Table 3. *Molecular thermal motion in the organic anion*

The analysis is carried out in the inertial frame with x along the elongated axis of the anion.

Translation tensor, **T** ($Å^2 \times 10^4$)

$$\begin{pmatrix} 181\,(20) & 37\,(14) & -33\,(12) \\ & 169\,(15) & -10\,(8) \\ & & 223\,(10) \end{pmatrix}$$

Libration tensor, L ($rad^2 \times 10^4$)

$$\begin{pmatrix} 21\,(3) & 19\,(3) & 15\,(3) \\ & 4\,(4) & 7\,(3) \\ & & 25\,(11) \end{pmatrix}$$

Cross tensor, **S** (rad $Å \times 10^4$)

$$\begin{pmatrix} 20\,(5) & -26\,(5) & 5\,(4) \\ 10\,(5) & -25\,(4) & 10\,(4) \\ 7\,(9) & -12\,(6) & 6\,(5) \end{pmatrix}$$

$R_{wU} = 0{\cdot}045$
$\langle \Delta^2 U_{ll} \rangle^{1/2} = 0{\cdot}0006$
$\langle \sigma^2 U_{ll} \rangle^{1/2} = 0{\cdot}0017$

(lower inertia moment) and the least librational motion (L_{22}) is also about a direction normal to the anion axis. A major limitation of the model is the assumption that the anionic groups in the crystal are vibrating independently, whereas they are actually coupled by ionic and H-bonding interactions.

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Structure of the 1:1 Adduct between Titanium(IV) Chloride and Pentanedinitrile

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Abstract. $TiCl_4.C_5H_6N_2$, $M_r = 283{\cdot}83$ orthorhombic, *Pbcm*, $a = 6{\cdot}009$ (1), $b = 12{\cdot}729$ (2), $c = 14{\cdot}243$ (2) Å, $V = 1089{\cdot}4$ (3) $Å^3$, $Z = 4$, $D_x = 1{\cdot}731$ g cm^{-3}, λ(Mo $K\alpha$) = $0{\cdot}7093$ Å, $\mu = 17{\cdot}20$ cm^{-1}, $F(000) = 560$, $T = 298$ K, $R = 0{\cdot}041$ for 1266 observed reflections. Equal amounts of $TiCl_4$ and $NC(CH_2)_3CN$ produce the 1:1 $TiCl_4$–$NC(CH_2)_3CN$ adduct whose crystal structure has been found to be one-dimensionally polymeric with $NC(CH_2)_3CN$ acting as a bridge between two $TiCl_4$ units. Ti atoms are octahedrally coordinated with N atoms in the *cis* configuration.

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Introduction. The interesting chemistry of transition-metal–nitrile complexes has been extensively reviewed (Storhoff & Lewis, 1977). With two —C≡N groups, a dinitrile is able to react with more than one transition-metal center, while titanium tetrachloride is coordinatively unsaturated, capable of increasing its coordination number from 4 to 6 by reacting with suitable organic ligands (Cotton & Wilkinson, 1980). The 1:1 $TiCl_4$–$NC(CH_2)_nCN$ adducts (n = 1–8) can be chelated complexes, cyclic di/trimers, or linear polymers based on spectroscopic data (Jain & Rivest, 1963). The 1:1 $TiCl_4$–$NC(CH_2)_nCN$ adducts (n = 2, 4, and 5), whose molecular weights as determined by cryoscopy are

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about half those of a formula weight, apparently have a dissociating nature in polar solvents (Jain & Rivest, 1963). The X-ray structure analysis of the 1:1 $TiCl_4$–$NC(CH_2)_3CN$ adduct as reported here serves as an essential study to decide which of the following would truly occur: chelate formation, cyclic structure, or linear polymer.

Experimental. The chemicals were purified and made anhydrous by suitable methods (Perrin, Armarego & Perrin, 1980). Being oxygen/moisture sensitive, the 1:1 $TiCl_4$–$NC(CH_2)_3CN$ adduct was handled in a glove box under a dry-nitrogen atmosphere or in evacuated glass flasks.

$TiCl_4$ solution (1·6 ml; 14·7 mmol, in 40 ml CH_2Cl_2) was gradually pipetted into $NC(CH_2)_3CN$ solution (1·4 ml; 14·7 mmol, also in 40 ml CH_2Cl_2) with stirring. With the yellow adduct precipitating immediately, the mixture was permitted to stand for 30 min to ensure complete conversion. The yellow precipitates, filtered on a sintered-glass filter, washed with 100 ml CH_2Cl_2, and then dried in a vacuum desiccator overnight, were purified by sublimation while single crystals of the adduct were obtained by slow sublimation under vacuum and controlled thermal gradient. Crystals taken out of the sublimate were immediately immersed in Nujol to avoid any decomposition. The data crystal (*ca* 0·5 × 0·4 × 0·3 mm) was sealed into a 0·3 mm lithium-glass capillary for X-ray structure analysis.

Nonius CAD-4 diffractometer data, $4 < 2\theta < 60°$, Mo $K\alpha$, ω–2θ scan with speeds 2·0–6·7° min^{-1}, $(\pm 1{\cdot}0 \pm 0{\cdot}35\tan\theta)°$ around maximum, h 0→8, k 0→17, l 0→19, 25 reflections ($14 < \theta < 21°$) used for measuring lattice parameters. Three standard reflections 031, 112, and $\bar{1}04$ after every 3600 s, no decay or decomposition found. 1641 unique reflections measured, 1266 observed with $I > 2\sigma(I)$. Structure solved by heavy-atom method, Ti on mirror ($Z = 4$), other non-H atoms found in Fourier map, H atoms found in difference Fourier map. No absorption corrections applied (data crystal coated with Nujol, sealed in capillary, shape regular). Structure refined by full-matrix least squares minimizing $\sum w||F_o|-|F_c||^2$, where weighting $w = 1/(\sigma_F^2 + 0{\cdot}000032|F_o|^2)$. Calculations carried out with anisotropic C, N, Cl and Ti and isotropic H. Scattering factors from *International Tables for X-ray Crystallography* (1974). Final $R = 0{\cdot}041$ and $wR = 0{\cdot}040$. Max. Δ/σ for last cycle 0·10. Max. and min. peak heights in final difference map 0·41 and −0·40 e $Å^{-3}$. Computations carried out on a PDP 11/23 with NRCC package (Lee & Gabe, 1978). *ORTEP* (Johnson, 1965) drawings are in Fig. 1. Final atomic fractional coordinates are in Table 1, bond lengths and angles in Table 2.*

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42600 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

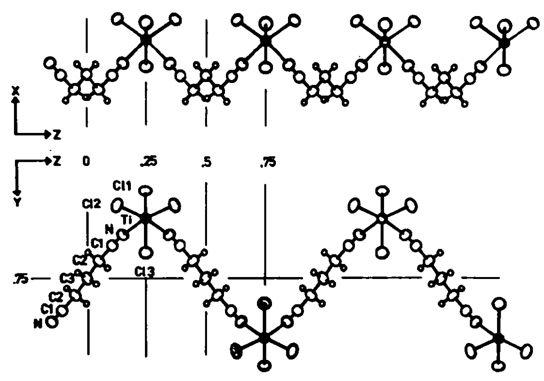

Fig. 1. *ORTEP* drawings of the 1:1 $TiCl_4$–$NC(CH_2)_3CN$ adduct as projected down the x and y axes.

Table 1. *Fractional atomic coordinates for the* 1:1 $TiCl_4$–$NC(CH_2)_3CN$ *adduct*

The equivalent B_{iso} for the anisotropic temperature factors is calculated from the equation $B_{iso} = 8\pi^2/3 \sum U_{ii}$.

	x	y	z	B_{iso} ($Å^2$)
Ti	0·15736 (5)	0·47353 (2)	0·25	2·36 (2)
Cl(1)	0·41551 (8)	0·34378 (3)	0·25	3·47 (2)
Cl(2)	−0·03936 (5)	0·41184 (3)	0·12970 (2)	4·13 (2)
Cl(3)	−0·00616 (9)	0·63354 (4)	0·25	4·33 (3)
N	0·3864 (2)	0·5498 (1)	0·1520 (1)	3·27 (5)
C(1)	0·5017 (2)	0·6004 (1)	0·1080 (1)	3·12 (6)
C(2)	0·6396 (2)	0·6712 (1)	0·0514 (1)	3·15 (7)
C(3)	0·4959 (4)	0·75	0·	3·34 (11)
H(2*a*)	0·759 (2)	0·704 (1)	0·089 (1)	3·6 (3)
H(2*b*)	0·718 (2)	0·633 (1)	0·005 (1)	3·9 (3)
H(3)	0·401 (2)	0·723 (1)	−0·038 (1)	4·8 (4)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *of the* 1:1 $TiCl_4$–$NC(CH_2)_3CN$ *adduct*

Ti—Cl(1)	2·2659 (6)	Ti—Cl(2)	2·2248 (5)
Ti—Cl(3)	2·2614 (6)	Ti—N	2·188 (1)
N—C(1)	1·134 (2)	C(1)—C(2)	1·466 (2)
C(2)—C(3)	1·513 (1)	C(2)—H(2*a*)	0·99 (1)
C(2)—H(2*b*)	0·95 (1)	C(3)—H(3)	0·86 (1)
Cl(1)—Ti—Cl(2)	96·11 (2)	Cl(1)—Ti—Cl(3)	162·55 (2)
Cl(1)—Ti—N	83·84 (3)	Cl(2)—Ti—Cl(2^{i})	100·73 (2)
Cl(2)—Ti—Cl(3)	94·99 (2)	Cl(2)—Ti—N	89·96 (3)
Cl(2)—Ti—N^{i}	169·24 (3)	Cl(3)—Ti—N	82·75 (3)
N—Ti—N^{i}	79·33 (4)	Ti—N—C(1)	171·3 (1)
N—C(1)—C(2)	176·2 (1)	C(1)—C(2)—C(3)	110·6 (1)
C(1)—C(2)—H(2*a*)	111·5 (6)	C(1)—C(2)—H(2*b*)	110·2 (6)
C(3)—C(2)—H(2*a*)	113·6 (6)	C(3)—C(2)—H(2*b*)	106·9 (6)
H(2*a*)—C(2)—H(2*b*)	103·7 (9)	C(2)—C(3)—C(2^{ii})	110·4 (2)
C(2)—C(3)—H(3)	115·2 (8)	C(2)—C(3)—H(3^{ii})	109·3 (8)
H(3)—C(3)—H(3^{ii})	97·1 (1)		

Symmetry code: (i) mirror-related atoms (from x, y, z to $x, y, \frac{1}{2} - z$); (ii) twofold-related atoms (from x, y, z to $x, \frac{1}{2} - y, -z$).

Discussion. As seen from Fig. 1 which includes projections down the x and y axes, $NC(CH_2)_3CN$ acts as a bridging ligand between two $TiCl_4$ units such that the 1:1 $TiCl_4$–$NC(CH_2)_3CN$ adduct is one-dimensionally polymeric in the solid state. Ti atoms are octahedrally coordinated with the N atoms being in the *cis* configuration. It should also be noted that C(3) is required to sit on a crystallographic twofold axis so that one half of $NC(CH_2)_2CN$ is related to the other half by the twofold symmetry.

The conformation of $NC(CH_2)_3CN$ in the adduct is *trans,trans* for the four C—C single bonds connecting C(1)—C(2)—C(3)—C(2)—C(1). The $NC(CH_2)_3CN$ molecule is nearly planar. The Ti—Cl distances of 2·225–2·266 Å are comparable to those obtained in previous works on $TiCl_4$ adducts, *e.g.* 2·174–2·190 Å in $(TiCl_4$–$NCCOOC_2H_5)_2$ (Constant, Cubaynes, Daran & Jeannin, 1974) and 2·226 Å in $TiCl_4$–$(NCH_2)_2$ (Constant, Daran & Jeannin, 1971). The Ti—N distance of 2·188 Å is similar to those found in $TiCl_4$–$(NCH_2)_2$, 2·198 Å, and $(TiCl_4$–$NCCOOC_2H_5)_2$, 2·240 Å. The C≡N triple-bond distance of 1·134 Å is slightly shorter than the 1·155 Å length observed in the equilibrium C≡N distance in CH_3CN (Cooney & Fraser, 1974). Such a shortening is expected because the C≡N bond strength increases upon coordination (Storhoff & Lewis, 1977). The N—C(1)—C(2) fragment is nearly linear as it should be [∠N—C(1)—C(2) 176·2°]. The departure from the ideal 180° of the Ti—N—C(1) angle (171·3°) is presumably a manifestation of crystal-packing effects caused primarily by the rigid nature of the N—C(1)—C(2) framework. It is noted that the linearity of the Ti—N—C(1)—C(2) segment prevents both ends of the dinitrile molecules from coordinating with the same Ti atom. To explain the slightly short C(1)—C(2) distance (1·466 Å) as compared to a typical C—C single-bond length of 1·54 Å, we may safely assume that there is a partial double-bond character due to the neighboring —C≡N group.

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Conformational Aspects of *meso*-Tartaric Acid. X.* Structure of Sodium Trihydrogen Di-*meso*-tartrate

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Abstract. $Na^+.C_8H_{11}O_{12}^-$, $M_r = 322·16$, monoclinic, $P2_1/n$, $a = 6·514$ (1), $b = 9·193$ (4), $c = 9·440$ (3) Å, $\beta = 96·38$ (2)°, $V = 561·8$ (4) Å^3, $Z = 2$, $D_x = 1·904$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 2·01$ mm^{-1}, $F(000) = 330$, $T = 295$ K, $R = 0·058$ for 989 diffractometer data with $I > 2·5\sigma(I)$. In this super-acid salt, the *meso*-tartrate anion adopts a dissymmetric conformation. The heavy atoms in one half of the anion are approximately coplanar, whereas the other glycolic-acid part is rather distorted from planarity owing to intermolecular H bonding. The H-bond scheme concerning the carboxyl-group coupling is of the mixed A/B type. The sodium-ion coordination is pseudo cubic with Na—O distances in the range 2·468–2·607 Å.

* Part IX: Moerman, Ouwerkerk & Kroon (1985).

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