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Dithiocarbamate complexes of trivalent aluminium and gallium via metal hydrides

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Abstract

Reaction of the thiurams $[R_2NC(=S)S]_2$ (R = Me, Et, Bz) with the trimethylamine complexes of alane (AlH₃) and gallane (GaH₃) results in the high yield production of the tris-dithiocarbamate complexes $[M(S_2CNR_2)_3]$ (M = Al, Ga) formed via the reductive cleavage of the S–S bond. Transmetallation reactions of $[(Et_2O)_k \cdot AlH_3]_n$ with $[M'(S_2CNEt_2)_n]$ (M' = As, Sb, n = 3, M' = Se, n = 2) also result in the synthesis of $[Al(S_2CNEt_2)_3]$ in high yield. A number of these complexes have been structurally characterised: $[Al(S_2CNEt_2)_3]$ (1), isomorphous with its chromium(III) analogue, belonging to the monoclinic P_{2_1}/n , Z = 4, form of the $[M(S_2CNEt_2)_3]$ family; Al–S are 2.377(6)–2.390(6) Å, similar to values previously established for $[Al(S_2CNMe_2)_3] \cdot CH_2Cl_2$, which is isostructural with its Ga analogue, **3**, (triclinic $P\overline{1}$, Z = 2), for which Ga–S are 2.418(2)–2.449(2) Å; solvent…tris-dithiocarbamate interactions in these species appear to be of negligible significance. Al–S are anomalously long cf. Ga–S in counterpart complexes ca. 2.37, 2.44 Å, Al, Ga–OH₂ in their alums being 1.877(3), 1.944(3) Å. These observations are reinforced by studies of $[M(S_2CNBz_2)_3]$, M = Al, Ga, **2**, **5**, monoclinic $P2_1$, Z = 4, isomorphous with previously reported M = Fe, Co, Ir complexes, and of orthorhombic *Fdd2* [Ga(S_2CNEt_2)_3]·2CHCl_3, **4**, in which the molecule lies on a crystallographic 2-axis, the hydrogen atoms of the chloroform molecules being wedged between the sulfur atoms of the pairs of ligands. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The N,N-disubstituted dithiocarbamate species $[{}^{-}S_2CNR_2]$ in its symmetrical chelating mode is one of the classical anionic bidentate ligands for which arrays of model complexes of bis(bidentate)metal(II) and tris(-bidentate)metal(III) form are found, with D_{2h} and D_3 core symmetry respectively having been extensively defined by numerous structural, magnetic, and spectroscopic studies [1]. Its unique bonding characteristics, and the potential for systematic symmetrical or unsymmetrical variation in the organic substituents R, R', further offer scope for accessing kinetic and thermody-

namic parameters for dynamic processes throughout the molecule. Symmetrical species of the above form are also found for some closed-shell main group metal ions. The most extensively studied are the heavier trivalent species of Group 13, only a few of which have been structurally characterised in the solid state, and almost all synthesised via the facile metathetical exchange reaction of the metal halide with the hydrated parent sodium dithiocarbamate. This method depended on the stability and ease of handling of the metal chloride and the subsequent dithiocarbamate derivative. The lattice water molecules in Group 1 dithiocarbamate salts are difficult to remove so that the resulting metal dithiocarbamate species must be stable to both hydrolysis and be able to be formed via sodium hydroxide elimination, if the metal halide first reacts with the entrained water molecules to form the metal hydroxide.

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It is not surprising therefore that those Group 13 complexes authenticated by single crystal X-ray diffraction are weighted towards the heavier metals, In and Tl, viz. $[M(S_2CNR_2)_3], M = In, R = Et [2], Pr [3]; NR_2 =$ pyrrolyl ($=C_5H_5N$) [3], pentamethylene ('pyrrolidyl') $(=C_5H_{10}N)$ [4], M = Tl, R = Me [5], Et [6], while for M = Al, Ga only one example is known for each metal, M = Al, R = Me [7]; M = Ga, R = Et [2]. The gallium derivative is formed from the metathetical exchange reaction of the trichloride and the sodium salt of the ligand in aqueous solution; however, this is not possible for Al due to the relative strength of the Al-O bond, meaning that the hydroxide is unreactive and that once formed $[Al(S_2CNR_2)_3]$ is susceptible to hydrolytic attack of the Al–S bonds. As such, $[Al(S_2CNMe_2)_3]$ has only been prepared via the insertion of carbon disulfide into the Al-N bonds of the aluminium amide, $[Al(NMe_2)_3].$

Herein we wish to report new, high yielding, synthetic routes to the homoleptic (trivalent) aluminium and gallium dithiocarbamates, involving Lewis base complexes of alane [L·AlH₃], and gallane, [L·GaH₃]. The first method involves the reductive cleavage of the S-S bonds in the parent thiuramdisulfides [R2NC- $(=S)S_{2}$, leading to the synthesis of $[Al(S_{2}CNEt_{2})_{3}]$ (1), $[Al(S_2CNBz_2)_3]$ (2), $[Ga(S_2CNMe_2)_3]$ ·CH₂Cl₂ (3), $[Ga(S_2CNEt_2)_3]$ ·2CHCl₃ (4), and $[Ga(S_2CNBz_2)_3]$ (5) $(Bz = PhCH_2)$ which have been structurally characterised. Secondly, $[Al(S_2CNEt_2)_3]$ (1) has also been obtained from transmetallation reactions of $[L \cdot AlH_3]_n$ with $[M'(S_2CNEt_2)_n]$ (n = 3, M' = Sb, As: n = 2, M' =Se).

The present study provides the opportunity to secure a number of historical loose ends in the field:

(i) A single crystal X-ray study of $[Al(S_2CNMe_2)_3]$ · CH₂Cl₂ has been reported [7], giving $\langle Al-S \rangle 2.39_6$ Å; given that in $[M(OH_2)_6]^{3+}$ in various caesium α -alums, M–O are 1.877(3) (Al), 1.873(3) (Co), 1.944(3) Å (Ga) [8], it is remarkable that that Al–S distance more closely resembles $\langle Ga-S \rangle$ in $[Ga(S_2CNEt_2)_3]$ (2.43₆ Å) rather than $\langle Co-S \rangle$ in $[Co(S_2NR_2)_3]$, R = Me [9], Et [10] (2.26(4), 2.26(7) Å), a phenomenon deserving of confirmation in an independent system.

(ii) If a similar distance for Al–S were to be observed in $[Al(S_2CNEt_2)_3]$, its position in the wide-ranging $[M(S_2CNEt_2)_3] C2/c//P2_1/a//A2/a$ structural hierarchy would be of interest, such a value placing it close to the $C2/c//P2_1/a$ transition point.

(iii) In the course of the earlier study of unsolvated $[Ga(S_2CNEt_2)_3]$ [2], it was observed that that compound readily formed large crystals as a chloroform solvate; at that time the material, desolvating rapidly under ambient conditions, was difficult of determination and the then more desirable unsolvated form was successfully crystallised from a different solvent. Nevertheless, the chloroform solvate remained of interest in respect of

any further light that its structure determination might shed on the nature of possible solvent interactions associated with the anomalous, temperature-dependent proton NMR spectrum found for the analogous $[Co(S_2CNEt_2)_3]$ system in deuterochloroform but not other solvents [11]. While the structure determination of $2[Ru(S_2CN(CH_2)_4O)_3]$ ·5CHCl₃ remains a useful pointer as to a possible cause of this anomaly [11,12], the chloroform solvate of $[Ga(S_2CNEt_2)_3]$ may provide a more direct analogy, with its structure now more readily accessible with modern techniques.

2. Experimental

All reactions and compound manipulations were performed under inert atmosphere conditions (Ar gas) using standard Schlenk techniques. All solvents were dried by reflux over Na/K alloy prior to use. $Na(S_2CNR_2) \cdot (H_2O)_n$ (n = 2 or 3), $LiAlH_4$, $SbCl_3$, $AsCl_3$, SeO_2 (for use in synthesis of $Na_2SeS_4O_6$) were purchased from Aldrich. SbCl₃ was purified by sublimation prior to use with all other chemicals used as received. The dimethyl, diethyl and dibenzyl thiuramdisulfides were synthesised according to a general literature procedure [14] and water free $[As(S_2CNEt_2)_3]$, $[Sb(S_2CNEt_2)_3]$ and $[Se(SC_2NEt_2)_2]$ synthesised by variations on literature procedures [15]. All NMR spectra were recorded on a Bruker AM300 MHz spectrometer or Varian Mercury 200 MHz and are referenced to the deuterated solvent used.

2.1. Syntheses of tris(N,N-diethyldithiocarbamato)aluminium(III), $Al(S_2CNEt_2)_3$ (1)

2.1.1. Method (i)

A cooled yellow toluene solution of $[Sb(S_2CNEt_2)_3]$ (3.5 mmol, 1.98 g) was added to an Et₂O (20 ml) solution of $[(Et_2O)_k \cdot AlH_3]_n$ (3.5 mmol) at $-78^{\circ}C$. The reaction mixture was stirred and allowed to warm slowly over 4 h to room temperature. Over this time the solution colour changed from yellow to colourless. Above 30°C a grey solid formed with visible gas evolution and elemental antimony coating the flask. Filtration gave a clear, colourless solution. Et₂O was removed in vacuo and small colourless crystals of 1 obtained at 4°C. (Yield 0.94 g, 71%).

2.1.2. Method (ii)

A cooled yellow toluene solution of $[As(S_2CNEt_2)_3]$, (1.90 mmol, 0.94 g) was added to an Et₂O (20 ml) solution of $[(Et_2O)_k \cdot AlH_3]_n$ (1.9 mmol) at $-78^{\circ}C$. The reaction mixture was stirred and allowed to warm slowly over 4 h to room temperature. Over this time the solution colour changed from yellow to colourless. Above 0°C a brown suspension formed with visible gas evolution and elemental arsenic coating the flask. In vacuo removal of Et_2O followed by filtration gave a clear colourless solution from which a moderate yield of small colourless crystals of 1 were obtained at -25° C. (Yield 0.41 g, 58%).

2.1.3. Method (iii)

[Me₃N·AlH₃]₂ (4.2 mmol, 0.37 g) was dissolved in Et₂O (30 ml) and cooled to -78° C. [Se(SC₂NEt₂)₂] (6.3 mmol, 2.3 g) was added slowly as a solid resulting in an orange coloured suspension. Gas evolution was visible at this point. The reaction mixture was stirred and allowed to warm to room temperature. In doing so the colour of the solution became less orange, then slightly violet and finally light brown. Et₂O was removed in vacuo and thf (15 ml) added and filtered to give a clear colourless solution. Over 4 weeks at -25° C a crop of small colourless crystals of 1 were grown alongside an amorphous white solid. (Yield 0.48 g, 31%). M.p. 256-258°C (orange melt and gas evolution); ¹H NMR (300 MHz, C₇D₈, 25°C): δ 3.29 (3H, q, CH₃), 0.78 (2H, t, CH₂); ¹³C NMR (75.5 MHz, C₇D₈, 25°C): δ 48.5 (CH₃), 12.1 (CH₂). ¹H NMR (300 MHz, CD₂Cl₂, 25°C): δ 4.01 (3H, q, CH₃, J = 0.03 Hz), 1.37 (2H, t, CH_2 , J = 0.02 Hz); ¹³C NMR (75.5 MHz, CD₂Cl₂, 25°C): δ 201.1 (qC), 48.9 (CH₃), 12.3 (CH₂). ¹H NMR (300 MHz, CDCl₃, 25°C): δ 3.78 (3H, q, CH_3 , J = 0.03 Hz), 1.26 (2H, t, CH_2 , J = 0.02 Hz); ¹³C NMR (75.5 MHz, CDCl₃, 25°C): δ 200.5 (qC), 48.4 (CH₃), 12.3 (CH₂). Found: C, 37.9; H, 6.5; N, 8.9. C₁₂H₃₀AlN₃S₆ requires: C, 38.2; H, 6.4; N, 8.9%.

2.2. Synthesis of tris(N,N-dibenzyldithiocarbamato)aluminium(III), $[Al(S_2CNBz_2)_3]$ (2)

A colourless solution of $[Me_3N\cdotAlH_3]_2$ (0.09 g, 1.01 mmol) in toluene (ca. 15 ml) was gradually added to a yellow solution of $[Bz_2NC(=S)S]_2$ (1.04 g, 1.91 mmol) in toluene (ca. 35 ml) at room temperature. Gas evolution was observed. The resulting yellow solution was allowed to stir at room temperature for 15 h whereupon it was filtered and the solvent volume reduced in vacuo (ca. 15 ml). Recrystallisation from toluene at room temperature afforded cream prismatic crystals (Yield 0.47 g, 55%). M.p. 171–173°C (orange melt). ¹H NMR (200 MHz, C_7D_8 , 25°C): δ 7.16–7.03 (5H, m, C_6H_5), 4.81 (2H, s, CH_2); ¹³C NMR (50.3 MHz, C_7D_8 , 25°C): δ 140.4, 138.3, 132.2–130.4 (m, C_6H_5), 58.1 (CH_2). Found: C, 62.5; H, 5.4; N, 5.1. $C_{45}H_{42}AlN_3S_6$ requires: C, 64.0; H, 5.0; N, 5.0%.

2.3. Synthesis of tris(N,N-dimethyldithiocarbamato)gallium(III) dichloromethane monosolvate, $[Ga(S_2CNMe_2)_3 \cdot CH_2Cl_2]$ (3)

A chilled Et_2O (10 ml) solution of $Me_3N \cdot GaH_3$ (1.37 mmol, 0.18 g) was added to a cold (0°C) yellow Et_2O (20

ml) solution of $[Me_2NC(=S)S]_2$ (2.1 mmol, 0.50 g). The reaction mixture was stirred overnight with the yellow colour disappearing to leave a white precipitate. Et₂O was removed in vacuo and CH₂Cl₂ (15 ml) added causing immediate gas evolution and giving a pale yellow colour to the subsequent solution. On filtration and cooling to $-25^{\circ}C$ a crop of colourless crystals of **3** were obtained (Yield 0.4 g, 68%). M.p. $251-253^{\circ}C$ (orange melt); ¹H NMR (300 MHz, CD₂Cl₂, $25^{\circ}C$): δ 4.25 (2H, s, CH₂Cl₂) 2.48 (18H, s, CH₃). Found: C, 24.7; H, 4.1; N, 9.6. C₉H₁₈GaN₃S₆ (desolvated) requires: C, 24.1; H, 4.0; N, 2.8%.

2.4. Synthesis of tris(N,N-diethyldithiocarbamato)gallium(III)·bis(chloroform) solvate, $[Ga(S_2CNEt_2)_3 \cdot 2CHCl_3]$ (4)

A chilled Et₂O (30 ml) solution of Me₃N·GaH₃ (3.24 mmol, 0.43 g) was added to a cold (0°C) yellow Et₂O (20 ml) solution of [Me₂NC(=S)S]₂ (4.86 mmol, 1.45 g). On addition a white precipitate immediately formed which subsequently dissolved on warming to room temperature. After stirring for 2 h Et₂O was removed in vacuo and CHCl₃ (15 ml) added causing immediate gas evolution and giving pale vellow colour to the subsequent solution. On filtration and cooling to -25° C a crop of colourless crystals of 4 were obtained. (Yield 1.51 g, 62%) M.p. 239–240°C; ¹H NMR (300 MHz, CDCl₃, 25°C): δ 3.74 (2H, q, CH_2 , J = 0.025 Hz) 1.26 (3H, t, CH_3 , J = 0.025Hz); ¹³C NMR (75.5 MHz, CDCl₃, 25°C): δ 200.8 (qC), 49.5 (CH₂), 12.2 (CH₃). Found: C, 36.1; H, 5.6; N, 8.1. $C_{15}H_{30}GaN_3S_6$ (desolvated) requires: C, 35.0; H, 5.8; N, 7.8%.

2.5. Synthesis of tris(N,N-dibenzyldithiocarbamato)gallium(III), [Ga(S₂CNBz₂)₃] (5)

A colourless solution of $[Me_3N\cdot GaH_3]$ (0.11 g, 0.83 mmol) in toluene (ca. 10 ml) was gradually added to a yellow solution of $[Bz_2NC(=S)S]_2$ (0.61 g, 1.12 mmol) in toluene (ca. 20 ml) at room temperature. Gas evolution was observed. The resulting yellow solution was allowed to stir at room temperature for 16 h whereupon it was filtered and the solvent volume reduced in vacuo (ca. 15 ml). Recrystallisation at room temperature afforded cream prismatic crystals of **5** (Yield 0.45 g, 69%). M.p. 216–217°C (decomp. to orange melt); ¹H NMR (200 MHz, C₆D₆, 25°C): δ 7.17–7.13, 7.05–7.01 (5H, m, C₆H₅), 4.80 (2H, s, CH₂); ¹³C NMR (50.3 MHz, C₆D₆, 25°C): δ 206.6, 135.2, 129.0, 128.3, 128.0 (C₆H₅), 56.5 (CH₂); Found: C, 61.0; H, 4.7; N, 4.9. C₄₅H₄₂GaN₃S₆ requires: C, 60.9; H, 4.8; N, 4.7%.

2.6. Structure determinations

Unique room-temperature diffractometer data sets (monochromatic Mo K α radiation, $\lambda = 0.71073$ Å,

 $2\theta_{\text{max}} = 50^{\circ}, \ 2\theta/\theta \text{ scan mode; } T \sim 295 \text{ K}$) were measured on capillary-mounted specimens yielding N independent reflections, N_0 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinements after Gaussian absorption correction. Anisotropic thermal parameter forms were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_{H}$ being included at estimated values; difference map residues were modelled as appropriate in terms of CH₂Cl₂ or CHCl₃ solvent. Conventional residuals R, R_w (statistical weights, derivative of $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004 \sigma^4(I_{\text{diff}}))$ are quoted at convergence. Neutral atom complex scattering factors were employed, computation using the XTAL 3.2 program system [29]. Pertinent results are given in the Figures and Tables; individual variations in procedure (etc.) are noted below ('variata'). Cell and coordinate settings follow those of previously determined isomorphs where these exist; present numbering schemes are such that the ligands are numbered, a,b,c, followed by 1 or 2 designating association with the 'upper' or 'lower' triangle of sulfur atoms about the central metal.



2.6.1. Crystal/refinement data — (1)

 $[Al(S_2CNEt_2)_3] \equiv C_{15}H_{30}AlN_3S_6, \quad M_r = 375.6. \text{ Monoclinic, space group } P2_1/n \ (C_{2h}^5, \text{ no. 14, variant}), a = 14.37(1), b = 10.348(9), c = 17.14(1) \text{ Å}, \beta = 111.31(4)^\circ, V = 2375 \text{ Å}^3. D_c \ (Z = 4) = 1.05_1 \text{ g cm}^{-3}; F(000) = 808. \\ \mu_{Mo} = 6.3 \text{ cm}^{-1}; \text{ specimen: } 0.24 \times 0.24 \times 0.32 \text{ mm}; \\ A_{\min,max}^* = 1.07, 1.09. N = 4422, N_o = 1802; R, R_w = 0.071 \ (\times 2).$

2.6.1.1. Variata. Ethyl group c was modelled (with isotropic thermal parameter refinement) as disordered over two sets of sites, occupancies set at 0.5 after trial refinement. This complex is isostructural with its chromium(III) counterpart [16] and was refined in the same cell and coordinate setting. As in the Cr(III) structure, ethyl group C(2,3c) was disordered over a pair of sites, modelled with equal occupancies after trial refinement. Residuals are high because of the weak primitive lattice superimposed upon the basically C2/c array, characteristic of a smaller central metal atom (e.g. Co) [10]. Caveat: the $P2_1/a$ cell has similar dimensions.

2.6.2. Crystal/refinement data — (3) $[Ga(S_2CNMe)_3]$ ·CH₂Cl₂=C₁₀H₂₀Cl₂GaN₃S₆, $M_r = 515.3$. Triclinic, space group $P\overline{1}$ (C_i^1 , no. 2), a = 626 9.174(7), b = 9.604(4), c = 12.751(8) Å, $\alpha = 75.17(4)$, $\beta = 87.64(6)$, $\gamma = 82.70(4)^\circ$, V = 1077 Å³. D_c (Z = 2) = 1.589 g cm⁻³; F(000) = 524. $\mu_{Mo} = 21.0$ cm⁻¹; specimen: $0.42 \times 0.32 \times 0.38$ mm (capillary); $A_{\min,max}^* = 1.64$, 1.94. N = 3769, $N_o = 2993$; R = 0.042, $R_w = 0.049$.

2.6.2.1. Variata. The complex is isostructural with its aluminium analogue and was refined in that setting. The site occupancy of the solvent molecule was set at unity after trial refinement.

2.6.3. Crystal/refinement data — (4)

[Ga(S₂CNEt₂)₃]. 2CHCl₃=C₁₇H₃₂Cl₆GaN₃S₆, $M_r = 753.3$. Orthorhombic, space group *Fdd2* (C_{2v}^{19} , no. 43), a = 35.46(6), b = 18.30(2), c = 10.35(1) Å, V = 6717 Å³. D_c (Z = 8) = 1.490 g cm⁻³; *F*(000) = 3072. $\mu_{Mo} = 16.8$ cm⁻¹; specimen: $0.50 \times 0.62 \times 0.40$ mm (capillary); $A_{min,max}^* = 1.68, 1.93.$ $N = 1554, N_o = 1206; R = 0.051, R_w = 0.056$ (preferred hand).

2.6.3.1. Variata. As modelled in the present space group, the solvent is disordered with two sets of chlorine atoms disposed over two sets of sites rotationally related about H-C, site occupancies set at 0.5 after trial refinement.

2.6.4. Crystal/refinement data — (2), (5)

 $[M(S_2CN(CH_2Ph)_2)_3] = C_{45}H_{42}MN_3S_6, M = AI, Ga.$ Monoclinic, space group $P2_1$ (C_2^2 , no. 4), Z = 4. (2). M = AI. $-M_r = 844.2$. a = 11.900(2), b = 29.953(4), c = 12.480(2) Å, $\beta = 97.69(1)^\circ$ V = 4408 Å³. $D_c = 1.272$ g cm⁻³; F(000) = 1768. $\mu_{Mo} = 3.7$ cm⁻¹; specimen: $0.50 \times 0.45 \times 0.40$ mm; $A_{\min,max}^* = 1.13$, 1.16. N = 7893, $N_o = 4657$; R = 0.056, $R_w = 0.057$ (both hands). (5). M = Ga - $M_r = 887.0$. a = 11.885(6), b = 1000

(5). $M = Ga - M_r = 887.0$. d = 11.885(6), b = 29.87(1), c = 12.511(3) Å, $\beta = 97.58(3)^\circ$ V = 4402 Å³. $D_c = 2.427$ g cm⁻³; F(000) = 1840. $\mu_{Mo} = 9.4$ cm⁻¹; specimen: cuboid, ca. 0.2 mm; $A_{min,max}^* = 1.18$, 1.28. N = 7877, $N_o = 5394$; R = 0.046, $R_w = 0.048$ (preferred chirality).

2.6.4.1. Variata. These two complexes are isomorphous and isomorphous with the previously studied M = Co [10], Fe [17] analogues, and are presented in the same cell and coordinate setting.

3. Results and discussion

Complexes 1-5 were prepared by the general reaction procedures outlined in Schemes 1 and 2. The parent thiuramdisulfides were synthesised by known literature procedures. As noted above the only previously reported synthesis of an aluminium dithiocarbamate compound was of dichloromethane solvated $[Al(S_2CNMe_2)_3]$ prepared via the insertion of CS₂ into $[(Me_2N)_3Al]$ in petroleum ether (40–50°C) followed by recrystallisation from CH₂Cl₂. Our synthetic method exploited the reduction of thiuramdisulfides by Lewis base complexes of alane and gallane, in a similar manner to the formation of $[L \cdot M(ER)_3]$, M = Al, Ga, E =Se, Te from the same metal hydride and R₂E₂, and related compounds [18].

The dimethyl- and diethyl-thiuramdisulfides have considerable solubility in Et₂O and their reaction with $[Me_3N \cdot MH_3]_n$ (M = Al, n = 2, M = Ga, n = 1) could be carried out at low temperature $(-78^{\circ}C)$ in either Et₂O or toluene, or alternatively in situ with the alane etherate complex, $[(Et_2O)_k \cdot AlH_3]_n$ which is formed from the low temperature stoichiometric addition of H₂SO₄ (98%) to an ether solution of LiAlH₄ [19]. After allowing the reaction mixtures to warm to ambient temperature and stirring for a further 4-6 h the solutions could be filtered, volatiles removed and the remaining white powders recrystallised from either dichloromethane or chloroform. Thus [Ga(S₂CNMe₂)₃]·CH₂Cl₂ (3), and [Ga(S₂CNMe₂)₃]·2CHCl₃ (4) were isolated as their respective CH₂Cl₂ or CHCl₃ solvates. It should be noted though that with [NMe₃·AlH₃]₂ elimination of H₂ occurs at room temperature in Et_2O ; with $[Me_3N \cdot GaH_3]$ no gas evolution is evident under the same conditions. Instead, on removal of the Et₂O the white precipitate which is formed rapidly eliminates H₂ on addition of the CH₂Cl₂ or CHCl₃ at room temperature. The white precipitate is most likely a Lewis base complex of the thiuram of gallane formed at the expense of complexation of Me₃N, noting that gallane preferentially binds to third row elements in contrast to alane, and forms almost exclusively four-coordinate species [20]. Complexation of alane by the thiuram may be the primary process in the formation of 1 and 2 with subsequent facile reduction more favoured due to the greater polarisation of the Al-H bonds relative to Ga-H [20].



Scheme 2.

In consequence of the limited solubility of the dibenzyl dithiuram in Et₂O, the reaction of $[Bz_2NC(=S)S]_2$ with $[Me_3N\cdot MH_3]_n$ (M = Al, Ga) was carried out in toluene as the solvent. The reaction mixtures were allowed to stir for approximately 10–16 h at ambient temperature whereupon they were filtered and the toluene reduced in vacuo. Crystals of $[Al(S_2CNBz_2)_3]$ (2) and $[Ga(S_2CNBz_2)_3]$ (5) were obtained at 4°C.

Our current interest in targeting the synthesis of mixed Group 13/15 and Group 13/16 complexes [18] as potential binary compounds for thin film deposition [21] led to an examination of the reactions of $(Et_2O)_n$ ·AlH₃ with $[As(S_2CNEt_2)_3]$, $[Sb(S_2CNEt_2)_3]$ or $[Se(S_2CNEt_2)_2]$. However, in all cases, solvent free $[Al(S_2CNEt_2)_3]$, was the only stable crystalline product obtained, inclusive of reactions at low temperature. Moisture free yellow crystals of arsenic and antimony diethyldithiocarbamates were grown in pre-dried toluene after preparation in thf via the 1:2 addition of $Na(S_2CNR_2) \cdot 3H_2O$ to M'Cl₃ in the presence of Et₃N [15]. $[Se(S_2CNEt_2)_2]$ was synthesised via the reaction of $Na(S_2CNEt_2) \cdot (H_2O)_3$ with $Na_2SeS_4O_6$ [15]. Crystals were obtained from pre-dried toluene and dried in vacuo.

A toluene solution of $[M'(S_2CNEt_2)_3]$ (M' = Sb, As) was reacted with a cold $(-78^{\circ}C)$ solution of preformed $(Et_2O)_n$ ·AlH₃ in Et₂O. Transmetallation occurs below -30° C possibly producing volatile SbH₃ or AsH₃ as indicated by the coating of the Schlenk flask by a film of elemental arsenic or antimony as the hydrides slowly decompose. $[Al(S_2CNEt_2)_3]$ was crystallised from $Et_2O/$ toluene solution at 4C after filtration. The reaction of $[Me_3N \cdot AlH_3]_2$ with $[Se(S_2CNEt_2)_2]$ in Et_2O went through a variety of colour changes - orange, pale orange, violet, light brown — as the reaction mixture warmed from -78° C to room temperature. This was accompanied by visible gas evolution, presumably SeH₂. On removal of Et₂O the resulting precipitate was dissolved in thf. At 4°C this solution produced a moderate yield of crystalline [Al(S₂CNEt₂)₃] and an amount of white amorphous powder which is yet to be fully characterised.

The aluminium dithiocarbamate complexes are both air and moisture sensitive with the colourless crystals slowly becoming opaque on exposure to air. The gallium compounds are, as expected, more stable with no perceptible decomposition on exposure to air. All of the compounds melt at high temperature to pale yellow/orange melts with some evidence of gas evolution.

The ¹H and ¹³C NMR spectra of compounds 1-5 at 298 K are largely unexceptional with spectra obtained in C₆D₆, d₈-toluene, CDCl₃ and CD₂Cl₂ all giving the expected chemical shifts and splitting patterns associated with respective methyl, ethyl and benzyl groups. Low temperature ¹H NMR studies in the range 208–

Table 1 Metal atom environments

i.d./M/R(/S)	$-/Al/Me/CH_2Cl_2$	1/Al/Et	2/Al/Bz	$3/Ga/Me/CH_2Cl_2$	$4/Ga/Et/CHCl_3 \ ^a$	5/Ga/Bz
Distances (Å)						
M-S(1a)	2.404(2)	2.383(5)	2.370(4), 2.366(4)	2.449(2)	2.437(4)	2.389(2), 2.415(2)
M-S(2a)	2.388(2)	2.397(6)	2.420(4), 2.409(4)	2.418(2)		2.484(3), 2.419(2)
M-S(1b)	2.405(2)	2.377(6)	2.389(3), 2.384(4)	2.441(2)	2.421(4)	2.407(2), 2.440(2)
M-S(2b)	2.398(2)	2.387(5)	2.373(4), 2.390(4)	2.437(2)	2.434(4)	2.412(2), 2.411(2)
M-S(1c)	2.393(2)	2.384(6)	2.424(4), 2.410(4)	2.428(2)		2.461(3), 2.480(2)
M-S(2c)	2.386(2)	2.390(6)	2.383(3), 2.374(4)	2.425(2)		2.475(2), 2.391(2)
S(1a)…S(2a)(1a')	2.908(3)	2.894(6)	2.913(4), 2.917(4)	2.922(2)	2.915(6)	2.927(3), 2.919(3)
S(1b)…S(2b)	2.905(2)	2.889(6)	2.903(4), 2.895(4)	2.916(3)	2.910(5)	2.913(3), 2.919(3)
S(1c)S(2c)	2.902(3)	2.903(6)	2.912(3), 2.909(3)	2.912(2)		2.921(3), 2.921(3)
Angles (°)						
S(1a)-M-S(2a)(1a')	74.9(1)	74.5(2)	74.9(1), 75.3(1)	73.77(6)	73.5(1)	73.78(8), 74.31(8)
S(1b)-M-S(2b)	74.6(1)	74.7(2)	75.1(1), 74.7(1)	73.44(6)	73.6(1)	74.39(8), 73.74(7)
S(1c)-M-S(2c)	74.9(1)	74.9(2)	74.6(1), 74.9(1)	73.76(6)		73.25(8), 73.66(3)
S(1a)-M-S(2c)(1b')	100.0(1)	100.1(2)	94.7(1), 93.9(1)	100.61(7)	100.6(1)	94.30(8), 93.62(8)
S(1b)-M-S(2a)	96.7(1)	98.7(2)	100.2(1), 99.8(1)	96.84(6)		101.50(9), 100.66(9)
S(2b)-M-S(1c)(2b')	95.6(1)	98.9(2)	95.3(1), 95.5(1)	95.78(6)	99.6(2)	95.13(8), 95.00(8)
S(1a)–M–S(1b)	93.7(1)	93.8(2)	95.9(1), 96.6(1)	93.99(7)	93.8(1)	97.29(8), 96.37(8)
S(1b)-M-S(1c)	96.3(1)	94.7(2)	97.12(9), 96.3(1)	97.25(6)		98.38(8), 95.63(8)
S(1a)-M-S(1c)(2b')	95.3(1)	94.6(2)	89.8(1), 91.9(1)	95.74(6)	95.0(1)	89.95(8), 91.19(8)
S(2a)-M-S(2b)	96.5(1)	94.4(2)	99.5(1), 99.4(1)	97.36(6)		100.02(8), 101.90(8)
S(2b)-M-S(2c)(1b')	93.0(1)	93.7(2)	98.2(1), 95.7(1)	93.37(7)	94.6(2)	98.74(8), 97.10(8)
S(2c)-M-S(2a)	94.3(1)	94.1(2)	90.6(1), 91.0(1)	94.67(6)		90.70(8), 92.11(9)
S(1a)–M–S(2b)	164.8(1)	162.8(2)	168.6(2), 169.1(2)	163.92(6)	161.4(1)	168.69(9), 168.77(9)
S(1b)-M-S(2c)(1b')	164.2(1)	163.2(2)	166.5(2), 166.5(2)	163.47(5)	162.1(1)	165.73(9), 165.52(9)
S(1c)-M-S(2a)	164.2(1)	163.2(2)	157.8(1), 160.4(1)	162.98(6)		155.65(8), 159.20(8)

^a Here the molecule lies on a crystallographic 2-axis; for the angles, the second atom, given in parentheses (number only, primed), is generated by rotation about that axis. Entries for the $A1/Me/CH_2Cl_2$ complex are taken from the data of Ref. [1]. For the R = Bz complexes, the two values in each entry are for the two independent molecules of the asymmetric unit.



Figure 1. Unit cell contents of $[Ga(S_2CNMe_2)_3]$ -CH₂Cl₂ (3), projected down *a*; 20% thermal ellipsoids are shown for the non-hydrogen atoms, in this and subsequent figures, hydrogen atoms where shown having arbitrary radii of 0.1 Å.

323 K were carried out on $[Al(S_2CNEt_2)_3]$ in d₈-toluene and on $[M(S_2CNEt_2)_3]$ (M = Ga, Al) in CDCl₃ in the range 213–298 K. Taking first the spectra in d₈-toluene, we note that at 273 K the quartet related to the CH₃ is slightly broadened but becomes significantly sharper as the temperature is raised to 323 K. At the lowest observed temperature, 208 K, it separates into two equally intense broad quartets centered on 3.49 and 3.90 ppm with coalescence occurring at 253 K. While this type of phenomenon has been ascribed to be a



Figure 2. (a) Molecular projection of $[Ga(S_2CNEt_2)_3]$ (4) in association with the pair of (disordered) chloroform solvent molecules, down the quasi-3 axis; the crystallographic 2-axis lies vertically in the page. (b) Unit cell contents, 4, projected down c.



Figure 3. Unit cell contents of $[Al(S_2CNBz_2)_3]$ (2), projected down *a*.

result of hindered rotation around the C–N bond [22] it is also characteristic of labile tris(dithiocarbamato) metal(III) species involving rapid unidentate/bidentate interconversion [5,23] and/or rapid δ/λ equilibration via a trigonal prismatic transition state. Only at 208 K are there indications of the triplet (CH₂) beginning to broaden. In CDCl₃ the CH₃ quartet splits for the Al compound at the lowest recording temperature of 213 K, though not into two completely resolved signals. There is no evidence of splitting for the Ga compound at this temperature although the signal does broaden, perhaps indicating a lower coalescence temperature.

4. X-ray crystallography

Pertinent bond lengths and angles for compounds 1-5 are presented in Table 1. Despite the appealing simplicity of the system, relatively few tris(N,N-dimethyldithiocarbamato)metal(III) complexes, [M-(S₂CNMe₂)₃], have been characterised by single crystal X-ray studies. Possible reasons include their relatively low solubility in common crystallisation solvents, and the occurrence of twinning among many complexes

when crystals have been obtained. The only trivalent metal complexes thus studied to date are the complexes of aluminium(III) (as its dichloromethane monosolvate), iron(III) (unsolvated; a spin-crossover system studied at 25, 150, 295 and 400 K) [5,24] cobalt(III) [4], and thallium(III) (monohydrate) [5]. All contain neutral molecular species of quasi-32 symmetry, but, despite this, no examples of isomorphism are reported, not surprisingly at least, among the diverse solvation types; the present gallium(III)/dichloromethane monosolvate, 3, isostructural with its aluminium(III) counterpart, now provides the first such example, one [Ga(S₂CNMe₂)₃]·CHCl₂ aggregate, devoid of crystallographic symmetry, comprising the asymmetric unit of the structure. No close interactions are found between putative solvent hydrogen atom sites and any part of the $[Ga(S_2CN)_3]$ molecular core, a feature also true of the aluminium analogue; unit cell contents are depicted in Fig. 1 as an example of this structural type.

Symmetrical unsolvated complexes, $[M(S_2CNEt_2)_3]$, are more widely characterised, the majority falling within a monoclinic, Z = 4, unit cell, $a \sim 14$, $b \sim 10$, $c \sim 18$ Å, $\beta \sim 110$ or 118° , C2/c (or variant) for the smaller metal atoms (Co–S 2.267, Fe–S 2.306 Å (70 K), Ir-S 2.367 [25]) degraded to $P2_1/a$ for larger species (Fe-S 2.357 (297 K) [17], Ru-S 2.376 [23c,26] Cr-S 2.39₆ Å [16]) and A2/a (or variant) (Ga–S 2.436 [2], Mn-S 2.45 [27], In-S 2.597 [2], Tl-S 2.666 [6]). Other categories of a less systematic nature are found in other systems, most of which have some intrinsic capacity for distortion or intermolecular interaction, viz. As (Rh) [12] and Sb, Bi [28]. The present unsolvated $[Al(S_2CNEt_2)_3]$ (1) has $\langle Al-S \rangle$ 2.386 Å, in keeping with its status as a member of the $P2_1/n$ class, and in agreement with the previous record of the dimethyl analogue (see above). Presumably the 'long' Al-S distance as ascribed above in relation to cobalt(III) and gallium(III) homologues is to be attributed to the status of aluminium as a 'harder' acid vis-a-vis the others, with a greatly diminished propensity for π -bonding and concomitant enhanced reactivity. Molecular and cell projections for the chromium(III) counterpart are given in Ref. [16].

The gallium(III) analogue, 4, is defined here as its chloroform disolvate, one half of the complex molecule (the latter lying with a crystallographic 2-axis passing through the metal and the N-C bond of one ligand) (Fig. 2(a)) and one solvent molecule making up the asymmetric unit for the structure; this is a new structural type for $[M(S_2CNEt_2)_3]$, the cell contents being shown in projection in Fig. 2(b). $\langle Ga-S \rangle$, 2.431 Å, is comparable with the value observed in the unsolvated parent [3] and the dimethyl substituted/dichloromethane solvate analogue reported above. The chloroform molecule is rotationally disordered in the familiar way; as in $2[Ru(S_2CN(CH_2)_4O)_3]$ ·5CHCl₃ [13], we find the putative solvent hydrogen approaching so as to wedge between a pair of sulfur atoms from different ligands (H...S (1a, 1b) 2.88, 3.07 Å (est.)), reinforcing the earlier suggestion [11-13] of interactions of that type as a possible cause of the NMR anomalies found with some members of the series of complexes.

The complexes $[M(S_2CN(CH_2C_6H_5)_2)_3]$, [M = A1 (2), Ga (5)] are isostructural and crystallise as creamcoloured prismatic crystals from toluene in the monoclinic space group $P2_1$. Both complexes have four monomeric molecules in their unit cells with the asymmetric units comprised of two discrete such monomers and, as such, are isomorphous with their M = Co, Fe counterparts. Core geometries are similar to those of the other complexes studied in the present work. Molecular projections for the cobalt analogue are given in Ref. [10]; unit cell contents

for the type are shown in Fig. 3.

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