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The Structure of *trans*-Dichlorotetrakis(pyridine)gallium(III) Tetrachlorogallate(III)

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Abstract. $[Ga(C_5H_5N)_4Cl_2][GaCl_4]$, $C_{20}H_{20}Cl_6Ga_2N_4$, orthorhombic, $Pna2_1$, $a = 18{\cdot}453$ (3), $b = 15{\cdot}070$ (2), $c = 9{\cdot}536$ (1) Å, $Z = 4$, $D_x = 1{\cdot}675$, $D_m = 1{\cdot}65$ Mg m^{-3}. The structure has been solved from 1637 diffractometer-measured intensities with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) and refined by full-matrix least-squares calculations to $R = 0{\cdot}056$. The crystal structure shows that the complex is *trans*-dichlorotetrakis(pyridine)gallium(III) tetrachlorogallate(III) $\{[trans\text{-}Cl_2Ga(C_5H_5N)_4]^+GaCl_4^-\}$, the first example of a *trans*-octahedral complex of Ga^{III}. The Raman spectrum of the complex has also been recorded and is discussed.

Introduction. There have been two recent crystal-structure determinations of gallium(III) chloride complexes containing 'octahedral' Ga. $GaCl_3$.bpy (bpy = 2,2′-bipyridyl) has been shown to be $[cis\text{-}Cl_2Ga(bpy)_2]^+GaCl_4^-$ (Restivo & Palenik, 1972) and $GaCl_3$.tpy (tpy = 2,2′,2″-terpyridyl) is molecular (Beran, Carty, Patel & Palenik, 1970). The variation in the Ga—Cl bond distances in the terpyridyl complex was interpreted in terms of a *trans* effect and this hypothesis was then used to explain the *cis* configuration observed in $[GaCl_2(bpy)_2]^+$.

The crystal structure of $GaCl_3$.(pyridine)$_2$ was investigated because an ionic structure appeared possible in view of the significant electrical conductance observed in the molten complex (Greenwood & Wade, 1958).

The complex was very susceptible to moisture and was prepared in all-glass apparatus *in vacuo* and subsequent manipulations were carried out in a nitrogen-filled drybox. An excess of dry pyridine was condensed on to pure gallium trichloride. Crystals were obtained from the pyridine solution. The density of selected crystals was determined by flotation in a 1,2-dibromoethane/benzene mixture. Raman spectra were recorded on solid samples using a Carey 81 spectrometer.

Using a single crystal sealed in a Lindemann-glass tube, the crystal data were obtained from Weissenberg photographs taken with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}542$ Å). Intensity measurements were made on the Stoe STADI-2 two-circle automatic diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). Layers $l = 0$ to 9 with the crystal set about c were measured. The crystal size was 0·9 × 0·3 × 0·2 mm. Absorption corrections ($\mu = 2{\cdot}55$ mm^{-1}) and scaling of data were carried out with the *SHELX* suite of programs (Sheldrick, 1976); after elimination of those for which $I < 3\sigma(I)$ there remained 1637 unique reflections. The same programs were used for all other

Table 1. *Fractional atomic coordinates* (×10^4), *equivalent isotropic thermal parameters for* Ga *and* Cl (×10^4) *and isotropic thermal parameters for* C *and* N (×10^3)

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}/U (Å^2)
Ga(1)	2013 (1)	676 (1)	6320 (–)	390
Ga(2)	4771 (1)	1938 (1)	1861 (3)	591
Cl(1)	2081 (2)	474 (3)	8715 (5)	481
Cl(2)	1888 (3)	882 (3)	3924 (5)	534
Cl(3)	5665 (3)	1451 (5)	3101 (8)	1036
Cl(4)	5177 (3)	2756 (4)	179 (8)	941
Cl(5)	4046 (3)	2675 (3)	3203 (6)	684
Cl(6)	4149 (3)	870 (3)	962 (7)	767
N(1)	2097 (7)	9298 (8)	5968 (14)	46 (3)
N(2)	3160 (6)	760 (8)	6194 (16)	43 (3)
N(3)	1986 (7)	2069 (8)	6663 (15)	48 (3)
N(4)	893 (6)	601 (8)	6498 (16)	45 (3)
C(1)	1661 (9)	8908 (11)	5065 (21)	49 (4)
C(2)	1744 (10)	7993 (12)	4799 (21)	58 (5)
C(3)	2273 (10)	7522 (12)	5466 (21)	60 (5)
C(4)	2730 (8)	7935 (11)	6459 (21)	54 (4)
C(5)	2624 (8)	8848 (10)	6711 (20)	49 (4)
C(6)	3521 (9)	1148 (11)	7201 (19)	50 (5)
C(7)	4266 (10)	1243 (12)	7127 (22)	60 (5)
C(8)	4614 (9)	881 (11)	6034 (21)	53 (5)
C(9)	4241 (10)	476 (12)	4985 (22)	56 (5)
C(10)	3501 (8)	429 (10)	5098 (20)	45 (4)
C(11)	2406 (10)	2563 (12)	5652 (20)	53 (5)
C(12)	2380 (11)	3516 (13)	5764 (22)	65 (6)
C(13)	1939 (10)	3881 (12)	6893 (24)	68 (5)
C(14)	1528 (10)	3369 (13)	7750 (24)	67 (6)
C(15)	1591 (9)	2422 (11)	7577 (21)	51 (4)
C(16)	451 (10)	1194 (12)	5920 (21)	60 (5)
C(17)	9676 (10)	1151 (12)	6055 (24)	66 (5)
C(18)	9353 (11)	453 (13)	6718 (26)	78 (6)
C(19)	9838 (11)	−162 (13)	7383 (24)	71 (6)
C(20)	592 (9)	−59 (11)	7259 (19)	50 (5)

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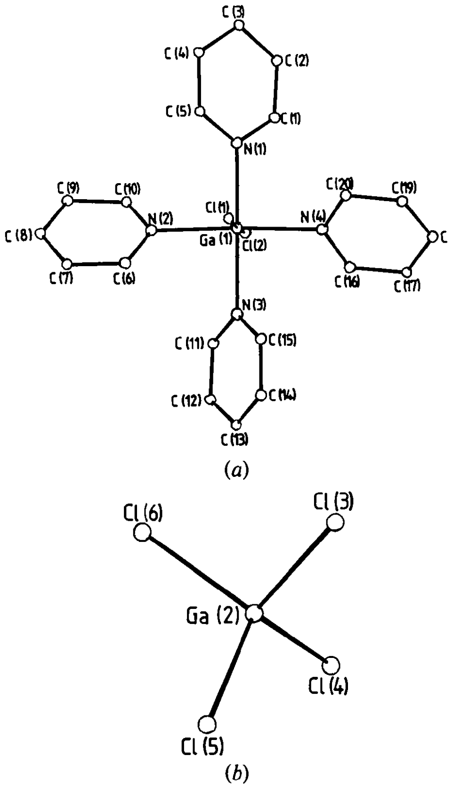
calculations. Ga atom positions obtained from Patterson maps were used to phase $(F_o - F_c)$ maps to give the positions of the remaining atoms (apart from H). Full-matrix least-squares refinement of all atomic positions, anisotropic U_{ij} values for Ga and Cl and isotropic U values for the remaining non-H atoms, were carried out until convergence was reached at R = 0·056. Throughout the refinement, z of Ga(1) was restrained at a constant value. As the space group is without a centre of symmetry, the enantiomorphous structure was also refined; the agreement was slightly worse (R = 0·059) although there were no significant changes of the structural parameters. Atomic scattering factors, including anomalous scattering, were those of Cromer & Mann (1968) and Cromer & Liberman (1970). Final coordinates and isotropic temperature factors are given in Table 1.*



(*a*)

(*b*)

Fig. 1. (*a*) $[Cl_2Ga(C_5H_5N)_4]^+$ ion. (*b*) $GaCl_4^-$ ion.

Table 2. *Bond distances* (Å) *and angles* (°) *around* Ga *atoms*

Ga(1)–Cl(1)	2·308 (5)	Ga(2)–Cl(3)	2·157 (7)
Ga(1)–Cl(2)	2·317 (5)	Ga(2)–Cl(4)	2·157 (6)
Ga(1)–N(1)	2·109 (13)	Ga(2)–Cl(5)	2·159 (5)
Ga(1)–N(2)	2·122 (11)	Ga(2)–Cl(6)	2·154 (5)
Ga(1)–N(3)	2·125 (12)		
Ga(1)–N(4)	2·074 (12)		
Cl(1)–Ga(1)–N(1)	91·3 (4)	Cl(2)–Ga(1)–N(4)	89·4 (4)
Cl(1)–Ga(1)–N(2)	90·5 (4)	N(3)–Ga(1)–N(4)	91·1 (5)
Cl(1)–Ga(1)–N(3)	88·8 (4)	N(2)–Ga(1)–N(3)	88·4 (5)
Cl(1)–Ga(1)–N(4)	88·1 (4)	N(2)–Ga(1)–N(4)	178·5 (6)
N(1)–Ga(1)–N(2)	88·6 (5)	Cl(3)–Ga(2)–Cl(4)	109·7 (3)
N(1)–Ga(1)–N(4)	91·9 (5)	Cl(3)–Ga(2)–Cl(5)	108·9 (3)
N(1)–Ga(1)–N(3)	177·1 (5)	Cl(4)–Ga(2)–Cl(5)	111·2 (2)
Cl(1)–Ga(1)–Cl(2)	177·5 (2)	Cl(4)–Ga(2)–Cl(6)	108·4 (2)
Cl(2)–Ga(1)–N(1)	89·0 (4)	Cl(3)–Ga(2)–Cl(6)	111·8 (3)
Cl(2)–Ga(1)–N(2)	92·0 (4)	Cl(6)–Ga(2)–Cl(5)	106·9 (2)
Cl(2)–Ga(1)–N(3)	91·0 (4)		

Discussion. The ions $[GaCl_2(C_5H_5N)_4]^+$ and $GaCl_4^-$ (Fig. 1) may be identified; the distances and angles around Ga are given in Table 2. The cation is approximately octahedral with the Cl atoms in *trans* positions. Ga—Cl distances (Å) in the cation [2·308 (5), 2·317 (5)] are, as expected, larger than those observed in the *cis* bipyridyl complex [2·265 (1)] and comparable with one of the *trans* distances [2·329 (3)] observed in the terpyridyl complex. The Ga—Cl distances in the $GaCl_4^-$ ion (approximately tetrahedral) have the expected values. The torsion angles listed in Table 3 show that the pyridine molecules are all twisted to give a propeller-type ion.

This pyridine complex is the first octahedral complex with *trans* geometry to be reported. It is able to adopt the expected *trans* geometry because α-hydrogen repulsions between pyridine rings have been minimized by ring twisting. A consideration of the *trans* effect (Beran *et al.*, 1970) would have predicted *cis* geometry. It now appears probable that the *cis* geometry adopted in $[GaCl_2(bpy)_2]^+$ (Restivo & Palenik, 1972) is due to other effects, the most likely being steric hindrance between α-hydrogens of *trans* bipyridyl ligands.

The Raman spectrum of the solid is given in Table 4. The four bands due to the anion (378, 347, 153, 120 cm^{-1}) are readily seen. The *trans* octahedral cation is expected to give Ga—N stretching modes (A_{1g} and B_{1g}) (Nakamoto, 1977) and these are assigned to the 263 and 248 bands. These were confirmed by recording the Raman spectrum of the deutero-pyridine complex where shifts of −7 cm^{-1} were observed for these bands. A strong band due to the Ga—Cl stretching modes

Table 3. *Torsion angles* (°) (*average e.s.d.* 0·7°)

Cl(1)–Ga(1)–N(1)–C(1)	134·8	Cl(1)–Ga(1)–N(2)–C(10)	144·3
Cl(1)–Ga(1)–N(3)–C(11)	138·9	Cl(2)–Ga(1)–N(4)–C(16)	130·9
Cl(2)–Ga(1)–N(1)–C(5)	136·8	Cl(2)–Ga(1)–N(2)–C(6)	143·4
Cl(2)–Ga(1)–N(3)–C(15)	133·6	Cl(2)–Ga(1)–N(4)–C(20)	133·0

Table 4. *Raman spectrum of* $[GaCl_3.2C_5H_5N]_2$ (cm^{-1})

378*m*	347*vs*	263*s*	248*m*	196*s*	153*s*	120*s*

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* Lists of structure factors, bond distances and angles not involving Ga and anisotropic U_{ij} have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35862 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(A_{1g}) is also expected to be observed in the Raman spectrum. There is only one other band observed in the spectrum at 194 cm^{-1}. This appears rather low for an octahedral Ga—Cl stretching vibration but in the absence of any strong band we tentatively ascribe it to this mode.

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Diethylenetriammonium Tetrachloromanganate(II) Chloride

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Abstract. $[(NH_3CH_2CH_2)_2NH_2Cl]MnCl_4$, $C_4H_{16}N_3^{3+}.Cl^-.MnCl_4^{2-}$, orthorhombic, *Pnma*, $a = 7{\cdot}116\ (1)$, $b = 24{\cdot}629\ (6)$, $c = 7{\cdot}201\ (2)$ Å, $Z = 4$, $D_c = 1{\cdot}78$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å. Final $R = 0{\cdot}051$ for a total of 1794 independent reflections. The compound is isostructural with the analogous Cu^{II} salt [Ferguson & Zaslow (1971). *Acta Cryst.* B**27**, 849–852; Greenhough & Ladd (1977). *Acta Cryst.* B**33**, 1266–1269] consisting of a laminar network of corner-sharing $MnCl_6$ octahedra. The bridging Mn—Cl distances are 2·5681 (5) and 2·5749 (6) Å while the terminal Mn—Cl distance is significantly shorter at 2·4978 (4) Å. The terminal NH_3^+ moieties hydrogen bond to chloride ions in the laminar network, while the NH_2^+ moiety hydrogen bonds to the lattice chloride ion.

Introduction. Crystals of $[(NH_3CH_2CH_2)_2NH_2Cl]$-$MnCl_4$ grow as flat pink plates from ethanolic solutions of equimolar mixtures of the ammonium chloride salt and $MnCl_4.4H_2O$.

Weissenberg and precession photographs exhibited *mmm* symmetry with systematic absences $0kl$, $k + l = 2n + 1$ and $hk0$, $h = 2n + 1$, indicating the space group *Pnma*. A crystal approximately $0{\cdot}055 \times 0{\cdot}037 \times 0{\cdot}118$ mm was selected and data were collected on a Picker diffractometer using a θ–2θ scan technique with Zr-filtered Mo $K\alpha$ radiation. A scan range of 1·6° with 0·05°/step and 3 s/step was used with 30 s background measurements before and after each scan. A total of 1794 independent reflections were measured at room temperature. Absorption corrections were applied ($\mu = 2{\cdot}106\ \text{mm}^{-1}$) with transmission factors ranging from 0·35 to 0·48. The unit-cell size and probable space group (*Pnma*) matched closely the Cu analog. Refinement was initiated using the coordinates from the structure of the Cu analog and rapidly converged. H atoms were found on a difference density map and included in the final refinement. A value of $R_1(=\sum||F_o| - |F_c||/\sum|F_o|) = 0{\cdot}051$ ($0{\cdot}038$ for $|F| > 3\sigma$) was obtained and $R_3\{=[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}\} = 0{\cdot}044$ where $w = 1/\sigma^2$ with $\sigma^2(I) = TC + 2{\cdot}56\ BK + (0{\cdot}04)^2I^2$ where TC = total counts, BK = total background counts, and $I = TC - 1{\cdot}6BK$. The standard error of an observation of unit weight was 1·34. Final parameters are listed in Table 1 and pertinent distances and angles are given in Table 2.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35947 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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