

Dialkyl- and Alkylenedithiophosphates of Gallium(III)

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Abstract

Gallium(III) tris-dialkyldithiophosphates, $\text{Ga}[\text{S}_2\text{P}(\text{OR})_2]_3$ ($\text{R} = \text{C}_2\text{H}_5$, $n\text{-C}_3\text{H}_7$, $i\text{-C}_3\text{H}_7$, $n\text{-C}_4\text{H}_9$ and $i\text{-C}_4\text{H}_9$) and gallium(III) tris-alkylenedithiophosphates, $\text{Ga}(\text{S}_2\text{P}-\text{O}-\text{G}-\text{O})_3$ [$\text{G} = -\text{CH}_2\text{C}(\text{C}_2\text{H}_5)_2\text{-CH}_2-$, $-\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2$ and $-\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)$] have been synthesized for the first time by the reactions of gallium(III) chloride with the alkali metal salt of the corresponding ligand in anhydrous benzene in 1:3 molar ratio respectively.

These compounds are crystalline solids or viscous liquids and are soluble in common organic solvents, in which they show monomeric behaviour. Based on elemental analyses, molecular weight determinations, IR and NMR (^1H and ^{31}P) spectral data, chelate octahedral structures have been proposed for these derivatives.

Introduction

As compared to the chemistry of gallium–oxygen bonded compounds, that of gallium–sulphur bonded compounds has been little explored. Gallium tends to form stronger bonds with oxygen than with sulphur. Thus, gallium is preferentially attached to oxygen in the monothiophosphinates [1–3] and monothiocarboxylate [4] derivatives, such as $\text{R}_2\text{-GaOP}(\text{S})\text{R}_2$ and $\text{R}_2\text{GaOC}(\text{S})\text{R}$. The latter derivatives appear to be monomeric, containing planar four membered, MOSC rings. Gallium, however, forms stable compounds with dithio ligands, e.g., dithiocarboxylates [5], xanthates [6] and dithiocarbamates [7–9]. $\text{Ga}(\text{S}_2\text{CNMe}_2)_3$ is monomeric [7] having bidentate chelating Me_2NCS_2 groups.

Dialkyldithiophosphate [10, 11], as well as alkylenedithiophosphate [12, 13], ligands exhibit bidentate behaviour and form stable complexes with transition and main group elements. Dialkyldithiophosphates of gallium are surprisingly still unknown. In view of the above, it was considered of interest to synthesize and characterize dialkyl- as well as alkylenedithiophosphates of gallium and compare their

structural features with the known complexes with other dithio ligands.

Experimental

Moisture was carefully excluded throughout the experimental manipulations. Solvents (benzene, petroleum-ether, chloroform and carbon tetrachloride) and alcohols (ethanol, n-propanol, isopropanol, n-butanol and iso-butanol) were dried before use, by standard methods. Gallium(III) chloride (Kochlight) was used as such. Gallium isopropoxide [14], dialkyl- [15–18] and alkylenedithiophosphoric acids [19] or their sodium/ammonium salts were prepared by the methods reported in the literature. Gallium [14] and sulphur [20] were estimated gravimetrically as gallium oxinate and barium sulphate respectively. Isopropanol was estimated by the method reported by Bradley *et al.* [21].

Measurements

Molecular weights were determined cryoscopically in benzene. IR spectra, using CsI cells, were recorded as neat liquids or in the form of Nujol mulls (in case of solid compounds) on a Perkin-Elmer 577 spectrometer in the range $4000\text{--}200\text{ cm}^{-1}$. ^1H NMR in CDCl_3 or CCl_4 were recorded on a Perkin-Elmer R 12B spectrophotometer using TMS as an external standard. ^{31}P NMR (proton decoupled) spectra in CDCl_3 were recorded on an FX 90 Q spectrometer using 85% H_3PO_4 as an internal standard.

Methods of Preparation

Reaction of gallium(III) chloride with sodium diethyldithiophosphate in 1:3 molar ratio

An exothermic reaction occurred when solid sodium diethyldithiophosphate (1.93 g, 9.28 mmol) was added to a benzene solution (~60 ml) of gallium(III) chloride (0.53 g, 3.01 mmol). The reaction mixture was refluxed for ~2 hr to ensure the completion of the reaction. The precipitate of NaCl (0.52 g) was filtered out and the removal of the solvent from the filtrate under reduced pressure yielded $\text{Ga}[\text{S}_2\text{P}(\text{OEt})_2]_3$ (1.67 g, 89% yield) as a

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colourless semisolid. *Anal.* Calcd. for $C_{12}H_{30}O_6P_3S_6Ga$: Ga, 11.16; S, 30.73%. Found: Ga, 11.40; S, 31.17%.

Other dialkyldithiophosphates of gallium were prepared similarly (Table I).

Reaction of gallium(III) chloride with ammonium hexylenedithiophosphate in 1:3 molar ratio

A suspension of ammonium alkylenedithiophosphate (2.50 g, 10.92 mmol) in benzene (~30 ml) was added to a solution of gallium(III) chloride (0.63 g, 3.58 mmol) in benzene (~30 ml). The reaction mixture was refluxed for ~3 hr. On separating out NH_4Cl (0.51 g) by filtration and removing the solvent from the filtrate under reduced pressure a crystalline white solid of gallium(III) tris-hexylenedithiophosphate was obtained (2.35 g, 96% yield). It was again purified by crystallization from a solution of benzene and n-hexane. *Anal.* Calcd. for $C_{18}H_{36}O_6P_3S_6Ga$: Ga, 9.92; S, 27.32%. Found: Ga, 9.97; S, 27.47%; M.P. 110–112 °C.

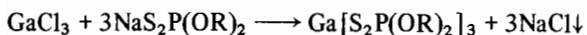
Physical and analytical data for other gallium(III) alkylenedithiophosphates have been described in Table I.

Reaction of gallium isopropoxide with pinacol-dithiophosphoric acid in 1:1 molar ratio

A mixture of gallium isopropoxide (0.68 g, 2.76 mmol) and pinacol-dithiophosphoric acid (0.59 g, 2.78 mmol) in ~70 ml anhydrous benzene was refluxed on the column and isopropanol (0.16 g), liberated during the course of the reaction, was collected azeotropically with benzene and estimated by the usual method. Removal of the solvent yielded diisopropoxy gallium mono(pinacol-dithiophosphate) as a white solid in quantitative yield. *Anal.* Calcd. for $C_{12}H_{26}O_4PS_2Ga$: Ga, 17.49; S, 16.05%. Found: Ga, 17.65; S, 15.86%. M.P. 180–5 °C dec.

Results and Discussion

Gallium(III) tris-dialkyldithiophosphates have been synthesized by the reactions of gallium(III) chloride and corresponding sodium salts of the dialkyldithiophosphoric acid in 1:3 molar ratio in refluxing benzene:

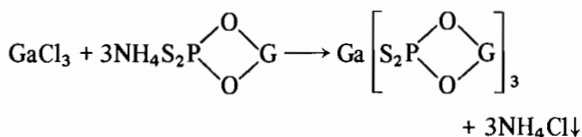


(Where R = C_2H_5 , $n-C_3H_7$, $i-C_3H_7$, $n-C_4H_9$ and $i-C_4H_9$).

Gallium(III) tris-diethyl and -diisopropyldithiophosphates are colourless semi-solids while other dialkyldithiophosphates are colourless viscous liquids. All these compounds are soluble in benzene, chloroform, carbon tetrachloride and acetonitrile. These derivatives show a tendency to decompose in air and turn blackish on keeping for a long time even in a

stopped flask; this property appears to be especially dominant in gallium(III) tris-diisopropyldithiophosphate.

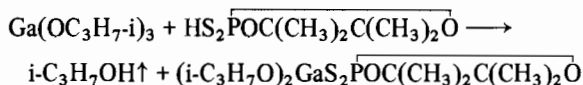
Adopting a similar route, gallium(III) tris-alkylene-dithiophosphates have also been prepared by the reactions of gallium(III) chloride and ammonium alkylenedithiophosphates in required molar ratio. Qualitatively these reactions appear to be somewhat less facile than the corresponding reactions of dialkyldithiophosphates:



[where G = $-CH_2C(C_2H_5)_2CH_2-$, $-C(CH_3)_2C(CH_3)_2-$ and $-C(CH_3)_2CH_2CH(CH_3)-$]

Gallium alkylenedithiophosphates are white crystalline solids which are soluble in benzene, chloroform and DMSO. A few of these could be crystallized from a mixture of benzene and n-hexane. Interestingly, their solubility decreases on keeping for a long period.

Mixed diisopropoxygallium mono(pinacol-dithiophosphate) could also be synthesized by the reaction of gallium isopropoxide, $Ga(OC_3H_7-i)_3$, with pinacol-dithiophosphoric acid in 1:1 molar ratio in refluxing benzene with fractionation of isopropanol azeotropically with the solvent. The mixed isopropoxy derivative, $(i-C_3H_7O)_2GaS_2POC(CH_3)_2C(CH_3)_2O$, was isolated as a white solid, soluble in benzene, chloroform and DMSO, from the resulting solution by removing the solvent under reduced pressure:



Spectroscopic Studies

The IR spectra of dialkyldithiophosphate derivatives of gallium have been measured in the range 4000–200 cm^{-1} and assignments have been made on the basis of earlier reports [10, 22]. The bands in the region 1030–975 and 870–770 cm^{-1} are assigned to (P)–O–C and P–O–(C) stretching modes respectively. A strong band due to P=S vibrations, observed in the region 680–660 cm^{-1} in the spectra of dialkyldithiophosphoric acids and their ammonium salts, is shifted to lower (~15 cm^{-1}) frequencies in these compounds. Bands of medium intensity present in the region 550–500 cm^{-1} have been assigned to P–S asymmetric and symmetric stretching vibrations.

The bands present in the regions 1060–980 and 835–770 cm^{-1} in the IR spectra of alkylenedithiophosphate derivatives may be assigned to (P)–O–C and P–O–(C) stretching vibrations respectively.

TABLE I. Syntheses and Characterisation of Dialkyl- and Alkylenedithiophosphates of Gallium(III).

Sl. No.	Reactants, g	Product, g Found (Calcd.)	NaCl/NH ₄ Cl (g) Found (Calcd.)	M.P. °C Found (Calcd.)	Physical state	% Analysis Found (Calcd.)		Molecular weight Found (Calcd.)
						Ga	S	
1	GaCl ₃ + 3NaS ₂ P(OCH ₂ CH ₃) ₂ 0.53 1.93	Ga[S ₂ P(OCH ₂ CH ₃) ₂] ₃ 1.67(1.88)	0.52 (0.53)		Colourless semisolid	11.40 (11.16)	31.17 (30.73)	635 (625)
2	GaCl ₃ + 3NaS ₂ P(OCH ₂ CH ₂ CH ₃) ₂ 0.67 2.77	Ga[S ₂ P(OCH ₂ CH ₂ CH ₃) ₂] ₃ 2.53(2.70)	0.60 (0.67)		Viscous liquid	9.82 (9.84)	27.11 (27.09)	720 (709)
3	GaCl ₃ + 3NaS ₂ P[OCH(CH ₃) ₂] ₂ 0.34 1.44	Ga[S ₂ P(OCH(CH ₃) ₂) ₂] ₃ 1.31(1.37)	0.31 (0.34)		Colourless semisolid	9.93 (9.84)	26.80 (27.09)	739 (709)
4	GaCl ₃ + 3NaS ₂ P(OCH ₂ CH ₂ CH ₂ CH ₃) ₂ 0.65 3.00	Ga[S ₂ P(OCH ₂ CH ₂ CH ₂ CH ₃) ₂] ₃ 2.80(2.93)	0.60 (0.65)		Viscous liquid	8.75 (8.80)	23.95 (24.22)	—
5	GaCl ₃ + 3NaS ₂ P[OCH ₂ CH(CH ₃) ₂] ₂ 0.45 2.15	Ga[S ₂ P(OCH ₂ CH(CH ₃) ₂) ₂] ₃ 2.01(2.03)	0.40 (0.45)		Viscous liquid	8.76 (8.80)	24.02 (24.22)	832 (793)
6	GaCl ₃ + 3NH ₄ S ₂ POCH ₂ C(C ₂ H ₅) ₂ CH ₂ O 0.52 2.21	Ga[S ₂ POCH ₂ C(C ₂ H ₅) ₂ CH ₂ O] ₃ 1.87(2.20)	0.42 (0.47)	115	White solid	9.28 (9.36)	25.39 (25.78)	780 (745)
7	GaCl ₃ + 3NH ₄ S ₂ POC(CH ₃) ₂ C(CH ₃) ₂ O 0.56 2.30	Ga[S ₂ POC(CH ₃) ₂ C(CH ₃) ₂ O] ₃ 2.05(2.23)	0.44 (0.51)	136	White solid	9.82 (9.92)	27.29 (27.32)	—
8	GaCl ₃ + 3NH ₄ S ₂ POC(CH ₃) ₂ CH ₂ CH(CH ₃)O 0.63 2.50	Ga[S ₂ POC(CH ₃) ₂ CH ₂ CH(CH ₃)O] ₃ 2.35(2.51)	0.51 (0.57)	110–2	White solid	9.97 (9.92)	27.47 (27.32)	722 (703)
9	Ga[OCH(CH ₃) ₂] ₃ + HS ₂ POC(CH ₃) ₂ C(CH ₃) ₂ O 0.68 0.59	[OCH(CH ₃) ₂ CHO] ₂ GaS ₂ POC(CH ₃) ₂ C(CH ₃) ₂ O 1.04(1.10)		180–5 dec	White solid	17.65 (17.49)	15.86 (16.05)	—

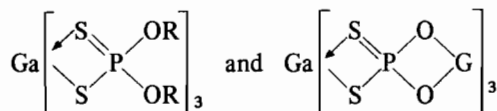
The bands of sharp to medium intensities in the region 950–900 cm^{-1} may be attributed to the ring vibrations of the dioxaphospholane and dioxaphosphorinane [23, 24] which are probably coupled with C–C stretching vibrations. A sharp band present in the region 660–630 cm^{-1} is due to $\nu(\text{P}=\text{S})$ vibrations (showing a shift to lower frequency with respect to corresponding parent acid) and the bands in the region 580–500 cm^{-1} may be assigned to P–S asymmetric and symmetric vibrations [12] (Table II).

^1H NMR spectra of the representative compounds, recorded in CDCl_3 or CCl_4 , are in accordance with the proposed formulae (Table III). The signals of hydrogen atoms, present at the α -carbon atom of P–O–C skeleton of alkyl or alkylene chains, become doubled due to coupling with ^{31}P nucleus.

Decoupled ^{31}P NMR spectra for these products give a singlet. The values of chemical shifts according to Glidewell's [25] observation indicates bidentate chelating behaviour of the ligand (Table III). It has

been observed that ^{31}P NMR chemical shifts for alkylenedithiophosphate derivatives are higher than those for dialkyldithiophosphate derivatives. An increase in ^{31}P chemical shift value for gallium(III) tris-alkylenedithiophosphates in comparison to corresponding ligand suggest a chelating behaviour of the ligand [25].

Molecular weight determination of gallium(III) tris-dialkyl and -alkylenedithiophosphates showed monomeric nature of these compounds in benzene. Thus, on the basis of our observations for IR, NMR (^1H and ^{31}P) and molecular weight determinations, the following structure (in which gallium is six-coordinated) is proposed for the tris-derivatives:



It is relevant to mention here that Coggon *et al.* [26] reported the single crystal structure for indium-

TABLE II. Some Relevant I.R. Frequencies (cm^{-1}) for Gallium(III) Dialkyl- and Alkylenedithiophosphates.^a

Sl. No.	Compound	$\nu(\text{P})-\text{O}-\text{C}$	$\nu\text{P}-\text{O}-(\text{C})$	Ring vibrations	$\nu\text{P}=\text{S}$	$\nu\text{P}-\text{S}$
1	$\text{Ga}[\text{S}_2\text{P}(\text{OCH}_2\text{CH}_3)_2]_3$	1015–30s	790s		655s	540s
2	$\text{Ga}[\text{S}_2\text{P}(\text{OCH}_2\text{CH}_2\text{CH}_3)_2]_3$	1000–990s	840s		660s	530m
3	$\text{Ga}[\text{S}_2\text{P}(\text{OCH}(\text{CH}_3)_2)_2]_3$	1005–975s	870s		640s	515m
4	$\text{Ga}[\text{S}_2\text{P}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2]_3$	1030–20s	840s		655s	530m
5	$\text{Ga}[\text{S}_2\text{P}(\text{OCH}_2\text{CH}(\text{CH}_3)_2)_2]_3$	1000–990s	840s		660s	535m
6	$\text{Ga}[\text{S}_2\text{P}(\text{OCH}_2\text{C}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{O})_2]_3$	1055s	800s	925m	680s	505m
7	$\text{Ga}[\text{S}_2\text{P}(\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O})_2]_3$	1035m	770s	950s	650s	570m
8	$\text{Ga}[\text{S}_2\text{P}(\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_2]_3$	1015–995s	780s	945m	630s	575m
9	$(i\text{-C}_3\text{H}_7\text{O})_2\text{GaS}_2\text{P}(\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O})$	1040s	785s	930s	640s	530s

^am = medium, s = strong, w = weak.

TABLE III. ^1H and ^{31}P NMR Spectral Data for Gallium(III) Dialkyl- and Alkylenedithiophosphates.^a

Sl. No.	Compound	^{31}P Chemical shift (δ ppm)	^1H Chemical shifts (δ ppm)
1	$\text{Ga}[\text{S}_2\text{P}(\text{OCH}_2\text{CH}_3)_2]_3$	93.89	1.30–1.55t, 18H(–CH ₃); 4.00–4.50m, 12H(–OCH ₂ –)
2	$\text{Ga}[\text{S}_2\text{P}(\text{OCH}_2\text{CH}_2\text{CH}_3)_2]_3$	94.09	0.90–1.35t, 18H(–CH ₃); 1.55–2.15m, 12H(–CH ₂ –); 3.95–4.40m, 12H(OCH ₂ –)
3	$\text{Ga}[\text{S}_2\text{P}(\text{OCH}(\text{CH}_3)_2)_2]_3$	90.59	1.20–1.60d, 36H(–CH ₃); 4.65–5.15m, 6H(–OCH–)
4	$\text{Ga}[\text{S}_2\text{P}(\text{OCH}_2\text{CH}(\text{CH}_3)_2)_2]_3$	91.67	0.90–1.20d, 36H(–CH ₃); 1.80–2.35m, 6H(–CH–); 3.75–4.20dd, 12H(–OCH ₂ –)
5	$\text{Ga}[\text{S}_2\text{P}(\text{OCH}_2\text{C}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{O})_2]_3$	90.93	0.65–1.00t, 18H(–CH ₃); 1.25–1.75q, 12H(–CH ₂ –); 4.05 and 4.25d, 12H(–OCH ₂ –), $J_{\text{POCH}_2} = 12$ Cps
6	$\text{Ga}[\text{S}_2\text{P}(\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O})_2]_3$		1.10s(–CH ₃) ₂
7	$\text{Ga}[\text{S}_2\text{P}(\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_2]_3$	81.44	1.30–1.90m, 33H[(CH ₃) ₂ CH ₂ C(CH ₃)], 4.65–5.20m, 3H(–OCH–)
8	$[(\text{CH}_3)_2\text{CHO}]_2\text{GaS}_2\text{P}(\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O})$		1.05s, 12H(–CH ₃) ₂ ; 1.10–1.15d, 12H(–CH ₃); 4.40–4.80m, 2H(–OCH–)

^as = singlet, d = doublet, t = triplet, q = quartet and m = multiplet; dd = double doublet.

(III) tris-diethyldithiophosphate, $\text{In}[\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2]_3$ and suggested an octahedral form with bidentate chelating behaviour of the ligand.

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