Synthesis, Crystal and Molecular Structure of a Stable Monomeric Five-co-ordinate Gallium–Amine Complex, Chloro(dimethyl)-1,10-phenanthrolinegallium(III)

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X-Ray single-crystal analysis, ^{1}H n.m.r., and molecular-weight measurements establish that the title compound has a trigonal bipyramidal structure in the solid state and in chloroform, but ionizes in water. Crystals are monoclinic, space group $P2_1/c$, with cell dimensions a = 10.75(1), b = 11.91(1), c = 15.59(1) Å, β = 134.8(1)°, Z = 4. The crystal structure was solved by the heavy-atom method and atomic parameters refined by full-matrix least-squares calculations to R 0.052 for 1 228 statistically significant reflections from diffractometer measurements. Two methyl groups [Ga–C 1.956(10) and 1.952(10) Å] and a 1,10-phenanthroline (phen) nitrogen atom [Ga–N 2.119(6) Å] define the basal plane of the trigonal bipyramid; axial sites are occupied by the second nitrogen of the bidentate phen ligand [Ga–N 2.433(6) Å] and the chlorine atom [Ga–Cl 2.440(3) Å]. Comparison of these dimensions with those in other gallium complexes indicates that only the Ga–N distances are significantly lengthened due to intramolecular ligand–ligand steric interactions.

In addition, ^{1}H n.m.r. spectral studies establish the *cis*-configuration of the octahedral complexes *cis*-$[GaCl_2(phen)_2]X$ (X = Cl, $GaCl_4$, or $MeGaCl_3$).

UNIDENTATE amines such as pyridine and trimethylamine react with gallium(III) hydride and gallium(III) halides to form stable four-co-ordinate 1 : 1 complexes.[1-5] Five-co-ordinate 2 : 1 complexes $[GaL_2X_3]$ have been detected, but these revert to the 1 : 1 complexes unless maintained at a low temperature in the presence of excess of amine. While bidentate amines, such as ethylenediamine (en),[6] 1,10-phenanthroline (phen),[7] and bipyridyl (bipy),[8,9] should favour formation of five-co-ordinate gallium(III) complexes, the observed products are six-co-ordinate complexes, formed by partial or complete displacement of the halide from the co-ordination sphere, *e.g.* $[GaCl_2(phen)_2]Cl$, $[Ga(phen)_3]Br_3$. Organogallium(III) halides are less well studied, although there is evidence[10] that the diammine and ethylenediamine complexes of dimethylgallium chloride are four-co-ordinate, *i.e.* $[GaMe_2(NH_3)_2]Cl$ and $[GaMe_2(en)]Cl$. All these observations would suggest that five-co-ordinate gallium(III) is kinetically labile and thermodynamically unstable relative to the four- and six-co-ordinate states. It is therefore of interest to report here the preparation and structural characterization of chloro(dimethyl)-1,10-phenanthrolinegallium(III), a rare example of a stable five-co-ordinate monomeric gallium(III) complex.

When dimethylgallium hydroxide was treated with an excess of hydrogen chloride or thionyl chloride, followed by 1,10-phenanthroline, a 75% yield of the partially demethylated complex, *cis*-$[GaCl_2(phen)_2]^+$-$[MeGaCl_3]^-$, was obtained. However, neutralization of dimethylgallium hydroxide with one equivalent of hydrochloric acid, followed by addition of 1,10-phenanthroline, gave a 65% yield of the desired 1 : 1 complex, $[GaMe_2(Cl)(phen)]$.

TABLE 1

^{1}H N.m.r. chemical shifts (p.p.m.) of gallium(III)–1,10-phenanthroline complexes [a]

Compound	H_2, H_9	H_3, H_8	H_4, H_7	H_5, H_6	Ga–CH_3
1,10-Phenanthroline [b]	9.03	7.57	8.23	7.74	
$[GaMe_2(Cl)(phen)]$;[b] $CDCl_3$	9.58	7.91	8.58	8.04	0.12
CD_3CN	9.28	7.88	8.60	8.03	−0.01
D_2O	9.07	7.88	8.44	7.62	−0.20
cis-$[GaCl_2(phen)_2]X$ [c,d] (X = Cl, $GaCl_4$, or $MeGaCl_3$)	10.08, 7.62	8.45, 7.60	9.16, 8.68	8.23, 8.36	0.04
cis-$[GaBr_2(phen)_2][GaBr_4]$ [c]	10.25, 7.63	8.47, 7.59	9.15, 8.67	8.25, 8.38	

[a] Determined in CD_3CN unless otherwise specified; correct signal intensities were observed. [b] J_{23}, J_{89} 4; J_{24}, J_{79} 2; J_{34}, J_{78} 8 Hz. [c] J_{23}, J_{89} = 5; J_{24}, J_{79} 1.5; J_{34}, J_{78} 8; $J_{5,6}$ 9 Hz. [d] Determined in CD_3CN/D_2O (3 : 1).

The ^{1}H n.m.r. spectra of the 1 : 1 complex in dichloromethane, acetonitrile, and water, showed magnetically equivalent methyl groups and a low-field aromatic pattern indicative of 1,10-phenanthroline in a symmetrical environment (Table 1). The spectra are equally compatible with a four-co-ordinate ionic structure, $[GaMe_2(phen)]^+$, a pseudo-rotating five-co-ordinate structure, and a symmetrical six-co-ordinate structure, *cis*-$[GaMe_2(Cl)(phen)(solvent)]$, although the latter is sterically unreasonable. Addition of an excess of 1,10-phenanthroline produced a time-averaged spectrum of the free and complexed amine, as a result of rapid ligand exchange.

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There was no evidence of a 2 : 1 complex, *e.g.* $[GaMe_2(phen)_2]^+$.

The 1 : 1 complex showed no Ga–Cl absorption [5-9] in the 300—400 cm^{-1} region of the far-i.r. spectrum (Nujol, KBr), favouring the ionic structure $[GaMe_2(phen)]^+Cl^-$. The measured molecular weight of 166 (calc. 315.4) in water also indicated an ionized structure in this medium. However, in acetonitrile and chloroform the molecular weights were 320 and 330, respectively, favouring a five- or six-co-ordinate (solvent associated) structure. In order to resolve these ambiguities an *X*-ray crystal-structure analysis was undertaken, and confirmed that $[GaMe_2(Cl)(phen)]$ is a discrete non-ionic monomeric complex. The atomic arrangement, atom numbering scheme, and packing of the monomeric units in the crystal are illustrated in the Figure. Interatomic distances and valency angles are in Table 2; displacements of atoms from least-squares planes are in Table 3.

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Bond lengths			
Ga–Cl	2.440(3)	C(4a)–C(10b)	1.397(11)
Ga–N(1)	2.119(6)	C(5)–C(6)	1.319(12)
Ga–N(10)	2.433(6)	C(6)–C(6a)	1.433(12)
Ga–C(11)	1.956(9)	C(6a)–C(7)	1.420(12)
Ga–C(12)	1.952(10)	C(6a)–C(10a)	1.421(10)
N(1)–C(2)	1.330(10)	C(7)–C(8)	1.316(14)
N(1)–C(10b)	1.367(8)	C(8)–C(9)	1.390(12)
C(2)–C(3)	1.382(12)	C(9)–N(10)	1.344(11)
C(3)–C(4)	1.372(12)	N(10)–C(10a)	1.346(10)
C(4)–C(4a)	1.411(12)	C(10a)–C(10b)	1.416(10)
C(4a)–C(5)	1.451(11)		
(*b*) Valency angles			
Cl–Ga–N(1)	91.2(2)	C(5)–C(4a)–C(10b)	118.6(7)
Cl–Ga–N(10)	161.0(2)	C(4a)–C(5)–C(6)	121.9(8)
Cl–Ga–C(11)	95.5(3)	C(5)–C(6)–C(6a)	121.1(8)
Cl–Ga–C(12)	99.4(3)	C(6)–C(6a)–C(7)	124.8(7)
N(1)–Ga–N(10)	71.9(2)	C(6)–C(6a)–C(10a)	118.2(7)
N(1)–Ga–C(11)	114.3(3)	C(7)–C(6a)–C(10a)	116.9(7)
N(1)–Ga–C(12)	108.4(3)	C(6a)–C(7)–C(8)	119.4(7)
N(10)–Ga–C(11)	84.3(3)	C(7)–C(8)–C(9)	121.4(9)
N(10)–Ga–C(12)	94.1(3)	C(8)–C(9)–N(10)	121.7(8)
C(11)–Ga–C(12)	134.2(4)	Ga–N(10)–C(9)	129.8(5)
Ga–N(1)–C(2)	122.6(5)	Ga–N(10)–C(10a)	109.8(5)
Ga–N(1)–C(10b)	119.6(5)	C(9)–N(10)–C(10a)	118.3(6)
C(2)–N(1)–C(10b)	117.6(6)	C(6a)–C(10a)–N(10)	122.1(6)
N(1)–C(2)–C(3)	123.2(7)	C(6a)–C(10a)–C(10b)	120.5(7)
C(2)–C(3)–C(4)	120.3(8)	N(10)–C(10a)–C(10b)	117.3(6)
C(3)–C(4)–C(4a)	117.8(8)	N(1)–C(10b)–C(4a)	122.2(6)
C(4)–C(4a)–C(5)	122.7(8)	N(1)–C(10b)–C(10a)	118.3(6)
C(4)–C(4a)–C(10b)	118.7(7)	C(4a)–C(10b)–C(10a)	119.5(6)
(*c*) Intermolecular separations < 3.6 Å			
C(3) · · · $C(7^I)$	3.48	C(2) · · · Cl^{II}	3.55
C(4) · · · $C(7^I)$	3.53	C(4a) · · · $C(10a^I)$	3.59
C(4) · · · $C(8^I)$	3.53		

Roman numeral superscripts refer to the following transformations of the co-ordinates of Table 4: I $1 - x, -y, 1 - z$; II $-x, -y, -z$.

TABLE 3

Equations of least-squares planes in the form: * $AX + BY + CZ + D = 0$; displacements (Å) of atoms from the plane are given in square brackets

Plane (I): phen

$$-0.7304X + 0.6580Y - 0.1834Z - 0.7439 = 0$$

[N(1) 0.109, C(2) 0.013, C(3) −0.090, C(4) −0.057, C(4a) 0.003, C(5) −0.004, C(6) 0.023, C(6a) 0.030, C(7) 0.015, C(8) −0.056, C(9) −0.055, N(10) −0.028, C(10a) 0.035, C(10b) 0.059, C(11) 2.244, C(12) −1.176, Ga 0.508, Cl 1.282]

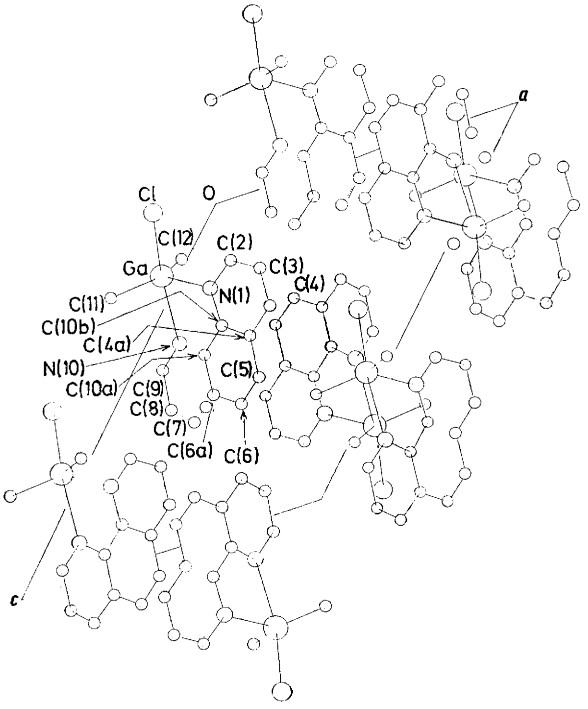
Plane (II): N(1), C(11), C(12)

$$0.1517X - 0.3554Y - 0.9223Z + 2.357 = 0$$

[N(1) 0.0, C(11) 0.0, C(12) 0.0, C(2) 1.014, N(10) −2.160, Ga 0.199, Cl 2.630]

Dihedral angle between planes (I) and (II): 73.0°

* Cartesian co-ordinates (*X*, *Y*, *Z*) are related to the fractional co-ordinates (*x*, *y*, *z*) of Table 4 by the transformation: $[X, Y, Z] = [xa + zc\cos\beta, yb, zc\sin\beta]$



Crystal structure of chloro(dimethyl)-1,10-phenanthroline-gallium, viewed in projection along the *b* axis

The gallium co-ordination geometry is distorted trigonal bipyramidal with two methyl groups and the phen nitrogen N(1) defining the basal plane and the axial sites occupied by the chlorine atom and the other nitrogen atom, N(10), of the bidentate phen ligand. Departures of the valency angles at gallium from ideal trigonal bipyramid values may be ascribed to minimization of intramolecular non-bonded interactions between the ligands and to the rigid nature of the bidentate phen ligand. The gallium atom lies 0.199 Å out of the basal plane in the direction of the axial chlorine, thereby decreasing interactions between the chlorine and the equatorial ligands and consequently increasing the Cl–Ga–C(Me) angles relative to the N(10)–Ga–C(Me) angles. Particularly severe overcrowding between the chlorine atom and the hydrogen atom H(2) is relieved through a combination of twisting of the phen ligand to give a Cl–Ga–N(1)–C(2) torsion angle of ±17° and rotation of the ligand away from the chlorine and approximately in the Cl–Ga–N(10) plane. The latter is manifested in the lengthened Ga–N bonds (see below) and the near-equality of the Ga–N(1)–C(2) and Ga–N(1)–C(10b) angles [122.6(5) and 119.6(5)°] in contrast to the significantly different values at N(10) [129.8(5) and 109.8(5)°] which conform to the normal pattern of phen ligands.[11] Significant departures [150.1(1)—175.9(1)°] of axial trigonal bipyramidal substituents from an ideal linear arrangement have been noted for all [12–16] previously characterized five-co-ordinate gallium complexes, in each of which constraints are imposed on the ligands through ring formation. A similar result is obtained in the present study where the Cl–Ga–N(10) angle [169.1(2)°] is a consequence of the rigid nature of the bidentate ligand.

Previous structural investigations on four-, five-, and six-co-ordinate gallium complexes [17–26] have revealed a wide range of Ga–Cl, Ga–O, and Ga–N distances, although Ga–C(Me) distances remain essentially constant. Such a variation indicates that in any particular complex the distances are strongly dependent upon co-ordination number, steric effects, and constraints imposed by ligand geometry. A trigonal bipyramidal arrangement at five-co-ordinate gallium would be expected to have two non-equivalent sets of distances comprising three strong equatorial and two weaker axial bonds.[27] Accordingly, these would be associated with two different gallium single-bond covalent radii for which the best estimates * from available structural data appear to be r_{eq} 1.21 and r_{ax} 1.41 Å.

In accord with the constancy of Ga–C(Me) distances [1.942(7) - 1.972(10) Å] reported previously [15,24,25] for both four- and five-co-ordinate gallium, the equatorial Ga–C bond lengths [1.956(9) and 1.952(10)Å] of the title compound lie within this range and are close to the sum of the single-bond covalent radii (1.98 Å).

The axial Ga–Cl length [2.440(3) Å] in the present complex is longer than the equatorial distance [2.190(2) Å] at five-co-ordinate gallium in [Ga(2-Mequin)$_2$Cl] by approximately the predicted $r_{ax} - r_{eq}$ difference (0.20 Å) and lies just outside the range [2.235(3)—2.403(3) Å] reported for a number of octahedral complexes.[19,20]

The two Ga–N distances [2.119(6) and 2.433(6) Å] differ significantly in accord with the fact that the bidentate phen ligand spans equatorial and axial trigonal bipyramidal sites. In contrast to the normal Ga–C(Me) and Ga–Cl distances found in the complex, both Ga–N distances are longer than the sums of the respective single-bond covalent radii (1.91 and 2.11 Å) but their ratio (1.15) remains close to the normal radius ratio (1.16), which indicates that both bonds suffer a similar degree of extension in order to reduce steric overcrowding. The extended equatorial bond length is comparable to the axial Ga–N distance in five-co-ordinate [Ga(2-Mequin)$_2$Cl] [2.106(5) Å] [12,13] and lies in the range of distances [2.034(7)—2.182(5) Å] in octahedral gallium complexes.[18–20] The long axial bond ranks with the longer Ga–N distances found in [$Me_2N{\cdot}CH_2{\cdot}CH_2{\cdot}OGaMe_2$] [2.471(4) Å],[15] and in a cage complex [2.778(3) Å].[16]

The means of chemically equivalent bonds in the phen ligand, assuming C_{2v} symmetry, are in excellent agreement with values for these parameters in other complexes:[11] N(1)–C(2) 1.337(11), N(1)–C(10b) 1.357(10), C(2)—C(3) 1.386(12), C(3)–C(4) 1.344(14), C(4)–C(4a) 1.416(12), C(4a)–C(5) 1.442(12), C(4a)–C(10b) 1.409(11), C(5)–C(6) 1.319(12), C(10a)–C(10b) 1.416(10) Å, where the quoted standard deviations are the larger of the individual values derived from the least-squares calculations. In accord with observations for other phen complexes, the ligand atoms depart by significant amounts from coplanarity (Table 3) with no clearly discernible pattern. The Ga–N–C angles are significantly different (see above) at N(1) and N(10), with those at the former being atypical owing to steric interactions between H(2) and the axial chlorine.

cis-[GaCl$_2$(phen)$_2$][GaMeCl$_3$].—The structure of this compound was assigned on the basis of its elemental composition and comparison of its ^{1}H n.m.r. and i.r. spectra with the spectra of [NBu$^n_4$][GaMeCl$_3$] and *cis*-[GaCl$_2$(phen)$_2$]Cl (Table 1). The *cis*-configuration of the latter cation could not be assigned in an earlier Raman and i.r. study [7] but is unambiguously established by its ^{1}H n.m.r. spectrum which consists of two independent ABX patterns ($H_{4,3,2}$ and $H_{7,8,9}$) and an AB quartet ($H_{5,6}$). This rules out a symmetrical *trans*-configuration

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* An estimate of these radii and the resulting normal bond lengths may be derived from consideration of the dimensions of the five-co-ordinate [Ga(2-Mequin)$_2$Cl] (2-Mequin = 2-methyl-8-hydroxyquinolinato) complex.[12,13] If the bond lengths in this complex are taken to represent the sums of the appropriate single-bond covalent radii then, by use of Pauling's values [28] for Cl, N, and O, the equatorial (r_{eq}) and axial (r_{ax}) radii for gallium(III) may be derived. d(Ga–Cl) = 2.19 Å = r_{eq} + 0.99 Å; d(Ga–O) = 1.87 Å = r_{eq} + 0.66 Å; d(Ga–N) = 2.11 Å = r_{ax} + 0.70 Å. These radii would then lead to predicted normal equatorial Ga–C (Me) and Ga–N distances of 1.98 and 1.91 Å, and an axial Ga–Cl distance of 2.40 Å.

[11] See *e.g.*, G. P. Khare and R. Eisenberg, *Inorg. Chem.*, 1970, **9**, 2211; D. L. McFadden and A. T. McPhail, *J.C.S. Dalton*, 1975, 1993.

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and conforms with the spectra of other known bis(phen) octahedral complexes with *cis*-configurations.[29]

EXPERIMENTAL

Dimethylgallium hydroxide [30] and 1,10-phenanthroline complexes of gallium trichloride and tribromide [7] were prepared by literature procedures. ^{1}H N.m.r. spectra were recorded by use of a Varian HA 100 spectrometer with acetonitrile (2.00 p.p.m.) as internal standard. Chemical shifts and coupling constants of bis(1,10-phenanthroline) complexes were derived by computer-assisted least-squares fitting of the experimental and theoretical spectra, and proton assignments were confirmed by double-resonance experiments. I.r. spectra were obtained by use of a Perkin-Elmer 637 spectrophotometer with caesium iodide grating. Molecular weights were determined by vapour-phase osmometry. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

TABLE 4

Fractional atomic co-ordinates ($\times 10^4$) and anisotropic temperature factor parameters,* with estimated standard deviations in parentheses

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	1 521(5)	733(6)	2 521(4)	2.7(1)	1.7(3)	2.9(1)	−0.3(2)	1.8(1)	−0.3(2)
C(2)	1 737(7)	1 302(8)	1 883(5)	3.2(1)	3.4(6)	3.8(2)	0.0(2)	2.3(1)	−0.3(2)
C(3)	3 048(8)	2 088(8)	2 415(5)	4.9(2)	2.8(6)	5.1(2)	0.1(2)	3.8(1)	1.1(2)
C(4)	4 180(7)	2 341(8)	3 653(6)	3.5(1)	3.2(6)	5.2(2)	−0.5(2)	3.1(1)	−0.3(3)
C(4a)	4 020(7)	1 728(7)	4 363(5)	2.2(1)	1.7(5)	3.8(2)	−0.2(2)	1.7(1)	−0.7(2)
C(5)	5 180(8)	1 895(8)	5 687(5)	2.8(2)	3.0(6)	3.7(2)	−1.1(2)	1.7(1)	−1.3(3)
C(6)	5 036(8)	1 297(8)	6 343(5)	3.2(2)	3.2(6)	3.3(2)	−0.4(2)	1.5(1)	−1.2(2)
C(6a)	3 739(7)	432(7)	5 776(5)	2.7(1)	3.0(6)	2.5(1)	0.4(2)	1.4(1)	−0.4(2)
C(7)	3 534(8)	−276(9)	6 419(5)	4.1(2)	5.5(6)	3.5(1)	1.1(2)	2.8(1)	0.7(3)
C(8)	2 364(8)	−1 087(9)	5 814(5)	5.4(2)	5.1(6)	4.0(1)	−0.7(3)	3.4(1)	0.3(3)
C(9)	1 270(8)	−1 237(8)	4 546(5)	5.0(2)	3.2(6)	4.3(2)	−1.1(2)	3.2(1)	0.1(3)
N(10)	1 395(6)	−587(6)	3 889(4)	3.6(1)	2.9(4)	3.4(1)	−0.7(2)	2.3(1)	−0.3(2)
C(10a)	2 587(6)	246(7)	4 481(4)	1.9(1)	2.2(5)	2.2(1)	0.3(2)	1.1(1)	−0.5(2)
C(10b)	2 700(6)	919(7)	3 771(4)	1.8(1)	1.7(4)	2.5(1)	0.3(2)	1.2(1)	−0.1(2)
C(11)	−2 245(8)	220(9)	1 802(6)	3.6(2)	5.4(6)	4.9(2)	0.3(2)	3.0(1)	0.3(3)
C(12)	−215(8)	−1 779(8)	1 357(6)	4.8(2)	2.2(6)	4.5(2)	0.5(2)	3.0(1)	−0.4(3)
Cl	−2 279(3)	564(3)	−351(2)	3.63(7)	4.76(17)	2.74(6)	0.82(9)	1.55(3)	0.67(8)
Ga	−676(1)	−314(1)	1 656(1)	3.40(2)	3.12(6)	3.76(6)	−0.25(2)	2.25(2)	−0.33(3)

* In the form: $\exp\{-[\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]\}$.

Chloro(dimethyl)-1,10-phenanthrolinegallium.— Dimethylgallium hydroxide (233 mg, 2.00 mmol) was stirred with 0.1N-hydrochloric acid (20 ml) at 0 °C for 10 min. 1,10-Phenanthroline hydrate (396 mg, 2.00 mmol) and ethanol (50 ml) were added and the clear solution was stirred at 0 °C (10 min), and then 25 °C (1 h). Solvent was removed *in vacuo* and the residue crystallized from acetone (411 mg, 65%); m.p. 146 °C [Found: C, 53.25; H, 4.40; Cl, 11.35; N, 8.85. $C_{14}H_{14}ClGaN_2$ requires C, 53.30; H, 4.47; Cl, 11.24; N, 8.88%].

cis-*[Dichlorobis(1,10-phenanthroline)gallium] Methyltrichlorogallate.*—Dry hydrogen chloride was bubbled into a stirred solution of dimethylgallium hydroxide (482 mg, 4.12 mmol) in anhydrous diethyl ether for 1 h. Solvent was removed and the residue in diethyl ether–ethanol (8 : 1, 50 ml) was added to 1,10-phenanthroline hydrate (198 mg, 10 mmol) in the same solvent. After 30 min, the crystalline precipitate was filtered, washed with diethyl ether–ethanol, then diethyl ether, and recrystallized from 30% acetone–ethanol to give white needles (1 110 mg, 85%), m.p. 310 °C, $\nu_{max.}$ (KBr) 570 (Ga–Me), 330sh, 315 (Ga–Cl)cm^{-1} [Found: C, 42.95; H, 2.50; Cl, 24.95; N, 8.05%; *M* (MeCN), 309. $C_{25}H_{19}Cl_5GaN_4$ requires C, 43.48; H, 2.76; Cl, 25.61; N, 8.09%; *M*, 311).

The same product (75%) was obtained when a stirred mixture of dimethylgallium hydroxide (4.12 mmol) and thionyl chloride (8.2 mmol) was warmed from −80 to 25 °C, concentrated *in vacuo*, then treated with 1,10-phenanthroline.

Crystal Data.—$C_{14}H_{14}ClGaN_2$, $M = 315.5$, Monoclinic, $a = 10.75(1)$, $b = 11.91(1)$, $c = 15.19(1)$ Å, $\beta = 134.8(1)°$, $U = 1\,380$ Å^3, D_m (flotation) $= 1.52$ g cm^{-3}, $Z = 4$, $D_c = 1.52$ g cm^{-3}, $F(000) = 696$. Cu-K_α radiation, $\lambda = 1.5418$ Å, μ(Cu-K_α) $= 45.5$ cm^{-1}. Space group $P2_1/c$ (C_{2h}^5) from systematic absences: $0k0$ when $k \neq 2n$, $h0l$ when $l \neq 2n$.

Crystallographic Measurements.—A crystal of dimensions *ca.* 0.15 × 0.20 × 0.40 mm was oriented on a glass fibre such that the *b* axis was parallel to the spindle axis. Preliminary unit-cell dimensions and space-group data were obtained from rotation and Weissenberg photographs taken with Cu-K_α radiation and precession photographs taken with Mo-K_α ($\lambda = 0.7107$ Å) radiation. Accurate unit-cell dimensions were obtained by least-squares treatment of the θ, χ, and ϕ angles for 40 high-angle reflections measured on an Enraf–Nonius CAD 3 automated diffractometer (Ni-filtered Cu-K_α radiation, 3° take-off angle). Two octants of intensity data for reflections with $\theta < 67°$ were collected by use of the θ—2θ scanning technique with scanwidths $(1.0 + 0.50\tan\theta)°$. Attenuators were inserted automatically to ensure that counting rates did not exceed 2 500 counts s^{-1}; attenuation factors were derived experimentally. Background counts for a time equal to half the duration of the scan period were made at each end of the scan range. Crystal and instrument stability were monitored throughout by remeasurement of the intensity of a strong standard reflection after each batch of 99 reflections; no significant variation was noted, although the crystal visibly darkened during data collection. Absorption corrections were established experimentally from the ϕ dependence of the intensity of the $0\bar{4}0$ reflection measured at χ 90°. From a total of 1 885 independent measurements, 1 223 reflections with $I > 2.0\,\sigma(I)$ [$\sigma(I) = (\text{scan count} + \text{total background count})^{\frac{1}{2}}$]

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were corrected for Lorentz, polarization, and absorption effects, and used in the structure analysis.

Structure Analysis.—Initial co-ordinates for the gallium atom were obtained from the three-dimensional Patterson map. Approximate positions for the remaining non-hydrogen atoms were obtained from a gallium-phased three-dimensional F_o Fourier synthesis, and when structure factors were calculated R was 0.36.

Positional and isotropic thermal parameters were then refined by six cycles of full-matrix least-squares calculations which reduced R to 0.123. Six further cycles during which the atoms were allowed to assume anisotropic temperature factors decreased R to 0.076. Calculated positions (assuming C–H 1.05 Å) for the phenanthroline hydrogen atoms were found to coincide with regions of positive electron-density in a difference-Fourier synthesis; the methyl-group hydrogen atoms could not be placed with confidence. When the contributions of the phenanthroline hydrogen atoms, with isotropic thermal parameters of their bonded carbon atoms, were included in the structure-factor calculations R decreased to 0.069. Two further least-squares cycles during which the parameters of the non-hydrogen atoms were varied brought the refinement to convergence at R 0.068. Final atomic positional and thermal parameters are listed in Tables 4 and 5. Observed structure amplitudes and calculated structure factors are listed in Supplementary Publication No. SUP 21735 (8 pp., 1 microfiche).*

For the structure-factor calculations, scattering factors for carbon, nitrogen, chlorine, and gallium were taken from ref. 31, and for hydrogen from ref. 32; those of both chlorine and gallium were corrected for the effects of anomalous dispersion.[33] In the least-squares calculations, $\Sigma w\Delta^2$ was minimized with weights w given by $w^{\frac{1}{2}} = 1$ for $|F_o| \leqslant 17.7$ and $w^{\frac{1}{2}} = 17.7/|F_o|$ for $|F_o| > 17.7$; this scheme showed no systematic dependence of $\langle w\Delta^2 \rangle$ when analyzed in ranges of $|F_o|$.

TABLE 5

Calculated fractional co-ordinates ($\times 10^3$) and isotropic temperature factors for the hydrogen atoms labelled according to the carbon atom to which they are bonded

Atom	x	y	z	B/Å
H(2)	83	115	92	3.7
H(3)	322	254	190	4.7
H(4)	520	295	405	4.3
H(5)	616	252	614	3.7
H(6)	587	144	731	3.4
H(7)	439	−15	738	4.1
H(8)	222	−164	629	4.3
H(9)	32	−188	405	4.7

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* For details see Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue. (Items less than 10 pp. are supplied as full-size copies).

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