

# Evidence on Ligand Strengths from the Crystal Structures of $[\text{InCl}_3(\text{dmf})_3]$ , $[\text{InCl}_3(\text{dma})_3]$ , $[\{\text{InCl}_3(\text{PhCHO})_3\}_2]\cdot\text{PhCHO}$ and $[\text{InCl}_3(\text{PhCOMe})_2]$ from Dimethylformamide (dmf), Dimethylacetamide (dma), Benzaldehyde and Acetophenone †

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X-Ray crystal structure determinations have been made for the *fac* octahedral complexes  $[\text{InCl}_3(\text{dmf})_3]$  **1**,  $[\text{InCl}_3(\text{dma})_3]$  **2** and  $[\{\text{InCl}_3(\text{PhCHO})_3\}_2]\cdot\text{PhCHO}$  **3**, from dimethylformamide (dmf), dimethylacetamide and benzaldehyde and the trigonal-bipyramidal complex  $[\text{InCl}_3(\text{PhCOMe})_2]$  **4** from acetophenone. The average In–O bond length for **3** is *ca.* 0.07 Å greater than for **1** or **2**. In **4**, In–O is 0.07 Å longer than that known for  $[\text{InCl}_3(\text{tmu})_2]$  from tetramethylurea (tmu). An extension of the comparison to structures involving other ligands shows there to be a general correspondence between In–O bond lengths and ligand donor values. By contrast with the weak co-ordination of aldehydes and ketones, co-ordination of an amide is enhanced through polarisation. In the crystal of **3**, individual  $[\text{InCl}_3(\text{PhCHO})_3]$  molecules are paired, almost centrosymmetrically, with intermeshing of their PhCHO ligands.

The capacity of monodentate amides, aldehydes and ketones to form complexes through the carbonyl group has long been known.<sup>1</sup> Knowledge of amide complexes, including those from ureas, is more extensive than of aldehyde and ketone derivatives; the amides are more easily prepared and handled, with the metal–ligand bond seemingly more stable towards dissociation and hydrolytic decomposition. Driessen and Groeneveld<sup>2</sup> have commented particularly on the relative instability of aldehyde and ketone derivatives. With a background interest in indium complexes with oxo-ligands,<sup>3</sup> we examined any structural effects arising from amide *vs.* aldehyde (or ketone) behaviour. We obtained, and determined the crystal structures of what proved to be *fac* octahedral complexes  $[\text{InCl}_3(\text{dmf})_3]$  **1**,  $[\text{InCl}_3(\text{dma})_3]$  **2** and  $[\{\text{InCl}_3(\text{PhCHO})_3\}_2]\cdot\text{PhCHO}$  **3**, in turn from dimethylformamide (dmf), dimethylacetamide (dma) and benzaldehyde, and the trigonal-bipyramidal  $[\text{InCl}_3(\text{PhCOMe})_2]$  **4** from acetophenone (acp). The structures of  $[\text{InCl}_3(\text{dmsO})_3]$  **5** (dmsO = dimethyl sulfoxide) and some phosphine oxide derivatives, as well as a trigonal-bipyramidal (TBPY) compound  $[\text{InCl}_3(\text{tmu})_2]$  from tetramethylurea (tmu),<sup>4</sup> were already available, and this allows the present results on bond lengths around In centres to be seen against a broader background. We discuss this first, before commenting on individual features of the structures of the present compounds, **1–4**.

## Results and Discussion

**Significance of Indium Bond Lengths.**—Average bond lengths for these  $\text{InCl}_3$  complexes are given in Table 1. It will be seen that the In–O values are in line with perceptions of the lower stabilities of aldehyde/ketone complexes as compared with those from amides. The In–O bond (av.) for the benzaldehyde compound **3** is longer than for the dmf and dma compounds **1** and **2**, by 0.05 and 0.07 Å respectively. There is a similar bond

length relationship as between the TBPY compounds **4** and  $[\text{InCl}_3(\text{tmu})_2]$  **6** from tetramethylurea.

For the *fac*-octahedral derivatives, including those from dmsO, phosphine oxides, and water, there is seen to be an inverse relationship between In–O and In–Cl bond lengths. This points to the relevance of charge transfer and suggests further that there should be some correspondence with Gutmann's ligand donor values<sup>5</sup> which represent enthalpies of formation of adducts with  $\text{SbCl}_5$  in solution, and whose bearing on stabilities is reinforced by measurements of equilibrium constants.<sup>5,8</sup> Table 1 shows that there is a clear relationship. The short In–O bond lengths for dmf, dmsO, and phosphine oxide derivatives relate to ligand donor values of *ca.* 27–30. The longer bonds for the benzaldehyde compound **3**, and for the acetophenone derivative **4** as compared with TBPY counterpart **6** from tetramethylurea, correspond with lower donor values inferred to be in the range 17–20. As based on bond lengths, the hydrate  $[\text{InCl}_3(\text{H}_2\text{O})_3]\cdot\text{C}_4\text{H}_4\text{O}_2$  is intermediate,<sup>6</sup> but in this case the donor activity of the co-ordinated water (donor value 18) will be enhanced through hydrogen bonding with the lattice dioxane. As with any bond-strength criteria, bond lengths offer lesser discrimination as the ligands become more similar, so that distinctions between dmsO, dma and dmf may become uncertain. Their In–O lengths lie in the rather narrow range 2.195(2)–2.225(2) Å. Yet while too much should not be read into the result, the ordering from precisely determined bond lengths, dmsO > dma > dmf does correspond with that from donor values.

**Ligand Strength of Amide *vs.* Aldehyde or Ketone.**—Bond polarity and molecular polarisability both contribute to ligand strength.<sup>9</sup> They are often not easily quantifiable properties and usually can be placed only within probable ranges. For the aldehyde/ketone series RCHO and  $\text{R}_2\text{CO}$  (R = Me or Ph), the C=O bond polarity in these planar molecules can be placed in the range 2.6–2.9 D for all members (see Table 2). For amides there is a small polarity increment, with the C=O bond polarity for dmf probably low in a general range 3.0–3.4 D. This must augment ligand strength. Besides this however, there is an important contribution from polarisability over the whole amide group, as shown by bond length values. There is a sharp

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: D  $\approx 3.33 \times 10^{-30}$  C m.

**Table 1** Average<sup>a</sup> bond lengths (Å) and angles (°)

<i>fac</i> Octahedral complexes	In–O	In–Cl	In–O–E <sup>b</sup> (E = C, S, P)	Donor number <sup>c</sup>
<b>1</b> [InCl <sub>3</sub> (dmf) <sub>3</sub> ]	2.225(2)	2.435(1)	124.0(2)	26.6
<b>2</b> [InCl <sub>3</sub> (dma) <sub>3</sub> ]	2.204(3)	2.454(1)	139.6(3)	27.8
<b>5</b> [InCl <sub>3</sub> (dmsO) <sub>3</sub> ] <sup>d</sup>	2.195(2)	2.460(1)	124.1(1)	29.8
<b>3</b> [{InCl <sub>3</sub> (PhCHO) <sub>3</sub> ] <sub>2</sub> ·PhCHO	2.281(16)	2.406(6)	125.9(1.6)	17–20 <sup>e</sup>
	2.277(12) <sup>f</sup>	2.400(5) <sup>f</sup>	124.6(1.1) <sup>f</sup>	
[InCl <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ·C <sub>4</sub> H <sub>4</sub> O <sub>2</sub> <sup>g</sup>	2.244(7) <sup>g</sup>	2.422(3)	—	18
[InCl <sub>3</sub> (PhMe <sub>2</sub> PO) <sub>3</sub> ·H <sub>2</sub> O <sup>d</sup>	2.196(7)	2.484(4)	142.3(5)	—
[InCl <sub>3</sub> (Me <sub>3</sub> PO) <sub>3</sub> ] <sup>h</sup>	2.168(9)	2.477(5)	139.4(6)	> 29.8 <sup>h</sup>
<i>TBPY</i> complexes <sup>i</sup>				
<b>4</b> [InCl <sub>3</sub> (PhCOMe) <sub>2</sub> ]	2.250(2)	2.354(1)	134.6(2)	17–20 <sup>e</sup>
<b>6</b> [InCl <sub>3</sub> (tmu) <sub>2</sub> ] <sup>j</sup>	2.175(2)	2.387(1)	133.6(2)	29.6

<sup>a</sup> Individual values are given in Table 3. The averaging of the *fac* octahedral values eliminates small differences due to non-bonding interactions.

<sup>b</sup> These angles are included because they show that repulsions causing angle enlargement (ref. 3) do not lead to a correlative increase in In–O.

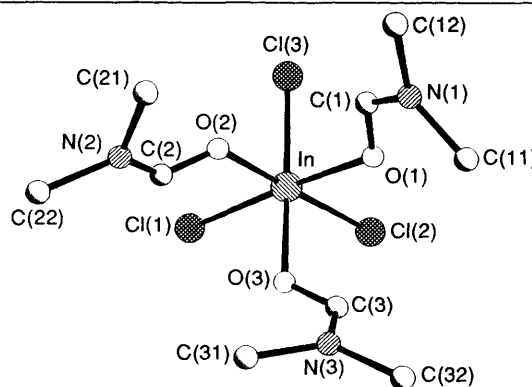
<sup>c</sup> Gutmann values (ref. 5). <sup>d</sup> Ref. 3. <sup>e</sup> Placed in this low range, matching values for acetone and benzophenone. <sup>f</sup> From a refinement giving  $R = 0.069$  with a larger data set. <sup>g</sup> Ref. 6. There may be some disturbance of In–O bond lengths through hydrogen bonding to lattice dioxane molecules. <sup>h</sup> A *mer* octahedral complex for which In–O lengths show no important variations from those in the *fac* octahedral [InCl<sub>3</sub>(Me<sub>3</sub>PO)<sub>2</sub>(H<sub>2</sub>O)]·H<sub>2</sub>O. Lindqvist and Zackrisson<sup>7</sup> place Me<sub>3</sub>PO above dmsO in the donor series. <sup>i</sup> Structural parameters from present data included for comparison. It is to be noted that the bonding orbitals for axial and equatorial positions are non-equivalent. <sup>j</sup> For low-temperature comparability, and to avoid crystal decomposition (ref. 4), values quoted are from a revised structure determination at 215 K [ $R(R') = 0.0206 (0.0283)$ ].

**Table 2** Estimated oxy-bond polarities in free ligands

Bond moment/D	Aldehydes, ketones	Amides
Charge transfer to oxygen <sup>c</sup>	2.6–2.9 <sup>a</sup>	3.0–3.4 <sup>b</sup>
	0.45–0.50	0.53–0.58 <sup>d</sup>

<sup>a</sup> Significant molecular dipole moments ( $\mu/D$ ) are: MeCHO, 2.69; Me<sub>2</sub>CO, 2.88; PhCHO, 2.8; PhCOMe, 3.02 (ref. 10). For MeCHO and PhCHO (ref. 11) the moment makes a low angle (15°) with the carbonyl bond and so the bond moment approaches the molecular moment.

<sup>b</sup> The amide (–CONH<sub>2</sub>) group moment has been deduced as 3.4 D (ref. 12) with a vector making an angle not greater than 30° with the C=O bond (ref. 13). For HCONH<sub>2</sub> and HCONMe<sub>2</sub>,  $\mu = 3.73$  and 3.82 D respectively (ref. 10). <sup>c</sup> Theoretical charge transfer ( $\delta e$ ) over the internuclear distance;  $\delta e = \text{bond moment}/\text{bond length}$ , with  $e = 4.8 \times 10^{-10}$  D Å<sup>-1</sup>. For dmsO, the probable value is only 0.39–0.45. <sup>d</sup> Range refers to formamide.



**Fig. 1** The *fac* octahedral molecule of [InCl<sub>3</sub>(dmf)<sub>3</sub>]. The dmf ligands are rigidly planar, but skewing and tilting at the oxygen 'ball-joint' differ for each of the three

decrease in the N–CO bond length from (an estimated) 1.36 Å in the dmf molecule\* to 1.305 Å in the InCl<sub>3</sub> complex **1** [individual values: 1.305(4), 1.308(4), 1.303(4) Å]. This indicates the importance of electron accession from nitrogen towards the carbonyl group, whose donor activity is thereby enhanced. Thus in the particular case of amides precise bond length measurements provide evidence on the co-ordinative polarisation contributing to ligand strength.

It is of interest that some 30 years ago the higher ligand strength of dmsO as compared with acetone was suggested by Lindqvist<sup>9</sup> to derive from higher polarisability, which in this case is provided by the second-row atom. There is evidence towards this from molecular refractivities,<sup>16</sup> although extraction of the polarisability of the S=O (or of the P=O bond in phosphine oxides) may still remain somewhat uncertain.

**Structures of Individual Compounds.**—[InCl<sub>3</sub>(dmf)<sub>3</sub>] **1**. This compound is analogous to the *fac*-octahedral [InCl<sub>3</sub>(dmsO)<sub>3</sub>] **5** and its detailed co-ordination geometry around In (Table 3)

\* Precise experimentally determined bond lengths for the free dmf molecule are not available (see ref. 14). A calculated geometry made by Dr. R. G. A. R. Maclagan using the HF 6–31 G\* basis set gave N–CO 1.348 Å, identical with that for formamide, for which the accurate experimental value is 1.368(3) Å (see ref. 15). This reference also contains a discussion of the effects of hydrogen bonding on bond lengths in crystalline formamide.

requires no comment. As is characteristic of amides, the co-ordinated ligands remain almost planar, with maximum atom displacements (apart from H atoms of methyl groups) from mean planes of only 0.024, 0.016 and 0.017 Å for ligand sets 1, 2 and 3 respectively. Each ligand behaves independently with respect to the orientation of its plane, to meet the needs of molecular packing. The torsion angles (Fig. 1) Cl(3)–In–O(1)–C(1), Cl(1)–In–O(2)–C(2), Cl(2)–In–O(3)–C(3) are 56.2, 35.6, 64.3°, and for In–O(1)–C(1)–N(1), In–O(2)–C(2)–N(2), In–O(3)–C(3)–N(3) the angles are 154.6, 166.6, 143.0°.

[InCl<sub>3</sub>(dma)<sub>3</sub>] **2**. With the introduction of the methyl group (acetyl *vs.* formyl) the molecules assume  $C_s$  symmetry in the crystal lattice. As will be seen from Fig. 2, the mirror plane contains the atom set O(2), C(2) *etc.* Moreover, a free refinement of the hydrogen atom positions showed the absence of methyl rotation, with the equilibrium position of one H atom of each of the three methyl groups in the mirror plane. The In–O(1)–C(1) and In–O(2)–C(2) angles have increased to 139.0 and 140.1° as compared with 122.5, 125.5 and 123.9° for the oxygen angles in **1**. Within the cell the molecules lie with their mirror planes parallel to [010], with  $y$  coordinates of the in-plane atoms 0.25, 0.75.

[[InCl<sub>3</sub>(PhCHO)<sub>3</sub>]<sub>2</sub>·PhCHO] **3**. There are two crystallographically independent, but near-equivalent molecules based on In(1) and In(2) within the asymmetric unit (Fig. 3). These molecules are paired in an almost centrosymmetric array with intermeshing of the rings of their nearly planar ligands [torsion angles of type In(1)–O(1)–C(1)–C(16) having low values in the

Table 3 Bond lengths (Å) and angles (°) for complexes 1-4

[InCl <sub>3</sub> (dmf) <sub>3</sub> ] 1				[InCl <sub>3</sub> (dma) <sub>3</sub> ] 2			
In-Cl(1)	2.439(1)	Cl(1)-In-Cl(2)	100.1(1)	In-Cl(1)	2.461(1)	Cl(1)-In-Cl(2)	97.3
In-Cl(2)	2.431(1)	Cl(1)-In-Cl(3)	100.4(1)	In-Cl(2)	2.440(1)	Cl(1)-In-Cl(1')	98.9(1)
In-Cl(3)	2.435(1)	Cl(2)-In-Cl(3)	98.1(1)	In-O(1)	2.217(3)	O(1)-In-O(2)	77.8(1)
In-O(1)	2.241(2)	O(1)-In-O(2)	79.0(1)	In-O(2)	2.180(3)	O(1)-In-O(1')	77.7(1)
In-O(2)	2.214(3)	O(1)-In-O(3)	80.1(1)	O(1)-C(1)	1.249(4)	In-O(1)-C(1)	139.0(2)
In-O(3)	2.220(2)	O(2)-In-O(3)	79.7(1)	O(2)-C(2)	1.254(4)	In-O(2)-C(2)	140.1(3)
O(1)-C(1)	1.264(4)	In-O(1)-C(1)	122.5(2)	C(1)-C(13)	1.503(6)	O(1)-C(1)-N(1)	119.6(3)
O(2)-C(2)	1.253(3)	In-O(2)-C(2)	125.5(2)	C(1)-N(1)	1.324(5)	C(13)-C(1)-N(1)	118.9(3)
O(3)-C(3)	1.257(4)	In-O(3)-C(3)	123.9(2)	C(2)-C(23)	1.493(8)	O(2)-C(2)-N(2)	118.1(4)
				C(2)-N(2)	1.333(6)	C(23)-C(2)-N(2)	119.7(3)
[InCl <sub>3</sub> (PhCHO) <sub>3</sub> ] <sub>2</sub> ·PhCHO 3				[InCl <sub>3</sub> (PhCOMe) <sub>2</sub> ] 4			
In(1)-Cl(1)	2.392(8)	Cl(1)-In(1)-Cl(2)	104.5(3)	In-Cl(1)	2.337(1)	Cl(1)-In-Cl(2)	120.4(1)
In(1)-Cl(1)	2.422(8)	Cl(1)-In(1)-Cl(3)	101.2(2)	In-Cl(2)	2.363(1)	Cl(2)-In-Cl(2')	119.2(1)
In(1)-Cl(3)	2.410(6)	Cl(2)-In(1)-Cl(3)	101.8(2)	In-O(1)	2.250(2)	O(1)-In-O(1')	173.7(1)
In(1)-O(1)	2.282(18)	O(1)-In(1)-O(2)	76.2(6)	O(1)-C(1)	1.241(3)	In-O(1)-C(1)	134.6(2)
In(1)-O(2)	2.273(16)	O(1)-In(1)-O(3)	76.5(6)	C(1)-C(2)	1.497(4)	O(1)-C(1)-C(16)	118.5(2)
In(1)-O(3)	2.280(14)	O(2)-In(1)-O(3)	76.7(4)	C(1)-C(16)	1.482(3)	O(1)-C(1)-C(2)	121.7(2)
In(2)-Cl(4)	2.402(8)	Cl(4)-In(2)-Cl(5)	102.9(3)			C(16)-C(1)-C(2)	114.8(2)
In(2)-Cl(5)	2.412(8)	Cl(4)-In(2)-Cl(6)	101.2(3)				
In(2)-Cl(6)	2.399(7)	Cl(5)-In(2)-Cl(6)	103.3(2)				
In(2)-O(4)	2.283(18)	O(4)-In(2)-O(5)	75.3(6)				
In(2)-O(5)	2.292(18)	O(4)-In(2)-O(6)	77.6(6)				
In(2)-O(6)	2.277(13)	O(5)-In(2)-O(6)	75.3(6)				

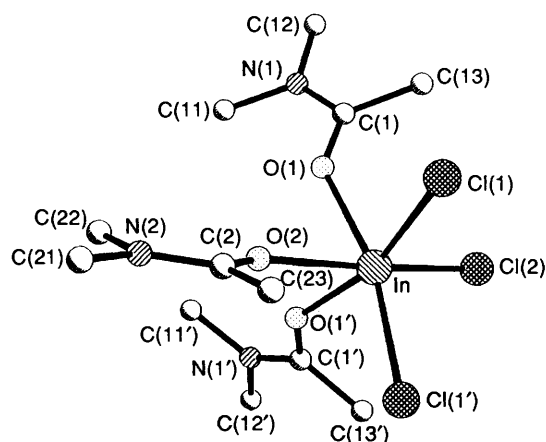


Fig. 2 The *fac* octahedral molecule of [InCl<sub>3</sub>(dma)<sub>3</sub>], showing the mirror plane containing Cl(2) and ligand 2. Ligands 1 and 1' are also planar

range 0.1–8.3°, and for the type O(1)–C(1)–C(16)–C(11), 1.2–2.6°. This pairing, which provides efficient packing of the rings, is promoted by the approach of the (positively charged) ring systems towards the oxygen atoms of the partner molecule. Shortest O...C approaches are in the range 3.31–3.38 Å.

The molecular pairs form clusters for which the enclosing envelope approximates to oblate spheroidal. The clusters are close-packed with an ABCA... layer sequence. The layers are parallel to [100] with the In(1)–In(2) vector almost perpendicular (89.1°) to this plane, and the Cl atoms from adjacent layers almost coplanar. The  $\beta$  angle of the cell, 113.8°, approaches the 109.5° value for close packing of perfect spheres. The free benzaldehyde molecules occupy recesses formed by the projecting Cl atoms, with which they too are almost coplanar (the *x* coordinates of all the atoms being close to 0.25 or 0.75).

[InCl<sub>3</sub>(PhCOMe)<sub>2</sub>] 4. The In atom is in *TBPY* co-ordination with the ligands in axial positions (Fig. 4). The molecule has *C*<sub>2</sub> symmetry about the In–Cl(1) vector, with all ligand atoms lying close to the InCl(1)O(1)O(1') plane. An H-atom refinement test showed that, as with compound 2, the methyl group is constrained against rotation at the temperature of data collection (150 K). The H(21) atom, for which *U*<sub>equiv</sub> refined at

only 0.033 Å<sup>2</sup>, is almost equidistant from Cl(2) and Cl(2'). As with 2 the introduction of the methyl group enlarges the In–O–C angle, so as to maintain minimum CH<sub>3</sub>...Cl approaches in the usual range 3.5–3.6 Å,<sup>3</sup> which matches van der Waals requirements.

## Experimental

**Preparation of Complexes.**—The compounds were obtained by dissolving finely divided anhydrous indium trichloride in the ligand (pre-dried over molecular sieve pellets) through stirring for a few minutes at 60–70 °C under dry nitrogen. For 3, lengthy heating must be avoided to minimise formation of condensation products. The crystalline compounds usually separated during slow cooling, or overnight. Solutions of 2 were prone to supersaturation, but addition of a few minute seed crystals produced a crop suitable for diffraction. (Other crystalline phases have been reported with dma,<sup>17</sup> but their identification was not pursued.) Using 3 cm<sup>3</sup> of ligand in each case, suitable quantities of InCl<sub>3</sub> for the preparations were (1) 0.10–0.12 g, (2) 0.25–0.30 g, (3) 0.17–0.20 g, (4) 0.27–0.30 g (Found: C, 24.8; H, 4.8; N, 9.6. Calc. for C<sub>6</sub>H<sub>21</sub>Cl<sub>3</sub>InN<sub>3</sub>O<sub>3</sub> 1: C, 24.5; H, 4.8; N, 9.5. Found: C, 2.95; H, 5.9; N, 8.6. Calc. for C<sub>12</sub>H<sub>27</sub>Cl<sub>3</sub>In<sub>3</sub>N<sub>3</sub>O<sub>3</sub> 2: C, 29.9; H, 5.4; N, 8.7%).

It can be noted that  $\nu$ (In–Cl) infrared wavenumbers for such products lie typically in the range 285–255 cm<sup>-1</sup> for octahedral co-ordination, and 335–315 cm<sup>-1</sup> for *TBPY* co-ordination.<sup>3</sup> For the present compounds, In–Cl wavenumbers (cm<sup>-1</sup>) are: (1) 289m, 280s; (2) 286s, 280 (sh); (3) 283s; [InCl<sub>3</sub>(tmu)<sub>2</sub>], 329s. A glassy residue from InCl<sub>3</sub> with *N,N*-dimethylbenzamide gave  $\nu$ (In–Cl) 337 cm<sup>-1</sup>, indicative of five-co-ordination.

**X-Ray Crystal Structure Determinations.**—A Nicolet R3M diffractometer was used, with the crystals mounted in a cold nitrogen stream (150 K). Crystals for diffraction were taken from the mother-liquor into fluorinated ether (Hoechst), quickly mounted, and transferred to the diffractometer where there was immediate cooling. The crystals were thus stabilised against hydrolytic decomposition and loss of ligand. The ensuing procedure was as previously described,<sup>3</sup> with detail for individual compounds given in Table 4. Indium atoms were located from Patterson maps and other (non-hydrogen) atoms from Fourier difference syntheses. For 1, 2 and 4, all non-

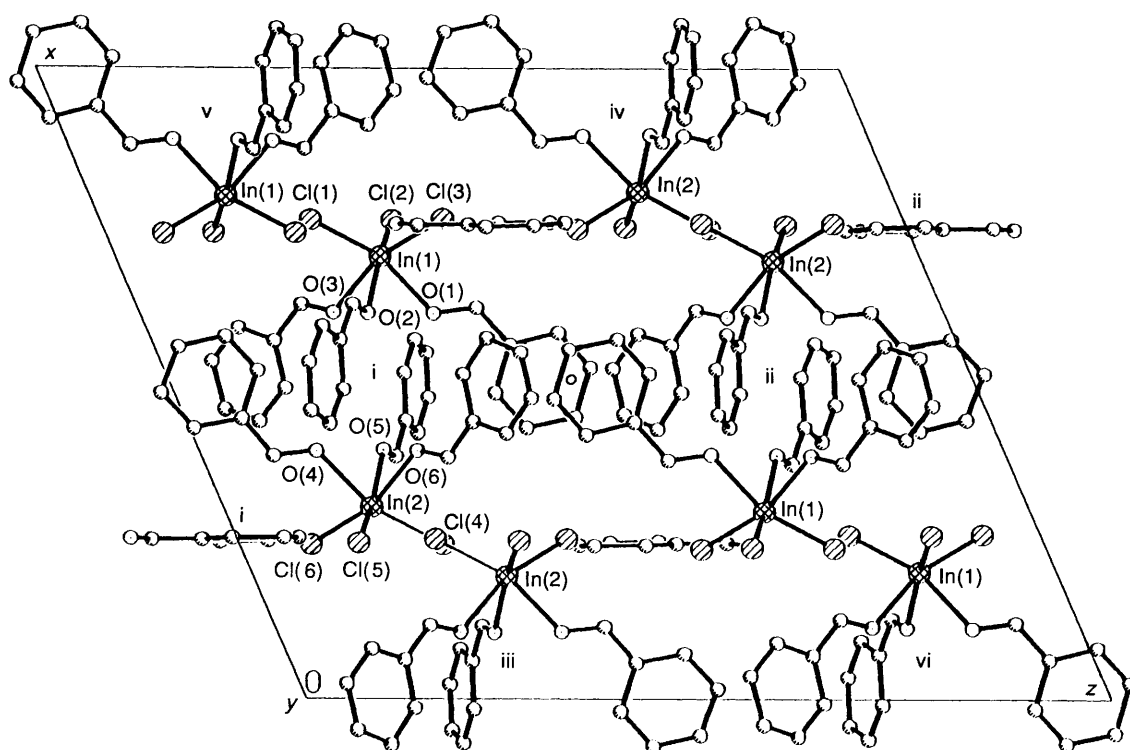


Fig. 3 The approximate centrosymmetric relationship of the two paired  $[\text{InCl}_3(\text{PhCHO})_3]$  molecules in the asymmetric unit of  $[\{\text{InCl}_3(\text{PhCHO})_3\}_2] \cdot \text{PhCHO}$ . Ligand attachment is seen to provide an *anti* disposition about the carbonyl bond. Symmetry codes are: (i),  $x, y, z$ ; (ii)  $1 - x, 1 - y, 1 - z$ ; (iii)  $0.5 - x, 0.5 + y, 0.5 - z$ ; (iv)  $0.5 + x, 0.5 - y, 0.5 + z$ ; (v)  $1.5 - x, 0.5 + y, 0.5 - z$ ; (vi)  $x - 0.5, 0.5 - y, 0.5 + z$

Table 4 Crystal data, experimental conditions, and refinements

	$[\text{InCl}_3(\text{C}_3\text{H}_7\text{NO})_3]$ 1	$[\text{InCl}_3(\text{C}_4\text{H}_9\text{NO})_3]$ 2	$[\text{InCl}_3(\text{C}_7\text{H}_6\text{O})_3] \cdot \text{C}_7\text{H}_6\text{O}$ 3	$[\text{InCl}_3(\text{C}_8\text{H}_8\text{O})_2]$ 4
<i>M</i>	440.5	482.4	1185.1	461.4
Crystal size/mm	$0.84 \times 0.8 \times 0.24$	$0.21 \times 0.18 \times 0.24$	$0.24 \times 0.18 \times 0.26$	$0.46 \times 0.42 \times 0.36$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group ( <i>Z</i> )	$P2_1/m(4)$	$P2_1/m(2)$	$P2_1/m(4)$	$C2/c(4)$
<i>a</i> /Å	9.987(3)	8.545(4)	19.530(7)	10.929(3)
<i>b</i> /Å	13.379(4)	14.113(8)	12.448(5)	13.480(5)
<i>c</i> /Å	13.193(6)	9.274(5)	22.391(9)	13.638(4)
$\beta$ /°	91.16(3)	116.47(4)	113.78(3)	112.57(2)
<i>U</i> /Å <sup>3</sup>	1762.4(1.1)	1001.2(9)	4981.3(3.4)	1855.4(1.1)
<i>D<sub>c</sub></i> ( <i>D<sub>m</sub></i> ) <sup>a</sup> /g cm <sup>-3</sup>	1.661(1.63)	1.60(1.55)	1.580	1.652
<i>F</i> (000)	880	488	2368	912
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	17.91	15.78	12.83	16.93
$\omega$ scan; $2\theta$ range/°	4–50	4–52	4–60	4–55
Range <i>h</i>	0–12	0–11	–26 to 26	–14 to 1
Range <i>k</i>	0–16	0–18	0–17	0–17
Range <i>l</i>	–16 to 16	–12 to 12	0–31	–16 to 17
<i>R</i> <sub>int</sub>	0.0193	0.0099	0.0949	0.019
Reflections total (unique)	2639	2061	7564	2134
Reflections used <sup>b</sup>	2327	1743	2382	2013
Transmission range	0.771–0.442	0.874–0.777	0.724–0.668	0.762–0.645
Parameters refined	172	169	297	101
Weighting factor <i>g</i> <sup>c</sup>	0.0004	0.000 17	0.0012	0.0006
Residual density/e Å <sup>-3</sup>	0.40, –0.44	0.37, –0.64	1.21, –1.30	0.64, –1.06
<i>S</i>	1.36	1.26	1.16	1.52
<i>R</i> ( <i>R'</i> ) <sup>d</sup>	0.0256 (0.0340)	0.0252 (0.0293)	0.0620 (0.0711)	0.0275 (0.0410)
$\Delta/\sigma_{\text{max}}$	< 0.001	0.006	< 0.001	< 0.001

<sup>a</sup> *D<sub>m</sub>* measured at room temperature. <sup>b</sup>  $I > 3\sigma(I)$ . <sup>c</sup> Values obtained by trial determination. <sup>d</sup>  $R = \Sigma(|F_o| - |F_c|)/\Sigma F_o$ ;  $R' = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$ .

Table 5 Atomic coordinates ( $\times 10^4$ ) for complexes 1-4

Atom	x	y	z	Atom	x	y	z
<b>[InCl<sub>3</sub>(dmf)<sub>3</sub>] 1</b>							
In	699(1)	2 430(1)	2 041(1)	C(1)	1 313(3)	4 040(2)	418(2)
Cl(1)	1 381(1)	1 108(1)	3 216(1)	C(11)	513(3)	4 027(2)	-1 317(2)
Cl(2)	-1 716(1)	2 363(1)	2 230(1)	C(12)	2 503(3)	5 038(2)	-794(3)
Cl(3)	1 143(1)	3 899(1)	3 084(1)	C(2)	3 573(3)	1 816(2)	1 412(2)
O(1)	423(2)	3 432(1)	693(2)	C(21)	5 046(4)	2 813(3)	394(3)
O(2)	2 781(2)	2 536(1)	1 505(2)	C(22)	5 616(3)	1 053(2)	832(2)
O(3)	640(2)	1 296(1)	812(2)	C(3)	67(3)	1 428(2)	-35(2)
N(1)	1 427(3)	4 367(2)	-508(2)	C(31)	1 778(3)	563(2)	-941(3)
N(2)	4 690(3)	1 887(2)	916(2)	C(32)	-197(4)	1 260(2)	-1 848(3)
N(3)	518(3)	1 096(2)	-891(2)				
<b>[InCl<sub>3</sub>(dma)<sub>3</sub>] 2</b>							
In	2 042(1)	2 500	8 492(1)	C(11)	57(5)	1 116(3)	12 069(4)
Cl(1)	2 113(1)	1 175(1)	6 797(1)	C(12)	2 227(5)	-160(3)	13 195(4)
Cl(2)	5 146(1)	2 500	10 370(1)	C(13)	3 623(5)	299(3)	10 971(5)
N(1)	1 517(3)	604(2)	12 022(3)	C(2)	-2 063(5)	2 500	5 928(5)
N(2)	-3 680(4)	2 500	5 799(4)	C(21)	-5 272(6)	2 500	4 286(6)
O(1)	1 422(3)	1 515(2)	10 028(3)	C(22)	-3 960(5)	2 500	7 248(5)
O(2)	-809(4)	2 500	7 313(3)	C(23)	-1 795(6)	2 500	4 443(5)
C(1)	2 121(4)	847(2)	10 984(4)				
<b>[{InCl<sub>3</sub>(PhCHO)<sub>3</sub>]<sub>2</sub>·PhCHO 3</b>							
In(1)	7 022(1)	2 427(2)	3 301(1)	C(34)	5 348(15)	-871(23)	644(10)
In(2)	3 050(1)	2 447(2)	1 847(1)	C(35)	5 884(17)	-286(22)	1 154(11)
Cl(1)	7 603(4)	3 134(6)	2 627(3)	C(36)	5 676(14)	424(19)	1 529(9)
Cl(2)	7 599(4)	685(6)	3 643(3)	C(4)	3 860(15)	3 013(21)	902(11)
Cl(3)	7 620(4)	3 477(6)	4 279(3)	C(41)	5 202(14)	3 254(20)	1 162(10)
Cl(4)	2 456(4)	1 816(6)	2 534(3)	C(42)	5 746(17)	3 486(24)	942(11)
Cl(5)	2 483(4)	4 184(6)	1 498(3)	C(43)	5 575(18)	3 686(26)	300(12)
Cl(6)	2 454(4)	1 347(6)	897(3)	C(44)	4 844(17)	3 683(26)	-166(12)
O(1)	6 117(9)	1 981(12)	3 658(6)	C(45)	4 292(12)	3 448(18)	57(9)
O(2)	6 124(9)	3 696(14)	2 844(6)	C(46)	4 440(14)	3 251(22)	707(9)
O(3)	6 137(9)	1 592(14)	2 422(7)	C(5)	3 851(14)	239(21)	2 420(10)
O(4)	3 941(9)	2 844(12)	1 463(6)	C(51)	4 223(14)	-1 582(20)	2 819(10)
O(5)	3 958(10)	1 170(15)	2 302(7)	C(52)	4 777(12)	-2 354(26)	3 137(9)
O(6)	3 944(9)	3 281(14)	2 717(6)	C(53)	5 495(16)	-2 068(22)	3 358(10)
C(1)	6 208(14)	1 815(19)	4 221(10)	C(54)	5 695(16)	-1 041(22)	3 283(10)
C(11)	4 846(14)	1 667(20)	3 994(10)	C(55)	5 166(16)	-272(23)	2 976(10)
C(12)	4 300(16)	1 504(22)	4 200(10)	C(56)	4 411(14)	-545(20)	2 734(10)
C(13)	4 463(15)	1 328(22)	4 857(10)	C(6)	3 838(14)	4 005(20)	3 064(9)
C(14)	5 251(15)	1 292(23)	5 312(11)	C(61)	5 148(16)	4 408(22)	3 697(10)
C(15)	5 809(16)	1 441(22)	5 101(11)	C(62)	5 722(16)	4 943(22)	4 186(10)
C(16)	5 615(12)	1 660(19)	4 437(9)	C(63)	5 492(17)	5 732(25)	4 526(11)
C(2)	6 264(14)	4 619(21)	2 705(10)	C(64)	4 769(16)	5 934(24)	4 414(11)
C(21)	5 917(15)	6 387(21)	2 208(10)	C(65)	4 216(16)	5 363(22)	3 916(10)
C(22)	5 337(14)	7 112(21)	1 849(10)	C(66)	4 394(15)	4 634(21)	3 562(10)
C(23)	4 573(14)	6 848(21)	1 611(10)	O(7)	2 545(11)	8 710(17)	-1 321(9)
C(24)	4 366(16)	5 857(23)	1 774(11)	C(7)	2 525(14)	7 853(23)	-1 066(11)
C(25)	4 903(16)	5 121(22)	2 129(11)	C(71)	2 495(16)	6 664(22)	-227(11)
C(26)	5 691(15)	5 402(22)	2 352(10)	C(72)	2 514(16)	6 470(25)	378(12)
C(3)	6 261(15)	972(22)	2 065(10)	C(73)	2 561(15)	7 329(25)	778(12)
C(31)	4 925(15)	558(22)	1 414(10)	C(74)	2 564(15)	8 371(25)	593(12)
C(32)	4 402(16)	-17(23)	917(11)	C(75)	2 558(18)	8 567(21)	-50(13)
C(33)	4 588(16)	-746(24)	544(1)	C(76)	2 530(12)	7 690(21)	-436(9)
<b>[InCl<sub>3</sub>(PhCOMe)<sub>2</sub>] 4</b>							
In(1)	0	757(1)	2 500	C(2)	2 857(3)	2 375(2)	3 209(2)
Cl(1)	0	-977(1)	2 500	C(12)	6 027(3)	-471(2)	4 037(2)
Cl(2)	168(1)	1 644(1)	4 041(1)	C(13)	7 085(3)	185(3)	4 337(2)
O(1)	2 218(2)	665(1)	3 038(2)	C(14)	6 869(3)	1 203(3)	4 302(2)
C(1)	3 127(2)	1 284(2)	3 275(2)	C(15)	5 581(2)	1 570(2)	3 961(2)
C(11)	4 740(3)	-112(2)	3 684(2)	C(16)	4 511(2)	920(2)	3 643(2)

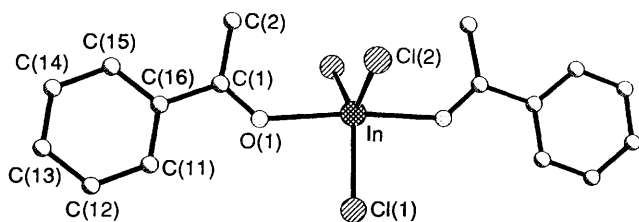


Fig. 4 The molecule  $[\text{InCl}_3(\text{PhCOMe})_2]$ , with the In-Cl(1) bond providing the  $C_2$  axis. The atoms of the ligand molecules are almost coplanar with InCl(1)O(1)O(1'). A spreading of the O(1)-In-O(1') angle arising from  $\text{CH}_3 \cdots \text{Cl}(2)/\text{Cl}(2')$  repulsions is apparent

hydrogen atoms were refined anisotropically. For **3** only In and Cl could be treated anisotropically. Hydrogen atoms, though almost always located, were held to idealised positions with constant thermal parameters. The SHELXTL PC package of integrated programs was used for data processing, structure solution and refinement.<sup>18</sup> Atomic coordinates are given in Table 5, with the more significant bond lengths and angles in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

#### Acknowledgements

The authors are grateful to Dr. R. G. A. R. Maclagan for running HF 6-31 G\* calculations and to Dr. H. K. J. Powell for use of the stability constant database. One of us (S. J.) participated during leave from the Changchun Institute for Applied Chemistry, Changchun, China.

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Received 9th March 1993; Paper 3/01404E