# Kuppukkannu Ramalingam\*, G.S. Sivagurunathan and Corrado Rizzoli Synthesis and characterization of gallium(III) dithiocarbamates as suitable nano-gallium(III) sulfide precursors

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Abstract: Gallium(III) complexes [Ga(chmdtc),] (1) and [Ga(chedtc)] (2) (where chmdtc=cyclohexylmethyldithiocarbamate and chedtc=cyclohexylethyldithiocarbamate) have been prepared and characterized by infrared, nuclear magnetic resonance (1H and 13C) spectra, thermogravimetry, X-ray photoelectron spectroscopy, and single crystal X-ray diffraction (XRD). The thermogravimetric curves obtained for both complexes are almost similar. The final residue corresponded to gallium sulfide (Ga<sub>2</sub>S<sub>2</sub>) above 700°C for complexes (1) and (2). In the single crystal X-ray structure of [Ga(chedtc)] (2), Ga-S bonds, and the associated C-S bonds show asymmetry as a requirement of packing. The complex shows distorted octahedral geometry due to its bite angle variations. Nano- $\alpha$ -Ga<sub>2</sub>S<sub>2</sub> was prepared from single source precursors  $[Ga(chmdtc)_{2}]$  (1) and [Ga(chedtc)<sub>3</sub>] (2). Prepared nano-Ga<sub>3</sub>S<sub>3</sub> have been characterized by powder XRD, energy-dispersive X-ray spectroscopy technique, and transmission electron microscopy (TEM)-selected area electron diffraction analysis showing the nano-sized nature of Ga<sub>2</sub>S<sub>2</sub>. TEM micrographs confirmed the size of the particles to be 50 nm.

**Keywords:** continuous shape measure; crystal structure; dithiocarbamate; gallium(III); nano-gallium(III) sulfide.

# Introduction

Dithiocarbamates of gallium, indium, and thallium have continued to attract attention in recent years on the account

of their industrial applications (Shen et al., 2009; Li, et al., 2011) and biological profiles (Bockman and Semin, 2003; Gabriel et al., 2007). Gallium is the instant metal ion, later than platinum, to be used in cancer dealing. Its activities are numerous and different. It adapts a 3D structure of DNA and inhibits its synthesis, modulates protein synthesis, and inhibits the activity of a number of enzymes, such as ATPases, DNA polymerases, ribonucleotide reductase, and tyrosine-specific protein phosphatase. Gallium toxicity is well documented in vitro and in vivo in animals. In humans, the oral administration of gallium is less toxic. Radioactive 67Ga and 68Ga show some promise in the study of bone cancer, as compounds of these isotopes are absorbed by the cancer deposits in the bone (Collery et al., 2002; Ismail et al., 2013). Group 13 sulfides are an interesting class of materials with promise in photovoltaic and optoelectronic applications. The related ternary and quaternary materials CuIn Ga Se, or CuIn Ga S, are of particular interest for solar cells (Nomura et al., 1992; Park et al., 2001). Relatively, fewer reports of dithiocarbamate compounds of gallium such as [Ga(S<sub>2</sub>CNEt<sub>2</sub>)]<sub>2</sub>, [Ga(S<sub>2</sub>CNCC<sub>4</sub>H<sub>4</sub>)<sub>2</sub>], [R,Ga(S,CNEt,)], and [R,Ga[S,CN(Me)CH,CH, CH,NMe,] and the growth of gallium sulfide (Ga,S<sub>3</sub>) from dithiocarbamate precursors have been reported in the recent past (Haggata et al., 1995). In our continued interest in the production of nano-Group 13 metal sulfides from the corresponding dithiocarbamates, structural and chemical investigations have been carried out (Sivagurunathan et al., 2013, 2014). In this paper, we report the synthesis, nuclear magnetic resonance (NMR) and infrared (IR) spectroscopic, thermogravimetric, and X-ray photoelectron spectroscopy (XPS) studies of  $[Ga(chmdtc)_3]$  (1) and  $[Ga(chedtc)_3]$  (2). The molecular structure of compound (2) was determined by single crystal X-ray diffraction (XRD) analysis. The dithiocarbamates are shown in Scheme 1.

# **Results and discussion**

The synthesis of tris(cyclohexylmethyldithiocarbamato) gallium(III) and its ethyl analogue has been accomplished

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**Scheme 1:** Schematic drawing of the dithiocarbamates and their abbreviations.



Scheme 2: Synthesis of gallium dithiocarbamates (1) and (2).

by the reaction of a methanolic solution of GaCl<sub>3</sub> and the corresponding freshly prepared dithiocarbamic acid in a 1:3 stoichiometric ratio (Scheme 2).

### IR spectroscopic studies

For complexes (1) and (2), the  $v_{C\cdot N}$  (thioureide) bands were observed at 1478 and 1474 cm<sup>-1</sup>, respectively. The  $v_{(C\cdot S)}$  stretching bands were observed at approximately 1000 cm<sup>-1</sup>, supporting the bidentate coordination mode (Baskaran et al., 2008; Arul Prakasam et al., 2009; Marimuthu et al., 2012) of the dithiocarbamate to the metal center, and the  $v_{C\cdot H}$  bands were observed in the range of 2852–2929 cm<sup>-1</sup>.

### NMR spectroscopic studies

NMR spectra were recorded at room temperature with tetramethylsilane as an internal reference and CDCl<sub>3</sub> as the solvent. The chemical shifts reported in the Spectral Data Base for Organic Compounds (SDBS) for the parent amines are shown in brackets for comparison. The <sup>1</sup>H NMR of complex (**1**) showed an intense signal at 4.57(m) ppm corresponding to a single proton integration due to  $\alpha$ -CH of the cyclohexyl ring, and CH<sub>3</sub> protons ( $\alpha$ -CH<sub>3</sub>) attached to the nitrogen appeared at 3.22(s) ppm with proton integration corresponding to three. The  $\alpha$ -CH and  $\alpha'$ -CH<sub>3</sub> protons were affected to a maximum extent on complexation. In the cyclohexyl ring, all equatorial protons were deshielded to a large extent compared to the axial protons. The <sup>13</sup>C NMR spectrum of (**1**) showed a weak signal at 201.1(3) ppm due to the characteristic thioureide

carbon (Van Gaal et al., 1979). In the case of (**2**), the <sup>1</sup>H NMR of α-CH proton of the cyclohexyl ring appeared at 4.56 ppm and α'-CH<sub>2</sub> protons at 3.73 ppm corresponding to two protons. The β'-CH<sub>3</sub> protons of the ethyl group appeared as a well-resolved triplet at 1.31–1.38 ppm. The proton signals in (**2**) appeared without much change as observed in (**1**) with slight deshielding. The <sup>13</sup>C NMR of (**2**) showed the characteristic thioureide signal at 201.09 ppm. β'(H<sub>3</sub>)C appeared at 13.99 ppm as a much shielded signal and the α'-CH<sub>2</sub> appeared highly deshielded at 44.15 ppm compared to complex (**1**). The <sup>13</sup>C chemical shifts of the cyclic ring appeared similar in (**1**) and (**2**).

### Thermogravimetric analysis

Thermograms of  $[Ga(chmdtc)_3]$  (1) and  $[Ga(chedtc)_3]$  (2) are shown in Figure 1A and B, respectively. Both complexes showed single-stage decompositions, and the thermogravimetric curves obtained for both complexes were almost similar. The percentages within the brackets refer to the moiety lost/residue left behind. The thermal decomposition of [Ga(chmdtc),] (1) started by losing the solvent toluene (0.5C,H,;% calcd.: 6.8, found: 6.5) in the first stage followed by the loss of chmdtc. The total mass loss corresponded to 78% and the final product of thermal decomposition was Ga<sub>2</sub>S<sub>2</sub> (% calcd.: 17.5, found: 17.4). In the second stage, decomposition occurred from 280°C to 320°C due to the loss of the chmdtc ligand. Compound (2) started decomposing by losing toluene (% calcd.: 6.3, found: 5.8) up to 290°C. Considerable mass loss was observed from 290°C to 320°C. The final residue corresponded to Ga<sub>2</sub>S<sub>2</sub> (% calcd.: 16.3, found: 16.1). The differential thermal analysis (DTA) curves of complex (1) showed exothermic signals at 290°C and 340°C. The exothermic signal indicates the decay of dithiocarbamates. Thermal analysis confirmed the proposed formulas of the compounds.

### **XPS** analysis

The survey scan of  $[Ga(chmdtc)_3]$  (1) and  $[Ga(chedtc)_3]$  (2) (Figure 2A and B) confirmed the presence of gallium, sulfur, nitrogen, and carbon in the samples. Gallium showed two signals corresponding to 2<sub>p</sub> electrons at 1120.0(2<sub>p3/2</sub>) and 1146.0(2<sub>p1/2</sub>) eV in (1) and (2) (Figure 2C and D). The gallium atom showed the binding energy at 1116.7(2<sub>p3/2</sub>) eV (Ghosh et al., 2007; Budz et al., 2009). The experimentally observed binding energies were significantly higher than those reported for the elemental gallium, indicating the increased positive nature of the metal ion in the



**Figure 1:** Thermogravimetry-DTA: (A) [Ga(chmdtc)<sub>3</sub>] and (B) [Ga(chedtc)<sub>3</sub>].

compounds. Elemental sulfur showed a binding energy corresponding to the removal of S2<sub>p</sub> electron at 164.0 eV. In compounds (1) and (2), the signals were observed at 166.5 eV for both compounds (Figure 2E and F). The increase in binding energy is an indication of the loss of electron density from the sulfur atoms to the coordinated gallium. A very highly significant increase in binding energy was observed in the removal of N<sub>1s</sub> electrons viz., 403.0 and 403.5 eV in (1) and (2), respectively, compared to the corresponding binding energy of the elemental N<sub>1s</sub> electron (398.4 eV). The observation signifies the delocalization of the lone pair of electrons on the nitrogen leading to the thioureide from of the structure. The binding energy of C<sub>1s</sub> electron in elemental carbon was 285.0 eV. In the present investigation, corresponding electrons were lost

at 287.5 eV for both compounds. The similarity in binding energies indicated similarity in the electronic environments of carbon atoms in both compounds.

### Structural analysis

Crystal data, data collection, and refinement parameters of complex (2) are given in Table 1. Selected bond parameters are given in Table 2. The ORTEP diagram of complex (2) is shown in Figure 3. In complex (2), the gallium center is coordinated by six sulfur atoms of three dithiocarbamate ligands. Four formula units are present in a unit cell. The compound is monomeric. Compound (2) crystallized with a toluene moiety, which was used for crystallization. A significant short contact of 2.855 Å was observed between H15B (cyclohexyl ring) and the S1 atom. Ga-S bonds and the associated C-S bonds showed asymmetry [Ga-S: 2.4164(12)-2.4481(12) Å and C-S: 1.714(4)–1.731(4) Å] as a requirement of packing. The mean Ga-S bond distance in the compound is 2.4362(13) Å. The complex shows distorted octahedral geometry due to its bite angle variations. The mean S-Ga-S and S-C-S angles are 73.64(2)° and 115.8(2)°, respectively. The thioureide bond shows a mean value of 1.332(4) Å and indicates a partial double-bonded nature of the C-N bond. The nature of the substituents associated with the dithiocarbamates does not alter the coordination environment around the gallium center to a large extent because of its relatively big ionic radius (76 nm; Andrews et al., 2000; Dutta et al., 2002; Goshal and Jain, 2007).

### Continuous shape measure (CShM)

CShM reckons the distance of a given structure from the desired ideal symmetry or from a reference shape (Zabrodsky et al., 1992; Keinan and Avnir, 2000; Alvarez et al., 2002; Ok et al., 2006). The descriptions of geometries such as 'slightly distorted' or 'severely distorted' relative to the reference polyhedron is qualitative in nature. The extent of distortion of a particular molecular structure from an ideal polyhedron can be quantified by symmetry measures. The CShM approach has been successful in such quantification in dealing with transition metal complexes and metal oxides. The ideal geometries associated with hexacoordinated atoms are ideal octahedron (iOh) or ideal trigonal prism (itp). In the present investigation, the coordination around gallium has been found to be distorted octahedron (dOh) in (2). In the present case, the CShM of GaS, core is 2.513. The observed CShM value clearly indicates the closeness of (2) to octahedral geometry.



**Figure 2:** XPS: (A and B) survey scans of  $[Ga(chmdtc)_3]$  and  $[Ga(chedtc)_3]$ , (C and D)  $2_{p3/2}$  electrons at 1120.0 eV and  $2_{p1/2}$  electrons at 1146.0 eV, and (E and F) S2<sub>p</sub> electron at 166.5 eV in (1) and (2).

### Bond valence sum (BVS) calculation

BVS calculations proffer a reliable method of assigning formal oxidation states of an atom in a compound from

the bond parameters. The method depends on the  $R_{ij}$  value for an *i*-*j* bond in a compound that is principally ionic (Brown and Altermatt, 1985; Bresse and O'Keefe, 1991; Brown, 2002, 2009). In a compound, the oxidation

 Table 1: Crystal data, data collection, and refinement parameters for [Ga(chedtc),] (2).

Empirical formula	C <sub>ao co</sub> H <sub>ca</sub> GaN <sub>a</sub> S <sub>c</sub>		
Formula weight	722.83		
Crystal dimensions (mm)	0.12×0.09×0.06		
Crystal system	Monoclinic		
Color	Colorless		
Space group	P2,/n		
a (Å)	9.826(3)		
b (Å)	21.166(6)		
<i>c</i> (Å)	18.236(5)		
α (°)	90		
β (°)	97.518(5)		
γ (°)	90		
<i>U</i> (ų)	3760.1(19)		
Ζ	4		
<i>D</i> <sub>c</sub> (g cm <sup>-3</sup> )	1.277		
μ (cm <sup>-1</sup> )	4.573		
<i>F</i> (000)	1532		
θ (°)	7.36-19.44		
Diffractometer	Bruker APEX-II CCD		
Scan type	ωscans		
Index ranges	$-11 \le h \le 11; -25 \le k \le 25; -21 \le l \le 21$		
Reflections collected	38537		
Unique reflections	3820		
Observed reflections	6810		
$F_{o} > 4\sigma (F_{o})$			
Weighting scheme	$w=1/[\sigma^2(F_0^2)+(0.0365P)^2+2.8992P],$		
	where $P = (F_0^2 + 2F_c^2)/3$		
Number of parameters refined	433		
Final R, R, (observed data)	0.0456, 0.0835		
Goodness-of-fit	0.997		

 Table 2:
 Selected bond distances (Å) and bond angles (°).

Bond distances (Å)		Bond angles (°)	
Ga(1)-S(1)	2.4203(13)	S(1)-Ga(1)-S(2)	73.63(4)
Ga(1)-S(2)	2.4481(12)	S(3)-Ga(1)-S(4)	73.52(4)
Ga(1)-S(3)	2.4529(13)	S(5)-Ga(1)-S(6)	73.77(3)
Ga(1)-S(4)	2.4164(12)	S(1)-C(1)-S(2)	115.6(2)
Ga(1)-S(5)	2.4262(13)	S(3)-C(10)-S(4)	115.8(2)
Ga(1)-S(6)	2.4353(12)	S(5)-C(19)-S(6)	116.1(2)
C(1)-N(1)	1.328(4)	C(1)-N(1)-C(2)	121.0(3)
C(10)-N(2)	1.335(4)	C(10)-N(2)-C(17)	119.8(3)
C(19)-N(3)	1.334(4)	C(19)-N(3)-C(20)	122.0(3)
S(1)-C(1)	1.717(4)	C(1)-S(1)-Ga(1)	85.84(13)
S(2)-C(1)	1.731(4)	C(1)-S(2)-Ga(1)	84.68(14)
S(3)-C(10)	1.714(4)	C(10)-S(3)-Ga(1)	84.76(13)
S(4)-C(10)	1.725(4)	C(10)-S(4)-Ga(1)	85.67(14)
S(5)-C(19)	1.721(4)	C(19)-S(5)-Ga(1)	85.16(13)
S(6)-C(19)	1.718(4)	C(19)-S(6)-Ga(1)	84.93(12)

state of a central atom *i* bonded to *j* matches the bond valence,  $S_{ij}$ , and the total valence of the central atom, which is its oxidation state,  $\sum S_{ij} = \exp[(R_o - R_{ij})/b]$ , and  $R_o$ 



**Figure 3:** ORTEP of [Ga(chedtc)<sub>3</sub>] (2). 40% probability ellipsoids were used for the presentation.

is used as reported (Brown and Altermatt, 1985) and  $R_{ij}$  is the experimentally determined bond distance. The constant *b* is assumed to be 0.37. For compound (**2**), BVS was calculated by summing up the bond valence contributions from six Ga-S interactions. The BVS value was found to be 2.987. In the present case, the BVS value clearly establishes the formal oxidation state of gallium as +3.0; therefore, a considerable ionic character to the predominantly covalent bonding in the compound is clear (Summers et al., 1994).

### Preparation of $Ga_2S_3$ by nonconventional solvothermal decomposition of [Ga(chmdtc)<sub>3</sub>]·0.5C<sub>7</sub>H<sub>8</sub> (1)/ [Ga(chedtc)<sub>3</sub>]·0.5C<sub>7</sub>H<sub>8</sub> (2)

A mixture of tris(cyclohexylmethyldithiocarbamato) gallium(III) or tris(cyclohexylethyldithiocarbamato) gallium(III) (1 g) as a clear solution in chloroform (100 mL) was heated with diethylenetriamine (2 mL) at 60°C for 45 min (Scheme 3). The solid black crystalline  $Ga_2S_3$  obtained was separated from chloroform, washed with ether and chloroform in a drop of dodecylamine, and dried in air. The ease of formation of the nanosulfide from (1) was greater than (2).



**Scheme 3:** Synthesis of nano-Ga<sub>2</sub>S<sub>3</sub>.

### **Powder XRD analysis**

The powder XRD pattern of the nano-Ga<sub>2</sub>S<sub>3</sub> corresponded to the hexagonal Ga<sub>2</sub>S<sub>3</sub> nanocrystals with lattice constants of *a*=11.120 Å, *b*= 6.395 Å, and *c*=7.002 Å, consistent with the JCPDS 16-0500. The signals from (110), (-311), (020), (-112), (310), and (221) planes are characteristic signals of  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub>, which are clearly distinguishable in the wurtzite form of Ga<sub>2</sub>S<sub>3</sub>. Solvothermally prepared Ga<sub>2</sub>S<sub>3</sub> showed sharp intense signals in its powder XRD, which indicates good crystalline nature of the material.

### High-resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray spectroscopy (EDX) analysis

The HRTEM and selected area electron diffraction (SAED) of the nano- $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> are shown in Figure 4. The partly spherical nature of the particles was confirmed by the TEM micrographs, and the particles are in the range of 50 nm. SAED confirmed the crystalline nature of the nano-sized  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub>. The SAED pattern can be indexed to the (110) and (-311) planes, confirming the wurtzite phase of  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> nanoparticles. The HRTEM images of  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> display fringes with interlayer spacing in the order of 0.50±0.01 nm, equal to the lattice spacing of the (110) planes of hexagonal  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> nanocrystals. The corresponding EDX (Figure 5) indicates that the nanoparticles consisted of Ga and S in the ratio of 2:3.

# Conclusions

The gallium dithiocarbamates [Ga(chmdtc)<sub>2</sub>] (1) and [Ga(chedtc)] (2) were prepared in good yields, characterized by IR, NMR, and XPS techniques, and used as Ga<sub>2</sub>S<sub>3</sub> precursor. Thermal analysis confirmed the proposed formulas of the compounds, and compound (1) is slightly thermally more stable than (2). In the XPS study, experimentally observed binding energies of gallium are significantly higher than those reported for the element, indicating the increased positive nature of the metal ion in the compounds. A similar increase in binding energy of sulfur is an indication of the loss of electron density from the sulfur atoms to the coordinated gallium. The molecular structure in the solid state of compound (2) was established by single crystal XRD analysis. Ga-S bonds and the associated C-S bonds showed significant asymmetry [Ga-S: 2.4164(12)–2.4481(12) Å and C-S: 1.714(4)–1.731(4) Å].



**Figure 4:** TEM-SAED patterns of nano- $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> (100 and 10 nm).



**Figure 5:** EDX of  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub>.

The mean Ga-S bond distance is 2.4362(13) Å. The complex showed distorted octahedral geometry due to the bite angle variations. The thioureide bond showed a mean value of 1.332(4) Å distance. The CShM of GaS<sub>6</sub> core is 2.513, which clearly indicates the closeness of (**2**) to octahedral geometry. BVS calculations proffer a value of 2.987, which clearly established the oxidation state of gallium as +3; therefore, the ionic interactions prevail in the compound. Nano- $\alpha$ -Ga,S<sub>2</sub> particles were found to be of 50 nm size.

# **Experimental**

### **Reagents and equipment**

Gallium(III) chloride (Sigma-Aldrich, India; assay: 99.99%) and the cyclohexylmethyl amine and cyclohexylethyl amine (Sigma-Aldrich; assay: 98%) were used as supplied without further purification. IR spectra were recorded on an Avatar Nicolet Fourier transform IR spectrometer (range, 4000-400 cm<sup>-1</sup>; USA) as KBr pellets of the compounds. Electronic spectra were recorded in CCl, on a Hitachi U-2001 double-beam spectrometer (Tokyo, Japan). Thermal analysis was carried out with NETZSCH STA 449F3 (Germany) instrument under nitrogen atmosphere with a heating rate of 20 K min<sup>-1</sup>. <sup>1</sup>H (400 MHz; CDCl.; Me, Si) and <sup>13</sup>C NMR (100.6 MHz; CDCl.) spectra were recorded on a Bruker AMX-400 spectrometer (USA) at room temperature using CDCl<sub>3</sub> as a solvent. The powder diffraction data were collected in the  $2\theta$  range=2-80° using Bruker D8 X-ray diffractometer (USA) equipped with CuKa radiation at fixed current and potential. The scan speed and step sizes were 0.05° min<sup>1</sup> and 0.00657, respectively. The scanning electron micrographs of the samples were recorded with JEOL JSM-5610Lv microscope (Tokyo, Japan). The HRTEM measurements were carried out on JEOL 2100 (field emission) with an accelerating voltage of 200 kV (Tokyo, Japan).

#### X-ray crystallography

Intensity data were collected at ambient temperature (295 K) on a Bruker APEX-II CCD diffractometer (USA) with graphite monochromated MoK $\alpha$  radiation ( $\lambda$ =0.71073 Å) and were corrected for absorptions with a multiscan technique (Walker and Stuart, 1983; Gluzinski, 1987). The structures were solved by direct methods using SIR97 (Altomare et al., 1999) and were refined by SHELX97 (Sheldrick, 2008). The nonhydrogen atoms were refined anisotropically and all hydrogen atoms were fixed geometrically. Molecular plots were obtained using the ORTEP-3 program (Farrugia, 1999).

#### Synthesis of the complexes

Synthesis of tris(cyclohexylmethyldithiocarbamato)gallium(III); [Ga(chmdtc)<sub>3</sub>]-0.5C<sub>7</sub>H<sub>8</sub> (1): Cyclohexylmethyl amine (30 mmol, 1.2 mL in 25 mL methanol) and carbon disulfide (30 mmol, 2.3 mL in methanol) were mixed under ice-cold condition  $(0-5^{\circ}C)$  to result in yellow dithiocarbamic acid solution. To the freshly prepared dithiocarbamic acid solution, GaCl<sub>3</sub> (10 mmol, 1.8 g in methanol) was added dropwise with constant stirring for approximately 3 h. A white precipitate separated from the mixture was filtered, washed with methanol, and dried in air. The solid was then recrystallized from dichloromethane/toluene (1:1, v/v) mixture. Yield 72%; dec. 232°C [anal. calcd. for  $C_{27.5}H_{46}N_3S_6Ga$  (680.79)% C, 48.51; H, 6.81; N, 6.17. Found C, 48.47; H, 6.78; N, 6.13].

Synthesis of tris(cyclohexylethyldithiocarbamato)gallium(III); [Ga(chedtc)<sub>3</sub>]-0.5C<sub>7</sub>H<sub>8</sub> (2): Cyclohexylethyl amine (30 mmol, 1.3 mL in 25 mL methanol), carbon disulfide (30 mmol, 2.3 mL), and GaCl<sub>3</sub> (10 mmol, 1.8 g) were used and a procedure as described above was followed. Yield 80%; dec. 220°C [anal. calcd. for  $C_{30.50}H_{52}GaN_3S_6$  (722.83)% C, 50.68; H, 7.25; N, 5.81. Found C, 50.63; H, 7.21; N, 5.76]. GaCl<sub>3</sub> in methanol will undergo extensive methanolysis and Ga(OCH<sub>3</sub>)<sub>3</sub> will be the true species reacting with the dithiocarbamate.

#### Supplementary material

CCDC **1025449** contains the supplementary crystallographic data for (**2**). The data can be obtained free of charge at http://www.ccdc.cam. ac.uk/con-ts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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