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ORIGINAL PAPER

NMR, X-Ray Crystal Structure Studies and Mechanism for Formation of a Novel Di-gallium Complex and 5-Methoxy-4,5,6-triphenyl-4,5-dihydro-1,2,4-triazene-3(2H)-thione

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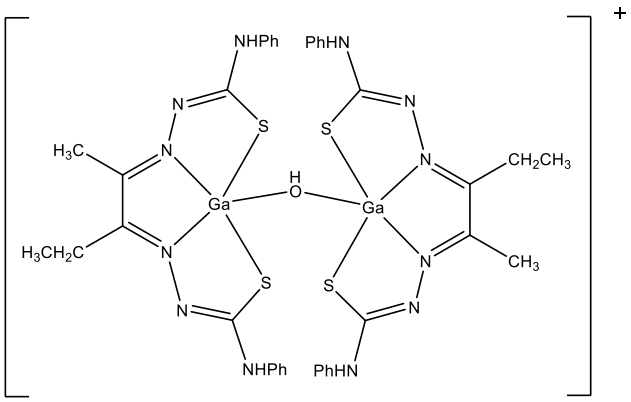
Abstract

Gallium complexes of bis-thiosemicarbazones were prepared and characterized using NMR and X-ray crystallography. Formation of a gallium nitrate complex was proven by NMR spectroscopy. Surprisingly, this complex was found to convert on standing to a new hydroxido-bridged di-gallium complex. The X-ray crystal structure of the digallium complex is described. Similarly, a triazene compound was formed during the preparation of the gallium complex comprising a tetraphenyl unit in the bis-thiosemicarbazone structure. We propose a mechanism for the formation of both the di-gallium species as well as triazene compound in solution. The lattice parameters for the digallium complex is as follows: a: 17.6854(13) Å, b:16.6492(7) Å, c: 21.4659(14) Å, β = 112.383(8)°.

Graphical Abstract



Gallium complexes of bis-thiosemicarbazones were prepared and were found to convert to a new hydroxido-bridged di-gallium complex

Keywords Synthesis · NMR · X-ray crystallography · Triazene · Mechanism

Introduction

Bis-thiosemicarbazones are a class of compound possessing N- and S-donor atoms that confer an ability to coordinate to a wide range of metal ions. These complexes can be prepared [1–3] with relative ease and often exhibit high stability. Some complexes with a thiosemicarbazone or bis-thiosemicarbazone framework also exhibit interesting biological characteristics [4–21] including potent anticancer activity. Recently, much attention has been devoted to metal

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coordinated thiosemicarbazones as potential imaging agents, with the introduction of radio metals [22]. A variety of radio metals can be used to coordinate with thiosemicarbazones. Pascu et al. prepared ^{68}Ga complexes as potential imaging agents [22–24]. They found that the ^{68}Ga complexes of tetradentate bis-thiosemicarbazones formed a square-based pyramidal chloridogallium(III) complex.

We were interested in developing imaging agents incorporating radio-metals, in gallium complexes of bis-thiosemicarbazones. Here, we describe the mechanism of formation of di-gallium complex and its X-ray crystal structure and the instability of the gallium nitrate complex resulting in formation of this di-gallium complex.

Experimental

All chemicals were purchased from Sigma-Aldrich Chemical Company and used as received. Anhydrous solvents were also obtained from Sigma-Aldrich in Sure/Seal™ bottles and transferred to reaction vessels via cannula under nitrogen atmosphere. Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker 700 MHz instrument and chemical shifts are reported in parts per million (ppm) relative to residual DMSO signal at 2.5 ppm, which was used as the internal standard. ^{13}C NMR spectra were recorded in d_6-DMSO on the same instrument by using a proton decoupling technique. The chemical shifts reported for ^{13}C NMR spectra are referenced to residual DMSO at 39.5 ppm. COSY, HSQC and HMBC spectra were acquired with a cryoprobe attachment.

DFT Calculations

Monte Carlo Conformational searching was performed using Macromodel [25]. Torsional sampling using a Monte Carlo Multiple Minimum (MCMM) search was performed with 1000 steps per rotatable bond. Each step was minimized with the OPLS-2005 force field using the Truncated Newton Conjugate Gradient (TNCG) method with a maximum number of iterations of 50,000 and an energy convergence threshold of 0.02. All other parameters were left at their default values. The lowest energy conformations (< 5 kcal/mol, 3 conformations) were optimized in Gaussian. All conformers were optimized with Gaussian 09 using B3LYP/631G(d) in vacuum and the vibrational frequencies were checked for a true minimum, i.e. no negative frequencies. All true minima were compared to remove identical conformations and conformations comprising < 1% of the Boltzmann populations. The single conformations were further optimized with B3LYP/6-311+G (2d,p) and a Polarizable Continuum Model (PCM) for chloroform and the vibrational frequencies where checked again for a true minimum.

NMR parameters (nmr = giao) were calculated with a single-point calculation, using the functional and basis set combinations, mpw1pw91/6-311+G(2d,p), using the optimized structures from the B3LYP/6-311+G(2d,p) calculation. This functional and basis set combination was selected in light of previous calculations which gave good agreement between experimentally measured and calculated chemical shifts. The integrated equation formalism polarized continuum model (IEFPCM) for chloroform was used in the NMR calculations. The computed NMR shielding tensors were converted to chemical shifts by using empirical scaling factors that are derived from linear regression analysis of a test set of molecules. The slope and intercept values of the scaling factors for proton chemical shifts were − 1.0719 and 31.8731 respectively and for carbon chemical shift were − 1.042 and 186.3569 respectively.

X-Ray Crystal Structure Determination

X-ray quality single crystals were obtained by slow diffusion of hexane into tetrahydrofuran solution. Crystallographic data were acquired at 190 K on an Oxford Diffraction Gemini CCD diffractometer employing graphite-monochromated Cu Kα radiation (1.5418 Å) and operating within the range $2 < 2\theta < 125$ Å. Temperature control was achieved with an Oxford Cryosystems Desktop Cooler. Data reduction and empirical absorption corrections (multiscan) were performed with Oxford Diffraction CrysAlisPro software. The structure was solved by direct methods with SHELXS and refined by full-matrix least-squares analysis with SHELXL-97 [26] within the WinGX graphical user interface [27]. All non-H atoms were refined with anisotropic thermal parameters. The molecular structure diagram was produced with ORTEP-3 [28]. The data in CIF format have been deposited at the Cambridge Crystallographic Data Centre with CCDC deposition number 1561094.

Bis-thiosemicarbazones

Bis-thiosemicarbazones were prepared (compounds **1**–**3**) by condensing appropriately substituted diketones with 4-phenyl-3-thiosemicarbazide in methanol medium containing a catalytic amount of dilute hydrochloric acid. The precipitated bis-thiosemicarbazone was washed with methanol, dried under vacuum and crystallized using methanol.

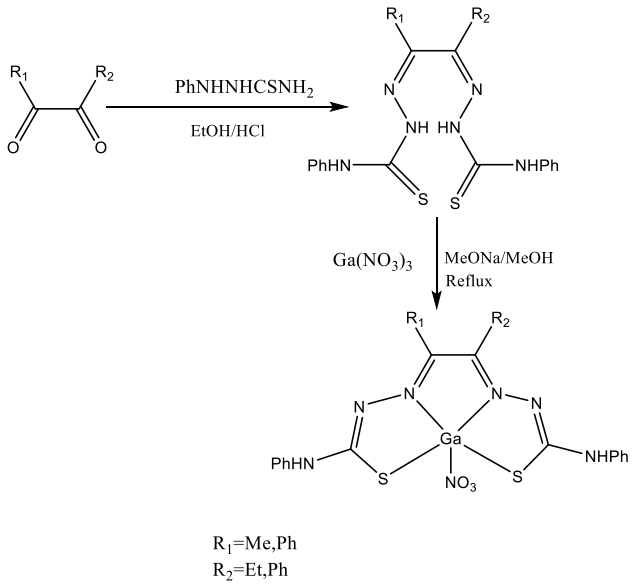
General Procedure for Preparation of Complexes of Gallium

Gallium complexes were made by reacting the bis-thiosemicarbazone with sodium methoxide in methanol and subsequently adding gallium nitrate. The mixture allowed to reflux for 4–6 h to yield highly colored solids with varying colors

from orange to red. The precipitated complex was filtered, washed with methanol and hexane and dried in vacuum [29].

Isolation of (S)-5-Methoxy-4,5,6-triphenyl-4,5-dihydro-1,2,4-tirazene-3(2H)-thione (Compound 4)

The prepared gallium methoxide complex (25 mg) was placed in a 20 mL scintillation vial. Using a dry syringe, 10 ml of dichloromethane was added to obtain an orange-red solution. Without disturbing the solution, 10 mL of ethanol was layered over the dichloromethane solution. The ethanol diffused into the mixture (5–7 days) and colorless crystals of (S)-5-methoxy-4,5,6-triphenyl-4,5-dihydro-1,2,4-tirazene-3(2H)-thione (7 mg) were obtained. The red solution was slowly pipetted out from the crystals and the crystals were washed with hexane and dried under vacuum before NMR and X-ray analysis. Of note, the red solution when left standing at room temperature for several days became completely colorless upon formation of the triazene.



Scheme 1 Synthetic scheme used for preparation of gallium complexes

Results and Discussion

The synthesis of gallium complexes of bis-thiosemicarbazone was accomplished following Scheme 1. In brief, the appropriately substituted diketones were condensed with thiosemicarbazide in acid medium to furnish the bis-thiosemicarbazones. This report describes specifically the single crystal X-ray structure of a novel di-gallium complex of bisthiosemicarbazone. Other structurally related gallium thiosemicarbazones did not produce X-ray quality crystals under our experimental conditions and therefore are not described in this report. Treatment of the bis-thiosemicarbazones with gallium nitrate in sodium methoxide in methanol yielded the gallium complexes as orange/red solids. The structures of compounds described in the present study are shown in Fig. 1.

During the preparation of these complexes, it is possible that the nitrate complex is formed initially and converted into the methoxide by substitution of the labile nitrate group. We have indeed isolated the methoxide complex in our earlier studies and confirmed the structure of the compound by single crystal X-ray crystallography [29]. In the initial experiments, we studied the NMR characteristics of this gallium

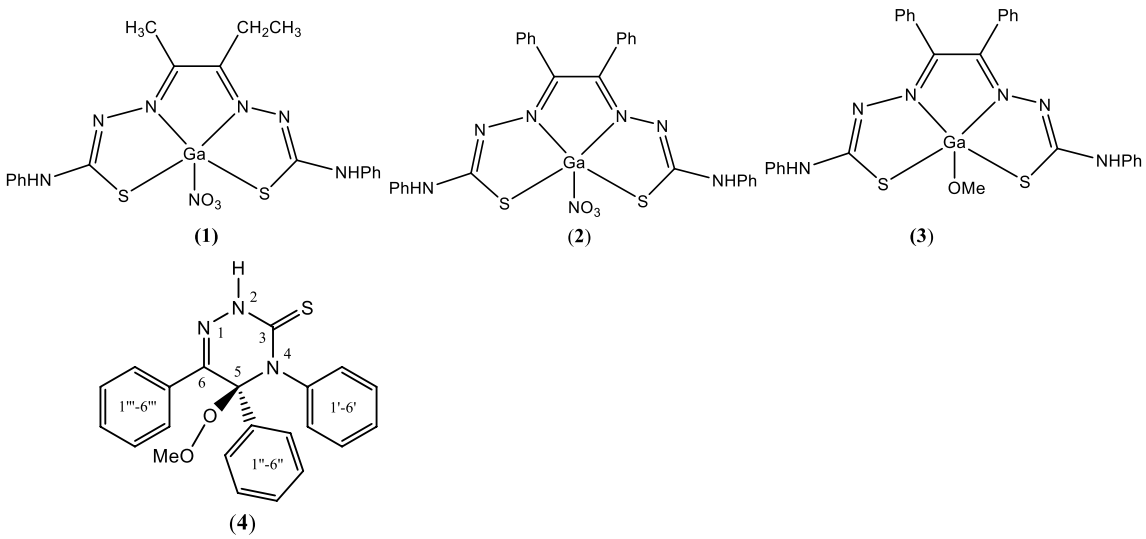


Fig. 1 Structures of compound described in the present study

complex. The ^{1}H NMR spectrum of the asymmetrically substituted (methyl/ethyl) diphenyl bis-thiosemicarbazone gallium complex (**1**) in d_6-DMSO is shown. (supplemental data).

The proton NMR spectrum showed two singlets at 10.3 ppm and 10.4 ppm corresponding to the NH protons associated with the aminophenyl moiety in the molecule. A doublet at 7.7 ppm corresponds to the ortho-protons of the phenyl ring, followed by two triplets assigned to the meta- and para-protons associated with the structure. A quartet at approximately 2.8 ppm indicated the presence of a CH_2 group; a singlet at 2.54 ppm corresponded to the isolated methyl group and finally a triplet at 1.2 ppm indicated the presence of the methyl group associated with the ethyl moiety. Further confirmation of the structure of the complex came from ^{13}C, COSY, HSQC and HMBC spectral data (supporting information). The methoxy group was absent based on the NMR data. The absence of any extra ^{13}C NMR peaks rules out coordination of d_6-DMSO so the likely ligand in the axial position is nitrate.

For single crystal X-ray crystallography, we dissolved this compound in THF followed by diffusion with hexane. After 10 days, dark orange colored crystals were obtained along with some precipitate in the vial. The colored crystals were carefully separated and subjected to X-ray crystallography (Fig. 2, 3). Based on the NMR data, we expected to observe the nitrate complex and were surprised to find that this crystal had two gallium atoms connected through hydrxido bridge as shown below. The crystal parameters are shown in Table 1.

There is extensive H-bonding in the structure. The hydroxido ligand donates an H-bond to one of the THF molecules O1–H1···O5′ 1.82 Å, 172.0° (see Fig. 4). The NH groups of both tetradentate ligands also act as H-bond donors to the other THF molecule (N1B–H1B···O6 1.99 Å, 163.6°) and to the nitrate anion which bridges adjacent complex cations (N1A–H1A···O2; 2.10 Å, 167.2°; N1B–H1B···O6 1.99 Å, 163.6°; N6A–H6G···O4 1.97 Å, 170.1°; N6B–H6H···O2′ 2.28 Å, 129.8°; N6B–H6H···O3′ 2.45 Å, 157.7°). The two Ga ions adopt close to square pyramidal geometries according to the well-established τ5 parameter [30] where τ5 = the difference between the two largest coordinate angles divided by 60; τ5 = 0 for square pyramidal and τ5 = 1 for trigonal bipyramidal). For Ga1 τ5 = 0.035 and for Ga2 τ5 = 0.104);

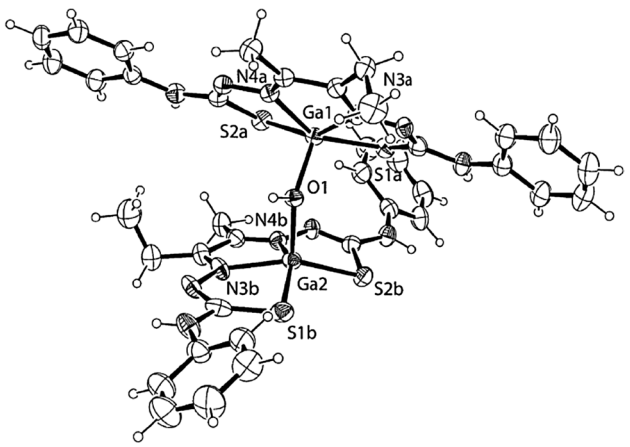


Fig. 2 X-ray crystal structure of asymmetrical methyl ethyl diphenyl bis-thiosemicarbazone gallium nitrate complex (compound **5**) after diffusion of solvent for 10 days (the compound has slowly hydrolyzed forming the dimeric compound)

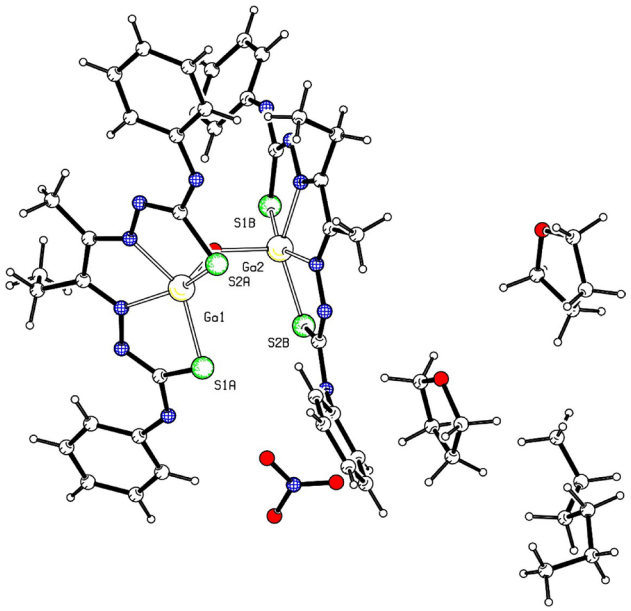


Fig. 3 The asymmetric unit showing the dimeric complex, two THF molecules, hexane and nitrate

Selected bond lengths and angles for this di-gallium bis-thiosemicarbazone complex (compound **5**) are shown in Table 2. The longest coordinate bond lengths are to the S-donors while the axial hydroxido ligand exhibits the shortest bonds; the two Ga-O bonds being the same within experimental uncertainty. Indeed, no differences are apparent between the two coordination spheres which are square-pyramidal as expected.

Based on our observations, we propose that formation of this gallium complex takes place according to the mechanism depicted in Scheme 2. The asymmetrical methyl ethyl diphenyl bis-thiosemicarbazone gallium nitrate is formed initially, according to the NMR evidence presented in this report. We postulate that the nitrate complex was hydrolyzed in the presence of THF (containing traces of water). Due to the high charge of the metal, the aqua ligand spontaneously ionizes then the hydroxido ligand thus formed reacts with another gallium nitrato complex resulting in the formation of the hydroxido-bridged digallium complex. This reaction

Table 1 Crystal data and structure refinement for 1705v5

Identification code	1705v5
Empirical formula	$C_{52}\ H_{71}\ Ga_2\ N_{13}\ O_6\ S_4$
Formula weight	1241.90
Temperature	190(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 17.6854(13) Å; α = 90°
	b = 16.6492(7) Å; β = 112.383(8)°
	c = 21.4659(14) Å; γ = 90°
Volume	5844.4(6) Å3
Z	4
Density (calculated)	1.411 Mg/m^3
Absorption coefficient	2.947 mm^{-1}
F(000)	2592
Crystal size	0.2 × 0.1 × 0.04 mm^3
Theta range for data collection	3.46 to 62.47°
Index ranges	−20 ≤ h ≤ 20, −18 ≤ k ≤ 19, −24 ≤ l ≤ 24
Reflections collected	35,379
Independent reflections	9284 [R(int) = 0.0783]
Completeness to theta = 62.47°	99.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.96902
Refinement method	Full-matrix least-squares on F2
Data/restraints/parameters	9284/9/669
Goodness-of-fit on F2	1.040
Final R indices [I > 2sigma(I)]	R1 = 0.0617, wR2 = 0.1531
R indices (all data)	R1 = 0.0972, wR2 = 0.1793
Largest diff. peak and hole	0.982 and −0.682 e/$Å^3$

(Compound # **5**) (digallium compound)

presumably occurred on standing of the nitrate complex in solution since NMR was performed in solvent immediately after the preparation of the compound and showed that the nitrate complex was intact. Therefore, we conclude that this reaction must be slow as evidenced from the formation of a fine white residue on the top of the crystals showing partial decomposition of the original nitrate complex. We note that the symmetrically ethyl substituted gallium nitrate complex was isolated and its X-ray crystal structure was solved demonstrating better stability. Thus, replacement of the ethyl group with a methyl group was associated with a change in the reactivity of the complex with moisture present in the solvent.

During the preparation of tetra phenyl substituted dithiosemicarbazone gallium chloride/methoxide complexes

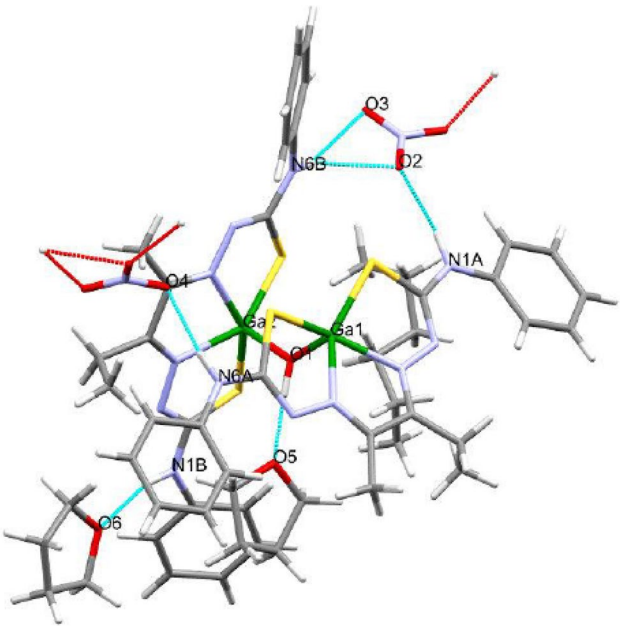


Fig. 4 Intermolecular interactions within the asymmetric unit of the Ga–OH–Ga dimer. Generated with Mercury vers. 3.10 and rendered with PovRay vers. 3.7

(compounds **2** & **3**), complexes were obtained as deep red colored solids. When this complex was subjected to solvent vapor diffusion during the preparation of X-ray crystals, colorless crystals were formed despite the solutions initially being highly colored and subsequently colorless on prolonged periods of time forming additional colorless crystals of triazene. (compound **4**) The crystals were separated from the solution and their NMR characteristics are illustrated (Supplemental data). Tables (Supplemental data) show the chemical shift obtained for each proton and carbon in the compound. It also shows DFT calculated chemical shifts for each proton in the compound. The DFT calculations were done to further assess the proton chemical shifts due to extreme over-lap of signals in the aromatic region. A single methoxy group was attached to a chirotopic carbon. In general, DFT calculated proton chemical shifts agreed well with the experimentally observed chemical shifts. We also examined the ^{13}C NMR chemical shifts and the values obtained along with DFT calculated chemical shifts are provided (Supplemental data).

The X-ray crystal structure of the triazene compound has been previously described [31]. The triazene possesses three aromatic rings and a methoxy group attached at the apex of the molecule. We postulate that the mechanism for the formation of the racemic mixture involves a planar transition

Table 2 Selected bond lengths (Å) and angles (°) for the Ga–OH–Ga complex

N(2A)–N(3A)	1.363(3)
N(2B)–N(3B)	1.374(7)
N(3A)–Ga(1)	2.057(4)
N(3B)–Ga(2)	2.041(5)
N(4A)–N(5A)	1.363(6)
N(4A)–Ga(1)	2.042(4)
N(4B)–N(5B)	1.367(6)
N(4B)–Ga(2)	2.043(4)
O(1)–Ga(1)	1.904(3)
O(1)–Ga(2)	1.908(3)
S(1A)–Ga(1)	2.2852(15)
S(1B)–Ga(2)	2.3329(16)
S(2A)–Ga(1)	2.2938(15)
S(2B)–Ga(2)	2.2842(15)
O(1)–Ga(1)–N(4A)	98.25(16)
O(1)–Ga(1)–N(3A)	98.93(16)
N(4A)–Ga(1)–N(3A)	75.86(17)
O(1)–Ga(1)–S(1A)	107.28(11)
N(4A)–Ga(1)–S(1A)	148.68(13)
N(3A)–Ga(1)–S(1A)	82.41(12)
O(1)–Ga(1)–S(2A)	103.80(11)
N(4A)–Ga(1)–S(2A)	82.90(13)
N(3A)–Ga(1)–S(2A)	150.81(14)
S(1A)–Ga(1)–S(2A)	107.55(6)
O(1)–Ga(2)–N(3B)	100.11(18)
O(1)–Ga(2)–N(4B)	100.28(16)
O(1)–Ga(1)–N(4A)	98.25(16)
O(1)–Ga(1)–N(3A)	98.93(16)
N(4A)–Ga(1)–N(3A)	75.86(17)
O(1)–Ga(1)–S(1A)	107.28(11)
N(4A)–Ga(1)–S(1A)	148.68(13)
N(3A)–Ga(1)–S(1A)	82.41(12)
O(1)–Ga(1)–S(2A)	103.80(11)
N(4A)–Ga(1)–S(2A)	82.90(13)
N(3A)–Ga(1)–S(2A)	150.81(14)
S(1A)–Ga(1)–S(2A)	107.55(6)
O(1)–Ga(2)–N(3B)	100.11(18)
O(1)–Ga(2)–N(4B)	100.28(16)

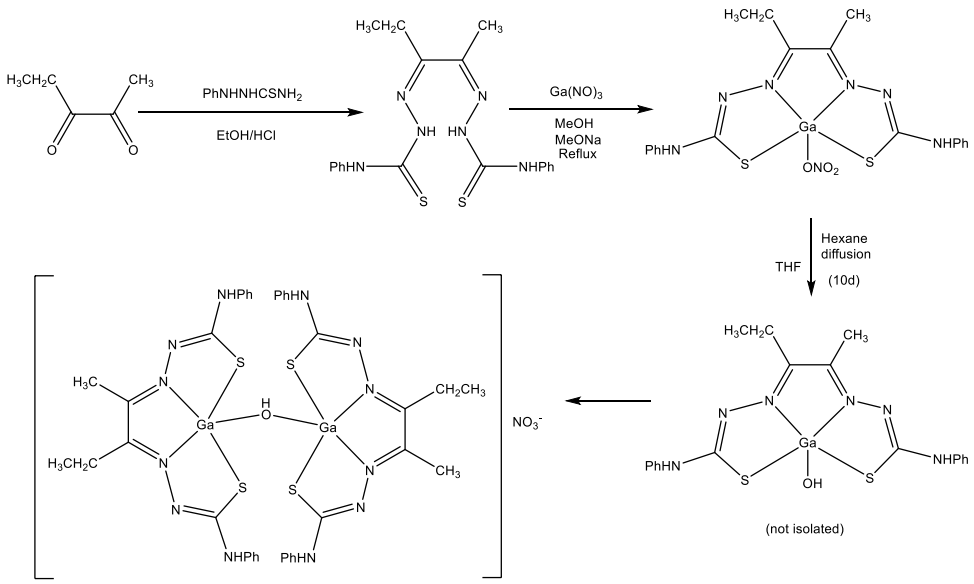
state. This allows the nucleophile to approach from either side of the plane of the molecule. We propose the following mechanism (Scheme 3) for the formation of the triazene from the gallium complex.

In Scheme 3, the gallium complexes are first formed as evidenced by the NMR data. X-ray crystal data shows that the compound slowly decomposes with time in the solvent. Previously, we observed that gallium nitrate and methoxide complexes of diphenyl substituted bis-thiosemicarbazone were not stable over prolonged periods in solution [29]. We propose that the partially decomposed bis-thiosemicarbazone cyclizes in the presence of methoxide and forms the tirazene molecule through a quaternary nitrogen as depicted in the scheme. This proposal is consistent with the formation of both "R" and "S" enantiomers in the final product. The transition state product, a tetracyclic planar compound, can be attacked by methanol from either side of the plane resulting in racemization.

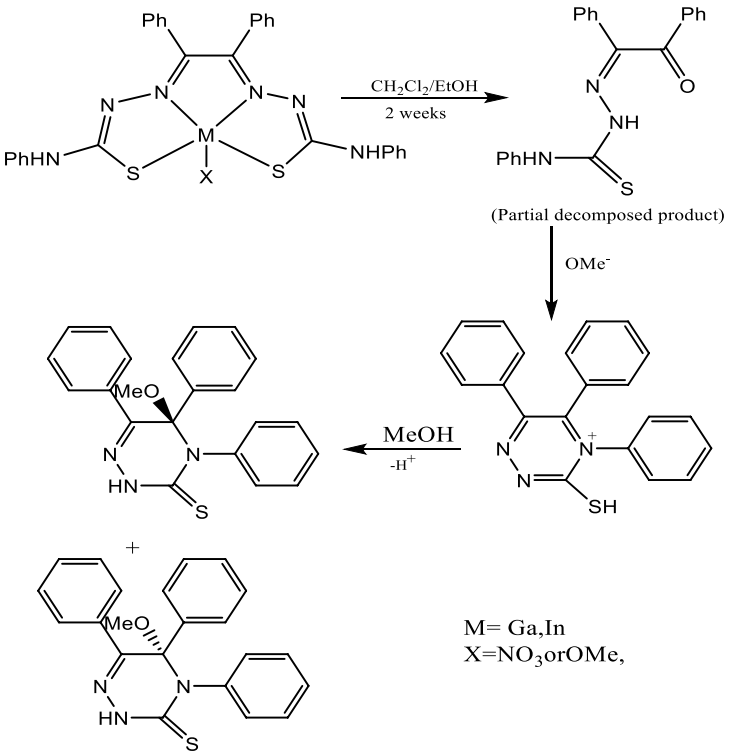
Previous authors used dilute hydrochloric acid to obtain the triazene compound and obtained the bis-thiosemicarbazone as a product when concentrated hydrochloric acid was used [31]. We used excess base in our experiments and therefore the triazene must have formed from the decomposition of the complex in the medium. Bermejo et al. [7] reported the formation of triazene compounds using copper acetate; it is likely that a similar reaction mechanism to that proposed above also applies in this setting. An alternative explanation is that during the synthesis of the gallium complexes, the gallium salts influenced the formation of the triazene product before the formation of the complex. Although the triazene formed easily with phenyl substituted bis-thiosemicarbazones, the methyl and ethyl substituted bis-thiosemicarbazone did not produce triazenes demonstrating the importance of multiple phenyl rings in the structure of the molecule.

In summary, we have demonstrated that certain gallium nitrate complexes of bis-thiosemicarbazones are not stable over prolonged periods in solvent and that the substituents play a major role in regard to stability. Additionally, we have provided experimental evidence that the tetraphenyl substituted bis-thiosemicarbazone gallium complexes can lead to structurally interesting triazene compounds. Further work is in progress to establish the structural features promoting stability for complexes with potential biological applications.

Scheme 2 Scheme illustrating the proposed pathway for formation of the di-gallium complex (compound **5**)



Scheme 3 Proposed mechanism of formation of (R) and (S)-5-methoxy-4,5,6-triphenyl-4,5-dihydro-1,2,4-tirazene-3(2H)-thione (compound **4**) showing the hydrogen bonding characteristics in the presence of base



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