. Removal of the solvent resulted in a white solid, which was washed with n-hexane (2 x 5 mL) and dried *in vacuo*. Yield: 215 mg, 80%. Required for C57H45F9GaO12P3S3⋅CH2Cl2 (1436.72): C, 48.49; H 3.30. Found: C, 48.02; H, 4.06%. 1H NMR (295 K, CD3CN): δ = 7.65 (m, [3H]), 7.45 (m, [12H]), 5.45 (s, CH2Cl2). 19F{1H} NMR (295 K, CD3CN): δ = −78.6 (s, OTf−). 31P{1H} NMR (295 K, CD3CN): δ = 44.6 (s, Ph3PO)). 71Ga NMR (295 K, CD3CN): not observed. IR spectrum (ν/cm-1): 1143 (P=O).

***2.3 [In(OTf)3(Ph3PO)3]***

In(OTf)3 (112 mg, 0.2 mmol) was dissolved in CH2Cl2 (10 mL) before the addition of triphenylphosphine oxide (167 mg, 0.6 mmol) and the mixture stirred for 2 h. Removal of solvent resulted in a white solid, which was washed with n-hexane (2 x 5 mL) and dried *in vacuo.* Yield: 245 mg, 88%. Required for C57H45F9InO12P3S3⋅0.5CH2Cl2 (1439.34): C, 47.98; H 3.22. Found: C, 48.63; H, 3.59%. 1H NMR (295 K, CD3CN): δ = 7.65 (m, [3H]), 7.50-7.40 (m, [12H]). 5.45 (s, CH2Cl2). 19F{1H} NMR (295 K, CD3CN): δ = −78.6 (s, OTf−).31P{1H} NMR (295 K, CD3CN): δ = 45.9 (s, Ph3PO). 115In NMR (295 K, CD3CN): not observed. IR spectrum (ν/cm-1): 1145 (P=O).

***2.4 [Al(OTf)3(Me3PO)3]***

Al(OTf)3 (95 mg, 0.2 mmol) was dissolved in CH2Cl2 (10 mL) before the addition of trimethylphosphine oxide (55 mg, 0.6 mmol) and stirred for 2 h. Removal of the volatiles *in vacuo,* followed by washing with hexane (2 x 5 mL) and drying *in vacuo* gave a white powdered solid*.* Yield: 134 mg, 84%**.** Required for C12H27AlF9O12P3S3 (750.4): C, 19.21; H 3.63. Found: C, 18.88; H, 3.50%.1H NMR (295 K, CD3CN): δ = 1.72 (d, 2JPH = 12 Hz, Me3PO). 13C{1H} NMR (295 K, CD3CN): δ = 15.85 (d, 1JPC = 73.5 Hz, Me3PO). 19F{1H} NMR (295 K, CD3CN): δ = −78.9 (s, OTf−). 31P{1H} NMR (295 K, CD3CN): δ = 60.9 (s, Me3PO). 27Al NMR (295 K, CD3CN): δ = –11.3 (br s). IR spectrum (ν/cm-1): 1103 vs (P=O).

***2.5 [Ga(OTf)3(Me3PO)3]***

Ga(OTf)3 (103 mg, 0.2 mmol) was dissolved in CH2Cl2 (10 mL) before the addition of trimethylphosphine oxide (55 mg, 0.6 mmol), and stirred for 2 h. Removal of the volatiles *in vacuo* resulted in a white solid, which was washed with n-hexane (2 x 5 mL) and dried *in vacuo.* Yield: 134 mg, 84%. Required for C12H27F9GaO12P3S3 (793.16): C, 18.17; H 3.43. Found: C, 18.11; H, 3.99%.1H NMR (295 K, CD3CN): δ = 1.75 (d, 2JPH = 12 Hz, Me3PO). 13C{1H} NMR (295 K, CD3CN): δ = 15.90 (d, 1JPC = 71 Hz, Me3PO). 19F{1H} NMR (295 K, CD3CN): δ = -78.8 (s, OTf−). 31P{1H} NMR (295 K, CD3CN): δ = 65.5 (s, Me3PO). 71Ga NMR (295 K, CD3CN): not observed. IR spectrum (ν/cm-1): 1108 s (P=O).

***2.6 [In(OTf)3(Me3PO)3]***

In(OTf)3 (112 mg, 0.2 mmol) was dissolved in CH2Cl2 (10 mL) before the addition of trimethylphosphine oxide (55 mg, 0.6 mmol), and stirred for 2 h. The solution was concentrated to ca. 5 mL *in vacuo*, before the addition of n-hexane (10 mL), which caused precipitation of a white solid. This was isolated by filtration and dried *in vacuo.* Yield: 113 mg, 71%. Required for C12H27F9InO12P3S3⋅CH2Cl2 (923.19): C, 16.91; H 3.17. Found: C, 16.90; H, 4.40%.1H NMR (295 K, CD3CN): δ = 1.71 (d, 2JPH = 16 Hz, Me3PO). 13C{1H} NMR (295 K, CD3CN): δ = 16.73 (d, 1JPC = 72 Hz, Me3PO). 19F{1H} NMR (295 K, CD3CN): δ = −78.6 (s, OTf−). 31P{1H} NMR (295 K, CD3CN): δ = 66.6 (s, Me3PO). 115In NMR (295 K, CD3CN): not observed. IR spectrum (ν/cm-1): 1104 s (P=O).

***2.7 [In(OTf)2(Me3PO)4][OTf].H2O***

In(OTf)3 (112 mg, 0.2 mmol) was dissolved in CH2Cl2 (10 mL) before the addition of trimethylphosphine oxide (74 mg, 0.8 mmol) and stirring for 2 h. The solution was concentrated to ca. 5 mL *in vacuo*, before the addition of n-hexane (10 mL) which caused precipitation of a white solid. This was isolated by filtration before drying *in vacuo.* Yield: 102 mg, 53%.Required for C15H40F9InO15P4S3⋅H2O (966.36): C, 18.64; H 4.17. Found: C, 18.63; H, 4.26%. 1H NMR (295 K, CD3CN): δ = 1.71 (d, 2JPH = 13.7 Hz, Me3PO). **1**3C{1H} NMR (295 K, CD3CN): δ = 16.75 (d, 1JPC = 70.4 Hz, Me3PO).19F{1H} NMR (295 K, CD3CN): δ = −78.6 (s, OTf−).31P{1H} NMR (295 K, CD3CN): δ = 65.3 (s, Me3PO).IR spectrum (ν/cm-1): 1106 s (P=O).

***2.8 [In(OTf)(Me3PO)5][OTf]2***

In(OTf)3 (112 mg, 0.2 mmol) was dissolved in CH2Cl2 (10 mL) before the addition of trimethylphosphine oxide (92 mg, 1.0 mmol) and stirring for 2 h. After filtering to remove particulates, the filtrate was concentrated to ca. 5 mL *in vacuo* before addition of n-hexane (10 mL), which caused precipitation of a white solid. This was isolated by filtration before drying *in vacuo.* Yield: 100 mg, 49%Required for C18H45F9InO14P5S3 (1022.41): C, 21.15; H 4.44. Found: C, 21.84; H, 5.07%.1H NMR (295 K, CD3CN): δ = 1.71 (d, 2JPH = 14 Hz, Me3PO). 13C{1H} NMR (295 K, CD3CN): δ = 16.75 (d, 1JPC = 70 Hz, Me3PO). 19F{1H} NMR (295 K, CD3CN): δ = −78.6 (s, OTf−). 31P{1H} NMR (295 K, CD3CN): δ = 63.9 (s, Me3PO). IR spectrum (ν/cm-1) 1111 s (P=O).

***2.9 [In(Me3PO)6][OTf]3***

In(OTf)3 (112 mg, 0.2 mmol) was dissolved in CH2Cl2 (10 mL) before addition of trimethylphosphine oxide (111 mg, 1.2 mmol) and stirred for 2 h. Concentration of solvent in vacuo to ca. 50%, followed by addition of hexane (10 mL) resulted in a white solid which was collected by filtration and dried *in vacuo.* Yield:148 mg, 66 %. Required for C21H64F9InO15P6S3 (1124.56): C, 22.43; H 5.74. Found: C, 22.69; H, 4.90%.1H NMR (295 K, CD3CN): δ = 1.70 (d, 2JPH = 13.6 Hz, Me3PO). 13C{1H} NMR (295 K, CD3CN): δ = 17.58 (d, 1JPC = 70.4 Hz, Me3PO). 19F{1H} NMR (295 K, CD3CN): δ = −79.9 (s, OTf−). 31P{1H} NMR (295 K, CD3CN): δ = 60.9 (s, Me3PO). 115In NMR (295 K, CD3CN): δ = –93.7 (s). IR spectrum (ν/cm-1): 1112 s (P=O).

***2.10 [Al(dppmO2)3][OTf]3***

Al(OTf)3 (47 mg, 0.1 mmol) was dissolved in CH2Cl2 (5 mL) before the addition of bis-(diphenylphosphino)methane dioxide (146 mg, 0.35 mmol) and the solution was stirred for 2 h. The solution was concentrated to ca. 50% volume *in vacuo* and the product was precipitated by the addition of n-hexane (5 mL). The white powder was collected by filtration and dried *in vacuo*. Yield: 86 mg, 50%. Required for C78H66AlF9O15P6S3⋅CH2Cl2 (1723.35): C, 52.47; H, 3.79. Found: 52.99; H, 3.84%. 1H NMR (295 K, CD3CN): δ = 7.78-7.60 (m, [8H]), 7.40-7.23 (m, [12H]), 5.45 (s, CH2Cl2), 4.08 (t, [2H], 2JPH = 12 Hz, CH2). 19F{1H} NMR (295 K, CD3CN): δ = −78.6 (s, OTf−). 31P{1H} NMR (295 K, CD3CN): δ = 44.2 (s, dppmO2). 27Al NMR (295 K, MeCN): δ = – 9.3. IR spectrum (ν/cm-1): 1141, ~1120 sh (P=O).

***2.11 [Ga(dppmO2)3][OTf]3***

Was made similarly to the aluminium analogue, using Ga(OTf)3 (51 mg, 0.1 mmol) and dppmO2 (125 mg, 0.3 mmol) in CH2Cl2 (5 mL), and precipitation with n-hexane (5 mL). Yield: 107 mg, 61%. Required for C78H66F9GaO15P6S3⋅CH2Cl2 (1851.03): C, 51.26; H, 3.70%. Found: C, 50.16; H, 3.71%. 1H NMR (295 K, CD3CN): δ = 7.76-7.65 (m, [8H]), 7.40-7.30 (m, [12H]), 5.45 (s, CH2Cl2), 4.27 (t, [2H], 2JPH = 12 Hz, CH2). 19F{1H} NMR (295 K, CD3CN): δ = –78.7 (s, OTf−). 31P{1H} NMR (295 K, CD3CN): δ = 46.3 (s, dppmO2). 71Ga NMR (295 K, CD3CN): δ = −43.4 (br s). IR spectrum (ν/cm–1): 1160, 1132 (P=O).

***2.12 [In(dppmO2)3][OTf]3***

Was made similarly to the aluminium analogue, using In(OTf)3 (56 mg, 0.1 mmol) and dppmO2 (146 mg, 0.35 mmol) in CH2Cl2 (5 mL), and precipitation with n-hexane (5 mL). Yield: 105 mg, 58%. Required for C78H66F9InO15P6S3⋅CH2Cl2 (1896.12): C, 50.04; H, 3.61. Found: 50.28, 3.86%. 1H NMR (295 K, CD3CN): δ = 7.53-7.62 (br m, [12H]), 7.27 (br s, [8H]), 5.45 (s, CH2Cl2), 4.52 (t, [2H], 2JPH = 12 Hz, CH2). 19F{1H} NMR (295 K, CD3CN): δ = –78.4 (s, OTf−). 31P{1H} NMR (295 K, CD3CN): δ = 48.0 (s, dppmO2). 115In NMR (MeCN): not observed. IR spectrum (ν/cm-1): 1160 (sh), 1137 (P=O).

***2.13 [Ga(OTf)2(dppmO2)2][OTf]***

Ga(OTf)3 (103 mg, 0.2 mmol) was dissolved in CH2Cl2 (10 mL) before the addition of dppmO2  (167 mg, 0.4 mmol) and stirring for 2 h. Removal of the solvent resulted in a white solid, which was washed with n-hexane (2 x 5 mL) and dried *in vacuo*. Yield: 221 mg, 77%. Required for C53H44F9GaO13P4S3⋅CH2Cl2 (1434.64): C, 45.21; H 3.23. Found: C, 45.14; H, 3.44%. 1H NMR (295 K, CD3CN): δ = 7.31-7.77 (m, [24H]), 5.45 (s, CH2Cl2), 4.25 (t, [2H], 2JPH = 13 Hz, CH2). 19F{1H} NMR (295 K, CD3CN): δ = –79.2 (s, OTf−). 31P{1H} NMR (295 K, CD3CN): δ = 44.8 (s, dppmO2). 71Ga NMR (295 K, MeCN): not observed. IR spectrum (ν/cm-1): 1163, 1132 (P=O).

***2.14 [In(OTf)3(PyNO)3]***

In(OTf)3 (112 mg, 0.2 mmol) was dissolved in CH2Cl2 (5 mL) before addition of freshly sublimed pyridine N-oxide (57 mg, 0.6 mmol) and stirred for 2 h. Addition of n-hexane (10 mL) caused the precipitation of a white solid which was collected by filtration and dried *in vacuo.* Crystals suitable for X-ray analysis were grown by slow evaporation of a CH2Cl2 solution. Yield: 66mg, 36%. Required for C18H15F9InN3O12S3⋅CH2Cl2 (932.26): C, 24.48; H, 1.84; N, 4.51. Found: 23.94; H, 2.43; N, 4.33%. 1H NMR (295 K, CD3CN): δ = 8.64 (br s, [2H]), 8.07 (br t, [1H]), 7.79 (br t, [2H]), 5.45 (s, CH2Cl2). 13C{1H} NMR (295 K, CD3CN): δ = 142.44, 139.05, 128.80. 19F{1H} NMR (295 K, CD3CN): δ = –78.3 (s, OTf−). IR spectrum (ν/cm-1): 1204 (N=O).

**3. Results and Discussion**

The reaction of the metal triflates, M(OTf)3 (M = Al, Ga, In) with three molar equivalents of R3PO (R = Me or Ph) in dichloromethane solution afforded high yields of white [M(OTf)3(R3PO)3] (Scheme 1), several of which were isolated as CH2Cl2 solvates, with the lattice CH2Cl2 identified by microanalysis and 1H NMR spectroscopy (δ1H = 5.35). [In(OTf)3(PyNO)3] was obtained similarly from In(OTf)3 and 3 mol. eq. of PyNO (pyridine-N-oxide), whereas using Al(OTf)3 or Ga(OTf)3 gave mixtures (below). Higher Me3PO : In(OTf)3 ratios (from 3:1 to 6:1) were also explored, with pure samples of the 6:1 [In(Me3PO)6][OTf]3 being isolated relatively easily, whereas NMR spectroscopic data from the products from the 4:1 and 5:1 species also indicated the presence of minor amounts of the other complexes, consistent with facile ligand exchange in solution.



Scheme 1

Using the diphosphine dioxide, dppmO2 (Ph2PO(CH2)2POPh2) led to complete displacement of the OTf from the Group 13 metal to give the tris-chelate species, [M(dppmO2)3][OTf]3, whereas reaction of Ga(OTf)3 with two equivalents of dppmO2 gave [Ga(OTf)2(dppmO2)2][OTf], with retention of two OTf ligands in the coordination sphere (Scheme 2).



Scheme 2

In view of the relatively fast ligand substitution kinetics in trivalent Group 13 complexes, the information available from solution NMR data is less informative, hence the discussion begins with consideration of the solid state X-ray structural data.

***Crystallographic data***

Crystals of [In(OTf)3(PyNO)3] were obtained from CH2Cl2/hexane and the structure confirms the tris-PyNO coordination, giving a *mer* octahedral geometry with three κ1-OTf− ligands as seen in Figure 1. The In-OTf bond distances are slightly longer than the In-OPyNO distances.

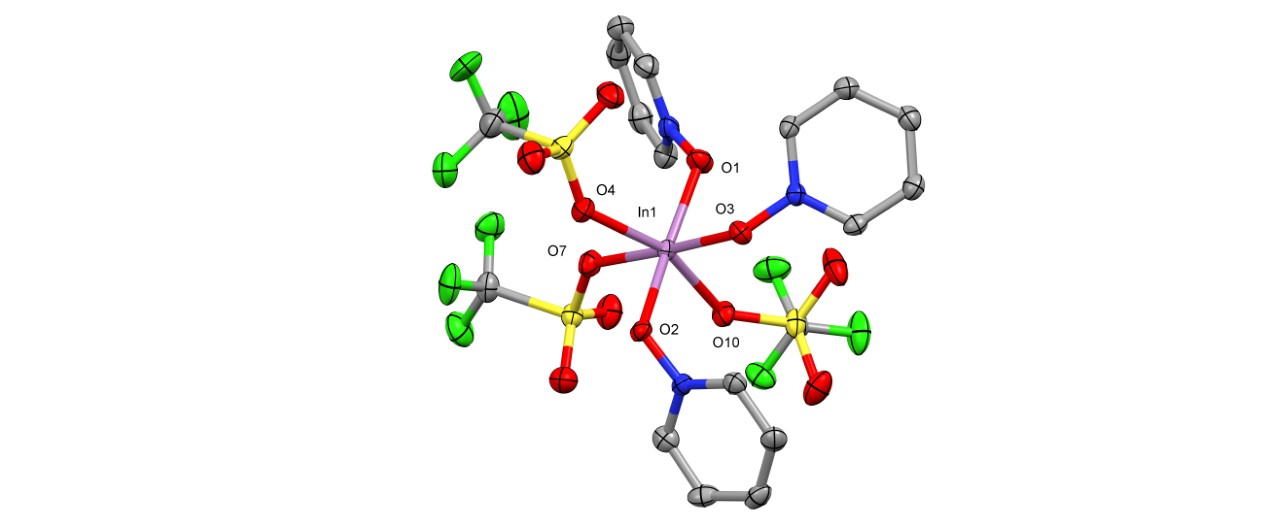


Figure 1 Structure of *mer*-[In(OTf)3(PyNO)3] showing the atom numbering scheme. Ellipsoids shown at 50% probability and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): In1–O1 = 2.096(3), In1–O2 = 2.105(2), In1–O3 = 2.133(2), In1–O10 = 2.163(3), In1–O4 = 2.166(3), In1–O7 = 2.168(3), O1–In1–O3 = 86.67(10), O2–In1– O3 = 82.95(10), O10–In1–O7 = 82.60(10), O4–In1–O7 = 81.53(11).

In contrast, similar preparations using a 3:1 ratio of PyNO : Al(OTf)3 or Ga(OTf)3 repeatedly gave mixtures containing two or three species based on the 1H NMR spectra, whether using CH2Cl2 or MeCN as the reaction solvent. A small number of crystals were grown from solutions of these in MeCN/Et2O, which turned out to be the *tetrakis* species, [Al(OTf)2(PyNO)4][OTf]⋅MeCN and [Ga(OTf)2(PyNO)4][OTf]⋅MeCN (Figure 2 (a) and (b), respectively), which are isostructural and contain distorted octahedral cations with the two coordinated OTf− groups mutually *trans* and the third OTf− acting as a discrete anion.

Chart, radar chart

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1. (b)

Figure 2 Crystal structures of the cations in isostructural complexes (a) *trans*-[Al(OTf)2(PyNO)4][OTf]⋅MeCN and (b) *trans*-[Ga(OTf)2(PyNO)4][OTf]⋅MeCN showing the atom numbering schemes. Ellipsoids shown at 50% probability and hydrogen atoms and lattice MeCN are omitted for clarity. In each structure there are two crystallographically independent ½ cations (centrosymmetric) in the asymmetric unit, only one of each is shown here. Selected bond lengths (Å) and angles (°): (a) Al1−O1 = 1.8613(9) , Al1−O2 = 1.8615(9), Al1−O3 = 1 .9571(10), Al2−O5 = 1.8632(9), Al2−O4 = 1.8597(9), Al2−O6 = 1.9508(9), O1−N1 = 1.3505(14), O5−N4 = 1.3488(14), O2−N2 = 1.3428(14), O4−N3 = 1.3429(14), O1−Al1−O2 = 89.19(4), O1−Al1−O3 = 89.06(4), O2−Al1−O3 = 91.46(4), O5−Al2−O6 = 88.26(4), O4−Al2−O5 = 89.06(4), O4−Al2−O6 = 88.50(4); (b) Ga1−O3 = 2.0397(17), Ga1−O2 = 1.9341(16), Ga1−O1 = 1.9318(17), Ga2−O4 = 1.9342(16), Ga2−O6 = 2.0427(19), Ga2−O5 = 1.9357(17), O4−N4 = 1.361(3), O2−N2 = 1.355(3), O1−N1 = 1.345(3), O5−N3 = 1.347(3), O2−Ga1−O3 = 91.78(7), O1−Ga1−O3 = 91.96(8), O1−Ga1−O2 = 88.98(7), O4−Ga2−O6 = 91.65(7), O4−Ga2 = O5 = 90.75(7), O5−Ga2−O6 = 91.54(8).

From the reaction of Me3PO and In(OTf)3 in a 4:1 ratio, two distinct polymorphs of the tetrakis Me3PO complex formulated as, [In(OTf)2(Me3PO)4][In(OH2)2(Me3PO)4][OTf]4, were obtained. Single crystal X-ray analysis shows that each polymorph comprises a *trans*-[In(OTf)2(OPMe3)4]+ cation co-crystallised with a *trans*-[In(OH2)2(Me3PO)4]3+ trication, and with the four OTf− anions required to balance the charge each involved in significant H-bonding interactions between one O atoms from each triflate with the H atoms on the coordinated water ligands, as shown in Figures 3 and 4. These could alternatively be formulated as the monocation/monoanion salt: [In(OTf)2(Me3PO)4][In{(OH2)2(OTf)4}(Me3PO)4].

While both polymorphs contain very similar *trans*-[In(OH2)2)(Me3PO)4]3+ trications with the H-bonded OTf− anions, they differ in that polymorph 1 contains two centrosymmetric half-cations of [In(OTf)2(Me3PO)4]+, whereas in polymorph 2 the *trans*-[In(OTf)2(Me3PO)4]+ monocation occupies a general position.

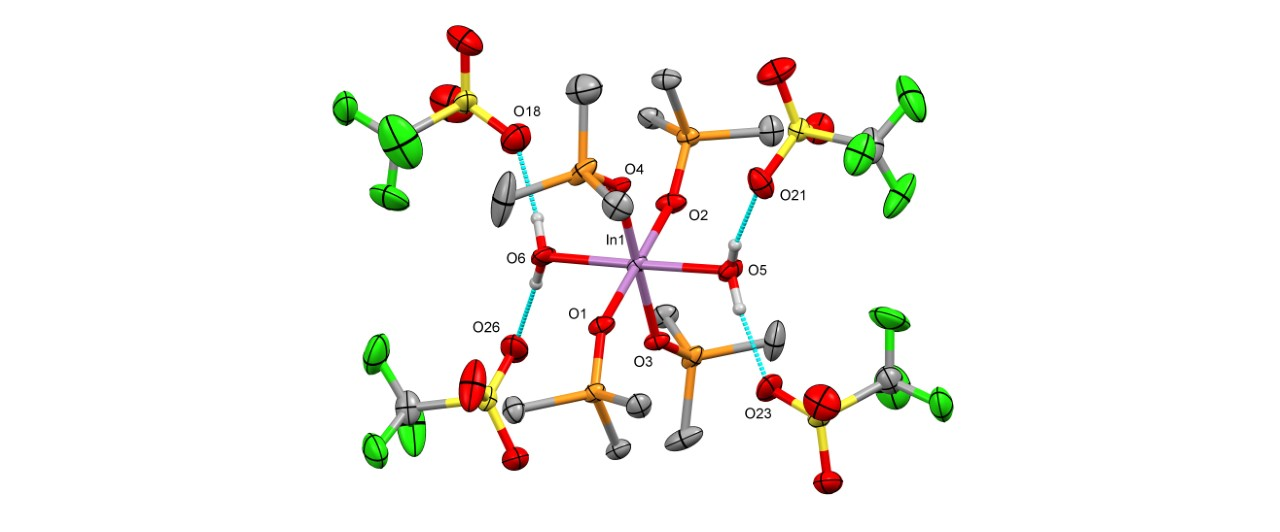
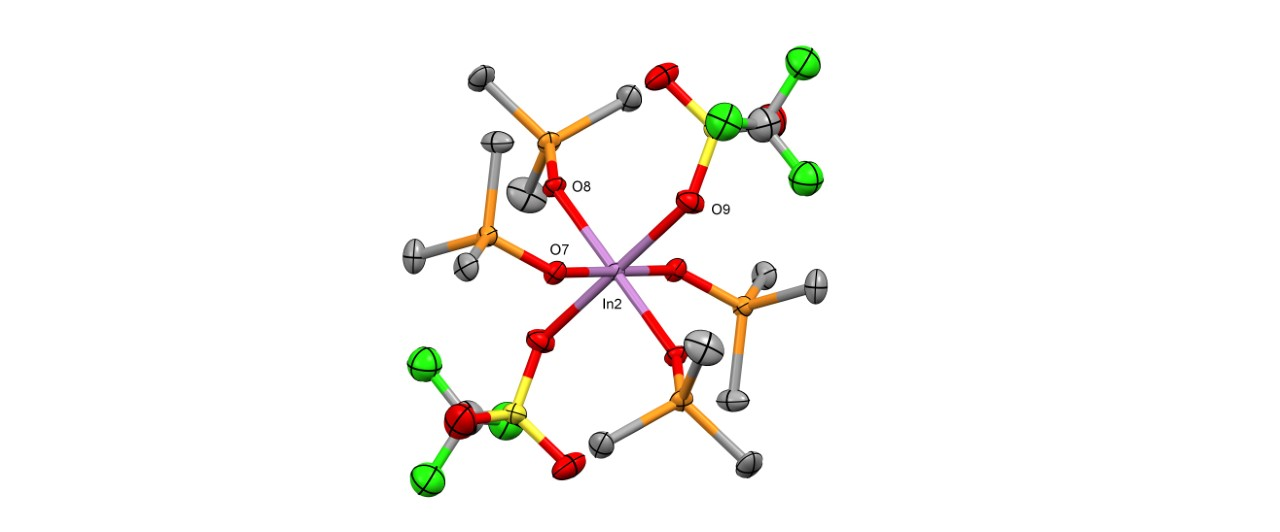


Figure 3 Crystal structure of polymorph 1 comprising *trans*-[In(OTf)2(Me3PO)4][In(OH2)2(Me3PO)4][OTf]4 showing the atom numbering schemes. Ellipsoids shown at 50% probability and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): In1-O1 = 2.120(3), In1-O2 = 2.114(3), In1-O3 = 2.102(3), In1-O4 = 2.102(3), In1-O5 = 2.153(4), In1-O6 = 2.155(4), O5⋅⋅⋅O21 = 2.702(6), O5⋅⋅⋅O23 = 2.669(6), O6⋅⋅⋅O18 = 2.671(6), O6⋅⋅⋅O26 = 2.941(7).

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Figure 4 Crystal structure of polymorph 2 comprising *trans*-[In(OTf)2(Me3PO)4][In(OH2)2(Me3PO)4][OTf]4 showing the atom numbering schemes and the H-bonded OTf− anions. Ellipsoids shown at 50% probability and hydrogen atoms (except those on the OH2 ligands) are omitted for clarity. Selected bond lengths (Å): In1-O1 = 2.099, In1-O2 = 2.101, In1-O6 = 2.165, In2-O3 = 2.108, In2–O4 = 2.118, In2-O5 = 2.164, O5⋅⋅⋅O9 = 2.837(8), O5⋅⋅⋅O12 = 2.675(7).

Using Ph3PO produced a related co-crystal, *trans*-[In(OTf)2(Ph3PO)4][In(OH2)4(Ph3PO)2][OTf]4⋅2CH2Cl2, as shown in Figure 5. In this case there is a [In(OTf)2(Ph3PO)4]+ cation, analogous to the Me3PO species discussed above, but the other cation is a tetra-aquo species, comprising a *trans*-octahedral [In(OH2)4(Ph3PO)2]3+ ion. The four OTf− anions required to balance the overall charge each show two O⋅⋅⋅H-bonding interactions, forming bridges that link the equatorial aquo ligands into a 24-membered ring. Thus, this complex could also be considered to be a salt derived from the [In(OTf)2(Ph3PO)4]+ cation with a [In{(OH2)4(OTf)4}(Ph3PO)2]− anion.

The prevalence for H-bonding between the aquo ligands and the O atoms of the OTf− anions in these species undoubtedly contributes significantly to the overall stability of the complexes, and therefore provides a driving force for their formation/crystallisation.

Diagram

Description automatically generatedFigure 5 Crystal structure of the two In(III) ions present in *trans*-[In(OTf)2(Ph3PO)4] [In(OH2)4(Ph3PO)2][OTf]4⋅2CH2Cl2 showing the atom numbering schemes and the H-bonded OTf− anions (turquoise dashed lines). Ellipsoids shown at 50% probability and hydrogen atoms (except those on the OH2 ligands) are omitted for clarity. There is a second crystallographically independent (In3-centred) centrosymmetric half-cation of [In(OH2)4(Ph3PO)2]3+ in the asymmetric unit, but the structural parameters are very similar to those in the In2-centred cation shown. Selected bond lengths (Å): In(1)-O(4) = 2.1059(19), In(1)-O(1) = 2.1113(19), In(1)-O(3) = 2.1139(19), In(1)-O(2) = 2.1154(19), In(1)-O(5) = 2.1623(18), In(1)-O(8) = 2.1695(18), In(2)-O(11) = 2.1009(18), In(2)-O(13) = 2.1487(18), In(2)-O(12) = 2.1553(19), In(3)-O(14) = 2.1243(19), In(3)-O(14) = 2.1243(19), In(3)-O(15) = 2.144(2).

Using a 5:1 Me3PO : In(OTf)3 ratio in CH2Cl2 led to formation of [In(OTf)(Me3PO)5][OTf]2. While we were unsuccessful in obtaining crystals of this pentakis species, we did manage to grow a crystal of the Ga(III) complex, [Ga(Me3PO)5(MeCN)][OTf]3, from a solution containing a few mg of Ga(OTf)3 layered with a solution of four equivalents of Me3PO in MeCN/Et2O. This structure also confirms that the MeCN solvent outcompetes OTf− for coordination at Ga(III) giving a near octahedral coordination environment (Fig. 6).

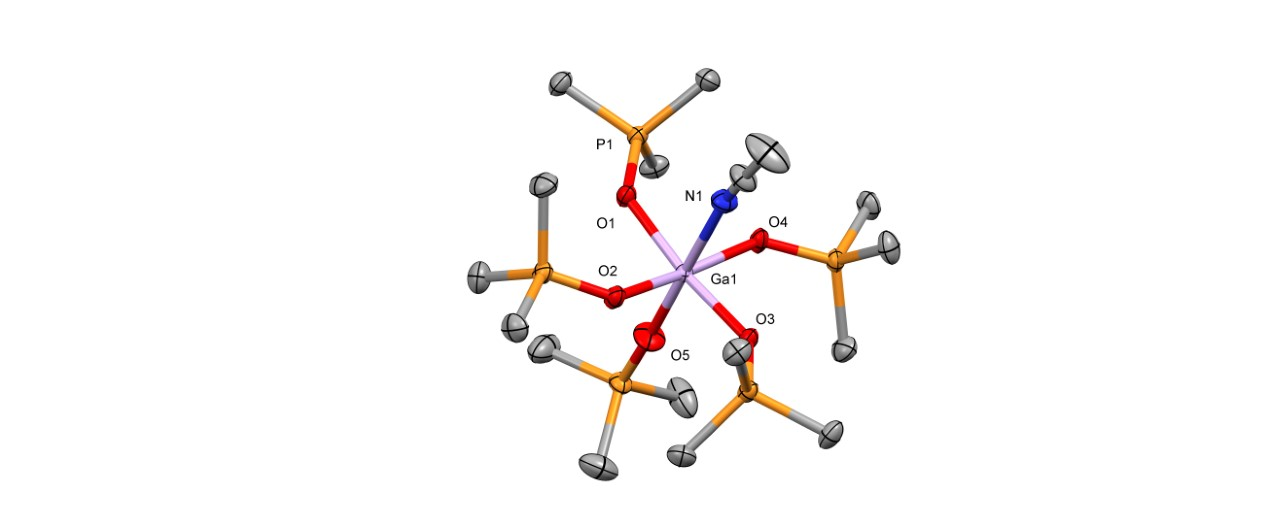
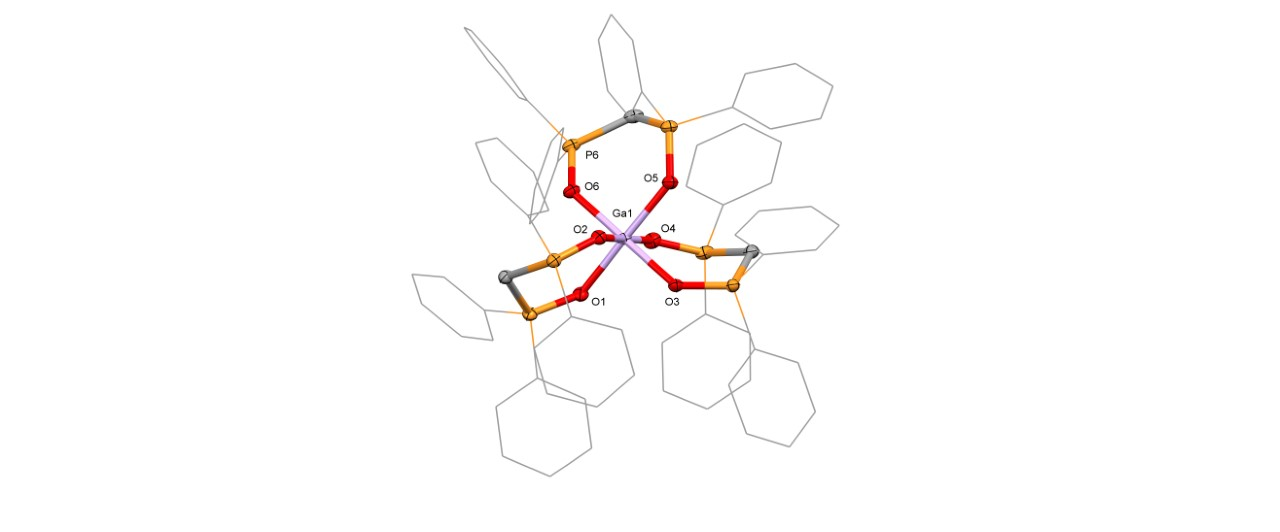


Figure 6 Crystal structure of the cation in [Ga(Me3PO)5(MeCN)][OTf]3 showing the atom numbering scheme. Ellipsoids are shown at 50% probability and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ga1–O1 = 1.9335(14), Ga1–O4 = 1.9295(14), Ga1–O3 = 1.9308(14), Ga1–O2 = 1.9205(14), Ga1–O5 = 1.8991(16), Ga1–N1 = 2.1985(18), P– O = 1.5007(16) – 1.5254(14), O1–Ga1–N1 = 86.62(7), O4–Ga1–N1 = 87.47(7), O3–Ga1–N1 = 84.24(7), O2–Ga1–N1 = 84.99(7), O4–Ga1–O1 = 89.81(6), O4–Ga1–O3 = 88.81(6), O2–Ga1–O1 = 90.23(6), O2–Ga1–O3 = 89.95(6), O5–Ga1–O1 = 94.60(7), O5–Ga1–O4 = 93.61(8), O5–Ga1–O3 = 94.56(7), O5–Ga1–O2= 93.92(8).

Using a 3:1 ratio of the diphosphine dioxide, dppmO2 : M(OTf)3 in CH2Cl2 solution led to the formation of the tris complexes, [M(dppmO2)3][OTf]3, and crystal structures were obtained for both M = Al and Ga, (Figures 7a and b), each of which confirm coordination is via three bidentate dppmO2, with the discrete OTf− anions present to balance the charge (although the data quality for the Al complex is rather poor – see Experimental). The structures of the cations are very similar to that reported previously for [Ga(dppmO2)3][NO3]3 [13].

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1. (b)

Figure 7 Crystal structures of the cations in (a) [Al(dppmO2)3][OTf]3⋅MeCN (the Al2-centred cation is not shown)and (b) [Ga(dppmO2)3][OTf]3⋅2CH2Cl2 showing the atom numbering schemes. Ellipsoids shown at 50% probability and hydrogen atoms and lattice solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): (a) Al1−O1 = 1.916(2), Al1−O2 = 1.872(2), Al1−O6 = 1.882(2), Al1−O3 = 1.865(2), Al1−O5 = 1.890(2), Al1−O4 = 1.905(2), Al2−O7 1.887(2), Al2−O9 = 1.898(2), Al2−O12 = 1.883(2), Al2−O11 = 1.911(2), Al2−O8 = 1.875(2), Al2−O10 = 1.875(2); (b) Ga1–O1 = 1.9372(14), Ga1–O2 = 1.9464(13), Ga1–O3 = 1.9567(13), Ga1–O4 = 1.9635(14), Ga1–O5 = 1.9681(13), Ga1–O6 = 1.9645(13), P–O = 1.5158(15) –1.5271(14), O1–Ga1–O2 = 92.63(6), O3–Ga1–O4 = 90.74(6), O6–Ga1–O5 = 90.51(6).

***Spectroscopic data***

The IR spectra of the isolated complexes each show bands associated with coordinated PyNO or R3PO to low frequency of the ligand itself, as expected and there was no evidence for uncoordinated ligand in the isolated complexes. However, using IR spectroscopy to provide a more detailed assignment of isomers or geometries was not possible due to the presence of OTf− bands in the same region and there was no significant change in the P=O stretching frequency with M.

The complexes are only modestly soluble in CH2Cl2, but dissolve readily in MeCN, and since previous studies of some Group 13 triflate complexes with N-donor ligands showed that the weakly coordinated OTf− groups were readily displaced [19], all solution data were obtained from anhydrous MeCN solutions to simplify comparisons. The 1H NMR spectra in CD3CN typically show one ligand environment to high frequency of the uncoordinated ligand and, like the 31P{1H} NMR spectra which each show a single resonance for each complex present (tris, tetrakis, etc.), do not appear to differentiate between different possible geometric isomers, but does identify different complexes. In the In(OTf)3 / nMe3PO system the solution NMR spectra typically show one major singlet resonance assigned to the target complex, but this was often accompanied by a second more minor singlet due to the next higher species, i.e. the 31P{1H} NMR spectrum of [In(OTf)(Me3PO)5]2+ also contains a small amount of [In(Me3PO)6]3+, due to mixtures forming in solution. The 31P{1H} NMR chemical shifts undergo a monotonic decrease as the number of Me3PO increases, from δ = 66.6 for the tris complex to δ = 60.9 for the hexakis species. Addition of excess Me3PO results in formation of the hexakis complex cation, but shows a separate resonance for the ‘free’ Me3PO that remains, indicating that exchange between ‘free’ and coordinated Me3PO is slow on the 31P NMR timescale.

The 19F{1H} NMR spectra for the complexes in MeCN each show one sharp singlet at ca. −79 ppm, due to the OTf− anions, consistent with these being ionic in all cases and hence displaced by MeCN, as expected.

The 27Al (I = 5/2), 71Ga (I = 3/2) and 115In (I = 9/2) isotopes all have significant quadrupole moments [20], hence as expected, spectra were typically only observed for high symmetry environments.

**Conclusions**

A range of new six-coordinate complexes of the Group 13 triflates containing phosphine oxide and pyridine-N-oxide ligands have been prepared and characterised structurally and spectroscopically. The OTf groups act as weakly coordinating ligands when there is insufficient neutral R3PO or PyNO completely fill the metal coordination sphere, but are readily displaced by solvent (MeCN or H2O). Crystallographic studies on the aquo complexes [In(OTf)2(Me3PO)4 and [In(OTf)2(Ph3PO)4][In{(OH2)4(OTf)4}(Ph3PO)2] reveal unexpected structures involving significant H⋅⋅⋅OTf hydrogen bonding interactions giving rise to unusual [In{(OH2)2(OTf)4}(Me3PO)4]− and [In{(OH2)4(OTf)4}(Ph3PO)2]− anions.

**Conflicts of interest**

The authors have none to declare.

**Acknowledgements**

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**Appendix A. Supplementary Information**

Contains the supplementary crystallographic data for this paper. CCDC reference numbers for the crystallographic information files in cif format are: [In(PyNO)3(OTf)3] – 2105962, [Al(OTf)2(PyNO)4][OTf]⋅MeCN – 2105964, [Ga(OTf)2(PyNO)4][OTf]⋅MeCN – 2105960, [In(OH2)2(Me3PO)4][In(OTf)2(Me3PO)4][OTf]4 (polymorph 2) – 2105965, [In(OTf)2(Me3PO)4][In(OH2)4(Me3PO)2][OTf]4 (polymorph 1) – 2105956, [In(OTf)2(Ph3PO)4][In(OH2)4(Ph3PO)2][OTf]2⋅CH2Cl2 – 2105975, [Ga(MeCN)(Me3PO)5][OTf]3 – 2105957, [Al(dppmO2)3][OTf]3⋅MeCN – 2105955, [Ga(dppmO2)3][OTf]3.2CHCl3 - 2105963. These data can be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ UK. Other supplementary materials include IR and NMR spectra for the complexes. Supplementary data associated with this article can be found in the online version, at http://.......

Table 1 Crystallographic dataa

|  |  |  |  |
| --- | --- | --- | --- |
| Compound | [In(PyNO)3(OTf)3] | [Al(OTf)2(PyNO)4][OTf]⋅MeCN | [Ga(OTf)2(PyNO)4][OTf] ⋅MeCN |
| Formula | C18H15F9InN3O1S3 | C25H23AlF9N5O13S3 | C25H23F9GaN5O13S3 |
| M | 847.33 | 895.64 | 938.72 |
| Crystal system | monoclinic | monoclinic | monoclinic |
| Space group (no) | P21/c (14) | P21/n (14) | P21/n (14) |
| a /Å | 9.6045(2) | 11.39200(10) | 11.3583(2) |
| b /Å | 27.2680(5) | 23.7735(3) | 23.7389(4) |
| c /Å | 11.0199(2) | 13.2470(2) | 13.4302(2) |
| α /° | 90 | 90 | 90 |
| β /° | 101.931(2) | 91.2530(10) | 91.435(2) |
| γ/° | 90 | 90 | 90 |
| U /Å3 | 2823.71(9) | 3586.80(8) | 3620.10(10) |
| Z | 4 | 4 | 4 |
| μ(Mo-ⱪα) /mm–1 | 1.183 | 0.347 | 1.048 |
| F(000) | 1672 | 1816 | 1889 |
| Total no. reflns | 50880 | 80071 | 45561 |
| Rint | 0.081 | 0.025 | 0.030 |
| Unique reflns | 5550 | 9273 | 9320 |
| No. of params, restraints | 415, 0 | 549, 21 | 509, 0 |
| GOF | 1.108 | 0.799 | 1.038 |
| R1, wR2 [I > 2σ(I)]b | 0.040, 0.092 | 0.033, 0.089 | 0.046, 0.118 |
| R1, wR2 (all data) | 0.044, 0.095 | 0.038, 0.093 | 0.060, 0.125 |

a common data: wavelength (Mo-Kα) = 0.71073 Å; θ(max) = 27.5°; b R1 = Σ||Fo|-|Fc||/Σ|Fo|; wR2=[Σw(Fo2-Fc2)2/ΣwFo4]1/2

Table 1 cont.

|  |  |  |  |
| --- | --- | --- | --- |
| Compound | [In(OH2)2(Me3PO)4] [In(OTf)2(Me3PO)4][OTf]4 (polymorph 2) | [In(OH2)2(Me3PO)4] [In(OTf)2(Me3PO)4][OTf]4 (polymorph 1) | [In(OTf)2(Ph3PO)4] [In(OH2)4(Ph3PO)2][OTf]4⋅2CH2Cl2 |
| Formula | C15H38F9InO14P4S3 | C30H76F18In2O28P8S6 | C116H102Cl4F18In2O28P6S6 |
| M | 948.33 | 1896.74 | 3035.60 |
| Crystal system | triclinic | triclinic | triclinic |
| Space group (no) | P-1 (2) | P-1 (2) | P-1 (2) |
| a /Å | 9.6477(3) | 11.2931(2) | 14.9532(3) |
| b /Å | 11.2964(2) | 18.4641(3) | 19.3894(5) |
| c /Å | 17.6524(4) | 19.3056(4) | 23.0722(6) |
| α /° | 83.7685(16) | 110.285(2) | 99.852(2) |
| β /° | 79.394(2) | 95.0470(10) | 106.775(2) |
| γ/° | 85.0987(18) | 93.4490(10) | 90.8505(19) |
| U /Å3 | 1875.57(7) | 3743.49(12) | 6295.7(3) |
| Z | 2 | 2 | 2 |
| μ(Mo-ⱪα) /mm–1 | 1.064 | 1.066 | 0.726 |
| F(000) | 956 | 1912 | 3072 |
| Total no. reflns | 49095 | 81590 | 81740 |
| Rint | 0.055 | 0.048 | 0.057 |
| Unique reflns | 11257 | 14680 | 24726 |
| No. of params, restraints | 514, 29 | 915, 210 | 1630, 0 |
| GOF | 1.053 | 1.253 | 1.006 |
| R1, wR2 [I > 2σ(I)]b | 0.056, 0.134 | 0.057, 0.148 | 0.035, 0.089 |
| R1, wR2 (all data) | 0.081, 0.151 | 0.062, 0.151 | 0.052, 0.067 |

Table 1 cont.

|  |  |  |  |
| --- | --- | --- | --- |
| Compound | [Ga(MeCN)(Me3PO)5][OTf]3 | [Al(dppmO2)3][OTf]3⋅MeCN | [Ga(dppmO2)3][OTf]3⋅2CHCl3 |
| Formula | C20H48F9GaNO14P5S3 | C80H69AlF9NO15P6S3 | C80H68Cl6F9GaO15P6S3 |
| M | 1018.34 | 1764.40 | 2004.76 |
| Crystal system | monoclinic | monoclinic | monoclinic |
| Space group (no) | P21/n (14) | P21/n (14) | P21/c (14) |
| a /Å | 15.7227(2) | 23.2259(3) | 27.2588(5) |
| b /Å | 17.5004(2) | 21.9395(3) | 18.9738(3) |
| c /Å | 15.8907(2) | 31.3366(5) | 17.3899(3) |
| α /° | 90 | 90 | 90 |
| β /° | 91.4170(10) | 92.1040(10) | 103.356(2) |
| γ/° | 90 | 90 | 90 |
| U /Å3 | 4371.05(9) | 15957.3(4) | 8750.8(3) |
| Z | 4 | 8 | 4 |
| μ(Mo-ⱪα) /mm–1 | 1.047 | 0.312 | 0.760 |
| F(000) | 2088 | 7273 | 4080 |
| Total number reflns | 99549 | 159139 | 75171 |
| Rint | 0.050 | 0.038 | 0.032 |
| Unique reflns | 11617 | 31271 | 22607 |
| No. of params, restraints | 525, 3 | 2478, 124 | 1081, 0 |
| GOF | 1.051 | 1.015 | 1.030 |
| R1, wR2 [I > 2σ(I)]b | 0.038, 0.091 | 0.061, 0.153 | 0.040, 0.097 |
| R1, wR2 (all data) | 0.044, 0.094 | 0.080, 0.167 | 0.061, 0.104 |

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