

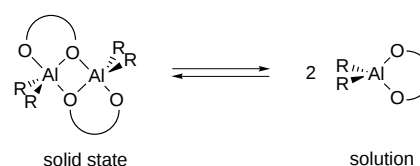
Structure investigation of dimethyl-aluminium, -gallium and -indium *O,O'*-chelate complexes in solution and the solid state. Molecular structure of five-co-ordinated $[\text{Me}_2\text{M}(\mu\text{-OC}_6\text{H}_4\text{CO}_2\text{Me-2})]_2$ adducts

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The reaction of trimethyl-aluminium, -gallium and -indium with an equimolar amount of methyl salicylate, 2-(HO)C₆H₄CO₂Me (Hmesal), gives $[\text{Me}_2\text{M}(\text{mesal})]_n$ chelate complexes in high yield (where $n = 1$ or 2, $\text{M} = \text{Al}$ **1** or Ga **2**; $n = 2$, $\text{M} = \text{In}$ **3**). The resulting compounds have been characterised in solution by NMR and IR spectroscopy as well as by cryoscopic molecular weight determinations in benzene; their molecular structures in the solid state were determined by single-crystal X-ray diffraction techniques. All three compounds are dimeric in the solid state, with five-co-ordinated metal centres. The deformation of the metal centre co-ordination sphere is discussed. In solution compounds **1** and **2** are monomeric, four-co-ordinated chelate complexes while **3** retains its dimeric structure. On the basis of the structural observation resulting from this study and with respect to related compounds the following sequence of the Group 13 metal centre Lewis acidity, in four-co-ordinated diorganometallic *O,O'*-chelate complexes is proposed: $\text{In} \geq \text{Al} > \text{Ga}$.

The past decade has brought a considerable increase in the number of examples of simple neutral monomeric five- and six-co-ordinated organometallic complexes of the Group 13 metals.^{1,2} The results indicate that the formation of compounds with higher co-ordination numbers is not limited to those containing macrocyclic ligands, and Group 13 organometallic chemistry has considerably broadened beyond the sphere of four-co-ordinated compounds that dominated previously. A large group of $[\text{R}_2\text{M}(\text{O},\text{X})]_2$ -type chelate complexes ($\text{M} = \text{Al}$, Ga or In, and $\text{O},\text{X} = \text{O},\text{O}'$ - or O,N -bidentate ligand), where diorganometallic alkoxides form oxygen-bridged dimers consisting of five-co-ordinated metal centres, are known.^{3,4} These Group 13 organometallic chelate complexes potentially create interesting possibilities for comparative studies of the reactivity of four- and five-co-ordinated compounds. In a previous paper we discussed the influence of *O,O'*-bidentate ligands on the structure of dialkylaluminium *O,O'*-chelate complexes in solution and in the solid state.⁴ Although this group of compounds has a tendency to form $[\text{R}_2\text{Al}(\text{O},\text{O})]_2$ -type adducts with five-co-ordinated metal centres in the solid state, in solution they exhibit a considerably greater structural variety depending on the nature of the chelating ligand. For instance, we have elucidated the electronic factors determining the rearrangement from the five-co-ordinated adduct to the four-co-ordinated monomeric chelate complex upon dissolution (Scheme 1).⁴ Such a rearrangement occurs for compounds with unsaturated *O,O'*-bidentate ligands, where the π interaction of the alkoxide oxygen lone electron pair with the chelate ligand unsaturated bond system considerably weakens the Lewis basicity of the bridging oxygen and simultaneously strengthens the basicity of the chelating oxygen owing to π delocalization. The role played by the nature of the bidentate ligand in related gallium and indium derivatives is less clear, because there are very few examples of structurally well characterised dialkylgallium *O,O'*-chelate complexes^{3f-3r} and only two examples of related indium compounds.^{3s,t} In view of this, it is of interest to know whether the factors affecting the structure of dialkylaluminium chelate complexes can be extended to gallium and indium derivatives. In this paper we present the structural investigation of the

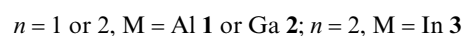


Scheme 1

Group 13 metal ($\text{M} = \text{Al}$, Ga or In) diorganometallic chelate complexes with the methyl salicylate anion (an unsaturated *O,O'*-bidentate ligand with a π conjugated system) in solution and in the solid state.

Results and Discussion

The interaction of Me_3M ($\text{M} = \text{Al}$, Ga or In) with an equimolar amount of methyl salicylate (Hmesal) results in the quantitative evolution of methane and formation of diorganometallic *O,O'*-chelate complexes according to equation (1). We reported



previously that the addition of 2 equivalents of Hmesal to Me_3Al yielded a monomeric five-co-ordinated chelate complex $\text{MeAl}(\text{mesal})_2$.^{2b} It should be noted that when similar reactions were attempted under identical conditions with trimethylgallium and trimethylindium, only the products corresponding to a 1 : 1 stoichiometry were obtained. Compounds **1**, **2** and **3** are stable as solids or in solution under an inert atmosphere. The resulting compounds have been characterised in solution by NMR and IR spectroscopy and by cryoscopic molecular weight measurements. The molecular structures of **1**, **2** and **3** have been determined by X-ray crystallography; selected bond lengths and angles are given in Table 1.

Structure of $[\text{Me}_2\text{Al}(\text{mesal})]_n$ **1**

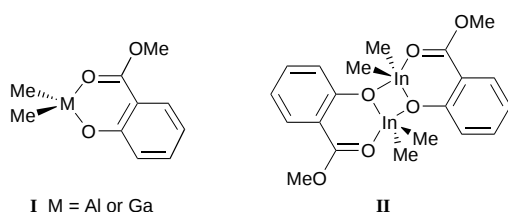
The ¹H NMR spectrum of complex **1** shows single resonances of Al-CH₃ and O-CH₃ protons and three well separated multiplets for the aromatic protons. The ²⁷Al NMR spectrum con-

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Table 1 Selected bond distances (Å) and angles (°) for [R₂M(O,O')]₂-type adducts studied and reported in the literature*

	1 [Me ₂ - Al(mesal)] ₂	2 [Me ₂ - Ga(mesal)] ₂	3 [Me ₂ - In(mesal)] ₂	4 ^{3f} [Me ₂ - Ga(salal)] ₂	5 ^{3f} [Me ₂ - In(salal)] ₂	6 ⁴ [Et ₂ - Al(trop)] ₂	7 ³ⁿ [Me ₂ - Ga(trop)] ₂	8 ^{3c} [Et ₂ - Al(gw)] ₂	9 ^{3c} [Me ₂ - Ga(gw)] ₂
M–O(1)	1.850(2)	1.924(2)	2.165(4)	1.927	2.188	1.902	1.974	1.859	1.957
M–O(2)	2.003(2)	2.157(2)	2.332(5)	2.120	2.341	1.936	2.025	1.952	2.046
M–O(1')	2.082(2)	2.354(2)	2.376(4)	2.462	2.383	2.093	2.463	2.249	2.521
M–C	1.952	1.947	2.19	1.939	2.122	1.971	1.960	1.955	1.946
O(1)–M–C(1)	114.93(14)	111.59(14)	104.2(4)	110.5	109.0	116.6	110.6	118.0	113.7
O(1)–M–C(2)	115.65(14)	111.73(14)	108.1(3)	111.9	109.1	118.3	112.9	117.5	111.3
C(1)–M–C(2)	129.4(2)	136.4(2)	147.6(5)	136.6	141.9	124.8	133.3	123.2	132.5
O(2)–M–O(1')	164.74(6)	162.58(7)	154.8(2)	164.4	154.7	151.9	150.0	150.4	145.8
O(2)–M–O(1)	88.61(6)	86.93(8)	78.7(2)	88.9	79.9	79.9	79.1	75.2	70.1
O(1)–M–O(1')	76.14(6)	75.66(8)	76.1(2)	75.5	74.8	72.1	71.0	73.3	75.6
M–O(1)–C(9)	132.54(13)	132.4(2)	134.0(4)	131.0	133.7	117.5	117.1	124.0	126.7
O(1)–C(9)–C(4)	122.5(2)	124.5(2)	125.6(5)	123.1	123.2	111.4	113.7	116.7	120.2
C(9)–C(4)–C(3)	121.5(2)	122.4(2)	123.1(5)	124.4	126.0	—	—	—	—
C(4)–C(3)–O(2)	124.8(2)	126.0(2)	126.7(6)	127.4	128.5	114.4	115.3	112.2	112.7
C(3)–O(2)–M	130.00(14)	127.7(2)	131.8(5)	125.1	128.2	116.7	114.9	111.9	109.0

* The literature values are presented according to the atom numbering scheme used in this work; Hsalal = salicylaldehyde, Htrop = α -tropolone (2-hydroxycyclohepta-2,4,6-trienone), Hgw = 2-methoxyphenol.



tains one resonance at δ 152, typical for a four-co-ordinated aluminium atom.⁵ The molecular weight determined for **1** by the cryoscopic method in benzene corresponds to a monomeric structure. In the IR spectrum of **1** in CH₂Cl₂ solution the carbonyl group stretching vibration bands are shifted towards higher frequencies as compared to those of free Hmesal, which indicates a co-ordination of this group to the aluminium atom. These results unequivocally confirm the monomeric structure of **1** in solution and are consistent with the tetrahedral chelate structure **I**.

In the solid state compound **1** has a dimeric structure, which has been confirmed by X-ray studies. The molecular structure of adduct **1** is shown in Fig. 1. The asymmetric unit comprises one half of the dimer, the other half being generated by the centre of symmetry on (0,0,0). Thus, the overall molecular symmetry is crystallographically constrained to be centrosymmetric with five-co-ordinated aluminium atoms. The two monomeric molecules are linked *via* oxygen bridges, which are formed by aryloxy oxygen atoms of the methyl salicylate anion. The resulting dimer features a nearly planar system of five fused rings. The largest deviation from this plane is 0.043(2) Å for the C(5) atom. The geometry of the aluminium co-ordination sphere can be described as a distorted trigonal bipyramid (*TBPY*). The equatorial plane is defined by the C(1) and C(2) carbon atoms and the aryloxy oxygen O(1). The Al(1) atom lies almost exactly in this plane with a negligible displacement of 0.026(1) Å towards the O(2) atom. The equatorial angles range from 114.9(1) to 129.4(2)°, the latter being the angle between the methyl groups. The axial positions are occupied by the O(2) atom of the carbonyl group and the aryloxy O(1') atom of the second monomeric molecule. The angle between the axial substituents is 164.74(6)°. The deformation of the aluminium co-ordination sphere from *TBPY* geometry is caused by constraints resulting from the presence of a four-membered Al₂O₂ central ring. As is shown in Fig. 2(a) the deviation of the internal axial Al–O bonds from a normal to the equatorial plane is significant only for the bond involved in the Al₂O₂ ring [13.0(1)°]. The deviation of the second axial

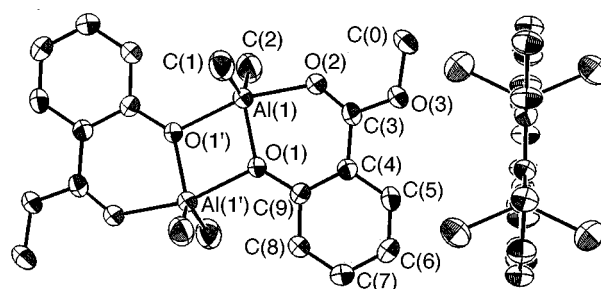


Fig. 1 An ORTEP⁶ diagram of [Me₂Al(mesal)]₂ **1** showing a 50% probability of thermal ellipsoids; view perpendicular and parallel to the Al₂O₂ plane. Hydrogen atoms are omitted for clarity

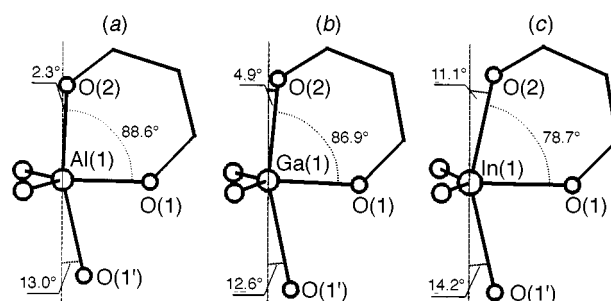


Fig. 2 Geometry of the co-ordination sphere of metal centres in adducts **1–3**

bond, being part of the six-membered chelating ring, is slight [2.3(1)°].

Owing to the participation of the O(1) atom in the formation of bridging bonds, the aryloxy Al(1)–O(1) [1.850(2) Å] and the ester Al(1)–O(2) [2.003(2) Å] bond distances in **1** are longer than the corresponding Al–O bond distances [1.773(2) and 1.968(1) Å, respectively] in the monomeric five-co-ordinated alkylaluminium compound with two chelating mesal ligands, MeAl(mesal)₂, where the aryloxy oxygen atom does not form bridging bonds.^{2b} The internal axial Al(1)–O(1') bond (bridging bond) [2.082(2) Å] is longer than the external axial Al(1)–O(2) bond. Thus, the internal axial bond joining two monomeric units is the weakest Al–O bond and undergoes cleavage upon dissolution of the solid in benzene or in other organic solvents. Weakening of the Al(1)–O(1') bond is due to the reduced Lewis basicity of the bridging aryloxy oxygen atoms resulting from the conjugation of the oxygen lone pair with the aromatic ring.

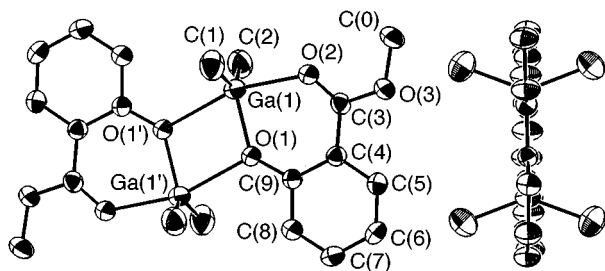


Fig. 3 An ORTEP diagram of $[\text{Me}_2\text{Ga}(\text{mesal})]_2$, **2** showing a 50% probability of thermal ellipsoids; view perpendicular and parallel to the Ga_2O_2 plane. Hydrogen atoms are omitted for clarity

The Al–O, C–O and C–C bond lengths observed in **1** are consistent with the fact that both functional groups of mesal are involved in the conjugated bond system within the chelate.

Structure of $[\text{Me}_2\text{Ga}(\text{mesal})]_n$, **2**

Compound **2** has the monomeric chelate structure **I** in solution, which was confirmed on the basis of cryoscopic molecular weight investigations and IR spectroscopy. In the ^1H NMR spectrum of **2** a downfield shift of the Ga–CH₃ and O–CH₃ resonances was observed as compared to those of the related aluminium compound (see Experimental section). However, compound **2** crystallises as a dimer, as indicated in Fig. 3. The atomic arrangement in the crystal of adduct **2** is entirely analogous to that found in **1**, the unit cell dimensions of these two crystals are nearly the same. The largest differences are observed for the metal–oxygen bond length, while the metal–carbon bond distances are comparable in both compounds. The Ga(1)–O(1) bond distance in the equatorial plane [1.924(2) Å] is only slightly longer than the corresponding bond distance in **1** (the difference is 0.074 Å), while the external axial Ga(1)–O(2) bond distance [2.157(2) Å] is longer by 0.154 Å and the internal axial Ga(1)–O(1') bond distance [2.354(2) Å] longer by 0.272 Å (Table 1). Since the Ga and Al covalent radii are very similar (1.25 Å)⁷ the significant lengthening of the axial Ga–O bonds observed in adduct **2** indicates that the gallium atom in the four-co-ordinated dimethylgallium chelate complex is a much weaker Lewis acid in comparison with the aluminium atom in the related complex. Thus, the remarkable lengthening of the Ga–O bonds linking the monomeric units (the lengths of these bonds are comparable with those of corresponding bonds in the dimethylindium analogue, despite the fact that the atomic radius of gallium is much smaller than that of indium, see below) results from the low Lewis acidity of the gallium atom and not from steric hindrance, as had been suggested previously when analysing the structure of the salicylaldehyde dialkylgallium derivative.^{3f} The deformation of the gallium co-ordination sphere in adduct **2** with respect to the *TBPY* geometry is similar to that observed in the related aluminium compound. The equatorial angles range from 111.6(1) to 136.4(2)°, the latter being the angle between the methyl groups. In the case of **2** some displacement [0.0595(4) Å] of the gallium atoms from the equatorial plane towards the O(2) chelating atom is observed. The angle formed by the axial bonds, O(2)–Ga(1)–O(1'), is 162.58(7)° and the difference in comparison to the ideal value of 180° is mainly caused by the inclination of the Ga(1)–O(1') bond being part of the central four-membered Ga₂O₂ ring [Fig. 2(b)]. On the other hand, despite the considerable lengthening of the Ga–O bonds, the O(1)–Ga(1)–O(2) angle in the six-membered heterocyclic ring and deviation of the axial Ga(1)–O(2) bond from a normal to the equatorial plane are comparable with the corresponding values in adduct **1**. This is possible owing to an increase in the O(1)–C(9)–C(4) and C(9)–C(4)–C(3) angles within the chelating mesal ligand of **2**, which is illustrated by a comparison of corresponding angle values in both compounds (Table 1).

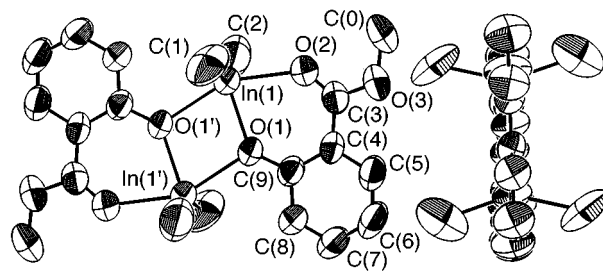


Fig. 4 An ORTEP diagram of $[\text{Me}_2\text{In}(\text{mesal})]_2$, **3** showing a 50% probability of thermal ellipsoids; view perpendicular and parallel to the In_2O_2 plane. Hydrogen atoms are omitted for clarity

Structure of $[\text{Me}_2\text{In}(\text{mesal})]_2$, **3**

Compound **3** has the dimeric structure **II** in solution, contrary to the analogous aluminium and gallium derivatives, which was confirmed on the basis of cryoscopic molecular weight investigations. In the IR spectrum of **3** in CH_2Cl_2 the frequency of the carbonyl group stretching vibration band is consistent with the co-ordination of the ester group to indium. In the ^1H NMR spectrum of **3** one can observe a further downfield shift of the In–CH₃ and O–CH₃ methyl proton resonances. The dimeric structure of this compound in the solid state is however in agreement with the structures of the aluminium and gallium adducts described above.

The molecular structure of **3** is shown in Fig. 4. The structure is centrosymmetric with five-co-ordinated indium atoms. The resulting dimer also features a nearly planar system of five fused rings. The largest deviation from this plane is 0.045(7) Å for the C(5) atom. In **3** an elongation of the In–C and In–O bonds is observed within the $\text{Me}_2\text{In}(\text{mesal})$ unit with respect to corresponding bonds in the aluminium and gallium adducts **1** and **2** (Table 1). This elongation of bonds in the indium derivative can be attributed to the larger covalent radius of indium (1.50 Å)⁷ with respect to aluminium and gallium. There is one remarkable exception, the In(1)–O(1') [2.376(4) Å] bond linking the two monomeric units has a length comparable to that of the corresponding Ga–O bond, which clearly indicates a larger Lewis acidity of indium in comparison with that of gallium in a four-co-ordinated chelate complex. The internal axial bond (bridging one) in **3** is only slightly longer than the external axial In(1)–O(2) bond and this bridging bond is strong enough to maintain a dimeric structure in solution.

The geometry of the indium co-ordination sphere can be described as a highly distorted trigonal bipyramid. The distortions in **3** are the largest among the compounds studied. The most significant deviation from the *TBPY* geometry is found in the O(2)–In(1)–O(1') angle [154.8(2)°] and represents the constraints imposed by both the central four-membered In_2O_2 and the six-membered InOCCCO rings. As shown in Fig. 2(c) both axial bonds in **3** are inclined from the normal to the equatorial plane essentially to the same extent. The deviation of the internal axial In(1)–O(1') bond is consistent with the results observed for the aluminium and gallium derivatives. On the other hand, the inclination from the ideal value of the external axial bond results from strains in the six-membered chelate ring, upon which considerable elongation of the In–O bonds occurs. This elongation is so large that it cannot be compensated by an increase in the bond angle values within the chelate. The O(1)–In(1)–O(2) angle [78.7(2)°] in the six-membered heterocyclic ring is in the range typical for corresponding angles in aluminium and gallium derivatives with a five-membered MOCCO chelate ring: $[\text{Et}_2\text{Al}(\text{trop})]_2$, **6**,⁴ $[\text{Et}_2\text{Al}(\mu\text{-OC}_6\text{H}_4\text{OMe-2})]_2$, **8**,^{3c} $[\text{Me}_2\text{Ga}(\mu\text{-OC}_6\text{H}_4\text{OMe-2})]_3$, **9**^{3c} (see Table 1). Thus, the elongation of the In–O bonds and limited flexibility of the chelating mesal ligand causes a considerable deformation of the co-ordination sphere of indium.

It is worthy to note that anisotropic thermal parameters

observed for **3** are very high and far larger than those observed for **1** and **2**. The value of these parameters is especially high in the direction perpendicular to the mean molecule plane and for methyl carbon atoms C(1), C(2) and the O(2) atom. In our opinion these high thermal parameters result from the non-rigidity of the indium complex due to the constraints within the chelate mesal ring mentioned above.†

Although the indium atom lies essentially in the plane defined by the C(1), C(2) and O(1) atoms, another significant deviation from the *TBPY* geometry is found for the bond angle within this equatorial plane. The two equatorial O–In–C bond angles are 104.2(4) and 108.1(3)°, and the C(1)–In(1)–C(2) angle is as large as 147.6(5)°. The question of which factor influences the value of the C–In–C angle cannot be answered unequivocally. However, this widening of the C–In–C angle in **3** fits well to that for analogous angles in other five-co-ordinated monomeric and dimeric diorganotin chelate compounds, where these angles fall in the range 134.8–153.3°. ^{1c,2i,3s,t} Comparison of the bond angles for five-co-ordinated diorganometallic adducts consisting of five- and six-membered chelate rings shows that there are minor changes at the C–M–C angle as a result of changes in geometrical constraints imposed by different heterocyclic rings (not greater than 6.2°, see Table 1). It should be noted that significant widening of the C–M–C angle in dimeric five-co-ordinated diorganometallic compounds is observed when passing from Al to Ga and In derivatives. Thus, the electron-pair repulsion of the M–C bonds may affect the C–M–C angles. It is worth noting that the C–In–C angle in four-co-ordinated dialkylindium compounds varies significantly, from 110.8(3) to 152.2(6)°, and there is some indication that this angle is sensitive to the degree of aggregation and to the substituents on the bridging moiety.⁸

Conclusion

The differences in the M–O bond lengths in the dimeric structures of **1**, **2** and **3** discussed above indicate that the monomeric dimethylgallium chelate complex forms the weakest adduct and gallium is the weakest Lewis acid metal centre in $[R_2M(O,O')]_n$ -type complexes. Further, despite the fact that the $[Me_2In(mesal)]_2$ adduct maintains a dimeric structure and $[Me_2Al(mesal)]_2$ dissociates to a monomeric complex in solution, the related tropolonato derivatives $[Et_2Al(trop)]$ **6**⁴ and $[Me_2In(trop)]$ **3**ⁿ occur as monomers in solution. Thus, it is reasonable to conclude that the Lewis acidities of the aluminium and indium atoms in diorganometallic chelate complexes are similar to one another. These structural observations lead to the following order of the Lewis acidity of the Group 13 metal centres in four-co-ordinated diorganometallic *O,O'*-chelate complexes: In ≥ Al > Ga. This sequence contradicts the commonly presented order of Group 13 metal acidity Al > Ga > In, which remains valid for the metal Lewis acidity in the adduct formation reactions from three- to four-co-ordinated compounds.⁹ Thus, various metals may display different susceptibility towards the Lewis acidity changes depending on the nature and number of co-ordinated ligands.

It should be noted that methyl salicylate and tropolonate anions are chelating ligands consisting of two bonding oxygens connected by a π conjugated system, which leads to weakening

of the alkoxide oxygen (bridging one) Lewis basicity and simultaneous strengthening of the carbonyl oxygen (chelating one) basicity. As we have recently reported, dialkylaluminium compounds with this type of chelating ligand, where simultaneous weakening of the internal axial Al–O bond (bridging one) and strengthening of the external axial Al–O bond occur owing to the π interaction, afford monomeric $[R_2Al(O,O')]_n$ -type chelate complexes in solution.⁴ Thus our consideration concerning the Lewis acidity of the Group 13 metal in four-co-ordinated diorganometallic *O,O'*-chelate complexes indicates that a similar structural effect may be expected for the analogous gallium complexes, while the structure of the related indium compounds appears not to be fully correlated with the aluminium derivatives. In further papers we will show how the degree of aggregation of diorganometallic chelate complexes influences the reactivity with Lewis bases and acids.

Experimental

All operations were carried out under nitrogen. Solvents were purified and dried by standard techniques. Trimethylaluminium, -gallium, and -indium and methyl salicylate were distilled before use. Standard Schlenk-line techniques were employed. The NMR spectra were recorded on a Varian 300VXL spectrometer. Chemical shifts are reported relative to external SiMe₄ (for H) and $[Al(H_2O)_6]^{3+}$ (for Al). The IR spectra were recorded on a Specord-75IR spectrophotometer. Molecular weight measurements were carried out cryoscopically in benzene.

Preparations

[Me₂Al(mesal)]_n 1. Methyl salicylate (1.07 g, 7.0 mmol) was dissolved in toluene (10 cm³) and Me₃Al (0.50 g, 7.0 mmol) was added dropwise at –78 °C. After the addition was completed the reaction mixture was allowed to warm to room temperature. The solvent was then removed under vacuum, leaving a white solid that was crystallised from a toluene–hexane solution at 0 °C. Yield: 85% (Found: C, 57.7; H, 6.4; Al, 12.9. Calc. for C₁₀H₁₃AlO₃: C, 57.7; H, 6.3; Al, 13.0%). ¹H NMR (C₆D₆): δ 0.24 (6 H, s, Al–CH₃), 3.17 (3 H, s, O–CH₃), 6.40 (1 H, t, CH), 6.98 (1 H, d, CH), 7.10 (1 H, t, CH), 7.60 (1 H, d, CH). ²⁷Al NMR (C₆D₆): δ 152. IR (CH₂Cl₂): $\tilde{\nu}_{C=O}$ = 1655 and 1643 cm^{–1}. Molecular weight (benzene): Found 209, Calc. 208.2.

[Me₂Ga(mesal)]_n 2. The reaction was carried out by using the same procedure as described for **1**, using methyl salicylate (1.14 g, 8.4 mmol) and Me₃Ga (0.96 g, 8.4 mmol). The solid was isolated and purified as described for **1**. The yield was essentially quantitative (Found: C, 47.9; H, 5.3; Ga, 27.6. Calc. for C₁₀H₁₃GaO₃: C, 47.9; H, 5.2; Ga, 27.8%). ¹H NMR (C₆D₆): δ 0.04 (6 H, s, Ga–CH₃), 3.03 (3 H, s, O–CH₃), 6.43 (1 H, t, CH), 7.03 (1 H, d, CH), 7.12 (1 H, t, CH), 7.62 (1 H, d, CH). IR (CH₂Cl₂): $\tilde{\nu}_{C=O}$ = 1659 and 1647 cm^{–1}. Molecular weight (benzene): Found 251, Calc. 250.9.

[Me₂In(mesal)]₂ 3. The preparation was the same as described for **1**, using methyl salicylate (1.04 g, 6.8 mmol) and Me₃In (1.09 g, 6.8 mmol). The yield was essentially quantitative (Found: C, 40.7; H, 4.5; In, 38.7. Calc. for C₁₀H₁₃InO₃: C, 40.6; H, 4.4; In, 38.8%). ¹H NMR (C₆D₆): δ 0.32 (6 H, s), 3.24 (3 H, s), 6.52 (1 H, t), 7.13 (2 H, m), 7.71 (1 H, d). IR (CH₂Cl₂): $\tilde{\nu}_{C=O}$ = 1664 cm^{–1}. Molecular weight (benzene): Found 592, Calc. 296.0 (monomer).

Crystallography

The crystallographic data, the parameters for data collection, and the refinement procedure for compounds **1**, **2** and **3** are given in Table 2.

Data collection and processing. X-Ray data were collected on a Siemens P3 four-circle diffractometer at room temperature. Crystals of **1**, **2**, and **3** suitable for an X-ray structure deter-

† It can be assumed that for **3** constraints within the chelate ring cause it to adopt a non-planar structure due to twisting of the ester group along the C(4)–C(9) bond. This causes a deviation from planarity of other atoms of the five-fused rings system. As a consequence, the adduct becomes non-rigid with oscillations of the atoms in a perpendicular direction to the mean molecular plane. When analysing temperature factors it can be assumed that the oscillations are a superposition of the ester group twisting along the C(4)–C(9) bond and twisting in the molecule along the C(3)–C(4) and C(3')–C(4') bonds. Such a direction of oscillations is indicated by the relatively small values of temperature factors for C(3), C(4) and C(9) atoms, and especially high for the C(1), C(2) and O(2) atoms.

Table 2 X-Ray data collection and structure analysis parameters for adducts 1–3*

	1	2	3
Formula	C ₂₀ H ₂₆ Al ₂ O ₆	C ₂₀ H ₂₆ Ga ₂ O ₆	C ₂₀ H ₂₆ In ₂ O ₆
<i>M</i>	416.39	501.87	592.06
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)
<i>a</i> /Å	7.4602(12)	7.4351(12)	10.072(3)
<i>b</i> /Å	8.887(2)	8.8401(12)	14.498(4)
<i>c</i> /Å	9.377(2)	9.6474(12)	9.099(2)
α /°	78.30(2)	79.323(11)	
β /°	66.887(14)	67.674(11)	106.60(2)
γ /°	70.55(2)	69.696(11)	
<i>U</i> /Å ³	537.3(2)	549.07(13)	1273.4(6)
<i>T</i> /K	293(2)	298(2)	293(2)
<i>Z</i>	1 (dimer)	1 (dimer)	2 (dimer)
<i>D</i> _x /g cm ^{−3}	1.287	1.518	1.544
μ /mm ^{−1}	0.167	2.484	1.838
<i>F</i> (000)	220	256	584
Crystal size/mm	0.44 × 0.32 × 0.26	0.30 × 0.30 × 0.20	0.70 × 0.55 × 0.50
2 θ Range/°	4.7 to 50.1	4.6 to 50.1	4.2 to 50.1
<i>hkl</i> Ranges	0–8, −9 to 10, −10 to 11	0–9, −10 to 10, −11 to 11	−12 to 11, −17 to 0, 0–10
Reflections collected	2005	2334	2352
Independent reflections (<i>R</i> _{int})	1850 (0.0258)	2144 (0.0134)	2208 (0.0236)
Data, restraints, parameters	1850, 0, 180	2144, 0, 162	2205, 0, 133
Goodness of fit on <i>F</i> ²	0.999	1.121	1.041
Final <i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0393, 0.0881	0.0314, 0.0773	0.0489, 0.1329
Final <i>wR</i> 2 (all data)	0.0970	0.0809	0.1483
Extinction coefficient	0.012(5)	0.015(3)	—
Maximum, minimum $\Delta\rho$ /e Å ^{−3}	0.17 and −0.19	0.60 and −0.67	0.74 and −0.81

* Details in common: Siemens P3 diffractometer, Mo-K α radiation (λ = 0.7107 Å), graphite monochromated. *R*1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, *wR*2 = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_c^2)]^{1/2}$, goodness of fit *S* = $[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where *n* = number of data and *p* = total number of parameters refined.

mination were grown from toluene–hexane solutions at 0 °C and were sealed inside Lindemann glass capillaries under an inert atmosphere. An automatic search routine was used to locate up to 25, 27 and 35 reflections for **1**, **2**, and **3**, respectively, which were used for determination and least-squares refinement of the unit cell parameters. Lattice constants were verified by axial photographs. Intensity data were recorded using the ω –2 θ scan technique. The data were corrected for Lorentz and polarisation effects. In each case two standard reflections were measured after every 70 reflections in order to monitor the crystal decay. A meaningful crystal decay of 55% was noticed for **1**, (2.0 and 2.7% for **2** and **3**, respectively) and the intensities were scaled appropriately. For **3** an empirical absorption correction based on ψ scans (360 intensities) was applied. Maximum and minimum values of the transmission coefficients were 0.291 and 0.191, respectively.

Structure analysis and refinement. The structures were solved by direct methods using the SHELXS 86 program,^{10a} which readily revealed the positions of the metal and oxygen atoms and the majority of the C atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms for **1** were located from the Fourier-difference map and isotropically refined. Methyl hydrogen atoms for **2** were calculated and refined as a disordered group with two positions rotated by 60° about the C–C bond. For **3**, all hydrogen atoms were introduced at geometrically idealised coordinates and allowed to ride on the appropriate carbon atoms. Full-matrix least-squares refinement method against *F*² values was carried out by means of the SHELXL 93 program.^{10b} Neutral-atom complex scattering factors were employed.^{10c} The final weighting schemes for **1**, **2** and **3** were $w^{-1} = \sigma^2(F_o^2) + (0.0532P)^2 + 0.0244P$, $w^{-1} = \sigma^2(F_o^2) + (0.0491P)^2 + 0.1845P$, and $w^{-1} = \sigma^2(F_o^2) + (0.0915P)^2 + 0.7682P$, respectively, where $P = \frac{1}{3}(F_o^2 + 2F_c^2)$. In all cases the largest positive and negative peaks on the final Fourier-difference maps have no significant chemical meaning, and the maximum shift/error ratios in the final cycles of refinement were less than 0.001.

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