Synthesis and Characterisation of Azido- and Thiocyanato-gallium(III) Porphyrins. Crystal Structure of Azido(2,3,7,8,12,13,17,18-octaethylporphyrinato)gallium(III) †

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Gallium(III) porphyrin complexes of the type Ga(por)X [por = 2,3,7,8,12,13,17,18-octamethyl-, 2,3,7,8,12,13,17,18-octaethyl-, 5,10,15,20-tetraphenyl-, 5,10,15,20-tetra-*m*-tolyl-, or 5,10,15,20-tetra-*p*-tolyl-porphyrinate(2−); X = N_3 or SCN] have been prepared. The stereochemistry of the metal has been established by i.r. and ^1H n.m.r. measurements and confirmed by the crystal structure determination of the title compound by *X*-ray diffraction methods using Cu-K_α radiation. Crystals are monoclinic, space group $P2_1/c$, with a = 13.469(1), b = 13.497(1), c = 19.050(2) Å, β = 106.28(1)°, and Z = 4; $R(F)$ = 0.041, $R'(F)$ = 0.044 for 6 295 reflections. The gallium atom is five-co-ordinated by the four nitrogen atoms (N_p) of the porphyrin plane and one nitrogen atom N(5) of the azido group: mean Ga–N_p 2.034(3), Ga–N(5) 1.955(2) Å, N(5)–Ga–N_p 100.3(10), Ga–N(5)–N(6) 120.8(1)°.

Recently hydrocarbon oxidations with oxometalloporphyrinates have been investigated extensively.[1–5] According to a similar approach Groves and Takahashi[6] have demonstrated that a reactive nitridomanganese(V) porphyrin complex induces direct oxidative amination of hydrocarbons. Other nitrido metalloporphyrins[7–10] and nitrido-bridged metalloporphyrin dimers[11–14] have been reported, the precursors often being the corresponding azido derivatives. Azido complexes of Mn,[15,16] Fe,[17–19] and Cr[20] are known and the thermal or photolytic decomposition of such complexes could lead also to reactive nitrido systems capable of direct autopolymerisation. In such inorganic–organic polymers, the metallic atom co-ordinated to the macrocycle would alternate in a linear chain with a nitrogen atom; these systems are good precursors of electrical conductors.

The main purposes of this paper are to report the synthesis and complete characterisation of the azidogallium(III) complexes Ga(por)N_3‡ and describe the *X*-ray structure of Ga(oep)N_3. Furthermore we describe also the isolation and spectroscopic properties of thiocyanatogallium(III) porphyrins.

Experimental

Synthesis.—The starting compounds Ga(por)Cl[21] and Ga(por)(O_2CMe)[22] were prepared according to the methods previously reported.

The azido and thiocyanato complexes were synthesised from Ga(por)Cl or Ga(por)(O_2CMe) by a general procedure which is detailed below.

(i) *Azido(porphyrinato)gallium*(III). Ga(por)X (X = Cl or O_2CMe) (0.55 mmol) was dissolved in dichloromethane (50 cm^3). NaN_3 (18.5 mmol) and H_2O (1 cm^3) were added. The mixture was stirred for 12 h and then washed three times with water (20 cm^3). The organic solution was dried, evaporated to dryness, and the residue recrystallised.

(ii) *Porphyrinato(thiocyanato)gallium*(III). The reaction was also run in dichloromethane. Ga(por)X (0.68 mmol) was dissolved in CH_2Cl_2 (100 cm^3); NaSCN (24.7 mmol) and H_2O (2 cm^3) were then added. After reaction (12 h) the organic phase was washed with water, dried, and evaporated.

The reaction conditions, yields, and elemental analyses for the two series of complexes are summarised in Table 1.

Analysis.—Elemental analyses were performed by the Service de Microanalyse du C.N.R.S. de Vernaison.

Physical Measurements.—Mass spectra were recorded in the electron-impact mode with a Finnigan 3300 spectrometer. All spectra were obtained by direct inlet under the following conditions: electron impact; ionising energy, 70—35 eV; ionising current, 0.4 mA; source temperature, up to 250 °C. ^1H N.m.r. spectra were taken on a JEOL FX 100 spectrometer. Samples (6 mg) were dissolved in $CDCl_3$ (0.5 cm^3) with $SiMe_4$ as internal reference. Infrared spectra were recorded on a Perkin-Elmer 580 B apparatus. Samples were prepared as 1% dispersions in CsI pellets or Nujol mulls. Electronic absorption spectra were recorded on a Perkin-Elmer 559 spectrophotometer using 5×10^{-3} mol dm^{-3} benzene solutions.

Crystal and Molecular Structure Determination.—A suitable crystal of Ga(oep)N_3 was obtained from a solution of toluene. Preliminary Weissenberg photographs along the *c* axis revealed a monoclinic unit cell and systematic absences of the type *h*0*l*, $l = 2n$ and 0*k*0, $k = 2n$ led to the centrosymmetric space group $P2_1/c$.

Crystal data. $C_{36}H_{44}GaN_7$, M = 644.4, monoclinic, space group $P2_1/c$, a = 13.469(1), b = 13.497(1), c = 19.050(2) Å, β = 106.28(1)°, U = 3 224 Å^3, Z = 4, D_c = 1.29 g cm^{-3}, $F(000)$ = 1 360, λ(Cu-K_α) = 1.540 5 Å, μ(Cu-K_α) = 14.91 cm^{-1}.

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† *Supplementary data available* (No. SUP 56566, 5 pp.): H-atom co-ordinates, thermal parameters, least-squares planes, dihedral angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. unit employed: eV ≈ 1.60×10^{-19} J.

‡ Abbreviations: por = unspecified porphyrinate(2−), omp = 2,3,7,8,12,13,17,18-octamethylporphyrinate(2−), oep = 2,3,7,8,12,13,17,18-octaethylporphyrinate(2−), tpp = 5,10,15,20-tetraphenylporphyrinate(2−), tmtp = 5,10,15,20-tetra-*m*-tolylporphyrinate(2−), tptp = 5,10,15,20-tetra-*p*-tolylporphyrinate(2−).

Table 1. Experimental data and yields

Complex	Recrystallisation solvent[a]	Yield (%)	Analysis (%)[b] C	H	N	S	Ga
(1a) Ga(omp)N_3	A–B (1:2)	85	63.1	5.1	18.4		12.4
			(63.2)	(5.30)	(18.40)		(13.10)
(1b) Ga(oep)N_3	A	91	67.0	6.5	15.0		10.5
			(67.1)	(6.90)	(15.20)		(10.80)
(1c) Ga(tpp)N_3	A–B (1:2)	88	72.8	4.0	13.7		8.9
			(72.95)	(3.90)	(13.55)		(9.60)
(1d) Ga(tptp)N_3	A–B (1:6)	89	73.8	4.6	12.3		8.2
			(73.85)	(4.65)	(12.55)		(8.95)
(1e) Ga(tmtp)N_3	A–B (1:5)	89	73.9	4.6	12.7		8.4
			(73.85)	(4.65)	(12.55)		(8.95)
(2a) Ga(omp)SCN	A	44	63.8	5.1	12.4	5.8	12.8
			(63.55)	(5.15)	(12.75)	(5.85)	(12.70)
(2b) Ga(oep)SCN	A	88	67.3	6.7	10.6	5.0	10.5
			(67.3)	(6.70)	(10.60)	(4.85)	(10.55)
(2c) Ga(tpp)SCN	A–B (1:5)	70	72.9	3.9	9.1	4.2	9.0
			(73.0)	(3.80)	(9.45)	(4.35)	(9.40)
(2d) Ga(tptp)SCN	A–B (1:5)	79	73.6	4.5	8.8	4.0	8.5
			(73.85)	(4.55)	(8.80)	(4.05)	(8.75)
(2e) Ga(tmtp)SCN	A–B (1:7)	80	73.8	4.5	8.7	4.0	8.7
			(73.85)	(4.55)	(8.80)	(4.05)	(8.75)

[a] Reaction solvents: A = toluene, B = heptane. [b] Calculated values are given in parentheses.

Table 2. Fractional co-ordinates with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Ga	0.838 93(3)	0.012 91(3)	0.561 93(2)	C(15)	0.881 7(2)	0.224 4(2)	0.476 4(2)
N(1)	0.726 6(2)	−0.093 2(2)	0.535 0(1)	C(16)	0.785 8(2)	0.180 2(2)	0.449 8(2)
N(2)	0.935 6(2)	−0.091 8(2)	0.621 4(1)	C(17)	0.702 3(2)	0.220 1(2)	0.391 7(2)
N(3)	0.965 6(2)	0.093 6(8)	0.560 8(1)	C(18)	0.623 2(2)	0.153 5(2)	0.379 7(2)
N(4)	0.757 8(2)	0.090 9(2)	0.473 2(1)	C(19)	0.657 2(2)	0.074 4(2)	0.431 4(2)
N(5)	0.795 0(2)	0.082 0(2)	0.638 4(1)	C(20)	0.597 3(2)	−0.004 8(2)	0.439 9(2)
N(6)	0.748 9(2)	0.040 3(2)	0.673 2(2)	C(25)	0.457 6(2)	−0.185 5(3)	0.444 9(2)
N(7)	0.703 2(3)	0.004 2(4)	0.708 9(2)	C(26)	0.454 9(3)	−0.225 5(4)	0.370 9(2)
C(1)	0.628 5(2)	−0.083 4(2)	0.487 4(2)	C(27)	0.598 8(3)	−0.328 9(3)	0.568 2(2)
C(2)	0.566 4(2)	−0.168 4(2)	0.492 0(2)	C(28)	0.632 1(4)	−0.415 0(3)	0.528 2(3)
C(3)	0.626 5(2)	−0.229 8(2)	0.543 5(2)	C(29)	0.990 7(3)	−0.320 7(3)	0.738 5(2)
C(4)	0.725 9(2)	−0.182 3(2)	0.570 0(2)	C(30)	1.013 6(3)	−0.407 9(3)	0.696 6(2)
C(5)	0.809 2(2)	−0.221 2(2)	0.622 5(2)	C(31)	1.181 5(2)	−0.171 6(3)	0.759 6(2)
C(6)	0.907 1(2)	−0.179 7(2)	0.646 4(2)	C(32)	1.193 4(4)	0.116 6(4)	0.830 4(3)
C(7)	0.993 0(2)	−0.223 6(3)	0.700 5(2)	C(33)	1.244 7(2)	0.170 4(3)	0.632 0(2)
C(8)	1.074 7(2)	−0.161 6(3)	0.707 4(2)	C(34)	1.270 9(3)	0.210 4(4)	0.708 7(2)
C(9)	1.039 4(2)	−0.080 6(2)	0.657 7(2)	C(35)	1.095 8(3)	0.327 0(3)	0.526 5(2)
C(10)	1.099 6(2)	−0.002 2(2)	0.647 2(2)	C(36)	1.072 4(5)	0.407 4(3)	0.576 7(3)
C(11)	1.066 5(2)	0.078 7(2)	0.603 0(2)	C(37)	0.705 4(3)	0.317 3(3)	0.353 4(2)
C(12)	1.130 3(2)	0.161 4(3)	0.595 4(2)	C(38)	0.680 8(4)	0.404 7(3)	0.396 1(3)
C(13)	1.068 1(2)	0.227 0(3)	0.549 3(2)	C(39)	0.521 6(3)	0.154 0(3)	0.321 0(2)
C(14)	0.965 7(2)	0.183 6(2)	0.527 2(2)	C(40)	0.519 7(3)	0.081 4(3)	0.260 0(2)

Data collection, structure solution and refinement. A crystal of dimensions 0.3 × 0.17 × 0.20 mm was mounted on a CAD 4F diffractometer with graphite-monochromatised Cu-K_α radiation (ω–2θ scan; 0.3 < scan speed < 2.5° min^{-1}; scan range, 0.8 + 0.14 tanθ; aperture, 3 + 1.0 tanθ mm; $\theta_{max.}$ = 70°). 7 295 Reflections were collected ($0 < h < 16$; $0 < k < 16$; $-23 < l < 23$) of which 6 295 [$I > 3\sigma(I)$] were used to solve and refine the structure. The crystal structure was solved by using MULTAN[23] and refined by the SDP[24] package. All the hydrogen atoms were found in difference Fourier maps and fixed during the refinement [B(H) = 3.16 Å^2]. The final agreement indexes are $R(F)$ = 0.041 and $R'(F)$ = 0.044. Fractional co-ordinates of the non-hydrogen atoms are given in Table 2. A selection of bond distances and bond angles is given in Table 3.

Table 3. Selection of bond distances (Å) and angles (°)

Ga–N(1)	2.041(1)	Ga–N(5)	1.955(2)
Ga–N(2)	2.037(1)	N(5)–N(6)	1.172(2)
Ga–N(3)	2.029(1)	N(6)–N(7)	1.146(3)
Ga–N(4)	2.031(1)	Ga–N_p mean	2.034(3)
N(1)–Ga–N(2)	88.1(1)	N(3)–Ga–N(4)	88.4(1)
N(2)–Ga–N(3)	88.3(1)	N(4)–Ga–N(1)	88.1(1)
N(1)–Ga–N(3)	160.0(1)	N(2)–Ga–N(4)	159.0(1)
N(1)–Ga–N(5)	99.5(2)	N(2)–Ga–N(5)	101.3(1)
N(3)–Ga–N(5)	100.5(2)	N(4)–Ga–N(5)	99.7(1)
Ga–N(5)–N(6)	120.8(1)		

Results and Discussion

Reaction of NaN_3 at room temperature on gallium(III) porphyrin complexes Ga(por)X (X = Cl or O_2CMe) affords

Table 4. Characteristic mass and i.r. spectral data

	Mass spectra			I.r. (cm^{-1})			
Complex	m/e	Relative intensity	Fragmentation pattern	ν_{asym}(NNN)	ν_{sym}(NNN)	δ(NNN)	ν(GaN)
(**1a**)	531	0.83	M^+	2 078	1 345	662	404
	489	100.00	$[M - N_3]^+$		1 298		344
					1 262		
(**1b**)	643	5.29	M^+	2 078	1 344	665	407
	644	7.15	$[M + 1]^+$		1 296		
	601	100.00	$[M - N_3]^+$				
(**1c**)	722	3.50	$[M - 1]^+$	2 088	1 296	741	436
	681	100.00	$[M - N_3]^+$		1 258	676	386
(**1d**)	778	1.64	$[M - 1]^+$	2 095	1 261		425
	777	2.19	$[M - 2]^+$				390
	737	11.53	$[M - N_3]^+$				
	738	100.00	$[M - N_3 + 1]^+$				
(**1e**)	779	2.71	M^+	2 095	1 263		394
	780	3.79	$[M + 1]^+$				
	737	71.06	$[M - N_3]^+$				
	738	100.00	$[M - N_3 + 1]^+$				
				ν(CN)	ν(CS)	δ(NCS)	ν(GaS)
(**2a**)	548	4.05	$[M + 1]^+$	2 091	805	396	315
	550	6.75	$[M + 3]^+$	2 050 (sh)			
	489	100.00	$[M - SCN]^+$				
(**2b**)	659	14.37	M^+	2 086	807		329
	660	18.30	$[M + 1]^+$	2 040 (sh)			290
	601	86.92	$[M - SCN]^+$				
	602	100.00	$[M - SCN + 1]^+$				
(**2c**)	639	16.73	M^+	2 074	805	412	304
	640	12.30	$[M + 1]^+$	2 025 (sh)			
	681	86.51	$[M - SCN]^+$				
	682	100.00	$[M - SCN + 1]^+$				
(**2d**)	796	8.82	$[M + 1]^+$	2 057	800		275
	798	8.82	$[M + 3]^+$	2 022			249
	737	35.29	$[M - SCN]^+$				
	738	100.00	$[M - SCN + 1]^+$				
(**2e**)	795	2.25	M^+	2 075		396	253
	796	16.45	$[M + 1]^+$	2 039			
	737	76.57	$[M - SCN]^+$				
	738	100.00	$[M - SCN + 1]^+$				

the azido compounds Ga(por)N$_3$ (**1**). The yields are high (85—91%) and are not dependent on the nature of the macrocycle. The complexes Ga(por)SCN (**2**) are prepared simply by substituting NaN$_3$ by NaSCN. The yields are satisfactory (70—88%) except for Ga(omp)SCN (44%).

The proposed formula for compounds (**1**) and (**2**) is in accordance with the analytical results (Table 1) and mass spectral data (Table 4). In all of the mass spectra of complexes (**1**) and (**2**) the molecular peak or its protonated (or deprotonated) form appears with a low intensity (0.83—16.73%). The parent peak corresponds to [Ga(por)]$^+$ or [Ga(por) + 1]$^+$ resulting from the fission of the metal ion and the axial ligand.

In addition to absorptions normally seen in gallium(III) porphyrin complexes, the i.r. spectra of (**1**) and (**2**) show characteristic absorptions of their respective pseudohalide ligands (Table 4). Most of the derivatives (**1**) exhibit four bands which are normally assigned to the asymmetric stretching (2 078—2 095), symmetric stretching (1 258—1 345), N$_3$ bonding (662—741), and Ga–N$_3$ stretching (344—436 cm^{-1}) modes.[25] The last ones may be due to the mixing of the Ga–N$_3$ and Ga–por stretching modes. These data suggest that the Ga–NNN bond is not linear.[26] Analysis of the results observed for (**2**) is more complicated but each complex exhibits generally four bands and a structural diagnosis between the bonding types of the NCS group is possible.[26,27] The high CN stretching frequency (2 022—2 050 cm^{-1}) is consistent with that in Ga–S–CN thiocyanato complexes.[27] The weak ν(CS) (800—807 cm^{-1}) and δ(NCS) (396—412 cm^{-1}) bands do not provide definitive structural information since for octaethylporphyrin and substituted tetraphenylporphyrin derivatives they are obscured by the presence of other bands in the same region. In the far-i.r. region some bands can be distinguished from the ν(Ga–N) (344—436 cm^{-1}) and attributed to the ν(Ga–S) vibrations (249—329 cm^{-1}). These observations and the analogy with other thiocyanatogallium complexes[26] lead us to propose Ga–S–CN bonding.

The complexes (**1**) and (**2**) exhibit characteristic electronic spectra for 'normal' metalloporphyrins[28,29] (Table 5). In the range 379—424 nm they show an intense Soret band (398—424 nm) and a blue-shifted band of lower intensity (379—401 nm). Three additional bands (or four) are red-shifted with respect to the Soret band. These are the Q(2,0), Q(1,0), and Q(0,0) bands [a fourth band appears only on the spectra of the thiocyanato derivatives (**2c**), (**2d**), and (**2e**)]. These spectra are similar to those displayed by the halogenogallium(III) porphyrins Ga(por)X (X = Cl, F, or I).[21]

Hydrogen-1 n.m.r. data for complexes (**1**) and (**2**) are presented in Table 5. The azido and thiocyanato derivatives (**1**) and (**2**) exhibit characteristic spectra of diamagnetic complexes and the n.m.r. data of these two series are very similar. For omp

Table 5. Proton n.m.r. and u.v.–visible data

			N.m.r.[a]			U.v.–visible (λ/nm)[b]					
			Protons of R^1		Protons of R^2						
Compd.	R^1	R^2				$B(1,0)$	$B(0,0)$	$Q(2,0)$	$Q(1,0)$	$Q(0,0)$	
(1a)	H	Me		s, 4, 10.15	s, 24, 3.64	379 (53.2)	399 (416.9)	481 (10.6)	530 (21.3)	569 (24.8)	
(1b)	H	Et		s, 4, 10.33	t, 24, 1.96 m, 16, 4.18	380 (43.6)	398 (270.7)	486 (4.4)	529 (12.9)	568 (19.8)	
(1c)	Ph	H	*o*-H *m,p*-H	m, 8, 8.20 m, 12, 7.76	s, 8, 9.10	400 (54.7)	418 (596.2)	505 (5.8)	555 (28.5)	584 (4.8)	
(1d)	*p*-MeC_6H_4	H	*o*-H *m*-H *p*-Me	m, 8, 8.09 d, 8, 7.55 s, 12, 2.70	s, 8, 9.06	401 (39.6)	424 (548.6)	511 (5.0)	551 (22.3)	591 (6.7)	
(1e)	*m*-MeC_6H_4	H	*o*-H *m,p*-H *m*-Me	m, 8, 8.03 m, 8, 7.63 m, 12, 2.63	s, 8, 9.11	399 (80.2)	419 (294.4)	505 (48.7)	545 (160.9)	583 (29.3)	
(2a)	H	Me		s, 4, 10.17	s, 24, 3.64	380 (15.2)	403 (234.4)	496 (2.4)	535 (8.2)	572 (11.9)	
(2b)	H	Et		s, 4, 10.32	t, 24, 1.98 m, 16, 4.17	383 (33.5)	402 (199.5)	487 (6.2)	532 (11.0)	570 (15.0)	
(2c)	Ph	H	*o*-H *m,p*-H	m, 8, 8.20 m, 12, 7.76	s, 8, 9.10	399 (53.7)	419 (520.6)	510 (9.9)	548 (21.2)	587 (6.6)	628(sh) (2.6)
(2d)	*p*-MeC_6H_4	H	*o*-H *m*-H *p*-Me	m, 8, 8.09 d, 8, 7.58 s, 12, 2.71	s, 8, 9.11	400 (37.7)	421 (443.5)	510 (7.4)	548 (20.7)	587 (7.4)	627(sh) (4.2)
(2e)	*m*-MeC_6H_4	H	*o*-H *m,p*-H *m*-Me	m, 8, 8.04 m, 8, 7.64 s, 12, 2.64	s, 8, 9.12	399 (51.2)	420 (434.7)	505 (13.6)	543 (23.9)	583 (9.1)	623(sh) (5.7)

[a] Spectra recorded in $CDCl_3$. Data given as multiplicity, intensity, δ/p.p.m. [b] 10^{-3} ε/dm^3 mol^{-1} cm^{-1} given in parentheses.

Table 6. Bond distances (Å) and angles (°) in some azidometalloporphyrins

Complexes	Ref.	M–N_p	M–N(5)	M–N(5)–N(6)	N(5)–N(6)	N(6)–N(7)	N(5)–N(6)–N(7)
$Fe^{III}(tpp)N_3(py)$[a]	19	1.989(6)	1.925(7)	125.6(7)	1.164(11)	1.111(12)	173.6(14)
$[Mn^{IV}(tpp)N_3]_2O$	15	2.014(9)	1.993(7)	128.3(7)	1.16(1)	1.19(1)	176.9(14)
$Ge^{IV}(tmtp)(N_3)_2$	*b*	1.983(3)	1.963(3)	124.8(4)	1.160(8)	1.154(13)	176.0(9)
$Ga^{III}(oep)N_3$	*c*	2.034(3)	1.955(2)	120.8(1)	1.172(2)	1.146(3)	176.4(2)

[a] py = Pyridine. [b] C. Lecomte, A. Boukhris, J. M. Barbe, and R. Guilard, unpublished work. [c] This work.

systems the morphology of the resonance signals is very simple since the *meso* and methyl protons appear as a singlet close to 10.15 and 3.65 p.p.m. respectively. For $Ga(oep)N_3$ and Ga(oep)-SCN, the resonance lines are typical of five-co-ordinate metallo-octaethylporphyrins:[30] the signal of the *meso* protons is located near to 10.30 p.p.m.; the methyl and the methylene protons of the ethyl groups give respectively a triplet (1.97 ± 0.01 p.p.m.) and an ABR_3 multiplet (4.17 ± 0.01 p.p.m.). The latter signal related to asymmetrical axial ligation indicates also that the gallium atom is out of the macrocycle plane.[30,31] These assumptions are confirmed by the spectra of tetraphenyl or substituted tetraphenyl complexes [(**1c**), (**1d**), (**1e**), (**2c**), (**2d**), and (**2e**)]: the resonance lines corresponding to the phenyl *o*-H atoms are broad and split into a doublet at high resolution; the pyrrolic protons give a singlet close to 9.1 p.p.m.

As no structure of an azido non-transition metal porphyrin had been studied, the crystal structure of $Ga(oep)N_3$ was solved. An ORTEP drawing of the molecule with the numbering scheme used is shown in the Figure. As expected the gallium atom is five-co-ordinated by the four nitrogen atoms (N_p) of the porphyrinato group and the N(5) nitrogen atom of the azido group; the co-ordination polyhedron is an almost perfect square pyramid [mean Ga–N_p 2.034(3), Ga–N(5) 1.955(2) Å, mean N(5)–Ga–N_p 100.3(10)°]. The gallium atom lies 0.362(1) Å from the $4N_p$ plane and 0.398(1) Å from the porphyrinato core whereas the N(5) atom is 2.318(2) Å above the $4N_p$ plane. For comparison, the distance of the gallium atom from the $4N_p$ plane is 0.317(1) Å in $Ga(tpp)Cl$[21] and 0.320(1) Å in Ga(oep)-(SO_3Me).[32] The difference observed with $Ga(oep)N_3$ may be

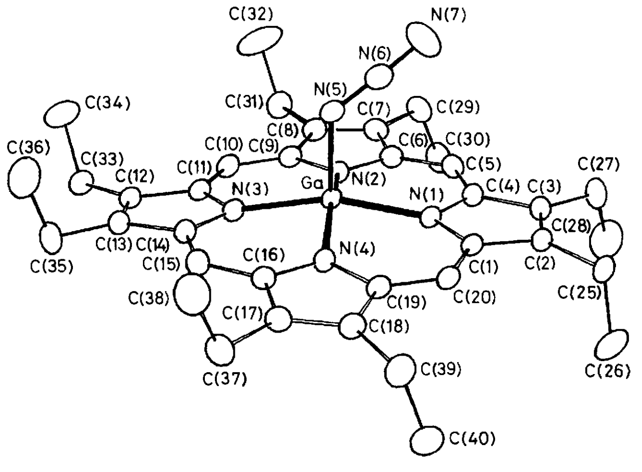

Figure. Molecular structure of $Ga(oep)N_3$

due to steric repulsive interactions between the azido-N(6) atom and the macrocycle [N(6)–C(4) 3.556(3) Å] pushing the gallium atom a little more out of the $4N_p$ plane. The azido group which eclipses the atoms C(4) and C(5) is almost linear [N(5)–N(6)–N(7) 176.4(2)°]. The metal–azido angle is small [Ga–N(5)–N(6) 120.8(1)°] compared to that in other azido-metalloporphyrins (Table 6). This geometry of the N_3 group puts the lone pair of the N(5) nitrogen atom exactly above the metal atom and suggests a metal donation (d_{xz}, d_{yz}) to the lowest unoccupied π^* molecular orbital of the azido group.

The carbon–carbon and carbon–nitrogen bond distances in the macrocycle are normal and there are no short inter-molecular distances.

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