

The mixed alkyl gallium or indium *N,N,N*-trimethylpropylenediaminedithiocarbamates. Crystal structure of diethyl(*N,N',N'*-trimethylpropylenediamine) dithiocarbamateindium(III)

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Abstract

A series of compounds with the general formula $(R_2MS_2CNMe(CH_2)_3NMe_2)$, $R = Me, Et, Np, C_5H_{11}$; $M = Ga, In$ have been synthesized and characterized. Their low melting points and reasonable volatility makes them potentially suitable as single-source precursors for III/VI materials. The crystal structure of $Et_2InS_2CNMe(CH_2)_3NMe_2$ has been determined.

Keywords: Alkyl; Indium; Gallium; Thiocarbonate; Crystal structure; Chemical vapour deposition

1. Introduction

Thin films of In_xS_x or Ga_xS_x have electrical, optical and photovoltaic properties which make them suitable for use in various opto-electronic devices [1]. Such materials may be classified as mid-band gap semiconductors, e.g. InS [2] (2.44 eV) [3] and β - In_2S_3 [4,5] (2.07 eV) [6] as compared with materials such as narrow band gap GaAs [7] (1.42 eV) or wide band gap ZnS [7] (3.68 eV). These materials may also be useful in passivating the surface of III/V materials [8,9]. There is only a small number of reports describing the deposition of these materials using organometallic precursors [2,4,10–17]. Recently III/VI materials have been deposited from single-source precursors such as $R_2MS_2CNEt_2$ ($M = Ga, In$; $R = Me, Et, Np$) [10], $Me_2InSePh$ [4], $In(SePh)_3$ [4], n - $BuIn(S-i-Pr)_2$ [2], $[In_2Se_2]_n$ [5,13] [$(^tBu)GaS$]₄ [11] and [$(^tBu)_2In(S^tBu)$]₂ [11].

In the present paper we report on the synthesis and characterisation of the unusually stable *N,N',N'*-trimethylpropylenediaminedithiocarbamic acid (TMP-

DAT) (1) and its subsequent reaction with the metal alkyls to give the alkylmetal dithiocarbamates of the general formula $(R_2MS_2CNMe(CH_2)_3NMe_2)$, $R = Me, Et, Np, C_5H_{11}$; $M = Ga, In$. The characterization of cadmium and zinc dithiocarbamates based on the diamines, *N,N',N'*-trimethylpropylenediamine and *N,N',N'*-trimethylethylenediamine and the deposition of the corresponding II/VI materials CdS and ZnS from these precursors have been reported [18,19]. The deposition behaviour of the new dithiocarbamate described here may be similar to the simpler diethyldithiocarbamates reported previously [10], which deposited crystalline indium sulphide films of good quality and varying phase over the temperature range 425–325°C.

2. Experimental

2.1. Chemicals

Bromoethane, 1-bromo-2,2-dimethylpropane, *N,N',N'*-trimethylpropanediamine, *N,N',N'*-trimethylethylenediamine, carbon disulphide, gallium(III) trichloride, indium(III) trichloride and magnesium turnings were purchased from Aldrich Chemical Co., Ltd. Trimethylgallium, trimethylindium and triethylindium were donated by Epichem, Ltd. The compounds Np_3In

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[20], Et₃Ga [21] and Np₃Ga [22], (*sec*-butyl)₃Ga [23] and (*sec*-butyl)₃In [23] were prepared by the literature methods.

2.2. Physical measurements

IR spectra were recorded on a Matteson Polaris FT-IR spectrometer as nujol mulls; ¹³C and ¹H solution NMR were recorded with a Bruker AM 250 pulsed Fourier-transform NMR instrument; solid state ¹³C NMR was recorded on a MSL-300 multinuclear instrument; mass spectra were recorded with a Kratos MS 50 TS instrument and microanalyses was performed by University College, London.

2.3. X-ray crystallography

X-ray measurements were made on a crystal (0.25 × 0.18 × 0.12 mm³), mounted in a glass capillary with an Enraf-Nonius CAD4 diffractometer operating in the ω-2θ scan mode with graphite-monochromated Mo K_α radiation as described previously [24]. The structures were solved via standard heavy-atom procedures and refined by using full-matrix least-squares methods [25] with scattering factors calculated by using the data from Ref. [26]. All non-hydrogen atoms were refined with anisotropic displacement factors. Hydrogen atoms were

Table 1
Crystals data, intensity measurement and structure refinement

Formula	C ₁₁ H ₂₅ InN ₂ S ₂
<i>M</i>	364.27
<i>T</i> (K)	293
Crystal size (mm)	0.25 × 0.18 × 0.12
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> (Å)	8.583(3)
<i>b</i> (Å)	9.647(4)
<i>c</i> (Å)	10.497(4)
α (°)	77.93(3)
β (°)	70.48(3)
γ (°)	85.83(4)
<i>V</i> (Å ³)	801.1(5)
<i>Z</i>	2
<i>D</i> _c (g cm ⁻³)	1.510
μ (mm ⁻¹)	1.716
<i>F</i> (000)	372
Radiation	Mo K _α
λ (Å)	0.71069
$\theta_{\min/\max}$	2.10, 24.98
Total no. of reflections	2115
No. of unique reflections	1884
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0207, <i>wR</i> ₂ = 0.0568
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0241, <i>wR</i> ₂ = 0.0576

$$R_1 = \frac{\sum \|F_o\| - |F_c|}{\sum \|F_o\|}, \quad wR_2 = \left[\frac{\sum \{w(F_o^2 - F_c^2)^2\}}{\sum w(F_o^2)^2} \right]^{1/2}, \quad w = 1/[\sigma(F_o^2) + (0.09P)^2], \quad \text{where } P = \frac{\max(F_o^2) + 2F_c^2}{3}.$$

Table 2

Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å² × 10³). *U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
In(1)	2187(1)	1534(1)	3321(1)	42(1)
S(1)	-262(1)	429(1)	2612(1)	44(1)
S(2)	2208(1)	2608(1)	842(1)	51(1)
N(1)	-390(3)	2014(3)	238(2)	42(1)
N(2)	-5338(3)	3269(3)	2871(3)	44(1)
C(1)	412(3)	1699(4)	1148(3)	37(1)
C(2)	224(4)	3080(5)	-1024(3)	63(1)
C(3)	-1955(3)	1339(4)	431(3)	44(1)
C(4)	-3456(3)	2294(4)	847(3)	49(1)
C(5)	-3686(3)	2696(5)	2213(3)	49(1)
C(6)	4408(5)	4652(5)	2080(5)	68(1)
C(7)	-5412(4)	3428(6)	4255(4)	67(2)
C(8)	417(4)	2689(5)	4724(3)	52(1)
C(9)	-627(5)	3744(5)	4099(5)	74(2)
C(10)	3684(4)	-338(5)	3568(4)	51(1)
C(11)	4018(5)	-1253(5)	2505(5)	75(2)

calculated geometrically using AFIX command on the SHELXL-93 program [27]. Empirical absorption correction (ψ -scan) was applied to *F* data with a transmission factor of 64.2% (min), 99.9% (max). The compound crystallizes in the space group *P*1, with *a* = 8.583(3) Å, *b* = 9.647(4) Å, *c* = 10.497(4) Å, α = 77.93(3)°, β = 70.48(3)°, γ = 85.83(4)°. The structure was refined to a final residual *R*_w = 0.0207. Crystal data and the details of the intensity measurements and refinement are given in Table 1; atomic coordinates and equivalent isotropic positional parameters are reported in Table 2. Tables of H-atom coordinates, all bond lengths and angles, and anisotropic displacement factors are included in supplementary material, deposited at the Cambridge Crystallographic Data Centre.

2.4. Synthesis

2.4.1. *N,N',N'*-trimethylpropylenediaminedithiocarbamic acid (1)

Carbon disulphide (3.27 g, 43.1 mmol) was added to a stirred solution of *N,N',N'*-trimethylpropylenediamine (5 g, 43.1 mmol) dissolved in dichloromethane (35 cm³) at 0°C. The mixture was allowed to warm to room temperature and was then stirred for about 20 min whereby a white compound had precipitated out of the solution. All solvents and volatiles were removed under vacuum leaving a white solid (1), yield 8.27 g, (92%), m.p. 160°C.

2.4.2. Alkyl-*N,N,N'*-trimethylpropylenediaminedithiocarbamatogallium or -indium(III) (*R*₂MS₂CN(Me)(CH₂)₃-NMe₂, *R* = Me, Et, Np, C₅H₁₁; *M* = Ga, In)

In a typical preparation of (Me₂GaS₂CN(Me)(CH₂)₃-NMe₂) (2) *N,N,N'*-trimethylpropylenediaminedithio-

carbamic acid (2.86 g, 14.95 mmol) was slowly added to a stirred solution of Me_3Ga (1.72 g, 14.95 mmol) in toluene (50 cm^3) at room temperature over a period of half an hour. The mixture was stirred under nitrogen for 18 h. The solvent and other volatiles were removed under vacuum at room temperature leaving a sticky yellow solid which was stirred with petroleum spirit (30 cm^3). The mixture was allowed to settle and the product was separated from any excess dithiocarbamic acid by filtration. A yellowish viscous liquid identified as methyl-*N,N,N*-trimethylpropylenediaminedithiocarbamatogallium(III) (**2**) was obtained, yield 3.01 g, (69.2%).

Other compounds were prepared by the same method using: Et_3Ga for $\text{Et}_2\text{GaS}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ (**3**), liquid, 90.8%; Et_3In for $\text{Et}_2\text{InS}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ (**4**), m.p. 46°C, 62%; Np_3Ga for $\text{Np}_2\text{GaS}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ (**5**), liquid, 55.4%; Np_3In for $\text{Np}_2\text{InS}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ (**6**), m.p. 52°C, 86%; (*sec*-butyl) $_3\text{Ga}$ for $(\text{C}_5\text{H}_{11})_2\text{GaS}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ (**7**), liquid, 97.3%; and (*sec*-butyl) $_3\text{In}$ for $(\text{C}_5\text{H}_{11})_2\text{InS}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ (**8**), m.p. 33°C, 86%.

All compounds have been characterized by IR, NMR and mass spectrometry. Compound (**2**) was additionally characterized by X-ray crystallography.

$\text{S}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ (**1**). ^{13}C NMR (solid state): δ (ppm) 23.57 ($\text{CH}_2\text{-CH}_2\text{-CH}_2$), 42.35, 42.85 ($-\text{N}(\text{CH}_3)_2$), 44.71 ($-\text{NCH}_3$), 54.21 ($-\text{CH}_2\text{N}(\text{CH}_3)_2$), 54.98 ($-\text{CH}_2\text{NCH}_3$), 211.94 ($-\text{CS}_2$). Major IR bands (cm^{-1}), nujol: 2942(s), 2858(s), 2815(s), 2785(s), 2497(vw), 2361(vw), 1458(m), 1378(w), 1366(m), 1298(w), 1257(m), 1225(w), 1139(m), 1084(w), 1060(w), 1037(w), 974(m), 901(w), 740(w), 610(w), 581(w), 507(w), 479(w), 433(w). Mass spectrum (m/z): $\text{HS}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ 192(8.9%), $\text{SCN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ 159(26.4%), $\text{CMeN}(\text{CH}_2)_3\text{NMe}_2$ 127(3.5%), $\text{MeN}(\text{CH}_2)_3\text{NMe}_2$ 115(3.0%), $^+\text{CH}_2\text{CH}_2\text{-CH}_2\text{NMe}_2$ 86(48.1%), $^+\text{CH}_2\text{CH}_2\text{NMe}_2$ 72(5.7%), $^+\text{CH}_2\text{NMe}_2$ 58(100%), $^+\text{NMe}_2$ 44(22.8%). Anal. Found: C, 42.32; H, 8.43; N, 13.80; S, 31.26%. $\text{C}_7\text{H}_{16}\text{N}_2\text{S}_2$. Calc.: for C, 43.7; H, 8.3; N, 14.6; S, 33.3%.

$\text{Me}_2\text{GaS}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ (**2**). ^1H NMR (C_6D_6): δ (ppm) 0.45 [6H, s, $\text{Ga}(\text{CH}_3)_2$], 1.44 [2H, quintet, $^3J(\text{H-H}) = 7.25$ Hz, ($\text{CH}_2\text{CH}_2\text{CH}_2$)], 1.96 [6H, s, $\text{N}(\text{CH}_3)_2$], 1.92 [2H, t, $^3J(\text{H-H}) = 6.5$ Hz, $\text{CH}_2\text{-N}(\text{CH}_3)_2$], 2.75 [3H, s, NCH_3], 3.41 [2H, t, $^3J(\text{H-H}) = 7.5$ Hz, CH_3NCH_2]. ^{13}C NMR (C_6D_6): δ (ppm) -1.42 [$\text{Ga}(\text{CH}_3)_2$], 25.38 [($\text{CH}_2\text{CH}_2\text{CH}_2$)], 45.81 [$\text{N}(\text{CH}_3)_2$], 56.89 [$\text{CH}_2\text{N}(\text{CH}_3)_2$], 41.08 [NCH_3], 53.98 [CH_3NCH_2], 201.15 [CS_2]. Major IR bands (cm^{-1}), neat: $\nu(\text{C-N})$ 1510(s), $\nu(\text{C=S})$ 989(m), $\nu(\text{Ga-C})$ 538(s), $\nu(\text{Ga-S})$ 382(m). Mass spectrum (m/z): $(\text{CH}_3)_2\text{-}^{71}\text{GaS}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ 292(0.4%), $\text{CH}_3\text{-}^{71}\text{Ga}^+\text{S}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ 277(56.1%), $^+\text{SCN-}$

$(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ 159(8.7%), $\text{CN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ 127(2.8%), $\text{HN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ 116(4.5%), $\text{MeN}(\text{CH}_2)_3\text{NMe}_2$ 115(3.0%), $^+\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$ 86(44.5%), $\text{CH}_3^+\text{Ga}^{69}$ 84(30.6%), $^+\text{CH}_2\text{CH}_2\text{NMe}_2$ 72(4.2%), $^{71}\text{Ga}^+$ 71(1.4%), $^{69}\text{Ga}^+$ 69(0.5%), $^+\text{CH}_2\text{NMe}_2$ 58(100%), $^+\text{NMe}_2$ 44(9.9%).

$\text{Et}_2\text{GaS}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ (**3**). ^1H NMR (C_6D_6): δ (ppm) 1.0 [4H, q, $^3J(\text{H-H}) = 8.0$ Hz, $\text{Ga}(\text{CH}_2\text{CH}_3)$], 1.53 [6H, t, $^3J(\text{H-H}) = 8.0$ Hz, $\text{Ga}(\text{CH}_2\text{CH}_3)$], 1.50 [2H, quintet, $^3J(\text{H-H}) = 7.25$ Hz, ($\text{CH}_2\text{CH}_2\text{CH}_2$)], 1.99 [6H, s, $\text{N}(\text{CH}_3)_2$], 1.95 [2H, t, $^3J(\text{H-H}) = 6.5$ Hz, $\text{CH}_2\text{N}(\text{CH}_3)_2$], 2.80 [3H, s, NCH_3], 3.47 [2H, t, $^3J(\text{H-H}) = 7.5$ Hz, CH_3N_2]. ^{13}C NMR (C_6D_6): δ (ppm) 8.51 [$\text{Ga}(\text{CH}_2\text{CH}_3)$], 11.31 [$\text{Ga}(\text{CH}_2\text{CH}_3)$], 25.51 [$\text{CH}_2\text{CH}_2\text{CH}_2$], 45.87 [$\text{N}(\text{CH}_3)_2$], 56.96 [$\text{CH}_2\text{N}(\text{CH}_3)_2$], 41.08 [NCH_3], 53.99 [CH_3NCH_2], 201.41 [CS_2]. Major IR bands (cm^{-1}), neat: $\nu(\text{C-N})$ 1505(s), $\nu(\text{C=S})$ 999(m), $\nu(\text{Ga-C})$ 515(s), $\nu(\text{Ga-S})$ 380(s). Mass spectrum (m/z): $\text{C}_2\text{H}_5\text{-}^{69}\text{GaS}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ 289(99.5%), $\text{C}_2\text{H}_5\text{-}^{71}\text{Ga}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ 159(8.7%), $^+\text{CN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ 127(8.8%), $\text{HN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ 116(2.0%), $\text{Me}^+\text{N}(\text{CH}_2)_3\text{NMe}_2$ 115(1.9), $^+\text{CN}(\text{H})(\text{CH}_2)_3\text{NMe}_2$ 113(16.4%), $^+\text{N}(\text{H})(\text{CH}_2)_3\text{NMe}_2$ 101(9.2%), $^+(\text{CH}_2)_3\text{NMe}_2$ 86(18.9%), $^+(\text{CH}_2)_2\text{NMe}_2$ 72(2.8%), $^{71}\text{Ga}^+$ 71(1.8%), $^+\text{CH}_2\text{-NMe}_2$ 58(100%), $^+\text{NMe}_2$ 44(9.9%).

$\text{Et}_2\text{InS}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ (**4**). ^1H NMR (C_6D_6): δ (ppm) 1.05 [4H, q, $^3J(\text{H-H}) = 8.0$ Hz, $\text{In}(\text{CH}_2\text{CH}_3)$], 1.66 [6H, t, $^3J(\text{H-H}) = 8.0$ Hz, $\text{In}(\text{CH}_2\text{CH}_3)$], 1.62 [2H, quintet, $^3J(\text{H-H}) = 7.25$ Hz, ($\text{CH}_2\text{CH}_2\text{CH}_2$)], 2.01 [6H, s, $\text{N}(\text{CH}_3)_2$], 1.99 [2H, t, $^3J(\text{H-H}) = 6.5$ Hz, $\text{CH}_2\text{N}(\text{CH}_3)_2$], 2.94 [3H, s, NCH_3], 3.60 [2H, t, $^3J(\text{H-H}) = 7.5$ Hz, CH_3NCH_2]. ^{13}C NMR (C_6D_6): δ (ppm) 10.74 [$\text{In}(\text{CH}_2\text{CH}_3)$], 13.09 [$\text{In}(\text{CH}_2\text{CH}_3)$], 25.57 [$\text{CH}_2\text{CH}_2\text{CH}_2$], 45.90 [$\text{N}(\text{CH}_3)_2$], 57.15 [$\text{CH}_2\text{N}(\text{CH}_3)_2$], 42.02 [NCH_3], 54.74 [CH_3NCH_2], 204.18 [CS_2]. Major IR bands (cm^{-1}), nujol: $\nu(\text{C-N})$ 1492(s), $\nu(\text{C=S})$ 997(m), $\nu(\text{In-C})$ 458(m), $\nu(\text{In-S})$ 365(w). Mass spectrum (m/z): $\text{C}_2\text{H}_5\text{-}^{115}\text{InS}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ 335(7.6%), $^+\text{SCN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ 159(2.0%), $^{115}\text{In}^+$ 115(2.0%), $^+(\text{CH}_2)_3\text{NMe}_2$ 86(4.6%), $^+\text{CH}_2\text{NMe}_2$ 58(8.4%). Microanalysis: Anal. Found: C, 36.26; H, 6.92; N, 7.69%. $\text{C}_{11}\text{H}_{25}\text{NS}_2\text{In}$. Calc.: C, 36.84; H, 6.80; N, 7.78%.

$\text{Np}_2\text{GaS}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ (**5**). ^1H NMR (C_6D_6): δ (ppm) 1.33 [4H, s, $\text{Ga}(\text{CH}_2\text{C})$], 1.34 [18H, s, $\text{GaCH}_2\text{C}(\text{CH}_3)_3$], 1.48 [2H, quintet, $^3J(\text{H-H}) = 7.25$ Hz, ($\text{CH}_2\text{CH}_2\text{CH}_2$)], 1.99 [6H, s, $\text{N}(\text{CH}_3)_2$], 1.95 [2H, t, $^3J(\text{H-H}) = 6.5$ Hz, $\text{CH}_2\text{N}(\text{CH}_3)_2$], 2.76 [3H, s, NCH_3], 3.44 [2H, t, $^3J(\text{H-H}) = 7.5$ Hz, CH_3NCH_2]. ^{13}C NMR (C_6D_6): δ (ppm) 38.82 [$\text{Ga}(\text{CH}_2\text{C})$], 33.12 [GaCH_2C], 34.81 [$\text{GaCH}_2\text{C}(\text{CH}_3)_3$], 25.59 [($\text{CH}_2\text{CH}_2\text{CH}_2$)], 45.89 [$\text{N}(\text{CH}_3)_2$], 56.99 [$\text{CH}_2\text{N}(\text{CH}_3)_2$], 40.91 [NCH_3],

53.84 [CH₃NCH₂], 200.47 [CS₂]. Major IR bands (cm⁻¹), neat: 2950(s), ν(C–N) 1505(s), ν(C=S) 986(m), ν(Ga–C) 533(w), ν(Ga–S) 380(m). Mass spectrum (*m/z*): Np ⁷¹GaS₂CN(Me)(CH₂)₃NMe₂ 333(100%), Np ⁶⁹GaN(Me)(CH₂)₃NMe₂ 255(18.1%), Np₂ ⁶⁹Ga 211(7.5%), ⁺SCN(Me)(CH₂)₃NMe₂ 159(9.7%), CN(Me)(CH₂)₃NMe₂ 127(2.8%), HNMe-(CH₂)₃NMe₂ 116(2.7%), ⁺N(Me)(CH₂)₃NMe₂ 115(3.4%), ⁺CH₂CH₂CH₂NMe₂ 86(32.9%), ⁺CH₂-CH₂NMe₂ 72(2.8%), ⁷¹Ga⁺ 71(6.9%), ⁶⁹Ga⁺ 69(1.0%), ⁺CH₂NMe₂ 58(57.5%), ⁺NMe₂ 44(8.2%).

Np₂InS₂CN(Me)(CH₂)₃NMe₂ (6). ¹H NMR (C₆D₆). δ (ppm) 1.47 [4H, s, In(CH₂C)], 1.29 [18H, s, InCH₂C(CH₃)₃], 1.58 [2H, quintet, ³J(H–H) = 7.25 Hz, (CH₂CH₂CH₂)], 2.01 [6H, s, N(CH₃)₂], 1.99 [2H, t, ³J(H–H) = 6.5 Hz, CH₂N(CH₃)₂], 2.90 [3H, s, NCH₃], 3.57 [2H, t, ³J(H–H) = 7.5 Hz, CH₃NCH₂]. ¹³C NMR (C₆D₆): δ (ppm) 41.91 [In(CH₂C)], 33.49 [InCH₂C], 35.37 [InCH₂C(CH₃)₃], 25.66 [(CH₂CH₂CH₂)], 45.92 [N(CH₃)₂], 57.12 [CH₂N(CH₃)₂], 41.59 [NCH₃], 54.66 [CH₃NCH₂], 203.07 [CS₂]. Major IR bands (cm⁻¹), nujol: ν(C–N) 1494(m), ν(C=S) 982 (m), ν(In–C) 452(w), ν(In–S) 377(m). Mass spectrum (*m/z*): Np ¹¹⁵InS₂CN(Me)(CH₂)₃NMe₂ 377(100%), (H)Np₂ ¹¹⁵In⁺ 258(0.6%), Np₂ ¹¹⁵In⁺ 257(4.1%), ⁺SCN(Me)(CH₂)₃NMe₂ 159(3.3%), CN(Me)(CH₂)₃NMe₂ 127(0.7%), HN(Me)(CH₂)₃NMe₂ 116(0.8%), ⁺N(Me)CH₂)₃NMe₂ 115(0.5%), ¹¹⁵In 115(2.7%), ⁺CH₂CH₂CH₂NMe₂ 86(10.6%), ⁺CH₂CH₂NMe₂ 72(1.6%), ⁺CH₂NMe₂ 58(19.8%), ⁺NMe₂ 44(3.1%).

(C₅H₁₁)₂GaS₂CN(Me)(CH₂)₃NMe₂ (7). ¹H NMR (C₆D₆): δ (ppm) 1.02 [2H, dd, ²J(HA–HB) = 13.75 Hz, ³J(HA–HC) = 7.75 Hz, Ga(CH₂^A)], 1.19 [2H, dd, ²J(HB–HA) = 13.75 Hz, ³J(HB–HC) = 5.5 Hz, Ga(CH₂^B)], 2.03 [2H, m, CH], 1.18 [6H, d, CCH₃], 1.44 [4H, m, CCH₂] 1.03 [6H, t, CCH₂CH₃], 1.44 [2H, quintet, ³J(H–H) = 7.25 Hz, (CH₂CH₂CH₂)], 1.96 [6H, s, N(CH₃)₂], 1.91 [2H, t, ³J(H–H) = 6.5 Hz, CH₂N(CH₃)₂], 2.77 [3H, s, NCH₃], 3.41 [2H, t, ³J(H–H) = 7.5 Hz, CH₃NCH₂]. ¹³C NMR (C₆D₆): δ (ppm) 25.57 [Ga(CH₂C)], 34.78 [CH], 28.09 [CCH₃], 35.01 [CCH₂], 13.01 [CCH₂CH₃], 24.84 [(CH₂CH₂CH₂)], 45.90 [N(CH₃)₂], 56.99 [CH₂N(CH₃)₂], 41.04 [NCH₃], 53.95 [CH₃NCH₂], 201.09 [CS₂]. Major IR bands (cm⁻¹), neat: ν(C–N) 1505(s), ν(C=S) 987(m), ν(Ga–C) 532(w), ν(Ga–S) 379(m). Mass spectrum (*m/z*): C₅H₁₁ ⁶⁹Ga⁺S₂CN(Me)(CH₂)₃NMe₂ 331(37.1%), C₅H₁₁ ⁶⁹GaN(Me)(CH₂)₃NMe₂ 255(7.3%), (C₅H₁₁)₂ ⁶⁹Ga⁺ 211(4.5%), ⁺SCN(Me)-(CH₂)₃NMe₂ 159(3.2%), ⁺CH₂CH₂CH₂NMe₂ 86 (25.4%), ⁺CH₂CH₂NMe₂ 72(2.0%), ⁷¹Ga⁺ 71(24.2%), ⁶⁹Ga⁺ 69(9.3%), ⁺CH₂NMe₂ 58(9.5%), C₄H₉⁺ 57(100%), ⁺NMe₂ 44(1.8%), C₃H₇⁺ 43(82.9%).

(C₅H₁₁)₂InS₂CN(Me)(CH₂)₃NMe₂ (8). ¹H NMR (C₆D₆): δ (ppm) 1.23 [2H, dd, ²J(HA–HB) = 12.5 Hz, ³J(HA–HC) = 7.0 Hz, In(CH₂^A)], 1.34 [2H, dd, ²J(HB–HA) = 12.5 Hz, ³J(HB–HC) = 5.5 Hz, In(CH₂^B)], 2.10 [2H, m, CH], 1.13 [6H, d, CCH₃], 1.41 [4H, m, CCH₂] 0.99 [6H, t, CCH₂CH₃], 1.53 [2H, quintet, ³J(H–H) = 7.25 Hz, (CH₂CH₂CH₂)], 1.97 [6H, s, N(CH₃)₂], 1.95 [2H, t, ³J(H–H) = 6.5 Hz, CH₂N(CH₃)₂], 2.89 [3H, s, NCH₃], 3.52 [2H, t, ³J(H–H) = 7.5 Hz, CH₃NCH₂]. ¹³C NMR (C₆D₆): δ (ppm) 30.29 [In(CH₂C)], 34.83 [CH], 24.97 [CCH₃], 34.95 [CCH₂], 12.36 [CCH₂CH₃], 24.92 [(CH₂CH₂CH₂)], 45.15 [N(CH₃)₂], 56.45 [CH₂N(CH₃)₂], 41.15 [NCH₃], 53.95 [CH₃NCH₂], 202.87 [CS₂]. Major IR bands (cm⁻¹), nujol: ν(C–N) 1495(m), ν(C=S) 981(m), ν(In–C) 465(w), ν(In–S) 378(m). Mass spectrum (*m/z*): (C₅H₁₁)₂ ¹¹⁵In⁺S₂CN(Me)(CH₂)₃NMe₂ 337(100%), (C₅H₁₁)₂ ¹¹⁵In⁺ 257(100%), ⁺CN(Me)-(CH₂)₃NMe₂ 127(1.5%), HN(Me)(CH₂)₃NMe₂ 116(1.3%), ⁺N(Me)(CH₂)₃NMe₂ 115(1.1%), ¹¹⁵In 115(3.8%), ⁺CH₂CH₂CH₂NMe₂ 86(16.5%), ⁺CH₂CH₂NMe₂ 72(4.0%), ⁺CH₂NMe₂ 58(31.4%), C₄H₉⁺ 57(3.1%), ⁺NMe₂ 44(4.5%), C₃H₇⁺ 43(12.2%).

3. Results and discussion

The physical properties of compounds **2** to **8** range from high boiling liquids to low melting solids. Steric hindrance and the degree of coordination exhibited by the metal centre appear to be important factors in determining the physical state of the compound. The unusually stable dithiocarbamic acid, *N,N',N'*-trimethylpropylenediaminedithiocarbamate has been isolated and used in alkane elimination reactions with various trialkyls producing the respective alkylmetaldithiocarbamates.

Elemental analysis of these compounds were not reliable except compounds **2** and **4** due to their higher reactivity towards oxygen, moisture and light. In all cases freshly prepared samples gave clear NMR spectra.

4. Spectroscopic studies

The IR spectra for the dithiocarbamic acid shows C–S stretching at 974 cm⁻¹ and a larger number of vibrations in the lower region between 800 and 400 cm⁻¹. Weak bands in the region between around 2400 cm⁻¹ and 2700 cm⁻¹ could be due to either N–H⁺ or S–H stretching. The dithiocarbamic acid is stable in air and soluble in water. This suggests that the compound behaves in a similar way to an amino acid, as a zwitterion, possibly with a H⁺ attached to a nitrogen and the sulphur carrying a negative charge, Fig. 1.

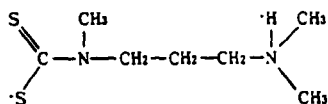


Fig. 1. Molecular diagram of *N,N,N'*-trimethylpropylenediamine-dithiocarbamic acid.

The IR spectrum of the chloride salt of *N,N',N'*-trimethylpropylenediamine ligand shows vibrations in the region 2400 to 2700 cm^{-1} which, due to the absence of sulphur, correspond to N-H^+ stretching only. Therefore, one can postulate that the bands observed in this region are the same bands observed at similar wavenumbers in the IR of the dithiocarbamic acid which are also assigned as N-H^+ vibrations. The results of the

elemental analyses and mass spectra are also in good agreement (see Section 2).

Alkyltrimethylpropylenediaminedithiocarbamateindium or gallium(III) show M-S (365–380 cm^{-1}), Ga-C (530 cm^{-1}) and In-C (450 cm^{-1}) symmetric stretches comparable with those of the simpler diethyldithiocarbamates of indium and gallium [10]. The higher value (365 cm^{-1}) for In-S symmetric stretch for compound 4 may be due to the polymeric nature of this compound. The terminal nitrogen which donates the five-coordinate indium weakens the In-S bond, and consequently lowers the frequency of vibration.

The mass spectra of the dithiocarbamic acid gives a base peak for the $^+\text{CH}_2\text{NMe}_2$ fragment which is also observed for the compounds 2 to 8. The molecular ion

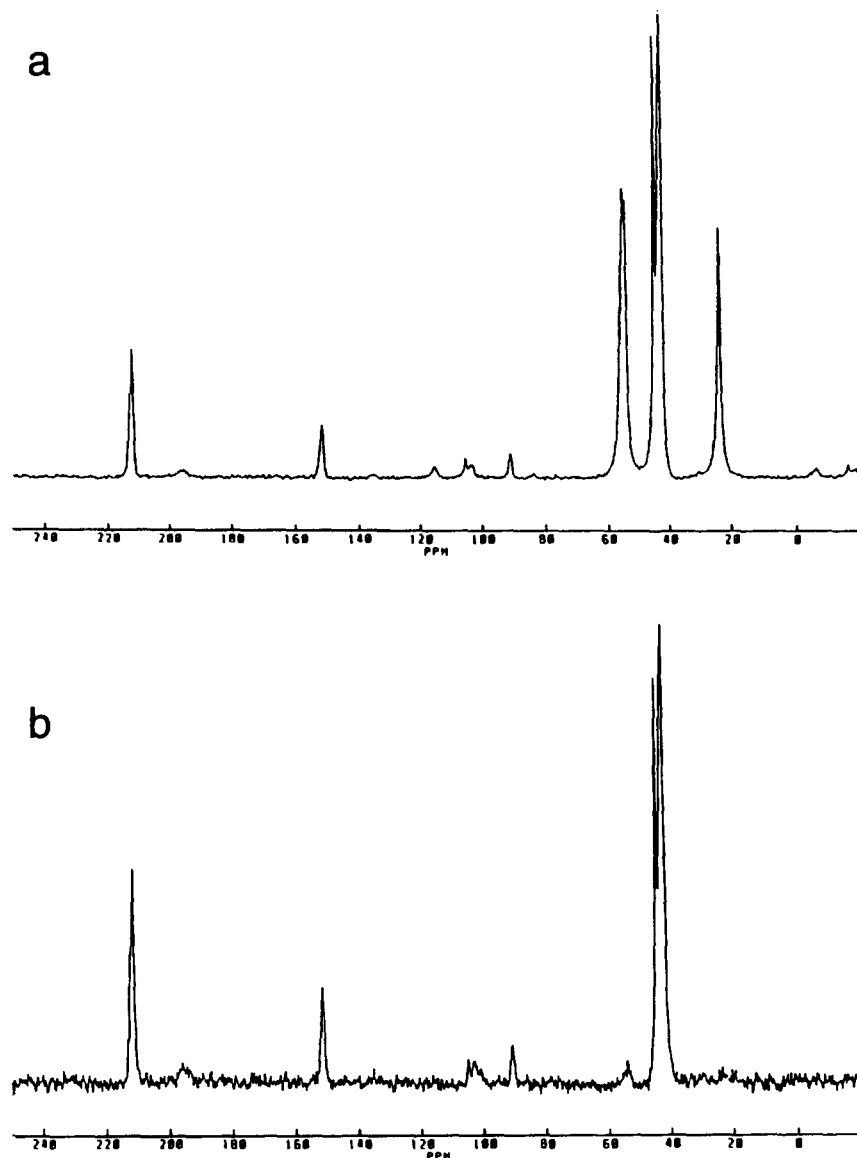


Fig. 2. (a) ^{13}C NMR spectrum (solid state) of *N,N,N'*-trimethylpropylene-diaminedithiocarbamic acid (1). (b) Nuclear quadrupole splitting in ^{13}C NMR spectrum (solid state) of *N,N,N'*-trimethylpropylenediaminedithiocarbamic acid (1).

peak for the majority of compounds **2** to **8** appears at a molecular mass less than the mass of one alkyl group from the metal to give an $R^+MS_2CN(Me)(CH_2)_nNMe_2$ ($n = 2, 3$) ion. Compound **4** gives several peaks of high molecular mass relating to fragments of a polymer. Only compound **2** shows the molecular ion peak at the molecular mass, 292 (0.4%) ($Me_2GaS_2CN(Me)CH_3-NMe_2$) which was also observed for dimethylgalliumdiethylthiocarbamate [10].

The analysis of the dithiocarbamic acid by solution NMR proved difficult as the compound was insoluble in most common deuterated solvents. Deuterated water dissolved the sample but unfortunately initiated decomposition at the same time. Solid state ^{13}C NMR showed seven clear signals, one for each carbon (Fig. 2(a)). The signal at the highest field corresponds to the middle methylene carbon and the two overlapping signals at δ 42.35 and δ 42.85 are assigned to $N(CH_3)_2$, showing that these methyls groups are non-equivalent in the solid state as observed previously [18]. The other two methylene carbons show very close chemical shifts as expected, and the carbamate carbon appears at δ 211.94. Fig. 2(b) shows the nuclear quadrupole splitting which suppresses the signals from CH and CH_2 groups.

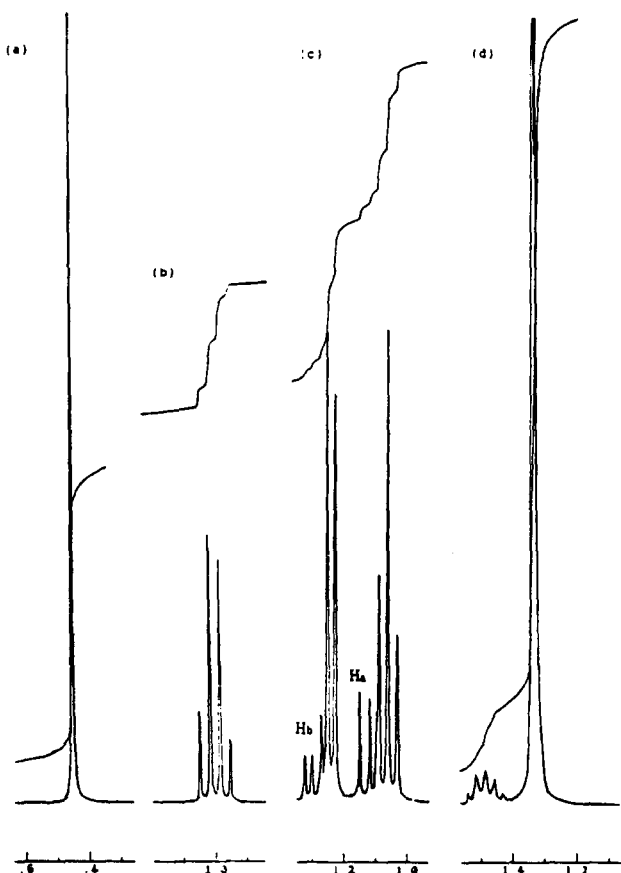


Fig. 3. α -Protons of gallium compounds: (a) **2**, (b) **3**, (c) **5**, (d) **7** showing the difference in chemical shifts.

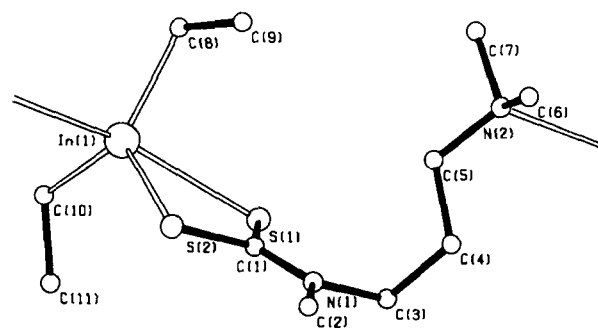


Fig. 4. Molecular structure of $Et_2InS_2CN(Me)(CH_2)_3NMe_2$.

The NMR spectra of the thiocarbamates **2** to **8** show interesting changes in the chemical shift of $M-CH_2$ protons. The chemical shifts for these protons are listed in Table 1, and 1H NMR spectra showing the changes in chemical shifts of these protons in various compounds are shown in Fig. 3. These protons are non-equivalent in chiral compounds **7** and **8** and hence show two multiplets (Fig. 3) but the chemical shift is taken as the mid-point between the two multiplets assigned as HA and HB.

The gallium compounds shift the $M-CH_2$ to a higher field with respect to the analogous indium derivatives. Compounds **2**, **3**, **5** and **7** listed in Table 1 are all gallium derivatives with the alkyl substituent varying from methyl to ethyl to (*S*)-2-methylbutyl and neopentyl. This variation of substituent shows a change in the chemical shift of $Ga-CH_2$ protons to a lower field: (a) 0.45 ppm in the $Me-Ga$, (b) 1.0 ppm for the $Et-Ga$, (c) 1.18 ppm for *sec*-butyl- Ga and (d) 1.33 ppm for $Np-Ga$ (Fig. 2).

Chemical shifts of the $M-C$ in the ^{13}C NMR spectra follow the same pattern as shifts observed in the 1H NMR spectra. Gallium compounds shift the $M-C$ to a higher field than indium. The $Ga-C$ resonance in compound **5** is observed at 38.82 ppm, whereas for analogous $In-C$ in compound **6** it is at 41.90 ppm. The CS_2 resonances in the indium derivatives are found at a

Table 3
Selected bond lengths (\AA) and angles ($^\circ$) for **4**

$In-C(8)$	2.16(3)	$In-C(10)$	2.16(4)
$In-S(1)$	2.79(1)	$In-S(2)$	2.59(1)
$S(1)-C(1)$	1.71(3)	$S(2)-C(1)$	1.73(3)
$In-N(2)$	2.66(1)		
$C(8)-In-C(10)$	134.55(1)	$C(8)-In-S(2)$	108.55(1)
$C(10)-In-S(2)$	116.63(1)	$C(8)-In-S(1)$	92.89(1)
$C(10)-In-S(1)$	100.21(1)	$S(1)-In-S(2)$	66.56(4)
$C(1)-S(1)-In$	83.71(1)	$C(1)-S(2)-In$	89.97(1)
$S(1)-C(1)-S(2)$	118.6 (2)	$S(1)-In-N(2)$	153.98(1)
$S(2)-In-N(2)$	87.49(1)	$N(2)-In-C(10)$	92.87(1)
$N(2)-In-C(8)$	93.78(1)		

lower field than gallium derivatives but are close to those reported previously [10].

5. Structure of $\text{Et}_2\text{InS}_2\text{CN}(\text{Me})(\text{CH}_2)_3\text{NMe}_2$ (4)

The structure of 4 is polymeric and a repeating unit is shown in Fig. 4. Each indium is five-coordinate and bound to two sulphurs, two carbons and one nitrogen from an adjacent complex. The polymer is linear, unlike the helical $\text{MeCd}(\text{TMPDAT})$ [14]. The indium adopts a distorted trigonal bipyramidal coordination. S(2), C(8) and C(10) are in the same plane. The terminal nitrogen, N(2), and the second bridging sulphur, S(1), are in axial positions. Details of intensity measurements and refinement are given in Table 1. Selected bond lengths and angles are listed in Table 3.

The In–S bond lengths of 4 are similar to those in $\text{Me}_2\text{InS}_2\text{CNEt}_2$ rather than $\text{Et}_2\text{InS}_2\text{CNEt}_2$ [10]. In the polymer, the similarity with $\text{Me}_2\text{InS}_2\text{CNEt}_2$ lies with the substantial difference in bond lengths between In–S(1) and In–S(2), which are 2.79(13) Å and 2.59(13) Å respectively for 4 and 2.67(10) Å and 2.56(10) Å for $\text{Me}_2\text{InS}_2\text{CNEt}_2$. This similarity of the polymer with $\text{Me}_2\text{InS}_2\text{CNEt}_2$ continues with the In–C bond lengths. In–C bond lengths of 4 are found to be identical to each other, In–C(8) and In–C(10) are both 2.16(4) Å. The S–In–S and C–In–C angles of 66.56(4)° and 134.55(14)° respectively are both similar to related angles for $\text{Me}_2\text{InS}_2\text{CNEt}_2$ and $\text{Et}_2\text{InS}_2\text{CNEt}_2$.

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References

- [1] S.M. Sze, *Semiconductor Devices, Physics and Technology*; Wiley, Chichester, 1985.
- [2] R. Nomura, S. Fuji, K. Kanaya and H. Matsuda, *Polyhedron*, 9 (1990) 361.
- [3] T. Nishino and Y. Hamakawa, *Jpn. J. Appl. Phys.*, 16 (1977) 1291.
- [4] R. Nomura, K. Konishi and H. Matsuda, *Thin Solid Films*, 198 (1991) 339.
- [5] Wha-Tek. Kim and Chang-Dae. Kim, *J. Appl. Phys.*, 60(7) (1986) 2631.
- [6] R.S. Becker, T. Zheng, J. Elton, M. Saeki, *Sol. Energ. Mater.*, 13 (1986) 97.
- [7] P. O'Brien, in D.W. Bruce and D. O'Hare (eds.), J. Wiley, 1992, Chapter 9, p. 491.
- [8] A.N. MacInnes, M.B. Power, A.R. Barron, P.P. Jenkins and A.F. Hepp, *Appl. Phys. Lett.*, 62 (1993) 711.
- [9] M. Tabib-Azer, S. Kang, A.A. MacInnes, M.B. Power, A.R. Barron, P.P. Jenkins and A.F. Hepp, *Appl. Phys. Lett.*, 63 (1993) 625.
- [10] S.W. Haggata, M.A. Malik, M. Motevalli and P. O'Brien, *Chem. Mater.*, 7 (1995) 716.
- [11] H.J. Gysling, A.A. Wernberg and T.N. Blanton, *Chem. Mater.*, 4 (1992) 900.
- [12] A.N. MacInnes, M.B. Power and A.R. Barron, *Chem. Mater.*, 5 (1993) 1344.
- [13] M.G. Kanatzidis and S. Diringra, *Inorg. Chem.*, 28 (1989) 2024.
- [14] R. Nomura, A. Moritake, K. Kanaya and H. Matsuda, *Thin Solid Films*, 167 (1988) L27–L29.
- [15] A.N. MacInnes, W.M. Cleaver, A.R. Barron, M.B. Power and A.F. Hepp, *Adv. Mater. Optic. and Electron.*, 1 (1992) 229.
- [16] R. Nomura, K. Kanaya and H. Matsuda, *Chem. Lett.*, (1988) 1849–1850.
- [17] R. Nomura, S. Inazawa, K. Kanaya and H. Matsuda, *Polyhedron*, 8 (1989) 763.
- [18] M.A. Malik, T. Saeed and P. O'Brien, *Polyhedron*, 12 (1993) 1533.
- [19] M.A. Malik, T. Saeed and P. O'Brien, *Adv. Mater.*, 9 (1993) 653.
- [20] O.T. Beachley, Jr., E.F. Spiegel, J.P. Kopaz and R.D. Rogers, *Organometallics*, 8 (1989) 1915.
- [21] F. Maury and G. Constant, *Polyhedron*, 3 (1984) 581.
- [22] O.T. Beachley, Jr. and J.C. Pazik, *Organometallics*, 7 (1988) 1516.
- [23] S.W. Haggata, M.A. Malik, M. Motevalli and P. O'Brien, submitted to *Organometallics*.
- [24] R.A. Jones, M.B. Hursthouse, K.M. Malik and G. Wilkinson, *J. Am. Chem. Soc.*, 101 (1979) 4128.
- [25] G.M. Sheldrick, *SHELX-76, Program for Crystal Structure Determination*, University of Cambridge, 1979.
- [26] *International Tables for X-ray Crystallography*, Vol. 4, Kynoch, Birmingham, 1974.
- [27] G.M. Sheldrick, *SHELXL-93 Program for Crystal Structure Refinement*, University of Gottingen, 1993.