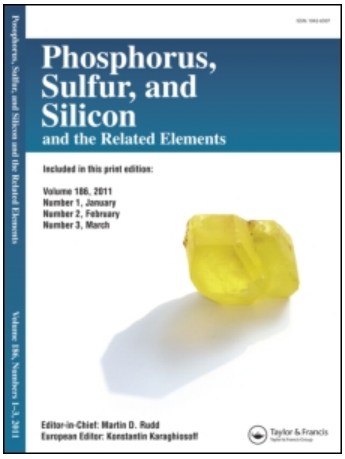

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TRIS(N-/S-ALKYL AMINOCYCLOPENTENE-1-CARBODITHIATO)GALLIUM(III): SYNTHESIS AND STRUCTURAL ELUCIDATION

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TRIS(N-/S-ALKYL AMINOCYCLOPENTENE-1-CARBODITHIATO)GALLIUM(III): SYNTHESIS AND STRUCTURAL ELUCIDATION

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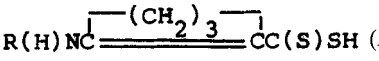
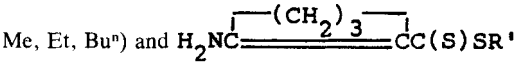
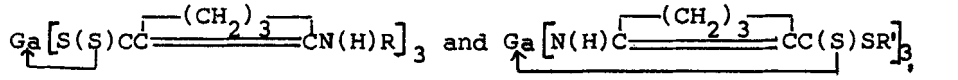
Reactions of gallium isopropoxide with 2N-alkyl and S-alkyl-aminocyclopentene-1-carbodithioic acids,  (R = H, Me, Et, Bu^n) and  (R' = Me, CH_2NEt_2), in 1:3 molar ratio in refluxing benzene lead to the formation of *tris*-derivatives,  respectively.

These compounds have been characterized by elemental analyses and molecular weight measurements and their probable structures have been proposed by IR and NMR (^1H and ^{13}C) spectral studies. In these complexes two different proposed bonding modes around the central gallium atom are discussed.

Key words: Gallium isopropoxide; 2N-alkyl aminocyclopentene-1-carbodithioic acid; spectral studies; four-membered chelate ring; six-membered chelate ring.

INTRODUCTION

Although the chemistry of gallium complexes with either sulfur or nitrogen donor ligands has been explored,[1–4] reports on complexes with ligands having both donor atoms are rather scanty.[5,6]

In continuation of our studies on comparative ligating capabilities of 2-aminocyclopentene-1-carbodithioic acid (ACDA) and its N-/S-alkyl derivatives with main group elements, (B[7], In[8], As[9], Sb[9], Ph_2Sb[10] and Bi[11]) in +3 oxidation state, we describe here investigations on synthetic and structural aspects of gallium(III) complexes.

RESULTS AND DISCUSSION

Out of various tautomeric forms reported[12,13] for 2-aminocyclopentene-1-carbodithioic acid (ACDA), the following tautomer(A) appears to predominate in solution[8]:

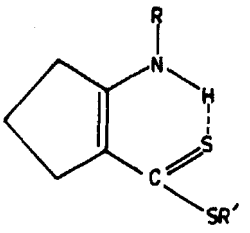


Fig.A
where R = H(ACDA), Me(MeACDA), Et(EtACDA), Bu(BuACDA); R' = H and R' = Me(ACDE'), $-CH_2NEt_2$(ACDE"); R = H, respectively

The reactions of gallium isopropoxide with the above ligands in 1:3 molar ratio in refluxing benzene solution, lead to the formation of *tris*-complexes of the type (I) and (II):

$$Ga(OPr^i)_3 + 3R(H)NC\overset{\overset{(CH_2)_3}{\frown}}{=\!=\!=}CC(S)SH \longrightarrow Ga\left[S(S)CC\overset{\overset{(CH_2)_3}{\frown}}{=\!=\!=}CN(H)R\right]_3 + 3Pr^iOH$$

(I)

where R = H, Me, Et and n-Bu

$$Ga(OPr^i)_3 + 3H_2NC\overset{\overset{(CH_2)_3}{\frown}}{=\!=\!=}CC(S)SR' \longrightarrow Ga\left[N(H)C\overset{\overset{(CH_2)_3}{\frown}}{=\!=\!=}CC(S)SR'\right]_3 + 3Pr^iOH$$

Where R' = Me and CH_2NEt_2

The elemental analyses of these complexes correspond to *tris*-derivatives of gallium within experimental error (±0.5%). These yellow coloured solids having solubility in common organic solvents are monomeric in nature and undergo decomposition above 20°C, even under reduced pressure.

(I) Structural elucidation of tris-2N-alkylaminocyclopentene-1-carbodithiolato-SS gallium (III); $Ga\left[S(S)CC\overset{\overset{(CH_2)_3}{\frown}}{=\!=\!=}CN(H)R\right]_3$.

IR SPECTRA

A comparison of IR spectra of these complexes with the spectra of corresponding ligands shows the absence of ν SH band (observed at ~2550 cm^{-1} in the spectra

TABLE I

IR data of gallium (III) complexes of 2-alkylaminocyclopentene-1-carbodithioic acids and their esters

$Ga(ACDA)_3$	$Ga(MeACDA)_3$	$Ga(EtACDA)_3$	$Ga(BuACDA)_3$	$Ga(ACDE')_3$	Assignment
3350 b	3350 b	3360 b	3360 b	3200 b	ν NH_2/NHR
1600 s	1605 s	1600 s	1605 s	1590 s	ν NH + C = C
1490 s	1490 s	1480 s	1496 s	1480 s	ν CH_2 + C = C
1350 s	1360 s	1360 s	1320 s	1270 s	νC = N + C = S
1280 s	1270 s	1280 s	1270 s	1160 s	νC = S + C = N
920 m	930 m	950 m	940 m	980 m	ν Asym CSS
610 b	610 b	605	610	615	ν Sym CSS
335 s	340	350	350	335	ν Ga - S
..	..	..	..	550	νGa - N

of ligands[9,13]) indicating deprotonation of —SH and formation of Ga—S bond. This has been supported by the appearance of new band at 355–350 cm^{-1} for ν Ga—S (Table I). Further, the appearance of a single band in the region 950 ± 30 cm^{-1} assigned to ν asy CSS, suggests the involvement and equivalent nature of both the sulfur atoms of dithiocarboxylate group.[14,15] However, the unaltered positions of bands due to NH_2 and NHR groups indicate the non-involvement of the amino group in bonding.

TABLE II

^1H NMR data of gallium (III) complexes of 2-alkylaminocyclopentene-1-carbodithioic acid and their esters

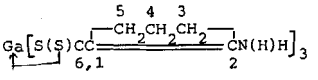
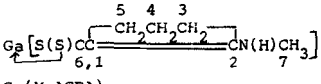
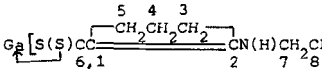
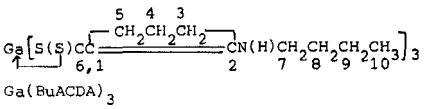
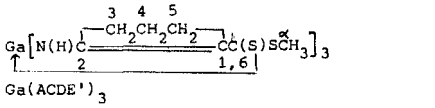
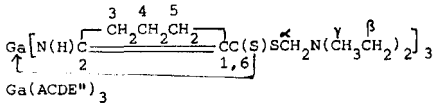
Sl.No.	Compound	Solvent	Chemical Shifts in (δ) ppm
1.	 $Ga(ACDA)_3$	Polysol	1.5-1.9, q , 2H-$CH_{2(4)}$; 2.5-2.8, m , 4H-$CH_{2(3\ \&\ 5)}$; 8.7, bs , 1H-NH (free) ; 8.9, bs , 1H-NH
2.	 $Ga(MeACDA)_3$	Polysol	1.81, q , 2H-$CH_{2(4)}$; 2.6-2.8, m , 2H-$CH_{2(3)}$; 2.9-3.3, m , 2H-$CH_{2(5)}$; 3.4, s , 3H-$NCH_{3(7)}$; 9.3, bs , 1H-NH
3.	 $Ga(EtACDA)_3$	$CDCl_3$	1.8, q , 2H-$CH_{2(4)}$; 2.6-2.8, m , 4H-$CH_{2(3\ \&\ 5)}$ 2.8-3.2, q ; 2H-$CH_{2(7)}$; 1.21, t , 3H-$CH_{3(8)}$; 9.2, bs , 1H-NH

TABLE II (*Continued*)

4.	 $Ga(BuACDA)_3$	$CDCl_3$	1.5-2.1, m , $6H-CH_{2(4,8\ \&\ 9)}$; 2.6-2.9, m , $4H-CH_{2(3\ \&\ 5)}$; 3.0-3.5, q , $2H-CH_{2(7)}$; 0.93, t , $3H-CH_{3(10)}$; 9.5, bs , 1H-NH
5.	 $Ga(ACDE')_3$	Polysol	1.6-2.0, q , $2H-CH_{2(4)}$; 2.5-2.9, m , $4H-CH_{2(3\ \&\ 5)}$; 2.7, s , $3H-SCH_{3(\alpha)}$; 6.8, bs , 1H-NH
6.	 $Ga(ACDE'')_3$	Polysol	1.4-1.8, m , $2H-CH_{2(4)}$; 2.1-2.9, m , $6H-CH_{2(3,5\ \&\ \beta)}$; 4.3, s , $2H-SCH_2N(\alpha)$; 8.5, bs , 1H-NH(free) ; 0.1-1.2, t , $3H-CH_{3(\gamma)}$

^{1}H NMR SPECTRA

The absence of the signal for —SH proton in the spectra of complexes (Table II) further supports its deprotonation and the formation of Ga—S bond.

In the spectra of free ligands, the appearance of the signal for the amino proton in the NHR group in the downfield region (δ11.2–12.0 ppm, where R = Me, Et and Bu) has been attributed to hydrogen bonding (Figure A). The upfield shifting of this signal in the complexes to δ8.7–9.5 ppm may, therefore, be ascribed to the breaking of hydrogen bond (Figure B):

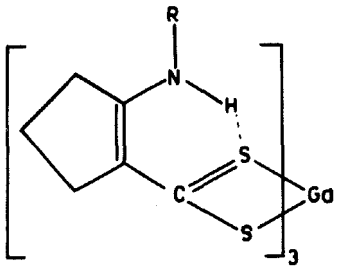


Fig. B

(where R = Me, Et and Bu)

The appearance of two signals due to NH_2 protons in the ligand (ACDA) at δ11.2 and 6.2 ppm has been ascribed to one of the protons being hydrogen bonded. Appearance of two close (in place of one) proton signals in $Ga(ACDA)_3$ at δ8.9 and 6.7 ppm indicates weak interaction between one of these protons with the sulfur atom of dithiocarboxylate groups.

^{13}C NMR SPECTRA

A comparison of ^{13}C NMR spectra of the complexes with the parent N-alkyl ligands reveals that the signals for alkyl and cyclopentene ring carbons do not show any significant shift in their positions (Table III). Only the signal due to C(6) atom shows a downfield shift of 4–8 ppm indicating its deshielding as a result of deprotonation of —SH group and coordination through free sulfur atom of dithiocarboxylate group and weakening of inherent hydrogen bonding in the parent ligand (Figure A).

These results are in contrast to our earlier reports for analogous boron derivatives[7] in which a six-membered chelate ring involving amino group and sulfur atom has been proposed. However, it resembles closely the structural features observed in the case of analogous indium[8], antimony[9], arsenic[9] and bismuth[11] complexes.

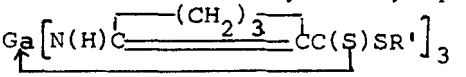
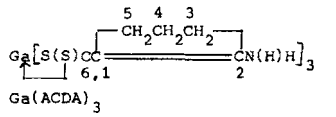
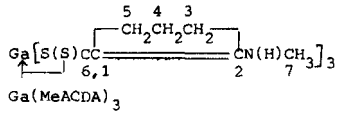
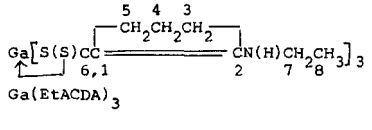
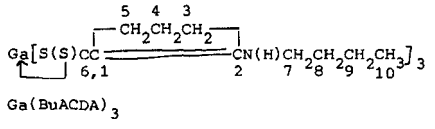
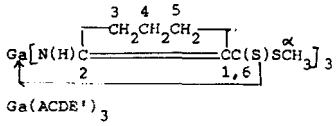
(II) Structural elucidation of tris-S-alkylaminocyclopentene-1-carbodithiotato-N,S gallium (III): 

TABLE III

^{13}C spectral data of gallium (III) complexes of 2-alkylaminocyclopentene-1-carbodithioic acids and their esters

Sl.No.	Compound	Solvent	Chemical Shift Values (δ) in ppm
1.	 Ga(ACDA)$_3$	Polysol	$C_{(1)}$, 116.9 ; $C_{(2)}$, 168.6 ; $C_{(3)}$, 39.4 ; $C_{(4)}$, 18.9 ; $C_{(5)}$, 30.6 ; $C_{(6)}$, 201.2
2.	 Ga(MeACDA)$_3$	Polysol	$C_{(1)}$, 117.1 ; $C_{(2)}$, 170.7 ; $C_{(3)}$, 34.7 ; $C_{(4)}$, 18.9 ; $C_{(5)}$, 33.1 ; $C_{(6)}$, 197.2
3.	 Ga(EtACDA)$_3$	$CDCl_3$	$C_{(1)}$, 118.1 ; $C_{(2)}$, 171.2 ; $C_{(3)}$, 33.4 ; $C_{(4)}$, 18.9 ; $C_{(5)}$, 33.2 ; $C_{(6)}$, 196.9 ; $C_{(7)}$, 39.8 ; $C_{(8)}$, 15.4
4.	 Ga(BuACDA)$_3$	$CDCl_3$	$C_{(1)}$, 118.2 ; $C_{(2)}$, 171.1 ; $C_{(3)}$, 33.0 ; $C_{(4)}$, 20.1 ; $C_{(5)}$, 32.5 ; $C_{(6)}$, 200.0 ; $C_{(7)}$, 46.1 ; $C_{(8)}$, 31.6 ; $C_{(9)}$, 22.1 ; $C_{(10)}$, 13.7
5.	 Ga(ACDE')$_3$	$CDCl_3$	$C_{(1)}$, 117.8 ; $C_{(2)}$, 166.2 ; $C_{(2)}$, 36.2 ; $C_{(4)}$, 20.3 ; $C_{(5)}$, 35.8 ; $C_{(6)}$, 207.8 ; $C_{(\alpha)}$, 17.2

IR SPECTRA

In the IR spectra of the above class of complexes, a lowering of 50 cm^{-1} in the position of NH_2 group (observed at 3250 cm^{-1} in parent ligands) indicates the involvement of amino group in bonding (Table I). The presence of a splitted band for ν asy CSS in the range 940–970 cm^{-1} reveals the non-equivalent nature of the two sulfur atoms of dithiocarboxylate group and supports the participation of one sulfur atom in complex formation.[14,15] The positions of other bands are found to be similar to those observed for N-alkyl derivatives.

^{1}H NMR SPECTRA

In the ^{1}H NMR spectrum of the complex, $GA(ACDE')_3$, only one signal for NH proton is observed at δ6.1 ppm (Table II) whereas in the parent ligand,[8] ACDE', two signals are being observed at δ11.2 and 6.1 ppm indicating the removal of one of the amino protons during complexation. A downfield shift in SCH_3 signal further supports the participation of C=S in bonding.

^{13}C NMR SPECTRA

The signals for the carbon atoms C_2, C_6 and C_7 (Table III) in $Ga(ACDE')_3$ type complexes show a downfield shift in comparison to the parent ligands and are observed at δ166.2 (C_2), 207.8 (C_6) and 17.2 (C_α) ppm, respectively. This downfield shift supports the presence of nitrogen and sulfur atoms along with gallium in a six-membered chelate ring (Figure C).

The mode of bonding in these complexes appears to be similar to that observed in the analogous complexes of boron[7] and indium[8], but it differs markedly with the complexes of group VA elements like Sb(III)[9], Ph_2Sb[10] and Bi[11] in which adducts are formed in preference to substituted complexes.

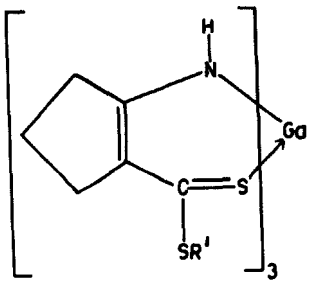


Fig. C

(where R' = Me and $-CH_2NEt_2$)

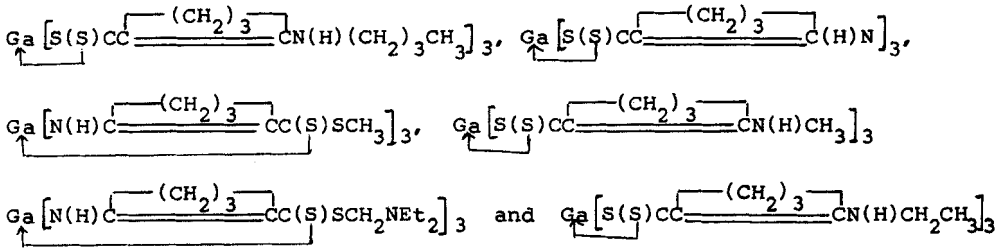
EXPERIMENTAL

Stringent precautions were taken to exclude moisture during the course of synthesis of the extremely hydrolysable nature of the starting material, gallium isopropoxide. All the chemicals used were of reagent grade. Gallium isopropoxide[16] and 2-alkylamino-cyclopentene-1-carbodithioic acids and their esters[13,17] have been synthesized by the reported methods.

Since a similar method has been adopted in the synthesis of gallium complexes, the synthetic procedure of only one compound has been described for brevity.

Synthesis of tris-(2-aminocyclopentene-1-carbodithiolato-S,S) Gallium (III). A mixture of gallium isopropoxide (0.89 g, 3.61 mmole) and the ligand ACDA (1.72 g, 10.79 mmole) in benzene (~60 ml) solution was refluxed under a fractionating column. The liberated isopropanol was fractionated out as azeotrope and the progress of the reaction was monitored by estimating the isopropanol in the azeotrope. After the completion of the reaction, the volatile constituents were removed under reduced pressure and the resultant yellow coloured solid was recrystallized from hot chloroform solution (yield ~90%). The compound on analysis was found to have Ga, 12.7; N, 2.5; S, 11.6%. Calcd. for $Ga(S_2NC_6H_8)_3$: Ga, 12.8; N, 2.6; S, 11.8%. Mol. wt. found 560.5, Calcd. 543.7.

Using the above procedure the compounds having the following molecular formulae have been synthesized and characterized:



Analytical methods and physical measurements. The isopropanol in the azeotrope was estimated by the oxidimetric method,[18] gallium as gallium oxinate,[19] nitrogen by the Kjeldahl's method,[19] and sulfur gravimetrically.[19]

Molecular weight measurements have been carried out on Knauer Vapour Pressure Osmometer at 45°C in chloroform solution. IR spectra have been recorded on Perkin Elmer 577 Spectrophotometer as CsI pellets or nujol mulls.

The ^1H and ^{13}C NMR spectra of the ligands have been recorded on a Bruker 270 MHz NMR Spectrometer and those of gallium complexes on Jeol FX 90Q NMR Spectrometer, in $CDCl_3$ or Polysol solution using TMS as an internal standard.

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