Synthesis and Crystal Structure of a Quinolinolato-complex of Dicyclopentylgallium†

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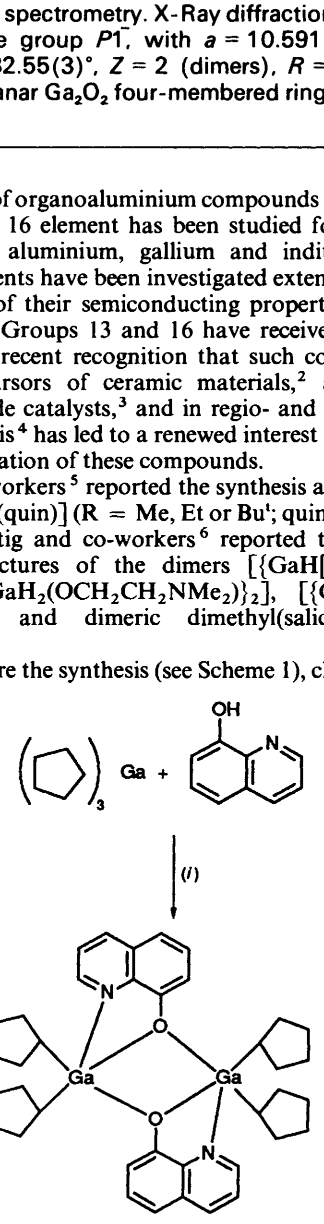
Tricyclopentylgallium reacts with 8-hydroxyquinoline in 1:1 ratio to yield quantitatively bis[dicyclopentyl(quinolin-8-olato)gallium] which has been characterized by elemental analysis, IR, ^{1}H NMR and mass spectrometry. X-Ray diffraction analysis indicated that the compound belongs to the triclinic system, space group $P\bar{1}$, with $a = 10.591(4)$, $b = 12.065(4)$, $c = 13.941(4)$ Å, $\alpha = 81.92(2)$, $\beta = 87.83(3)$, $\gamma = 82.55(3)°$, $Z = 2$ (dimers), $R = 0.0608$ ($R' = 0.0871$). The molecule contains an oxygen-bridged coplanar Ga_2O_2 four-membered ring.

The chemistry of organoaluminium compounds bound either to a Group 15 or 16 element has been studied for many years. Derivatives of aluminium, gallium and indium containing Group 15 elements have been investigated extensively in recent years because of their semiconducting properties.[1] However, compounds of Groups 13 and 16 have received only limited attention. The recent recognition that such compounds may serve as precursors of ceramic materials,[2] as models for aluminium oxide catalysts,[3] and in regio- and stereo-selective organic synthesis[4] has led to a renewed interest in the synthesis and characterization of these compounds.

Sen and co-workers[5] reported the synthesis and characterization of $[GaR_2(quin)]$ (R = Me, Et or Bu^t; quin = quinolin-8-olate) and Rettig and co-workers[6] reported the crystal and molecular structures of the dimers $[\{GaH[(OCH_2CH_2)_2NMe]\}_2]$, $[\{GaH_2(OCH_2CH_2NMe_2)\}_2]$, $[\{GaMe_2(OCH_2CH_2NMe_2)\}_2]$ and dimeric dimethyl(salicylaldehydato)gallium.[6]

We report here the synthesis (see Scheme 1), characterization and crystal and molecular structure of the quinolinolato-complex of dicyclopentylgallium.



Scheme 1 (*i*) Hexane, toluene, 60–70 °C, 4 h

Table 1 Experimental parameters for the X-ray diffraction study

Formula	$C_{38}H_{48}Ga_2N_2O_2$
M	708.3
Crystal colour	Yellow
Crystal size/mm	0.20 × 0.20 × 0.35
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.591(4)
b/Å	12.065(4)
c/Å	13.941(4)
α/°	81.92(2)
β/°	87.83(3)
γ/°	82.55(3)
U/Å^3	1748.6(10)
D_c/g cm^{-3}	1.345
Z	2 (dimers)
F(000)	744
Radiation	Mo-Kα (λ = 0.710 73 Å)
T/°C	20
2θ range/°	3.0–45.0
Scan type	2θ–θ
ω Scan speed/° min^{-1}	Variable, 6.51–29.30
Reflections collected	5989
Independent reflections	5623 (R_{int} = 0.0201)
Observed reflections	3991 [$F > 4.0\sigma(F)$]
Parameters refined	397
R	0.0608
R'	0.0871

Experimental

Tricyclopentylgallium was prepared by the reaction of cyclopentylmagnesium bromide [from magnesium (0.4 g, 166.7 mmol) and cyclopentyl bromide (23.1 g, 155 mmol)] with gallium trichloride in diethyl ether at room temperature for 16 h. After removal of the solvent under vacuum the residue was extracted with hexane (60 cm^3) and purified by distillation in vacuum [150–155 °C, 0.1 mmHg (*ca.* 13.3 Pa)]. Yield 10.40 g (92.4%).

Proton NMR spectra were recorded on a Varian XL-200 instrument in $CDCl_3$ with tetramethylsilane as internal

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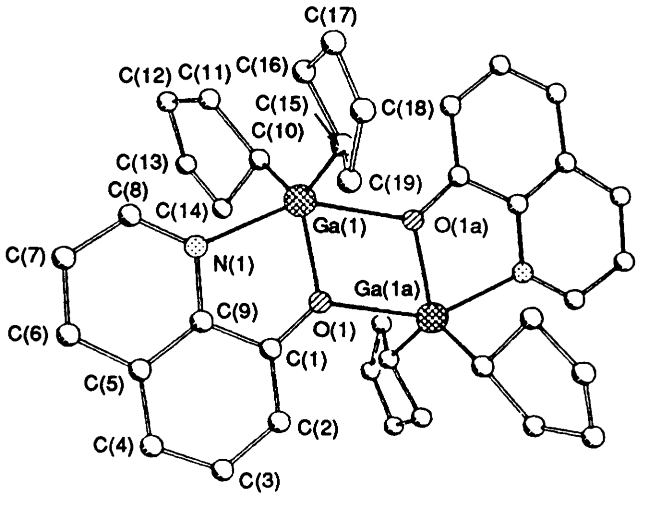
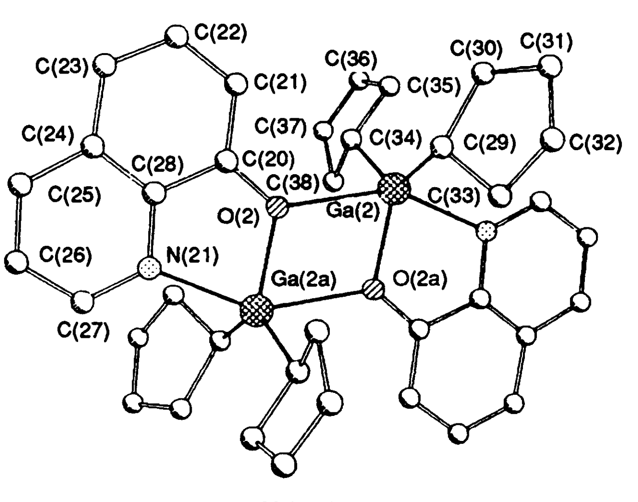
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 2 Atomic coordinates (× 10^4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ga(1)	−90(1)	3753(1)	806(1)	Ga(2)	4691(1)	1384(1)	5245(1)
O(1)	1123(4)	4521(3)	−19(3)	O(2)	3966(4)	−107(3)	4637(3)
N(1)	1660(5)	2530(4)	1002(3)	N(2)	3770(5)	−2085(5)	4120(4)
C(1)	2311(6)	4042(5)	−89(4)	C(20)	2846(6)	−252(5)	4320(4)
C(2)	3266(6)	4512(6)	−624(5)	C(21)	1806(6)	561(5)	4252(4)
C(3)	4499(7)	3941(7)	−663(6)	C(22)	654(6)	321(6)	3907(4)
C(4)	4795(7)	2883(7)	−164(6)	C(23)	528(7)	−690(7)	3626(5)
C(5)	3861(6)	2370(6)	406(5)	C(24)	1567(7)	−1548(6)	3682(5)
C(6)	4051(8)	1284(6)	969(6)	C(25)	1533(8)	−2623(7)	3428(6)
C(7)	3093(8)	884(6)	1520(6)	C(26)	2576(9)	−3386(7)	3529(7)
C(8)	1895(7)	1527(5)	1522(5)	C(27)	3698(8)	−3100(6)	3863(6)
C(9)	2625(6)	2954(5)	452(4)	C(28)	2717(6)	−1322(5)	4022(4)
C(10)	−1139(7)	2811(5)	173(5)	C(29)	3422(6)	1384(6)	6335(4)
C(11)	−1517(8)	1758(7)	773(6)	C(30)	2708(8)	2555(7)	6415(6)
C(12)	−1767(8)	967(6)	83(6)	C(31)	2303(11)	2505(11)	7491(7)
C(13)	−1359(9)	1470(7)	−904(6)	C(32)	2906(12)	1464(12)	7979(7)
C(14)	−554(9)	2374(7)	−728(6)	C(33)	3897(9)	974(8)	7314(5)
C(15)	−327(8)	4201(6)	2135(5)	C(34)	4653(7)	2327(7)	3929(5)
C(16)	−843(14)	3369(12)	2844(7)	C(35)	4297(14)	3510(8)	3890(8)
C(17)	−623(14)	3749(11)	3829(7)	C(36)	4758(14)	4021(10)	2895(8)
C(18)	305(13)	4442(13)	3680(7)	C(37)	5531(13)	3232(9)	2544(7)
C(19)	690(12)	4508(12)	2601(8)	C(38)	5791(11)	2217(8)	3343(7)



Molecule 1



Molecule 2

Fig. 1 The molecular structure of the quinolinolato-complex

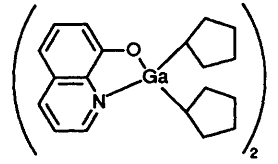
Table 3 Selected bond lengths (Å) and angles (°)

Ga(1)–O(1)	1.932(4)	Ga(2)–O(2a)	1.950(4)
Ga(1)–O(1a)	2.365(4)	Ga(2)–O(2)	2.320(5)
Ga(1)–N(1)	2.215(5)	Ga(2a)–N(2)	2.198(6)
Ga(1)–C(10)	1.996(8)	Ga(1)–C(15)	2.000(7)
Ga(2)–C(29)	1.991(6)	Ga(2)–C(34)	2.017(7)
O(1)–C(1)	1.321(7)	O(2)–C(20)	1.321(7)
Ga(1)–O(1)–Ga(1a)	109.4(2)	Ga(2)–O(1)–Ga(2a)	108.7(2)
O(1)–Ga(1)–O(1a)	70.6(2)	O(2)–Ga(2)–O(2a)	71.3(2)
O(1)–Ga(1)–N(1)	78.1(2)	O(2)–Ga(2a)–N(2a)	78.2(2)
N(1)–Ga(1)–O(1a)	148.6(2)	N(2a)–Ga(2)–O(2)	149.5(2)
C(15)–Ga(1)–O(1a)	94.6(2)	C(29)–Ga(2)–O(2)	94.0(2)
C(10)–Ga(1)–O(1a)	93.9(2)	C(34)–Ga(2)–O(2)	92.2(3)
O(1)–Ga(1)–C(15)	115.0(3)	O(2a)–Ga(2)–C(29)	115.1(2)
O(1)–Ga(1)–C(10)	116.4(2)	O(2a)–Ga(2)–C(34)	113.6(2)
N(1)–Ga(1)–C(10)	98.1(2)	N(2a)–Ga(2)–C(34)	98.9(3)
N(1)–Ga(1)–C(15)	100.6(2)	N(2a)–Ga(2)–C(29)	100.1(2)
C(10)–Ga(1)–C(15)	127.7(3)	C(29)–Ga(2)–C(34)	130.3(3)
C(16)–C(15)–C(19)	104.2(8)	C(30)–C(29)–C(33)	104.4(6)
O(1)–C(1)–C(9)	117.0(5)	O(2)–C(20)–C(28)	117.8(5)
O(1)–C(1)–C(2)	125.4(5)	O(2)–C(20)–C(21)	124.0(6)
C(1)–C(9)–N(1)	115.9(5)	C(20)–C(28)–N(2)	115.0(6)
C(9)–N(1)–Ga(1)	109.2(3)	C(28)–N(2)–Ga(2a)	110.4(4)

standard, IR spectra (Nujol mull, NaCl) on a Shimadzu IR-440 spectrophotometer and mass spectra on a Finigan 4021 spectrometer.

Synthesis of the Quinolinolato-complex of Dicyclopentylgallium.—A solution of 8-hydroxyquinoline (0.219 g, 1.510 mmol) in hexane–toluene (1 : 1, 20 cm^3) was added dropwise with stirring to a solution of tricyclopentylgallium (0.420 g, 1.517 mmol) in hexane (10 cm^3) during 15 min. The resulting solution was allowed to stir at 60–70 °C for 4 h. After removal of the solvent under vacuum, the yellow crystalline residue was washed with hexane and recrystallized from hexane, giving 0.480 g (91%) of product, m.p. 92–93 °C. ^1H NMR: δ 0.98 (m, 2 H), 1.42 (s, 12 H), 1.86 (m, 4 H), 7.12 (m, 2 H), 7.52 (s, 2 H) and 8.40 (m, 2 H). IR: 2900s, 1470s, 1380s, 1300m, 1100m, 805m, 795m and 740m cm^{-1}. Mass spectrum (^{69}Ga, ^{71}Ga isotopes): *m*/*z* (relative intensity) 352, 354 (0.66, 0.42), 351, 353 (2.61, 1.74), 283, 285 (18.03, 10.36), 282, 284 (100, 64.63), 214, 216 (27.55, 17.39), 213, 215 (11.20, 9.36), 69, 71 (34.49, 19.02) (Found: C, 64.80; H, 6.60; N, 4.15. Calc. for $C_{19}H_{24}GaNO$: C, 64.85; H, 6.80; N, 4.00%).

Table 4 Comparison of the bond parameters in Ga_2O_2 rings

	Bond length (Å)		Bond angle (°)	
Compound	Ga–O	Ga–N	O–Ga–O′	Ref.
$[\{GaH[(OCH_2CH_2)_2NMe]\}_2]$	1.843, 2.019	2.187 2.196	76.2	6(*a*)
$[\{GaH_2(OCH_2CH_2NMe_2)\}_2]$	1.911, 2.053	2.279	74.7	6(*b*)
$[\{GaMe_2(OCH_2CH_2NMe_2)\}_2]$	1.913, 2.078	2.471	74.6	6(*c*)
	1.932, 2.365 1.950, 2.320	2.215 2.198	70.6 71.3	This work

Crystal-structure Determination of the Quinolinolato-complex of Dicyclopentylgallium.—Single crystals, collected by recrystallization in hexane at −10 °C, were sealed in thin-walled glass capillaries under an argon atmosphere. Diffraction data were collected on a Siemens R3m/V four-circle diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). 5989 Reflections were measured ($1.5 \leqslant \theta \leqslant 22.5°$) of which 3991 had $F > 4.0\,\sigma(F)$ and were considered observed. The structure was solved using direct methods (Ga atoms) followed by normal heavy-atom procedures. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions with one overall refined U_{iso} (= 0.08 Å^2). The weighting scheme $w^{-1} = \sigma^2(F) + 0.0050F^2$ was employed. Final R and R' values 0.0608, 0.0871. Other details are given in Table 1.

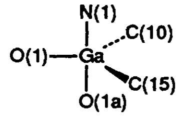
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The structure of the quinolinolato-complex features centrosymmetric dimeric units involving the formation of a four-membered Ga_2O_2 ring. The five-co-ordinated gallium atoms have distorted trigonal-bipyramidal geometry. The two quinoline rings and the Ga_2O_2 ring are in the same plane.

The crystal structure is shown in Fig. 1, experimental parameters in Table 1, atomic coordinates in Table 2 and bond lengths and angles in Table 3. For comparison, the Ga–O and Ga–N bond lengths and O–Ga–O′ bond angle in some known compounds are listed in Table 4. The Ga–O bond lengths of our product in molecules 1 and 2 [1.932(4), 2.365(4); and 1.950(4), 2.320(5) Å respectively] are longer than those in the known compounds. The Ga–N bond lengths [2.215(5) and 2.198(6) Å] fall in the range of those of the analogues (2.187–2.471 Å).

The gallium atom has a distorted trigonal-bipyramidal coordination as shown (exemplified by molecule 1). It deviates by 0.10 Å from the plane defined by C(10), C(15), O(1) towards N(1) (0.11 Å in another dimeric unit). The bond angle O(1)–Ga(1)–N(1) is 78.1(2)°, in between those of analogues, and O(1)–Ga(1)–O(1a) is 70.6(2)°, the lowest angle when compared with those of analogues, probably due to the influence of both the quinoline and cyclopentane rings. Another deformation of bond angles is noteworthy: O(1)–C(1)–C(9) [117.0(5)°], C(1)–C(9)–N(1) [115.9(5)°] and C(9)–N(1)–Ga(1) [109.2(3)°] deviate from 120°. The angles C(11)–C(10)–C(14) [102.7(6)°] and C(16)–C(15)–C(19) [104.2(8)°] also deviate from the standard values.



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