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Formation and Crystal Structure of the Pyridine (py) Adduct of Trimeric Gallium Sulfide Chloride, $(GaSCl{\cdot}py)_3$

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The reaction of a toluene solution of $Ga[GaCl_4]$ with elemental sulfur at ambient temperature gave GaSCl, to which pyridine (py) could be added to yield a crystalline adduct $(GaSCl{\cdot}py)_3$ featuring a boat-shaped gallium–sulfur ring structure.

Gallium–sulfur compounds are of considerable current interest, since they may be useful as single source precursors for semiconducting materials such as GaS and Ga_2S_3.[1] In this context, the reaction of trialkylgallium compounds with elemental sulfur has recently been studied, which leads to several kinds of organogallium sulfides depending on the stoichiometry and conditions employed in the process.[2]

In extensive investigations[3] of the structure and properties of the complexes of low- and mixed-valent gallium halides with aromatic hydrocarbons we were able to demonstrate that solutions of compounds like $Ga[GaCl_4]$ in such hydrocarbons are particularly convenient for homogeneous reaction with a wide variety of substrates. Thus the reaction with elemental sulfur described herein, which leads to the formation of a novel trimeric gallium sulfide chloride, serves as a good example for the advantages of such a process.

Treatment of a clear, colourless solution of Ga_2Cl_4 in toluene, which is now known[4–6] to contain the dimeric arene complex $[\{[Ga(C_6H_5Me)_2]^+[GaCl_4]^-\}_2]$, with yellow elemental sulfur affords a colourless precipitate of GaSCl, whose composition was confirmed by elemental analysis. This compound has previously been identified as an incongruous melting-point compound in the phase diagram of the $GaCl_3$–Ga_2S_3 system.[7]

The GaSCl product obtained is stable in air, but sensitive to moisture (hydrogen chloride forms in the hydrolysis) and insoluble in common organic solvents such as diethyl ether, hydrocarbons and halogenocarbons. A slurry in toluene reacts exothermally with pyridine (py) to give an adduct, which can be crystallized from acetonitrile containing 5% v/v pyridine [equation (1)]. The same adduct is also generated directly if pyridine is added to a mixture of Ga_2Cl_4 and sulfur in toluene [equation (2)]†

$$Ga[GaCl_4] + S \longrightarrow GaCl_3 + GaSCl \xrightarrow{py} (GaSCl{\cdot}py)_3 \quad (1)$$

$$Ga[GaCl_4] + S + 2py \longrightarrow GaCl_3{\cdot}py + (GaSCl{\cdot}py)_3 \quad (2)$$

The adduct, m.p. 179–180 °C (decomp.) has the composition GaSCl·py according to elemental analysis. The ^1H and ^{13}C NMR spectra of solutions in CD_3CN give only pyridine resonances with the expected co-ordination shifts as compared to free pyridine,‡ and the IR absorptions also show the conventional co-ordination effects. Attempts to determine the molecular mass by cryoscopy or mass spectrometry afforded no conclusive results regarding the degree of association of the compound, and therefore a single-crystal X-ray diffraction study was undertaken.

Crystals of the complex are monoclinic, space group $P2_1/a$, with four trimeric formula units in the unit cell.§ The molecules have no crystallographic symmetry. The structure is based on a

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† The compound $Ga[GaCl_4]$ (1.26 g, 4.48 mmol) and sulfur (1.00 g, 3.90 mmol) were treated with toluene (50 cm^3) at room temperature for 10 h under a dry nitrogen atmosphere. A white precipitate formed, which was filtered off, washed with toluene and dried *in vacuo*. Yield: 0.40 g (65%) (Found: Cl, 25.70; S, 23.40. Calc. for GaSCl Cl, 25.85; S, 23.40%). An amount of this product (0.240 g, 1.75 mmol) was then dispersed in toluene (5 cm^3) and treated with pyridine (1.41 cm^3). An oil formed which soon resolidified. The product was filtered off, washed with toluene and dried *in vacuo*. Yield 0.320 g (85%). The same product was obtained from $Ga[GaCl_4]$ (2.52 g, 8.96 mmol), sulfur (2.00 g, 7.80 mmol) and pyridine (7.90 cm^3, 98.0 mmol) in toluene (120 cm^3). It was recrystallized from dry acetonitrile. Yield 1.31 g (68%).

‡ ^1H NMR (CD_3CN): δ 7.66 [d, *m*-H, *J*(HH) 4.89], 8.13 [t, *p*-H, *J*(HH) 6.84 Hz], 8.90 (br s, *o*-H); IR (KBr): 3040w, 1610s, 1490m, 1450s, 1060w, 1050m, 1030w, 770m, 760m, 700s, 680m and 650m cm^{-1}.

§ Crystal data. $C_{15}H_{15}Cl_3Ga_3N_3S_3$, $M_r = 649.01$, colourless crystal (0.2 × 0.3 × 0.35 mm), monoclinic, space group $P2_1/a$ (no. 14), $a = 12.638(1)$, $b = 13.427(1)$, $c = 13.727(1)$ Å, $\beta = 96.61(1)°$, $U = 2319.9$ Å^3, $Z = 4$, $D_c = 1.863$ g cm^{-3}. Enraf-Nonius CAD4 diffractometer, graphite monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å), μ(Mo-Kα) = 40.76 cm^{-1}, $T = -55$ °C, θ–2θ scan mode. During data collection three standard reflections were periodically measured as a general check of crystal and instrument stability. No significant change was observed. Reduced cell calculations did not indicate any higher symmetry (DELOS, LEPAGE). Intensity data were corrected for absorption effects (ψ-scans). The structure was solved by Patterson methods and refined by full-matrix least-squares calculations (SHELXS 86,[8] SHELX 76[9]). After merging of equivalent data 3946 independent structure factors were considered 'observed' [$F_o \geqslant 4\sigma(F_o)$] and used for refinement. The thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were located in the difference Fourier maps but were included in the refinement with fixed isotropic displacement parameters ($U_{iso} = 0.05$ Å^2). Number of refined parameters 244. The function minimized was $[\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^{\,2}]^{\frac{1}{2}}$, $w = 1/\sigma^2(F_o)$. Final R and R' values 0.0341 and 0.0289, respectively. Residual electron density ±0.71 e Å^{-3}. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

cyclic trimer $(GaSCl)_3$, with the gallium and sulfur atoms forming a boat-shaped six-membered ring, and the chlorine atoms in quasi-equatorial positions at the gallium atoms. The three pyridine molecules occupy the axial positions at gallium, two above and one below the puckered ring system (Fig. 1). The atoms Ga(1), Ga(2), S(2) and S(3) are almost coplanar, with a maximum deviation of 0.102 Å from this plane for Ga(2). Atoms Ga(3) and S(1) lie 0.84 and 0.93 Å below this plane, respectively. Not unexpectedly,[2] the internal ring angles S–Ga–S are larger than the angles Ga–S–Ga.

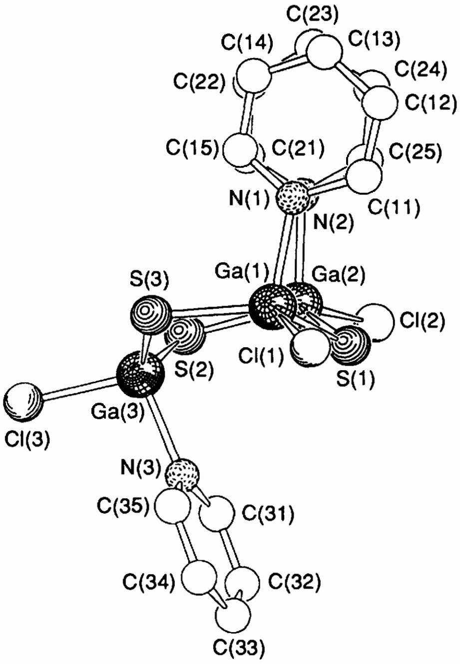

Fig. 1 Molecular structure of $(GaCl{\cdot}py)_3$. Selected bond lengths (Å) and angles (°): Ga(1)–S(1) 2.216(1), Ga(1)–S(3) 2.210(1), Ga(2)–S(1) 2.215(1), Ga(2)–S(2) 2.213(1), Ga(3)–S(2) 2.213(1), Ga(3)–S(3) 2.222(1), Ga(1)–Cl(1) 2.204(1), Ga(2)–Cl(2) 2.205(1), Ga(3)–Cl(3) 2.195(1), Ga(1)–N(1) 2.042(3), Ga(2)–N(2) 2.020(3), Ga(3)–N(3) 2.018(3); S(1)–Ga(1)–S(3) 123.2(1), S(1)–Ga(2)–S(2) 122.3(1), S(2)–Ga(3)–S(3) 123.6(1), Ga(1)–S(1)–Ga(2) 101.9(1), Ga(2)–S(2)–Ga(3) 100.1(1), Ga(1)–S(3)–Ga(3) 100.6(1), S(1)–Ga(1)–Cl(1) 107.1(1), S(2)–Ga(2)–Cl(2) 108.6(1), S(3)–Ga(1)–Cl(1) 111.1(1), S(2)–Ga(3)–Cl(3) 107.2(1), S(1)–Ga(2)–Cl(2) 109.4(1), S(3)–Ga(3)–Cl(3) 108.5(1), S(1)–Ga(1)–N(1) 107.4(1), S(2)–Ga(2)–N(2) 106.7(1), S(3)–Ga(1)–N(1) 104.6(1), S(2)–Ga(3)–N(3) 108.7(1), S(1)–Ga(2)–N(2) 107.7(1), S(3)–Ga(3)–N(3) 105.6(1), N(1)–Ga(1)–Cl(1) 100.4(1), N(2)–Ga(2)–Cl(2) 99.8(1), N(3)–Ga(3)–Cl(3) 100.9(1)

The structure of the pyridine adduct of a *tert*-butylgallium sulfide trimer reported recently[2] is based on a similar $(GaS)_3$ unit, but the six-membered ring for this molecule adopts a twist conformation with the alkyl groups in axial positions.

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