Neutral five-co-ordinate gallium(III) and indium(III) complexes derived from sulfur ligands†

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Five-co-ordinated gallium(III) and indium(III) complexes, $GaCl[PhC(S)CHC(O)Ph]_2$, $GaCl(S_2CNR_2)_2$ (R = Me, Pr^i or NR_2 = pyrrolyl) and $InCl(S_2CNPr^i{}_2)_2$, have been synthesized and characterized. X-Ray crystallographic studies revealed a trigonal-bipyramidal structure for $GaCl[PhC(S)CHC(O)Ph]_2$ and square-pyramidal structures for $GaCl(S_2CNMe_2)_2$ and $InCl(S_2CNPr^i{}_2)_2$. Also, $Ga(S_2CNC_4H_4)_3$ has been synthesized. Its molecular structure shows a GaS_6 core approaching a trigonal-prismatic geometry.

Five-co-ordinate complexes of Group 13 metals are still not very common. Those with bidentate amines, such as 1,10-phenanthroline and bipyridyl, and gallium(III) centres have been suggested to be kinetically labile[1,2] and thermodynamically unstable relative to the four- and six-co-ordinate states. However, a few stable five-co-ordinate gallium and indium complexes have been synthesized and characterized crystallographically where the geometries have been stabilized by either deployment of bulky ligands[3–5] or by using macrocyclic ligands.[6,7] Introduction of alkyl groups has also been found useful in stabilizing these structures by reducing Lewis acidity at the metal centre.[8] The first structurally characterized five-co-ordinate gallium complex was chlorobis(2-methylquinolin-8-olato)gallium(III)[9] where the orientation of ligand atoms is that of a trigonal bipyramid (*TBPY*) around the central Ga atom. As expected, most other five-co-ordinated gallium and indium complexes have similar *TBPY* structures. The other geometric alternative, *i.e.* the square pyramid, is still rare and has been found for a (dibenzotetramethyltetraaza[14]annulene) complex of Ga.[7] Also, there are a few complexes which have a stereochemistry intermediate between these two forms.[6] However, the effect of different ligand factors, particularly the effect of donor atoms, in attaining a particular geometrical form is still not clear. It is, therefore, of interest to report here the synthesis and structural characterization of some five-co-ordinate gallium and indium complexes which have been derived from the asymmetric compound benzoyl(thiobenzoyl)methane and symmetric dithiocarbamates. These are of interest because no neutral five-co-ordinate gallium complex with sulfur donor ligands has been reported so far, and the only indium complex of this type is $InEt_2[S(O)CMe]$[10] which is a polymer. Moreover, our earlier studies[11–13] on six-co-ordinated complexes with these ligands have been found to display interesting structural variations as well as stability. In this paper the synthesis and molecular structures of $GaCl[PhC(S)CHC(O)Ph]_2$ **1**, $GaCl(S_2CNMe_2)_2$ **2a** and $InCl(S_2CNPr^i{}_2)_2$ **3** as determined by X-ray crystallography are reported. Also, the tris-chelated $Ga(S_2CNC_4H_4)_3$ **4a** has been characterized crystallographically.

Experimental

All experimental manipulations using organic solvents were performed under anhydrous conditions under a dinitrogen atmosphere. Solvents were dried by standard procedures. Gallium and indium trichloride (Aldrich) were used as supplied. Sodium salts of benzoyl(thiobenzoyl)methane[14] and dimethyl-[15] and diisopropyl-dithiocarbamates[16] and potassium pyrrole-1-carbodithioate[17] were prepared by reported procedures. Carbon, hydrogen and nitrogen analyses were carried out on a Perkin-Elmer 240C analyser. Infrared spectra were recorded on Perkin-Elmer 783 and JASCO FT IR-5300 instruments as Nujol mulls over CsI plates or as KBr pellets, NMR spectra in $CDCl_3$ using $SiMe_4$ as an internal reference on a JEOL 90Q spectrometer.

Preparations

General method for gallium and indium complexes 1–4 (Table 1). A solution of potassium pyrrole-1-carbodithioate or the sodium salt of all other thio proligands in methanol (*ca.* 20 cm^3) was added to a solution of gallium or indium trichloride in methanol (20–25 cm^3) with stirring at room temperature ($\approx$30 °C). Stirring was continued for 3–4 h. After evaporation of the solvent the residue was extracted with chloroform and filtered. The filtrate was freed from the solvent under reduced pressure at $\approx$30 °C (1 mmHg) in 1–3 h. The residue was crystallized from CH_2Cl_2–hexane (1 : 1), except for **1** which was crystallized from $CHCl_3$–MeOH (1 : 1). Single crystals formed such as **1**$\cdot$$CHCl_3$.

Compound 4c. An aqueous solution of gallium trichloride was added to a solution of $NaS_2CNPr^i{}_2$ in water ($\approx$30 cm^3) with stirring at room temperature (30 °C). Stirring was continued for 0.5 h and the resulting white precipitate was filtered off and dried in vacuum for 2 h at 30 °C (0.01 mmHg) and crystallized from CH_2Cl_2–hexane (1 : 1).

Tris[benzoyl(thiobenzoyl)methanato]gallium(III) (attempted). A solution of gallium trichloride (0.15 g, 0.85 mmol) in methanol ($\approx$10 cm^3) was added to a solution of Na[PhC(S)CHC(O)Ph] (0.67 g, 2.56 mmol) in methanol ($\approx$20 cm^3) with stirring. The reaction mixture was refluxed for 6 h and the resulting yellow-orange precipitate was filtered off and dried for 5 h at 30 °C (2 mmHg). It was identified by elemental analysis as $GaCl[PhC(S)CHC(O)Ph]_2$.

Bis[benzoyl(thiobenzoyl)methanato]ethoxogallium(III) (attempted). A solution of compound **1** (0.30 g, 0.51 mmol) in

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† *Non-SI unit employed:* mmHg ≈ 133 Pa.

Table 1 Preparation and analytical data for the complexes

Reactants (g, mmol)		Product (yield/g, %)	Nature (m.p./°C)	Analysis (%)* C	H	N	Cl
$GaCl_3$ + Na[PhC(S)CHC(O)Ph]	**1**	GaCl[PhC(S)CHC(O)Ph]$_2$	Yellow-orange solid	29.15	2.10	—	5.9
(0.25, 1.41) (0.74, 2.82)		(0.73, 88)	(195–197)	(30.85)	(1.90)		(6.1)
$GaCl_3 + NaS_2CNMe_2$	**2a**	$GaCl(S_2CNMe_2)_2$	Blue-green solid	21.25	3.50	8.10	9.7
(0.18, 1.02) (0.29, 2.03)		(0.27, 77)	(250, decomp.)	(20.85)	(3.45)	(8.10)	(10.3)
$GaCl_3 + NaS_2CNPr^i_2$	**2b**	$GaCl(S_2CNPr^i_2)_2$	Green solid	36.10	6.40	6.70	7.5
(0.17, 0.96) (0.38, 1.91)		(0.38, 87)	(224, decomp.)	(36.30)	(6.10)	(6.10)	(7.7)
$GaCl_3 + KS_2CNC_4H_4$	**2c**	$GaCl(S_2CNC_4H_4)_2$	Purple solid	30.00	2.50	6.55	9.2
(0.09, 0.51) (0.18, 0.99)		(0.18, 89)	(165–166, decomp.)	(30.80)	(2.05)	(7.20)	(9.1)
$InCl_3 + NaS_2CNPr^i_2$	**3**	$InCl(S_2CNPr^i_2)_2$	Green solid	33.30	5.40	5.75	6.9
(0.34, 1.53) (0.62, 3.11)		(0.40, 96)	(260, decomp.)	(33.45)	(5.55)	(5.55)	(7.0)
$GaCl_3 + KS_2CNC_4H_4$	**4a**	$Ga(S_2CNC_4H_4)_3$	Off-white solid	36.85	2.45	8.00	—
(0.35, 1.98) (1.09, 6.00)		(0.95, 97)	(195–197)	(36.30)	(2.40)	(8.40)	
$GaCl_3 + NaS_2CNMe_2$	**4b**	$Ga(S_2CNMe_2)_3$	Green solid	25.85	4.45	9.25	—
(0.20, 1.13) (0.48, 3.35)		(0.48, 81)	(262, decomp.)	(25.10)	(4.20)	(9.75)	
$GaCl_3 + NaS_2CNPr^i_2$	**4c**	$Ga(S_2CNPr^i_2)_3$	White solid	42.85	7.60	7.95	—
(0.12, 0.68) (0.40, 1.92)		(0.35, 87)	(179, decomp.)	(42.10)	(7.05)	(7.00)	

* Calculated values in parentheses.

benzene (≈ 10 cm^3) was added to a suspension of NaOEt (0.04 g, 0.58 mmol) in benzene with stirring. The reaction mixture was then refluxed for 12 h but no change could be seen. The insoluble material was filtered off and the solvent stripped from the filtrate under reduced pressure at 35 °C (0.1 mmHg) in 1 h. The residue (0.28 g) was identified by elemental analysis (C, 29.75; H, 2.05%) and melting point (195 °C) as the starting material GaCl[PhC(S)CHC(O)Ph]$_2$.

Crystallography

The structure determinations were performed by using automated four-circle diffractometers (Siemens R3m for compounds **1**, **3** and **4a**, and P4 for **2a**) operating with graphite monochromators and Mo-Kα radiation (λ = 0.710 73 Å) for data collection at ambient temperature. Unit-cell parameters were refined from the setting angles of 16–25 centred reflections by the least-squares method. Lorentz and polarisation correction was employed as well as empirical absorption correction (ψ-scans). Non-hydrogen atoms were refined anisotropically and hydrogen atoms in calculated positions. Computer calculations were carried out by using the SHELXTL PLUS[18] computer program package. Details of crystallographic data, data collection and structure solution are given in Table 2. Refinements were performed on *F*.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/83.

Results and Discussion

The reaction of gallium trichloride with the sodium salt of benzoyl(thiobenzoyl)methane, NaL, gave invariably compound **1** even in refluxing toluene [equation (1)]. The Ga–Cl bond in **1**

$$GaCl_3 + 2Na[PhC(S)CHC(O)Ph] \longrightarrow \underset{\mathbf{1}}{GaCl[PhC(S)CHC(O)Ph]_2} + 2NaCl \qquad (1)$$

seems to be kinetically inert as it did not even react with sodium ethoxide. The most reasonable explanation for this observation is that the nucleophilic attack is sterically hindered in this case. Indium trichloride is known under similar conditions to give tris[benzoyl(thiobenzoyl)methanato]indium(III);[11] the chloro analogue $InClL_2$ disproportionates readily to give the tris product InL_3. That steric control for the formation of chlorobis-substituted products plays an important role for obtaining $MCl(S_2CNR_2)_2$ is evinced in the preparation of dithiocarbamate complexes of gallium and indium [equations (2) and (3); M = Ga or In]. The gallium compounds **2a**–**2c**

$$MCl_3 + 2M'(S_2CNR_2) \longrightarrow \underset{\mathbf{2, 3}}{MCl(S_2CNR_2)_2} + 2M'Cl \qquad (2)$$

$$GaCl_3 + 3M'(S_2CNR_2) \longrightarrow \underset{\mathbf{4}}{Ga(S_2CNR_2)_3} + 3M'Cl \qquad (3)$$

could be conveniently prepared from the sodium salt of the appropriate proligand. However, only with diisopropyldithiocarbamate could the indium analogue **3** be isolated.

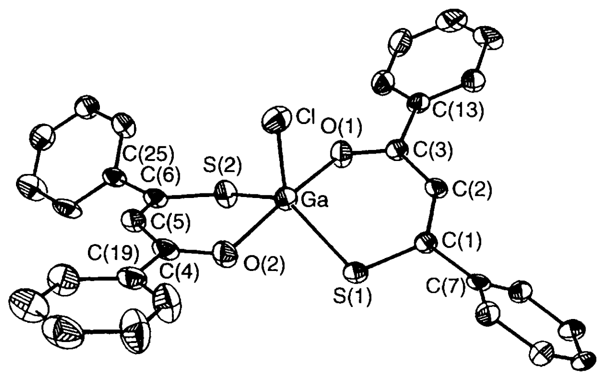

Fig. 1 Molecular structure of GaCl[PhC(S)CHC(O)Ph]$_2$ **1** in the crystal. Thermal ellipsoids are drawn at 25% probability. Hydrogen atoms are omitted for clarity

Molecular structures

The molecular structure of compound **1** is shown in Fig. 1 and selected bond parameters are reported in Table 3. The gallium atom is located in the centre of a trigonal bipyramid with the two oxygen atoms of the ligands occupying the axial positions consistent with the rules for a *TBPY* geometry with axial positioning of the more electronegative ligand atoms. The two sulfur and chlorine atoms complete the equatorial plane with planar disposition of gallium. The two equatorial angles, S(1)–Ga–Cl 117.4(1) and S(2)–Ga–Cl 114.5(1)°, are smaller than the angle S(2)–Ga–S(1) 128.1(1)°. The reason for this 'deviation' could be the larger van der Waals radius of sulfur as compared to chlorine. The angles formed from the equatorial to

Table 2 Crystallographic data, data collection and structure solution of complexes **1**, **2a**, **3** and **4a**

	1	**2a**	**3**	**4a**
Formula	$C_{31}H_{23}Cl_2GaO_2S_2$	$C_6H_{12}ClGaN_2S_4$	$C_{14}H_{28}ClInN_2S_4$	$C_{15}H_{12}GaN_3S_6$
M	703.1	345.6	502.9	496.4
Crystal symmetry	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	10.294(4)	6.500(1)	9.380(2)	14.379(4)
b/Å	11.005(3)	13.753(2)	17.745(4)	9.644(5)
c/Å	14.955(5)	15.197(3)	13.910(3)	14.699(4)
α/°	97.05(2)			
β/°	102.58(3)	95.53(1)	107.81(1)	91.18(2)
γ/°	105.05(3)			
U/Å^3	1567.6(9)	1352.2(6)	2204.5(9)	2038(2)
D_c/Mg m^{-3}	1.490	1.698	1.515	1.618
Z	2	4	4	4
μ/mm^{-1}	1.373	2.817	1.570	1.969
F(000)	712	696	1024	1000
Crystal size/mm	0.4 × 0.3 × 0.2	0.3 × 0.28 × 0.6	0.18 × 0.22 × 0.35	0.30 × 0.22 × 0.55
2θ Range/°	3.0–55.0	2.0–52.0	2.0–50.0	2.0–50.0
hkl Ranges	−13 to 9, −10 to 12, 0–17	−1 to 8, −1 to 16, −18 to 18	−1 to 11, −1 to 21, −16 to 16	0–17, −1 to 11, −17 to 17
Scan range/°	1.4	2	1.0	1.1
Scan speed/min^{-1}	4.00–15.00	2.30–60.00	2.30–60.00	2.70–60.00
Reflections collected	4093	3114	5129	3868
Independent reflections (R_{int})	3940 (0.0206)	2630 (0.0184)	3883 (0.089)	3587 (0.108)
Observed reflections	2619 [$F > 4.0\sigma(F)$]	2065 [$F > 4.0\sigma(F)$]	2853 [$F > 4.0\sigma(F)$]	2829 [$F > 3.0\sigma(F)$]
Structure solution	Patterson method	Direct method	Direct method	Direct method
Variables	361	127	199	226
R	0.049	0.035	0.035	0.045
R′	0.050	0.063	0.044	0.059
Goodness of fit	1.57	0.95	0.99	0.85
Largest residual electron density/e Å^{-3}	0.46	0.33	1.66	0.74

$R = [\Sigma(||F_o| - |F_c||)/\Sigma|F_o|]$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w^{-1} = \sigma^2(F_o) + gF_o^2$.

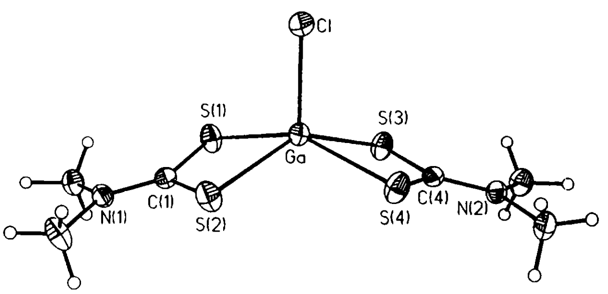

Fig. 2 Molecular structure of $GaCl(S_2CNMe_2)_2$ **2a** in the crystal. Thermal ellipsoids represent 25% probability

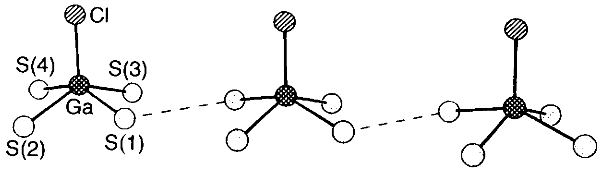

Fig. 3 Arrangement of three $GaClS_4$ cores of molecule **2a** to demonstrate the intermolecular S ··· S contacts

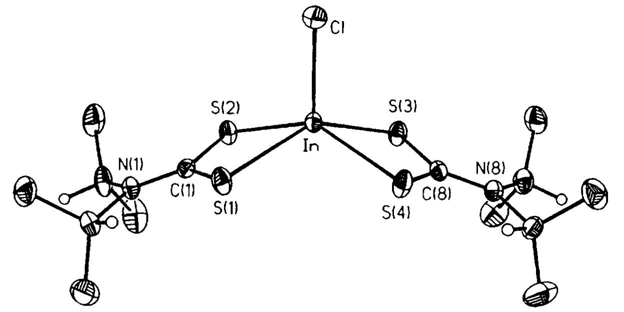

Fig. 4 Molecular structure of $InCl(S_2CNPr^i_2)_2$ **3**. Thermal ellipsoids are drawn at 25% probability. Some of the H atoms are omitted for clarity

axial bonds range from 84.3 to 93.6°. The two oxygen atoms deviate from linearity by 6.9(2)°.

The Ga–Cl distance, 2.193(3) Å, is similar to those for other equatorial bonds in trigonal-bipyramidal environments such as in chlorobis(2-methylquinolin-8-olato)gallium(III) (2.190 Å)[9] and chlorobis[dihydrobis(pyrazolyl)borato]gallium(III) (2.195 Å).[5] However, the average Ga–O bond length of 2.041 Å is much longer than the two *cis* Ga–O bonds (average 1.871 Å) reported for five-co-ordinated chloro[*N*,*N*′-bis(salicylidene)ethane-1,2-diaminato]gallium(III),[6] and even in six-co-ordinate complexes such as tris(acetylacetonato)gallium(III)[19] (average 1.950 Å). This may arise due to the *trans* orientation of the two Ga–O bonds and also from the ligand effect of the thio-β-diketone. In the ligand framework (Table 3) the C–C bond adjacent to the C–S bond being slightly shorter than the C–C bond adjacent to the CO group indicates that the negative charge essentially resides at the sulfur atoms in the conjugated ring.[20,21] On the other hand, the average Ga–S bond length of 2.273 Å is significantly shorter than that of the hitherto described only example of a structurally characterized five-co-ordinate sulfur complex $GaCl(S_2CNMe_2)_2$ **2a** (average Ga–S 2.389 Å).

Compound **2a** crystallizes as a discrete monomer (Figs. 2, 3) and its co-ordination polyhedron around the Ga atom is distorted square pyramidal. The plane through the four sulfur atoms is not perfect with an average deviation of 0.087 Å. The gallium atom is displaced by 0.46 Å from the basal plane of the four sulfur atoms towards the apical chlorine atom and consequently the interplanar angle between the two S_2CN units is compressed to 148.3°. The Ga–Cl distance of 2.209(1) Å is not much different from the corresponding bond length of **1** and other reported five-co-ordinated complexes.[5,9] It seems that the difference between axial and equatorial gallium–chlorine bond lengths noted earlier becomes insignificant in case of the sulfur chelates. It should be noted that the **2a** molecules are oriented in the crystal in the manner as shown in Fig. 3. The intermolecular

S $\cdots$ S atom distances are 3.53 Å, shorter than the longest intramolecular S $\cdots$ S atom distances (3.56 Å) between S atoms of different S_2CNMe_2 ligands.

The Ga–S bond lengths within a chelate ring display considerable asymmetry in compound **2a**, on average by 0.09 Å [Ga–S 2.431(1) and Ga(1)–S(2) 2.340(1) Å]. However, the corresponding C–S bond lengths in one of the chelate rings [C(1)–S(1) and C(1)–S(2)] are identical (1.729 Å). As expected, the NCS_2 units are truly planar and each of the Cl–Ga–C planes is almost perpendicular to the S_4 plane (89.7°).

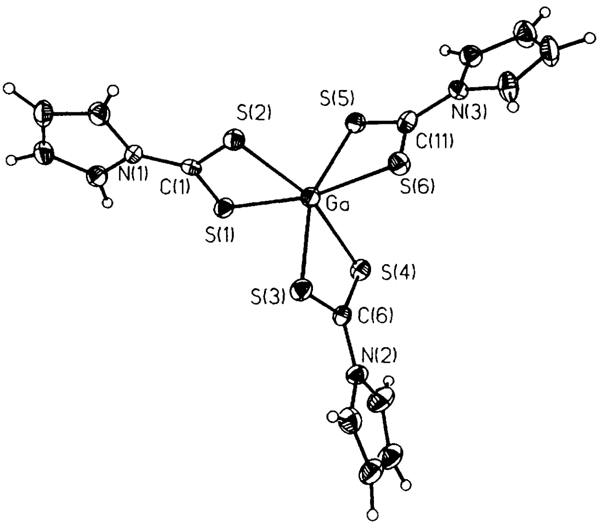

Fig. 5 An ORTEP plot of the molecular structure of $Ga(S_2CNC_4H_4)_3$ **4**. Thermal ellipsoids are drawn at the 25% probability level

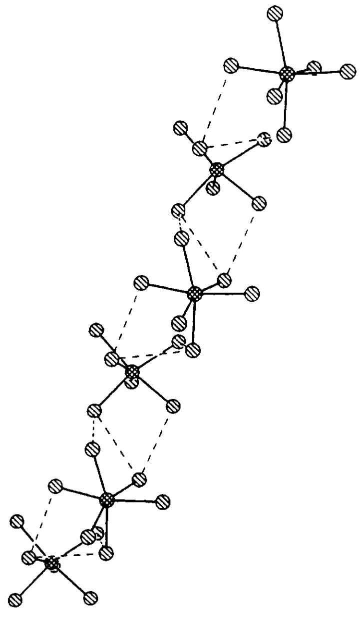

Fig. 6 Alignment of the GaS_6 cores of compound **4** demonstrating intermolecular S $\cdots$ S contacts

The crystals of chlorobis(diisopropyldithiocarbamato)-indium(III) **3** are also composed of discrete molecules with five-co-ordinated square-pyramidal geometry as shown in Fig. 4. The four sulfur atoms constitute an almost perfect plane (mean deviation 0.013 Å) and the indium atom lies 0.79 Å above the mean S_4 plane, and as a result the interplanar angle between the two chelate ring planes is only 140.1°. The In–Cl bond length, 2.380(2) Å, is comparable to the average equatorial distances in the trigonal-bipyramidal adducts $InCl_3{\cdot}2PPh_3$[22] (2.383 Å), $InCl_3{\cdot}2NMe_3$[23a] (2.365 Å) and $InCl_3{\cdot}2SPMe_3$ (2.397 Å),[23b] but shorter than the axial distance in $[NEt_4]_2[InCl_5]$ (2.415 Å)[24] as well as in the anionic bis(dicyanoethylenedithiolato) complex (2.418 Å)[25] or even in $InCl(C_6H_4CH_2NMe_2\text{-}o)_2$.[26] This may arise as a consequence of the negative charge at the five-co-ordinated anions. Unlike **2a**, the asymmetry in the In–S bond lengths in a ligand is relatively small, average difference 0.026 Å. Notably, the In–S bond lengths in this compound are much shorter than in the corresponding tris complex (by about 0.09 Å).[27] However they are significantly longer than in the five-co-ordinated indium tris(1,5-diphenylthiocarbazonate) [In–S 2.477(3) and 2.467(3) Å] with *TBPY* geometry.[28] This may be attributed to inductive effects of the chlorine atom, to the decrease in co-ordination number from six to five as well as to the distorted square-pyramidal geometry. It should be noted

Table 3 Selected bond lengths (Å) of compounds **1**, **2a**, **4a** and **3**

1			
Ga–S(1)	2.274(2)	Ga–S(2)	2.273(2)
Ga–Cl	2.193(3)	Ga–O(1)	2.031(6)
Ga–O(2)	2.051(6)	S(1)–C(1)	1.738(7)
S(2)–C(6)	1.735(8)	O(1)–C(3)	1.282(8)
O(2)–C(4)	1.287(10)	C(1)–C(2)	1.383(11)
C(2)–C(3)	1.379(10)	C(4)–C(5)	1.411(10)
C(5)–C(6)	1.364(11)		
2a			
Ga–Cl	2.209(1)	Ga–S(1)	2.431(1)
Ga–S(2)	2.340(1)	Ga–S(3)	2.348(1)
Ga–S(4)	2.440(1)	S(1)–C(1)	1.729(3)
S(2)–C(1)	1.729(4)	S(3)–C(4)	1.727(4)
S(4)–C(4)	1.714(3)	N(1)–C(1)	1.317(4)
N(2)–C(4)	1.327(4)		
4a			
Ga–S(1)	2.414(2)	Ga–S(2)	2.452(2)
Ga–S(3)	2.422(2)	Ga–S(4)	2.471(2)
Ga–S(5)	2.412(2)	Ga–S(6)	2.438(2)
S(1)–C(1)	1.682(4)	S(2)–C(1)	1.706(5)
C(1)–N(1)	1.365(6)		
3			
In–Cl	2.380(2)	In–S(1)	2.561(1)
In–S(2)	2.533(1)	In–S(3)	2.552(1)
In–S(4)	2.537(1)	S(1)–C(1)	1.733(4)
S(2)–C(1)	1.737(4)	C(1)–N(1)	1.316(5)
S(3)–C(8)	1.734(4)	S(4)–C(8)	1.733(4)
C(8)–N(8)	1.323(5)		

Table 4 Selected IR absorption bands (cm^{-1}) of gallium(III) and indium(III) complexes

Compound	$\nu(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{O})$	$\nu(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{C})$	$\nu(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{N})$	ν(N–C)	ν(C–S)	ν(Ga–O)	ν(M–Cl)	ν(M–S)
1	1586s	1525s			830w	500m	375w	352m
2a			1452s	1151s	980m		388m	401w, 344w
2b			1449s	1145s	941m		380w	407w, 352w
2c			1339s		1007s		374m	405w, 303w
3			1458s	1139s	936w		359m	398w, 310w
4a			1330s		998m			340w
4b			1460s	1155s	947s			409w, 345w
4c			1479s	1148s	948m			405w, 351w

that there are no short heavy-atom contacts between molecules of **3** in the lattice.

The product of the reaction of gallium trichloride with potassium pyrrole-1-carbodithioate, **4a** crystallizes also in the monoclinic space group $P2_1/n$. Its ORTEP[29] plot and numbering scheme is given in Fig. 5. The co-ordination environment around the gallium atom consists of six sulfur atoms of three dithiocarbamate moieties. The GaS_6 polyhedron approximates D_3 symmetry. In the unit cell a number of intermolecular $S \cdots S$ contacts ranging from 3.58 to 3.93 Å are found. These contacts are depicted in Fig. 6. However, the observed distortion in the polyhedron arises more likely from the small bite angle of the bidentate ligand (average 73.6°) (Table 3). Asymmetry is observed in the Ga–S distances with an average deviation of 0.031 Å, significantly much less than in **2a**. Consistent with the diminished contribution of the CN double-bonded canonical form ($N{=}C \longleftrightarrow N{-}C$), the C–N bond lengths ranging from 1.363 to 1.381 Å are significantly longer than that for $Ga(S_2CNEt_2)_3$ (average 1.324 Å).[30]

Vibrational spectra

Infrared spectroscopic data (Table 4) of the complexes investigated are consistent with the X-ray structural results. For **1** the presence of an intense IR absorption at 1586 cm^{-1} assignable to ν(C⋯O) strongly suggests a bidentate ligand anion.[31] Similarly, for compounds **2a**, **2b**, **3** and **4a**, **4b**, a strong single ν(C–S) band between 936 and 980 cm^{-1} is characteristic for bidentate bonding of the dithiocarbamate.[32] All the chloro complexes **1**–**2c** show an absorption in the far-IR region at 374–388 cm^{-1} due to ν(Ga–Cl) which is in between the stretching modes for a tetrahedral species ($\approx$410 cm^{-1}) and for an octahedral species ($\approx$300 cm^{-1}) and is, therefore, indicative of five-co-ordination around the metal centre.[33] In the IR spectra of complexes **2c** and **4a** the ν(C–N) band was found at comparably lower frequencies (1339 and 1330 cm^{-1}) and the ν(C–S) band at higher frequencies (1007 and 998 cm^{-1}) as compared to their dialkyl analogues **2a**, **2b** owing to the lesser contribution of the dianionic canonical form in **2c** and **4a**.

NMR spectra

A temperature-dependent NMR investigation on some five-co-ordinated compounds established a trigonal bipyramidal $\rightleftharpoons$ square pyramidal isomerization in solution.[34] However, ^1H NMR spectra of **2a** show only a single absorption at δ 3.38 without any line broadening in the temperature range +45 to −45 °C. Strikingly, the ^1H NMR spectrum of **3** at −45 °C shows absorptions for the methyl protons as two doublets centred at δ 1.30 and 1.53 of nearly equal intensity. The lines broadened with increase in temperature and finally coalesced at +45 °C. This coalescence can be interpreted in terms of hindered rotation about the isopropyl–nitrogen (C–N) single bond: $S_2C{\cdots}N$ rotation does not exchange the isopropyl groups.[16] It is evident from the present findings that the sulfur-donor atoms in four-membered strained rings such as dithiocarbamate can stabilize the square-pyramidal geometry in Group 13 metal ions. That the ligand factor is largely predominant is also evident by comparison with isostructural iron(III) compounds.[35,36] The extent to which the metal atom is above the S_4 plane towards the apical substituents is a consequence of its size. Steric constraints imposed by the ligand side-group have an effect, and it is conceivable that the five-co-ordinate structures are more labile in case of indium than of gallium.

Discussion

The two gallium complexes **1** and **2a** constitute the first examples of five-co-ordinate Ga^{III} bonded to sulfur ligands. While **1** belongs to the polyhedron *TBPY* found for the majority of five-co-ordinated compounds, **2a** is a rare example of a gallium complex with square-pyramidal geometry. The other two reported distorted square-pyramidal structures, one[6] with a $ClGaN_2O_2$ core and one[7] with a $ClGaN_4$ core, essentially involve planar orientations of the donor atoms. Here, the presence of four-membered strained rings with some degree of unsaturation may be an overriding factor in stabilizing the square-pyramidal structures.[34] The indium complex **3** is the first neutral five-co-ordinate example with a sulfur bidentate ligand. Further insight into the factors governing the structure for five-co-ordination of Group 13 elements should be forthcoming as additional structural reports become available. It may, however, be emphasized that the ligand effect seems to be predominant since chlorobis(diethyldithiocarbamato)iron(III)[35] and its nitroso analogue, $[Fe(NO)(S_2CNEt_2)_2]$[36] are isostructural with **2a** and **3**. In all these complexes the metal atom sits in a position above the basal plane (toward the axial ligand), and this is also true for the Ga or In in the dicyanodithiolato complexes $MCl[S_2C_2(CN)_2]$.[25]

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