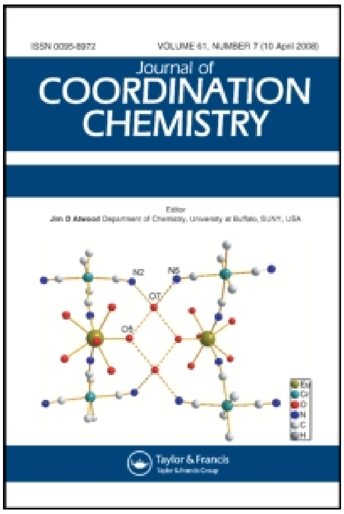

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Georges Constant[a]; Jean-Jacques Cubaynes[a]; Jean-Claude Daran[a]; Yves Jeannin[a]
[a] Centre National de la Recherche Scientifique, Laboratoire de Chimie de Coordination, TOULOUSE CEDEX

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THE CRYSTAL STRUCTURE OF DI-μ-CHLORO-HEXACHLORO-BIS (ETHYL-CYANOFORMATE-N) DITITANIUM (IV)

GEORGES CONSTANT, JEAN-JACQUES CUBAYNES, JEAN-CLAUDE DARAN and YVES JEANNIN

Centre National de la Recherche Scientifique, Laboratoire de Chimie de Coordination
B.P. 4142 – 31030 TOULOUSE CEDEX

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Crystals of the adduct titanium tetrachloride-ethylcyanoformate (1–1) are monoclinic $a = 9.06$ A, $b = 18.36$ A, $c = 13.83$ A, $\beta = 113°.2$, space group C2/c, $Z = 8$. The structure was solved by application of X-Ray diffraction techniques at room temperature. Atomic positions were refined by a full-matrix least-squares method to a final R of 0.049 using 829 non-zero independent reflections. This compound is dimeric with a double chlorine bridge between titanium atoms. Titanium is octahedrally coordinated to five chlorine atoms and to the nitrogen atom of the nitrile group and not to the oxygen atom of the carbonyl group. Thus in this complex the nitrogen atom is a better donor than the carbonyl oxygen.

INTRODUCTION

Nitriles such as HCN, CH_3CN, C_2H_5CN react as Lewis bases toward covalent transition metal halides such as $FeCl_3$, $TiCl_4$, and VCl_4. This was demonstrated by the preparation of single crystals of $VCl_4(NCH)_2$,[1] $TiCl_4(NCH)_2$,[2] $Fe_3Cl_8(NCH)_6$,[3] $Fe_3Cl_8(NCCH_3)_6$,[4] $Fe_3Cl_9(NCC_2H_5)_5$[5] and the elucidation of their structures.

For all of the complexes we have established that the nitrile is bound to the metal atom through the nitrogen lone pair. In order to determine the donor force of the nitrile group with respect to other donating groups, a structural study was initiated on the adduct of titanium tetrachloride and ethylcyanoformate. Indeed this ligand possesses two donor groups, the nitrile one and the carbonyl one. Let us point out that Chenard, Commereuc and Chauvin[6] prepared complexes by reacting this ligand with molybdenum, tungsten and manganese carbonyls. They concluded that π bonding between the CN group and metal atoms is involved. However such a π bonding scheme seems unlikely in our case since it usually is observed with metals in a low oxidation state.

EXPERIMENTAL PART

Because of the extreme sensitivity of titanium tetrachloride to moisture, synthesis is carried out in a sealed evacuated glass system. Titanium tetrachloride is twice distilled before reacting with ethylcyanoformate which has been dried over P_2O_5. Yellow prismatic crystals, obtained by cooling the solution, are very sensitive to moisture and heat. This makes it difficult to carry out density measurements and to record the IR spectrum. Chemical analysis leads to the empirical formula $TiCl_4C_4H_5NO_2$, which corresponds to a 1–1 addition compound. Laue and precession photographs show the lattice constants to be:

$a = 9.06 \pm 0.01$ Å $\beta = 113.2° \pm 0.15$
$b = 18.36 \pm 0.02$ Å Cc or C2/c
$c = 13.83 \pm 0.02$ Å $d_x = 1.81 \pm 0.01$

The films were measured to the nearest 1/100 millimeter and a correction for film shrinkage was applied.

A density of 1.76 ± 0.02 was determined by the flotation technique using a mixture of 1,2 dibromoethane and carbon tetrachloride. This result is very close to the calculated density of 1.81 ± 0.01 for 8 molecules per unit cell.

A 0.6 x 0.5 x 0.5 mm single crystal used for data collection was placed in a glass capillary in a dry box. This sealed tube was set on a 30 cm diameter eulerian cradle. MoKα radiation (λ = 0.71069) was supplied by a stabilized CGRθ 60 generator. Diffracted intensities were measured with a scintillation counter and a pulse height analyser set of the MoKα energy in such a way that 90% of diffracted intensity was counted.

An oriented graphite monochromator was placed in front of the counter window.

The diffractometer was set manually and all 957 independent reflections having a Bragg angle of less than 20°, were recorded at room temperature using a θ-2θ scan at a rate of 0.97° per 100 seconds in Bragg angle. The take-off angle was 3°. Background counts were measured for 30 seconds at both ends of scan.

Three reflections (6,0,0) (0,12,0) (0,0,2) were chosen as standards and their intensities measured twice a day. No anomaly was observed. Twenty eight reflections for which counting rates were greater than 10000 c/s, were corrected for counting losses.[7] For every structure factor F, a standard deviation σ is computed:

$$\sigma = \frac{Fx\sqrt{\Delta C}}{2C}$$

Where C is the integrated intensity and ΔC the statistical error on integrated intensity.[7]

If the observed structure factor was less or equal to its standard deviation σ, the structure factor was set at one half the value of the standard deviation which is then equal to $\sqrt{(\Delta C/LP)}$ where LP is Lorentz polarization factor. During least squares refinement, the reciprocal of the standard deviation was used as a weighting factor.

STRUCTURE DETERMINATION AND REFINEMENT

The test of Howells, Phillips and Rogers[8] suggested a centered space group. Therefore $C\ 2/c$ was chosen. Titanium and chlorine positions clearly show up on a three dimensional Patterson map. All atoms are in general positions. Titanium appears octahedrally surrounded with five corners occupied by chlorine atoms. Thus, the adduct is a dimer $(TiCl_4, 1L)_2$ and the ligand is monocoordinated.

After partial refinement, a Fourier difference map showed all other atoms but hydrogens. A linear chain of three atoms was found attached to each titanium atom. This implies a Ti–N≡C–C chain with the ligand attached to the metal atom by the nitrogen lone pair. Atomic positions of all atoms were refined by a least squares technique[9] using the form factors of Cromer and Waber[10] and isotropic temperature factors. An R factor, $R = \Sigma\ |\text{Fcalc-Fobs})|/\Sigma\text{Fobs}$, of 0.13 was obtained. Anisotropic temperature factors were introduced and the form factors corrected for the real part of the anomalous dispersion.

TABLE 1

Atomic parameters and anisotropic thermal vibration components
$\exp\left(-2\pi^2\left(U_{11}(ha^*)^2 + U_{22}(kb^*)^2 + U_{33}(lc^*)^2 + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*\right)\right)$
standard deviations are between parentheses

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti	0.1896(1)	0.04487(6)	0.0998(1)	0.0305(8)	0.0495(8)	0.0518(8)	0.0009(7)	0.0113(6)	−0.0082(6)
Cl_1	0.2712(2)	0.0437 (1)	0.2715(1)	0.054 (1)	0.081 (1)	0.049 (1)	0.012 (1)	0.004 (1)	−0.008 (1)
Cl_2	0.0181(2)	0.04548(9)	−0.0894(1)	0.043 (1)	0.049 (1)	0.050 (1)	−0.001 (1)	0.0186(9)	0.0004(9)
Cl_3	0.3098(2)	0.1433 (1)	0.0793(1)	0.065 (1)	0.072 (1)	0.103 (1)	−0.029 (1)	0.040 (1)	−0.018 (1)
Cl_4	0.3496(2)	−0.0373 (1)	0.0816(1)	0.037 (1)	0.080 (1)	0.085 (1)	0.008 (1)	0.015 (1)	−0.028 (1)
N_1	−0.0062(7)	0.1190 (3)	0.1019(4)	0.040 (4)	0.049 (3)	0.042 (4)	0.002 (4)	0.016 (3)	−0.005 (2)
C_1	−0.1028(9)	0.1548 (4)	0.1060(5)	0.045 (4)	0.056 (6)	0.035 (4)	−0.003 (5)	0.014 (4)	−0.004 (3)
C_2	−0.2383(9)	0.2006 (3)	0.1077(6)	0.047 (4)	0.041 (5)	0.056 (5)	0.005 (5)	0.028 (4)	0.011 (4)
O_1	−0.3596(6)	0.2050 (2)	0.0339(4)	0.043 (3)	0.085 (4)	0.056 (3)	0.014 (3)	0.002 (3)	−0.002 (3)
O_2	−0.1903(5)	0.2353 (2)	0.1962(3)	0.050 (3)	0.059 (3)	0.053 (3)	0.020 (3)	0.017 (2)	−0.004 (3)
C_3	−0.306 (1)	0.2859 (5)	0.2085(8)	0.058 (4)	0.084 (8)	0.112 (8)	0.036 (7)	0.038 (6)	−0.009 (5)
C_4	−0.225 (1)	0.3272 (5)	0.3028(8)	0.116 (8)	0.073 (8)	0.069 (7)	0.021 (7)	0.023 (7)	−0.031 (6)
H_{31}	−0.34 (1)	0.316 (5)	0.145 (7)	0.058 (4)	0.084 (8)	0.112 (8)	0.036 (7)	0.038 (6)	−0.009 (5)
H_{32}	−0.40 (1)	0.262 (5)	0.196 (7)	0.058 (4)	0.084 (8)	0.112 (8)	0.036 (7)	0.038 (6)	−0.009 (5)
H_{41}	−0.19 (1)	0.298 (5)	0.373 (7)	0.116 (8)	0.073 (8)	0.069 (7)	0.021 (7)	0.023 (7)	−0.031 (6)
H_{42}	−0.28 (1)	0.365 (5)	0.321 (7)	0.116 (8)	0.073 (8)	0.069 (7)	0.021 (7)	0.023 (7)	−0.031 (6)
H_{43}	−0.09 (1)	0.345 (5)	0.329 (7)	0.116 (8)	0.073 (8)	0.069 (7)	0.021 (7)	0.023 (7)	−0.031 (6)

4 cycles of a full-matrix least squares refinement yielded an R value of 0.056. A Fourier difference synthesis showed peaks higher than the error on electron density (0.02 $eÅ^{-3}$) in positions which could be those of hydrogen atoms. A refinement including hydrogen atom positions reduces R to 0.049. According to Hamilton's test,[11] this is significant at the 0.005 level. Thermal parameters of the hydrogen atoms were set equal to these of the carbon atoms to which they are bonded.

The final refinement based upon 942 data leads to:

non weighted R, including 113 zeros 0.057
non weighted R, excluding 113 zeros 0.049
weighted R, including 113 zeros 0.050
weighted R, excluding 113 zeros 0.049

$R_W = (\Sigma(w|Fcalc\text{-}Fobs|)^2/\Sigma(wFobs)^2)^{1/2}$

Atomic parameters are listed in Table I, bond lengths and bond angles in Table II.

DESCRIPTION AND DISCUSSION OF STRUCTURE

The adduct of titanium tetrachloride and ethylcyanoformate is a dimer $(TiCl_4NCCOOC_2H_5)_2$. Its structure is shown in figure 1. This dimeric form is typical of 1–1 adducts of titanium tetrachloride such as $(TiCl_4CH_3COOC_2H_5)_2$[12] and $(TiCl_4POCl_3)_2$.[13]

Differences in lengths between non-bridging Ti–Cl bonds (2.174(2), 2.187(2), 2.190(2)) and bridging Ti–Cl bonds (2.463(5), 2.469(2)) have almost the same magnitude as those of $(TiCl_4CH_3COOC_2H_5)_2$ and $(TiCl_4POCl_3)_2$.

An interesting point is the Ti–Cl bond length in trans position to nitrogen; it is slightly shorter (2.174) than equatorial ones (2.187 and 2.190). A similar shortening occurs in $NbCl_5HCN$ (2.25 instead of 2.31).[14] It is interpreted considering chlorine atoms as weak π donors. When two chlorines are trans to each other their donor effects are balanced through metal d-orbital. On the opposite, when chlorine is in trans position of nitrile group which is not π donor, its weak π donation induces some shortening in the metal-chlorine bond length.

The titanium-nitrogen distance (2.240(3)) is longer than the one found in $TiCl_4(NCH)_2$ (2.198(7)). Under the influence of five chlorine atoms which surround titanium, nitrogen moves away from titanium in order to maintain normal Van der Waals contacts as shown in table III. Indeed in both compounds, the average interatomic Cl–N distances are similar, 3.03 Å for $(TiCl_4NCCOOC_2H_5)_2$ and 3.04 Å for $TiCl_4(NCH)_2$. This is attributed to the effects of valence shell electron repulsion.

The N(1)–C(1) triple bond distances of 1.112 Å is

TABLE II
Interatomic distances (Å) and bond angles (°) with standard deviations σ

Bond	Length (Å)	σ	Angle	Degree	σ
Ti(1)–Cl(2)	2.463	0.005	Cl(2)–Ti(1)–Cl(2′)	78.1	0.2
Ti(1)–Cl(2′)	2.469	0.003	Cl(1)–Ti(1)–Cl(2)	162.6	0.1
Ti(1)–Cl(1)	2.190	0.002	Cl(1)–Ti(1)–Cl(2′)	88.9	0.2
Ti(1)–Cl(3)	2.187	0.002	Cl(1)–Ti(1)–Cl(3)	100.1	0.1
Ti(1)–Cl(4)	2.174	0.002	Cl(1)–Ti(1)–Cl(4)	99.3	0.2
Ti(1)–N(1)	2.240	0.003	Cl(1)–Ti(1)–N(1)	85.6	0.2
N(1)–C(1)	1.112	0.003	Cl(2)–Ti(1)–Cl(3)	89.8	0.2
C(1)–C(2)	1.505	0.003	Cl(2)–Ti(1)–Cl(4)	92.9	0.2
C(2)–O(1)	1.160	0.004	Cl(2)–Ti(1)–N(1)	80.8	0.2
C(2)–O(2)	1.309	0.003	Cl(3)–Ti(1)–Cl(2′)	162.8	0.1
O(2)–C(3)	1.466	0.003	Cl(3)–Ti(1)–Cl(4)	99.7	0.3
C(3)–C(4)	1.473	0.004	Cl(3)–Ti(1)–N(1)	86.5	0.3
			Cl(4)–Ti(1)–Cl(2′)	93.2	0.3
			Cl(4)–Ti(1)–N(1)	171.2	0.1
			Cl(2′)–Ti(1)–N(1)	79.6	0.3
			Ti(1)–N(1)–C(1)	178.1	0.2
			N(1)–C(1)–C(2)	177.1	0.2
			C(1)–C(2)–O(1)	121.8	0.3
			C(1)–C(2)–O(2)	108.1	0.3
			O(1)–C(2)–O(2)	129.8	0.3
			C(2)–O(2)–C(3)	116.5	0.3
			O(2)–C(3)–C(4)	108.5	0.3

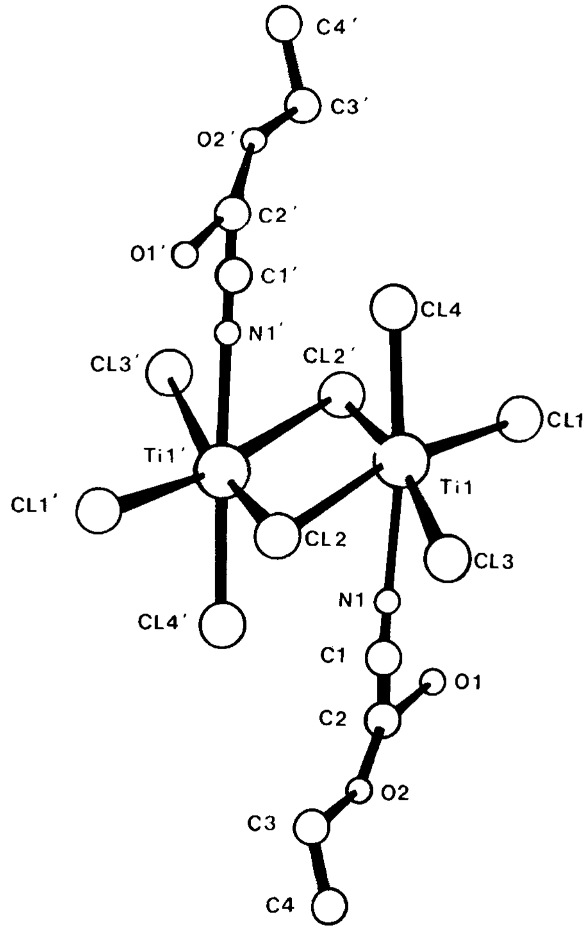

FIGURE 1 Molecular structure of $(TiCl_4NCCOOC_2H_5)_2$

shorter than the 1.155 Å length observed in gaseous hydrogen cyanide. Such a shortening has been observed for all adducts of nitriles coordinated through the nitrogen. Shortening is due to a contraction of valence electron shell of C≡N bond when the nitrogen gives its lone pair. In free nitrile this lone pair occupies a large volume which somewhat repulses π electrons of the triple bond, making some stretching. When the nitrile is bonded, the lone pair is concentrated between nitrogen and metal atoms. Repulsion is diminished and the N≡C bond is shortened.

Since nitrogen in bonded to titanium, it behaves as a better donor atom than the oxygen of the carbonyl group. However in compounds such as $SbCl_5HCON(CH_3)_2$[16] or $FeCl_2(HCONH_2)_2$[17] where nitrogen belongs to an amide group, the better donor is oxygen belonging to the carbonyl group. Then we can compare donicity. The nitrogen atom of a nitrile group is a better donor than the oxygen atom of a carbonyl group, which is a better donor than the nitrogen atom of an amide group.

TABLE III

Van der Waals contacts between chlorine and nitrogen atoms (Å) with standard deviations σ

Bond	Length	σ
Cl(3)–N(1)	3.033	0.005
Cl(1)–N(1)	3.010	0.007
Cl(2)–N(1)	3.052	0.004
Cl(2')–N(1)	3.018	0.003
Cl(3)–Cl(4)	3.335	0.003
Cl(1)–Cl(4)	3.326	0.005
Cl(2)–Cl(4)	3.367	0.007
Cl(2')–Cl(4)	3.378	0.004
Cl(1)–Cl(3)	3.355	0.004
Cl(3)–Cl(2)	3.288	0.006
Cl(1)–Cl(2)	3.269	0.006
Cl(2)–Cl(2')	3.105	0.004

CONCLUSION

The adduct compound of titanium tetrachloride with ethyl cyanoformate is a dimer. The ligand is linked by the nitrogen lone pair. Thus the nitrogen atom of a nitrile group is a better donor than the nitrogen atom of an amide group.

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