

## COMPLEXES OF ALUMINUM, GALLIUM AND INDIUM WITH PYRONE DERIVATIVES

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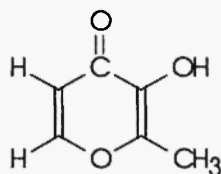
### Abstract

The reaction of aluminum and gallium trichlorides with 3-hydroxy-2-methyl-4H-pyran-4-one (HMa) in benzene yields  $M(\text{HMa})_3\text{Cl}_3$  ( $M = \text{Al}$  or  $\text{Ga}$ ) adducts, whereas with indium trichloride the  $\text{In}(\text{HMa})_2\text{Cl}_3$  complex has been isolated. In analogous conditions the other aluminum trihalides yielded complexes containing the maltolato ion, as  $\text{Al}(\text{HMa})_2(\text{Ma})\text{Br}_2$  or  $\text{Al}(\text{Ma})_2\text{I}$ . Moreover by using the neutral ligand 2,6-dimethyl-4H-pyran-4-one (DMP) the adducts  $\text{Al}(\text{DMP})_2\text{Cl}_3$ ,  $\text{Al}(\text{DMP})_3\text{X}_3$  ( $\text{X} = \text{Br}$  or  $\text{I}$ ),  $\text{Ga}(\text{DMP})_{1.5}\text{Cl}_3$  and  $\text{In}(\text{DMP})_2\text{Cl}_3$  have been obtained. The compounds have been characterized by IR and proton NMR spectroscopy and by thermogravimetric (TG and DTA) analysis. The behaviour of the HMa complexes in deuterated dimethyl sulfoxide is discussed on the basis of proton NMR spectra.

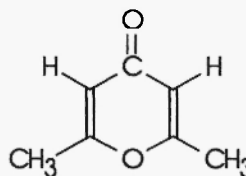
### Introduction

Maltol (3-hydroxy-2-methyl-4H-pyran-4-one, HMa) can act as either neutral or anionic donor toward lanthanide trichlorides or tin and germanium tetrachlorides. Complexes like  $\text{Ln}(\text{HMa})_3\text{Cl}_3 \cdot n\text{H}_2\text{O}$  ( $\text{Ln} = \text{Pr}$ ,  $\text{Nd}$  or  $\text{Eu}$ ;  $n = 0, 1$ ) or  $\text{M}(\text{HMa})_4\text{Cl}_4 \cdot \text{C}_6\text{H}_6$  ( $M = \text{Ge}$  or  $\text{Sn}$ ) have been isolated in benzene (or acetone), whereas organotin moieties did not show any tendency to form HMa adducts [1-3]. In either water or alcoholic media the maltolato derivatives  $\text{M}(\text{Ma})_2\text{Cl}_2$  ( $M = \text{Ge}$  or  $\text{Sn}$ ),  $\text{R}_2\text{Sn}(\text{Ma})_2$ ,  $\text{R}_2\text{Sn}(\text{Ma})\text{X}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) and  $\text{R}_3\text{SnMa}$  were obtained, as observed for lanthanides, which form generally hydrated 1:3 maltolates. In the  $\text{Pr}(\text{Ma})_3(\text{H}_2\text{O})_2$  complex the praseodymium atom is eight-coordinated, one of the bidentate ligand molecules being disordered into two possible positions [3]. 3-Hydroxy-4-pyrones (HL) have been found to suppress hydrolysis of trivalent ions forming the water soluble neutral complexes  $\text{ML}_3$  ( $M = \text{Al}$ ,  $\text{Ga}$ ,  $\text{In}$  or  $\text{Fe}$ ) suitable for medical applications [4-9]. In particular the  $\text{Al}(\text{Ma})_3$  complex shows a *mer* geometry, one of the ligands being disordered, as for the praseodymium analogue [8].

In this paper we report the interaction of aluminum group trihalides with either maltol and the parent neutral ligand 2,6-dimethyl-4H-pyran-4-one (DMP) in non aqueous media.



HMa



DMP

Literature reports on complexes of this class of metal with monodentate O-donors concern mainly phosphine oxide derivatives. Aluminum and gallium trihalides give the  $\text{MX}_3 \cdot \text{R}_3\text{PO}$  ( $\text{M} = \text{Al}$ ,  $\text{X} = \text{Cl}$  or  $\text{Br}$ ;  $\text{M} = \text{Ga}$ ,  $\text{X} = \text{Cl}$ ) complexes [10], whereas indium displays a versatile behaviour yielding, along with neutral 1:2 and 1:3 adducts, the ionic complex  $[\text{In}(\text{Ph}_3\text{PO})_4\text{Cl}_2][\text{InCl}_4]$  [11,12]. Along with the dimethyl sulfoxide derivatives  $\text{In}(\text{Me}_2\text{SO})_3\text{X}_3$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ), the *N,N*-dimethylacetamide (dma) complexes  $\text{In}(\text{dma})_2\text{X}_3$  and  $\text{In}(\text{dma})_{1.5}\text{X}_3$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) have been reported, which should contain bridging ligand molecules [11,12]. From X-ray structure data, the  $\text{In}(\text{Me}_3\text{AsO})_{1.5}\text{Cl}_3$  complex is actually a dimer in which two terminal  $\text{InCl}_3$  molecules are linked by three bridging oxygen atoms, each indium centre being six-coordinated [13]. In the  $\text{In}(\text{hmpa})_2\text{Cl}_3$  (hmpa = hexamethylphosphoramide) adduct the indium atom is five-coordinated with three chlorine atoms in the equatorial position of a trigonal bipyramidal arrangement [14]. As regards aldehyde or ketone coordination, aluminum triiodide forms 1:2 adducts, whereas 1:1 complexes are obtained with the chloro and bromo analogues [15,16].

## Experimental

$\text{AlCl}_3$  and  $\text{AlI}_3$  (Aldrich),  $\text{AlBr}_3$  (Ventron),  $\text{GaCl}_3$  (Aldrich) and  $\text{InCl}_3$  (Ventron) were used as supplied. Ligands were 3-hydroxy-2-methyl-4H-pyran-4-one (HMa, Aldrich) and 2,6-dimethyl-4H-pyran-4-one (DMP, Ega Chemie). Syntheses were performed in a dry box line under dinitrogen atmosphere. Anhydrous solvents were distilled under dinitrogen.

### Preparation of the complexes

The DMP adducts of aluminum trihalides were prepared in benzene by reaction of the appropriate  $\text{AlX}_3$  with the ligand in a molar ratio 1:3. As an example, the  $\text{Al}(\text{DMP})_2\text{Cl}_3$  complex was prepared by mixing  $\text{AlCl}_3$  (1.91 mmol) and DMP (5.74 mmol) in benzene (8  $\text{cm}^3$ ). A beige oil was formed within a few minutes, which, by addition of *n*-hexane (2  $\text{cm}^3$ ), turned into a white solid. The compound was filtered and washed with benzene and *n*-hexane. Yield, 80 %. In analogous conditions aluminium tribromide yielded the  $\text{Al}(\text{DMP})_3\text{Br}_3$  complex, whereas the  $\text{AlI}_3$  reaction required longer reaction times. In this case a suspension of  $\text{AlI}_3$  (1.15 mmol) and DMP (3.7 mmol in 10  $\text{cm}^3$  of benzene) was allowed to react for three days. A nutmeg powder formed gradually which was separated mechanically from a few crops of residual  $\text{AlI}_3$ . The  $\text{Al}(\text{DMP})_3\text{I}_3$  complex was filtered, washed with benzene and *n*-hexane and dried under reduced pressure.

The  $\text{Ga}(\text{DMP})_{1.5}\text{Cl}_3$  complex was prepared by reaction of  $\text{GaCl}_3$  (1.1 mmol) and DMP (3.3 mmol) in benzene (8  $\text{cm}^3$ ) with vigorous stirring (16 h). The white fine powder was filtered, washed with benzene and *n*-hexane and dried *in vacuo*. The same compound separated overnight from an ethanol solution containing  $\text{GaCl}_3$  (0.6 mmol) and DMP (1.8 mmol in 12  $\text{cm}^3$ ).

The  $\text{In}(\text{DMP})_2\text{Cl}_3$  complex was obtained by reacting  $\text{InCl}_3$  and DMP (molar ratio 1:3) in benzene, in ethanol or in acetone. The white compound separated from the acetone (or ethanol) solution as

a fine powder which was separated by centrifugation. The reaction in benzene went on in heterogeneous phase with stirring (24 h).

All the HMa complexes were prepared in benzene. The reaction of  $\text{AlCl}_3$  (1.2 mmol) with HMa (3.6 mmol in  $10\text{ cm}^3$ ) yielded a white solid (2h) which was filtered, washed with *n*-pentane and dried under reduced pressure. The  $\text{Al}(\text{HMa})_3\text{Cl}_3$  complex characterization was carried out immediately after synthesis, because solid samples release hydrochloric acid on standing to form mixed species containing the maltolato ion. Mixed species were also obtained when the benzene suspension was kept under stirring overnight. In this case a white solid separated whose analytical and proton NMR data supported the formulation  $\text{Al}(\text{HMa})_{2.2}(\text{Ma})_{0.8}\text{Cl}_{2.2}$ . The  $\text{Al}(\text{Ma})_3$  complex was prepared by thermal degradation of the parent  $\text{Al}(\text{HMa})_3\text{Cl}_3$  species. Samples of the HMa adduct were heated directly on the thermobalance crucible up to  $170^\circ\text{C}$  (see discussion).

The complex  $\text{Ga}(\text{HMa})_3\text{Cl}_3$  was prepared by reaction of  $\text{GaCl}_3$  (1.24 mmol) and HMa (3.75 mmol) in benzene ( $5\text{ cm}^3$ ). An oil was formed initially which, by addition of *n*-pentane ( $5\text{ cm}^3$ ) with stirring, turned into a white powder. The solid was filtered, washed with *n*-pentane and dried *in vacuo* (5 min). In the same conditions the reaction of  $\text{InCl}_3$  with HMa yielded the white complex  $\text{In}(\text{HMa})_{2.5}\text{Cl}_3$ .

The reaction of  $\text{AlBr}_3$  or  $\text{AlI}_3$  with HMa in benzene gave always mixed species. By stirring overnight a  $\text{AlBr}_3$  (1.15 mmol) and HMa (3.50 mmol) suspension in benzene ( $15\text{ cm}^3$ ) a white solid separated which was filtered, washed with *n*-pentane and characterized as  $\text{Al}(\text{HMa})_2(\text{Ma})\text{Br}_2 \cdot 0.5\text{C}_6\text{H}_6$ . In analogous conditions aluminium triiodide yielded a yellow powder whose analytical and spectroscopic data supported the formulation  $\text{Al}(\text{HMa})_n(\text{Ma})_2\text{I}$  (*n*, from 0.3 to 0.8). By heating samples from different preparations up to  $150^\circ\text{C}$  the yellow  $\text{Al}(\text{Ma})_2\text{I}$  complex was obtained.

### Measurements

Infrared spectra were recorded using Nicolet 5SXC FT-IR and Nicolet 20F far-IR spectrometers, in nujol mulls between KBr and polyethylene discs.  $^1\text{H}$  nmr spectra were obtained with a JEOL FX90Q spectrometer (in ppm from  $\text{SiMe}_4$  as internal standard). The TG and DTA curves in air (flow rate  $250\text{ cm}^3\text{ min}^{-1}$ , heating rate  $5^\circ\text{C min}^{-1}$ ) were recorded on a Netzsch STA 429 thermoanalytical instrument (reference material  $\text{Al}_2\text{O}_3$ ).

### Results and discussion

The  $\text{M}(\text{HMa})_3\text{Cl}_3$  (*M* = Al or Ga) complexes have been prepared by reaction of metal trihalide with maltol in benzene (Table 1). Also if kept under dinitrogen, samples of these species tend to release hydrochloric acid with time giving mixed species containing either maltol or maltolato ion, the effect being particularly evident for  $\text{Al}(\text{HMa})_3\text{Cl}_3$ . The thermograms of freshly prepared  $\text{Al}(\text{HMa})_3\text{Cl}_3$  (Fig. 1) show an initial step ( $60$ – $180^\circ\text{C}$ ) caused by evolution of three HCl molecules (weight loss, 20.8 % against a calculated value of 21.4 %), the related endotherm being at  $130^\circ\text{C}$  (shoulders at  $122^\circ\text{C}$  and  $160^\circ\text{C}$ ). The  $\text{Al}(\text{Ma})_3$  intermediate is stable up to  $240^\circ\text{C}$ , subsequent combustion originating the broad exotherm at  $360^\circ\text{C}$ . Pyrolysis ends at  $540^\circ\text{C}$  with a total weight loss of 90.6 % against a calculated value for  $\text{Al}_2\text{O}_3$  as final product of 90.0 %. Thermograms of aged samples are unchanged, apart for a less marked initial step due to progressive formation of maltolato moieties on standing. As an example, after one week at room temperature sealed samples of  $\text{Al}(\text{HMa})_3\text{Cl}_3$  contain about 1.3 maltolato ions whereas after one month the residue is almost  $\text{AlMa}_3$ . The  $\text{Ga}(\text{HMa})_3\text{Cl}_3$  complex shows a quite different thermal behaviour (Fig. 2). In this case, the initial evolution of one HCl molecule ( $50$ – $150^\circ\text{C}$ ; endotherms at  $54$ ,  $74$  and  $86^\circ\text{C}$ ; weight loss, 6.2 % against calculated 6.6 %) to give  $\text{Ga}(\text{HMa})_2(\text{Ma})\text{Cl}_2$  is followed by release of

1HMa + 1HCl (30.5 % against calculated 29.3 %). The Ga(Ma)<sub>2</sub>Cl intermediate melts at 294°C, the following exothermic process being caused by combustion (540°C, total weight loss, 83.4 % against calculated 83.1 % for Ga<sub>2</sub>O<sub>3</sub> as pyrolysis residue). Thermograms of samples kept under dinitrogen atmosphere show an identical trend up to ca. 300°C. At higher temperatures the DTA curve is shapeless, owing to incomplete combustion. The In(HMa)<sub>2.5</sub>Cl<sub>3</sub> complex undergoes gradual decomposition in the 80-580°C temperature interval (weight loss, 74.8 against calculated 74.1 for In<sub>2</sub>O<sub>3</sub> as residue) the related DTA peaks being at 189°C (endotherm), 343°C (weak

Table 1. Analytical data<sup>a</sup> and selected IR frequencies (cm<sup>-1</sup>) for the complexes.

Compound	Formula	C %	H %	hal %	IR (cm <sup>-1</sup> )
Al(DMP) <sub>2</sub> Cl <sub>3</sub>	C <sub>14</sub> H <sub>16</sub> AlCl <sub>3</sub> O <sub>4</sub>	44.7 (44.1)	4.4 (4.2)	27.2 (27.9)	1649vs, 1568m, 1548vs
Al(DMP) <sub>3</sub> Br <sub>3</sub>	C <sub>21</sub> H <sub>24</sub> AlBr <sub>3</sub> O <sub>6</sub>	39.6 (39.5)	4.1 (3.8)	- (37.5)	1652vs, 1564m, 1542s
Al(DMP) <sub>3</sub> I <sub>3</sub>	C <sub>21</sub> H <sub>24</sub> AlI <sub>3</sub> O <sub>6</sub>	32.5 (32.3)	3.2 (3.1)	- (48.8)	1651vs, 1564m, 1542s
Ga(DMP) <sub>1.5</sub> Cl <sub>3</sub>	C <sub>10.5</sub> H <sub>12</sub> Cl <sub>3</sub> GaO <sub>3</sub>	35.3 (34.8)	3.3 (3.4)	30.1 (29.4)	1652vs, 1595w, 1569m, 1533vs
In(DMP) <sub>2</sub> Cl <sub>3</sub>	C <sub>14</sub> H <sub>16</sub> Cl <sub>3</sub> InO <sub>4</sub>	36.1 (35.8)	3.3 (3.4)	22.7 (22.6)	1649vs, 1573m, 1537vs
Al(HMa) <sub>3</sub> Cl <sub>3</sub>	C <sub>18</sub> H <sub>18</sub> AlCl <sub>3</sub> O <sub>9</sub>	42.7 (42.2)	3.7 (3.6)	19.6 (20.8)	1629s, 1579vs, 1524w
Al(Ma) <sub>3</sub>	C <sub>18</sub> H <sub>15</sub> AlO <sub>9</sub>	52.9 (53.7)	3.8 (3.8)	- -	1616m, 1577s, 1521w 1470s
Al(HMa) <sub>2</sub> (Ma)Br <sub>2</sub> 0.5C <sub>6</sub> H <sub>6</sub>	C <sub>21</sub> H <sub>20</sub> AlBr <sub>2</sub> O <sub>9</sub>	40.9 (41.8)	3.8 (3.3)	26.2 (26.5)	1635s, 1575vs, 1530m, 1478vs
Al(Ma) <sub>2</sub> I	C <sub>12</sub> H <sub>10</sub> AlIO <sub>6</sub>	35.5 (35.7)	3.0 (2.5)	30.2 31.4)	
Ga(HMa) <sub>3</sub> Cl <sub>3</sub>	C <sub>18</sub> H <sub>18</sub> Cl <sub>3</sub> GaO <sub>9</sub>	38.6 (39.0)	3.1 (3.3)	20.5 (19.2)	1617s, 1570vs, 1511w 1470s
In(HMa) <sub>2.5</sub> Cl <sub>3</sub>	C <sub>15</sub> H <sub>15</sub> Cl <sub>3</sub> InO <sub>7.5</sub>	33.3 (33.6)	2.7 (2.8)	19.9 (19.8)	1622s, 1568vs, 1511w 1474s

<sup>a</sup>Calculated values in parentheses.

exotherm) and 556°C (strong exotherm). Moreover the DTA curve shows a weak endotherm at 56°C, as for the  $\text{Ga}(\text{HMa})_3\text{Cl}_3$  adduct (Fig. 2). The absence of corresponding variations in the sample weight suggests rearrangement in the solid phase concerning probably hydrogen bridges. By reacting aluminum tribromide and HMa in benzene the  $\text{Al}(\text{HMa})_2(\text{Ma})\text{Br}_2$  complex is obtained, which generally retains one half benzene molecule, the related amount being estimated by proton NMR spectra. Thermal degradation of  $\text{Al}(\text{HMa})_2(\text{Ma})\text{Br}_2 \cdot 0.5\text{C}_6\text{H}_6$  (Fig. 3) is consistent with an initial evolution of  $0.5\text{C}_6\text{H}_6 + \text{HBr}$  (weight loss, 19.2 % against calculated 19.9 %; endotherm at 104°C) to form  $\text{Al}(\text{HMa})(\text{Ma})_2\text{Br}$ , followed by HMa release (130-220°C) to form  $\text{Al}(\text{Ma})_2\text{Br}$  (weight loss 21.0 % against calculated 20.9 %; endotherm at 187°C). The combustion process (exotherm

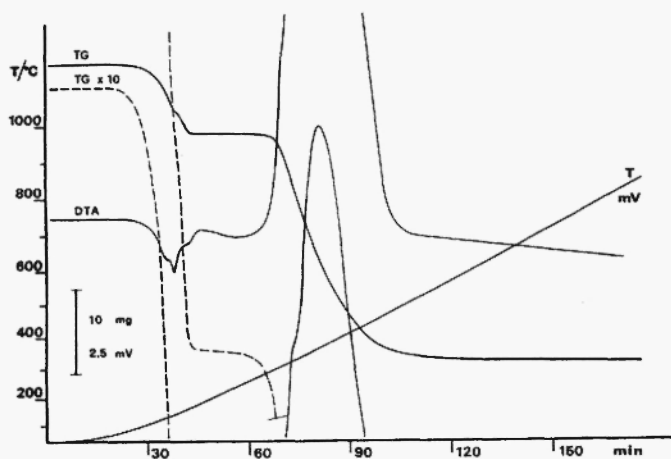


Figure 1. Thermograms of  $\text{Al}(\text{HMa})_3\text{Cl}_3$  (39.00 mg) in air.

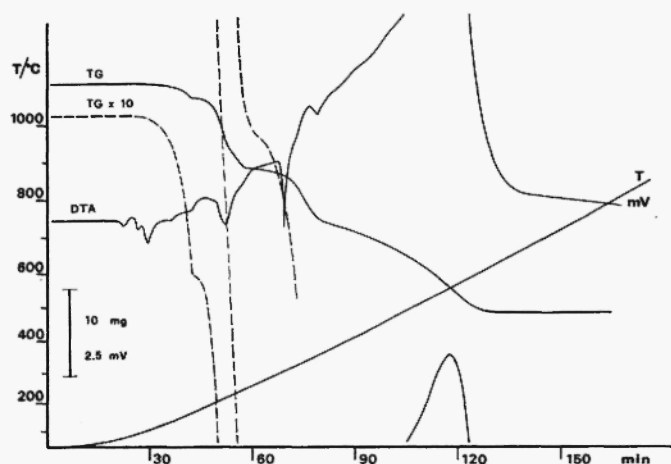


Figure 2. Thermograms of  $\text{Ga}(\text{HMa})_3\text{Cl}_3$  (38.83 mg) in air.

at 475°C) to  $\text{Al}_2\text{O}_3$  ends at 565°C. The reaction of aluminum triiodide with maltol in benzene yields essentially the  $\text{Al}(\text{Ma})_2\text{I}$  species, which contains variable not-stoichiometric amounts of HMa (from 0.3 to 0.8). Maltol can be removed by heating the compound at 150°C under reduced pressure. The  $\text{Al}(\text{Ma})_2\text{I}$  complex decomposes to  $\text{Al}_2\text{O}_3$  in the 200-550°C interval, the only significant DTA peak being the combustion exotherm at 375°C.

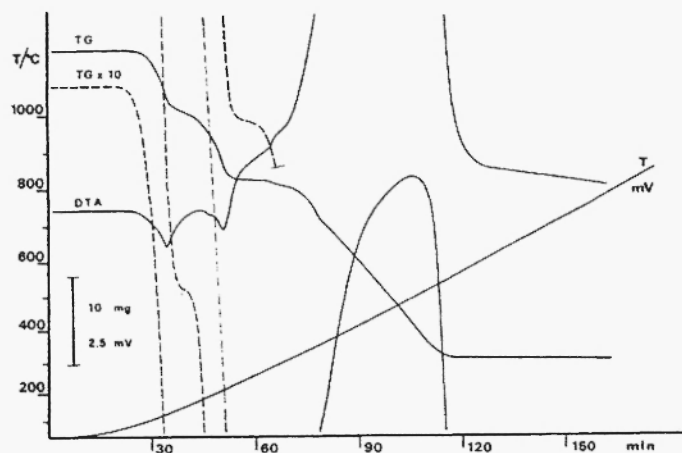


Figure 3. Thermograms of  $\text{Al}(\text{HMa})_2(\text{Ma})\text{Br}_2 \cdot 0.5\text{C}_6\text{H}_6$  (38.41 mg) in air.

No particularly significant feature is observed in the DMP adduct thermograms. As an example,  $\text{Al}(\text{DMP})_2\text{Cl}_3$  melts at 189°C, sample combustion (exotherm at 490°C) to  $\text{Al}_2\text{O}_3$  ending at 570°C (total weight loss, 86.6 % against a calculated value of 86.6 %). The thermograms of  $\text{Al}(\text{DMP})_3\text{Br}_3$  (m.p., 214°C) display an analogous trend (combustion exotherm, 450°C), whereas the  $\text{Al}(\text{DMP})_3\text{I}_3$  complex decomposes without melting in the 170-525°C interval (exotherms at 355°C and 460°C). Thermal degradation of  $\text{Ga}(\text{DMP})_{1.5}\text{Cl}_3$  (m.p., 129°C) and  $\text{In}(\text{DMP})_2\text{Cl}_3$  (m.p., 205°C) occurs with contemporaneous partial sublimation. The weight of the pyrolysis residue at ca 650°C is less than expected (20-40 %) for stoichiometric  $\text{M}_2\text{O}_3$ .

The IR spectrum of free DMP shows the strong band assigned to carbonyl group stretch at 1611  $\text{cm}^{-1}$ , whereas ring vibrations originate the absorptions at 1669 and 1599  $\text{cm}^{-1}$  [17, 18]. Carbonyl group coordination causes a low energy shift of  $\nu(\text{C}=\text{O})$  [18, 19], which is observed at ca 1540  $\text{cm}^{-1}$  in the complexes (Table 1). Ring absorptions undergo less marked shifts, being observed in the complexes at ca 1650 and 1570  $\text{cm}^{-1}$ . As regards metal-halide vibrations (Table 2), the spectrum of  $\text{Al}(\text{DMP})_2\text{Cl}_3$  contains a strong band at 497  $\text{cm}^{-1}$  assignable to Al-Cl stretch, the corresponding absorption in  $\text{Al}(\text{DMP})_3\text{Br}_3$  being at 427  $\text{cm}^{-1}$ . The assignment of the strong band at 347  $\text{cm}^{-1}$  (Cl) and 357  $\text{cm}^{-1}$  (Br) is uncertain, because other DMP adducts (i.e., with zinc and cadmium dihalides) present in the same range a ligand band of medium intensity [19]. Literature reports on Al-halide absorptions in complexes are scarce and concern mainly 1:1 adducts with ammonia, phosphine and thiol derivatives [10, 20-22]. Moreover 1:2 aluminum trihalide adducts can contain ionic moieties, as confirmed for  $\text{Al}(\text{CH}_3\text{CN})_2\text{X}_3$  (X = Cl or Br) by X-ray analysis [23]. The  $\text{Al}(\text{CH}_3\text{CN})_2\text{Cl}_3$  crystals consist of two  $[\text{AlCl}_4]^-$  anions and the  $[\text{Al}(\text{CH}_3\text{CN})_5\text{Cl}]^{2+}$  cation along with a crystallization molecule of  $\text{CH}_3\text{CN}$  [24]. Studies on the aluminum trichloride-tetrahydrofuran system have confirmed the versatility of this class of acceptors [25-28].

Table 2. Infrared bands in the 550-200  $\text{cm}^{-1}$  region for the pyrone complexes.

$\text{Al}(\text{DMP})_2\text{Cl}_3$	564 mw	554 sh	532 mw	497 s	414 m	393 sh	347 s <sup>b</sup>		
$\text{Al}(\text{DMP})_3\text{Br}_3$	564 mw	532 mw	518 sh	427 s	419 sh		357 s <sup>b</sup>		
$\text{Al}(\text{DMP})_3\text{I}_3$	565 mw	535 m	520 sh			370 w	345 w	330 w	
$\text{Ga}(\text{DMP})_{1.5}\text{Cl}_3$	562 w	552 sh	528 w			375 s		266 m	
$\text{In}(\text{DMP})_2\text{Cl}_3$		547 mw	523 mw			373 w	342	m298w	285 sh 228, 219 w

<sup>a</sup>Metal-halide in italic. <sup>b</sup>Tentative assignment

In particular two species with 1:2 stoichiometry have been isolated, the molecular one,  $\text{Al}(\text{THF})_2\text{Cl}_3$ , showing a trigonal bipyramidal geometry with equatorial chlorine atoms, and the ionic complex  $[\text{Al}(\text{THF})_4\text{Cl}_2][\text{AlCl}_4]$ , in which the octahedral cation contains apical chlorine atoms. The Al-Cl absorptions of the ionic species are at  $494\text{ cm}^{-1}$  ( $[\text{AlCl}_4]^-$ ) and  $457\text{ cm}^{-1}$  ( $\nu_{\text{asym}}(\text{AlX}_2)$  of the cation). The  $\text{Al}(\text{THF})_2\text{Cl}_3$  spectra have been measured in  $\text{AlCl}_3/\text{THF}$  solutions, which contain both *cis*- and *trans*- isomers of the complex, the related Al-Cl absorptions being at  $490\text{ cm}^{-1}$  (*cis*) and  $494\text{ cm}^{-1}$  (*trans*). It is evident that infrared data do not allow to state the monomeric or ionic nature of the complex. The In-Cl absorptions are observed at 305 and  $182\text{ cm}^{-1}$  in the molecular complex  $\text{In}(\text{hmpa})_2\text{Cl}_3$ , whereas they are present at 340, 320 and  $302\text{ cm}^{-1}$  in the ionic compound  $[\text{In}(\text{Ph}_3\text{PO})_4\text{Cl}_2][\text{InCl}_4]$  [11, 14]. The position of the bands for  $\text{In}(\text{DMP})_2\text{Cl}_3$  (342 and  $298\text{ cm}^{-1}$ ) could be in favour of an ionic arrangement. The infrared absorptions of maltol complexes in the  $1650\text{--}1450\text{ cm}^{-1}$  region are hardly correlable to coordination sites, especially for mixed species (Table 1). In fact free maltol displays a strong band at  $1652\text{ cm}^{-1}$ , assigned as mainly  $\nu(\text{C}=\text{O})$ , whereas the bands at  $1616\text{ cm}^{-1}$  (strong) and  $1559\text{ cm}^{-1}$  (medium) belong to strongly mixed  $\nu(\text{C}=\text{C})$  and  $\nu(\text{C}=\text{O})$  modes. Carbonyl coordination, along with possible formation of phenol hydrogen-halide bridges, causes a slight shift of the ligand band at  $1616\text{ cm}^{-1}$ , the  $\nu(\text{C}=\text{O})$  originating the strong absorption at *ca*  $1570\text{ cm}^{-1}$ . The spectrum of maltol below  $500\text{ cm}^{-1}$  is very simple with a medium intensity band at  $321\text{ cm}^{-1}$  and a weak one at  $215\text{ cm}^{-1}$ . The  $\nu(\text{M}-\text{O})$  absorptions in  $\text{Al}(\text{Ma})_3$  ( $464$ ,  $445$  and  $410\text{ cm}^{-1}$ ) and in  $\text{Ga}(\text{Ma})_3$  ( $360$ ,  $270$  and  $230\text{ cm}^{-1}$ ) [4] are quite different from those of the related HMa adducts, whose spectra contain strong M-Cl bands at  $479$ ,  $470\text{ cm}^{-1}$  (Al) and  $374\text{ cm}^{-1}$  (Ga), present for  $\text{In}(\text{HMa})_2\text{Cl}_3$  at  $301$ ,  $294$  and  $288\text{ cm}^{-1}$ . The proton NMR spectrum of maltol in deuterated dimethyl sulfoxide gives  $\text{CH}_3$  and OH singlets at 2.22 and 8.80 ppm respectively, along with ring CH doublets at 6.31 ppm (CH bound to carbonyl) and 7.99 ppm (CH bound to ring oxygen) (Table 3). As expected, the OH proton signal is absent in the  $\text{Al}(\text{Ma})_3$  spectrum, the resonances of the other proton groups being observed downfield with respect to free maltol. The  $\text{Al}(\text{Ma})_2\text{I}$  spectrum displays an analogous trend, proton resonances being observed at 2.35 ppm ( $\text{CH}_3$ ) and 6.65 and 8.23 ppm (CH). The spectrum of  $\text{Al}(\text{HMa})_3\text{Cl}_3$  in  $d_6$ -DMSO, registered for freshly prepared samples, coincides with that of free maltol. In fact the strongly coordinating solvent replaces immediately the ligand in the metal coordination sphere. On standing, the NMR solution separates a white solid, the supernatant solution showing weak maltolato signals at 2.40, 6.82 and 8.50 ppm. The  $\text{Ga}(\text{HMa})_3\text{Cl}_3$  complex shows a similar behaviour, the reaction to form maltolato species being slower than for aluminum. Maltol should not be removed by acetone, as shown by the corresponding spectrum, in which all resonances are well downfield with respect of those of free ligand in the same solvent. The spectrum of  $\text{Al}(\text{HMa})_2(\text{Ma})\text{Br}_2$  in  $d_6$ -DMSO contains two sets of signals, the downfield one belonging to coordinated maltolato and the upfield one (having a double intensity) belonging to free HMA

Table 3. Proton NMR data in  $d_6$ -DMSO (ppm; ca 25°C)

Compound	CH <sup>a</sup>	CH	CH <sub>3</sub>	OH <sup>b</sup>
HMa	7.99	6.31	2.22	8.8
HMa <sup>c</sup>	7.95	6.32	2.29	7.4
AlMa <sub>3</sub>	8.33	6.74	2.31	
Al(HMa) <sub>3</sub> Cl <sub>3</sub>	8.0	6.31	2.22	d
Ga(HMa) <sub>3</sub> Cl <sub>3</sub>	8.0	6.30	2.23	d
Ga(HMa) <sub>3</sub> Cl <sub>3</sub> <sup>c</sup>	8.33	6.83	2.45	9.25
Al(HMa) <sub>2</sub> (Ma)Br <sub>2</sub> <sup>e</sup>	8.0	6.31	2.21	8.7
	8.43	6.79	2.41	
Al(Ma) <sub>2</sub> I	8.23	6.65	2.35	

<sup>a</sup>The downfield signal in maltol and complexes belongs to ring CH near the ring oxygen. <sup>b</sup>The signal position varies with concentration. <sup>c</sup>In  $d_6$ -acetone. <sup>d</sup>Very broad signal centered at 8.5 ppm. <sup>e</sup>The intensity of HMa signals is twice the intensity of the maltolato resonances.

removed by solvent. The DMP complexes dissolve in dimethyl sulfoxide and N,N-dimethylformamide with decomposition, as confirmed by proton NMR spectra, which contain free DMP signals (CH<sub>3</sub>, 2.22 ppm; CH, 6.01 ppm). The spectra of saturated solutions in deuterated acetone, a solvent in which the complexes are slightly soluble, contain coordinated DMP signals, free ligand being absent. One signal for each proton group is observed for Al(DMP)<sub>2</sub>Cl<sub>3</sub> (2.31 and 6.21 ppm), Ga(DMP)<sub>1.5</sub>Cl<sub>3</sub> (2.50 and 6.61 ppm) and In(DMP)<sub>2</sub>Cl<sub>3</sub> (2.39 and 6.50 ppm), downfield with respect to the corresponding resonances for free DMP, as expected on coordination. Conversely, the spectra of the Al(DMP)<sub>3</sub>X<sub>3</sub> complexes contain several signals due to coordinated ligand. In particular Al(DMP)<sub>3</sub>I<sub>3</sub> displays two signals of different intensity for the CH<sub>3</sub> protons (2.59 and 2.67 ppm), the corresponding CH resonances being at 7.43 and 6.91 ppm. The stronger signals in the Al(DMP)<sub>3</sub>Br<sub>3</sub> spectrum are at 2.66 and 7.32 ppm, whereas weak CH<sub>3</sub> proton resonances at 2.52, 2.56 and 2.59 ppm appear as shoulders of the main signal. The corresponding broad resonances related to CH protons are observed in the 6.9-7.50 ppm range. Such a behaviour supports the presence in solution of more species with different coordination environments.

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### References

1. D. Fregona, Z. J. Guo, G. Faraglia and S. Sitran, *J. Coord. Chem.*, 28 (1993) 73.
2. D. Fregona, G. Faraglia and S. Sitran, *J. Coord. Chem.*, 30 (1993) 221.
3. D. Fregona, G. Faraglia, R. Graziani, U. Casellato and S. Sitran, *Gazz. Chim. Ital.*, 124 (1994) 55.
4. M. M. Finnegan, T. G. Lutz, W. O. Nelson, A. Smith and C. Orvig, *Inorg. Chem.*, 26 (1987) 2171.



5. C. A. Matsuba, W. O. Nelson, S. J. Rettig and C. Orvig, *Inorg. Chem.*, **27** (1988) 3935.
6. M. T. Ahmet, C. S. Frampton and J. Silver, *J. Chem. Soc., Dalton Trans.*, (1988) 1159.
7. T. G. Lutz, D. J. Clevette, S. J. Rettig and C. Orvig, *Inorg. Chem.*, **28** (1989) 715.
8. M. M. Finnegan, S. J. Rettig and C. Orvig, *J. Am. Chem. Soc.*, **108** (1986) 5033.
9. M. Shah, PCT Int. Appl. WO 91; C.A., **116** (1992) 136251d.
10. N. Burford, B. W. Royan, R. E. v. H. Spence, T. S. Cameron, A. Linden and R. D. Rogers, *J. Chem. Soc., Dalton Trans.*, (1990) 1521.
11. W. T. Robinson, C. J. Wilkins and Z. Zeying, *J. Chem. Soc., Dalton Trans.*, (1990) 219.
12. A. J. Carty and D. G. Tuck, *J. Chem. Soc. (A)*, (1966) 1081.
13. A. G. Groves, W. T. Robinson and C. J. Wilkins, *Inorg. Chim. Acta*, **114** (1986) L29.
14. S. P. Sinha, T. T. Pakkanen, T. A. Pakkanen and L. Niinistö, *Polyhedron*, **1** (1982) 355.
15. L. A. Lobanova, E. N. Gur'yanova, A. F. Volkov and R. R. Shifrina, *Russ. J. Gen. Chem., (Engl. Transl.)* **45** (1975) 1819.
16. F. J. Arnàiz, J. M. Bustello and R. Lopez, *Synth. React. Inorg. Met.-Org. Chem.*, **22** (1992) 371.
17. A. R. Katritzky and R. A. Jones, *Spectrochim. Acta*, **17** (1961) 64.
18. D. Fregona, Z. J. Guo, G. Faraglia, and S. Sitran, *Transition Met. Chem.*, **17** (1992) 242.
19. G. Faraglia, D. Fregona, Z. J. Guo and S. Sitran, *Thermochim. Acta*, **191** (1991) 95.
20. G. G. Hoffmann, *Z. Anorg. Allg. Chem.*, **558** (1988) 160.
21. G. G. Hoffmann, *Chem. Ber.*, **118** (1985) 3320.
22. C. E. Sjøgren and E. Rytter, *Spectrochim. Acta*, **41A** (1985) 1277.
23. M. Dalibart, J. Derouault, M. T. Forel and P. Caillet, *J. Mol. Struct.*, **63** (1980) 233.
24. J. A. K. Howard, L. E. Smart and C. J. Gilmore, *J. Chem. Soc., Chem. Commun.*, (1976) 477.
25. J. Derouault and M. T. Forel, *Inorg. Chem.*, **16**, (1977) 3207.
26. J. Derouault, P. Granger and M. T. Forel, *Inorg. Chem.*, **16**, (1977) 3214.
27. A. H. Cowley, M. C. Cushner, R. E. Davis and P. E. Riley, *Inorg. Chem.*, **20**, (1981) 1179.
28. N. Carlene Means, C. Mitchell Means, S. G. Bott and J. L. Atwood, *Inorg. Chem.*, **26** (1987) 1466.

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