Synthesis and characterization of organoindium complexes derived from internally functionalized anionic ligands

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Reactions of triorganoindium etherate with protic ligands in benzene at room temperature have afforded diorganoindium complexes of the type, [R2In(L)]n (R = Me, Et; L = (CH2)4NCH2O, (CH2)4CH2CH2O; 2-MeOC6H4O’; C6H5CO2; 2-MeOC6H4CO2; 2-(CH2)3NCO2; 2-(C6H5N)CO2; 2-(C6H5O)CO2). These complexes have been characterized by indium analysis, IR, NMR (1H, 13C{1H}) and mass spectral data. The mass spectra reveal that these complexes are associated in the solid state. The complex Et2In(O2C-C6H4N) shows photoluminescence on excitation with 370 nm radiation.

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The chemistry of organo-aluminium, -gallium and -indium compounds with group 15 and 16 donor ligands has been the subject of considerable research for several years1,2. The interest in these compounds appears to be due to their rich structural diversity and their potential applications as catalysts as well as possible precursors for III-V (e.g., GaN, GaP, InSb, InP, etc.) and III-VI (e.g., Ga2O3, In2O3, In2S2, In2Se3, etc.) materials2-5. The compounds of the type R2ML have been isolated as mono-, di- and tri-meric species with the metal coordination varying between four and six. The structural preferences are usually dictated by the nature of R, M and L. For instance, while [R2Ga(acac)] (R = Me or Et) are monomeric with four coordinate gallium atom6, the corresponding indium derivative, [Me2In(acac)]2 is dimeric with five coordinate indium7. The ligand (L) also greatly influences the molecularity of the complex. Monomeric complexes with four coordinate metal atom are often isolated with the bidentate ligands forming six-membered chelates, e.g., [R2M(OCH2CH2NMe2)]8, [Me2M(OCR=CH=CR=NR)]9. Ligands capable of forming five-membered chelates afford both discrete four coordinate monomers (e.g., [Me2Ga(OCH2CH2NH2)]10,11, [Me2Ga(O2CCH2NH2)]12) as well as dimers containing five coordinate metal atom, e.g., [Me2Ga(OCh2CHMeNH2)]13, Me2GaL (L = OC6H4CHO-214, OC6H4OMe-2 (Ref. 15), C6H5NCH2O16), [Et2InOx]17, [Me2In[OCH2CH2(C6H5N)]]18. With monofunctional organic ligands (alkoxy) and four membered bidentate chelating ligands, dimeric derivatives are generally isolated, e.g., [Bu3In(OEt)]19, [Bu3Ga(OBu)]20 and [Me2M(O2PPh2)]21 (M = Ga or In)22. For assessing metal coordination preferences vis-a-vis molecularity of the complex, and in persuasion of our work on group 13 compounds, we have synthesized and characterized diorganoindium complexes with internally functionalized anionic ligands (1-8):

**Materials and Methods**

All experiments employing organoindium compounds were performed in Schlenk flasks under anhydrous conditions in a nitrogen atmosphere. Solvents were dried using standard procedures. The ligands 2-pyridine methanol, 2-(2-hydroxyethyl)pyridine and 2-methoxy phenol and benzoic, 2-methoxy benzoic, 2-furoic, 2-picolinic and 2-quinoidal acids were obtained from commercial sources. R3In.OEt (R = Me, Et) were usually co-distilled with 3-5 equivalents of ether which was ascertained every time by 1H NMR integration, were prepared by the reaction of
RMgI with InCl₃ in dry diethylether. Infrared spectra were recorded between CsI plates on Bomen MB-102 FT IR spectrometer. NMR spectra (¹H, ¹³C{¹H}) were recorded on Bruker AC-200 NMR spectrometer in 5 mm tube in CDCl₃ solution. Chemical shifts were referenced to the internal chloroform peak (δ 7.26 and 8 77.0 ppm) for IH and ¹³C{¹H}, respectively. Mass spectra were recorded on a time of flight mass spectrometer Waters Q-TOF micro (YA-105).

Preparation of [Me₂In(OCH₂C₆H₄0Me-2)]

To a benzene solution (20 cm³) of trimethylindium etherate (3.506 g, containing 1.137 g Me₃In, 7.1 mmol), a solution of 2-methoxy phenol (881 mg, 7.1 mmol) in the same solvent was added dropwise over a period of 10 min with stirring under a nitrogen atmosphere. The contents were stirred for 4 h at room temperature. The solvent was stripped off under reduced pressure leaving behind a colourless solid (yield 1.845 g, 97%). This can be sublimed under vacuum at 130 °C in a poor yield. Similarly, all other compounds were prepared in 92-96% yield and were recrystallized from benzene hexane as colourless crystalline solids. Pertinent data are given in Table 1.

Results and Discussion

Diorganoindium complexes of the type R₂InL have been synthesized in 92-96% yield by the metathetical reaction between trialkylindium diethyl ether adduct and free ligand (LH) in 1:1 stoichiometry in benzene (Eq.1). All complexes were isolated as colourless crystalline solids. These compounds are soluble in unsaturated hydrocarbons such as benzene or toluene, but almost insoluble in saturated hydrocarbons such as hexane or pentane.

\[ R₂In.OE₃ + LH \rightarrow R₂InL + RH + Et₂O \]  \hspace{1cm} (1)

\[ R = Me, Et; L = (C₉H₆N)CH₂O'; (C₉H₆N)CH₂CH₂O'; 2-MeOC₆H₄0'; 2-MeOC₆H₅CO₂'; C₆H₅CO₂'; 2-(C₉H₆N)CO₂'; 2-(C₉H₈N)CO₂'; 2-(C₄H₃O)CO₂'. \]

The IR spectra of the complexes displayed an absorption band of medium to strong intensity in the range 505-535 cm⁻¹ attributed to In-C stretchings. IR spectra of picolinic and quinaldic acids complexes exhibited C=O stretchings at 1660 cm⁻¹ indicating the presence of unchelated carboxylate group. In contrast, for benzoic, 2-methoxy benzoic and furoic acids complexes, the v CO has been assigned in the region 1590-1606 cm⁻¹.

The ¹H and ¹³C{¹H} NMR spectra (Figs 1 and 2) exhibited characteristic peaks attributable to R₂In and the ligand moiety. The ¹H NMR resonance for Me₂In and the methylene protons of Et₂In showed ligand dependence and were deshielded which is the order of increasing acid strength of the ligand:

\[ (C₉H₆N)CO₂' > (C₆H₅H)CO₂' > (C₄H₃O)CO₂' > 2-(C₉H₆N)CO₂' > 2-(C₉H₈N)CO₂' > (C₉H₈N)CH₂CH₂O' > (C₉H₈N)CH₂O'. \]

<table>
<thead>
<tr>
<th>Complex</th>
<th>% yield</th>
<th>m.p. °C</th>
<th>% In Found (Calcd)</th>
<th>δ in ppm</th>
<th>δ in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Me₂In(OCH₂C₆H₄N)]ₙ</td>
<td>93</td>
<td>194</td>
<td>44.6</td>
<td>-0.35</td>
<td>-8.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(45.4)</td>
<td>5.00 (br, s, OCH₃); 7.11-7.24 (m, 2H, H-3,5); 7.65 (m, 1H, H-4); 8.34 (br, 1H, H-6)</td>
<td>64.3 (s, Me₂In); 120.8 (C-5); 122.4 (C-3); 156.7 (C-4); 145.6 (C-6); 162.7 (C-2)</td>
</tr>
<tr>
<td>[Et₂In(OCH₂C₆H₄N)]ₙ</td>
<td>94</td>
<td>118</td>
<td>40.5</td>
<td>0.53 (q, 8.0 Hz, InCH₃); 1.13 (t, 8.0 Hz, InCH₃CH₂); 5.06 (s, OCH₃); 7.11-7.22 (m, 2H, H-3,5); 7.67 (t, 7Hz, 1H, H-4); 8.36 (br, 1H, H-6)</td>
<td>-6.0 (s, Me₂In); 46.0 (s, OCH₃CH₂); 62.2 (s, OCH₃); 121.6 (s, C-5); 123.8 (C-3); 137.1 (C-4); 148.0 (C-6); 161.7 (C-2)</td>
</tr>
<tr>
<td>[Me₂In(OCH₂CH₂C₆H₄N)]ₙ</td>
<td>95</td>
<td>105</td>
<td>43.0</td>
<td>-0.31 (s, Me₂In); 2.97 (5Hz, OCH₂CH₂); 4.04 (t, 5 Hz, OCH₂); 7.11-7.19 (m, 2H, H-3,5); 7.62 (t, 7.5 Hz, 1H, H-4); 8.36 (br, 1H, H-6)</td>
<td>-6.0 (s, Me₂In); 46.0 (s, OCH₃CH₂); 62.2 (s, OCH₃); 121.6 (s, C-5); 123.8 (C-3); 137.1 (C-4); 148.0 (C-6); 161.7 (C-2)</td>
</tr>
</tbody>
</table>
### Table 1 — Yield, analysis and $^{1}H$ and $^{13}C$($^{1}H$) NMR data for diorganoindium complexes — Contd.

<table>
<thead>
<tr>
<th>Complex</th>
<th>% yield</th>
<th>m.p. °C</th>
<th>% Found (Calcd)</th>
<th>$^{1}H$ NMR dataδ in ppm</th>
<th>$^{13}C$($^{1}H$) NMR dataδ in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Et}_2\text{In(OCH}_2\text{CH}_2\text{C}_5\text{H}_4\text{N})]_n$</td>
<td>95</td>
<td>87</td>
<td>38.9 (38.9)</td>
<td>0.51 (q, br, InCH$_2$); 1.17 (t, 8.0 Hz, InCH$_3$Me); 2.98 (br, OCH$_2$CH$_3$); 4.06 (br, OCH$_2$); 7.11-7.19 (m, 2H, H-3,5); 7.62 (t, 7.3 Hz, 1H, H-4); 8.38 (br, 1H, H-6)</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Me}_2\text{In(OC}_6\text{H}_4\text{OMe}-2)]_n$</td>
<td>97</td>
<td>175</td>
<td>43.5 (42.8)</td>
<td>-0.04 (s, Me$_2$In); 3.84 (s, OMe); 0.51 (q, 8 Hz, InCH$_2$-); 1.17 (t, 8.0 Hz, (38.9) InCH$_2$Me); 2.98 (br, OCH$_2$CH$_2$); 4.06 (br, OCH$_2$); 7.11-7.19 (m, 2H, H-3,5); 7.62 (t, 7.3 Hz, 1H, H-4); 8.38 (br, 1H, H-6)</td>
<td>-5.1 (s, Me$_2$In); 54.7 (s, OMe); 110.9 (C-6); 116.8 (C-3); 122.4 (C-4,5); 147.5 (C-1); 150.3 (C-2)</td>
</tr>
<tr>
<td>$[\text{Et}_2\text{In(OC}_6\text{H}_4\text{OMe}-2)]_n$</td>
<td>96</td>
<td>123</td>
<td>39.6 (38.8)</td>
<td>0.82 (q, 8 Hz, InCH$_2$-); 1.21 (t, 8 Hz, (38.9) InCH$_2$Me); 2.98 (br, OCH$_2$CH$_2$); 4.06 (br, OCH$_2$); 7.11-7.19 (m, 2H, H-3,5); 7.62 (t, 7.3 Hz, 1H, H-4); 8.38 (br, 1H, H-6)</td>
<td>9.0 (s, InCH$_2$); 11.3 (s, InCH$_3$Me); 55.5 (s, OMe); 110.3 (C-6); 116.6 (C-3); 122.2 (s,C-4,5); 147.7 (C-1); 151.1(C-2)</td>
</tr>
<tr>
<td>$[\text{Me}_3\text{In}[\text{O}_2\text{C(}C_5\text{H}_4\text{N})-2)]_n$</td>
<td>95</td>
<td>243-245</td>
<td>42.8 (43.0)</td>
<td>-0.02 (s, Me$_3$In); 7.57-7.68 (m, 1H, H-5); 8.01 (dt, 7.8 Hz t, 1 Hz, d, 1H, H-4); 8.35 (dd, 7, 1Hz, 1H, H-3); 8.43 (dd, 5,1Hz, 1H, H-6)</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Et}_3\text{In[O}_2\text{C(}C_5\text{H}_4\text{N}-2)]_n$</td>
<td>95</td>
<td>201</td>
<td>38.7 (38.9)</td>
<td>0.84 (q, 8 Hz, InCH$_2$-); 1.07 (t, 8Hz, InCH$_3$Me); 7.57-7.63 (m, 1H, H-5); 8.02 (dt, 7.8 Hz t, 1.6 Hz, d, 1H, H-4); 8.37 (d, 7.8 Hz, 1H, H-3); 8.44 (d, 4.8 Hz, 1H, H-6)</td>
<td>9.0 (s, InCH$_2$); 11.3 (s, InCH$_3$Me); 125.5 (C-5); 126.9 (C-3); 139.3 (C-4); 146.2 (C-2); 149.3 (C-6); 165.7 (C=O)</td>
</tr>
<tr>
<td>$[\text{Me}_3\text{In[O}_2\text{C(}C_6\text{H}_4\text{N})-2)]_n$</td>
<td>93</td>
<td>&gt;300</td>
<td>35.7 (36.2)</td>
<td>0.11 (s, Me$_3$In); 7.73 (t, 7 Hz, 1H, H-6); 7.89 (dt, 7 Hz t, 1.5 Hz d, 1H, H-7); 8.00 (d, 8 Hz, 1H, H-5); 8.12 (d, 8 Hz, 1H, H-3); 8.47 (br, 2H, H-4,8)</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Et}_3\text{In[O}_2\text{C(}C_6\text{H}_4\text{N})]-3)]_n$</td>
<td>94</td>
<td>265</td>
<td>32.7 (33.3)</td>
<td>0.88-1.14 (m, InCH$_3$Me), 7.74 (dt, 7 Hz t, 1H d, 1H, H-6); 7.90 (dt, 7 Hz t, 1.5 Hz d, 1H, H-7); 8.00 (dd, 8, 1.5 Hz, 1H, H-5); 8.11 (d, 8.4 Hz, 1H, H-3); 8.43 (s, 2H, H-4,8)</td>
<td>9.8 (s, InCH$_2$); 11.4 (s, InCH$_3$Me); 121.4 (C-3); 126.4 129.4, 129.1, 129.6, 131.4 (C-7); 139.6 (C-4); 144.6; 150.0 (C-2); 166.1 (C=O)</td>
</tr>
<tr>
<td>$[\text{Me}_3\text{In[O}_2\text{C(}C_5\text{H}_4\text{O})]-3)]_n$</td>
<td>92</td>
<td>231*</td>
<td>45.3 (44.8)</td>
<td>0.09 (s, Me$_3$In); 6.52 (m, 1H); 7.16 (m, 1H), 7.52 (br, 1H)</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Et}_3\text{In[O}_2\text{C(}C_5\text{H}_4\text{O})]-3)]_n$</td>
<td>95</td>
<td>180</td>
<td>39.3 (40.4)</td>
<td>0.88 (q, 8 Hz, InCH$_2$-); 1.19 (t, 8 Hz, InCH$_3$Me); 6.52 (br, 1H); 7.16 (d, 3 Hz, 1H, H-7); 7.51 (br, 1H)</td>
<td>-3.8 (s, Me$_3$In); 128.1, 130.2, 132.4 (Ph); 175.5 (CO)</td>
</tr>
<tr>
<td>$[\text{Me}_3\text{In[O}_2\text{C(}C_6\text{H}_4\text{OMe}-2)]_n$</td>
<td>95</td>
<td>180</td>
<td>41.9 (43.1)</td>
<td>0.10 (s, Me$_3$In); 7.36 - 7.51 (m, 3H); 7.94 (d, 8Hz 2H) (Ph)</td>
<td>-3.7 (s, Me$_3$In); 56.0 (s, OMe); 112.3, 121.3, 122.3, 133.4, 157.9 (C$_3$H$_4$); 173.4 (CO)</td>
</tr>
</tbody>
</table>

*decomposed with melting
Table 2 - Mass spectral data of diorganoinium(III) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>m/e (species)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Me2In(OC6H4OMe-2)]_n</td>
<td>331 [In(OC6H4py)2+; 253 (molecular ion, M'); 238 (M-Me); 145 (Me2In); 115 (In')</td>
</tr>
<tr>
<td>[Me2In(OC6H4OMe-2)]_n</td>
<td>462; 432; 340; 145 (Me2In'); 115 (In')</td>
</tr>
<tr>
<td>[Me2In(O2C-(C6H4N)_1)h]_n</td>
<td>893; 786 ([Me2In pic]2-; Me); 519 ([Me2In pic]2-; Me); 412 ([Me2In pic]2-; pic); 290; 268 (M); 145 (Me2In')</td>
</tr>
<tr>
<td>[Et2In(O2C-(C6H4N)]_n</td>
<td>894; 856 ([Et2In pic]2-; Et); 762 ([Et2In pic]2-; pic); 561 ([Et2In pic]2-; pic); 295 (M); 266 (Et2In pic-Et); 173 (Et2In')</td>
</tr>
<tr>
<td>[Et2In(O2C-(C6H4N)]_n</td>
<td>863 ([Et2In Qua]2-; Qua); 713; 661 ([Et2In Qua]2-; Qua); 518 ([Et2In Qua]2-; Qua); 368; 346 (M'); 173 (Et2In'); 172 (Et2In')</td>
</tr>
</tbody>
</table>

*M = for monomeric (formula weight) unit; pic = 2- picolnic acid; Qua = C9H6N2CO2

The methyl resonance for Me2In for these compounds and for those having 4- or 5-coordinate indium in mono-, di- or tri-meric derivatives reported in literature, exists in a narrow range of -0.5 ppm (δ - 0.35 to 0.15 ppm). Thus, the methyl chemical shift appears to provide little information with regards to either coordination number of indium or nuclearity of the compound. The ligand proton and carbon resonances for [R2In(O(CH2)2C6H4N-2)] (n = 1 or 2) can be compared with the corresponding organogallium complexes24 for which a dimeric structure has been established by X-ray diffraction analysis19. Although a dimeric structure for [Me-In(OCH2CH2(C6H4N))]2 has been reported18, the 1H NMR chemical shifts for R2In protons are different from those reported here. The methyl proton/carbon and C-2 carbon resonances of 2-methoxy phenolate ligand in [Me2In(OC6H4OMe-2)] are considerably deshielded from the corresponding resonances for dimeric [Me2Ga(OC6H4OMe-2)]13. Deshielding of C-4 carbon resonance in the 13C{1H} NMR spectra of the complexes containing nitrogen heterocyclic ligands relative to the corresponding resonance for the free ligand suggests that nitrogen is coordinated to the metal atom15,16,23,25. The mass spectra (Table 2) of these complexes indicate that they are associated in the solid state as they displayed peaks greater than their formula weights. The complexes showed fragments formed by cleavage of R-In and L-In linkages. In every case, peak due to R2In+ was identified suggesting its high stability. The mass spectra of the complexes derived from alcoholic/phenolic ligands indicate that they may be dimeric. A dimeric structure for [Me2In(OCH2CH2(C6H4N))]2 has been established by X-ray crystallography18. The spectra of picolinic and quinaldic acids complexes, however, exhibited fragments originating from trimeric species. The complexes may be compared with [Me2Sn(pic)2]n which is a linear polymer formed by chelating picolinolate group and the free carbonyl coordinating to adjacent tin atom26. This complex shows carbonyl absorption at 1667 and 1618 cm⁻¹ in the IR
The presence of free carbonyl absorption in the IR spectra of $[\text{R}_3\text{In(O}_2\text{C} \text{Ar)}]$ (Ar = C$_8$H$_6$N; C$_9$H$_7$N and m/e peaks for the fragments of trimers indicate that these ligands are chelated with indium and the free carbonyl coordinating to the adjacent indium atom.

The electronic spectra of $[\text{R}_3\text{In(O}_2\text{C} \text{Ar)}]$ (Ar = C$_8$H$_6$N ($\lambda_{max}$ = 280 nm); C$_9$H$_7$N ($\lambda_{max}$ = 311, 317, 330 nm)) and the corresponding free ligands benzene were similar and the absorptions have been attributed to $\pi-\pi^*$ transition in the ligand moiety. Benzene solutions of quinaldic acid and $[\text{Et}_2\text{In(O}_2\text{C} \text{C}_9\text{H}_6\text{N})]$ showed photoluminescence on excitation with 370 nm radiation. The indium complex exhibited an emission at 381 nm with an intensity of 1.6 a.u. The photoluminescence in organogallium and indium complexes has been reported recently.

From the foregoing discussion, it can be concluded that except picolinic and quinaldic acids derivatives, these complexes have a dimeric structure stabilized by bridging ligands. For picolinic and quinaldic acids derivatives, a polymeric structure may be suggested based on mass spectral and IR data as well as by analogy with $[\text{Me}_2\text{Sn(pic)}_2]$.

Acknowledgement

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References