

Organic compounds of gallium. III. Reactions of gallium alkoxides with acetylacetone, ethyl acetoacetate, methyl acetoacetate, and methyl salicylate

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Received November 5, 1968

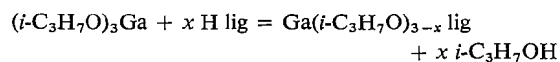
Derivatives of gallium of the type: $\text{Ga}(i\text{-C}_3\text{H}_7\text{O})_{3-x}\text{lig}_x$ ($x = 1, 2, \text{ or } 3$; and H lig = acetylacetone, methyl and ethyl acetoacetate, or methyl salicylate) have been synthesized by reacting gallium alkoxides with ligands in various molar ratios. The compounds are soluble in organic solvents and could be volatilized under reduced pressure. Their molecular weights have been determined ebullioscopically. The infrared spectra of some of the compounds have been studied.

Canadian Journal of Chemistry, 47, 2661 (1969)

Introduction

The reactions of alkoxides of aluminium, lanthanum, neodymium, preseodymium, titanium, niobium, and tantalum (1-7) with bidentate monofunctional ligands like β -diketones and β -ketoesters have recently been studied in these laboratories with interesting results regarding the volatility and coordination number of the products. In the cases of the first 4 elements, all the 3 isopropoxy groups could be replaced by the chelating ligands, but in the cases of the last 3, only partial replacement was possible; e.g. the final end products were $\text{Ti}(\text{OR})_2\text{lig}_2$ and $\text{Nb}(\text{OR})_2\text{lig}_3$.

In view of the above studies, it was considered of interest to carry out similar reactions with gallium alkoxides. The synthesis of gallium tris-acetylacetonate was reported as early as 1921 by Morgan and Drew (14). In the present investigation, the acetylacetone and β -ketoester derivatives of gallium have been prepared by the following reactions in benzene solution



where $x = 1, 2, \text{ or } 3$; and H lig = acetylacetone, methyl acetoacetate, ethyl acetate, or methyl salicylate.

Isopropanol liberated was fractionated azeotropically and estimated. The products obtained by the above general reactions are soluble in benzene and except those of methyl salicylate can be distilled or sublimed under reduced pressure. All the products obtained in a molar ratio of 1:1 showed dimeric association and the 1:3 derivatives are monomers. However, the

TABLE I
Infrared analysis of compounds*

$\text{Ga}(i\text{-C}_3\text{H}_7\text{O})_2\text{-(acac)}$ (in KBr)	$\text{Ga}(i\text{-C}_3\text{H}_7\text{O})\text{-(acac)}_2$ (in CHCl_3 soln.)	$\text{Ga}(\text{acac})_3$ (in Nujol mull at 4000-400 cm^{-1})
3500 sb	3710 m†	3350 wb
2975 s (A)	2975 s (A)†	2960 s (A)
1950 w	—	2925 sb†
—	—	2850 sb
1600 s (B)	1600 s (B)	1575 sb (B)
1510 w (C)	1545 s (C)	1515 mb (C)
1460 w (D)	1470 w†	1450 s†
—	—	—
1400 sb (E)	1440 m (D)	—
1280 s	1385 w†	1380 s†
1260 m	1335 w (E)	1275 m
1250 w	1295 m	1190 w
1200 w	1270 m	1150 w
1180 w (G)	1180 w (G)	1015 s (F)
1150 s (G)	1130 s (G)	925 s
1100 mb	1050 w (F)†	790 m
1035 s (F)	1035 w (F)	760 s
965 m (G)	935 s†	715 w
935 s	880 m†	670 w (H)
835 w	855 m†	650 w (H)
825 w	680-760 sb†	570 m
805 m	—	455 w (H)
770 m	—	430 mb (H)
680 m (H)	—	—

*Modes assigned on the basis of previous measurements are given in parentheses:

(A), $\nu(\text{C-H})$; (B), $\nu(\text{C}=\text{C})$ and chelated ketone $-\text{C}=\text{O}-$; (C), $\nu(\text{C}=\text{C})$; (D), $\nu(\text{C}=\text{O}) + \text{CH}$; (E), $\delta(\text{C-H})$; (F), $\nu(\text{C-O})$;

(G), $-\text{CH}-\begin{matrix} \text{CH}_3 \\ | \\ \text{CH}_3 \end{matrix}$, skeletal; (H), $\nu(\text{Ga-O})$ and ring deformation.

s, strong; m, medium; w, weak; b, broad.
†Bands of the solvent used.

compounds obtained in a molar ratio of 1:2 varied in molecular complexity as the ligands were changed; the methyl acetoacetate, the ethyl acetoacetate, and the acetylacetonate derivative showed molecular complexities of 2, 1.3, and 1, respectively.

TABLE II
Reactions of gallium alkoxides with β -ketoesters and acetylacetone

Ligand	Wt. of compound (g)	Wt. of ligand (g)	Molar ratio	Product	Yield (g)	State	Analysis (%)				Mol. wt.		Wt. of $i\text{-C}_3\text{H}_7\text{OH}$ in azeotrope (g)		Boiling point ($^{\circ}\text{C}/\text{mm}$)		
							Ga		Isopropoxy		Found	Calcd.	Found	Calcd.		Found	Calcd.
							Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.			
Compound = $\text{Ga}(i\text{-C}_3\text{H}_7\text{O})_3$																	
Methyl acetoacetate	2.13	1.00	1:1	$\text{Ga}(i\text{-C}_3\text{H}_7\text{O})_2(\text{meacac})$	2.61	Yellow liquid	23.06	23.02	37.88	37.98	617	303	0.52	0.52	160/0.6		
	2.76	2.62	1:2	$\text{Ga}(i\text{-C}_3\text{H}_7\text{O})(\text{meacac})_2$	4.5	"	19.35	19.43	17.69	17.48	718	359	1.35	1.36	172/0.4		
	1.12	1.58	1:3	$\text{Ga}(\text{meacac})_3$	1.87	"	16.79	16.81	—	—	406	413	0.81	0.82	182/2.5		
Ethyl acetoacetate	2.70	1.42	1:1	$\text{Ga}(i\text{-C}_3\text{H}_7\text{O})_2(\text{etacac})$	3.40	Colorless liquid	22.04	22.01	37.17	37.26	632	317	0.65	0.66	136/0.5		
	2.03	2.15	1:2	$\text{Ga}(i\text{-C}_3\text{H}_7\text{O})(\text{etacac})_2$	3.20	"	18.07	18.02	15.37	15.26	504	387	0.99	0.99	170/0.5		
	1.23	1.94	1:3	$\text{Ga}(\text{etacac})_3$	2.30	White solid	15.23	15.25	—	—	433	457	0.52	0.52	136/0.1		
Compound = $\text{Ga}(i\text{-C}_3\text{H}_7\text{O})(\text{meacac})_2$																	
Methyl salicylate	2.14	1.35	1:1	$\text{Ga}(i\text{-C}_3\text{H}_7\text{O})_2(\text{mesyl})$	2.94	White foamy solid	20.66	20.58	33.70	34.05	680	339	0.51	0.52	285/0.2 (decomp.)		
	1.05	1.94	1:3	$\text{Ga}(\text{mesyl})_3$	2.26	"	13.26	13.32	—	—	507	523	0.75	0.76	330/0.5 (decomp.)		
Acetyl acetone	2.20	0.89	1:1	$\text{Ga}(i\text{-C}_3\text{H}_7\text{O})_2(\text{acac})$	2.56	Brown liquid	24.33	24.31	38.27	41.25	613	287	0.53	0.54	151/0.8		
	2.00	1.62	1:2	$\text{Ga}(i\text{-C}_3\text{H}_7\text{O})(\text{acac})_2$	2.56	Yellow solid	21.22	21.32	18.68	18.48	324	327	0.97	0.97	171/0.5 (Sublimed)		
	1.13	1.39	1:3	$\text{Ga}(\text{acac})_3$	1.70	"	18.92	19.00	—	—	352	367	0.81	0.82	197-198 (m.p.)		
Acetyl acetone	2.21	1.20	Excess ligand	$\text{Ga}(\text{acac})(\text{meacac})_2$	2.30	Yellow liquid	17.69	17.48	—	—	404	399	—	—	170/0.9		
Compound = $\text{Ga}(\text{OC}_2\text{H}_5)_3$																	
Acetyl acetone	2.37	1.16	1:1	$\text{Ga}(\text{OC}_2\text{H}_5)_2(\text{acac})$	3.01	Brown liquid	27.01	26.95	—	—	626	259	0.52	0.53	170/0.9		
	1.62	1.58	1:2	$\text{Ga}(\text{OC}_2\text{H}_5)(\text{acac})_2$	2.48	Cream crystals	22.15	22.29	—	—	422	313	0.72	0.73	175-176 (m.p.)		
	1.76	2.58	1:3	$\text{Ga}(\text{acac})_3$	3.16	Yellow crystals	19.13	19.01	—	—	377	367	1.18	1.19	190-200/0.2 (Sublimed) 197-198 (m.p.)		

The derivatives could be distilled at higher temperatures compared to gallium isopropoxide indicating that chelation has the expected effect of lowering the volatility.

A mixed ligand product $\text{Ga}(\text{acac})(\text{meacac})_2$ was also obtained by reacting $\text{Ga}(i\text{-C}_3\text{H}_7\text{O})(\text{meacac})_2$ and acetylacetone in excess (acac = acetylacetone, meacac = methyl acetoacetate). The compound is monomeric in benzene.

Infrared spectra of some of the derivatives have been recorded in the range $4000\text{--}670\text{ cm}^{-1}$ ($2.5\text{--}15\ \mu$). The data and the modes assigned on the basis of previous measurements (8–13) are given in Table I. The bands at about $3400\text{--}3500\text{ cm}^{-1}$ may be due to slight hydrolysis of isopropoxy derivatives during handling and recording of the spectra.

Experimental

An all-glass apparatus fitted with interchangeable joints was used, special precautions being taken to exclude moisture. All reactions were carried out in a flask under a column packed with Rasching rings and fitted to a total condensation variable take-off stillhead.

Molecular weights were determined ebullioscopically in boiling benzene by means of a semimicro (Gallenkamp) ebulliometer using thermistor sensing. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer model 137B.

Gallium isopropoxide was prepared as previously described (8) and benzene was dried similarly. Methyl acetoacetate, ethyl acetoacetate, and methyl salicylate were distilled over aluminium isopropoxide. Acetylacetone was fractionated over aluminium isopropoxide.

Gallium and isopropanol were estimated as described earlier (8). Isopropoxy in mixed β -diketonate compounds was estimated by liberating the isopropanol with excess of the ligand.

The same synthetic procedure was used in all the cases. Details are, therefore, given for the typical derivatives only; the other reactions are summarized in Table II.

Synthetic Reactions

Reaction of Gallium Isopropoxide and Acetylacetone in Molar Ratio 1:2

Gallium isopropoxide (2.00 g) and acetylacetone (1.62 g) were refluxed in benzene (60 ml) followed by slow distillation of isopropanol azeotropically between $72\text{--}80\text{ }^\circ\text{C}$. The remaining solvent was removed under reduced pressure and the product dried at room temperature ($35\text{ }^\circ\text{C}$) at 0.5 mm pressure for 2 h. A yellow solid (2.56 g) was obtained.

The analysis of isopropanol in azeotrope required for 2 moles of isopropanol, 0.97 g. Found: 0.97 g.

Anal. Calcd. for $\text{C}_{13}\text{H}_{21}\text{O}_5\text{Ga}$: Ga, 21.32; isopropoxy, 18.48. Found: Ga, 21.22; isopropoxy, 18.68.

This compound (2.0 g) was distilled under reduced pressure at $171\text{ }^\circ\text{C}/0.5\text{ mm}$ as a brown liquid (0.85 g); it solidified after a few minutes on cooling, m.p. $148\text{--}149\text{ }^\circ\text{C}$, and this solid was found to be 21.42% Ga.

Reaction of Gallium Ethoxide and Acetylacetone in Molar Ratio 1:2

Gallium ethoxide (1.62 g) and acetylacetone (1.58 g) were refluxed in benzene (55 ml) and ethanol was removed azeotropically between $68\text{--}80\text{ }^\circ\text{C}$ followed by excess of benzene. On leaving the clear solution overnight, cream colored crystals appeared. The mother liquor was decanted off and the crystals were dried at room temperature ($35\text{ }^\circ\text{C}$) at 0.4 mm pressure yielding a crystalline solid (1.58 g). The analysis of ethanol in the azeotrope required for 2 moles of ethanol, 0.73 g. Found: 0.72 g.

The solid was recrystallized from benzene giving crystals (m.p. $175\text{--}176\text{ }^\circ\text{C}$) having the same appearance and analysis.

Acknowledgments

The authors are grateful to the Chemical Society, London, for a research grant for chemicals. One of the authors S.R.B. is grateful to the Council of Scientific and Industrial Research, New Delhi, for the award of a Junior Research Fellowship. The authors' thanks are due to Mr. Bhagirath Singh for recording the infrared spectra.

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