Crystal Structure of *cis*-Dichlorobis-(2,2′-bipyridyl)gallium(III) Tetrachlorogallate(III)

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The compound of empirical formula $GaCl_3$(bipy) (bipy = 2,2′-bipyridyl) has been shown by *X*-ray single-crystal study to be *cis*-$[Cl_2Ga(bipy)_2]^+[GaCl_4]^-$. The crystals are orthorhombic with cell dimensions $a = 14{\cdot}900 \pm 0{\cdot}002$, $b = 12{\cdot}469 \pm 0{\cdot}002$, and $c = 13{\cdot}561 \pm 0{\cdot}002$ Å, space group *Pccn*, $Z = 8$. Diffractometer data were refined by least-squares methods to a final *R* of 0·052 for 1907 observed reflections. The cation and anion are required to have symmetry C_2. The cation has a *cis*-configuration with Ga–Cl 2·265 ± 0·001 and Ga–N 2·095 ± 0·004 and 2·111 ± 0·004 Å. The N–Ga–N angle of 77·2 ± 0·1° is a consequence of the rigid nature of the bipyridyl ligand. The remaining angles are much closer to the idealized values. The Ga–Cl distances in the tetrahedral $GaCl_4^+$ ion are 2·171 and 2·162 Å (both ±0·002 Å) with the Cl–Ga–Cl angles varying from 107·0—110·9 ± 0·1°. The distances in the two ions are compared with each other and also with those of other gallium compounds.

STRUCTURAL studies of complexes of gallium and indium with co-ordination numbers greater than four are relatively rare. Three examples are known for indium(III) [1] but only one for gallium(III).[2] However, many adducts of gallium trihalides, GaX_3 (X = Cl, Br, or I), have been reported which apparently are five- or six-co-ordinate. We have therefore undertaken *X*-ray studies of gallium and indium complexes with higher co-ordination numbers to establish the existence of these species and to elucidate the bonding of non-transition elements with high co-ordination numbers.

The reaction of GaX_3 with 2,2′-bipyridyl(bipy) gives a series of GaX_3(bipy) complexes.[3] A survey of the i.r. data of GaX_3 adducts [4] suggested an ionic formulation, *trans*-$[GaCl_2(bipy)_2]^+[GaCl_4]^-$, for the compound of empirical formula $GaCl_3$(bipy), although a study of $[Me_3N]_2GaCl_3$ was interpreted in terms of a trigonal bipyramidal geometry.[5] A single-crystal study revealed that the ionic formulation was correct for $GaCl_3$(bipy) but that the cation has a *cis*-configuration.[6]

EXPERIMENTAL

Colourless, needle-shaped crystals of $[GaCl_2(bipy)_2]^+$-$[GaCl_4]^-$ were grown by slowly cooling an acetone solution of the compound. Preliminary unit-cell and space-group data were determined from Weissenberg and precession photographs.

Crystal Data.—$C_{10}H_8Cl_3GaN_2$, $M = 332{\cdot}2$, Orthorhombic, $a = 14{\cdot}900 \pm 0{\cdot}002$, $b = 12{\cdot}469 \pm 0{\cdot}002$, $c = 13{\cdot}561 \pm 0{\cdot}002$ Å, $U = 2519{\cdot}4$ Å^3, D_m (by flotation) $= 1{\cdot}75 \pm 0{\cdot}01$, $Z = 8$, $D_c = 1{\cdot}752 \pm 0{\cdot}001$, $F(000) = 1312$. Cu-K_α radiation, $\lambda(\alpha_1) = 1{\cdot}54051$, $\lambda(\beta) = 1{\cdot}39217$ Å, μ(Cu-K_α) $= 85{\cdot}4$ cm^{-1}. Systematic absences, $0kl$ if $l = 2n + 1$, $h0l$ if $l = 2n + 1$, and $hk0$ if $h + k = 2n + 1$ indicate space-group *Pccn* (D_{2h}^{10}).

The crystal used for intensity measurements had dimensions 0·11 × 0·11 × 0·12 mm (parallel to $\tilde{a}$, $\tilde{b}$, and $\tilde{c}$). The intensity data were measured by use of the stationary-crystal–stationary-counter technique with Cu-K_α radiation and three nickel foils (0·35 mils) at the counter window. All the unique reflections with $2\theta \leq 135°$ were measured first and then one-half of the hemisphere was remeasured, giving up to three measurements for most reflections. A small correction (maximum 3·2%) was applied for the variation of the four standard reflections which were measured after every 100 reflections. From the 7810 measurements, a total of 2275 independent reflections was obtained after averaging equivalent reflections. The 1907 reflections $\geqslant 1{\cdot}2$ times the respective background count were considered as observed. The remaining 368 unobserved reflections were entered as 0·1 times the appropriate background count and were flagged with a minus sign. These data were corrected for $\alpha_1 - \alpha_2$ splitting at high 2θ values and then converted to a set of structure amplitudes by standard means.

Structure Analysis.—A sharpened three-dimensional Patterson function with the origin peak removed was calculated. The Ga ··· Ga vectors could not be located with all eight

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gallium atoms in general positions. However, when they were in two sets of four-fold positions, two possible values for the z parameters could be deduced: the first did not lead to a reasonable solution but the second easily led to a trial structure. After a Fourier synthesis based on phases computed from all the atoms, R was 0·185. After 6 cycles of full-matrix least-squares refinement with individual isotropic thermal parameters, R was 0·122 and after 4 cycles with anisotropic thermal parameters, 0·062.

A difference Fourier synthesis indicated positions for all eight hydrogen atoms. The hydrogen-atom contributions were included in the structure-factor calculation with isotropic thermal parameters but their parameters were not refined. Four additional least-squares cycles reduced R to 0·052 and since the shifts were small (largest $<\sigma/50$), the refinement was considered complete.

TABLE 1

Final positional and thermal parameters ($\times 10^{+4}$) * with estimated standard deviations in parentheses for $[GaCl_2(bipy)_2]^+[GaCl_4]^-$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ga(1)	$\frac{1}{4}$ †	$\frac{3}{4}$ †	2360(1)	30(1)	44(1)	50(1)	8(1)	0 †	0 †
Ga(2)	$\frac{3}{4}$ †	$\frac{3}{4}$ †	4064(1)	48(1)	75(1)	65(1)	38(1)	0 †	0 †
Cl(1)	6563(1)	1721(1)	1256(2)	48(1)	63(1)	63(1)	5(1)	−34(1)	−11(1)
Cl(2)	6930(1)	6246(2)	4982(2)	75(1)	137(2)	109(1)	65(2)	57(2)	119(3)
Cl(3)	8523(1)	6759(1)	3161(1)	58(1)	75(1)	81(1)	39(1)	27(1)	−5(2)
N(1)	8302(2)	1134(3)	2538(3)	35(2)	49(3)	58(2)	19(3)	6(3)	12(4)
N(2)	8383(2)	2955(2)	3503(3)	32(2)	58(3)	51(2)	−2(3)	0(3)	−2(4)
C(12)	9019(3)	1255(4)	3128(4)	28(2)	67(3)	64(3)	12(4)	12(4)	40(5)
C(13)	9652(4)	442(5)	3211(5)	39(2)	88(4)	89(4)	34(5)	8(5)	41(7)
C(14)	9525(5)	−497(5)	2696(5)	67(4)	76(4)	102(5)	65(7)	39(7)	45(8)
C(15)	8775(4)	−622(4)	2118(5)	67(3)	66(4)	78(4)	44(6)	38(6)	14(6)
C(16)	8176(4)	219(4)	2044(4)	54(3)	51(3)	64(3)	26(5)	10(5)	−2(5)
C(22)	9070(3)	2272(4)	3675(4)	32(2)	74(4)	52(3)	−12(4)	2(4)	33(5)
C(23)	9740(4)	2507(5)	4354(5)	38(2)	97(5)	81(4)	−36(5)	−26(5)	48(7)
C(24)	9672(4)	3470(6)	4866(5)	64(4)	123(6)	69(4)	−93(8)	−46(6)	52(8)
C(25)	8987(4)	4154(5)	4702(4)	65(3)	89(5)	60(3)	−63(7)	−12(5)	6(6)
C(26)	8358(4)	3880(4)	4009(4)	46(2)	68(4)	69(3)	−21(5)	4(5)	−18(6)

* The temperature factor for an atom is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. † Value required by space group symmetry.

The quantity $\Sigma w(F_o - F_c)^2$ was minimized in the least-squares calculations. The weighting scheme used was $\sqrt{w} = F_o/8.5$ if $F_o < 8.5$, $\sqrt{w} = 1$ if $8.5 \leq F_o \leq 25.7$, and $\sqrt{w} = 25.7/F_o$ if $F_o > 25.7$. The scattering factors were taken from ref. 7, with the gallium atom being corrected for the real part of the anomalous dispersion.[8] The final positional and thermal parameters for the non-hydrogen atoms are given in Table 1, and the hydrogen-atom parameters in Table 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20253 (4 pp., 1 microfiche).*

TABLE 2

Probable hydrogen-atom positions. The hydrogen atom is given followed by the atom to which it is bonded, the position parameters $\times 10^3$, the isotropic thermal parameter used in the calculation, and the corresponding C–H distance

Atom	x	y	z	B	C–H (Å)
H(13)–C(13)	1028	54	358	5·43	1·06
H(14)–C(14)	989	−116	289	6·23	1·02
H(15)–C(15)	854	−136	177	5·58	1·10
H(16)–C(16)	756	18	166	4·54	1·06
H(23)–C(23)	1026	207	457	5·20	0·99
H(24)–C(24)	1022	360	530	5·98	1·02
H(25)–C(25)	895	503	509	5·85	1·22
H(26)–C(26)	786	444	385	4·76	1·05

DISCUSSION

The crystal consists of dichlorobis-(2,2′-bipyridyl)-gallium(III) cations and tetrachlorogallate(III) anions separated by normal van der Waals forces. Both ions lie on two-fold axes and the molecular packing and atomic numbering are illustrated in Figure 1. An ORTEP drawing of the individual ions showing the atomic numbering and the vibration ellipsoids is given in Figure 2.

The cation *cis*-$[GaCl_2(bipy)_2]^+$ has C_2 symmetry as required by the space-group. The *cis*-configuration was unexpected since the i.r. spectra had been interpreted[3,4] in terms of a *trans*-configuration. The *trans*-configuration was assigned because only one Ga–Cl frequency was observed in the far-i.r., illustrating the danger of determining structures on the basis of missing frequencies. Subsequently, the existence of *trans*-bipyridyl or *o*-phenanthroline configurations has been challenged[9] on the basis of steric hindrance. Unfortunately insufficient structural data are available at present to support or refute these arguments.

The distances and angles in the bipyridyl group (Table 3) are in agreement with those found in other bipy complexes[10] and in bipy itself.[11] The two rings are planar (Table 4) but twisted by 5° 52′ about the C(12)–C(22) bond between the two rings. A similar twist has been observed in other bipy complexes. In bipy the molecule is planar but the nitrogen atoms are

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* For details of Supplementary Publications, see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

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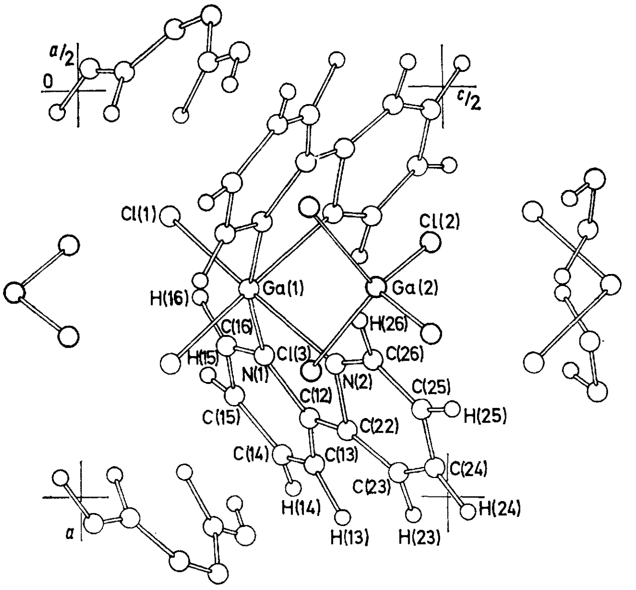

FIGURE 1 A projection of the structure on 010 illustrating the molecular packing and atomic numbering

TABLE 3

Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for $[GaCl_2(bipy)_2]^+[GaCl_4]^-$

(*a*) In $[GaCl_2(bipy)_2]^+$			
(i) Distances			
N(1)–C(12)	1·343(6)	N(2)–C(22)	1·351(6)
C(12)–C(13)	1·389(7)	C(22)–C(23)	1·390(7)
C(13)–C(14)	1·376(9)	C(23)–C(24)	1·390(10)
C(14)–C(15)	1·373(9)	C(24)–C(25)	1·349(9)
C(15)–C(16)	1·380(8)	C(25)–C(26)	1·371(8)
C(16)–N(1)	1·335(6)	C(26)–N(2)	1·342(7)
Ga(1)–N(1)	2·095(4)	Ga(1)–N(2)	2·111(4)
Ga(1)–Cl(1)	2·265(1)	C(12)–C(22)	1·471(7)
(ii) Angles			
Ga(1)–N(1)–C(12)	115·5(3)	Ga(1)–N(2)–C(22)	115·4(3)
Ga(1)–N(1)–C(16)	123·8(3)	Ga(1)–N(2)–C(26)	126·1(3)
C(12)–N(1)–C(16)	120·5(4)	C(22)–N(2)–C(26)	118·4(4)
N(1)–C(12)–C(13)	120·4(4)	N(2)–C(22)–C(23)	121·7(5)
C(12)–C(13)–C(14)	119·1(5)	C(22)–C(23)–C(24)	117·5(5)
C(13)–C(14)–C(15)	119·8(6)	C(23)–C(24)–C(25)	121·2(6)
C(14)–C(15)–C(16)	118·7(6)	C(24)–C(25)–C(26)	118·2(6)
C(15)–C(16)–N(1)	121·4(5)	C(25)–C(26)–N(2)	123·0(5)
Cl(1)–Ga(1)–N(1)	94·5(1)	N(1)–Ga(1)–N(1′)	166·8(1)
Cl(1)–Ga(1)–N(2)	169·9(1)	N(1)–Ga(1)–N(2′)	93·0(1)
Cl(1)–Ga(1)–Cl(1′)	97·3(1)	N(1)–C(12)–C(22)	116·0(4)
Cl(1)–Ga(1)–N(1′)	94·2(1)	C(13)–C(12)–C(22)	123·6(4)
Cl(1)–Ga(1)–N(2′)	89·2(1)	N(2)–C(22)–C(12)	114·7(4)
N(1)–Ga(1)–N(2)	77·2(1)	C(12)–C(22)–C(23)	123·6(5)
C(12)–C(13)–H(13)	123	C(22)–C(23)–H(23)	130
C(14)–C(13)–H(13)	117	C(24)–C(23)–H(23)	113
C(13)–C(14)–H(14)	119	C(23)–C(24)–H(24)	112
C(15)–C(14)–H(14)	119	C(25)–C(24)–H(24)	127
C(14)–C(15)–H(15)	127	C(24)–C(25)–H(25)	123
C(16)–C(15)–H(15)	114	C(26)–C(25)–H(25)	119
C(15)–C(16)–H(16)	124	C(25)–C(26)–H(26)	118
N(1)–C(16)–H(16)	114	N(2)–C(26)–H(26)	119
(*b*) In $[GaCl_4]^-$			
(i) Distances			
Ga(2)–Cl(2)	2·171(2)	Ga(2)–Cl(3)	2·162(2)
(ii) Angles			
Cl(2)–Ga(2)–Cl(3)	107·0(1)	Cl(2)–Ga(2)–Cl(3′)	110·9(1)
Cl(2)–Ga(2)–Cl(2′)	110·0(1)	Cl(3)–Ga(2)–Cl(3′)	111·0(1)

trans rather than *cis*, as required by complex formation. The hydrogen atom H(13) is bent out of the plane of the ring [N(1)—C(16)] away from H(23) which lies approximately in the plane of the second ring [N(2)—C(26)].

TABLE 4

Least-squares planes. The deviations from the plane (Å) are given for the specified atom

(*a*) Deviation from plane

Atom	(I)	(II)	(III)
N(1)	0·029 *	0·008 *	−0·157
C(12)	0·054 *	−0·011 *	−0·088
C(13)	0·047 *	0·003 *	−0·119
C(14)	−0·014 *	0·009 *	−0·250
C(15)	−0·079 *	−0·012 *	−0·360
C(16)	−0·041 *	0·003 *	−0·295
N(2)	0·052 *	−0·093	−0·003 *
C(22)	0·063 *	−0·072	−0·004 *
C(23)	0·021 *	−0·166	0·007 *
C(24)	−0·055 *	−0·306	−0·002 *
C(25)	−0·072 *	−0·333	−0·005 *
C(26)	−0·004 *	−0·212	0·008 *
H(13)	0·218	0·141	0·085
H(14)	−0·264	−0·226	−0·517
H(15)	−0·294	−0·173	−0·630
H(16)	−0·150	−0·075	−0·433
H(23)	−0·013	−0·200	−0·030
H(24)	0·003	−0·283	0·092
H(25)	−0·045	−0·362	0·080
H(26)	0·057	−0·159	0·080

(*b*) Parameters for plane †

	(I)	(II)	(III)
A	0·5241	0·5094	0·5363
B	0·4120	0·3748	0·4509
C	−0·7454	−0·7746	−0·7134
D	4·471	4·147	4·974
Atoms in plane	N(1)—C(26)	N(1)—C(16)	N(2)—C(26)

* Atom used to define the plane. † Equation of the plane in the form $AX + BY + CZ = D$ where XYZ are the orthogonal co-ordinates (in Å) relative to *a*, *b*, and *c*.

However, the C(22)–C(23)–H(23) (130°) is much larger than the corresponding C(12)–C(13)–H(13) angle (123°). These observations suggest that steric repulsions between H(13) and H(23) are reduced by a combination of out-of-plane [H(13)] and in-plane bending [H(23)].

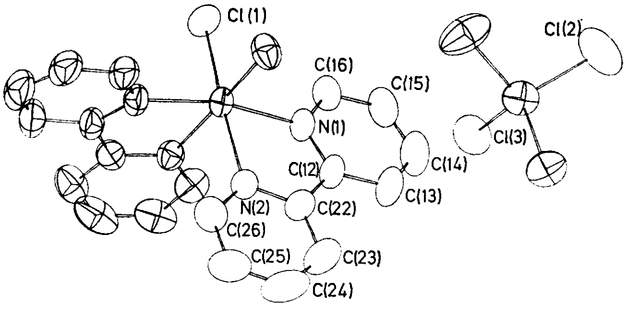

FIGURE 2 An ORTEP drawing of the $[GaCl_2(bipy)_2]^+$ cation and $[GaCl_4]^-$ anion showing the atomic numbering and vibration ellipsoids. The central Ga atom in each ion has not been labelled for clarity. Both ions have C_2 symmetry as required by the space group

The two Ga–N bonds in the cation appear to be significantly different (t_0 2·82) [12] although no chemically reasonable explanation is obvious. However, the N(2) atom [Ga–N(2) 2·111 Å] is *trans* to Cl(1) while N(1) is *trans* to N(1) related by the two-fold axis. In $GaCl_3$(terpy) (terpy = 2,2′,2″-terpyridyl) the outer Ga–N bonds (mutually *trans*) average 2·112 ± 0·006 Å; in (hydrogen ethylenediaminetetra-acetato)aquogallium(III) the Ga–N bonds are 2·182 ± 0·005 and 2·097 ± 0·006 Å, with the short bond opposite the water molecule.[13] Therefore, the Ga–N bond length appears to be dependent upon both the nature of the atom *trans* to the bond as well as the other atoms in the co-ordination sphere. However, the variation of the Ga–N distance in the compounds studied (2·097—2·112 Å) is small compared to the variation in the Ga–Cl distances (*vide infra*). An explanation for these observations may be premature because of the lack of data.

The Ga–Cl bond distance of 2·265 ± 0·001 Å found in the cation was the first measurement of a Ga–Cl bond in an octahedral gallium species. The values reported recently in $GaCl_3$(terpy) [13] of 2·235, 2·329, and 2·403 Å (all ±0·003 Å) show a wide range, with two of the bonds significantly longer than in $[Cl_2Ga(bipy)_2]^+$. The difference in the chlorine and nitrogen bond radius is *ca.* 0·29 Å * but the difference in the Ga–Cl and Ga–N distances is only 0·159 Å. This comparison suggests that either the Ga–N bond is longer than or the Ga–Cl bond is shorter than a single bond. The consistency of the Ga–N bond distance in the various molecules together with the change in Ga–Cl bonds suggests that the Ga–Cl bonds are shorter than a normal single bond. This conclusion may be premature since only three observations are involved in the comparison.

The two Ga–Cl distances in the anion appear to be significantly different (t_0 3·18) [12] although no reasonable explanation is possible. The value of 2·19 Å (no estimated standard deviation was given [14]) found in $Ga^+[GaCl_4]^-$ is probably not significantly different from the present value. The value reported for the terminal Ga–Cl bonds in Ga_2Cl_6 of 2·09 ± 0·02 Å [15] is significantly shorter but the shortening may be related to the presence of the long Ga–Cl bond of 2·29 ± 0·02 Å to the bridging chlorine atoms. The only other tetrahedral gallium species reported is $(Me)_3NGaH_3$ [16] where the Ga–N distance is 1·97 ± 0·09 Å. The relatively large estimated standard deviation of the Ga–N bond precludes any useful comparison. However, the difference between the Ga–N and Ga–Cl bond distances in the tetrahedral molecules is 0·20 Å, close to the difference of 0·16 Å observed in the octahedral cation $[GaCl_2(bipy)_2]^+$. A tetrahedral gallium species containing both Cl and N atoms would make a useful comparison with the two ions in the present study.

TABLE 5

Interatomic distances (Å)

$C(23) \cdots Cl(1^{I})$	3·374(6)	$H(25) \cdots C(24^{III})$	2·78
$C(24) \cdots Cl(1^{I})$	3·420(7)	$H(25) \cdots H(24^{III})$	2·17
$Cl(1) \cdots H(24^{II})$	2·85	$H(25) \cdots C(15^{III})$	2·86
$H(24) \cdots Cl(3^{III})$	2·84		

Roman numerals as superscripts denote the following equivalent positions relative to the reference molecule at x, y, z:

I $\frac{3}{2} - x, y, \frac{1}{2} + z$
II $\frac{3}{2} + x, -y, \frac{1}{2} - z$
III $2 - x, 1 - y, 1 - z$
IV $x, \frac{1}{2} - y, \frac{1}{2} + z$

All the intermolecular distances <4·0 Å were calculated and surveyed for any unusual interactions. Interatomic distances less than the appropriate sum of the radii [17] are tabulated in Table 5. None of the distances appear short enough to suggest any unusual intermolecular interactions, hence the packing appears normal.

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* The difference can be estimated by a comparison of C–Cl and C–N bond lengths in compounds where the bonds are expected to be single bonds.

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