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# Racemic *cis*-Dichlorobis(2,2,6,6-tetramethyl-3,5-heptanedionato)titanium(IV)

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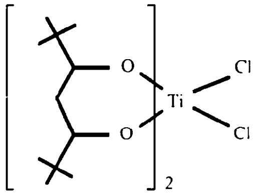
## Abstract

The title compound, [Ti($C_{11}H_{19}O_2$)$_2$Cl$_2$], has a *cis* configuration. The racemic compound crystallizes in space group $P2_1/c$ with two molecules in the asymmetric unit: the mean Ti—Cl distance is 2.266 (5) Å and the mean Ti—O distances are (*trans* to O) 1.919 (7) and (*trans* to Cl) 1.999 (9) Å.

## Comment

Pentane-2,4-dione ($CH_3COCH_2COCH_3$, Hacac) reacts with both titanium(IV) chloride and titanium(IV) alkoxides to yield neutral products [Ti(acac)$_2X_2$], where $X$ = Cl (Dilthey, 1904) or $X$ = O$R$ (Yamamoto & Kambara, 1957). NMR studies suggest that, in solution, these products and the analogous complexes derived from other 1,3-diketones are all octahedral, containing bidentate $O,O'$-chelating diketonate ligands with a *cis* arrangement of the two ligands $X$ (Fay & Lowry, 1967; Serpone & Fay, 1967; Bradley & Holloway, 1969). Structure analyses of the alkoxide complexes [Ti(acac)$_2${OC$_6$H$_3$(CHMe$_2$)$_2$}$_2$] (Bird, Fraser & Lau, 1973), [Ti(PhCOCHCOCF$_3$)$_2$(OEt)$_2$] (Wang, Miao, Fan, Feng & Wang, 1990) and [Ti(PhCOCHCOCH$_3$)$_2$(OCMe$_3$)$_2$] (Schubert, Buhler & Hirle, 1992) have shown unambiguously that these complexes all adopt *cis* configurations in the solid state. However, no X-ray structure analysis of any complex of type [Ti(1,3-diketonate)$_2$Cl$_2$] has been reported; an attempted structure analysis of [Ti(acac)$_2$Cl$_2$] was thwarted by hydrolysis, and the compound actually studied was [Ti(acac)$_2$Cl]$_2$O (Watenpaugh & Caughlin, 1967), where the chloride and bridging oxide ligands occupy *cis* sites. The title compound [Ti(Me$_3$CCOCHCOCMe$_3$)$_2$Cl$_2$], (I), is much less susceptible to hydrolysis than [Ti(acac)$_2$Cl$_2$] and is thus more amenable to X-ray structure analysis. Moreover, the structure of (I) is of considerable interest since the analogous niobium(IV) complex [Nb(Me$_3$CCOCHCOCMe$_3$)$_2$Cl$_2$] was found to adopt the *trans* configuration (Cotton, Diebold & Roth, 1985).



(I)

Compound (I) crystallizes in the monoclinic space group $P2_1/c$, with two molecules in the asymmetric unit (Fig. 1). The Ti atoms are octahedrally coordinated forming the chromophore TiCl$_2$O$_4$ with the two Cl ligands *cis*, so that the molecules are chiral; the centrosymmetric space group accommodates the equal numbers of L and D enantiomers expected in a racemic product, and the asymmetric unit has been chosen to contain one complex of L and one complex of D helicity.

The bond angles around the Ti atom (Table 2) indicate significant distortion from the ideal octahedral geometry: in particular the *trans* O—Ti—O angles are 164.05 (13) and 163.44 (12)° in the two independent molecules, while the corresponding Cl—Ti—Cl angles are 96.97 (9) and 95.50 (6)°; the intraligand O—Ti—O angles range from 82.60 (12) to 83.03 (11)°, associated with O···O 'bites' in the range 2.588 (4)–2.597 (4) Å. The Ti—Cl distances all lie between the mean and lower quartile values for such bonds involving six-coordinate Ti$^{IV}$ (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989), although they are longer than the bonds in TiCl$_4$ [2.170 (2) Å] (Morino & Uehara, 1966). However, the Ti—O bonds show significant differences between those *trans* to oxygen [mean value 1.919 (7) Å] and those *trans* to chlorine [mean value 1.999 (9) Å]; the bonds *trans* to oxygen are much shorter than the lower quartile value of 1.941 Å (Orpen *et al.*, 1989). A comparable difference was observed in the alkoxide complex [Ti(PhCOCHCOCH$_3$)$_2$(OCMe$_3$)$_2$] (Schubert *et al.*, 1992) where the Ti—O distances involving the diketonate ligand have a mean value of 2.001 (6) Å when *trans* to another diketonate oxygen, but a mean value of 2.086 (6) Å when *trans* to an alkoxide oxygen. Similarly, in the bridged oxo complex $[Ti(acac)_2O]_2$ (Smith, Caughlan & Campbell, 1972), the diketonate Ti—O bonds *trans* to another diketonate oxygen are much shorter [1.971 (4) Å] than those *trans* to a $\mu_2$-oxo ligand. The higher *p*-donor capacity of the *trans* ligands chloride, oxide and alkoxide oxygen compared with diketonate oxygen may account for these differences (Huffman, Molay, Marsella & Caulton, 1980).

It is of interest to compare the structure of compound (I) with that of the niobium analogue $[Nb(Me_3CCOCHCOCMe_3)_2Cl_2]$ (Cotton *et al.*, 1985). The niobium complex crystallizes in two forms, orthorhombic and monoclinic, but in both polymorphs the configuration is *trans*. In the monoclinic form the complex is centrosymmetric, with almost perfect $D_{2h}$ (*mmm*) molecular symmetry; however, the mean distances and angles in the orthorhombic polymorph are virtually identical to those of the monoclinic polymorph, so that comparison may be restricted to the monoclinic form. In the Nb complex, all Nb—O bonds are *trans* to another diketonate oxygen, and are thus expected to be only a little weakened by *trans* influences: accordingly, although the Nb—O bonds [1.983 (4) Å] are longer than the mean Ti—O distance in (I), they are actually shorter than the Ti—O bonds *trans* to oxygen. On the other hand, the Nb—Cl bonds are *trans* to another chloride ligand, and are expected to be weakened thereby: the Nb—Cl distance [2.410 (2) Å] is thus significantly longer than the Ti—Cl bonds in (I). The *trans* geometry of $[Nb(Me_3CCOCHCOCMe_3)_2Cl_2]$, compared with the *cis* geometry of (I), is possibly a consequence of higher crystal-field stabilization energy (CFSE) in the *trans* isomer than in the *cis* isomer of the $4d^1$ $Nb^{IV}$ complex; application of the angular overlap model (Schäffer, 1973; Larsen & La Mar, 1974) to the *cis* and *trans* isomers of a $d^1$ octahedral complex $MX_4Y_2$ shows that the *trans* isomer has the higher CFSE if the ligand *Y* (here chloride) is the better *p*-donor.

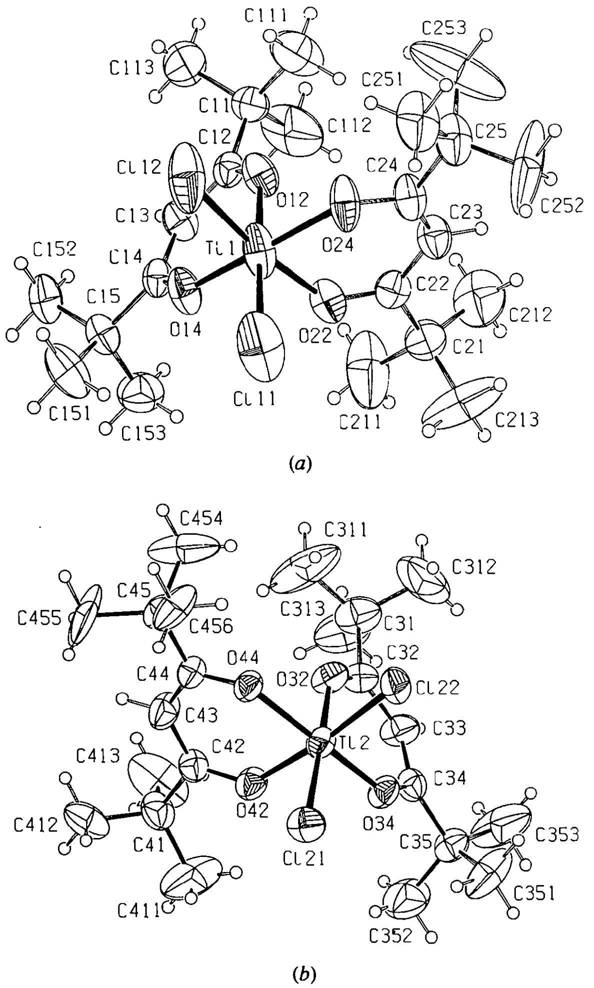


Fig. 1. Views (*a*) and (*b*) of the two independent molecules of (I) with the numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. In each molecule only one conformer is shown for the disordered *tert*-butyl groups.

Although $Ti^{IV}$ has the electronic configuration $3d^0$, complexes of type $[Ti(diketonate)_2X_2]$ are generally coloured. There are no features of the structure analysis reported here which support any mechanism other than ligand–metal charge transfer as the source of this colour. Such a mechanism is consistent with the colour variations in the series $[Ti(CF_3COCHCOCF_3)_2Cl_2]$ (yellow), $[Ti(acac)_2Cl_2]$ (orange) and $[Ti(Me_3CCOCHCOCMe_3)_2Cl_2]$ (orange–red), and the series $[Ti(acac)_2F_2]$ (yellow), $[Ti(acac)_2Cl_2]$ (orange) and $[Ti(acac)_2Br_2]$ (dark red) (Fay & Lowry, 1967).

## Experimental

Compound (I) was prepared by slow addition, under nitrogen, of titanium(IV) chloride to a threefold molar excess of 2,2,6,6-tetramethyl-3,5-heptanedione in sodium-dried toluene, followed by heating under reflux for 20 min. The solvent was removed under reduced pressure and orange–red crystals were grown by slow evaporation of a solution in toluene. Elemental analysis: found C 54.4, H 7.8%; $C_{22}H_{38}Cl_2O_4Ti$ requires C 54.4, H 7.9%. NMR ($CDCl_3$): $\delta_H$ 1.18 (*s*, 36H, $CH_3$), 6.17 p.p.m. (*s*, 2H, CH); $\delta_C$ 27.6 (*q*, $CH_3$), 40.7 (*s*, $CMe_3$), 99.0 (*d*, CH), 201.1 p.p.m. (*s*, CO).

*Crystal data*

$[Ti(C_{11}H_{19}O_2)_2Cl_2]$
$M_r = 485.32$
Monoclinic
$P2_1/c$
$a = 18.028\ (2)$ Å
$b = 18.173\ (3)$ Å
$c = 18.856\ (3)$ Å
$\beta = 113.985\ (11)°$
$V = 5644.1\ (14)$ Å$^3$

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 9.55–12.35°$
$\mu = 0.513$ mm$^{-1}$
$T = 294\ (1)$ K
Block cut from a larger crystal

$Z = 8$
$D_x = 1.142$ Mg m$^{-3}$
$D_m$ not measured

0.42 × 0.38 × 0.35 mm
Orange–red

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: three $\psi$ scans at 4° steps (North, Phillips & Mathews, 1968)
$T_{\min} = 0.752$, $T_{\max} = 0.858$
12645 measured reflections
12271 independent reflections

3897 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.026$
$\theta_{\max} = 26.9°$
$h = -23 \rightarrow 21$
$k = 0 \rightarrow 23$
$l = 0 \rightarrow 24$
3 standard reflections
frequency: 120 min
intensity decay: 3.8%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.0650$
$wR(F^2) = 0.2157$
$S = 0.884$
12271 reflections
639 parameters
H atoms riding [*SHELXL*93 (Sheldrick, 1993) defaults, C—H 0.93–0.96 Å]
$w = 1/[\sigma^2(F_o^2) + (0.1090P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.055$

$\Delta\rho_{\max} = 0.364$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.339$ e Å$^{-3}$
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0010 (2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| Ti1 | 0.70829 (6) | 0.23618 (4) | 0.21146 (7) | 0.1039 (3) |
| Cl11 | 0.69020 (12) | 0.31363 (9) | 0.11212 (14) | 0.1778 (8) |
| Cl12 | 0.82840 (9) | 0.28350 (10) | 0.29605 (14) | 0.1663 (8) |
| O12 | 0.7154 (2) | 0.1577 (2) | 0.2893 (2) | 0.0880 (9) |
| O14 | 0.7540 (2) | 0.1604 (2) | 0.1710 (2) | 0.0935 (9) |
| O22 | 0.6010 (2) | 0.1888 (2) | 0.1506 (2) | 0.0921 (9) |
| O24 | 0.6474 (2) | 0.28901 (15) | 0.2573 (2) | 0.1020 (11) |
| C11 | 0.72390 (7) | 0.04844 (7) | 0.36041 (9) | 0.0861 (14) |
| C12 | 0.73359 (11) | 0.08978 (10) | 0.29458 (9) | 0.0664 (11) |
| C13 | 0.7585 (3) | 0.0564 (2) | 0.2428 (2) | 0.0789 (13) |
| C14 | 0.77063 (12) | 0.09180 (13) | 0.18443 (12) | 0.0694 (11) |
| C15 | 0.79779 (9) | 0.05426 (9) | 0.12699 (11) | 0.0765 (12) |
| C111† | 0.7073 (2) | 0.10177 (12) | 0.41309 (12) | 0.152 (4) |
| C112 | 0.65428 (11) | −0.00469 (12) | 0.3279 (2) | 0.178 (6) |
| C113 | 0.80023 (11) | 0.00649 (14) | 0.40642 (15) | 0.204 (7) |
| C114 | 0.64121 (10) | 0.0629 (2) | 0.3589 (2) | 0.126 (7) |
| C115 | 0.7335 (3) | −0.03275 (8) | 0.3518 (2) | 0.110 (6) |
| C116 | 0.7873 (2) | 0.0736 (2) | 0.43699 (9) | 0.204 (14) |
| C151 | 0.83694 (15) | 0.10937 (13) | 0.0937 (2) | 0.131 (2) |
| C152 | 0.85788 (14) | −0.00552 (12) | 0.1670 (2) | 0.111 (2) |
| C153 | 0.72570 (13) | 0.0209 (2) | 0.06215 (13) | 0.116 (2) |
| C21 | 0.46672 (11) | 0.14217 (11) | 0.10032 (12) | 0.101 (2) |
| C22 | 0.53453 (13) | 0.18867 (12) | 0.15805 (13) | 0.0788 (13) |
| C23 | 0.5215 (3) | 0.2329 (2) | 0.2131 (3) | 0.0861 (14) |
| C24 | 0.57619 (11) | 0.28158 (9) | 0.25874 (10) | 0.0817 (13) |
| C25 | 0.56403 (7) | 0.33067 (8) | 0.31845 (9) | 0.105 (2) |
| C211 | 0.50200 (14) | 0.08048 (15) | 0.0710 (2) | 0.235 (5) |
| C212 | 0.4155 (2) | 0.1104 (2) | 0.1389 (2) | 0.164 (3) |
| C213 | 0.4140 (2) | 0.1890 (2) | 0.0330 (2) | 0.258 (6) |
| C251 | 0.62576 (11) | 0.39151 (11) | 0.3422 (2) | 0.144 (6) |
| C252 | 0.48042 (9) | 0.3637 (2) | 0.2844 (2) | 0.287 (14) |
| C253 | 0.5735 (2) | 0.2863 (2) | 0.38884 (12) | 0.295 (13) |
| C254 | 0.5715 (2) | 0.41006 (8) | 0.3001 (2) | 0.225 (9) |
| C255 | 0.48132 (11) | 0.3179 (2) | 0.3175 (2) | 0.126 (5) |
| C256 | 0.6273 (2) | 0.3136 (2) | 0.39807 (9) | 0.189 (9) |
| Ti2 | 0.22633 (4) | 0.24698 (4) | 0.24515 (4) | 0.0674 (2) |
| Cl21 | 0.27434 (7) | 0.27371 (7) | 0.15421 (7) | 0.0917 (4) |
| Cl22 | 0.28785 (8) | 0.34292 (6) | 0.32400 (7) | 0.0990 (4) |
| O32 | 0.1742 (2) | 0.2173 (2) | 0.3159 (2) | 0.0834 (9) |
| O34 | 0.1238 (2) | 0.29478 (15) | 0.18979 (15) | 0.0736 (8) |
| O42 | 0.1739 (2) | 0.15695 (15) | 0.1859 (2) | 0.0778 (9) |
| O44 | 0.3094 (2) | 0.17833 (14) | 0.30597 (14) | 0.0716 (8) |
| C31 | 0.09094 (10) | 0.19798 (10) | 0.38403 (13) | 0.113 (2) |
| C32 | 0.10532 (14) | 0.22532 (15) | 0.31443 (11) | 0.0809 (13) |
| C33 | 0.0440 (3) | 0.2635 (3) | 0.2557 (2) | 0.0881 (15) |
| C34 | 0.05444 (13) | 0.29848 (12) | 0.19616 (12) | 0.0694 (11) |
| C35 | −0.01137 (10) | 0.33733 (10) | 0.12851 (12) | 0.0747 (12) |
| C311 | 0.16057 (13) | 0.15035 (15) | 0.4342 (2) | 0.255 (5) |
| C312 | 0.0839 (2) | 0.26235 (14) | 0.4309 (2) | 0.237 (4) |
| C313 | 0.01385 (12) | 0.1539 (2) | 0.3570 (2) | 0.168 (3) |
| C351 | 0.02368 (14) | 0.40281 (12) | 0.1043 (2) | 0.150 (3) |
| C352 | −0.0469 (2) | 0.28552 (14) | 0.06080 (13) | 0.160 (3) |
| C353 | −0.07778 (15) | 0.3628 (2) | 0.1515 (2) | 0.224 (4) |
| C41 | 0.13116 (7) | 0.03741 (8) | 0.13993 (9) | 0.0913 (15) |
| C42 | 0.18949 (10) | 0.08943 (9) | 0.19981 (10) | 0.0701 (11) |
| C43 | 0.2536 (3) | 0.0641 (2) | 0.2630 (3) | 0.0857 (14) |
| C44 | 0.31203 (9) | 0.10829 (11) | 0.31456 (9) | 0.0705 (12) |
| C45 | 0.38532 (8) | 0.08077 (7) | 0.38435 (10) | 0.0887 (15) |
| C411 | 0.0843 (2) | 0.07823 (12) | 0.06583 (10) | 0.244 (11) |
| C412 | 0.17767 (12) | −0.02414 (12) | 0.1236 (2) | 0.126 (4) |
| C413 | 0.07264 (13) | 0.0054 (2) | 0.1700 (2) | 0.178 (7) |
| C414 | 0.16139 (14) | 0.0209 (2) | 0.07821 (13) | 0.226 (13) |
| C415 | 0.1245 (2) | −0.03327 (11) | 0.1783 (2) | 0.233 (15) |
| C416 | 0.04855 (9) | 0.0722 (2) | 0.1028 (2) | 0.143 (8) |
| C451 | 0.4069 (2) | 0.13504 (11) | 0.44983 (11) | 0.141 (7) |
| C452 | 0.3663 (2) | 0.00782 (10) | 0.4105 (2) | 0.206 (11) |
| C453 | 0.45652 (10) | 0.0719 (2) | 0.3630 (2) | 0.148 (6) |
| C454 | 0.36830 (15) | 0.0846 (2) | 0.45592 (10) | 0.202 (10) |
| C455 | 0.4033 (2) | 0.00240 (10) | 0.3714 (2) | 0.245 (12) |
| C456 | 0.45808 (11) | 0.1275 (2) | 0.3960 (2) | 0.135 (6) |

† Occupancies for the disordered *tert*-butyl C atoms are: C111–C113/C114–C116 0.655 (8)/0.345 (8); C251–C253/C254–C256 0.478 (9)/0.522 (9); C411–C413/C414–C416 0.586 (10)/0.414 (10); C451–C453/C454–C456 0.471 (10)/0.529 (10).

Table 2. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Ti1—Cl11 | 2.258 (2) | Ti2—Cl21 | 2.2654 (15) |
| Ti1—Cl12 | 2.273 (2) | Ti2—Cl22 | 2.2671 (14) |
| Ti1—O12 | 2.014 (3) | Ti2—O32 | 1.994 (3) |
| Ti1—O14 | 1.916 (3) | Ti2—O34 | 1.922 (3) |
| Ti1—O22 | 1.998 (3) | Ti2—O42 | 1.990 (3) |
| Ti1—O24 | 1.910 (3) | Ti2—O44 | 1.928 (3) |
| O12—C12 | 1.270 (3) | O32—C32 | 1.239 (4) |
| O14—C14 | 1.283 (3) | O34—C34 | 1.305 (3) |
| O22—C22 | 1.262 (4) | O42—C42 | 1.262 (3) |
| O24—C24 | 1.301 (3) | O44—C44 | 1.282 (3) |
| C11—C12 | 1.521 (2) | C31—C32 | 1.521 (2) |
| C12—C13 | 1.370 (5) | C32—C33 | 1.392 (5) |
| C13—C14 | 1.367 (5) | C33—C34 | 1.368 (5) |
| C14—C15 | 1.520 (2) | C34—C35 | 1.518 (2) |
| C21—C22 | 1.520 (2) | C41—C42 | 1.520 (2) |
| C22—C23 | 1.406 (5) | C42—C43 | 1.359 (4) |
| C23—C24 | 1.344 (5) | C43—C44 | 1.366 (4) |
| C24—C25 | 1.521 (2) | C44—C45 | 1.521 (2) |
| Cl11—Ti1—Cl12 | 96.97 (9) | Cl21—Ti2—Cl22 | 95.50 (6) |
| Cl11—Ti1—O12 | 172.46 (11) | Cl21—Ti2—O32 | 173.60 (10) |
| Cl11—Ti1—O14 | 93.32 (11) | Cl21—Ti2—O34 | 94.07 (9) |
| Cl11—Ti1—O22 | 90.74 (11) | Cl21—Ti2—O42 | 89.50 (10) |
| Cl11—Ti1—O24 | 98.43 (12) | Cl21—Ti2—O44 | 98.39 (10) |
| Cl12—Ti1—O12 | 89.80 (11) | Cl22—Ti2—O32 | 90.42 (10) |
| Cl12—Ti1—O14 | 96.32 (11) | Cl22—Ti2—O34 | 96.59 (9) |
| Cl12—Ti1—O22 | 171.72 (12) | Cl22—Ti2—O42 | 174.05 (9) |
| Cl12—Ti1—O24 | 92.94 (11) | Cl22—Ti2—O44 | 93.04 (9) |
| O12—Ti1—O14 | 82.60 (12) | O32—Ti2—O34 | 82.82 (11) |
| O12—Ti1—O22 | 82.69 (13) | O32—Ti2—O42 | 84.72 (12) |
| O12—Ti1—O24 | 84.48 (13) | O32—Ti2—O44 | 83.68 (12) |

| | | | |
|---|---|---|---|
| O14—Ti1—O22 | 86.21 (13) | O34—Ti2—O42 | 86.23 (11) |
| O14—Ti1—O24 | 164.05 (13) | O34—Ti2—O44 | 163.44 (12) |
| O22—Ti1—O24 | 82.90 (13) | O42—Ti2—O44 | 83.03 (11) |

The compound crystallized in the monoclinic system; space group $P2_1/c$ was determined from the systematic absences. The crystal did not diffract well (only 32% of the data were classified as 'observed' at the $2\sigma$ level) presumably because the molecules take part in no significant intermolecular interactions.

Four of the eight independent *tert*-butyl groups showed clear evidence of rotational disorder and this was allowed for using the *DFIX* options in *SHELXL*93 (Sheldrick, 1993) with suitable distance and occupancy constraints. For all *tert*-butyl groups, free variables were refined for the C—C(methyl) [1.502 (1) Å], methyl···methyl [2.447 (1) Å] and C($sp^2$)··· C(methyl) [2.474 (1) Å] distances to ensure approximate tetrahedral geometry.

Examination of the structure with *PLATON* (Spek, 1994*a*) showed that there were no solvent accessible voids in the crystal lattice.

Data collection: Enraf–Nonius (1992) *CAD*-4 *PC Software*. Cell refinement: Enraf–Nonius (1992) *SET*4 and *CELDIM*. Data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX*94 (Patterson heavy-atom method). Program(s) used to refine structure: *NRCVAX*94 and *SHELXL*93. Molecular graphics: *NRCVAX*94, *PLUTON* (Spek, 1994*b*) and *ORTEP*II (Johnson, 1976) as implemented in *PLATON*. Software used to prepare material for publication: *NRCVAX*94 and *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1297). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Tetramethylammonium Lithium Zinc Cyanide, $[N(CH_3)_4]LiZn(CN)_4$

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## Abstract

The title crystal has a diamond-type framework structure with $Zn^{2+}$ and $Li^+$ ions on tetrahedral atom sites and $(CN)^-$ anions as bridging 'rods' between them. The charge-balancing $[N(CH_3)_4]^+$ cations are located in half of the adamantane cages.

## Comment

This work is part of our efforts to synthesize diamond-type structures with variable adamantane cage sizes. The X-ray powder diffraction study of the $[N(C_2H_5)_4]^+$ templated sample shows that it has the same cubic diamond-type structure as $[N(CH_3)_4]LiZn(CN)_4$ with a sightly expanded cage (3% volume increase per cell). The cubic structure (possibly the diamond-type framework) is lost when other organic templates, such as $[N(C_3H_7)_4]^+$, are used.

In diamond-type frameworks, the number of the adamantane cages is the same as the number of tetrahedral atom sites. Thus, in the title compound, only half of the adamantane cages are occupied. The crystal structure of $[N(CH_3)_4]CuZn(CN)_4$ has been reported previously (Hoskins & Robson, 1991). By replacing $Cu^+$ with $Li^+$, we were able to distinguish two different tetrahedral atom sites and prove that $N(CH_3)_4^+$ cations are located

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