

Synthesis and Characterization of Aluminum and Gallium Complexes of Heterocyclic Thiosemicarbazones. Crystal Structures of $\text{Me}_2\text{M}[\text{SC}_4\text{H}_3\text{CHNNC}(\text{S})\text{SCH}_3]$ ($\text{M}=\text{Al}$, Ga)

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The synthesis and characterization of the monomeric group 13 heterocyclic thiosemicarbazone complexes $\text{Me}_2\text{M}[\text{SC}_4\text{H}_3\text{CHNNC}(\text{S})\text{SCH}_3]$ ($\text{M}=\text{Al}$ (2), Ga (3)) are described. Compounds 2-3 were prepared using MMe_3 ($\text{M}=\text{Al}$, Ga) in toluene with 2-thiophenecarboxaldehyde-*S*-methylthiocarbamate under anaerobic conditions. These complexes have been characterized by ^1H NMR, ^{13}C NMR, elemental analyses, and single-crystal X-ray diffraction. 2 crystallizes in the monoclinic space group $\text{P}2_1/c$ with unit cell parameters $a=10.2930(5)$ Å, $b=18.564(1)$ Å, $c=7.3812(6)$ Å, $V=1347.9(2)$ Å³, $D_{\text{calc}}=1.342$ gcm⁻³ for $Z=4$, 9281 reflections with $I_o < 3\sigma(I_o)$, $R1=0.0500$ and $wR2=0.0526$. 3 crystallizes in the orthorhombic space group P_{bca} with unit cell parameters $a=13.340(3)$ Å, $b=19.9070(5)$ Å, $c=11.3690(2)$ Å, $V=2673.88(9)$ Å³, $D_{\text{calc}}=1.511$ gcm⁻³ for $Z=8$, 17004 reflections with $I_o > 3\sigma(I_o)$, $R1=0.0480$ and $wR2=0.0524$. Compound 3 is a monomeric gallium compound with a weak interaction between the pendant thiophene and the gallium center.

Introduction

Studies relating the nature of metal complexes to an aspect of their biological activity are increasingly important. Extensive literature on the antitumor properties of many α -*N*-heterocyclic carboxaldehyde thiosemicarbazones is now available. The terdentate heterocyclic thiosemicarbazones have been shown to form complexes with various transition metal ions including Cu(II),¹ Ni(II),² Co(II),³ Fe(II),⁴ Hg(I),⁵ and Tl(I).⁵ Gallium(III) complexes of heterocyclic thiosemicarbazones have been given increased attention due to the facts that radioactive congeners of gallium (^{67}Ga) are γ -ray emitters with energy which make them useful for medical diagnostic agent.⁶ Recently, Kepper and coworkers⁷ developed gallium(III) complexes employing ligands which themselves had antiviral and antitumor activity such as α -*N*-heterocyclic thiosemicarbazones.⁸ We have prepared a series of dinuclear group 13 heterocyclic carboxaldehyde thiosemicarbazones complexes ($\text{Me}_2\text{M}[\text{NC}_5\text{H}_4\text{CMeNNC}(\text{S})\text{NR}]$ (MMe_2)⁹ and trinuclear aluminum and gallium complexes of bis (thiosemicarbazones).¹⁰ However, the coordination chemistry of the functionalized thiosemicarbazones system with novel substitution patterns remains unexplored.

Motivated by an interest in the effects of α -*N*-heterocyclic thiosemicarbazones geometry on the coordination environments of aluminum and gallium specifically,¹¹ we began a systematic study of the use of terdentate ligands by replacing the pyridine moiety with thiophene moiety and replacing the RNH groups at the terminal (N) position of the thiosemicarbazone with methylthio group for organometallic aluminum and gallium compounds. We have now described the interaction of the trimethylaluminum and gallium with *S*, *N*, *S*-terdentate ligand thiophene-2-carboxaldehyde-*S*-methylthio-carbazate.

Experimental Section

All reactions and manipulations were conducted under a dry argon atmosphere either using an inert atmosphere glovebox or standard Schlenk techniques. Toluene and hexane were distilled from Na/Ph₂CO. NMR solvent was degassed by freeze-pump-thaw cycles. All other starting materials were purchased in reagent grade and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker WH-300 spectrometer and referenced to residual protic solvent with chemical shifts being reported as δ ppm from TMS. IR spectra were recorded on a Shimadzu FT IR-8501 spectrometer. Mass spectra were recorded on a high resolution VG70-VSEG mass spectrometer. Elemental analyses were performed by the Basic Science Center. The ligand [$\text{SC}_4\text{H}_4\text{CHNNHC}(\text{S})\text{SMe}$] was prepared by the literature method.¹² AlMe_3 and GaMe_3 were purchased from Strem Chemicals.

Synthesis of $\text{SC}_4\text{H}_3\text{CHNNHC}(\text{S})\text{SMe}$ (1). In a 100 mL Schlenk flask with a stirring bar were placed 0.80 g (7.13 mmol) of 2-thiophenecarboxaldehyde, 0.87 g (7.13 mmol) of methylhydrazine-carbadithiolate, and 40 mL of *i*-PrOH. The mixture was stirred for 2 h. The reaction solution was filtered, and the pale yellow solid was dried under vacuum to give 2-thiophenecarboxaldehyde-*S*-methylthiocarbamate in 86% yield. This compound can be recrystallized from hot ethanol. ^1H NMR (300 MHz, CDCl_3) δ 10.50 (s, 1H, NH), 8.09 (d, 1H, CH), 7.50 (d, 1H of thiophene), 7.12 (dd, 1H of thiophene), 2.72 (s, 3H, CH₃).

Synthesis of $\text{Me}_2\text{Al}[\text{SC}_4\text{H}_3\text{CHNNC}(\text{S})\text{SCH}_3]$ (2). To a stirred suspension of 1 (0.45 g, 2.08 mmol) in toluene (30 mL) was added trimethylaluminum (0.15 g, 2.12 mmol) at 0 °C. The mixture was warmed to 35 °C and was stirred for 2 h at that temperature. Concentration of the solution afforded compound 2 as a crystalline yellow solid. Yield: 88%. mp 113-117 °C. ^1H NMR (300 MHz, C_6D_6): δ 7.42 (s, 1H, CH), 7.08 (d, 1H of thiophene), 6.78 (d, 1H of thio-

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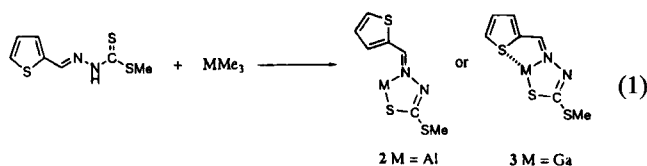
phene), 2.45 (s, 3H, CH₃), 0.12 (s, 6H, Al-CH₃); ¹³C NMR (C₆D₆): δ 186.29, 145.97, 137.45, 136.28, 132.76, 127.68, 17.33, -2.88; IR (on KBr pellet; cm⁻¹): 3321(br), 3104(w), 2982(w), 1592(m), 1542(m), 1503(w), 1471(w), 1382(m), 1374(m), 1304(s), 1221(w), 1087(w), 952(m), 882(w), 821(w), 770(m), 712(s), 623(w), 521(w). MS(EI): m/z 272[M⁺]. Anal. Calcd. for C₉H₁₃N₂S₃Al: C, 39.69; H, 5.18. Found: C, 39.42; H, 5.28.

Synthesis of Me₂Ga[SC₄H₃CHNNC(S)SCH₃] (3). 3 was prepared according to the same method used for 2, except that trimethylgallium was used instead of trimethylaluminum. Yield: 82%. mp 127-130 °C. ¹H NMR (300 MHz, C₆D₆): δ 7.48 (s, 1H, CH), 7.05 (d, 1H of thiophene), 6.74 (d, 1H of thiophene), 6.57 (dd, 1H of thiophene), 2.32 (s, 3H, CH₃), 0.14 (s, 6H, Ga-CH₃); ¹³C NMR (C₆D₆): δ 186.31, 145.96, 137.44, 136.28, 132.27, 126.80, 17.33, -2.88; IR (on KBr pellet; cm⁻¹): 3008(w), 2992(w), 1594(s), 1448(s), 1402(s), 1372(m), 1312(w), 1304(s), 1250(m), 1211(w), 1188(w), 1068(m), 1041(m), 952(m), 912(w), 817(m), 762(m), 710(m), 602(m), 588(m), 532(m), 478(m). MS(EI): m/z 315[M⁺]. Anal. Calcd. for C₉H₁₃N₂S₃Ga: C, 34.19; H, 4.46. Found: C, 33.92; H, 4.52.

X-ray structure analysis of compounds 2 and 3. The crystals of compounds 2-3 were grown from toluene. Diffraction data were collected on a Rigaku/RAXIS IIC area detector by employing graphite-monochromated Mo K_α radiation (λ=0.71069 Å) at a temperature of 228 K for both crystals. Indexing was performed from a series of 1 oscillation images with exposures of 5 min/frame. A total of 9281 reflections of 2 and 17004 reflections of 3 were measured over the following ranges: 0.0 ≤ 2θ ≤ 49.9°, -29 ≤ h ≤ 29.0, 0 ≤ k ≤ 8, -15 ≤ l ≤ 15. Of the reflections measured, a total of 1507 unique reflections of 2 and 1706 reflections of 3 with F² > 3.0σ (F²) were used during subsequent structure refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques based on F to minimize the quantity Σw(F_o-F_c)² with w=1/σ²(F). Non-hydrogen atoms were anisotropically refined, and hydrogen atoms were included as constant contributions to the structure factors and were not refined. Refinement converged to R₁=0.050 and R₂=0.053 for 2, and R₁=0.048 and R₂=0.052 for 3.

Results and Discussion

The reaction of 2-thiophenecarboxaldehyde-S-methylthiocarbamate with trimethylaluminum or gallium in toluene at 30-40 °C affords the corresponding organoaluminum and gallium complexes, in which one hydrogen atom has been lost from the azahydrogen atom via the methane elimination reaction according to Eq. (1). The resulting yellow products 2-3 were isolated as air-sensitive crystalline solids in high yield.



These compounds are readily soluble in benzene, toluene,

and THF. Compounds 2-3 were characterized by ¹H, ¹³C NMR, mass spectrometry, and elemental analysis. The structures of compounds 2-3 were determined by single-crystal X-ray diffraction. The initial indication of the mononuclear formulation for 2 stemmed from the observation of a parent ion in the mass spectrum at m/z 272. In the ¹H NMR spectrum of 2, the methyl group of the aluminum moiety gives rise to one signal at δ 0.12; the region expected for a σ-bonded species due to the hydrogen atoms of the Al-Me group. The chemical shift of this kind of Al-CH₃ is consistent with prior observations of four-coordinate Al atoms.¹³ The ¹³C NMR spectrum of 2 shows one resonance at -2.88 ppm which is due to the carbon atom of the Al-CH₃ group. The carbons (C9), C(6)) attached to the imine groups appear at δ 186.29 and 145.97. The ¹H and ¹³C NMR spectra of the complex 3 are in good agreement with those of 2. The infrared spectrum of 2 indicates the mode of the ligand coordination. The peak at 1587 cm⁻¹ is assigned to the ring deformation mode. Positive shift of the mode compared to that of ligand indicates that the pyridyl nitrogen coordinates in the complex. The stretching mode of ν(CS) at 770 cm⁻¹ is significantly decreased. This could involve a tautomerism for the semicarbazone-3-thiol, i.e., a 1,3-proton shift. Although all the spectra are consistent with the proposed formulation, the bonding mode in 2 is still unclear. Therefore, we decided to determine the structures of 2 and 3 by X-ray crystallography.

Compound 2 crystallizes in the space group P2₁/c with four molecules per unit cell. The molecular structure and atom numbering schemes for 2 are given in Figure 1. Selected bond distances and angles are given in Table 2. The packing diagram of compound 2 (view down the C-axis) is shown in Figure 2. The molecule consists of one five-membered AlN₂CS ring. The coordination environment about Al may be described as a distorted tetrahedron. The Al(1)-N(1) distance is 1.971(4) Å. The Al-N bond distance is shorter than distances observed for four coordinate aluminum compounds such as Me₃N-AlMe₃ (2.099(10) Å),¹⁴ and the pyridyl compound Al(CH₃)₂(NHCH₂-4-Py)₂ (2.248(4) Å).¹⁵ The Al-N bond distance is comparable to those of [Me₂NAlMe₂]₂ (1.958(7) Å),¹⁶ and [Ad(H)NAlMe₂]₂ (1.963(2) Å).¹⁷ The Al-S bond distance (2.288(2) Å) is com-

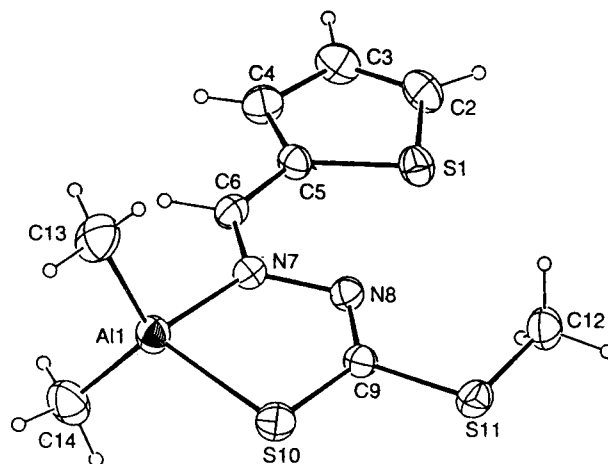


Figure 1. ORTEP diagram showing the structure of 2 with labeling scheme and 30% thermal ellipsoids.

Table 1. Crystallographic data for the structural studies of compounds **2** and **3**

| | 2 | 3 |
|-------------------------------------|---|---|
| Empirical formula | C ₉ H ₁₃ N ₂ S ₃ Al | C ₉ H ₁₃ N ₂ S ₃ Ga |
| Molecular weight | 272.38 | 315.11 |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | P2 ₁ /c | P _{bca} |
| Cell constant | | |
| a, Å | 10.2930(5) | 13.1340(3) |
| b, Å | 18.564(1) | 19.9070(5) |
| c, Å | 7.3812(6) | 11.3690(2) |
| V, Å ³ | 1347.9(2) | 2673.88(9) |
| D _c , g cm ⁻³ | 1.342 | 1.511 |
| μ(Mo Kα), cm ⁻¹ | 5.86 | 24.93 |
| F(000) | 188 | 136 |
| Z | 4 | 8 |
| No. of indep. reflns | 9281 | 17004 |
| Params refined | 1507 | 1706 |
| Goodness of fit | 1.85 | 1.95 |
| R ₁ ^a | 0.0500 | 0.0480 |
| wR ₂ ^a | 0.0526 | 0.0524 |

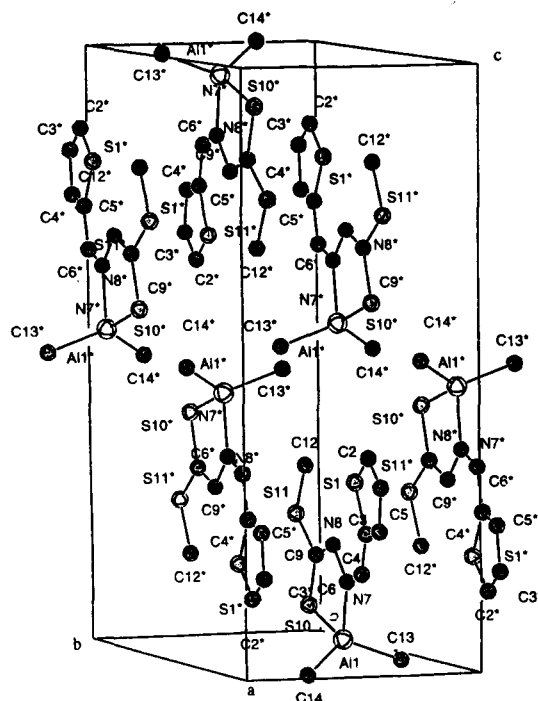
$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = \{[\sum w(F_o^2 - F_c^2)^2] / [\sum wF_o^2]\}^{1/2}$$

parable to that observed for the thiolate compound, AlH(SCH₂CH₂NEt₂)₂ (2.271(1) Å),¹⁸ the cubane compound [(^tBu)Al(μ₃-S)]₄ (2.316(9) Å)¹⁹ and the bridged sulfur compound [AlMe₂(μ-SC₆F₅)₂] (2.405 Å).²⁰ The Al(1)-C(13) bond distance (1.962(7) Å) is typical for four-coordinate aluminum complexes. The next question arises as to whether the Al...S interaction is present. It is well known that S-donor interactions for aluminum in general are weak and in the case of thiophene-dimethylaluminum species there is a reluctance to form any intimate metal-sulfur contact.²¹ There are not any Al...S intermolecular interactions (see Figure 2). This is in sharp contrast to the case of aluminum compound of 2-formylpyridine-S-methyldithiocarbamate,²² demonstrating adherence to the basicity series (N > O > S) established for donor complexes of aluminum Lewis acids.

Compound **3** crystallizes in the space group P_{bca} with

Table 2. Selected bond lengths (Å) and angles (deg) for compound **2**

| | | | | | |
|-------------------|----------|-------------------|----------|-------------|----------|
| S(1)-C(2) | 1.699(5) | S(1)-C(5) | 1.724(4) | S(10)-Al(1) | 2.288(2) |
| S(10)-C(9) | 1.734(5) | S(11)-C(9) | 1.735(5) | S(11)-C(12) | 1.781(6) |
| Al(1)-N(7) | 1.971(4) | Al(1)-C(13) | 1.962(7) | Al(1)-C(14) | 1.942(7) |
| N(7)-N(8) | 1.405(5) | N(7)-C(6) | 1.307(5) | N(8)-C(9) | 1.304(5) |
| C(2)-C(3) | 1.347(8) | C(4)-C(5) | 1.317(6) | C(3)-C(4) | 1.407(7) |
| C(5)-C(6) | 1.424(6) | | | | |
| C(2)-S(1)-C(5) | 90.8(3) | Al(1)-S(10)-C(9) | 93.0 (2) | | |
| C(9)-S(11)-C(12) | 103.6(2) | S(10)-Al(1)-N(7) | 85.7(1) | | |
| S(10)-Al(1)-C(13) | 114.7(2) | S(10)-Al(1)-C(14) | 115.8(2) | | |
| N7-Al(1)-C(13) | 109.2(2) | N(7)-Al(1)-C(14) | 107.7(2) | | |
| C(13)-Al(1)-C(14) | 118.2(3) | Al(1)-N(7)-N(8) | 120.7(3) | | |
| Al(1)-N(7)-C(6) | 124.3(3) | N(8)-N(7)-C(6) | 115.0(4) | | |
| N(7)-N(8)-C(9) | 112.0(4) | S(1)-C(2)-C(3) | 113.7(4) | | |
| S(1)-C(5)-C(6) | 126.2(3) | C(4)-C(5)-C(6) | 122.7(4) | | |
| C(2)-C(3)-C(4) | 111.6(5) | S(10)-C(9)-N(8) | 128.3(4) | | |
| S(11)-C(9)-N(8) | 118.9(4) | C(3)-C(4)-C(5) | 112.9(5) | | |
| S(10)-C(9)-S(11) | 112.8(3) | N(7)-C(6)-C(5) | 130.0(4) | | |

**Figure 2.** Packing diagram of **2** (view down the C-axis).

eight molecules per unit cell. The molecular structure and atom numbering schemes for **3** are given in Figure 3. Selected bond distances and angles are given in Table 3. The packing diagram of compound **3** is shown in Figure 4. The molecule consists of a five-membered GaN₂CS ring. In the solid state, the Ga(1) center is coordinated by one nitrogen, one sulfur, and two methyl groups in a distorted tetrahedral configuration. The Ga(1)-S(10) bond distance (2.317(2) Å) is comparable to that observed for [py(^tBu)GaS]₃ (2.231(3)-2.253(3) Å)²³ and for the thiolate-bridged complexes Ga₄L₄(SMe)₄S₂ (2.204(8) Å).²⁴ The Ga(1)-N(7) bond distance (2.084(4) Å) is comparable to that of the pyridine-2-thiol complex Ga(SC₆H₄N)₃ (2.062(8) Å).¹⁵

The primary coordination sphere of Ga(1) consists of a

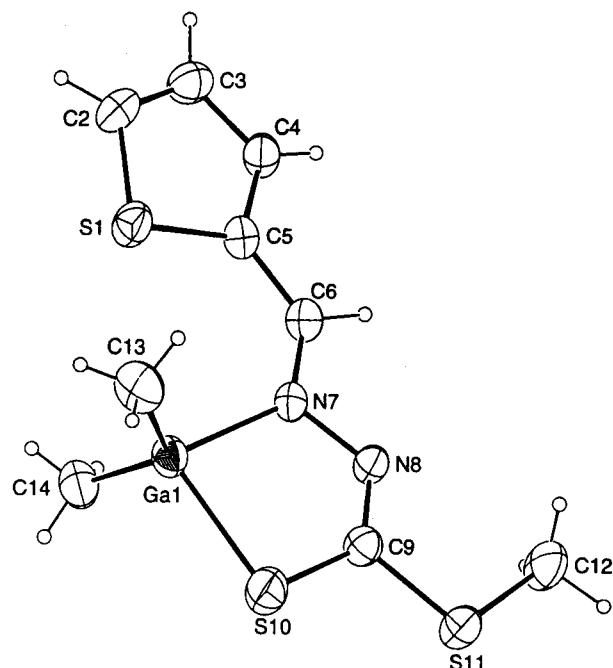


Figure 3. ORTEP diagram showing the structure of **3** with labeling scheme and 30% thermal ellipsoids.

distorted tetrahedral configuration. However, weak secondary interaction between the pendant thiophene and the gallium center is evident. The orientation of this interaction is such that the lone pairs of the thiophene group are directed toward the gallium center and Ga...S vector lies approximately *trans* to the Ga-S(10) bond with S...Ga-S angle of 152.8(2)°. Although the gallium-sulfur distance (3.33 Å) is less than the sum of van der Waals radii for gallium and sulfur (3.70 Å),²⁵ they exceed typical Ga-S covalent bond distance (2.22 Å). If this subsidiary Ga...S interaction is included, the overall geometry at gallium is that of a distorted trigonal bipyramid. Such weak interaction has been observed previously in group 13 compounds.

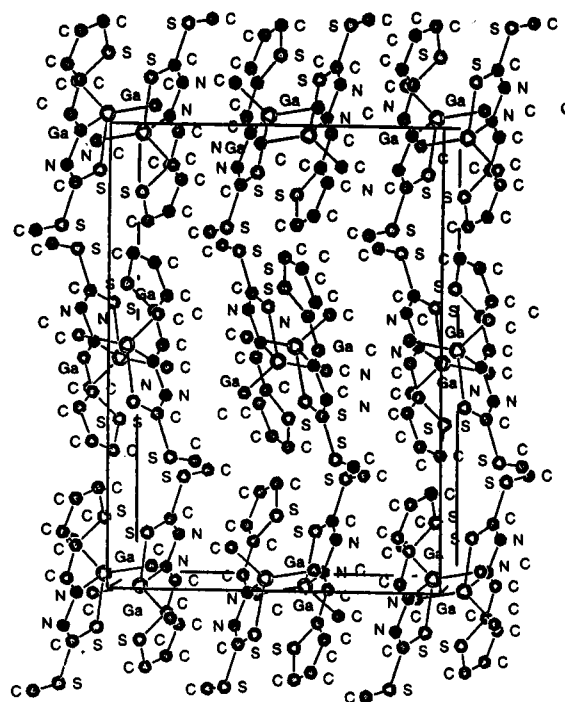


Figure 4. Packing diagram of **3** (view down the C-axis).

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Supporting Information Available. Text describing X-ray procedures and tables of bond distances and angles, atomic coordinates, fractional coordinates for hydrogen atom, thermal parameters, and X-ray data for compound **2** (15 pages) and **3** (14 pages) are available from the corresponding authors.

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Table 3. Selected bond lengths (Å) and angles (deg) for compound **3**

| | | | | | |
|-------------------|----------|------------|-------------------|-------------|----------|
| Ga(1)-S(10) | 2.317(2) | Ga(1)-N(7) | 2.084(4) | Ga(1)-C(13) | 1.951(7) |
| Ga(1)-C(14) | 1.946(6) | S(1)-C(2) | 1.695(6) | S(1)-C(5) | 1.725(5) |
| S(10)-C(9) | 1.727(5) | S(11)-C(9) | 1.752(5) | S(11)-C(12) | 1.789(6) |
| N(7)-N(8) | 1.411(5) | N(7)-C(6) | 1.298(6) | N(8)-C(9) | 1.293(7) |
| C(2)-C(3) | 1.337(8) | C(3)-C(4) | 1.409(7) | C(4)-C(5) | 1.369(7) |
| C(5)-C(6) | 1.422(7) | Ga(1)-S(1) | 3.780(4) | | |
| S(10)-Ga(1)-N(7) | | 84.6(1) | S(10)-Ga(1)-C(13) | | 109.8(2) |
| S(10)-Ga(1)-C(14) | | 111.72 | N(7)-Ga(1)-C(13) | | 113.4(2) |
| N7-Ga(1)-C(14) | | 105.0(2) | C(13)-Ga(1)-C(14) | | 124.9(3) |
| C(2)-S(1)-C(5) | | 91.3(3) | Ga(1)-S(10)-C(9) | | 94.0(2) |
| C(9)-S(11)-C(12) | | 102.5(3) | Ga(1)-N(7)-N(8) | | 117.0(3) |
| Ga(1)-N(7)-C(6) | | 131.2(4) | N(8)-N(7)-C(6) | | 111.5(4) |
| N(7)-N(8)-C(9) | | 115.0(4) | S(1)-C(2)-C(3) | | 113.2(4) |
| C(2)-C(3)-C(4) | | 112.2(5) | C(3)-C(4)-C(5) | | 112.8(5) |
| S(1)-C(5)-C(6) | | 110.5(4) | S(1)-C(5)-C(6) | | 126.3(4) |
| C(4)-C(5)-C(6) | | 123.2(5) | N(7)-C(6)-C(5) | | 127.9(5) |
| S(10)-C(9)-S(11) | | 112.3(3) | S(10)-C(9)-N(8) | | 129.1(4) |
| S(11)-C(9)-N(8) | | 118.6(4) | | | |

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