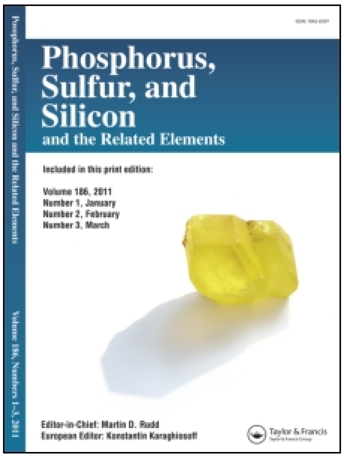

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Kaushik, Ajay , Singh, Yash Pal and Rai, Audhesh K.(2001) 'Synthesis and Characterisation of N-Alkyl-2-Mercaptoacetamide Complexes of Gallium (III)', Phosphorus, Sulfur, and Silicon and the Related Elements, 169: 1, 267 — 270

To link to this Article: DOI: 10.1080/10426500108546639

URL: http://dx.doi.org/10.1080/10426500108546639

Phosphorus, Sulfur and Silicon, 2001, Vol. 169, pp. 267-270
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Synthesis and Characterisation of N-Alkyl-2-Mercaptoacetamide Complexes of Gallium (III)

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N-alkyl-2-mercaptoacetamides of gallium having general formula $[RNHC(O)CH_2S]_3Ga$, where $R = C_2H_5$, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, $i\text{-}C_4H_9$, $sec\text{-}C_4H_9$ have been prepared and characterised by elemental analysis and spectral (IR, ^1H & ^{13}C NMR) studies. The complexes appear to exist in two conformational isomeric forms in solution and the probable structure for both the isomers have been proposed.

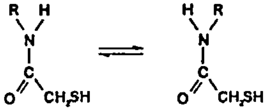
Keywords: Gallium isopropoxide; N-alkyl-2-mercaptoacetamides; conformational isomerism; spectral studies; five membered chelatering

INTRODUCTION

N-alkyl-2-mercaptoacetamides are known to behave as bidentate ligand and due to the presence of O, N and S atoms at suitable positions, these ligands are capable of showing linkage isomerism[1-3]. These ligands also exist in two conformational isomeric forms, which interact individually with metal ions and form two different isomers of metal complexes[4-7]. The present paper deals with synthesis, characterisation and structure elucidation of some gallium (III) complexes of N-alkyl-2-mercaptoacetamides.

RESULTS AND DISCUSSION

N-alkyl-2-mercaptoacetamides exist in the following two conformational isomeric forms[4-7].



These forms interact with gallium isopropoxide in 1:3 molar ratio in refluxing benzene solution :

$$Ga(OPr^i)_3 + 3RNHC(O)CH_2SH \longrightarrow Ga[SCH_2(O)CNHR]_3 + 3\,Pr^i(OH)\uparrow$$

Where $R = C_2H_5$, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, $i\text{-}C_4H_9$, $sec\text{-}C_4H_9$.

The resulting light yellow derivatives are found to be viscous, soluble in polar solvents like alcohols and DMSO. Molecular weight determination in methanol solution indicates their monomeric nature.

IR SPECTRA

In the infrared spectra of these complexes, disappearance of υ SH band (observed at ~ 2510 cm^{-1} in the spectra of the ligands) suggests the deprotonation of the mercapto group. This has been further supported by the appearance of a band at ~ 350 cm^{-1} which may be assigned to υ Ga-S[11]. A lower shift of 30-50 cm^{-1} in the position of υ NH band (2970-2040 cm^{-1}) in comparison to its position in parent ligands and the appearance of a new band at ~ 590 cm^{-1} for υ Ga – N[11] indicates the coordination of amide nitrogen with central gallium atom.

A comparison of the absorption bands observed at ~ 1640, ~ 1545 and ~ 1270 cm^{-1} in the spectra of the ligands and assigned to υ C=O, amide- II [υ (CN)+ δ (NH)] and amide-III [υ (CN)+ δ (NH)] respectively, with their corresponding position in the spectra of their gallium (III) derivatives show lower shift of 30-40 cm^{-1}. This shifting supports the participation of NH group in bonding with gallium atom. The absence of any appreciable shift in the position of amide-I [υ (C=O)] band confirms the non-participation of carbonyl oxygen in the bonding. The appearance of υ Ga-S and υ Ga-N absorption bands in the complexes and the absence of υ Ga-O band confirms that out of the three donor atoms viz. O, S and N present in ligands only N and S are involved in bonding with central gallium atom.

^{1}H NMR Spectra

The ^{1}H NMR spectra of these derivatives have been recorded in DMSO-d_6 solution using TMS as an internal reference (Table-1).

Table – 1 : ***^{1}H NMR Spectra (δ ppm) of gallium derivatives of N-alkyl-2-mercaptoacetamides***

S No.	Complex	$-CH_3$	$>CH_2$	$>CH$	$-CH_2S-$	$>NH$
1.	$(CH_3CH_2NHCOCH_2S)_3Ga$	1.27 (t)	3.24 (q)	–	3.34 (s)	8.10 (br) 9.40 (br)
2.	$(CH_3\overset{a}{C}H_2\overset{b}{C}H_2NHCOCH_2S)_3Ga$	0.89 (t)	(a) 1.20-1.74 (m) (b) 3.08 (t)	–	3.40 (s)	8.35 (br) 9.43 (br)
3.	$[(CH_3)_2CHNHCOCH_2S]_3Ga$	1.19 (d) 1.34 (d)	–	3.38 (sep) 4.00 (sep)	3.43 (s)	7.82 (br) 9.16 (br)
4.	$(CH_3\overset{a}{C}H_2\overset{b}{C}H_2\overset{c}{C}H_2NHCOCH_2S)_3Ga$	0.89 (t)	(a,b) 1.91-1.84 (m) (c) 3.10 (t)	–	3.31 (s)	7.51 (br) 9.03 (br)
5.	$[(CH_3)_2CHCH_2NHCOCH_2S]_3Ga$	0.89 (d) 0.97 (d)	2.54 (d) 2.59 (d)	2.00 (m)	3.42 (s)	8.18 (br) 8.29 (br)
6.	$(CH_3\overset{a}{C}H_2\overset{b}{C}H(CH_3)NHCOCH_2S)_3Ga$	(a) 0.96 (t) (b) 1.16 (t)	1.52 (m)	3.97 (m)	3.30 (s)	7.80 (br) 8.93 (br)

The spectra exhibit, two distinct NH signals with a downfield shift of δ 0.5 to δ 2.0 ppm in comparison to their position in the corresponding ligands. This indicates the existence of these derivatives in two isomeric forms and participation of nitrogen atom in bonding. Absence of SH proton signal at ~ δ 3.5 ppm., confirm the deprotonation of mercapto group and supports the formation of Ga-S bond.

The signals for alkyl protons show a downfield shift in comparison to their position in the ligands. The spectrum of the derivative where R = i-C_3H_7 exhibits two doublets and two septets for gem dimethyl and methine protons respectively. Whereas, in the spectrum of the complex where R = i-C_4H_9, two sets of doublts have been observed each for $(CH_3)_2$ and CH_2 proton but a clear resolution of CH proton signal could not be observed. The splitting of alkyl and NH proton signals provide further support to the existence of these derivatives in two conformational isomeric forms in the solution.

^{13}C NMR Spectra

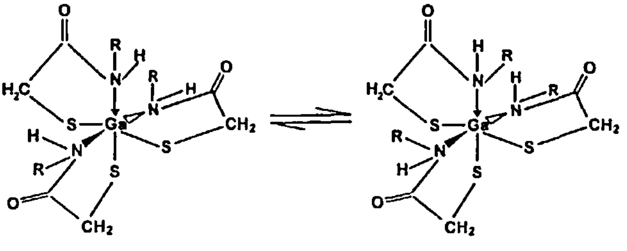
The ^{13}C NMR spectra of the complexes have been recorded in methanol solution (Table-2).

Table – 2 : *^{13}C NMR Spectra data (δ ppm) of gallium derivatives of N-alkyl-2-mercaptoacetamides*

S No.	Complex	-CH_3	>CH_2	→CH	-CH_2S-	-C=O
1.	$(CH_3CH_2NHCOCH_2S)_3Ga$	12.75, 14.48	3.28, 30.47	–	35.42 36.11	170.00 175.23
2.	$(CH_3\overset{a}{C}H_2\overset{b}{C}H_2NHCOCH_2S)_3Ga$	12.00, 12.48	(a) 21.88, 23.52 (b) 28.98, 29.12	–	43.26 44.29	169.68 175.00
3.	$[(CH_3)_2CHNHCOCH_2S]_3Ga$	21.11, 22.73	–	28.43 30.81	44.03 44.74	170.21 174.83
4.	$(CH_3\overset{a}{C}H_2\overset{b}{C}H_2\overset{c}{C}H_2NHCOCH_2S)_3Ga$	14.52, 14.61	(a) 20.60, 20.92 (b) 28.60, 28.91 (c) 30.43, 32.98	–	40.88 41.12	170.12 175.12
5.	$[(CH_3)_2CHCH_2NHCOCH_2S]_3Ga$	19.98, 20.00	28.32, 29.91	26.91 27.32	46.93 47.55	169.98 174.93
6.	$(\overset{a}{C}H_3CH_2CH(\overset{b}{C}H_3)NHCOCH_2S)_3Ga$	(a) 09.65, 09.99 (b) 18.20, 19.81	29.10, 29.68	41.18 43.69	47.18 47.72	170.00 175.12

The existence of two conformational isomers in these complexes have been further confirmed by the appearance of two signals for each carbonyl and alkyl carbons (R) in their ^{13}C NMR spectra. A downfield shift of about δ 0.5 ppm to δ 2.0 ppm in the position of the -CH_2S- carbon signals indicates the involvement of sulphur atom in complexation. A downfield shift in the position of the alkyl carbons attached to nitrogen further supports the involvement of nitrogen in bond formation.

The presence of υ Ga-N and υ Ga-S absorption bands along with the shift of amide- II and amide-III absorption bands to lower wave number and no shift in the position of amide-I [υ (C=O)] band supports the chelation of the ligand with central gallium atom through nitrogen and sulphur. Since both the isomeric forms of the ligand individually interact with central gallium atom and form the corresponding complexes and therefore they may be assigned the following structures :



EXPERIMENTAL

All the operations were carried out under strictly anhydrous condition and the chemical used were of reagent grade. Gallium trichloride was distilled before use.Gallium isopropoxide[8] and N-alkyl-2-mercaptoacetamides[9] were prepared by the literature method. Sulphur and Gallium were estimated gravimetrically whereas nitrogen was determined by Kjeldahl's method[10]. Molecular weights were determined by Knaur vapour pressure osmometer in methanol solution at 45° C.The IR spectra were recorded on a carl zeiss Jena specord M-80 instrument as nujol mull and ^{1}H and ^{13}C NMR spectra on a JEOL FX90Q spectrometer.All the derivatives were synthesised by the reactions of $Ga(OPr^i)_3$ with the ligands in 1 : 3 molar ratio in benzene solution and the preparation of only one representative complex is being discussed below.

Preparation of $[i\text{-}C_3H_7NHC(O)CH_2S]_3Ga$ **:** A mixture of Gallium triisopropoxide (0.53 gm. 2.14 mM) and the ligand N-(isopropyl)-2-mercaptoacetamide (0.96 gm. 6.42 gmM) in ~ 50 ml benzene was refluxed under fractionating column. The isopropanol liberated during the course of the reaction was fractionated off azeotropically with benzene. The progress of the reaction was monitored by estimating the isopropanol in the azeotrope. After the completion of reaction, the precipitated product was filtered off, washed with benzene and dried under reduced pressure. A compound, thus obtained was purified by washing with benzene. Repeated washing with benzene purified the light yellow coloured viscous mass (yield 97 %). Analysis : found % Ga, 14.91; S,20.55; N, 8.85; Cal.% for $C_{15}H_{30}S_3N_3O_3Ga$; Ga, 14.97; S,20.61; N,9.01.

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