# Crystal and Molecular Structure of Trichloro(2,5,8-trioxanonane)-titanium(III)

By **Michael G. B. Drew** * and **Jennifer A. Hutton**, Department of Chemistry, The University, Whiteknights, Reading RG6 2AD

Crystals of the title compound are orthorhombic, $a = 11.38(1)$, $b = 28.77(3)$, $c = 7.125(10)$ Å, space group $Pbn2_1$ with $Z = 8$. 1 094 Above-background reflections collected on a diffractometer have been refined by full-matrix least squares to $R$ 0.062. There are two molecules in the asymmetric unit. In both, the titanium(III) atoms are six-co-ordinate with a *fac* arrangement of ligands. The metals are bonded to three chlorine atoms [2.31(1)—2.35(1) Å] and to three oxygen atoms of the trioxanonane ligand [2.115(13)—2.182(13) Å]. The ligand conformation is different in the two molecules, being $\delta\delta$ in one and $\delta\lambda$ in the other.

COMPOUNDS of titanium(III) are rarely studied and only a few structures have been determined. Among the six-co-ordinate molecules are [Ti(urea)$_6$]$^{3+}$,[1] [TiCl$_2$(HOPr$^i$)$_4$]$^+$,[2] [TiCl$_3$(py)$_3$]·py (py = pyridine),[3] and [TiCl$_3$(Me$_2$dpma)] {Me$_2$dpma = *NN*-bis[(6-methyl-2-pyridyl)methyl]amine}.[4] In the latter two molecules the ligand arrangement is predictably *mer*, because a *fac* arrangement in [TiCl$_3$(py)$_3$] would lead to close contacts between pyridine rings and in [TiCl$_3$(Me$_2$dpma)] the tridentate ligand is too rigid. With a more saturated tridentate ligand the *fac* arrangement was considered more likely. Accordingly, when crystals of [TiCl$_3$(diglyme)] (diglyme = 2,5,8-trioxanonane) were prepared it was decided to carry out a crystal-structure determination to see whether the ligands were *mer* or *fac* and also to study the conformations of the diglyme ligands.

## EXPERIMENTAL

During a study of the reactions between TiCl$_3$ and the benzoic acid–benzoic anhydride system [5] the tridentate ether diglyme O(CH$_2$CH$_2$OMe)$_2$ was used as a high-boiling point solvent. Thus TiCl$_3$ (1.5 g), benzoic acid (2 g), and benzoic anhydride (2 g) in dry diglyme (20 cm$^3$) were heated under reflux (5 h) *in vacuo* and a dark brown suspension was obtained. On cooling overnight under a nitrogen atmosphere, extremely air- and moisture-sensitive needles of [TiCl$_3$(diglyme)] separated out. These were filtered off, pumped dry, and loaded into thin capillaries under nitrogen for *X*-ray examination. Attempts to obtain the adduct from neat diglyme and TiCl$_3$ were unsuccessful, the preparation yielding a mixture of oxidation products (Found: C, 25.2; H, 4.90; Cl, 36.1; Ti, 16.3. C$_6$H$_{14}$Cl$_3$O$_3$Ti requires C, 25.0; H, 4.90; Cl, 36.85; Ti, 16.6%).

*Crystal Data.*—C$_6$H$_{14}$Cl$_3$O$_3$Ti, $M = 288.4$, Orthorhombic, $a = 11.38(1)$, $b = 28.77(3)$, $c = 7.125(10)$ Å, $U = 2\,340.9$ Å$^3$, $D_c = 1.64$, $Z = 8$, $D_m = 1.61(3)$, $F(000) = 1\,176$, Mo-$K_\alpha$ radiation, $\lambda = 0.710\,7$ Å, $\mu$(Mo-$K_\alpha$) = 13.9 cm$^{-1}$, space group $Pbn2_1$ (no. 33) from systematic absences $h0l$ where $h + l = 2n + 1$ and $0kl$ where $k = 2n + 1$ and the successful structure determination.

A crystal of dimensions 1.25 × 0.25 × 0.05 mm was mounted with the $a$ axis parallel to the instrument axis of a General Electric XRD5 apparatus which was used to measure diffraction intensities and cell dimensions. The diffractometer was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. The stationary-crystal–stationary-counter method was used with a 4° take-off angle and a counting time of 10 s. 1 204 Independent reflections were measured with $2\theta < 40°$ of which 1 094 with $I > \sigma(I)$ were used in the subsequent calculations. No crystal decay was observed during data measurement. Individual backgrounds were taken for those reflections whose counts were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of background as a function of $2\theta$. Absorption and extinction corrections were not applied.

*Structure Determination.*—The Patterson function indicated that the correct space group was $Pbn2_1$ with two independent titanium atoms in the asymmetric unit. Least-squares refinement verified this interpretation and Fourier syntheses revealed the positions of the remaining atoms. The structure was refined by full-matrix least squares. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of $F_o$ and $(\sin\theta)/\lambda$, was $w^{\frac{1}{2}} = 1$ for $F_o < 60$ and $w^{\frac{1}{2}} = 60/F_o$ for $F_o > 60$. Calculations were made on the CDC 7600 computer at the University of London Computer Centre using the 'Shel-X 76' system of programs.[6] Atomic scattering factors and dispersion corrections were taken from ref. 7. All the atoms except those of hydrogen were refined anisotropically. These were positioned in tetrahedral sites and given thermal parameters equivalent to those of the carbon atoms to which they were bonded, but their parameters were not refined. Two models were refined with opposite signs for all the co-ordinates but no significant difference between them was found and the set of co-ordinates with the lowest value for $R$ was chosen (0.062 2, 0.062 6). The final difference-Fourier map was featureless and in the final cycle of refinement all the shifts were $< 0.1\sigma$. The zero-weighted reflections showed no large discrepancies. Final positional parameters are listed in Table 1 and molecular dimensions in Table 2. Thermal parameters and structure factors are given in Supplementary Publication No. SUP 22283 (9 pp.).*

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[1] B. N. Figgis, L. G. B. Wadley, and J. Graham, *Acta Cryst.*, 1972, **B28**, 187.

[2] M. Hanlovic and F. Hanic, *J. Cryst. Mol. Struct.*, 1975, **4**, 327.

[3] M. G. B. Drew and R. K. Collins, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 975.

[4] R. K. Collins, M. G. B. Drew, and J. Rodgers, *J.C.S. Dalton*, 1972, 899.

[5] J. A. Hutton, Ph.D. Thesis, University of Reading, 1975.

[6] 'Shel-X 76' system of programs, G. M. Sheldrick, 1976.

[7] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

## DISCUSSION

The two molecules A and B in the asymmetric unit (Figures 1 and 2) are numbered identically. While the arrangement of ligands in both molecules is *fac*, their ring conformations differ considerably.

TABLE 1

Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Ti(A) | 2 317(3) | 0 516(1) | 0 000 * |
| Cl(1A) | 3 844(4) | 0 938(2) | 1 398(10) |
| Cl(2A) | 2 200(5) | −0 081(3) | 2 191(9) |
| Cl(3A) | 0 724(4) | 0 927(2) | 1 182(10) |
| O(1A) | 1 289(10) | 0 142(5) | −1 960(20) |
| O(2A) | 2 284(11) | 0 951(4) | −2 406(20) |
| O(3A) | 3 588(10) | 0 131(4) | −1 663(20) |
| C(21A) | 1 732(20) | 0 778(8) | −4 045(34) |
| C(22A) | 0 846(16) | 0 435(7) | −3 481(31) |
| C(23A) | 2 632(25) | 1 419(8) | −2 552(38) |
| C(31A) | 3 086(19) | −1 216(7) | −2 969(37) |
| C(32A) | 1 878(18) | −0 304(6) | −2 372(35) |
| C(33A) | 4 719(20) | 0 312(8) | −2 288(46) |
| Ti(B) | 2 489(3) | 3 018(1) | 0 731(7) |
| Cl(1B) | 4 455(5) | 3 256(2) | 0 702(12) |
| Cl(2B) | 1 518(6) | 3 664(2) | −0 433(12) |
| Cl(3B) | 2 486(5) | 2 638(2) | −2 191(9) |
| O(1B) | 0 912(11) | 2 717(5) | 1 754(22) |
| O(2B) | 2 990(11) | 2 362(4) | 2 040(21) |
| O(3B) | 2 274(11) | 3 285(4) | 3 492(21) |
| C(21B) | 2 067(15) | 2 028(4) | 2 515(35) |
| C(22B) | 0 977(16) | 2 212(6) | 1 480(27) |
| C(23B) | 4 019(18) | 2 263(8) | 3 164(35) |
| C(31B) | 1 067(19) | 3 315(7) | 4 034(35) |
| C(32B) | 0 523(20) | 2 849(8) | 3 615(36) |
| C(33B) | 2 951(21) | 3 664(8) | 4 357(38) |

* Fixed parameter.

The geometry of [M(L−L−L)$L_3$] molecules (L and L−L−L = uni- and tri-dentate ligands) has been recently discussed [8] and known examples are equally divided between *mer* and *fac* isomers. The choice between the two is primarily dependent on the design of the tridentate ligand. Indeed, of the four quoted [8] examples with *mer* geometry only one, namely [Rh{HN($CH_2CH_2NEt_2$)$_2$}($N_3$)$_3$],[9] is flexible enough to be able to adopt the alternative *fac* arrangement.

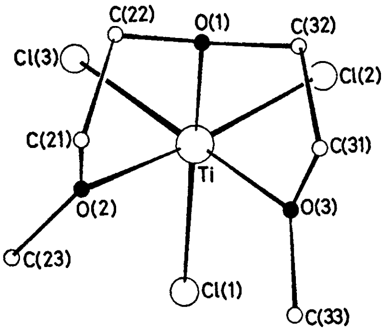

FIGURE 1 Molecule A

Examples with *fac* geometry are listed in Table 3. All the known examples of [$ML_3$(dien)] (dien = 3-azapentane-1,5-diamine) have this geometry although it is likely that the ligand is flexible enough to be *mer* if required, particularly as the tetramethyl-substituted ligand is *fac* in the afore-mentioned rhodium complex.[9] Additional evidence for the flexibility of dien in this regard is provided by work on [$CrCl_3$(dien)]. Two isomers have been reported [10] which are presumed to have the *mer* and *fac* geometries although only the latter has been characterised by an *X*-ray study.

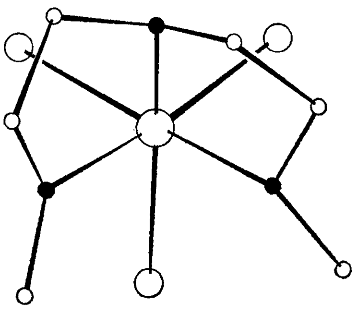

FIGURE 2 Molecule B

TABLE 2

Molecular dimensions (distances in Å, angles in °)

| | Molecule A | Molecule B |
|---|---|---|
| Ti−O(1) | 2.115(13) | 2.122(13) |
| Ti−O(2) | 2.123(14) | 2.182(13) |
| Ti−O(3) | 2.169(12) | 2.125(15) |
| Ti−Cl(1) | 2.343(6) | 2.340(6) |
| Ti−Cl(2) | 2.326(7) | 2.316(7) |
| Ti−Cl(3) | 2.323(6) | 2.352(7) |
| O(1)−C(22) | 1.46(2) | 1.47(2) |
| O(1)−C(32) | 1.47(2) | 1.45(2) |
| O(2)−C(21) | 1.42(2) | 1.46(2) |
| O(2)−C(23) | 1.41(2) | 1.45(2) |
| O(3)−C(31) | 1.48(2) | 1.43(2) |
| O(3)−C(33) | 1.46(2) | 1.47(2) |
| C(21)−C(22) | 1.47(3) | 1.54(3) |
| C(31)−C(32) | 1.46(3) | 1.51(3) |
| O(1)−Ti−O(2) | 75.9(5) | 73.8(5) |
| O(1)−Ti−O(3) | 75.6(5) | 74.5(6) |
| O(1)−Ti−Cl(1) | 162.6(4) | 158.6(5) |
| O(1)−Ti−Cl(2) | 92.0(4) | 92.7(4) |
| O(1)−Ti−Cl(3) | 93.8(4) | 96.5(4) |
| O(2)−Ti−O(3) | 82.8(6) | 87.0(5) |
| O(2)−Ti−Cl(1) | 92.9(4) | 90.4(4) |
| O(2)−Ti−Cl(2) | 167.6(4) | 166.5(4) |
| O(2)−Ti−Cl(3) | 88.8(4) | 88.7(4) |
| O(3)−Ti−Cl(1) | 90.0(4) | 90.7(4) |
| O(3)−Ti−Cl(2) | 91.5(4) | 89.2(4) |
| O(3)−Ti−Cl(3) | 167.8(4) | 170.8(4) |
| Cl(1)−Ti−Cl(2) | 98.0(2) | 102.6(3) |
| Cl(1)−Ti−Cl(3) | 99.2(2) | 97.4(3) |
| Cl(2)−Ti−Cl(3) | 95.0(2) | 93.2(3) |
| Ti−O(1)−C(22) | 112.8(11) | 108.4(10) |
| Ti−O(1)−C(32) | 108.8(11) | 117.7(13) |
| C(32)−O(1)−C(22) | 120.6(16) | 113.4(16) |
| Ti−O(2)−C(21) | 117.8(12) | 118.6(10) |
| Ti−O(2)−C(23) | 128.2(14) | 128.2(12) |
| C(21)−O(2)−C(23) | 113.5(17) | 108.9(14) |
| Ti−O(3)−C(31) | 115.5(11) | 112.5(13) |
| Ti−O(3)−C(33) | 125.1(12) | 126.6(13) |
| C(31)−O(3)−C(33) | 112.5(17) | 110.2(16) |
| O(1)−C(22)−C(21) | 110.8(16) | 108.6(14) |
| O(1)−C(32)−C(31) | 109.6(16) | 106.9(19) |
| O(2)−C(21)−C(22) | 108.4(19) | 104.0(14) |
| O(3)−C(31)−C(32) | 107.1(19) | 106.7(17) |

---

[8] M. C. Favas, D. L. Kepert, A. H. White, and A. C. Willis, *J.C.S. Dalton*, 1977, 1350.

[9] R. F. Ziolo, R. M. Shelby, R. H. Stanford, and H. B. Gray, *Cryst. Struct. Comm.*, 1974, **3**, 469.

[10] M. Konno, F. Marumo, and Y. Saito, *Acta Cryst.*, 1973, **B29**, 739.

The relative stability of the *fac* and *mer* isomers is difficult to assess but it was suggested [8] that for $R \leqslant 1$ ($R$ = M-L/M-$L_t$, $L_t$ being a donor atom in the tridentate ligand) and for normalised bites * of <1.3 the *fac* isomer is the more stable. However, there are not yet enough examples to be able to assess the validity of such calculations. In the present molecules $R$ is *ca.* 1.08, a value for which ref. 8 predicts little difference between *mer* and *fac* energies. Ref. 8 also predicts that in the *fac* geometry the unique L-M-L angle will be smaller than the other two and that there will be a significant difference in M-L bond lengths. (The calculation assumes $C_{2v}$ geometry in the co-ordination sphere.) Angle differences are found (Table 3) in all the molecules including [$TiCl_3$(diglyme)] where Cl(2)-Ti-Cl(3) is smaller [95.0(2) in A, 93.2(3)° in B] than the Cl(1)-Ti-Cl(3) and Cl(1)-Ti-Cl(2) angles in both molecules. However, none of the molecules in Table 3 shows any significant differences in M-L bond lengths as predicted by the potential-energy calculations.[8]

TABLE 3

Configuration of *fac*-[M(L-L-L)$L_3$] molecules

| Compound | Ref. | M-$L_t$/Å unique | M-$L_t$/Å others | L-M-L/° unique | L-M-L/° others | $L_t$-M-$L_c$/° unique | $L_t$-M-$L_c$/° others | Ring conformation |
|---|---|---|---|---|---|---|---|---|
| [$TiCl_3$(diglyme)] A | *a* | 2.115 | 2.15 | 95.0 | 98.6 | 83 | 76 | δδ |
| B | *a* | 2.122 | 2.15 | 93.2 | 100.0 | 87 | 74 | δλ |
| [Cr(dien)$Cl_3$] | 12 | 2.10 | 2.08 | 92.2 | 95.4 | 89.7 | 83.2 | δδ |
| [Zn{S($CH_2CO_2$)$_2$}($OH_2$)$_3$] | *b* | | | 85.1 | 98.1 | | | |
| [Cr(dien)$(CO)_3$] | 13 | 2.187 | 2.184 | 81.7 | 85.9 | 87.6 | 78.4 | δλ |
| [Mo(dien)$(CO)_3$] | *c* | 2.31 | 2.33 | 82.4 | 86.7 | 87.5 | 74.2 | δλ |
| [Mo(dien)$O_3$] | 11 | 2.33 | 2.32 | 105.3 | 106.8 | 80.0 | 73.1 | δδ |

[a] This work. [b] M. G. B. Drew, D. A. Rice, and C. W. Timewell, *J.C.S. Dalton*, 1975, 144. [c] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 314.

Table 3 also shows differences among $L_t$-M-$L_t$ angles although these are very much dependent on the ligand design. Thus in [$TiCl_3$(diglyme)] the unique angle O(2)-Ti-O(3) is considerably larger [82.8(6), 87.0(5)°] than the O(1)-Ti-O(3) and O(1)-Ti-O(2) angles [75.9(5) and 75.6(5) in A, 73.8(5) and 74.5(6)° in B]. A similar pattern is observed for the other molecules in Table 3. In [$TiCl_3$(diglyme)] the unique M-$L_t$ bond Ti-O(1) is shorter than the other two. However, this difference is not observed for all the other molecules in Table 3, distances being equivalent to within experimental error.

The two molecules A and B of [$TiCl_3$(diglyme)] have different ring conformations δδ and δλ respectively. This is apparent both from the torsion angles (Table 4) and Figures 1 and 2. The presence of both δδ and δλ conformations in the same unit cell implies that there is very little potential-energy difference between the two forms. This is also suggested for the analogous [$ML_3$(dien)] molecules for which there are two known examples of δδ and two of δλ conformations (Table 3). There are no examples of the λλ conformation among these [M(L-L-L)$L_3$] molecules although it has been observed in an [M(L-L-L)$_2$] molecule, namely *fac*-[Co(dien)$_2$]$^{2+}$.[10] There are also two molecules in the asymmetric unit for this molecule; in one both dien rings have the δλ configuration and in the other the λλ configuration; *fac* and *mer* isomers of [Co(dien)$_2$]$^{3+}$ are also known. It is hardly surprising, however, that the interaction of two dien ligands in [M(L-L-L)$_2$] might lead to different ring conformations from those found in [$ML_3$(L-L-L)] molecules.

Indeed molecular mechanics calculations for [$ML_3$(L-L-L)] molecules † show potential energies in the order δλ < δδ < λλ. In comparing the δλ and δδ forms, it is apparent that the most significant non-bonded contact is that between hydrogen atoms on C(21) and C(31) in the δδ form. In molecule A of [$TiCl_3$(diglyme)] these are 2.15 Å apart while in [Mo(dien)$O_3$],[11] which has crystallographically imposed $C_s$ symmetry, they are only 1.90 Å apart. This suggests that the reason for the large dis-

TABLE 4

Torsion angles (°) in molecules A and B compared to those in similar molecules

(*a*) Conformation of the two five-membered rings compared to those in [Cr(dien)$(CO)_3$] (2) and [Cr(dien)$Cl_3$] (3)

| | A | (3) | B | (2) |
|---|---|---|---|---|
| O(3)-Ti-O(1)-C(32) | 32.4 | 21.9 | 1.7 | 7.2 |
| O(1)-Ti-O(3)-C(31) | −8.5 | 2.8 | −29.0 | −27.3 |
| Ti-O(3)-C(31)-C(32) | −17.3 | −27.5 | 50.1 | 45.4 |
| O(1)-C(32)-C(31)-O(3) | 45.3 | 47.5 | −45.7 | −40.3 |
| Ti-O(1)-C(32)-C(31) | −54.0 | −44.1 | 23.4 | 14.8 |
| O(2)-Ti-O(1)-C(22) | −18.1 | −12.1 | −37.3 | −28.2 |
| O(1)-Ti-O(2)-C(21) | −5.0 | −11.9 | 13.1 | 3.4 |
| Ti-O(2)-C(21)-C(22) | 26.3 | 32.7 | 12.8 | 20.7 |
| O(2)-C(21)-C(22)-O(1) | −40.7 | −44.4 | −44.2 | −45.6 |
| C(21)-C(22)-O(1)-Ti | 38.2 | 33.8 | 57.9 | 48.5 |

(*b*) Conformation of diglyme

$$C(23)-O(2)\overset{a}{-}C(21)\overset{b}{-}C(22)\overset{c}{-}O(1)\overset{d}{-}C(32)\overset{e}{-}C(31)\overset{f}{-}O(3)-C(33)$$

Torsion angles around bonds *a*—*f*

| | *a* | *b* | *c* | *d* | *e* | *f* |
|---|---|---|---|---|---|---|
| A | −147.1 | −40.7 | −92.7 | 78.5 | 45.3 | −169.7 |
| B | 171.5 | −44.2 | −74.8 | 151.4 | −45.7 | −162.8 |
| [K(diglyme)]$^+$ | 177.8 | 64.4 | 177.0 | −177.0 | −64.4 | −177.8 |
| [K(diglyme)]$^+$ | 165.6 | 1.0 | 170.0 | −156.2 | −9.60 | −175.9 |
| [$HgCl_2$(tge)] * | −174 | 72 | 176 | −179 | −71 | −178 |
| [($HgCl_2$)$_2$(hge)] | −176 | −67 | −88 | −88 | −67 | −176 |
| [($HgCl_2$)$_2$(hge)] | 173 | 77 | −176 | −169 | −74 | 172 |

* The conformation in [$HgCl_2$(tgm)] (tgm = 2,5,8,11,14-pentaoxapentadecane) is very similar.[18]

---

* Defined [8] as ($L_t \cdots L_t$)/(M-$L_t$).

† In ref. 5 using the method of R. H. Boyd, *J. Chem. Phys.*, 1968, **49**, 2574.

[11] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, 1964, **3**, 397.

tortion from $C_s$ symmetry in molecule A {and in [Cr(dien)$Cl_3$] [12]} is so that this H · · · H contact is increased.

It is noticeable that despite the differences between diglyme and dien the ring conformations as described quantitatively by the torsion angles are very similar in both the δδ and δλ compounds. We have therefore included the torsion angles of [Cr(dien)$(CO)_3$] [13] and [Cr(dien)$Cl_3$] [12] in Table 4 to illustrate this point.

There are a number of compounds containing the diglyme ligand whose structures have been determined. There are two examples of $[K(diglyme)]^+$ cations [14,15] and the conformation of the ligands are compared with those in [$TiCl_3$(diglyme)] in Table 4. Also in this Table are torsion angles from the central C–O–C–C–O–C–C–O–C fragment in [$HgCl_2$(tge)] [16] (tge = 3,6,9,12,15-pentaoxaheptadecane) and from two such fragments in [$(HgCl_2)_2$(hge)] (hge = 3,6,9,12,15,18,21-heptaoxatricosane).[17] While clearly there are three very similar conformations exemplified by the first $[K(diglyme)]^+$, [$HgCl_2$(tge)], and [$(HgCl_2)_2$(hge)], the diverse conformations in the other fragments suggest that any order of stabilities (as in ref. 16) is speculative, particularly in a metal complex since these ligands can adopt many different conformations dependent on the stoicheiometry of the complete complex. The conformation of the central fragment in metal complexes of polyethylene oxides has also been discussed.[16-18]

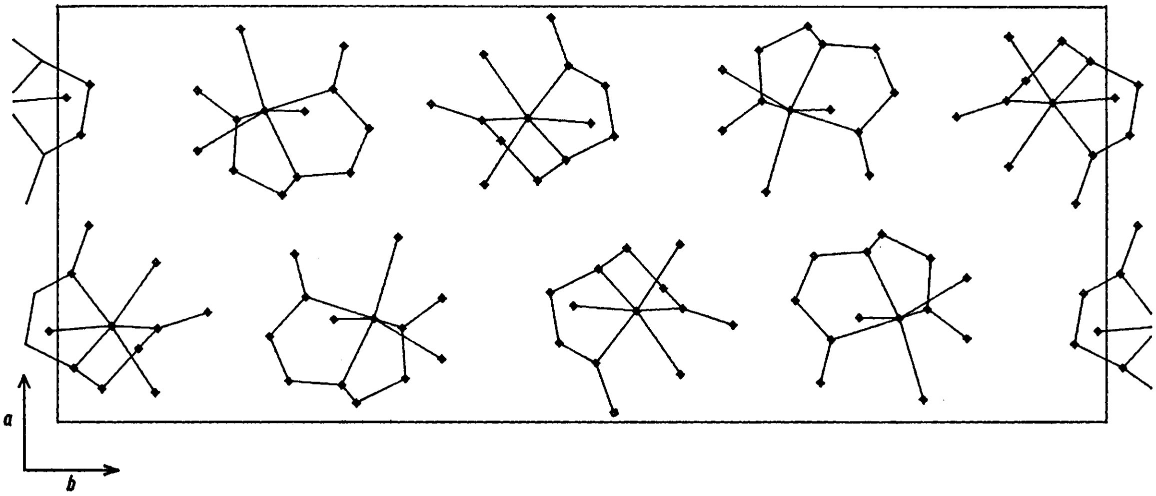

FIGURE 3 Unit cell in the *c* projection

Despite the differences in conformation there are no major differences in bond lengths and angles around the metal atom in the [$TiCl_3$(diglyme)] molecules. Ti–Cl and Ti–O bond lengths are comparable to those observed in other titanium(III) molecules.[1-4] There are no distances less than the sum of van der Waals contacts between molecules. The packing diagram in the *c* projection is shown in Figure 3.

We thank Professor G. W. A. Fowles for his interest in this work, and A. W. Johans for his assistance with the crystallographic investigations.

[7/2044 *Received, 21st November*, 1977]

---

[12] A. D. Fowlie, D. A. House, W. T. Robinson, and S. S. Rumball, *J. Chem. Soc.* (*A*), 1970, 803.

[13] F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, 1966, **5**, 1851.

[14] S. Z. Goldberg, K. N. Raymond, C. A. Harmon, and D. H. Templeton, *J. Amer. Chem. Soc.*, 1974, **96**, 1348.

[15] K. O. Hodgson and K. N. Raymond, *Inorg. Chem.*, 1972, **11**, 3030.

[16] R. Iwamoto, *Bull. Chem. Soc. Japan*, 1973, **46**, 1118.

[17] R. Iwamoto, *Bull. Chem. Soc. Japan*, 1973, **46**, 1123.

[18] R. Iwamoto, *Bull. Chem. Soc. Japan*, 1973, **46**, 1114.